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Журнал публикует рецензированные статьи по научным исследованиям, выполненным в различных отраслях химической науки: неорганическая химия, органическая химия, аналитическая химия, физическая химия и химия твёрдого тела. Приветствуется публикация статей по смежным отраслям. Редакционная коллегия поддерживает высокий уровень публикаций, строго придерживаясь политики независимой сторонней экспертизы, выполненной специалистами в соответствующей области, квалификация которых подтверждена общепризнанными наукометрическими показателями.

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The journal publishes peer-reviewed papers on scientific research in various branches of chemical science: inorganic chemistry, organic chemistry, analytical chemistry, physical chemistry and solid-state chemistry. The papers in related branches are welcome. The editorial board keeps the high quality of publications, strictly adhering to the policy of independent third-party expert opinion, expressed by specialists in the corresponding branches, whose qualification is confirmed by generally recognized scientometrical indicators.

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Organometallic Chemistry

*The issue is composed of papers
dedicated to the memory of
the outstanding chemist
academician G.A. Razuvaev
in relation to 120th anniversary
of his birthday*

Grigory Alekseyevich Razuvaev

(1895–1989)



On August 23, 2015, is the 120th anniversary from the birthday of academician Grigory Alekseyevich Razuvaev, who was an outstanding scientist, one of the founders of the modern organometallic chemistry.

Grigory Alekseyevich Razuvaev was born on August 23, 1895, in Moscow. He graduated from Leningrad University (1925). From 1927 he worked in the laboratory of research in high pressures (State Institute of High Pressures from 1929) and Leningrad Technological Institute.

Since 1946 he was a professor of Gorky State University and simultaneously the director of Scientific Research Institute of the university in 1956–1962. In 1963 he was made the head of the laboratory of polymer stabilization of the USSR Academy of Sciences. In 1969–1988 he was the director of Chemistry Institute of the USSR Academy of Sciences in Gorky. Since 1988 he was the honorary director of Institute of Organometallic Chemistry of the USSR Academy of Sciences.

His fundamental research was in chemistry of organometallic compounds, organic peroxides and in the study of free radicals in solutions. He determined the relative rate of their formation during thermal decomposition of organomercury compounds and compiled the activity series for radicals. Together with M.M. Koton he discovered the method of generation of free aliphatic radicals (1931–1935). He established the mechanism (1940s) of free radical formation in photolysis reactions of organometallic compounds in liquid medium, as well as the character of their interaction with each other and the solvents. He developed a new accessible synthesis method of mercury organic compounds (1954) by the action of free radicals formed from peroxides upon mercury salts. He discovered fundamentally new ways of transformations in the series of arsenic organic derivatives. He suggested synthesis methods (1963–1969) of organometallic compounds with a chain containing from two to four heteroatoms of the $R_3SiHgGeR_3$ type. Together with his collaborators (1963–1970) he originated various ways to obtain filamentary single crystals and layered films of germanium and other metals for semiconductor technology and electronics. He obtained organometallic compounds, used as polymerization initiators and catalysts and as monomer stabilizers. In 1967–1974 he developed synthesis methods of ceryl aryl compounds of tetravalent titanium, zirconium, vanadium and trivalent titanium.

G.A. Razuvaev was awarded the title of Hero of Socialist Labour (1969), Lenin Prize (1958), State Prizes of the USSR (1971, 1985).

KEEPING RAZUVAEV'S TRADITIONS ALIVE

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The role of Grigory Alekseyevich Razuvaev in establishment of organometallic chemistry at the subdepartment of organic chemistry and chemistry department of Lobachevsky State University of Nizhny Novgorod is in arrangement of indissoluble connection between academic activity and scientific research work.

On September the 1st the academic year for the first-year students of the chemical department of Lobachevsky UNN traditionally begins in the memorial lecture room named after academician Grigory Alekseyevich Razuvaev, an honorary freeman of Nizhny Novgorod, a laureate of Lenin Prize and three State Prizes of the USSR, an outstanding scientist, the founder of organometallic chemistry in Nizhny Novgorod region.

G.A. Razuvaev appeared in Gorky State University in 1946 as a mature man that had studied in the school of the famous Russian chemist Professor Vladimir Nikolayevich Ipatiev (Leningrad Technological Institute, Petersburg), of Professor Georg Wieland (Germany), and after that in survival school in radium plant in Ukhta. He started his work in the capacity of the head of organic chemistry laboratory of the Scientific Research Institute at GSU, after which he took the baton of the head of organic chemistry subdepartment from the associate member of the USSR Academy of Sciences Professor Aleksandr Dmitrievich Petrov.

G.A. Razuvaev always was of opinion that it was possible to teach a student, to make him or her a self-sufficient thinking specialist, only by involving the student into research work, making it necessary to "stew" in a scientific research group of the world level. This idea was put into practice by him incessantly, in both his positions as the head of organic chemistry subdepartment (1946–1971) and the head of organic chemistry laboratory of the Scientific Research Chemistry Institute in GSU (from 1946). For a long time, from 1956 to 1962, Grigory Alekseyevich was the head of the Scientific Research Chemistry Institute; he initiated the scientific collaboration of organic chemists with physicochemists, polymer chemists, analytical chemists and other specialists in the institute, involving them in widening of the field of scientific development in the new branch of organometallic chemistry. The new round of widening the connection between academic activity of chemical department and research activity in synthesis and reactions of organometallic compounds began in 1963, when the Laboratory of Polymer Stabilization of the USSR Academy of Sciences had been established in Gorky city under the direction of G.A. Razuvaev. Later it became the basis of formation of Chemistry Institute of the USSR Academy of Sciences (1969), and later still – of Institute of Organometallic Chemistry of the Russian Academy of Sciences (1988). The lecturers of the organometallic chemistry subdepartment and the researches in organometallic chemistry of the laboratories in Chemistry Institute within GSU and the research institute of the Academy. From 2005 to the present the filial branch of the organic chemistry subdepartment of UNN carries out its activities in Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, under the direction of V.K. Cherkasov, the associate member of the Russian Academy of Sciences (Agreement dated 11.03.2005 between UNN and IOMC). In 2004 according to the order No. 2004-OD dated 02.12.2004 of UNN rector the base laboratory of coordination compounds of IOMC has been set up within the UNN chemistry department (the head of the laboratory is A.A. Trifonov, Doctor of Science (Chemistry), Professor).



Organometallic chemistry

Institute of Organometallic Chemistry regularly hosts "Razuvaev Readings" once in 3 years in the format of all-Russian scientific conferences with international participation, on a Volga motor ship. For a week the leading world and Russian scientists in organometallic chemistry gather to discuss the problems of synthesis, study, coordination chemistry of organometallic compounds, their application in catalysis, synthesis of polymers and advanced materials. Postgraduate students and young scientists have the opportunity to communicate with distinguished scientists, to arrange for study courses and cooperative investigations, to participate in competitions of young researchers.

Close relationships between the Chemistry Institute of the Academy and the chemical department have been of great help in organization of access to modern research equipment, without which it is impossible to prepare the graduation papers by undergraduate and postgraduate students to an accomplished standard. In the hard period of "equipment hunger" the instruments for NMR, EPR, X-ray investigation in Razuvaev IOMC were placed at the disposal of the faculty and the students for free. Equipping of the department by its own top-class instrumentation began in 2006, when the presidential program for priority development of universities "Education" started (2006–2007), and then it continued with the program "National Research University" from 2009.

Within the program "Russian Academic Excellence Project" in 2014 the laboratory "High-technology materials on the basis of functional polymers and metal complex compounds (UNN – IMOC)" was opened under the direction of associate member of the Russian Academy of Sciences D.F. Grishin, the head of subdepartment of petrochemistry and petrochemical synthesis; as well as the laboratory "Composite acrylate adhesives (UNN – IMOC – Kargin Polymer Research Institute)" under the direction of Professor V.A. Dodonov, the head of subdepartment of organic chemistry.

On terms of secondary employment, spare time work or in other forms many scientists were involved in research with the chemistry department students on the subject of chemistry of organometallic compounds: academician of the Russian Academy of Sciences G.A. Abakumov, associate members of the Academy G.A. Domrachev, V.K. Cherkasov, I.L. Fedyushkin, professors L.N. Zakharov, A.N. Egorochkin, M.N. Bochkarev, L.N. Bochkarev, B.B. Troitskiy, Yu.A. Kurskiy, A.A. Trifonov, M.P. Bubnov, A.G. Poddel'skiy, V.V. Semyonov, A.N. Kornev, A.V. Piskunov; the scientists of the Research Chemistry Institute of UNN: associate member of the Academy D.F. Grishin, professors I.V. Spirina, S.A. Bulgakova, N.N. Smirnova. That helped in improvement of education quality and ensured influx into student body.

Many organometallic chemists that consider themselves the disciples of Razuvaev school, have become the heads of subdepartments and laboratories of other higher education institutions of Nizhny Novgorod and Russia, they have always made efforts to continue the scientific collaboration with the University of Nizhny Novgorod. Among them there are doctors of science V.A. Yablokov (State Architectural Building University of Nizhny Novgorod), S.F. Zhiltsov (Minin State Pedagogical University of Nizhny Novgorod), V.N. Latyaeva, A.S. Gordetsov (State Medical Academy of Nizhny Novgorod), V.V. Sharutin (South Ural State University), E.S. Klimov (Ul'yanovsk State Technical University), Yu.A. Ol'dekop, N.A. Mayer (Physical Organic Chemistry Institute of the Belarus National Academy of Sciences, Minsk), N.S. Vyazankin (Organic Chemistry Institute of the Academy of Sciences, Irkutsk), M.M. Koton (Institute of Macromolecular Compounds of the Academy of Sciences, Saint Petersburg), V.S. Etlis (Kargin Polymer Chemistry and Technology Research Institute, Dzerzhinsk in Nizhny Novgorod region), etc.

After G.A. Razuvaev from 1971 to 2015 the head of the subdepartment of organic chemistry was Professor Viktor Alekseyevich Dodonov, D.Sc.(Chem.), Honored Science Worker of the Russian Federation, the full member of the Russian Academy of Engineering Sciences, Honorable Professor of UNN, Honored Worker of UNN, Fulbright professor (1996, 2001), Soros professor, who qualified 3 Doctors of Science, 27 Candidates of Science; he is an author of 40 patents and author's certificates, 450 scientific papers. From 2015 the position has been held by Aleksey Yurievich Fyodorov, D.Sc.(Chem.), Professor, the head of the Chemistry Thesis Board.

The organic chemistry subdepartment qualifies bachelors and masters majoring in "Chemistry", specialists in "Fundamental and applied chemistry", candidates and doctors of sciences in "Organic chemistry" and "Organometallic chemistry". Guideline courses in organic chemistry, organometallic chemistry and life-science chemistry. Special courses for specialists, masters and postgraduate students have been prepared: "Metal complex catalysis", "Application of organometallic compounds of transition

metals in organic synthesis", "Reactions of organoelemental compounds of non-transition metals with oxygen and peroxides". Joint Russian-French post-graduate studies are in practice.

Scientific research is carried out in the field of synthesis and study of structure and properties of organoelemental compounds of non-transition metals and peroxides, application of organometallic compounds in organic synthesis and catalysis, in production of biologically active substances and macromolecular compounds [1–7].

Lately, from 2006, the subdepartment has successfully been modernized and equipped with the modern instruments. All exhaust ventilation systems, the laboratories of student classes in organic chemistry, and a part of research laboratories have been repaired; costly equipment for physicochemical analysis of organic compounds has been established: IR-Fourier- and UV-spectrometers, as well as Shimadzu gas chromatographs, Knauer liquid chromatograph, NMR spectrometer Agilent DD2 400 MHz, CHNS analyzer Vario EL Cube (Germany). Various instruments for laboratory practical training and graduation work has been acquired, such as modern rotary evaporators, magnetic stirrers, electronic balances, ultrasonic baths, muffle furnaces and drying cabinets, thermostats.

Young lecturers and postgraduate students work as trainees in the best laboratories and centers in Moscow, Saint Petersburg, England, Germany, France, USA.

Every year the subdepartment of organic chemistry carries out research work in grants and commercial contracts for approximately 10 million rubles, 20–25 scientific papers are published in the leading Russian and foreign journals, 2–4 patents and "know-hows" are registered, 1–2 theses are defended.

Along with other colleagues in the subdepartment of organic chemistry and chemistry department, I keep the memories of academician G.A. Razuvaev as a great scientist, one of the founders of the Russian organometallic chemistry, who was an indispensable member of organizing committees of Russian national and international conferences, who excelled in plenary reports demonstrating the vigor of Nizhny-Novgorod school of organometallic and peroxidic chemists. In my student days I was lucky to attend a few of Razuvaev's lectures. For a lifetime I have remembered his regular and serious "rounds of scientific groups", when the academician visited his original subdepartment. It was so amazing and unusual, that we, the members of students' scientific society, along with the instructors, were inquired about powders and solutions of reaction products standing under an exhaust hood. He intently examined them through thick lenses of his spectacles, offered advice what to study in literature, and in passing he instructed our supervisor (associate professor T.G. Brilkina) to train students to be more orderly, not to let them draw skull and crossbones on weighing bottles with substances... He noticed everything, remembered everything, in a week he asked what was new in your work, passed a note with a reference to an interesting paper.

References

1. Sharutin V.V., Senchurin V.S. *Imennye reaktsii v khimii elementoorganicheskikh soedineniy* [Name Reactions in Chemistry of Organoelemental Compounds]. Chelyabinsk, South Ural St. Univ. Publ., 2011. 426 p. (in Russ.)
2. Razuvaev G.A., Gribov B.G., Domrachev G.A., Salamatin B.A. *Metallorganicheskie soedineniya v elektronike* [Organometallic Compounds in Electronics]. Moscow, Nauka Publ., 1972. 479 p. (in Russ.)
3. Nefedov O.M. *Vospominaniya ob akademike Grigorii Alekseeviche Razuvaeve* [Reminiscences about Academician Grigory Alekseyevich Razuvaev]. Moscow, Nauka Publ., 1992. 349 p. (in Russ.)
4. Petukhov G.G. *Laureat Leninskoy premii professor G.A. Razuvaev* [Laureate of Lenin Prize Professor G.A. Razuvaev] *Trudy po khimii i khimicheskoy tekhnologii* [Papers on Chemistry and Chemical Technology], 1958, vol. 1, pp. 439–444. (in Russ.)
5. Ol'dekop Yu.A., Mayer N.A. [To the 70th birthday and the 40th anniversary of scientific and pedagogical work]. *Russian Journal of General Chemistry*, 1966, vol. 36, iss. 2, pp. 3–6. (in Russ.)
6. Vasileyskaya N.S. Grigoriy Alekseevich Razuvaev [To the 80th birthday and the 50th anniversary of scientific and pedagogical work]. *Russian Journal of Organic Chemistry*, 1976, vol. 12, iss. 1, pp. 3–6. (in Russ.)
7. Tyutyunnik V.M. *Khimiki – laureaty Leninskoy premii* [Laureates of Lenin Prize in Chemistry]. Moscow, Znanie Publ., 1978. pp. 5–10. (in Russ.)

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1. Шарутин, В.В. Именные реакции в химии элементоорганических соединений / В.В. Шарутин, В.С. Сенчурин. – Челябинск: Издательский центр ЮУрГУ, 2011. – 426 с.
2. Металлорганические соединения в электронике / Г.А. Разуваев, Б.Г. Грибов, Г.А. Домрачев, Б.А. Саламатин. – М.: Наука, 1972. – 479 с.
3. Нефедов, О.М. Воспоминания об академике Григории Алексеевиче Разуваеве / О.М. Нефедов. – М.: Наука, 1992. – 349 с.
4. Петухов, Г.Г. Лауреат Ленинской премии профессор Г.А. Разуваев / Г.Г. Петухов // Труды по химии и химической технологии. – 1958. – Т. 1. – С. 439–444.
5. Ольдекоп, Ю.А. Григорий Алексеевич Разуваев (К 70-летию со дня рождения и 40-летию научной и педагогической деятельности) / Ю.А. Ольдекоп, Н.А. Майер // Журн. общ. химии. – 1966. – Т. 36. – Вып. 2. – С. 3–6.
6. Василейская, Н.С. Григорий Алексеевич Разуваев (К 80-летию со дня рождения и 50-летию научной и педагогической деятельности) / Н.С. Василейская // Журн. орг. химии. – 1976. – Т. 12. – Вып. 1. – С. 3–6.
7. Тютюнник, В.М. Химики – лауреаты Ленинской премии / В.М. Тютюнник. – М.: Знание, 1978. – С. 5–10.

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SOME REACTIONS OF *BIS*(CYCLOPENTADIENYL)DIFERROCENYL TITAN¹

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Reaction of *bis*(cyclopentadienyl)diferrocenyltitanium Cp_2TiFc_2 (**1**) with iodine (toluene, 20°C, 24 h) proceeds with formation of *bis*(cyclopentadienyl)titanium diiodide Cp_2TiI_2 (**2**) and diferrocenyl Fc-Fc (**3**); a byproduct of the reaction is the salt Fc-Fc·I₃ (**4**). Interaction of **1** with carbon monoxide (100 bar, benzene, 50 °C, 3 h) leads to the synthesis of diferrocenylketone (**5**) and *bis*(cyclopentadienyl) titanium dicarbonyl (**6**).

Keywords: *bis*(cyclopentadienyl)diferrocenyltitanium, reaction, iodine, carbonyl carbon.

Introduction

It is known that alkyl and aryl compounds of titanium are especially labile complexes, sensitive to heating and action of oxygen and atmospheric moisture [1]. Introduction of the ligands, stabilizing σ -bonds C–Ti, into the coordination sphere of titanium makes it possible to increase the stability of titanium complexes [2,3]. The most thermally stable of this series is *bis*(cyclopentadienyl)-diferrocenyltitanium Cp_2TiFc_2 (**1**), its decomposition temperature reaches 156 °C [3].

Note that complex **1** is one of only a few titanium compounds, for which high-temperature pyrolysis leads to formation of metallic titanium films [4], hence the investigation of complex **1** reactivity is undeniably urgent.

Experimental

Reaction of 1 with iodine. To the solution of 0.65 g (1.20 mmol) complex **1** in 50 mL toluene at 20 °C 0.30 g (1.20 mmol) iodine in 20 mL toluene was added. In 24 h the solvent was removed, the residue was sequentially extracted by hexane and benzene. From benzene solution 0.31 g (0.60 mmol) complex **1** and 0.22 g (0.51 mmol) *bis*(cyclopentadienyl)titanium (**2**, decomposition temperature 314 °C) were isolated by fractional crystallization. Found, %: C 27.11, H 2.38, I 57.86. Calculated for $\text{C}_{10}\text{H}_{10}\text{I}_2\text{Ti}$, %: C 27.77, H 2.31, I 58.79. After evaporation of hexane extracts diferrocenyl was isolated (**3**, m.p. 231°C). Found, %: C 64.90, H 4.79, Fe 29.55. Calculated for $\text{C}_{20}\text{H}_{18}\text{Fe}_2$, %: C 64.86, H 4.86, Fe 30.28. The residue, insoluble in benzene (0.07 g) constituted a black crystal substance with decomposition temperature 172°C. Found, %: C 32.69, H 2.75, I 49.89. Calculated for $\text{C}_{20}\text{H}_{18}\text{Fe}_2\text{I}_3$, %: C 31.98, H 2.27, I 50.73.

Reaction of 1 with carbon monoxide. The sample 0.65 g (1.20 mmol) complex **1** in 15 mL benzene was placed into 50 mL autoclave. The pressure of carbon monoxide was increased up to 100 atm, the temperature was 50°C. After agitation of the reaction mixture during 3 h it was cooled, the pressure was released, 0.15 g (1.20 mmol) iodine was added in order to confirm the formation of *bis*(cyclopentadienyl)titanium dicarbonyl. Liberation of 45 mL (2.00 mol) carbon monoxide was observed. The reaction mixture was sequentially extracted by benzene and chloroform. After evaporation of benzene 0.35 g (0.88 mmol) diferrocenylketone was obtained (**3**, m.p. 210 °C). Found, %: C 63.02, H 4.73, Fe 28.07. Calculated for $\text{C}_{21}\text{H}_{18}\text{Fe}_2\text{O}$, %: C 63.29, H 4.52, Fe 28.14. Chloroform extracts were used to isolate 0.46 g (1.06 mmol) complex **2**.

Results and Discussion

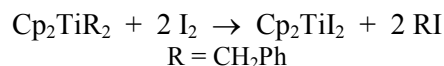
Synthesizing a number of ferrocenyl compounds of transition metals has revealed the research objects in chemistry of metallocenes containing metal-ferrocenyl σ -bonds [4]. Studying the peculiarities of their structure has helped to determine the character of the abovementioned bond that is of π -character to

¹ The research was carried out by V.V. Sharutin under supervision of academician G.A. Razuvaev in 1982.

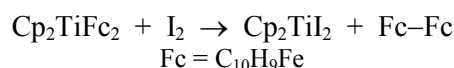
Organometallic chemistry

some extent [4,5], so it is important to study reactivity of ferrocenyl compounds on the example of *bis*(cyclopentadienyl)diferrocenylyltitanium (**1**) reactions with iodine and carbon monoxide.

It is known that the action of halogenes (Hal_2) on many organometallic compounds containing M-R σ -bonds leads to bond-breaking with formation of RHal and metal halogenides, *e.g.* in the reaction of Cp_2TiR_2 with iodine [6]:

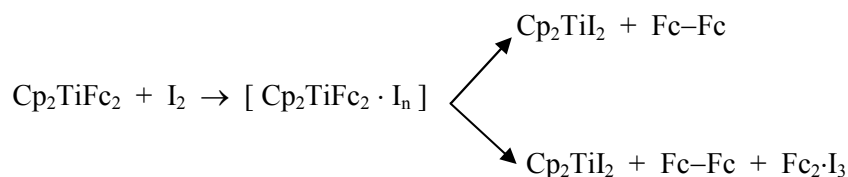


The interaction of **1** with iodine, studied by us, proceeds in somewhat different way, which obviously points at the reaction direction being governed by the kind of σ -bonded ligand at the titanium atom. Thus, apart from the initial complex **1** isolated from the reaction mixture, titanocene diiodide and diferrocenyl have been identified:



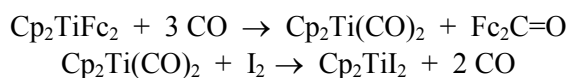
Besides, a minor amount of diferricinium salt $\text{Fc}_2\cdot\text{I}_3$ has been separated from the reaction mixture. Its presence among the reaction products suggests the direct participation of the oxidized form of ferrocenyl ligand in the process course, as it was earlier shown that at the same conditions iodine and diferrocenyl, when taken separately, did not react with each other [4].

Increase of percent yield for diferricinium salt $\text{Fc}_2\cdot\text{I}_3$ at excess amount of iodine in this reaction, as well as the familiar property of ferrocene treated with iodine to produce compounds $\text{FcH}\cdot\text{I}_n$ ($n = 3-10$), speaks for intermediate complex of *bis*(cyclopentadienyl)diferrocenylyltitanium with iodine, which decomposes next, according to the scheme:



As far as is known, the interaction of *bis*(cyclopentadienyl)diphenyltitanium with carbon dioxide (toluene, 80°C , 1 atm) is accompanied by elimination of benzene and formation of titanocyclic compound [7,8], therefore it is of interest to investigate how such a titanium complex with σ -bonded ferrocenyl ligands reacts with carbon dioxide.

We have found that at the abovementioned conditions complex **1** does not react with carbon dioxide. Increase of reaction temperature up to 160°C is accompanied by removal of σ -bonded ferrocenyl ligands in the form of ferrocene and by breakdown of the initial biscyclopentadienyl structure into titanium-containing remainder with the empirical formula « $\text{C}_{10}\text{H}_8\text{Ti}$ ». At the same time the interaction of *bis*(cyclopentadienyl)diferrocenylyltitanium with carbon monoxide (benzene, 100 atm, 50°C , 3 h) leads to the synthesis of diferrocenylketone and titanocene dicarbonyl, the presence of which has been proved by chemical method:



Conclusions

Thus, the nature of the ligands, σ -bonded with the central atom in titanium complexes of the general formula Cp_2TiR_2 ($\text{R}=\text{Fc}$, Ph), determines the scheme of their interaction with iodine and carbon oxides.

References

1. Nesmeyanov A.N. *Metody elementoorganicheskoy khimii. Podgruppy medi, skandiya, titana, vanadiya, khroma, margantsa* [Methods of Organoelemental Chemistry. Copper, Scandium, Titanium, Vanadium, Chromium, Manganese Groups]. Moscow, Nauka Publ., 1974. 470 p. (in Russ.)
2. Burger H., Kluess C. Titan-stickstoff-verbindungen. XVII. σ -(Ferrocenyl)-titan-dialkylamide. *J. Organometal. Chem.*, 1973, vol. 56, pp. 269–277. doi:10.1016/S0022-328X(00)89975-1
3. Razuvaev G.A., Domrachev G.A., Sharutin V.V., Suvorova O.N. Ferrocenyl Derivatives of Dicyclopentadienyltitanium, -Zirconium and -Hafnium. *J. Organometal. Chem.*, 1977, vol. 141, pp. 313–317. DOI: doi:10.1016/S0022-328X(00)90854-4
4. Sharutin V.V. *Ferrotsenil'nye i tsimantrenil'nye soedineniya metallov IV-V grupp*: Diss. kand. khim. nauk [Ferrocenyl and Cymantrenyl Compounds of Metals of Groups IV-V. Cand. Sci. Diss.]. Gorky, 1982. 112 p.
5. Zakharov L.N., Struchkov Yu.T., Sharutin V.V., Suvorova O.N. Diferrocenyltitanocene, $C_{30}H_{28}Fe_2Ti$. *Cryst. Struct. Comm.*, 1979, vol. 8, pp. 439–444.
6. Razuvaev G.A., Latyaeva V.N., Vyshinskaya L.I. [Benzyl Derivative of Titanocene]. *Dokl. AN SSSR* [Proceedings of the USSR Academy of Sciences], 1969, vol. 189, pp. 103–104. (in Russ.)
7. Kolomnikov I.S., Lobeveva T.S., Gorbachevskaya V.V., Aleksandrov G.G., Struchkov Yu.T., Vol'pin M.E. Reaction of Carbon Dioxide with Diphenyltitanocene and X-ray Crystal Structure of the Product. *J. Chem. Soc. D*, 1971, pp. 972–973. DOI: 10.1039/C29710000972
8. Sharutin V.V., Senchurin V.S. *Imennye reaktsii v khimii elementoorganicheskikh soedineniy* [Name Reactions in Chemistry of Organoelemental Compounds]. Chelyabinsk, South Ural St. Univ. Publ., 2011. 426 p. (in Russ.)

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**НЕКОТОРЫЕ РЕАКЦИИ
БИС(ЦИКЛОПЕНТАДИЕНИЛ)ДИФЕРОЦЕНИЛТИТАНА¹****Г.А. Разуваев, В.В. Шарутин²**² Южно-Уральский государственный университет, г. Челябинск

Взаимодействие бис(циклопентадиенил)диферроценилтитана Cr_2TiFe_2 (1) с иодом (толуол, 20 °С, 24 ч) протекает с образованием диодида бис(циклопентадиенил)титана Cr_2TiI_2 (2) и диферроценила $Fe-Fe$ (3); побочным продуктом реакции является соль $Fe-Fe-I_3$ (4). Взаимодействие 1 с оксидом углерода (100 атм, бензол, 50 °С, 3 ч) приводит к синтезу диферроценилкетона (5) и дикарбонила бис(циклопентадиенил)титана (6).

Ключевые слова: бис(циклопентадиенил)диферроценилтитан, реакция, иод, карбонил углерода.

Литература

1. Несмеянов, А.Н. Методы элементоорганической химии. Подгруппы меди, скандия, титана, ванадия, хрома, марганца / А.Н. Несмеянов. – М.: Наука, 1974. – 470 с.
2. Burger, H. Titan-stickstoff-verbindungen. XVII. σ -(Ferrocenyl)-titan-dialkylamide / H. Burger, C. Kluess // *J. Organometal. Chem.* – 1973. – V. 56, № 2. – P. 269–277.

¹ Исследования проводились В.В. Шарутиным под руководством акад. Г.А. Разуваева в 1982 г.

Organometallic chemistry

3. Ferrocenyl derivatives of dicyclopentadienyltitanium, -zirconium and -hafnium / G.A. Razuvaev, G.A. Domrachev, V.V. Sharutin, O.N. Suvorova // *J. Organometal. Chem.* – 1977. – V. 141, № 3. – P. 313–317.
4. Шарутин, В.В. Ферроценильные и цимантренильные соединения металлов IV-V групп: дисс. ... канд. хим. наук / В.В. Шарутин. – Горький, 1982. – 112 с.
5. Diferrocenyltitanocene, $C_{30}H_{28}Fe_2Ti$ / L.N. Zakharov, Yu.T. Struchkov, V.V. Sharutin, O.N. Suvorova // *Cryst. Struct. Comm.* – 1979. – V. 8. – P. 439–444.
6. Разуваев, Г.А. Бензильное производное титаноцена / Г.А. Разуваев, В.Н. Латяева, Л.И. Вышинская // *Докл. АН СССР.* – 1969. – Т. 189, № 1. – С. 103–104.
7. Reaction of carbon dioxide with diphenyltitanocene and X-ray crystal structure of the product / I.S. Kolomnikov, T.S. Lobeeva, V.V. Gorbachevskaya et al // *Chem. Comm.* – 1971. – № 16. – P. 972–973.
8. Шарутин, В.В. Именные реакции в химии элементоорганических соединений / В.В. Шарутин, В.С. Сенчурин. – Челябинск: Издательский центр ЮУрГУ, 2011. – 426 с.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Razuvaev, G.A. Some reactions of bis(cyclopentadienyl)diferrocenyltitan / G.A. Razuvaev, V.V. Sharutin // *Вестник ЮУрГУ. Серия «Химия».* – 2015. – Т. 7, № 4. – С. 9–12. DOI: 10.14529/chem150401

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SYNTHESIS AND STRUCTURE OF OSMIUM COMPLEX $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$ V.V. Sharutin, vvsharutin@rambler.ruO.K. Sharutina, sharutinao@mail.ruV.S. Senchurin, senvl@rambler.ru

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Tetraphenylphosphonium hexabromoosmate, $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$ (**1**), has been structurally characterized after synthesis by interaction of sodium hexabromoosmate with tetraphenylphosphonium bromide in dimethyl sulfoxide. The phosphorus atoms of $[\text{Ph}_4\text{P}]^+$ cations have distorted tetrahedral coordination geometry (CPC angles are $106.23(11)^\circ$ – $113.23(10)^\circ$), the P–C bond lengths are 1.791(2)–1.801(2) Å. In octahedral $[\text{OsBr}_6]^{2-}$ anions the Os–Br bond lengths equal 2.4752(2)–2.5020(3) Å, *trans*-BrOsBr angles are 180° .

Keywords: sodium hexabromoosmate, tetraphenylphosphonium bromide, dimethyl sulfoxide, complex $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$, crystal structure, X-ray diffraction analysis.

Introduction

Complexes containing $[\text{OsBr}_6]^{2-}$ anions are some of the least structurally characterized ionic osmium complexes [1]; among them there is only one complex with phosphonium cations, $[\text{Ph}_3\text{PH}]^+_2[\text{OsBr}_6]^{2-}$ [2].

In the present paper the synthesis and structure of osmium complex $[\text{Ph}_4\text{P}]^+_2[\text{OsBr}_6]^{2-}$ (**1**) has been described.

Experimental

Synthesis of $[\text{Ph}_4\text{P}]^+_2[\text{OsBr}_6]^{2-}$ (1**).** A mixture of 0.035 g (0.08 mmol) of tetraphenylphosphonium bromide and 0.030 g (0.04 mmol) of sodium hexabromoosmate was dissolved by stirring in 2 mL of dimethyl sulfoxide. After evaporation of the solvent, formation of dark brown crystals was observed; they were filtered off and dried. 0.046 g (82%) of the complex was obtained, m.p. 320°C . IR (ν , cm^{-1}): 3053, 1583, 1482, 1437, 1313, 1186, 1107, 1025, 995, 761, 752, 721, 690, 663, 531, 522. Found, %: C 42.49, H 3.06. Anal. calc. for $\text{C}_{48}\text{H}_{40}\text{P}_2\text{Br}_6\text{Os}$ ($M = 1348.37$), %: C 42.74, H 2.97.

IR-spectrum was recorded on a Bruker Tensor 27 IR spectrometer in KBr pellet.

The X-ray diffraction experiment for crystal **1** was carried out on a Bruker D8 Quest diffractometer (Mo K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). Data collection, their editing, and refinement of the unit cell parameters, as well as accounting for absorption, were carried out using the *SMART* and *SAINT-Plus* programs [3]. All calculations for structure determination and refinement were carried out using the *SHELXL/PC* program [4]. Structure **1** was determined by the direct method and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms. The main crystallographic data and structure refinement details are given in Table 1. The main bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (№ 1000138; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Table 1
Crystallographic data, the experimental and structure refinement parameters for compound **1**

Parameter	Value
Formula	$\text{C}_{48}\text{H}_{40}\text{P}_2\text{Br}_6\text{Os}$
M	1348.37
T , K	296(2)
Crystal system	Triclinic
Space group	P-1

Parameter	Value
<i>a</i> , Å	10.2879(4)
<i>b</i> , Å	10.5331(4)
<i>c</i> , Å	12.1824(5)
<i>α</i> , deg	92.7640(10)
<i>β</i> , deg	99.9850(10)
<i>γ</i> , deg	116.3110(10)
<i>V</i> , Å ³	1153.68(8)
<i>Z</i>	1
<i>ρ</i> (calc.), g/cm ³	1.941
<i>μ</i> , mm ⁻¹	8.061
<i>F</i> (000)	644.0
Crystal size, mm	0.32 × 0.26 × 0.13
θ Range of data collection, deg	5.92 – 52.86
Range of refraction indices	-12 ≤ <i>h</i> ≤ 12, -13 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 15
Measured reflections	36441
Independent reflections	4730 (<i>R</i> _{int} = 0.0245)
Refinement variables	259
<i>GOOF</i>	1.105
<i>R</i> factors for <i>F</i> ² > 2σ(<i>F</i> ²)	<i>R</i> ₁ = 0.0171, <i>wR</i> ₂ = 0.0416
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.0195, <i>wR</i> ₂ = 0.0426
Residual electron density (min/max), e/Å ³	0.35/-0.66

Table 2

Selected bond lengths (*d*) and bond angles (*ω*) in the structure of compound 1

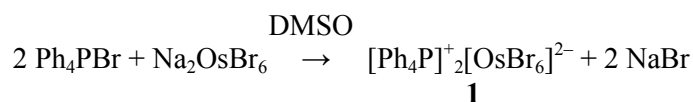
Bond	<i>d</i> , Å	Angle	<i>ω</i> , deg
Os(1)–Br(1 ¹)	2.4985(2)	Br(1 ¹)Os(1)Br1	180.0
Os(1)–Br(1)	2.4986(2)	Br(2)Os(1)Br1	91.620(8)
Os(1)–Br(2)	2.4752(2)	Br(2 ¹)Os(1)Br1	88.380(8)
Os(1)–Br(3)	2.5019(3)	C(1)P(1)C31	106.23(11)
Os(1)–Br(3 ¹)	2.5020(3)	C(1)P(1)C11	109.65(11)
P(1)–C(1)	1.798(2)	C(31)P(1)C11	109.57(11)
P(1)–C(31)	1.800(2)	C(21)P(1)C1	113.23(10)
P(1)–C(21)	1.791(2)	C(21)P(1)C31	108.47(10)
P(1)–C(11)	1.801(2)	C(21)P(1)C11	109.60(11)

Symmetry transformation: ¹-*x*, 1-*y*, 1-*z*

Results and Discussion

It is known that the synthesis of osmium complex [Ph₃PH]⁺₂[OsBr₆]²⁻ was carried out by consecutive addition of triphenylphosphine, glacial acetic acid and acetic anhydride to the dichloromethane solution of tetrabutylammonium hexabromoosmate, and heating of the reaction mixture for 3 days at 55–60 °C, with the yield equaling 29% [2].

We have ascertained that the reaction of sodium hexabromoosmate with tetraphenylphosphonium bromide in dimethyl sulfoxide leads to formation of air-stable dark brown crystals of tetraphenylphosphonium hexabromoosmate (**1**), isolated from the reaction mixture with the yield equaling 82 %:



According to the X-ray diffraction data, phosphorus atoms in tetraphenylphosphonium cations have slightly distorted tetrahedral coordination geometry: CPC angles lie within the range $106.23(11)^\circ$ – $113.23(10)^\circ$, P–C distances are 1.791(2)–1.801(2) Å (Fig. 1).

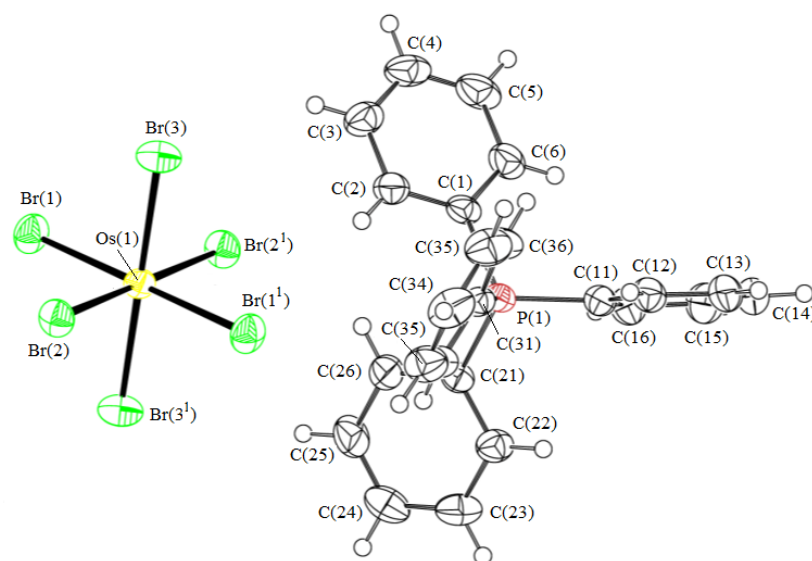


Fig. 1. Structure of complex 1

In centrosymmetric octahedral $[OsBr_6]^{2-}$ anions, the Os–Br bond lengths equal 2.4752(2)–2.5020(3) Å, *trans*-BrOsBr angles are 180° . Two tetraphenylphosphonium cations are bonded with hexabromoosmate anion by intermolecular H···Br hydrogen bonds (2.90 and 3.01 Å) (Fig. 2).

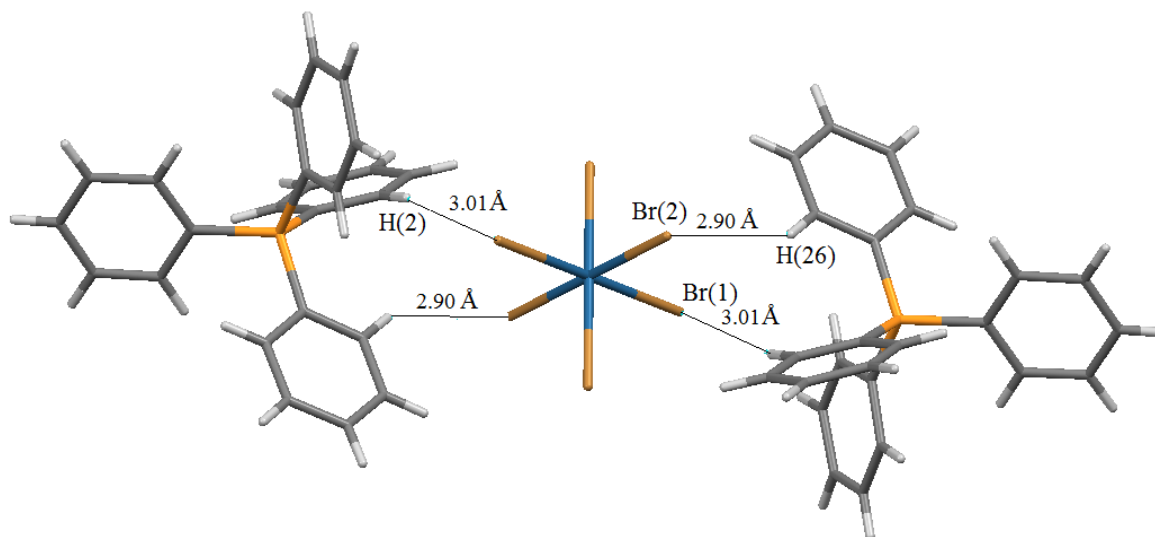


Fig. 2. The system of hydrogen bonds in the crystal of complex 1

Conclusions

Thus, the osmium complex with the tetrahedral tetraphenylphosphonium cation and the centrosymmetric octahedral Os-,Br-containing $[OsBr_6]^{2-}$ anion has been synthesized and structurally characterized for the first time. Formation of crystal structure occurs due to intermolecular H···Br hydrogen bonds between tetraphenylphosphonium cations and hexabromoosmate anions.

References

1. Cambridge Crystallographic Database. Release 2015. Cambridge.
2. Robinson P.D., Hinckley C.C., Matusz M., Kibala P.A. Acta Cryst. 1988. Vol. C44. P. 619–621.
3. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
4. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.

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СИНТЕЗ И СТРОЕНИЕ КОМПЛЕКСА ОСМИЯ $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$

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Взаимодействием гексабромосмата натрия с бромидом тетрафенилфосфония в диметилсульфоксиде синтезирован и структурно охарактеризован гексабромосмат тетрафенилфосфония $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$ (I). Атомы фосфора в катионах $[\text{Ph}_4\text{P}]^+$ имеют искаженную тетраэдрическую координацию (углы CPC $106.23(11)^\circ$ – $113.23(10)^\circ$), расстояния P–C составляют $1.791(2)$ – $1.801(2)$ Å. В октаэдрических анионах $[\text{OsBr}_6]^{2-}$ длины связей Os–Br равны $2.4752(2)$ – $2.5020(3)$ Å, углы *транс*-BrOsBr составляют 180° .

Ключевые слова: гексабромосмат натрия, бромид тетрафенилфосфония, диметилсульфоксид, комплекс $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$, структура, рентгеноструктурный анализ.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Sharutin, V.V. Synthesis and structure of osmium complex $[\text{Ph}_4\text{P}]_2[\text{OsBr}_6]$ / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 13–16. DOI: 10.14529/chem150402

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INTERACTION OF PENTAPHENYLANTIMONY WITH ACETYLENEDICARBOXYLIC ACID. MOLECULAR STRUCTURE OF BIS(TETRAPHENYLANTIMONY) ACETYLENEDICARBOXILATE

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Bis(tetraphenylantimony) acetylenedicarboxilate (1) has been synthesized by the interaction of pentaphenylantimony with acetylenedicarboxylic acid (mole ratio 2:1 or 1:1) in toluene. In molecule 1 the acid anion has the bridging role and bonds Ph₄Sb fragments. The antimony atoms have distorted trigonal bipyramidal coordination with the oxygen atom in the axial position. The Sb–O bond lengths are 2.287(4) and 2.389(4) Å, the Sb–C bond lengths are 2.110(7)–2.179(6) Å and 2.108(6)–2.165(6) Å.

Keywords: pentaphenylantimony, acetylenedicarboxylic acid, bis(tetraphenylantimony) acetylenedicarboxilate, molecular structure, X-ray diffraction analysis.

Introduction

It is known that the interaction of pentaarylantimony with dicarboxylic acid can give two types of compounds: acidic tetraarylantimony carboxilates and *bis*(tetraarylantimony) carboxilates [1–4]. According to the X-ray diffraction data, the coordination of antimony atoms in these types of molecules is significantly different. In the first case there is a tendency of the Ar₄Sb fragment to the transformation into the tetrahedric configuration, which is accompanied by increase of the distance between the antimony atom and the oxygen atom of the monodentate carboxylic ligand, which has the bond of coordinating character [1–3].

In binuclear *bis*(tetraarylantimony) carboxilates the antimony atom has a slightly distorted trigonal bipyramidal coordination [SbC₄O]. As a rule, the bridging carboxylic ligand has anisobidentate type of coordination caused by intramolecular interactions Sb···O=C between the antimony atoms and carbonyl oxygen atoms [2, 4–6]. Only oxalate ligand is coordinated to the antimony atom almost symmetrically, thus the antimony atom coordination transforms into the octahedral one [7].

In the continuation of our research of organoantimony dicarboxylic acid derivatives the reactions of pentaphenylantimony with acetylenedicarboxylic acid have been studied. The product structure has been determined by the X-ray diffraction analysis.

Experimental

Interaction of pentaphenylantimony with acetylenedicarboxylic acid. A) A mixture of 0.200 g (0.394 mmol) of pentaphenylantimony and 0.022 g (0.197 mmol) of acetylenedicarboxylic acid in 5 mL of toluene was kept in a sealed glass ampoule at room temperature for 24 h. The solution was concentrated, the crystals were filtered off and dried. The substance was isolated as 0.173 g (90 %) of colorless crystals **1** with $T_{\text{dec}} = 178$ °C. Found, %: C 64.09; H 4.23. For C₅₂H₄₀O₄Sb₂, anal. calcd, %: C 64.20; H 4.11. IR spectrum (ν , cm⁻¹): 3401, 3057, 2989, 1632, 1612, 1577, 1479, 1435, 1389, 1322, 1289, 1184, 1158, 1067, 1021, 996, 774, 731, 691, 670, 460.

B) A mixture of 0.200 g (0.394 mmol) of pentaphenylantimony and 0.044 g (0.394 mmol) of acetylenedicarboxylic acid in 5 mL of toluene was heated in a sealed glass ampoule in a boiling water bath for 15 min. Large crystals of *bis*(tetraphenylantimony) carbonate with $T_{\text{m}} = 234$ °C were observed on the ampoule walls during cooling. IR spectrum (ν , cm⁻¹): 3050, 1577, 1472, 1429, 1382, 1332, 1304, 1264, 1186, 1157, 1067, 1021, 997, 830, 730, 691, 653, 457.

The supernatant toluene solution was concentrated, the crystals were filtered off and dried. The substance was isolated as 0.149 g (76 %) of colorless crystals of tetraphenylantimony propiolate with

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$T_m = 174$ °C (with decomposition). Found, (%): C 64.81; H 4.29. For $C_{27}H_{21}O_2Sb$, anal. calcd, (%): C 64.96; H 4.21. IR spectrum (ν , cm^{-1}): 3277, 3053, 3010, 2990, 2917, 2591, 2361, 2178, 2091, 1967, 1885, 1819, 1621, 1575, 1562, 1477, 1433, 1377, 1333, 1301, 1187, 1158, 1070, 1057, 1020, 997, 883, 782, 737, 693, 658, 643, 601, 586, 462, 447.

IR spectra were recorded in KBr pellets on the IR Fourier-transform spectrometer Bruker Tensor 27.

The X-ray diffraction analyses of crystal **1** was performed on the Bruker D8 Quest diffractometer (Mo K_α -radiation, $\lambda = 0.71073$ Å, graphite monochromator). The data collection and editing as well as the refinement of unit cell parameters and the absorption accounting were carried out using SMART and SAINT *Plus* program packages [8]. All calculations for the structure determination and refinement were carried out using the SHELXTL/PC [9] and OLEX2 [10] programs packages. The structures were determined by the direct method and refined by least-squares method calculations in anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement results for compounds **I** and **II** are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 994821; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Table 1

Crystallographic data and the experimental and structure refinement parameters for compound 1

Parameter	Value
Empirical formula	$C_{52}H_{40}O_4Sb_2$
Formula weight	972.34
T , K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a , Å	10.0115(4)
b , Å	21.1868(8)
c , Å	22.6148(9)
α , deg	90.00
β , deg	91.530(2)
γ , deg	90.00
V , Å ³	4795.2(3)
Z	4
ρ (calcd.), g/cm ³	1.347
μ , mm ⁻¹	1.167
$F(000)$	1944.0
Crystal size, mm	0.92×0.18×0.09
2 θ Range of data collection, deg	6.64 – 46.62°
Range of refraction indices	$-9 \leq h \leq 11$, $-23 \leq k \leq 22$, $-25 \leq l \leq 23$
Measured reflections	12802
Independent reflections	6525
R_{int}	0.0282
Refinement variables	523
<i>GOOF</i>	1.095
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0401$, $wR_2 = 0.1132$
R factors for all reflections	$R_1 = 0.0576$, $wR_2 = 0.1226$
Residual electron density (min/max), e/Å ³	1.02/−0.41

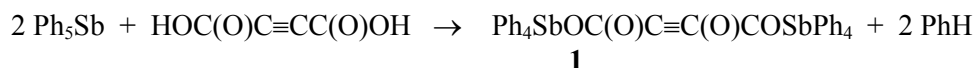
Table 2

Selected bond lengths and bond angles in the structure of compound 1

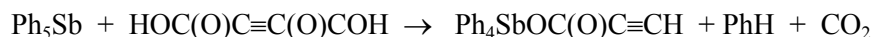
Bond	<i>d</i> , Å	Angle	ω, deg
Sb(1)–O(1)	2.287(4)	C(1)Sb(1)O(1)	84.7(2)
Sb(1)–C(1)	2.110(7)	C(1)Sb(1)C(31)	96.7(2)
Sb(1)–C(31)	2.179(6)	C(1)Sb(1)C(11)	114.6(2)
Sb(1)–C(11)	2.118(6)	C(1)Sb(1)C(21)	124.6(2)
Sb(1)–C(21)	2.133(6)	C(31)Sb(1)O(1)	175.20(18)
Sb(2)–O(3)	2.389(4)	C(11)Sb(1)O(1)	81.91(18)
Sb(2)–C(51)	2.108(6)	C(11)Sb(1)C(31)	93.3(2)
Sb(2)–C(41)	2.119(6)	C(11)Sb(1)C(21)	117.8(2)
Sb(2)–C(61)	2.102(6)	C(21)Sb(1)O(1)	85.49(19)
Sb(2)–C(71)	2.165(6)	C(21)Sb(1)C(31)	97.3(2)
C(7)–O(1)	1.293(7)	C(51)Sb(2)O(3)	89.54(19)
C(7)–O(2)	1.212(7)	C(51)Sb(2)C(41)	119.6(2)
C(10)–O(3)	1.255(7)	C(51)Sb(2)C(71)	94.5(2)
C(10)–O(4)	1.224(7)	C(41)Sb(2)O(3)	82.4(2)
Sb(1)⋯O(2)	3.297(6)	C(41)Sb(2)C(71)	98.5(2)

Results and Discussion

We have found that the reaction of pentaphenylantimony with dicarboxylic acid (mole ratio 2:1 or 1:1) proceeds in toluene solution at room temperature with the substitution of hydrogen atoms in two carboxyl groups and the formation of *bis*(tetraphenylantimony) acetylenedicarboxylate (**1**). The yield of compound **1** is up to 90%:



Only one carboxyl group reacts with pentaphenylantimony after short-duration heating of equimolar quantities in toluene solution. The second group is decarboxylated in this case.



The yield of tetraphenylantimony propiolate isolated from the reaction mixture is 76%. Its IR spectrum, melting point and parameters of crystal cell correspond to the similar characteristics of the compound synthesized from pentaphenylantimony and propiolic acid [11]. *Bis*(tetraphenylantimony) carbonate ($\text{Ph}_4\text{Sb})_2\text{CO}_3$ is the second product of this reaction with the yield about 10%. This product has been identified by its melting point and IR spectrum. As shown by X-ray diffraction, the obtained *bis*(tetraphenylantimony) carbonate has triclinic modification described in the paper [12].

According to the X-ray diffraction data, the acid anion in molecule **1** has the bridging role and bonds Ph_4Sb fragments. The Sb(1,2) atoms have distorted trigonal bipyramidal coordination with carboxylate and phenyl ligands in the axial positions (Fig. 1).

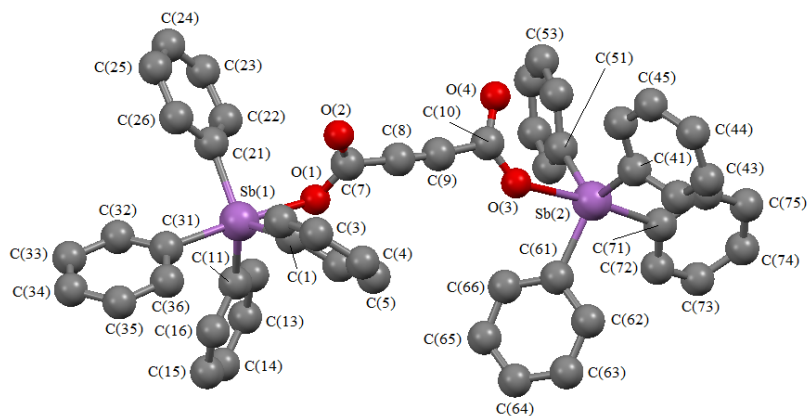


Fig. 1. The structure of compound 1

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The axial angles OSb(1,2)C are equal to $175.2(2)^\circ$ and $174.7(2)^\circ$. The sums of the CSbC angles in the equatorial planes are $357.0(2)^\circ$ and $356.2(2)^\circ$, respectively. There is deviation of Sb(1,2) atoms from the equatorial plane towards the carbon atom in the axial position up to $0.218(2)$ Å and $0.237(2)$ Å. The angles between the axial and equatorial bonds of OSb(1,2)C are less than 90° ($81.9(2)$ – $85.5(2)^\circ$, ($78.8(2)$ – $89.5(2)^\circ$), for CSb(1,2)C they are more than 90° ($93.3(2)$ – $97.3(2)^\circ$, $94.5(2)$ – $98.5(2)^\circ$). The length of Sb(1,2)–C equatorial bonds changes in the ranges $2.110(7)$ – $2.133(6)$ Å, $2.108(6)$ – $2.119(6)$ Å. The axial distances Sb(1,2)–C ($2.179(6)$ Å and $2.165(6)$ Å) are greater than equatorial ones. The Sb(1)–O(1) ($2.287(4)$ Å) and Sb(2)–O(3) ($2.389(4)$ Å) bonds are longer than the sum of covalent radii of antimony and oxygen (2.05 Å [13]). As one would expect, the C(7)–O(1) ($1.293(7)$ Å), C(10)–O(3) ($1.255(7)$ Å) distances in the carboxyl group are greater than the C(7)–O(2) ($1.212(7)$ Å) and C(10)–O(4) ($1.224(7)$ Å) distances. In structure **1** bidentate properties of the carboxylate ligands almost do not appear. The intramolecular Sb(1)···O(2) and Sb(2)···O(4) distances are $3.297(6)$ and $3.794(6)$ Å, while the sum of antimony and oxygen van der Waals radii equals 3.70 Å [13]. For comparison: in the *bis*(tetraphenylantimony) maleinate molecule the Sb–O and Sb···O distances equal 2.206 , 2.218 Å and 3.236 , 3.259 Å [2].

The torsion angle in the dicarboxylic acid anion O(2)C(7)C(10)O(4) is $-50.3(7)^\circ$. Acetylene fragment has almost linear structure: the angles C(7)C(8)C(9) and C(10)C(9)C(8) are $177.8(7)^\circ$ and $175.2(7)^\circ$, the distance C(8)–C(9) ($1.177(9)$ Å) corresponds to the triple bond.

The structural organization of the crystal is formed with the participation of weak hydrogen bonds of (Ph)C–H···O(=C) type.

Conclusions

Thus, the interaction between pentaphenylantimony with acetylenedicarboxylic acid has the specific feature: under mild conditions both carboxylic groups react. We did not succeed in isolation of acidic tetraphenylantimony carboxylate. Even short-duration heating of reaction mixture is accompanied by the decarboxylation of a carboxyl group in the acid and the formation of tetraphenylantimony propiolate.

In the *bis*(tetraphenylantimony) acetylenedicarboxylate molecule the carboxylate groups are characterized by the monodentate type of the bond.

References

1. Sharutin V.V., Sharutina O.K., Mel'nikova I.G., Fukin G.K., Zaharov L.N., Janovskij A.I., Struchkov Ju.T. Synthesis and Structure of Tetraphenylantimony Hydrogen Phthalate. *Russian Chemical Bulletin*. 1996, vol. 45, no. 8, pp. 1977–1980. DOI: 10.1007/bf01457791.
2. Sharutin V.V., Sharutina O.K., Pakusina A.P., Belsky V.K. Reactions of Pentaphenylantimony with Dicarboxylic Acids. *J. Organometal. Chem.* 1997, vol. 536-537, no. 1-2, pp. 87–92. DOI: 10.1016/s0022-328x(96)06463-7.
3. Sharutin V.V., Senchurin V.S., Sharutina O.K. Synthesis and Structure of Tetraphenylantimony Hydrogenmalonate. *Russian Journal of Inorganic Chemistry*, 2014, vol. 59, no. 2, pp. 115–118. DOI: 10.1134/S003602361402017X.
4. Sharutin V.V., Sharutina O.K. Bis(tetraphenylantimony) Succinate, Malate and Tartrate: Synthesis and Structures. *Russian Journal of Coordination Chemistry*, 2014, vol. 40, no. 9, pp. 643–647. DOI: 10.1134/S1070328414090073.
5. Sharutin V.V., Sharutina O.K., Senchurin V.S., Platonova T.P., Nasonova N.V., Pakusina A.P., Gerasimenko A.V., Sergienko S.S. μ -Oxo-bis(Tetraphenylantimony): Synthesis, Structure, and Reactions. *Russian Journal of Coordination Chemistry*, 2001, vol. 27, no. 9, pp. 669–675. DOI: 10.1023/a:1017909824029.
6. Sharutin V.V., Sharutina O.K., Bondar' E.A., Senchurin V.S., Pakusina A.P., Gatilov Ju.V., Adonin N.Ju., Starichenko V.F. Synthesis and Structure of Bis(tetraphenylantimony) Tetrafluorophthalate. *Russian Journal of General Chemistry*, 2002, vol. 72, no. 12, pp. 1920–1924. DOI: 10.1023/A:1023411228493.

7. Millington P.L., Sowerby D.B. Phenylantimony (V) Oxalates: Isolation and Crystal Structures of $[\text{SbPh}_4][\text{SbPh}_2(\text{ox})_2]$, $[\text{SbPh}_3(\text{OMe})_2]\text{ox}$ and $(\text{SbPh}_4)_2\text{ox}$. *J. Chem. Soc., Dalton Trans.*, 1992, no. 7, pp. 1199–1204.
8. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
10. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341. doi:10.1107/S0021889808042726.
11. Sharutin V.V., Sharutina O.K., Senchurin V.S. Tri- and Tetraphenylantimony Propiolates: Synthesis and Structures. *Russian Journal of Coordination Chemistry*, 2014, vol. 40, no. 2, pp. 109–114. DOI: 10.1134/S1070328414020109.
12. Ferguson G., Hawley D. M. The Crystal and Molecular Structure of μ -Carbonato-Bis(tetraphenylantimony): a System Containing Penta- and Hexacoordinated Antimony. *Acta Crystallogr.*, 1974, vol. 30B, no. 1, pp. 103–111.
13. Cordero B., Gomez V., Platero-Prats A.E., Reyes M., Echeverria J., Cremades E., Barragan F., Alvarez S. Covalent Radii revisited. *Dalton Trans.*, 2008, pp. 2832–2838. DOI: 10.1039/b801115j.

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ВЗАИМОДЕЙСТВИЕ ПЕНТАФЕНИЛСУРЬМЫ С АЦЕТИЛЕНДИКАРБОНОВОЙ КИСЛОТОЙ. МОЛЕКУЛЯРНАЯ СТРУКТУРА АЦЕТИЛЕНДИКАРБОКСИЛАТА БИС(ТЕТРАФЕНИЛСУРЬМЫ)

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Взаимодействием пентафенилсурьмы с ацетилендикарбоновой кислотой (2:1 или 1:1 мольн.) в толуоле получен ацетилендикарбоксилат бис(тетрафенилсурьмы) (1). В молекуле 1 остаток кислоты выполняет мостиковую функцию, соединяя фрагменты Ph_4Sb . Атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомом кислорода в аксиальном положении. Длина связей $\text{Sb}-\text{O}$ 2.287(4) и 2.389(4) Å, $\text{Sb}-\text{C}$ 2.110(7)–2.179(6) Å и 2.108(6)–2.165(6) Å.

Ключевые слова: пентафенилсурьма, ацетилендикарбоновая кислота, ацетилендикарбоксилат бис(тетрафенилсурьмы), молекулярная структура, рентгеноструктурный анализ.

Литература

1. Синтез и строение кислого фталата тетрафенилсурьмы / В.В. Шарутин, О.К. Шарутина, И.Г. Мельникова и др. // Известия Академии наук. Серия Химическая. – 1996. – Т. 8. – Вып. 10. – С. 2082–2085.
2. Reactions of Pentaphenylantimony with Dicarboxylic Acids / V.V. Sharutin, O.K. Sharutina, A.P. Pakusina et al. // *J. Organometal. Chem.* – 1997. – V. 536–537. – № 1–2. – P. 87–92. DOI: 10.1016/s0022-328x(96)06463-7.

3. Шарутин, В.В. Синтез и строение кислого малоната тетрафенилсурьмы / В.В. Шарутин, В.С. Сенчурин, О.К. Шарутина // Журн. неорган. химии. – 2014. – Т. 59. – № 2. – С. 247–250. DOI: 10.7868/S0044457X14020184.
4. Шарутин, В.В. Синтез и строение сукцината, малата и тартрата бис(тетрафенилсурьмы) / В.В. Шарутин, О.К. Шарутина // Корд. химия. – 2014. – Т. 40. – № 9. – С. 559–563. DOI: 10.7868/S0132344X14090072.
5. Синтез, строение и реакции μ -оксо-бис(тетрафенилсурьмы) / В.В. Шарутин, О.К. Шарутина, В.С. Сенчурин и др. // Корд. химия. – 2001. – Т. 27. – № 9. – С. 710–716.
6. Синтез и строение тетрафторфталата бис(тетрафенилсурьмы) / В.В. Шарутин, О.К. Шарутина, Е.А. Бондарь и др. // Журн. общ. химии. – 2002. – Т. 72. – № 12. – С. 2029–2032.
7. Millington, P.L. Phenylantimony (V) Oxalates: Isolation and Crystal Structures of $[\text{SbPh}_4][\text{SbPh}_2(\text{ox})_2]$, $[\text{SbPh}_3(\text{OMe})_2]\text{ox}$ and $(\text{SbPh}_4)_2\text{ox}$. / P.L. Millington, D.B. Sowerby // J. Chem. Soc., Dalton Trans. – 1992. – N. 7. – P. 1199–1204.
8. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
10. OLEX2: a Complete Structure Solution, Refinement and Analysis Program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341. DOI: 10.1107/S0021889808042726.
11. Шарутин, В.В. Синтез и строение пропиолатов три- и тетрафенилсурьмы / В.В. Шарутин, О.К. Шарутина, В.С. Сенчурин // Корд. химия. – 2014. – Т. 40. – № 2. – С. 108–112. DOI: 10.7868/S0132344X14020108.
12. Ferguson, G. The Crystal and Molecular Structure of μ -Carbonato-Bis(tetraphenylantimony): a System Containing Penta- and Hexacoordinated Antimony / G. Ferguson, D.M. Hawley // Acta Crystallogr. – 1974. – V. 30B. – N. 1. – P. 103–111.
13. Covalent Radii revisited / B. Cordero, V. Gomez, A.E. Platero-Prats et al. // Dalton Trans. – 2008. – P. 2832–2838. DOI: 10.1039/b801115j.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

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OXIDATION OF TRI(O-TOLYL)ANTIMONY BY *TERT*-BUTYL HYDROPEROXIDE. MOLECULAR STRUCTURES OF *BIS*[μ_2 -OXO- TRI(O-TOLYL)ANTIMONY] AND μ_2 -OXO-*BIS*[(*TERT*-BUTYLPEROXY)TRI(O-TOLYL)ANTIMONY]

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Tri(*o*-tolyl)antimony oxidation by equimolar amount of *tert*-butyl hydroperoxide in diethyl ether led to the formation of *bis*[μ_2 -oxo-tri(*o*-tolyl)antimony] (1). At the molar ratio of reactants 1:2 or 1:4 μ_2 -oxo-*bis*[(*tert*-butylperoxy)tri(*o*-tolyl)antimony] (2) has been formed. According to the X-ray analysis data, antimony atoms are in the trigonal bipyramidal coordination in molecules 1 and 2. The bond lengths Sb–O vary within the ranges 1.937(2)–2.078(2) Å (1) and 1.975(17)–2.216(15) Å (2).

Keywords: tri(ortho-tolyl)antimony, *tert*-butyl hydroperoxide, oxidation, *bis*[μ_2 -oxo-tri(*o*-tolyl)antimony], μ_2 -oxo-*bis*[(*tert*-butylperoxy)tri(*o*-tolyl)antimony], molecular structures, X-ray analysis.

The interactions between triarylantimony and inorganic and organic oxidizing agents were investigated by many authors, for example [1–4]. The studies of reactions of triarylantimony with hydroperoxides are of great importance, as the products are useful precursors of derivatives with general formula Ar_3SbX_2 (X = acid radical HX) [5–10]. It has been found that hydrogen peroxide oxidizes triarylantimony to produce oxide Ar_3SbO (Ar = Ph, *p*-Tol) or dihydroxide $\text{Ar}_3\text{Sb}(\text{OH})_2$ (Ar = 2,4,6-Me₃C₆H₂), depending on the volume of organic radical bonded with antimony atom, it is believed [10, 11]. The interaction of triarylantimony with *tert*-butyl hydroperoxide was studied on the example of triphenylantimony only. The molecular structure of the reaction product was found to depend on the amount of an oxidizing agent. Triphenylantimony oxide was formed at stoichiometric ratio of reactants and may be dimerized or polymerized [12–14]. Stable antimony peroxides $\text{Ph}_3\text{Sb}(\text{OOBu-}t)_2$ and $(\text{Ph}_3\text{SbOOBu-}t)_2\text{O}$ are formed in the presence of the excess of *tert*-butyl hydroperoxide [15].

The reactions of tri(*o*-tolyl)antimony with *tert*-butyl hydroperoxide at various molar ratios of the reactants have been investigated and crystal and molecular structures of the products have been determined in the present paper.

Experimental

Synthesis of *bis*[μ_2 -oxo-tri(*o*-tolyl)antimony] (1). Tri(*o*-tolyl)antimony (200 mg, 0.50 mmol) was dissolved in diethyl ether (20 mL). Then *tert*-butyl hydroperoxide (66 mg of 70 % aqueous solution, 0.50 mmol) was added. The solution was left to stand for 24 hours at temperature 20 °C. When the solvent evaporated, colourless crystalline substance **1** was obtained; the product yield was 199 mg (95 %), MP: 216 °C.

IR spectrum (ν , cm⁻¹): 3048, 2921, 2854, 1584, 1446, 1280, 1202, 1160, 1120, 1031, 935, 918, 890, 764, 750, 740, 655, 636, 491, 471, 435.

Synthesis of μ_2 -oxo-*bis*[(*tert*-butylperoxy)tri(*o*-tolyl)antimony] 2. Tri(*o*-tolyl)antimony (200 mg, 0.50 mmol) was dissolved in diethyl ether (20 mL). Then *tert*-butyl hydroperoxide (132 mg of 70 % aqueous solution, 1.00 mmol) was added. The solution was left to stand for 24 hours at temperature 20 °C. Colorless crystals **2** were obtained; yield 230 mg (92 %), MP: 162 °C.

The reaction with the molar ratio 1:4 was carried out at the same conditions. The product yield of substance **2** was 87 %.

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IR spectrum of the substance **1** was recorded on the Bruker Tensor 27 FT-IR (KBr pellets; 4000–400 cm^{-1}).

The X-ray diffraction analyses of crystalline substances **1** and **2** were made on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_{α} -emission, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the *SMART* and *SAINTE-Plus* programs [16]. All calculations for structure determination and refinement were performed using the *SHELXL/PC* programs [17]. The structures **1** and **2** were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms.

The main crystallographic data and refinement results for structures **1** and **2** are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

Table 1
Crystallographic data and the experimental and structure refinement parameters for compound **1**

Parameter	Value	
	1	2
Empirical formula	$\text{C}_{42}\text{H}_{42}\text{O}_2\text{Sb}_2$	$\text{C}_{50}\text{H}_{60}\text{O}_5\text{Sb}_2$
Formula weight	822.26	984.48
T , K	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P1
a , \AA	11.0684(3)	10.3355(4)
b , \AA	11.1721(3)	11.0049(5)
c , \AA	17.0248(5)	11.0848(4)
α , deg	80.7820(10)	69.771(2)
β , deg	86.0600(10)	84.636(2)
γ , deg	61.0370(10)	81.907(2)
V , \AA^3	1818.06(9)	1169.88(8)
Z	2	1
ρ (calcd.), g/cm^3	1.502	1.397
μ , mm^{-1}	1.520	1.198
$F(000)$	824.0	502.0
Crystal size, mm	0.17×0.09×0.08	0.55×0.38×0.21
2 θ Range of data collection, deg	7.38 – 58.28°	3.98 – 47.5°
Range of refraction indices	$-15 \leq h \leq 15, -15 \leq k \leq 15,$ $-23 \leq l \leq 23$	$-11 \leq h \leq 11, -12 \leq k \leq 12,$ $-12 \leq l \leq 12$
Measured reflections	32558	14775
Independent reflections	9014	6981
R_{int}	0.0480	0.0245
Refinement variables	421	521
$GOOF$	1.030	1.159
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0314, wR_2 = 0.0551$	$R_1 = 0.0511, wR_2 = 0.1274$
R factors for all reflections	$R_1 = 0.0564, wR_2 = 0.0611$	$R_1 = 0.0589, wR_2 = 0.1361$
Residual electron density (min/max), $e/\text{\AA}^3$	0.49/–0.33	1.04/–2.17

Table 2
Selected bond lengths and bond angles in the structures of compounds **1–2**

Bond	d , \AA	Angle	ω , deg	Bond	d , \AA	Angle	ω , deg
1				2			
Sb(1)–Sb(1a)	3.1409(4)	O(1a)Sb(1)C(1)	165.14(10)	Sb(1)–O(1)	1.997(17)	O(1)Sb(1)C(11)	93.7(9)
Sb(1)–O(1)	1.9372(18)	O(1)Sb(1)C(11)	114.54(10)	Sb(1)–C(11)	2.145(14)	O(1)Sb(1)O(2)	167.6(6)
Sb(1)–O(1a)	2.0784(18)	O(1a)Sb(1)C(11)	89.40(9)	Sb(1)–O(2)	2.143(18)	O(1)Sb(1)C(21)	86.7(7)
Sb(1)–C(1)	2.180(3)	O(1)Sb(1)C(21)	130.04(10)	Sb(1)–C(21)	2.166(17)	O(1)Sb(1)C(1)	95.3(8)
Sb(1)–C(11)	2.135(3)	C(11)Sb(1)C(1)	103.30(11)	Sb(1)–C(1)	2.18(2)	C(11)Sb(1)C(21)	116.3(10)

Table 2 (end)

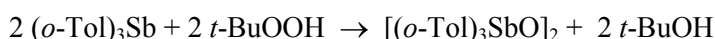
Bond	<i>d</i> , Å	Angle	ω, deg	Bond	<i>d</i> , Å	Angle	ω, deg
1				2			
Sb(1)–C(21)	2.150(3)	C(11)Sb(1)C(21)	111.93(11)	Sb(2)–O(1)	1.951(18)	C(11)Sb(1)C(1)	124.4(12)
Sb(2)–Sb(2b)	3.1441(3)	C(21)Sb(1)Sb(1a)	110.58(8)	Sb(2)–C(41)	2.150(17)	O(2)Sb(1)C(11)	87.2(9)
Sb(2)–O(2)	2.0585(17)	C(21)Sb(1)C(1)	96.05(11)	Sb(2)–C(61)	2.114(12)	O(2)Sb(1)C(21)	81.9(7)
Sb(2)–O(2b)	1.9473(17)	O(2b)Sb(2)C(31)	89.87(9)	Sb(2)–C(51)	2.114(12)	O(2)Sb(1)C(1)	94.3(8)
Sb(2)–C(31)	2.186(3)	O(2)Sb(2)C(31)	163.65(9)	Sb(2)–O(4)	2.129(17)	C(1)Sb(1)C(21)	118.9(10)
Sb(2)–C(41)	2.131(3)	O(2b)Sb(2)C(41)	108.70(10)	O(2)–O(3)	1.337(17)	Sb(2)O(1)Sb(1)	169.2(6)
Sb(2)–C(51)	2.151(3)	O(2)Sb(2)C(41)	92.51(10)	O(4)–O(5)	1.356(17)	C(22)C(21)Sb(1)	127.0(19)
O(1)–Sb(1a)	2.0784(18)	O(2b)Sb(2)C(51)	130.20(9)	O(5)–C(35)	1.51(2)	C(46)C(41)Sb(2)	114.2(15)
O(2)–Sb(2b)	1.9473(17)	O(2)Sb(2)C(51)	87.24(9)	O(3)–C(31)	1.451(17)	C(42)C(41)Sb(2)	124.6(15)

Symmetry relation: a) 1–*x*, –*y*, 2–*z*; b) 2–*x*, 1–*y*, 1–*z*

The full tables of atomic coordinates, bond lengths, and bond angles for the substance **1** was deposited with the Cambridge Crystallographic Data Centre (№ 1052677; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Results and Discussion

It has been found that the oxidation of tri(*o*-tolyl)antimony by *tert*-butylhydroperoxide at the molar ratio 1:1 in diethyl ether goes with the formation of tri(*o*-tolyl)antimony oxide with dimeric structure: bis[μ₂-oxo-tri(*o*-tolyl)antimony] (**1**):



According to X-ray diffraction data the crystal of compound **1** contains two types of crystallographically independent molecules (**A**, **B**). The antimony atoms have intermediate coordination between trigonal-bipyramidal and square-pyramidal coordination (Fig. 1).

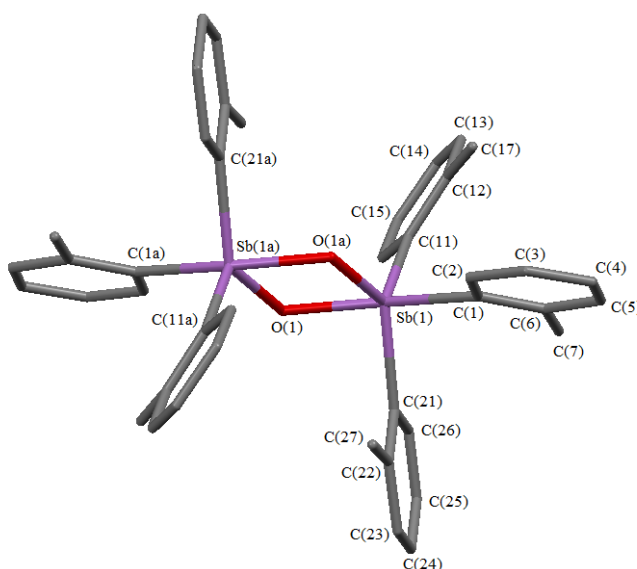


Fig. 1. The structure of compound **1A** (hydrogen atoms aren't shown)

Two carbon atoms of the aryl substituents and μ₂-bridging oxygen atom are placed in equatorial plane, the second μ₂-bridging oxygen atom and carbon atom are in axial positions. The sum of equatorial OSbC and CSbC angles is 356.57(10)° for **A** and 350.83(10)° for **B**. The axial OSbC angles are significantly distorted, they are equal to 165.14(10)° and 163.65(9)°. The OSbO and SbOSb angles in the flat cyclic fragment [Sb₂O₂] equal 77.14(8)°, 102.86(8)° (**A**) and 76.62(8)°, 103.13(7)° (**B**). The Sb–C_{eq} bond

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lengths (2.135(3), 2.150(3) Å **A**; 2.131(3), 2151(3) Å **B**) and Sb–O_{eq} (1.937(2) Å **A**; 1.943(2) Å **B**) are less than Sb–C_{ax} (2.180(3) Å **A**; 2.186(3) Å **B**) and Sb–O_{ax} (2.078(2) Å **A**; 2.058(2) Å **B**). The distances between antimony atoms in the cycle (3.1409(5) (A), 3.1441(3) Å (B)) are considerably less than the double Van der Waals radius of antimony atom (4.4 Å [18]). The *o*-Tol₃Sb fragments in compound **1** are in staggered conformation with respect to each other. Geometrical parameters of complex **1** are close to geometrical parameters of such compounds as (Ph₃SbO)₂ [19] and [(2-MeOC₆H₄)₃SbO]₂ [20].

When the concentration of *tert*-butylhydroperoxide has increased (1:2 or 1:4) the single organoantimony product in the reaction mixture is μ₂-oxo-*bis*[(*tert*-butylperoxo)tri(*o*-tolyl)antimony] (**2**), the product yield is 92 %:



The coordination polyhedron of antimony atoms in binuclear molecule **2** is an insignificantly distorted trigonal bipyramid (Fig. 2). The bipyramid distortion is characterized by deflection of Sb(1) and Sb(2) atoms from their respective equatorial planes by 0.02 Å and 0.08 Å to the direction of the bridging oxygen atom O(1), which leads to angle deviation between axial and equatorial bonds from the theoretical value 90°. The axial OSb(1,2)O angles are equal to 167.6(6)° and 159.5(5)°.

The equatorial CSb(1,2)C angles are changed in the range of 116.3(8)°–124.4(12)°. The Sb(1)O(1)Sb(2) angle is 169.2(6)°. The SbOSb fragment has linear structure in the centrosymmetric molecule of μ₂-oxo-*bis*[(*tert*-butylperoxo)triphenylantimony] [21].

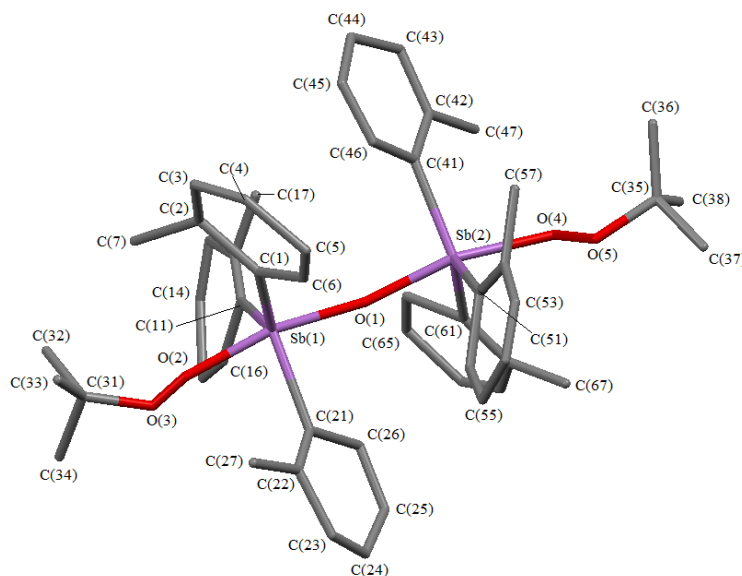


Fig. 2. The structure of compound **2** (hydrogen atoms aren't shown)

The equatorial bonds Sb(1)–C_{eq} and Sb(2)–C_{eq} are changed in the range of 2.14(1)–2.18(2) Å and 2.10(1)–2.15(1) Å.

The Sb(1,2)–O(1) distances are equal to 1.997(7) and 1.951(18) Å, and they are less than terminal distances Sb(1)–O(2) (2.143(18) Å) and Sb(2)–O(4) (2.129(17) Å) like in the molecule of μ₂-oxo-*bis*[(*tert*-butylperoxo)triphenylantimony].

Conclusions

Thus, *tert*-butylhydroperoxide oxidizes tri(*o*-tolyl)antimony at the molar ratio of the reactants 1:1 into tri(*o*-tolyl)antimony oxide, which dimerizes into *bis*[μ₂-oxo-tri(*o*-tolyl)antimony]. With *tert*-butylhydroperoxide in excess (1:2 and 1:4) the reaction proceeds with the formation of the single organoantimony compound: μ₂-oxo-*bis*[(*tert*-butylperoxo)tri(*o*-tolyl)antimony].

References

1. Bhattacharya S.N., Singh M. Oxidative Addition Reactions of Triarylsarsines and Triarylstibines with Copper (II) and Mercury(II) Salts. *Indian J. Chem.*, 1979, vol. 18A, no. 6, pp. 515–516.
2. Sharma H.K., Singh S., Dubey S.N., Puri D.M. Metal Derivatives of Organoantimony Compounds; Reactions of Anhydrous Ferric Chloride with Arylantimony Compounds. *Indian J. Chem.*, 1982, vol. 21A, no. 6, pp. 619–621.
3. Alberola A., Gonzaleer A.M., Pulido F.G. The Reaction of *p*-Quinones with Triphenylstibine. *Rev. Roum. Chim.* 1984, vol. 29, no. 5, pp. 441–446.
4. Cherkasov V.K., Grunova E.V., Poddel'sky A.I., Fukin G.K., Kurskii Y.A., Abakumova L.G., Abakumov G.A. Oxidative Addition Reaction of *o*-Quinones to Triphenylantimony. Novel Triphenylantimony Catecholate Complexes. *J. Organomet. Chem.* 2005, vol. 690, no. 5, pp. 1273–1281.
5. Goel R.G., Ridlej D.R. Organoantimony Compounds. *J. Organomet. Chem.* 1979, vol. 182, no. 2, pp. 207–212.
6. Bajpai K., Srivastava R.S. Synthesis and Reactions of *o*-Triorganoantimony Dioximates. *Inorg. Met.-Org. Chem.*, 1981, vol. 11, no. 1, pp. 7–13.
7. Chang M.-M.Y., Kai S., Musher J.I. Some New Organoantimony (V) Compounds. *Isr. J. Chem.*, 1974, vol. 12, no. 5, pp. 967–970.
8. Domagala M., Huber F., Preut H. Triorganoantimon- und Triorganobismutderivate von Carbonsauren funfgliedriger Heterocyclen Kristall- und Molekulstruktur von $(C_6H_5)_3Sb(O_2C-2-C_4H_3S)_2$ und $(CH_3)_3Sb(O_2C-2-C_4H_3S)_2$. *Z. Anorg. Allg. Chem.*, 1989, Bd. 574, ss. 130–142.
9. Domagala M., Huber F., Preut H. Triorganoantimon- und Triorganobismutderivate von 2-Pyridincarbonsaure und 2-Pyridinlessigsaeure. Kristall- und Molekulstrukturen von $Ph_3Sb(O_2C-2-C_5H_4N)_2$ und $Me_3Sb(O_2CCH_2-2-C_5H_4N)_2$. *Z. Anorg. Allg. Chem.*, 1990, Bd. 582, ss. 37–50.
10. Ruther R., Huber F., Preut H. Triorganoantimon- und Triorganobismutdisulfonate Kristall- und Molekulstrukturen von $(C_6H_5)_3M(O_3SC_6H_5)_2$ ($M=Sb, Bi$). *Z. Anorg. Allg. Chem.* 1986, Bd. 539, ss. 110–126.
11. Westhoff T., Huber F., Preut H. Syntesis of Tris(2,4,6-trimethylphenyl)hydroxoantimony Carboxylates. Crystall Structure of Tris(2,4,6-trimethylphenyl)hydroxoantimony 1-Adamantylcarboxylate. *J. Organomet. Chem.*, 1988, vol. 348, no. 2, pp. 185–191.
12. Hiatt R., McColeman C., Howe G.R. The Reaction of Hydroperoxides with Triphenylarsine and Triphenylstibine. *Canad. J. Chem.*, 1975, vol. 53, no. 4, pp. 559–563.
13. Cvetkov V.G., Aleksandrov Ju.A., Glushakova V.N., Skorodumova N.A., Koll'jakova G.M. Thermochemistry of Reaction Triphenylphosphorus -arsenic and -antimony with tert-butyl hydroperoxide. [Termohimija reakcii trifenilfosfora, -mysh'jaka i -sur'my s gidrolerekis'ju tretichnogo butila] *Zhurn. obshh. Himii [Russian Journal of General Chemistry]*, 1980, vol. 50, no. 2, pp. 256–258. (in Russ.)
14. Razuvaev G.A., Shushunov V.A., Dodonov V.A., Briikina T.G. Reactions of Organometallic Compounds with Organic peroxides. In: *Organic Peroxides*. N.Y.: J. Willey and Sons., 1972, vol. 3, pp. 141–270.
15. Pokrovskaja I.E., Dodonov V.A., Starikova Z.A., Kanunnikova E.N., Shhegoleva T.M., Lebedev G.P. The Peroxide Compounds of Triphenylantimony: Their Synthesis and Structure. [Peroksidnye soedinenija trifenil'sur'my, ih sintez i stroenie]. *Zhurn. obshh. Himii [Russian Journal of General Chemistry]*, 1981, vol. 51, no. 6, pp. 1247–1253. (in Russ.)
16. Bruker (2000) SMART. Bruker Molecular Analysis Research Tool, Versions 5.625 Bruker AXS, Madison, Wisconsin, USA.
17. Bruker (2000) SAINTPlus Data Reduction and Correction Program Versions 6.02a, Bruker AXS, Madison, Wisconsin, USA.
18. Bacanov S.S. Atomic Radii of the Elements [Atomnye radiusy jelementov]. *Zhurn. Neorgan. Himii [Russian Journal of Inorganic Chemistry]*, 1991, vol. 36, no. 12, pp. 3015–3037. (in Russ.)
19. Bordner J., Doak G.O., Everett T. S. Crystal Structure of 2,2,2,4,4,4-Tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane (Triphenylstibine Oxide Dimer) and Related Compounds. *J. Am. Chem. Soc.*, 1986, vol. 108, no. 14, pp. 4206–4213.
20. Matano Y., Nomura H., Hisanaga T., Nakano H., Shiro M., Imahori H. Diverse Structures and Remarkable Oxidizing Ability of Triaryl bismuthane Oxides. Comparative Study on the Structure and Reactivity of a Series of Triaryl pnictogen Oxides. *Organometallics*, 2004, vol. 23, no. 23, pp. 5471–5480.

21. Starikova Z.A., Shhegoleva T.M., Trunov V.K., Pokrovskaja I.E. The crystal and molecular structure of oxa-bis (tret.butilperoksitriphenilsurmy) [Kristallicheskaja i molekularnaja struktura oksa-bis(tret.butilperoksitriphenilsur'my)]. *Kristallografija [Crystallography Reports]*, 1978, vol. 23, no. 5, pp. 969–973. (in Russ.)

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ОКИСЛЕНИЕ ТРИ(О-ТОЛИЛ)СУРЬМЫ ТРЕТБУТИЛГИДРОПЕРОКСИДОМ. МОЛЕКУЛЯРНЫЕ СТРУКТУРЫ БИС[μ_2 -ОКСО-ТРИ(О-ТОЛИЛ)СУРЬМЫ] И μ_2 -ОКСО-БИС[(ТРЕТБУТИЛПЕРОКСО)ТРИ(О-ТОЛИЛ)СУРЬМЫ]

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Окисление три(о-толил)сурьмы эквимольным количеством третбутилгидропероксида в эфире приводит к образованию бис[μ_2 -оксо-три(о-толил)сурьмы] (1). При соотношении реагентов 1:2 или 1:4 (мольн.) продуктом реакции является μ_2 -оксо-[три(о-толил)третбутилпероксо]-сурьма (2). По данным РСА, в молекулах 1 и 2 атомы Sb имеют искаженную тригонально-бипирамидальную координацию. Длина связей Sb–O изменяется в интервалах 1.937(2)–2.078(2) Å (1) и 1.975(17)–2.216(15) Å (2).

Ключевые слова: три-о-толилсурьма, третбутилгидропероксид, окисление, бис[μ_2 -оксо-три(о-толил)сурьма], μ_2 -оксо-бис[(третбутилпероксо)три(о-толил)-сурьма], молекулярные структуры, рентгеноструктурный анализ.

Литература

1. Bhattacharya, S.N. Oxidative Addition Reactions of Triarylsines and Triarylstibines with Copper (II) and Mercury(II) Salts / S.N. Bhattacharya, M. Singh // *Indian J. Chem.* – 1979. – V. 18A, N. 6. – P. 515–516.
2. Metal Derivatives of Organoantimony Compounds; Reactions of Anhydrous Ferric Chloride with Arylantimony Compounds / H.K. Sharma, S. Singh, S.N. Dubey, D.M. Puri // *Indian J. Chem.* – 1982. – V. 21A, N. 6. – P. 619–621.
3. Alberola, A. The Reaction of *p*-Quinones with Triphenylstibine / A. Alberola, A.M. Gonzalez, F.G. Pulido // *Rev. Roum. Chim.* – 1984. – V. 29, N. 5. – P. 441–446.
4. Oxidative Addition Reaction of *o*-Quinones to Triphenylantimony. Novel Triphenylantimony Catecholate Complexes / V.K. Cherkasov, E.V. Grunova, A.I. Poddel'sky et al. // *J. Organomet. Chem.* – 2005. – V. 690. – N. 5. – P. 1273–1281.
5. Goel, R.G. Organoantimony Compounds / R.G. Goel, D.R. Ridlej // *J. Organomet. Chem.* – 1979. – V. 182. – N. 2. – P. 207–212.
6. Bajpai, K. Synthesis and Reactions of *o*-Triorganoantimony Dioximates / K. Bajpai, R.S. Srivastava // *Synth. Inorg. Met.-Org. Chem.* – 1981. – V. 11, N. 1. – P. 7–13.
7. Chang, M.-M.Y. Some New Organoantimony (V) Compounds / M.-M.Y. Chang, S. Kai, J.I. Musher // *Isr. J. Chem.* – 1974. – V. 12, N. 5. – P. 967–970.
8. Domagala, M. Triorganoantimon- und Triorganobismutderivate von Carbonsauren funfgliedriger Heterocyclen Kristall- und Molekulstruktur von $(C_6H_5)_3Sb(O_2C-2-C_4H_3S)_2$ und $(CH_3)_3Sb(O_2C-2-C_4H_3S)_2$ / M. Domagala, F. Huber, H. Preut // *Z. Anorg. Allg. Chem.* – 1989. – Bd. 574. – S. 130–142.
9. Domagala, M. Triorganoantimon- und Triorganobismutderivate von 2-Pyridincarbonsaure und 2-Pyridinlessigsaeure. Kristall- und Molekulstrukturen von $Ph_3Sb(O_2C-2-C_5H_4N)_2$ und $Me_3Sb(O_2CCH_2-2-C_5H_4N)_2$ / M. Domagala, F. Huber, H. Preut // *Z. Anorg. Allg. Chem.* – 1990. – Bd. 582. – S. 37–50.

10. Ruther, R. Triorganoantimon- und Triorganobismutdisulfonate Kristall- und Molekülstrukturen von $(C_6H_5)_3M(O_3SC_6H_5)_2$ ($M=Sb, Bi$) / R. Ruther, F. Huber, H. Preut // *Z. Anorg. Allg. Chem.* – 1986. – Bd. 539. – S. 110–126.
11. Westhoff, T. Synthesis of Tris(2,4,6-trimethylphenyl)hydroxoantimony Carboxylates. Crystal Structure of Tris(2,4,6-trimethylphenyl)hydroxoantimony 1-Adamantylcarboxylate / T. Westhoff, F. Huber, H. Preut // *J. Organomet. Chem.* – 1988. – V. 348, N. 2. – P. 185–191.
12. Hiatt, R. The Reaction of Hydroperoxides with Triphenylarsine and Triphenylstibine / R. Hiatt, C. McColeman, G.R. Howe // *Canad. J. Chem.* – 1975. – V. 53, N. 4. – P. 559–563.
13. Термохимия реакции трифенилфосфора, -мышьяка и -сурьмы с гидроперекисью третичного бутила / В.Г. Цветков, Ю.А. Александров, В.Н. Глушакова и др. // *Журн. общ. химии.* – 1980. – Т. 50. – № 2. – С. 256–258.
14. Reactions of Organometallic Compounds with Organic peroxides / G.A. Razuvaev, V.A. Shushunov, V.A. Dodonov, T.G. Brillkina // *Organic Peroxides.* – N.Y.: J. Willey and Sons. – 1972. – V. 3. – P. 141–270.
15. Пероксидные соединения трифенилсурьмы, их синтез и строение / И.Е. Покровская, В.А. Додонов, З.А. Старикова и др. // *Журн. общ. химии.* – 1981. – Т. 51, № 6. – С. 1247–1253.
16. Bruker (2000) SMART. Bruker Molecular Analysis Research Tool, Versions 5.625 Bruker AXS, Madison, Wisconsin, USA.
17. Bruker (2000) SAINTPlus Data Reduction and Correction Program Versions 6.02a, Bruker AXS, Madison, Wisconsin, USA.
18. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // *Журн. неорган. химии.* – 1991. – Т. 36, № 12. – С. 3015–3037.
19. Bordner, J. Crystal Structure of 2,2,2,4,4,4-Tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane (Triphenylstibine Oxide Dimer) and Related Compounds / J. Bordner, G.O. Doak, T.S. Everett // *J. Am. Chem. Soc.* – 1986. – V. 108, N. 14. – P. 4206–4213.
20. Diverse Structures and Remarkable Oxidizing Ability of Triarylbi-muthane Oxides. Comparative Study on the Structure and Reactivity of a Series of Triaryl-pnictogen Oxides / Y. Matano, H. Nomura, T. Hisanaga et al. // *Organometallics.* – 2004. – V. 23, N. 23. – P. 5471–5480.
21. Кристаллическая и молекулярная структура окса-бис(трет.бутилперокситрифенилсурьмы) / З.А. Старикова, Т.М. Щеголева, В.К. Трунов и др. // *Кристаллография.* – 1978. – Т. 23, № 5. – С. 969–973.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Oxidation of Tri(*o*-tolyl)antimony by *Tert*-butyl Hydroperoxide. Molecular Structures of *Bis*[μ_2 -oxo-tri(*o*-tolyl)antimony] and μ_2 -oxo-*bis*[(*tert*-butylperoxy)tri(*o*-tolyl)antimony] / V.V. Sharutin, O.K. Sharutina, E.V. Artem'eva, M.S. Makerova // *Вестник ЮУрГУ. Серия «Химия».* – 2015. – Т. 7, № 4. – С. 23–29. DOI: 10.14529/chem150404

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CHEMISTRY OF UNSATURATED ARENETRICARBONYLCHROMIUM COMPOUNDS. PART 3. SYNTHESIS, CHARACTERISTICS AND SPECTROSCOPIC RESEARCH OF η^6 -(ARENE)TRICARBONYLCHROMIUM DERIVATIVES OF ISOXAZOLIDINES

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The series of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines has been obtained by 1,3-dipolar cycloaddition. The obtained compounds have been investigated by IR spectroscopy, ^1H NMR spectroscopy and mass spectrometry. It has been shown that $\text{Cr}(\text{CO})_3$ group significantly influences the structure and spectral characteristics of synthesized heterocycles.

Keywords: 1,3-dipolar cycloaddition, nitron, isoxazolidine, η^6 -(arene)tricarbonylchromium, IR spectroscopy, ^1H NMR spectroscopy, mass spectrometry.

Introduction

The reaction of 1,3-dipolar cycloaddition are of fundamental importance, from theoretical and practical points of view alike, it is a classical synthesis method for five-membered heterocyclic compounds. One of its essential parts is the interaction between nitrones and alkenes leading to formation of isoxazolidines [1–3]. The enormous number of various functionally substituted compounds notwithstanding, the π -complexes containing tricarbonylmetal groups are practically absent among them. Fundamental interest in π -complexes of such kind is in establishment of the influence of electron and steric factors peculiar to η^6 -(arene)tricarbonyl group upon the selectivity of 1,3-dipolar addition and the structure of the formed products.

Recently we have reported [4–6] that the introduction of $\text{Cr}(\text{CO})_3$ group into phenyl rings of both nitron and alkene leads to significant increase of regio- and diastereoselectivity for the 1,3-dipolar cycloaddition reactions, at that nothing but C(3),C(5)-substituted isoxazolidines with predominantly *cis*-structure is formed. In the present paper we describe the investigation of these compounds in detail, using various physicochemical methods of analysis.

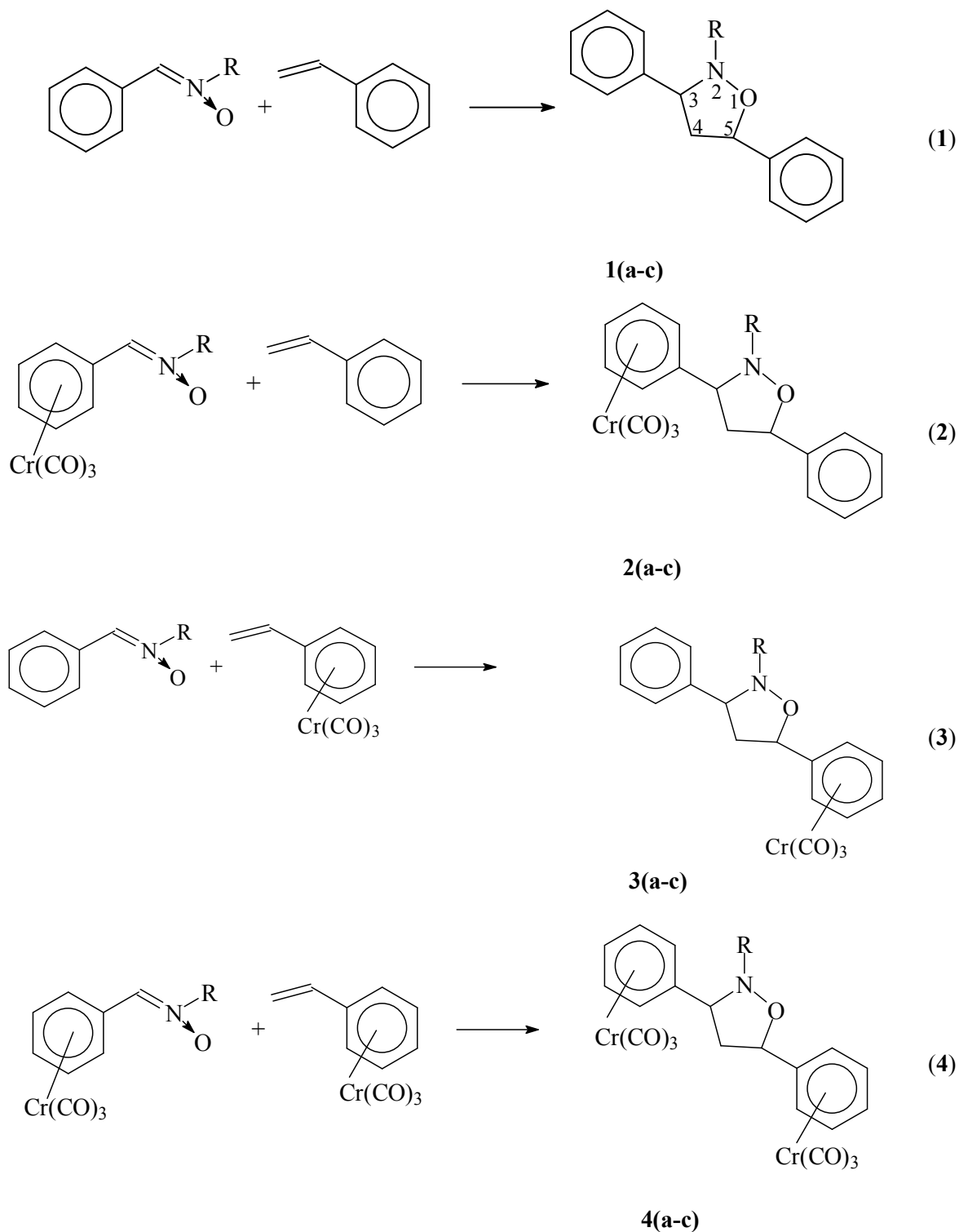
Results and Discussion

The initial isoxazolidines have been obtained in accordance with the previously developed procedure [4,5] (reactions (1)–(4), Scheme 1), in which a number of free and coordinated nitrones have been used as dipoles in the 1,3-dipolar cycloaddition reactions:



R=CH₃ (**a**); t-C₄H₉ (**b**); C₆H₅ (**c**)

Styrene and η^6 -(styrene)tricarbonylchromium have been used of in this reaction as dipoles (Scheme 1) [7].



R=CH₃ (a); t-C₄H₉ (b); C₆H₅ (c)

Scheme 1

All the processes, except reaction (1), have led to formation of isoxazolidines containing Cr(CO)₃ groups. The obtained arenetricarbonylchromium complexes of those heterocycles look like yellow crystalline substances that are comparatively stable in air. All isoxazolidines are isolated in the pure state and investigated using various physicochemical methods of analysis.

The reaction conditions and some properties of isoxazolidines **2a-c-4a-c** are represented in Table 1.

The reaction conditions and some properties of π -complexes of isoxazolidines 2a-c-4a-c

Compound	Reaction conditions		Yield, %	M.p., °C
	Time, h	Temperature, °C		
2a	6	90	25	94–95
2b	6	90	30	40–41
2c	6	90	62	121–122
3a	40	105	66	91–92
3b	40	105	47	104–105
3c	40	105	42	112–113
4a	40	80	20	155–156
4b	40	80	36	136–137
4c	40	80	38	132–133

The IR spectra of each π -complex (**2a-c** – **4a-c**) show the expected pair of stretching vibrations from A_1 and E bands of tricarbonylchromium group. Repositioning of these bands in the spectrum often provides valuable information concerning the electronic effects of a system. From the measurement results presented in Table 2 it follows that the values of stretching ν_{CO} vibrations of the complexes suffer comparatively small though reasonably regular changes that far exceed experimental error, under the influence of a heterocyclic ring as a substituent. Repositioning of stretching ν_{CO} vibrations inside the isostructural series can be considered as the result of electron influence of the heterocyclic ring. It is known [8, 9] that the frequencies of carbonyl vibrations in IR spectra of the compounds of $\eta^6\text{-(C}_6\text{H}_5\text{X)Cr(CO)}_3$ type are sensitive to electronic effects of the substituent X. Thus, π -donor groups, which increase the negative charge on the oxygen atom, shift the ν_{CO} vibrations towards increasing wavelengths. To the contrary, the substituents with acceptor properties produce the opposite effect, *viz.* heighten the frequencies of stretching vibrations. Correlation of the stretching vibration frequencies in the IR spectra of the investigated series and the IR spectrum of $\eta^6\text{-(benzene)tricarbonylchromium}$ ($\nu_{\text{CO}} = 1972, 1891 \text{ cm}^{-1}$) makes it easy to see that the isoxazolidine ring is a weak donor with respect to Cr(CO)_3 group.

Another characteristic feature of IR spectra of some compounds in this series is considerable splitting of ν_{CO} bands of degenerate carbonyl vibrations. Doubling of E bands in IR spectra of carbonyl metal complexes is not anything exceptional, it is explained by violation of the C_{3v} rule – the local symmetry of tricarbonylchromium group. This rule holds quite well for the cases, in which it can be supposed that M(CO)_3 group rotates freely and carbonyl groups do not interact with other parts of a molecule. Such splitting of E band for carbonyl vibrations has also been observed for many other complexes of transition metals, as an example, the substitution derivatives of $\eta^5\text{-(cyclopentadienyl)tricarbonylmanganese}$ and $-\text{rhenium}$ [8, 9], as well as the series of $\eta^6\text{-(benzene)tricarbonylchromium}$ [8]. Thus, in paper [10] it has been shown that E band significantly splits for $\eta^6\text{-(arene)tricarbonylchromium}$ alcohols containing hydroxyl groups in α -position in relation to π -arene ring ($\nu_{\text{CO}} - A_1: 1960, E: 1870, 1720 \text{ cm}^{-1}$), while for the alcohols containing OH groups in β - and γ -positions any similar splitting of bands of degenerate vibrations is nonexistent.

In order to establish why E bands broaden and split in the series of π -complexes of isoxazolidines, we carried out the investigation of IR spectra of these compounds in various media: in the solid state (in potassium bromide pellets), as well as in cyclohexane and carbon tetrachloride solutions. As Table 2 suggests, for the solid samples of compounds **2a-c** – **3a-c** intensive splitting of E band is observed, in the case of **3c** it reaches the difference of wavenumbers $\Delta(\nu(E)) = 47 \text{ cm}^{-1}$. Carbonyl area in IR spectra of compound **3c** is shown in Fig. 1. This appearance of the spectrum can be explained both by intermolecular interactions (crystalline factor) and by intramolecular interactions between one of carbonyl groups and the oxygen atom of the heterocyclic ring.

It is known that during transition from solid samples to solutions crystalline factors cease to act, which results in spectra with better resolution. As a rule, significant increase of the frequencies of carbonyl vibrations occurs at that (Table 2). By way of example, for isoxazolidine **3a** the frequencies of symmetrical ν_{CO} vibrations (A_1) in cyclohexane and carbon tetrachloride solutions increase by 25 cm^{-1} , while the frequencies of degenerate vibrations increase by 34 cm^{-1} on average, in each case they constitute only one unsplit signal.

Table 2

The frequencies of the symmetric (A_1) and asymmetric (E) stretching carbonyl vibrations
in IR-spectra of isoxazolidines cis-2-4

Compound	$\nu_{\text{CO}}, \text{cm}^{-1}$					
	A_1			E		
	KBr	n-C ₆ H ₁₂	CCl ₄	KBr	n-C ₆ H ₁₂	CCl ₄
2a	1956	1979	1975	1875, 1862	1912	1905
2b	1961	1976	1972	1885, 1871	1909, 1903	1901
2c	1957	1980	1976	1882, 1865	1914, 1905	1905
3a	1955	1980	1977	1894, 1875	1912	1906
3b	1951	1979	1975	1885, 1872	1911	1904
3c	1970	1981	1978	1904, 1857	1914	1907
4a	1953	–	–	1885, 1877	–	–
4b	1963	–	–	1886, 1865	–	–
4c	1961	–	–	1887, 1870	–	–

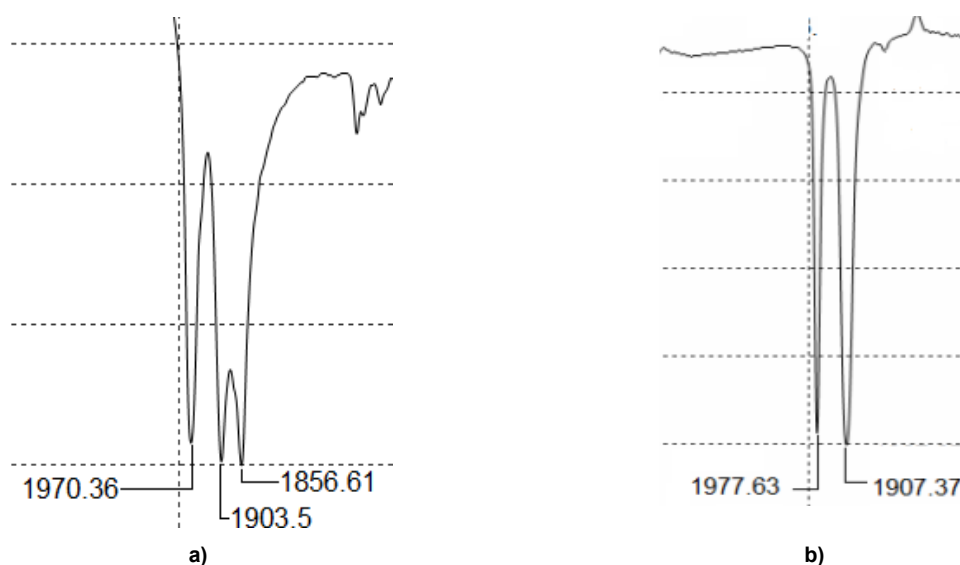


Fig. 1. The IR-spectrum of isoxazolidine 3c in the area of carbonyl vibrations:
a – in the tablet of KBr, b – in the solution of CCl₄

Therefore, owing to the investigation of IR spectra in crystalline state and in solutions it has been shown that splitting of the bands of degenerate vibrations, observed for the solid samples, does not take place in solutions, because of solvation of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines by the solvent molecules.

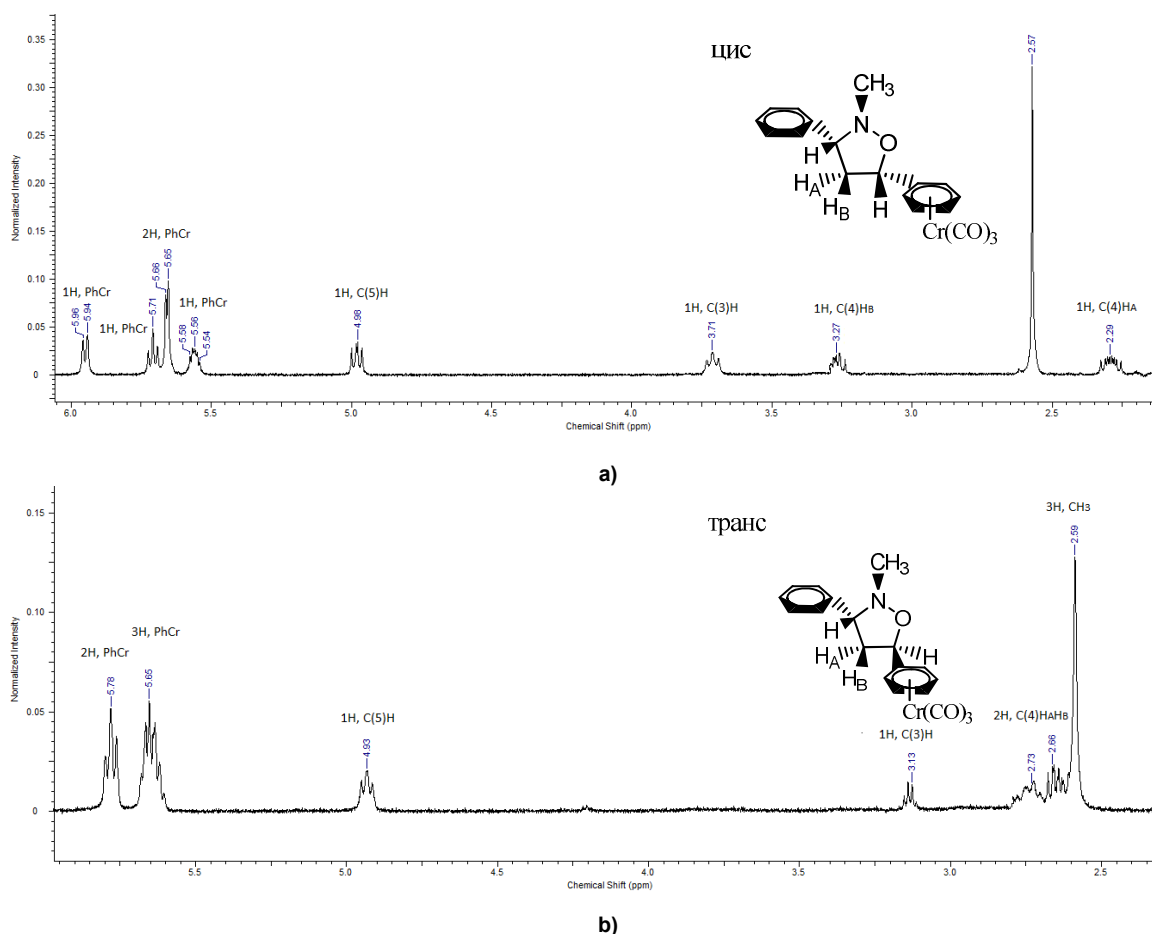
The structure and configuration of all obtained compounds have been established with the use of ¹H NMR spectroscopy as well. In the spectra of all complex isoxazolidines six groups of resonance signals are observed: from the protons of a substituent at the nitrogen atom (CH₃, t-C₄H₉, C₆H₅), from the methylene protons at the fourth carbon atom of the heterocycle (2H, C(4)), from the single protons of the ring (1H, C(3) and 1H, C(5)), as well as the protons of the free and coordinated phenyl rings (Table 3 and Experimental). The ¹H NMR spectroscopy data, represented in Table 3, unambiguously prove that the substituents in the isoxazolidine ring are located in positions 2,3,5. This assignment has been suggested on the basis of resonance position for two protons of the methylene group and their spin-spin interaction constants. If the configuration of the substituents in isoxazolidine is taken to be 2,3,4, then in such NMR spectrum the complex multiplet in the area 4.0–4.5 ppm should be observed, which is actually observed for all 2,3,4-trisubstituted isoxazolidines. Instead of this, the spectra of all obtained coordinated compounds have two quite narrow multiplets in the area $\delta = 2.2$ –3.5 ppm, peculiar to 2,3,5-substituted isoxazolidines.

The chemical shifts and the view of NMR H^1 -spectra of the protons of heterocyclic rings of the isoxazolidines cis-2-4

Compound	2H(C(4))	HC(3)	HC(5)
2a	2.28, 3.24 (t.d, t.d)	3.78 (t)	5.27-5.38 (m)
2b	2.18-2.52, 3.20-3.44 (m, m)	4.53 (d.d)	5.26 (t)
2c	2.39, 3.15-3.53 (d.d.d, m)	5.04 (d.d)	5.13-5.33 (m)
3a	2.29, 3.22-3.29 (d.d.d, m)	3.71 (t)	4.98 (d.d)
3b	2.19, 3.16 (d.t, d.t)	4.49 (d.d)	4.88 (d.d)
3c	2.37, 3.37 (d.t, d.t)	5.00 (t)	5.00 (t)
4a	2.31, 3.43 (d.t, d.t)	3.83 (t)	5.07 (t)
4b	2.26-2.50, 3.14-3.70 (m, m)	4.51 (d.d)	4.99 (t)
4c	2.41, 3.40 (d.d.d, d.d.d)	4.82-5.19 (m)	7.09-7.46 (m)

Another important aspect of the structure of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines is the arrangement of the substituents in relation to the heterocyclic ring plane. Assignment of the studied compound to cis- or trans-series (in this case it means the relative position of substituents at C(3) and C(5) carbon atoms of the heterocyclic ring) can be obtained on the basis of the well-known Karplus relationship for vicinal proton-proton constants: $3J_{H-H} = f(\theta)$, also, mainly, from the analysis of qualitative difference of chemical shifts ($\Delta\delta$) of methylene protons at atom C(4).

In the case of cis-arrangement of the substituents at C(3) and C(5) of the isoxazolidine ring, chemical shifts of protons H_A and H_B (Fig. 2) strongly differ, as H_A interacts only with the protons that lie on the same side with it in relation to the heterocyclic ring plane, while H_B interacts with the protons on the other side of the cycle. In this case the difference of chemical shifts usually falls within 0.7–1.2 ppm.

Fig. 2. The fragments of NMR H^1 -spectra (400 MHz, acetone- d_6) of isoxazolidines cis-3a (a) and trans-3a (b)

The interaction of protons H_A and H_B with the protons at carbon atoms C(3) and C(5) in the case of trans-arrangement of the substituents is symmetrical, that is, the values of their screening are close and equal 0.2–0.3 ppm, sometimes one complex multiplet can be observed. Indeed, comparison of the spectra represented in Fig. 2 shows that the abovementioned rule is valid for them. Trans-2-methyl-5- η^6 -(phenyltricarbonylchromium)-3-phenylisoxazolidine (trans-**3a**), which is absent in Table 3, has been obtained with low yield as a by-product of the reaction between C-phenyl-N-methylnitrone and η^6 -(styrene)tricarbonylchromium (ref. Experimental section), it has been separated from its mixture with cis-**3a** with the use of column chromatography on silica gel (by hexane/ethylacetate = 4:1 as the eluent). As can be seen from Fig. 2, the spectrum of cis-**3a** isomer illustrates the strong magnetic nonequivalence of two protons located at C(4) ($\Delta\delta_{AB} \sim 0.97$ ppm), which proves the cis-configuration of this isomer. At the same time trans-**3a** isomer has one broad unresolved multiplet in the range 2.62–2.79 ppm. Therefore, 1H NMR spectra make it possible not only to establish the composition of the obtained components, but also to prove their spatial structure unambiguously. The same purpose is served by mass spectra of these complexes.

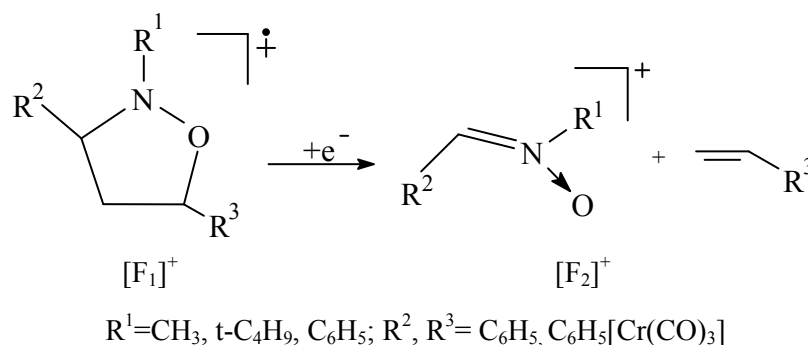
For the obtained series of isoxazolidines with tricarbonylchromium groups the electron impact mass spectra have been registered and their fragmentation has been studied. As in the case of other carbonyl complexes of transition metals, the primary fragmentation consists in dissociation of three carbonyl groups that occurs in stages, at that the successful removal of the first CO group from the molecular ion $[M]^+$ brings leads to corresponding decrease in dissociation energy of the remaining M–CO bonds. It is expressed in increasing intensity of the peaks in this sequence:



Indeed, all obtained isoxazolidine complexes form molecular ions $[M]^+$, which are principally transformed into fragments $[M-3CO]^+$ by way of elimination of three carbon monoxide molecules, either simultaneously or sequentially in the fast two-stage process:



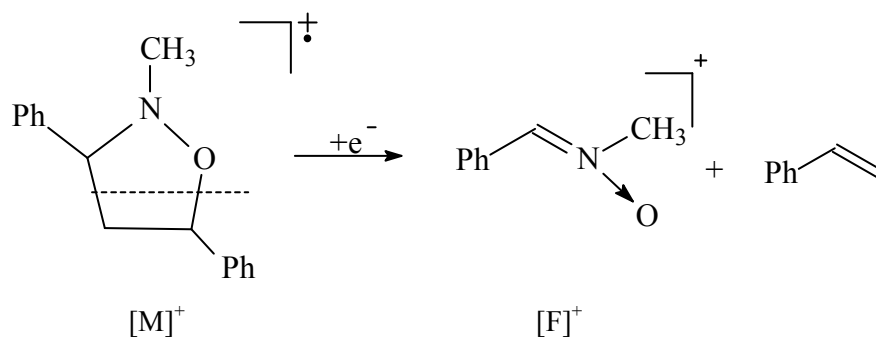
After elimination of three CO groups (fragment $[F_1]^+$) the disintegration of the heterocyclic ring follows, essentially into two particles with formation of fragment ions $[F_2]^+$, which correspond to retro-disintegration (Scheme 2):



Scheme 2

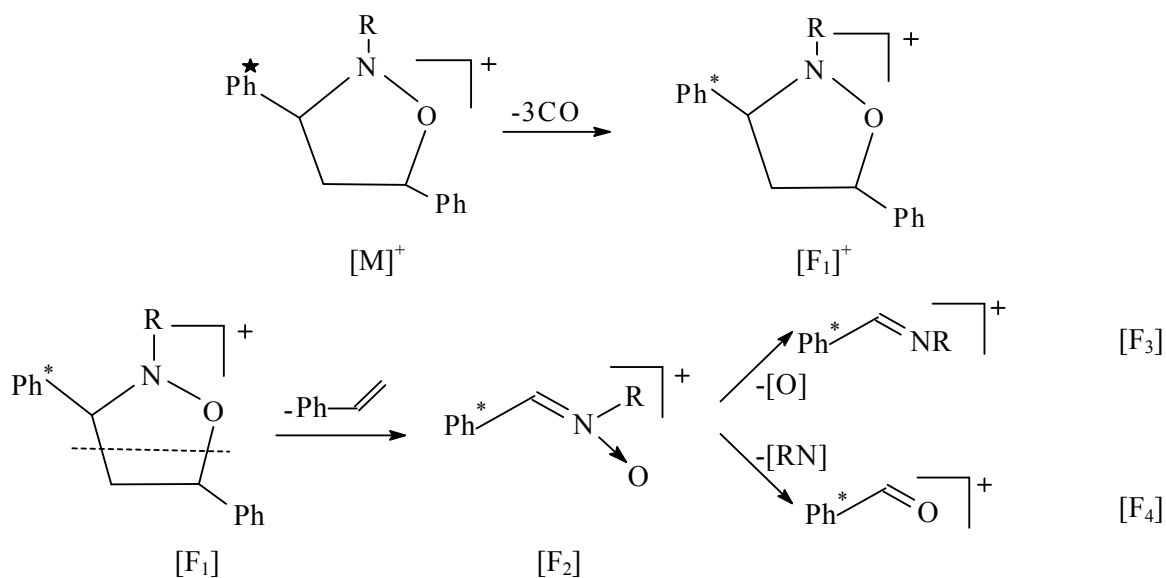
Previously it has been shown that cis-2-methyl-3,5-diphenylisoxazolidine is ionized at electron impact with the formation of molecular ion $[M]^+ = 239$ (24%), with the most intensive fragment ion in the spectrum $[F]^+ = 135$ (100%). Fragmentation of this compound can be represented by the following simple scheme 3.

Introduction of $Cr(CO)_3$ groups into isoxazolidines decidedly complicates the pattern of disintegration through appearance of additional peaks as the result of sequential elimination of carbon monoxide, as well as specific interaction of the metal. It is known that the primary ionization of a compound usually proceeds by way of the detachment of an electron from the higher bonding orbital of the organometallic complex, which is of predominantly metal character. That is why during disintegration of the molecular ion the charge usually remains on the metal-containing fragment. So the greater part of ion current consists of metal-containing ions.



Scheme 3

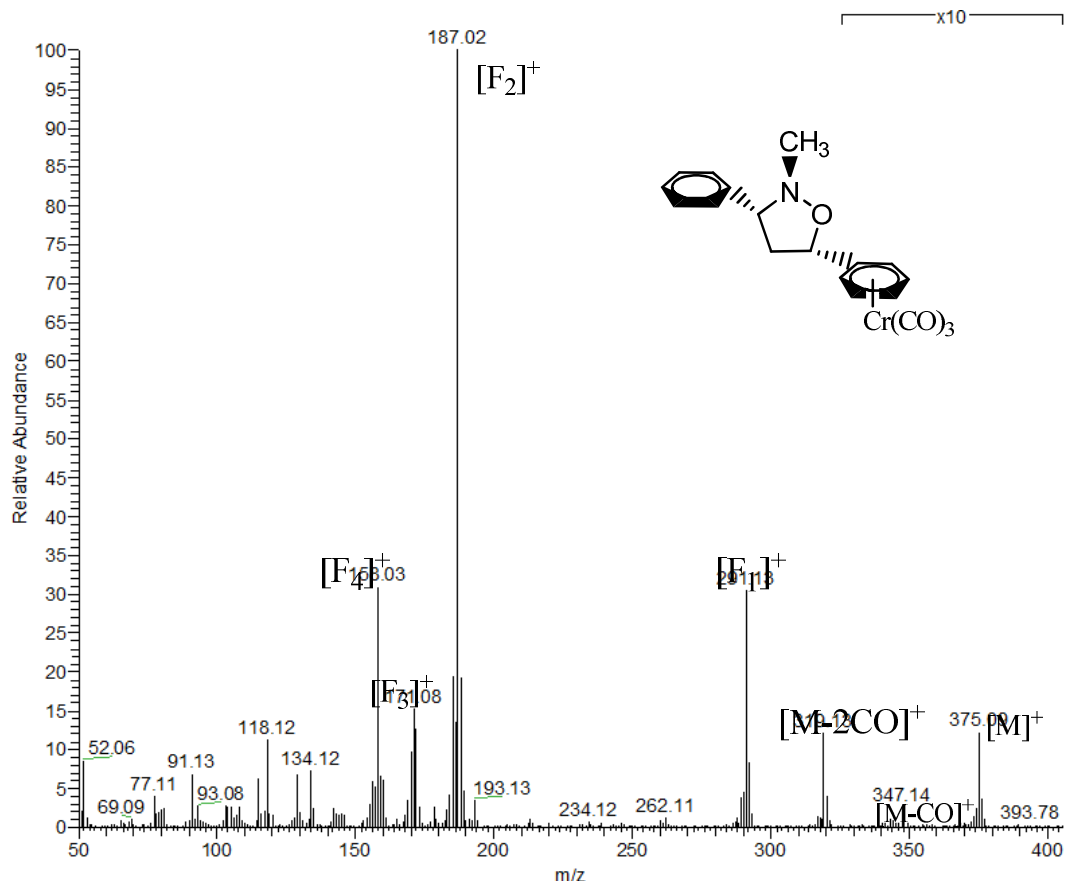
Investigation of the influence of $\text{Cr}(\text{CO})_3$ groups upon the fragmentation process for isoxazolidines under electron impact has shown that the peaks of molecular ions have low intensity; much more intensive are the peaks of ions $[\text{F}_1]^+$ that correspond to the molecular ion after elimination of three carbonyl groups $[\text{M}-3\text{CO}]^+$, as well as the ions resulting from disintegration of the heterocyclic ring. Just as with uncoordinated isoxazolidines the main (the most intensive) peaks in the mass spectra of all the studied compounds correspond to fragment ions $[\text{F}_2]^+$, which are formed after disintegration of $[\text{F}_1]^+$ with elimination of styrene molecule. The direction of the following fragmentation depends on the structure of the formed ion. In a general way the fragmentation of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines can be represented by the dissociative scheme 4.



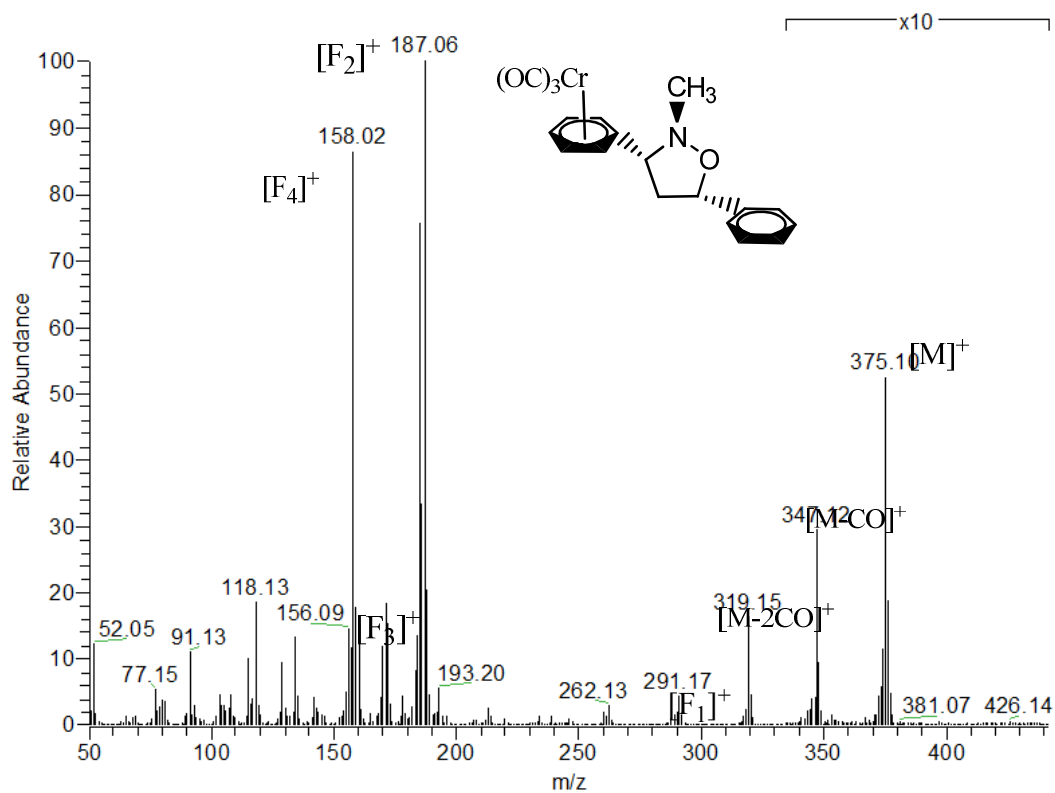
here $\text{Ph}^* = \text{C}_6\text{H}_5[\text{Cr}(\text{CO})_3]$, $\text{Ph} = \text{C}_6\text{H}_5\text{Cr}$, $\text{R} = \text{CH}_3, t\text{-C}_4\text{H}_9, \text{C}_6\text{H}_5$; the masses of the corresponding ions and their intensities are shown in Table 4

Scheme 4

For example, in the mass spectrum of 2-methyl-3- η^6 -(phenyltricarbonylchromium)-5-phenylisoxazolidine (**2a**) (Fig. 3, Table 4) there is the peak of the molecular ion $[\text{M}]^+ = 375$ (1.2%), as well as the peaks corresponding to elimination of CO molecules. The peak of $[\text{F}_2]^+$ with $m/z = 187$ (100.0%) is the maximal; it forms from $[\text{F}_1]^+$ when neutral styrene (C_8H_8) is removed from it. In its turn $[\text{F}_2]^+$ is subject to further disintegration by way of donor-acceptor bond $\text{N} \rightarrow \text{O}$ with removal of the oxygen atom and formation of $[\text{F}_3] = 171$ (16.0%) (Scheme 5), and also as the result of rearrangement with removal of particle $[\text{NCH}_3]$ and formation of ion $[\text{F}_4]^+$.



a)

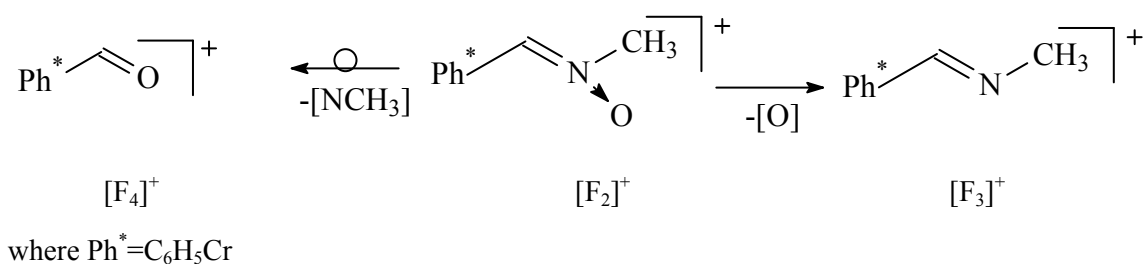


b)

Fig. 3. Mass-spectra of isoxazolidines *cis*-2a (a) and *cis*-3a (b)

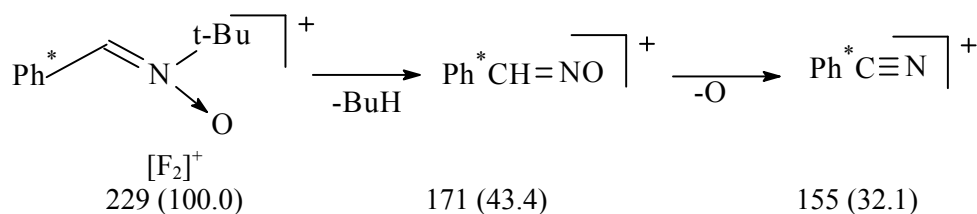
Data of mass-spectra of isoxazolidines cis-2-3

Compound	Characteristics of the ions: m/z (I,%)						
	[M] ⁺	[M-CO] ⁺	[M-2CO] ⁺	F ₁	F ₂	F ₃	F ₄
2a	375 (1.2)	347 (0.3)	319 (13.2)	291 (31.2)	187 (100)	171 (16.0)	158 (31.1)
2b	417 (1.1)	389 (0.5)	361 (19.8)	333 (65.1)	229 (100)	212 (22.6)	–
2c	437 (1.8)	–	381 (5.7)	353 (47.2)	249 (82.1)	233 (57.6)	–
3a	375 (5.3)	347 (2.9)	319 (16.0)	291 (4.7)	187 (100)	171 (18.9)	158 (86.8)
3b	417 (5.0)	–	361 (11.3)	333 (62.3)	229 (100)	212 (32.1)	–
3c	437 (2.4)	–	381 (6.7)	353 (52.8)	249 (85.3)	233 (66.0)	–

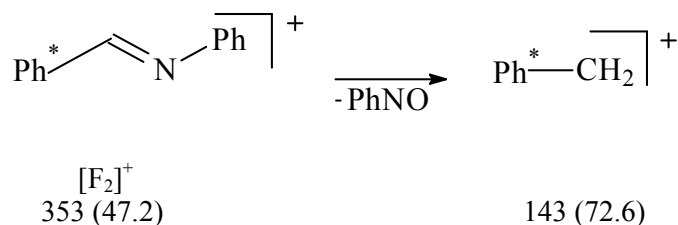


Scheme 5

Similar to the example described above (complex **2a**), tert-butyl (**2b**) and phenyl (**2c**) analogues of this compound completely copy the fragmentation of **2a** up to formation of ions [F₂]⁺ and [F₃]⁺, however, instead of the rearrangement process leading to [F₄]⁺, they are better characterized by: removal of isobutane (fragmentation of **2b**, Scheme 6) and removal of nitrobenzene C₆H₅NO (fragmentation of **2c**, Scheme 7).



Scheme 6



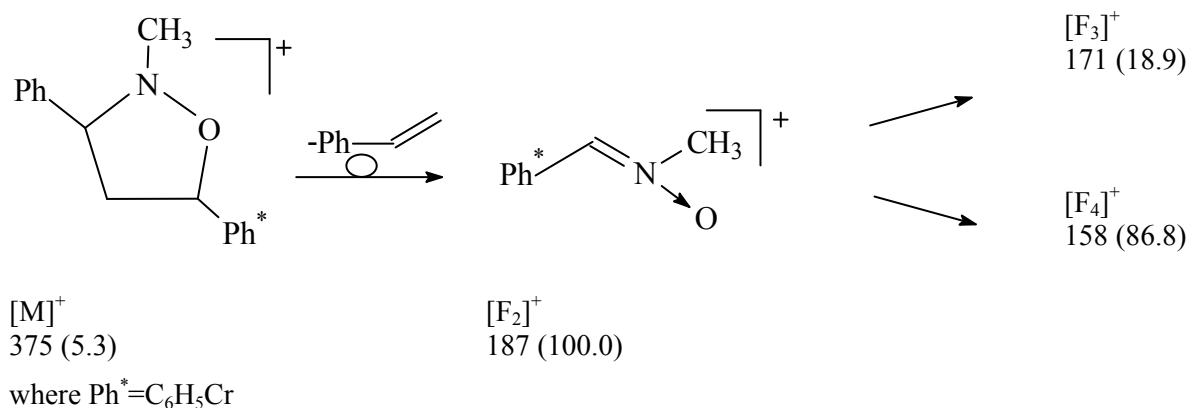
where Ph* = C₆H₅Cr

Scheme 7

It is of interest to compare the mass spectra of two isomeric compounds **2a** and **3a**, which differ from each other by the arrangement of Cr(CO)₃ groups in the complex (Fig. 3). As can be seen in Fig. 3, the mass number of ions have equal values, while the intensities of molecular ions in the mass spectra of **2a** and **3a** strongly differ. The fragmentation of isoxazolidine **3a** is represented in Scheme 8.

Compounds **3b** and **3c** are fragmented according to the same scheme. Their mass spectra practically completely coincide with the mass spectra of the isomeric compounds **2b** and **2c** (Table 4). Unfortunately-

ly, we failed to get satisfactory mass spectra for binuclear complexes **4a-c**, because of lesser stability and low volatility of these compounds. They all decomposed in the process of evaporation in the ion source of the mass spectrometer.



Scheme 8

Experimental

The synthesis of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines (**2a-c** – **4a-c**) was carried out according to the procedure described in papers [4, 5]. IR spectra were registered on the "Infralume FT-801" spectrometer in the range 4000–400 cm⁻¹ in KBr pellets, cyclohexane and CCl₄ solutions. ¹H NMR spectra were registered on the "Bruker DPX 200" and "Bruker Avance DPX 400" spectrometers, with acetone-d₆ as the solvent. Field tailoring was conducted at the signal of deuterium nuclei of the solvent. Mass spectrometric analysis was performed on DSQ II mass spectrometer: a few micrograms of the studied substance was placed into a test microtube of the direct injection system, which was introduced through the vacuum lock directly into the ion source of the spectrometer. The microtube was heated from 50 to 450 °C at the rate 100 °C/min, mass spectra were registered in the range of mass numbers 50–700 under the energy of ionizing electrons equaling 70 eV.

Cis-2-methyl-3-(η^6 -phenyltricarbonylchromium)-5-phenylisoxazolidine (cis-2a). Yield 25%, m.p. 94-95 °C. IR spectrum (KBr), ν /cm⁻¹: 2952, 2839 (ν (C-H)), 1956, 1875, 1862 (ν (C≡O)), 1458, 1444, 1420 (ν (C-C)), 764, 702, 664, 630 (ω (C_{Ar}-H)). IR spectrum (n-C₆H₁₄), ν /cm⁻¹: 1979, 1912 (ν (C≡O)). IR spectrum (CCl₄), ν /cm⁻¹: 1975, 1905 (ν (C≡O)). ¹H NMR spectrum (400 MHz, δ , ppm, J /Hz): 2.28 (t.d., 1H, HC(4), J =12.6, J =7.6); 2.90 (s, 3H, CH₃); 3.24 (t.d., 1H, HC(4), J =12.6, J =7.6), 3,78 (t, 1H, HC(3), J =7.6); 5.23 (d, 1H, C(3)PhCr, J =6.4.); 5.27-5.38 (m, 4H, C(3)PhCr, HC(5)); 5.67 (d, 1H, C(3)PhCr, J =6.4.); 7.27-7.38 (m, 5H, PhN). Mass spectrum (EI, 70 eV, m/z (I_{rel} (%))): 375 [M]⁺ (1.2), 347 [M-CO]⁺ (0.3), 319 [M-2CO]⁺ (13.2), 291 [M-3CO]⁺ (31.2), 187 [M-3CO-PhCHCH₂]⁺ (100.0), 171 [M-3CO-PhCHCH₂-O]⁺ (16.0), 158 [M-3CO-PhCHCH₂-NCH₃]⁺ (31.1), 118 [M-3CO-PhCHCH₂-Cr-H-O]⁺ (12.1), 91 [PhCH₂]⁺ (7.8), 52 [Cr⁺] (9.0).

Cis-2-tertbutyl-3-(η^6 -phenyltricarbonylchromium)-5-phenylisoxazolidine (cis-2b). Yield 30%, m.p. 40-41 °C. IR spectrum (KBr), ν /cm⁻¹: 3070, 3033, 2984, 2917, 2850 (ν (C-H)); 1961, 1885, 1871 (ν (C≡O)); 1531, 1455, 1421 (ν (C-C)); 758,697,663, 632 (ω (C_{Ar}-H)). IR spectrum (n-C₆H₁₄), ν /cm⁻¹: 1976, 1909, 1903 (ν (C≡O)). IR spectrum (CCl₄), ν /cm⁻¹: 1972, 1901 (ν (C≡O)). ¹H NMR spectrum (200 MHz, δ , ppm, J /Hz): 1.21 (s, 9 H, t-C₄H₉); 2.18-2.52 (m, 1 H, HC(4)); 3.20-3.44 (m, 1 H, HC(4)); 4.53 (d.d, 1 H, HC(3), J = 8.5, J = 6.0); 5.26 (t, 1 H, HC(5), J = 7.6); 5.43-5.59 (m, 2 H, m -C(3)PhCr); 5.66 (t, 1 H, n -C(3)PhCr, J = 6.3); 5.91 (br. d, 1 H, o -C(3)PhCr, J = 6.5); 6.10 (br. d, 1 H, o -C(3)PhCr, J = 6.5); 7.04-7.66 (m, 5 H, C(5)Ph). Mass spectrum (EI, 70 eV, m/z (I_{rel} , %)): 417 [M]⁺ (1.1), 389 [M-CO]⁺ (0.5), 361 [M-2CO]⁺ (19.8), 333 [M-3CO]⁺ (65.1), 229 [M-3CO-PhCHCH₂]⁺ (100.0), 212 [M-3CO-PhCHCH₂-O]⁺ (22.6), 171 [M-3CO-PhCHCH₂-C₄H₉-H]⁺ (43.4), 155 [M-3CO-PhCHCH₂-O-C₄H₉-H]⁺ (32.1), 129 [PhCr]⁺ (12.0), 93 [C₆H₅CH₂H₂]⁺ (13.0), 52 [Cr]⁺ (8.7).

Cis-3-(η^6 -phenyltricarbonylchromium)-2,5-diphenylisoxazolidine (cis-2c). Yield 62%, m.p. 121-122 °C. IR spectrum (KBr), ν /cm⁻¹: 2983 (ν (C-H)); 1957, 1882, 1865 (ν (C≡O)); 1594, 1488, 1454

($\nu(\text{C-C})$); 763, 702, 656, 632 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). IR spectrum ($n\text{-C}_6\text{H}_{14}$), ν/cm^{-1} : 1980, 1914, 1905 ($\nu(\text{C}\equiv\text{O})$). IR spectrum (CCl_4), ν/cm^{-1} : 1976, 1905 ($\nu(\text{C}\equiv\text{O})$). ^1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 2.39 (d.d, 1 H, HC(4), $J = 12.8, 9.0, 5.0$); 3.15-3.53 (m, 1 H, HC(4)); 5.04 (d.d, 1 H, HC(3), $J = 9.0, J = 5.0$); 5.13-5.33 (m, 1 H, HC(5)); 5.57-5.80 (m, 3 H, C(3)PhCr); 5.91 (br. d, 1 H, $o\text{-C}(3)\text{PhCr}$, $J = 5.9$); 6.05-6.19 (m, 1 H, C(3)PhCr); 6.99 (t, 1 H, $n\text{-PhN}$, $J = 7.0$); 7.11-7.58 (m, 9 H, PhN, PhC(5)). Mass spectrum (EI, 70 eV, m/z ($I_{\text{rel.}}$, %)): 437 $[\text{M}]^+$ (1.8), 381 $[\text{M-2CO}]^+$ (5.7), 353 $[\text{M-3CO}]^+$ (47.2), 249 $[\text{M-3CO-PhCHCH}_2]^+$ (82.1), 247 $[\text{M-3CO-PhCHCH}_2\text{-2H}]^+$ (100.0), 233 $[\text{M-3CO-PhCHCH}_2\text{-O}]^+$ (57.6), 180 $[\text{M-3CO-PhCHCH}_2\text{-O-Cr-H}]^+$ (11.3), 143 $[\text{M-3CO-PhCHCH-O-NPh}]^+$ (72.6), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (9.3), 52 $[\text{Cr}]^+$ (8.7).

Cis-2-methyl-5-(η^6 -phenyltricarbonylchromium)-3-phenylisoxazolidine (cis-3a). Yield 66%, m.p. 91-92 °C. IR spectrum (KBr), ν/cm^{-1} : 3020, 2992, 2877 ($\nu(\text{C-H})$); 1955, 1894, 1875 ($\nu(\text{C}\equiv\text{O})$); 1454, 1384 ($\nu(\text{C-C})$); 771, 660, 633 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). IR spectrum ($n\text{-C}_6\text{H}_{14}$), ν/cm^{-1} : 1980, 1912 ($\nu(\text{C}\equiv\text{O})$). IR spectrum (CCl_4), ν/cm^{-1} : 1977, 1906 ($\nu(\text{C}\equiv\text{O})$). ^1H NMR spectrum (400 MHz, δ , ppm, J/Hz): 2.29 (d.d, 1 H, HC(4), $J = 12.6, J = 9.5, J = 6.3$); 2.57 (s, 3H, CH_3); 3.22-3.29 (m, 1 H, HC(4)); 3.71 (br. t, 1 H, HC(3), $J = 8.4$); 4.98 (d.d, 1 H, HC(5), $J = 8.5, J = 6.3$); 5.52-5.59 (m, 1 H, C(5)- m -PhCr); 5.66 (d, 2 H, C(5)- o -PhCr, $J = 3.8$); 5.71 (t, 1 H, C(5)- m -PhCr, $J = 6.4$); 5.95 (d, 1 H, C(5)- p -PhCr, $J = 6.4$); 7.29 (d, 1 H, p -PhC(3), $J = 7.0$); 7.34 (d.d, 2 H, m -PhC(3), $J = 7.3, J = 7.0$); 7.39 (br. d, 2 H, o -PhC(3), $J = 7.3$). Mass spectrum (EI, 70 eV, m/z ($I_{\text{rel.}}$, %)): 375 $[\text{M}]^+$ (5.3), 347 $[\text{M-CO}]^+$ (2.9), 319 $[\text{M-2CO}]^+$ (16.0), 291 $[\text{M-3CO}]^+$ (4.7), 187 $[\text{M-3CO-PhCHCH}_2]^+$ (100.0), 171 $[\text{M-3CO-PhCHCH}_2\text{-O}]^+$ (18.9), 158 $[\text{M-3CO-PhCHCH}_2\text{-NCH}_3]^+$ (86.8), 134 $[\text{M-3CO-PhCHCH}_2\text{-Cr-H}]^+$ (13.2), 118 $[\text{M-3CO-PhCHCH}_2\text{-Cr-H-O}]^+$ (17.9), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (10.8), 77 $[\text{Ph}]^+$ (5.2), 52 $[\text{Cr}]^+$ (11.8).

Trans-2-methyl-5-(η^6 -phenyltricarbonylchromium)-3-phenylisoxazolidine (trans-3a). Yield 14%, m.p. 112-113 °C. IR spectrum (KBr), ν/cm^{-1} : 1956, 1895, 1878 ($\nu(\text{C}\equiv\text{O})$); 1384 ($\nu(\text{C-C})$); 706, 661, 633 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). ^1H NMR spectrum (400 MHz, δ , ppm, J/Hz): 2.59 (s, 3 H, CH_3N); 2.62-2.79 (m, 2 H, HC(4)); 3.13 (d.d, 1 H, HC(3), $J = 10.8, J = 5.3$); 4.93 (br. t, 1 H, HC(5), $J = 7.2$); 5.57-5.71 (m, 3 H, C(5)PhCr); 5.78 (t, 2 H, C(5)PhCr, $J = 7.7$); 7.30 (d, 1 H, o -PhC(3), $J = 7.0$); 7.36-7.52 (m, 4 H, o -, m -, p -PhC(3)).

Cis-2-*tert*butyl-5-(η^6 -phenyltricarbonylchromium)-3-phenylisoxazolidine (cis-3b). Yield 47%, m.p. 104-105 °C. IR spectrum (KBr), ν/cm^{-1} : 3079, 2981, 2921 ($\nu(\text{C-H})$); 1951, 1885, 1872 ($\nu(\text{C}\equiv\text{O})$); 1632 ($\nu(\text{C-C}_{\text{Ar}})$); 1490, 1455 ($\nu(\text{C-C})$); 767, 707, 660, 633 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). IR spectrum ($n\text{-C}_6\text{H}_{14}$), ν/cm^{-1} : 1979, 1911 ($\nu(\text{C}\equiv\text{O})$). IR spectrum (CCl_4), ν/cm^{-1} : 1975, 1904 ($\nu(\text{C}\equiv\text{O})$). ^1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 1.08 (s, 9 H, $t\text{-C}_4\text{H}_9$); 2.19 (br. d.t, 1 H, HC(4), $J = 12.0, J = 9.0$); 3.16 (br. d.t, 1 H, HC(4), $J = 12.0, J = 7.0$); 4.49 (d.d, 1 H, HC(3), $J = 9.0, J = 7.5$); 4.88 (d.d, 1 H, HC(5), $J = 8.2, J = 7.0$); 5.58 (m, 2 H, $m\text{-C}(5)\text{PhCr}$); 5.63 (d, 1 H, $o\text{-C}(5)\text{PhCr}$, $J = 4.0$); 5.71 (t, 1 H, $p\text{-C}(5)\text{PhCr}$, $J = 6.0$); 5.99 (d, 1 H, $o\text{-C}(5)\text{PhCr}$, $J = 6.0$); 7.32 (m, 3 H, m -, p -PhC(3)); 7.48 (d, 2 H, o -PhC(3), $J = 7.0$). Mass spectrum (EI, 70 eV, m/z ($I_{\text{rel.}}$, %)): 417 $[\text{M}]^+$ (5.0), 361 $[\text{M-2CO}]^+$ (11.3), 333 $[\text{M-3CO}]^+$ (62.3), 229 $[\text{M-3CO-PhCHCH}_2]^+$ (100.0), 212 $[\text{M-3CO-PhCHCH}_2\text{-O}]^+$ (32.1), 172 $[\text{M-3CO-PhCHCH}_2\text{-C}_4\text{H}_9]^+$ (41.5), 155 $[\text{M-3CO-PhCHCH}_2\text{-O-C}_4\text{H}_9\text{-H}]^+$ (33.0), 129 $[\text{PhCr}]^+$ (14.2), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (5.2), 52 $[\text{Cr}]^+$ (13.2).

Cis-5-(η^6 -phenyltricarbonylchromium)-2,3-diphenylisoxazolidine (cis-3c). Yield 42%, m.p. 112-113 °C. IR spectrum (KBr), ν/cm^{-1} : 3092, 2916, 2923, 2849 ($\nu(\text{C-H})$); 1970, 1904, 1857 ($\nu(\text{C}\equiv\text{O})$); 1595, 1540, 1489 ($\nu(\text{C-C})$); 761, 699, 663, 622 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). IR spectrum ($n\text{-C}_6\text{H}_{14}$), ν/cm^{-1} : 1981, 1914 ($\nu(\text{C}\equiv\text{O})$). IR spectrum (CCl_4), ν/cm^{-1} : 1978, 1907 ($\nu(\text{C}\equiv\text{O})$). ^1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 2.37 (d.t, 1 H, HC(4), $J = 12.4, J = 8.8, J = 7.2$); 3.37 (d.t, 1 H, HC(4), $J = 12.4, J = 7.2, J = 6.0$); 5.00 (br. t, 2 H, HC(3), HC(5), $J = 7.2$); 5.50-5.80 (m, 4 H, o -, m -, p -C(5)PhCr); 5.85 (d, 1 H, $o\text{-C}(5)\text{PhCr}$, $J = 6.0$); 6.94 (t, 1 H, $p\text{-PhN}$, $J = 7.2$); 7.11 (d, 2 H, $o\text{-PhN}$, $J = 3.8$); 7.26 (m, 3 H, $m\text{-PhN}$, $p\text{-PhC}(3)$); 7.40 (m, 2 H, $m\text{-PhC}(3)$); 7.58 (d, 2 H, $o\text{-PhC}(3)$, $J = 7.4$). Mass spectrum (EI, 70 eV, m/z ($I_{\text{rel.}}$, %)): 437 $[\text{M}]^+$ (2.4), 381 $[\text{M-2CO}]^+$ (6.7), 353 $[\text{M-3CO}]^+$ (52.8), 249 $[\text{M-3CO-PhCHCH}_2]^+$ (84.9), 249 $[\text{M-3CO-PhCHCH}_2]^+$ (85.3), 247 $[\text{M-3CO-PhCHCH}_2\text{-2H}]^+$ (100.0), 233 $[\text{M-3CO-PhCHCH}_2\text{-O}]^+$ (66.0), 180 $[\text{M-3CO-PhCHCH}_2\text{-O-Cr-H}]^+$ (26.4), 143 $[\text{M-3CO-PhCHCH-O-NPh}]^+$ (62.2), 91 $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (16.5), 52 $[\text{Cr}]^+$ (16.0).

Cis-2-methyl-3,5-bis(η^6 -phenyltricarbonylchromium)isoxazolidine (cis-4a). Yield 20%, m.p. 155-156 °C. IR spectrum (KBr), ν/cm^{-1} : 2958, 2919, 2863 ($\nu(\text{C-H})$); 1953, 1885, 1877 ($\nu(\text{C}\equiv\text{O})$); 1636, 1493, 1454 ($\nu(\text{C-C})$); 699, 662, 633 ($\omega(\text{C}_{\text{Ar}}\text{-H})$). ^1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 2.08 (s, 3 H, CH_3N), 2.31 (d.t, 1 H, HC(4), $J = 12.6, J = 7.1$), 3.43 (d.t, 1 H, HC(4), $J = 12.6, J = 8.1$), 3.83 (br. t, 1

H, HC(3), $J = 8.1$), 5.07 (t, 1 H, HC(5), $J = 7.1$), 5.50-5.75 (m, 8 H, PhCr), 5.75-5.91 (m, 8 H, PhCr). Mass spectrum (EI, 70 eV, m/z ($I_{rel.}$, %)): 455 $[M-2CO]^+$ (12.5), 427 $[M-3CO]^+$ (25.0), 343 $[M-6CO]^+$ (100.0), 239 $[M-6CO-PhCHCH_2]^+$ (90.1), 212 (22.2), 187 $[M-6CO-PhCHCH_2-Cr]^+$ (40.3), 170 (34.0), 158 (25.0), 120 (38.9), 97 (49.3), 85 (23.6), 52 $[Cr]^+$ (20.1).

Cis-2-*tert*butyl-3,5-bis(η^6 -phenyltricarbonylchromium)isoxazolidine (cis-4b). Yield 36%, m.p. 136-137 °C. IR spectrum (KBr), ν/cm^{-1} : 2918, 2877 ($\nu(C-H)$); 1963, 1886, 1865 ($\nu(C\equiv O)$); 1633, 1462, 1408 ($\nu(C-C)$); 663, 632, 533 ($\omega(C_{Ar}-H)$). 1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 1.20 (s, 9H, C_4H_9), 2.26-2.50 (m, 1 H, HC(4)), 3.14-3.70 (m, 1 H, HC(4)), 4.51 (d.d, 1 H, HC(3), $J = 7.6$, $J = 6.1$), 4.99 (t, 1 H, HC(5) $J = 7.1$), 5.39-5.73 (m, 7 H, PhCr), 5.79 (d, 1 H, PhCr, $J = 6.1$), 5.95 (d, 1 H, PhCr, $J = 7.1$), 6.09 (d, 1 H, PhCr, $J = 6.6$). Mass spectrum (EI, 70 eV, m/z ($I_{rel.}$, %)): 455 $[M-3CO-CH_2]^+$ (10.0), 427 $[M-4CO-CH_2]^+$ (24.8), 343 (100.0), 239 (94.2), 212 (24.8), 187 (29.2), 170 (30.7), 158 (21.2), 125 (30.1), 111 (42.3), 97 (58.4), 85 (30.1), 52 $[Cr]^+$ (16.1).

Cis-3,5-bis(η^6 -phenyltricarbonylchromium)-2-phenylisoxazolidine (cis-4c). Yield 38%. m.p. 132-133 °C. IR spectrum (KBr), ν/cm^{-1} : 2874, 2723 ($\nu(C-H)$); 1961, 1887, 1870 ($\nu(C\equiv O)$); 1636, 1487 ($\nu(C-C)$); 661, 631, 536 ($\omega(C_{Ar}-H)$). 1H NMR spectrum (200 MHz, δ , ppm, J/Hz): 2.41 (d.d.d, 1 H, HC(4), $J = 12.6$, $J = 8.6$, $J = 4.6$), 3.40 (d.d.d, 1 H, HC(4), $J = 12.6$, $J = 8.6$, $J = 7.6$), 4.82-5.19 (m, 2 H, HC(3), HC(5)), 5.50-5.76 (m, 7 H, PhCr), 5.83 (br. d, 1 H, PhCr, $J = 6.6$), 5.92 (br. d, 1 H, PhCr, $J = 5.6$), 6.05-6.15 (br. d, 1 H, PhCr), 6.88-7.09 (m, 1 H, PhN), 7.09-7.46 (m, 4 H, PhN). Mass spectrum (EI, 70 eV, m/z ($I_{rel.}$, %)): 499 (3.6), 489 $[M-3CO]^+$ (8.2), 433 $[M-5CO]^+$ (2.5), 419 (4.5), 405 $[M-6CO]^+$ (38.4), 387 (22.4), 335 (100), 299 $[M-6CO-PhCHCH_2-2H]^+$ (31.5), 260 (65.9), 233 (34.0), 180 (21.0), 129 (18.8), 93 (31.9), 77 $[Ph]^+$ (13.0), 52 $[Cr]^+$ (23.2).

Conclusion

With the use of 1,3-dipolar cycloaddition reactions the series of η^6 -(arene)tricarbonylchromium complexes of isoxazolidines has been obtained. In the IR spectra of all obtained tricarbonylchromium complexes two strong (occasionally splitted) bands in the area of carbonyl vibrations are observed, which correlate to $Cr(CO)_3$ groups. Difference in position of these bands in relation to $C_6H_6Cr(CO)_3$ is consistent with the isoxazolidine system as a weak electron donor. It has been established that the study of 1H NMR spectra is an excellent analytical method making it possible not only to determine qualitative composition of π -complexes, but also to open the way of unambiguous demonstration of their spatial diastereomer structure. The electron impact mass spectra resemble other mass spectra of monosubstituted derivatives of benzenetricarbonylchromium. Their fragmentation proceeds by way of sequential removal of three CO groups and retro disintegration of the isoxazolidine ring according to the general scheme. The main peak is the fragment of the molecular ion after the loss of three CO groups and removal of styrene. Other peaks of smaller intensity are the derivatives of this fragment.

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References

1. Confalone P.N., Huie E.M. *The [3+2] Nitron-Olefin Cycloaddition Reaction in Organic Reactions*. USA, John Willy and Sons, 1988, vol. 36, 173 p. DOI:10.1002/0471264180.or036.01
2. Huisgen F., Grashey R., Sauer J. *Khimiya alkenov* [The Chemistry of Alkenes]. Leningrad, Khimiya publ., 1969, pp. 444-534.
3. Gilchrist T., Storr R. *Organicheskie reaktsii i orbital'naya simmetriya* [Organic Reactions and Orbital Symmetry]. Moscow, Mir publ., 1976, pp. 100-119.
4. Artemov A.N., Sazonova E.V., Mavrina E.A., Zarovkina N.Yu. [Synthesis of New η^6 -(arene)chromium Tricarbonyl Complexes of Isoxazolidines by 1,3-Dipolar Cycloaddition]. *Russian Chemical Bulletin*, 2012, no. 11, pp. 2076-2081. DOI: 10.1007/s11172-012-0290-4
5. Artemov A.N., Sazonova E.V., Zarovkina N.Yu. [1,3-Dipolar Cycloaddition Reactions of nitron η^6 -(arene)tricarbonylchromium Complexes of Nitrones with Styrene and η^6 -

(styrene)tricarbonylchromium]. *Russian Chemical Bulletin*, 2013, no. 6, pp. 1382–1387. DOI: 10.1007/s11172-013-0197-8

6. Zarovkina N.Yu., Sazonova E.V., Artemov A.N., Fukin G.K. [Chemistry of Unsaturated Arene-tricarbonylchromium Compounds. Part 1. Interaction of η^6 -(arene)tricarbonylchromium Complexes of Nitrones with Methyl Phenylpropiolate]. *Russian Chemical Bulletin*, 2014, no. 4, pp. 970–975. (in Russ.)

7. Raush M.D., Moses G.A., Zaiko E.S. Lipman Jr A.L. Organometallic π -Complexes. XX. The Preparation of Styrenetricarbonylchromium. *J. Organomet. Chem.*, 1970, vol.23, pp. 185–190. DOI:10.1016/S0022-328X(00)92813-4

8. Aleksanyan V.T., Lokshin B.V. *Itogi nauki i tekhniki. Seriya: Stroenie molekul i khimicheskaya svyaz'. T. 5: Kolebatel'nye spektry π -kompleksov perekhodnykh elementov* [Results of Scientific and Technical Research. Ser. Molecular Structure and Chemical Bond. Vol. 5. Vibrational Spectra of π -Complexes of Transition Elements]. Moscow, VINITI Publ., 1976. 178 p.

9. Nesmeyanov A.N., Anisimov K.N., Lokshin B.V., Kolobova N.E., Makarov Yu.V. [Influence Transfer of Substituents through the Metal Atom in Cyclopentadienyltricarbonylmanganese $RC_5H_4Mn(CO)_3$ Derivatives]. *Proceedings of the USSR Academy of Sciences*, 1967, vol. 176, no. 5, pp. 1082–1085. (in Russ.)

10. Bodrikov I. V., Grinval'd I.I., Artemov A. N., Bazhan L. I., Kalagaev I. Yu. Intramolecular CO \cdots H Interaction in Arene(tricarbonyl)-chromium Complexes. *Russian Journal of General Chemistry*, 2010, vol. 80, № 1, pp. 20–22. DOI: 10.1134/S1070363210010032

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ХИМИЯ НЕПРЕДЕЛЬНЫХ АРЕНХРОМТРИКАРБОНИЛЬНЫХ СОЕДИНЕНИЙ. СООБЩЕНИЕ 3. СИНТЕЗ, ХАРАКТЕРИСТИКА И СПЕКТРОСКОПИЧЕСКОЕ ИССЛЕДОВАНИЕ η^6 -(АРЕН)ХРОМТРИКАРБОНИЛЬНЫХ ПРОИЗВОДНЫХ ИЗОКСАЗОЛИДИНОВ

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Реакцией 1,3-диполярного циклоприсоединения получена широкая серия η^6 -(арен)хромтрикарбонильных комплексов изоксазолидинов. Полученные соединения изучались с помощью ИК-, ЯМР 1H -спектроскопии и масс-спектрометрии. Показано, что $Cr(CO)_3$ -группа оказывает существенное влияние на структуру и спектральные характеристики синтезированных гетероциклов.

Ключевые слова: 1,3-диполярное циклоприсоединение, нитрон, изоксазолидин, η^6 -(арен)хромтрикарбонил, ИК-спектроскопия, 1H ЯМР 1H -спектроскопия, масс-спектрометрия.

Литература

1. Confalone, P.N. The [3+2] Nitron-Olefin Cycloaddition Reaction in Organic Reactions / P.N. Confalone, E.M. Huie. – New York: John Willy and Sons, 1988. – V. 36. – 173 p.
2. Хьюзген, Ф. Химия алкенов / Ф. Хьюзген, Р. Грэши, Дж. Соейр. – Л.: Химия, 1969. – С. 444–534.
3. Джилкрист, Т. Органические реакции и орбитальная симметрия / Т. Джилкрист, Р. Сторр. – М.: Мир, 1976. – С. 100–119.

4. Синтез новых η^6 -(арен)хромтрикарбонильных комплексов изоксазолидинов реакцией 1,3-диполярного циклоприсоединения / А.Н. Артемов, Е.В. Сазонова, Е.А. Маврина, Н.Ю. Заровкина // Известия АН. Серия «Химия». – 2012. – № 11. – С. 2059–2064.
5. Артемов, А.Н. Реакции 1,3-диполярного циклоприсоединения η^6 -(арен)хромтрикарбонильных комплексов нитронов со стиролом и η^6 -(стирол)хромтрикарбонилем / А.Н. Артемов, Е.В. Сазонова, Н.Ю. Заровкина // Известия АН. Серия «Химия». – 2013. – № 6. – С. 1382–1387.
6. Химия непредельных аренхромтрикарбонильных соединений. Сообщ. 1. Взаимодействие η^6 -(арен) хромтрикарбонильных комплексов нитронов с метиловым эфиром фенолпропиоловой кислоты / Н.Ю. Заровкина, Е.В. Сазонова, А.Н. Артемов, Г.К. Фукин // Известия АН. Серия «Химия». – 2014. – № 4. – С. 970–975.
7. Organometallic π -Complexes. XX. The Preparation of Styrenetricarbonylchromium / M.D. Raush, G.A. Moser, E.S. Zaiko, Lipman Jr A.L. // J. Organomet. Chem. – 1970. – V. 23 – P. 185–190.
8. Алексанян, В.Т. Итоги науки и техники. Серия: Строение молекул и химическая связь. Т. 5: Колебательные спектры π -комплексов переходных элементов / В.Т. Алексанян, Б.В. Локшин. – М.: ВИНТИ, 1976. – 178 с.
9. Передача влияния заместителей через атом металла в производных циклопентадиенилмарганецтрикарбонила $RC_3H_4Mn(CO)_3$ / А.Н. Несмеянов, К.Н. Анисимов, Б.В. Локшин и др. // Докл. АН СССР. – 1967. – Т. 176. – № 5. – С. 1082–1085.
10. Внутримолекулярное взаимодействие $CO \cdots H$ в аренхромтрикарбонильных комплексах / И.В. Бодриков, И.И. Гринвальд, А.Н. Артемов и др. // Журн. общ. хим. – 2010. – Т. 80. – № 1. – С. 24–26.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Chemistry of Unsaturated Arenetricarbonylchromium Compounds. Part 3. Synthesis, Characteristics and Spectroscopic Research of H_6 -(Arene)Tricarbonylchromium Derivatives of Isoxazolidines / A.N. Artemov, E.V. Sazonova, N.Yu. Zarovkina, Faerman V.I. // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 30–43. DOI: 10.14529/chem150405

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SYNTHESIS AND STRUCTURE OF BISMUTH COMPLEXES [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P, Sb

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The interaction of equimolar amounts of tetra-*p*-tolylphosphonium and tetra-*p*-tolylstibonium iodides with bismuth triiodide in 2-ethoxyethanol leads to formation of the complexes [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P (I), Sb (II). X-ray diffraction analysis of compounds (I) and (II) has shown that in the cations of complexes I and II the coordination of phosphorus and antimony atoms is tetrahedral (angles equal: CPC 107.3(3)°–113.4(4)° (I), CSbC 105.4(3)°–113.7(3)° (II); bond lengths for P–C and Sb–C are 1.761(9)–1.815(7) Å and 2.085(8)–2.099(8) Å, respectively). In trinuclear anions [Bi₃I₁₂]³⁻ the terminal fragments BiI₃ (Bi–I_{term} 2.8714(5)–2.9181(5) Å (I), 2.8867(5)–2.9248(6) Å (II)) are bonded to the central bismuth atom through six μ₂-bridging iodine atoms (Bi–I_{br} 3.0454(6)–3.3891(6) Å (I), 3.0595(4)–3.3694(6) Å (II)).

Keywords: bismuth triiodide, bismuth complexes [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅, E=P, Sb, synthesis, structure.

Introduction

Ionic bismuth complexes with linear anions [Bi₃I₁₂]³⁻, in which the bismuth atoms are bonded through six μ₂-bridging iodine atoms, are described in the literature as separate examples, where nitrogen-containing acyclic or heterocyclic cations stand as counter-ions [1–3]. Thus far only one similar complex with phosphonium cation is known [4]; like complexes with organoantimony cations are not known.

In the present paper we have synthesized two new phosphorus- and antimony-containing bismuth complexes [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ (E=P, Sb) with the linear anion [Bi₃I₁₂]³⁻ and carried out X-ray diffraction analysis of these.

Experimental

tris(Tetra-*p*-tolylphosphonium) hexakis(μ₂-iodo)-hexaiodo-tribismuth 2-ethoxyethanol solvate (I). The solution of 0.100 g (0.19 mmol) tetra-*p*-tolylphosphonium and 0.113 g (0.19 mmol) bismuth triiodide in 15 mL 2-ethoxyethanol was obtained. The solvent was slowly evaporated. The yield was 0.142 g (65%) of orange-red crystals of complex **I** with decomposition temperature 195 °C. Found, %: C 30.83, H 2.74. For C₈₈H₉₄O₂P₃Bi₃I₁₂ calculated, %: C 30.54, H 2.85.

tris(Tetra-*p*-tolylstibonium) hexakis(μ₂-iodo)-hexaiodo-tribismuth 2-ethoxyethanol solvate (II). It was obtained by the similar procedure. Orange-red crystals of complex **II** were isolated (48%) with decomposition temperature 219 °C. Found, %: C 28.56, H 2.54. For C₈₈H₉₄O₂Sb₃Bi₃I₁₂ calculated, %: C 28.43, H 2.62.

The X-ray diffraction analyses of crystals **I** and **II** were performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_α-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [5]. All calculations for structure determination and refinement were performed using the SHELXL/PC [6] and OLEX2 programs [7]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for the structure are listed in Table 1, the selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1053856, 1049481; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic data and the experimental and structure refinement parameters for compounds I, II

Parameter	Value	
	I	II
Empirical formula	C ₈₈ H ₉₄ O ₂ P ₃ I ₁₂ Bi ₃	C ₈₈ H ₉₄ O ₂ Sb ₃ I ₁₂ Bi ₃
Formula weight	3426.28	3698.62
<i>T</i> , K	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	12.4517(6)	12.4055(4)
<i>b</i> , Å	18.0680(9)	18.3805(5)
<i>c</i> , Å	24.1711(10)	24.6523(7)
α , deg	87.532(2)	87.401(2)
β , deg	87.039(2)	87.049(2)
γ , deg	75.281(2)	74.124(2)
<i>V</i> , Å ³	5250.0(4)	5396.8(3)
<i>Z</i>	4	2
ρ (calcd.), g/cm ³	2.167	2.276
μ , mm ⁻¹	8.630	9.085
<i>F</i> (000)	3136.0	3352.0
Crystal size, mm	0.26×0.25×0.16	0.33×0.3×0.14
2 θ Range of data collection, deg	4.04 – 46.56	4.1 – 53.54
Range of refraction indices	-13 ≤ <i>h</i> ≤ 13 -20 ≤ <i>k</i> ≤ 20 -26 ≤ <i>l</i> ≤ 26	-15 ≤ <i>h</i> ≤ 15 -23 ≤ <i>k</i> ≤ 23 -31 ≤ <i>l</i> ≤ 31
Measured reflections	94609	102068
Independent reflections	15056	22967
<i>R</i> _{int}	0.0486	0.0587
Refinement variables	990	990
<i>GOOF</i>	1.036	1.007
<i>R</i> factors for <i>F</i> ² > 2 σ (<i>F</i> ²)	<i>R</i> ₁ = 0.0361 <i>wR</i> ₂ = 0.0817	<i>R</i> ₁ = 0.0382 <i>wR</i> ₂ = 0.0705
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.0579 <i>wR</i> ₂ = 0.0941	<i>R</i> ₁ = 0.0711 <i>wR</i> ₂ = 0.0811
Residual electron density (min/max), e/Å ³	1.42/-0.77	1.29/-0.92

Table 2
Selected bond lengths and bond angles in the structure of compounds 1, 2

Bond <i>d</i> , Å		Angle ω , deg	
I			
P(1) – C(1)	1.788(8)	C(1)P(1)C(11)	109.0(4)
P(1) – C(11)	1.800(7)	C(1)P(1)C(21)	110.0(4)
P(1) – C(21)	1.761(9)	C(1)P(1)C(31)	109.6(4)
P(1) – C(31)	1.799(8)	C(11)P(1)C(21)	110.3(4)
P(2) – C(41)	1.804(7)	C(11)P(1)C(31)	109.9(3)
P(2) – C(51)	1.791(6)	C(21)P(1)C(31)	108.0(4)

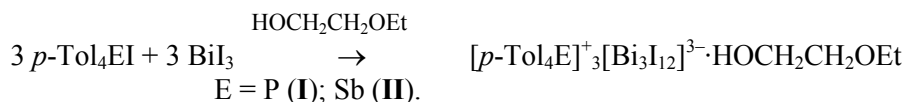
Bond d , Å		Angle ω , deg	
I			
P(2) – C(61)	1.770(7)	C(41)P(2)C(51)	107.5(3)
P(2) – C(71)	1.795(7)	C(41)P(2)C(61)	109.6(3)
P(3) – C(81)	1.800(7)	C(41)P(2)C(71)	111.7(3)
P(3) – C(91)	1.791(7)	C(51)P(2)C(61)	109.3(3)
P(3) – C(101)	1.815(7)	C(51)P(2)C(71)	111.4(3)
P(3) – C(111)	1.800(8)	C(61)P(2)C(71)	107.3(3)
Bi(1) – I (1)	3.0748(5)	C(81)P(3)C(91)	109.7(3)
Bi(1) – I (2)	3.0706(5)	C(81)P(3)C(101)	109.1(3)
Bi(1) – I (3)	3.0444(4)	C(81)P(3)C(111)	107.7(4)
Bi(2) – I (1)	3.3046(5)	C(91)P(3)C(101)	107.8(3)
Bi(2) – I (2)	3.2715(5)	C(91)P(3)C(111)	109.1(3)
Bi(2) – I (3)	3.3556(5)	C(101)P(3)C(111)	113.4(4)
Bi(2) – I (4)	2.9181(5)	I(1)Bi(1)I(2)	91.611(13)
Bi(2) – I (5)	2.8714(5)	I(7)Bi(3)I(9)	88.583(16)
Bi(2) – I (6)	2.9049(5)	I(7)Bi(3)I(8)	85.096(15)
Bi(3) – I (7)	3.0669(5)	I(8)Bi(3)I(9)	88.406(15)
Bi(3) – I (8)	3.0654(5)	I(2)Bi(2)I(3)	79.092(13)
Bi(3) – I (9)	3.0454(6)	I(2)Bi(2)I(4)	88.012(16)
Bi(4) – I (7)	3.3153(6)	I(2)Bi(2)I(5)	93.250(16)
Bi(4) – I (8)	3.3891(6)	I(2)Bi(2)I(6)	169.597(15)
Bi(4) – I (9)	3.2907(7)	I(3)Bi(2)I(4)	94.399(15)
Bi(4) – I (10)	2.8958(6)	I(3)Bi(2)I(5)	165.035(15)
Bi(4) – I (11)	2.9040(7)	I(3)Bi(2)I(6)	92.370(15)
Bi(4) – I (12)	2.9088(7)	I(4)Bi(2)I(5)	98.194(16)
		I(4)Bi(2)I(6)	98.652(17)
		I(5)Bi(2)I(6)	93.689(17)
		I(7)Bi(4)I(8)	76.406(14)
		I(7)Bi(4)I(9)	80.500(15)
		I(7)Bi(4)I(10)	87.219(17)
		I(7)Bi(4)I(11)	93.121(18)
		I(7)Bi(4)I(12)	170.78(2)
		I(8)Bi(4)I(9)	79.245(15)
		I(8)Bi(4)I(10)	163.130(16)
		I(8)Bi(4)I(11)	87.587(17)
		I(8)Bi(4)I(12)	101.94(2)
		I(9)Bi(4)I(10)	94.251(17)
		I(9)Bi(4)I(11)	166.381(18)
		I(9)Bi(4)I(12)	90.28(2)
		I(10)Bi(4)I(11)	97.464(19)
		I(10)Bi(4)I(12)	93.58(2)
		I(11)Bi(4)I(12)	95.88(2)
II			
Sb(1) – C(1)	2.089(6)	C(1)Sb(1)C(11)	107.6(3)
Sb(1) – C(11)	2.099(8)	C(1)Sb(1)C(21)	110.8(3)
Sb(1) – C(21)	2.091(7)	C(1)Sb(1)C(31)	108.8(3)

Table (end)

Bond <i>d</i> , Å		Angle ω, deg	
II			
Sb(1) – C(31)	2.085(8)	C(11)Sb(1)C(21)	112.0(3)
Sb(2) – C(41)	2.086(7)	C(11)Sb(1)C(31)	110.9(3)
Sb(2) – C(51)	2.097(7)	C(21)Sb(1)C(31)	106.9(3)
Sb(2) – C(61)	2.097(7)	C(41)Sb(2)C(51)	109.7(3)
Sb(2) – C(71)	2.086(7)	C(41)Sb(2)C(61)	106.1(3)
Sb(3) – C(81)	2.092(8)	C(41)Sb(2)C(71)	113.6(3)
Sb(3) – C(91)	2.073(9)	C(51)Sb(2)C(61)	110.2(3)
Sb(3) – C(101)	2.090(9)	C(51)Sb(2)C(71)	105.6(3)
Sb(3) – C(111)	2.085(8)	C(61)Sb(2)C(71)	111.7(3)
Bi(1) – I (1)	3.0785(5)	C(81)Sb(3)C(91)	113.7(3)
Bi(1) – I (2)	3.0866(5)	C(81)Sb(3)C(101)	113.1(3)
Bi(1) – I (3)	3.0595(4)	C(81)Sb(3)C(111)	105.4(3)
Bi(2) – I (2)	3.3341(5)	C(91)Sb(3)C(101)	107.9(3)
Bi(2) – I (3)	3.3376(5)	C(91)Sb(3)C(111)	109.6(3)
Bi(2) – I (4)	2.9191(5)	C(101)Sb(3)C(111)	106.8(4)
Bi(2) – I (5)	2.9234(6)	I(1)Bi(1)I(2)	92.813(14)
Bi(2) – I (6)	2.8867(5)	I(1)Bi(1)I(3)	93.202(13)
Bi(3) – I (7)	3.0754(5)	I(2)Bi(2)I(3)	78.388(13)
Bi(3) – I (8)	3.0672(5)	I(2)Bi(2)I(4)	92.235(15)
Bi(3) – I (9)	3.0750(6)	I(2)Bi(2)I(5)	167.390(16)
Bi(4) – I (8)	3.3694(6)	I(2)Bi(2)I(6)	89.205(16)
Bi(4) – I (9)	3.2947(6)	I(3)Bi(2)I(4)	91.055(14)
Bi(4) – I (10)	2.9086(8)	I(3)Bi(2)I(5)	93.163(15)
Bi(4) – I (11)	2.9248(6)	I(3)Bi(2)I(6)	166.958(16)
Bi(4) – I (12)	2.9032(6)	I(4)Bi(2)I(5)	97.312(17)
		I(4)Bi(2)I(6)	93.459(17)
		I(5)Bi(2)I(6)	98.383(17)
		I(7)Bi(3)I(8)	94.620(15)
		I(7)Bi(3)I(9)	91.955(16)
		I(8)Bi(3)I(9)	88.963(16)
		I(8)Bi(4)I(9)	80.444(15)
		I(8)Bi(4)I(10)	101.90(2)
		I(8)Bi(4)I(11)	86.408(17)
		I(8)Bi(4)I(12)	163.561(19)
		I(9)Bi(4)I(10)	89.58(2)
		I(9)Bi(4)I(11)	166.666(19)
		I(9)Bi(4)I(12)	94.318(16)
		I(10)Bi(4)I(11)	95.33(2)
		I(10)Bi(4)I(12)	93.58(2)
		I(11)Bi(4)I(12)	97.730(19)

Results and Discussion

It has been shown that the interaction of equimolar amounts of tetra-p-tolylphosphonium and tetra-p-tolylstybonium iodides with bismuth triiodide in 2-ethoxyetanol leads to formation of the ionic bismuth complexes with the anion [Bi₃I₁₂]³⁻, which contain the solvate molecule of the solvent:



According to X-ray diffraction data, the phosphorus and antimony atoms of the cations have weakly distorted tetrahedral coordination (Fig. 1 and 2). Angles CPC and CSbC equal $107.3(3)^\circ$ – $113.4(4)^\circ$ and $105.4(3)^\circ$ – $113.7(3)^\circ$, respectively. Bond lengths P–C (1.761(9)–1.815(7) Å) and Sb–C (2.085(8)–2.099(8) Å) are near to the sums of covalent radii of phosphorus, carbon (1.88 Å) and antimony, carbon (2.19 Å) [8]. In trinuclear centrosymmetrical anions $[\text{Bi}_3\text{I}_{12}]^{3-}$ the terminal fragments BiI_3 ($\text{Bi}-\text{I}_{\text{term}}$ 2.8714(5)–2.9181(5) Å (**I**), 2.8867(5)–2.9248(6) Å (**II**)) are bonded to the central bismuth atom through six μ_2 -bridging iodine atoms ($\text{Bi}-\text{I}_{\text{br}}$ 3.0454(6)–3.3891(6) Å (**I**), 3.0595(4)–3.3694(6) Å (**II**)). The terminal fragments BiI_3 are in the masked conformation.

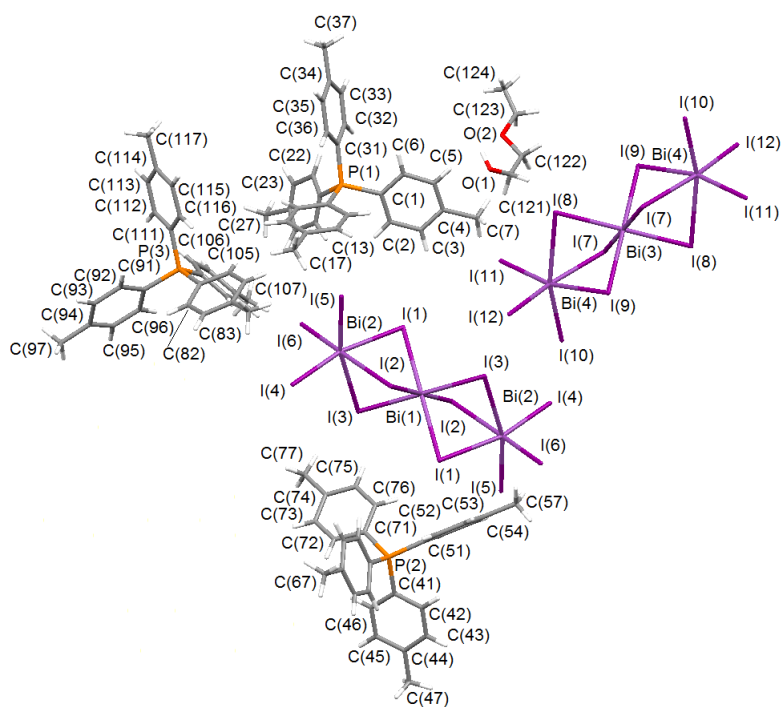


Fig. 1. The structure of complex I

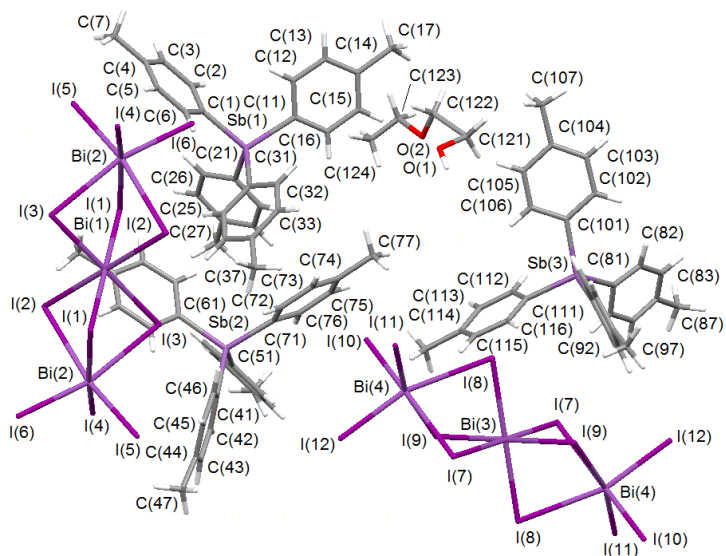


Fig. 2. The structure of complex II

The structural organization in crystals **I** and **II** results from weak interactions of the type H···I and H···O. In **I** the bridging μ₂-atoms of iodine in anions are bonded (2.86–3.16 Å) to the hydrogen atoms of phosphonium cations, in **II** the similar bonds are formed with participation of both bridging (3.10 Å) and terminal (3.15 Å) atoms of iodine (which is somewhat less than the sum of Van der Waals radii of hydrogen and iodine, namely, 3.3 Å [8]). No significant close contacts of the ions with the solvent molecules have been observed, but the molecules of 2-ethoxyethanol are bonded with each other by hydrogen bonds H···O (2.33 Å (**I**) and 2.62 Å (**II**)) (Fig. 3).

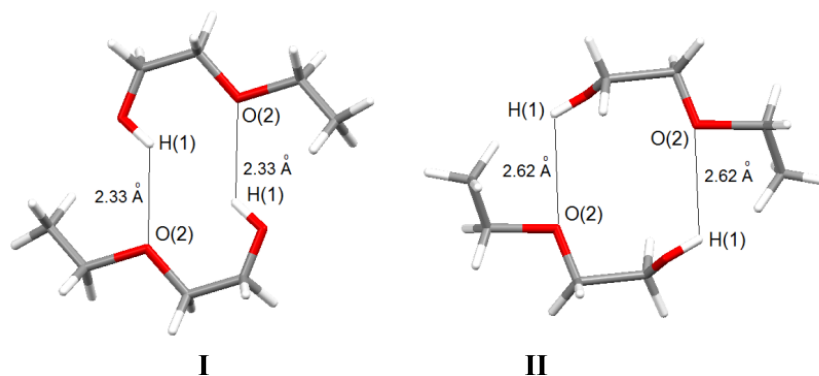


Fig. 3. Association of solvent molecules in crystals **I** and **II**

Conclusions

Complexes [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P (**I**), Sb (**II**) have been synthesized by interaction of equimolar amounts of tetra-*p*-tolylphosphonium and tetra-*p*-tolylstibonium iodides with bismuth triiodide in 2-ethoxyethanol. The structure of the products has been established by X-ray diffraction analysis.

References

1. Geiser U., Wade E., Wang H.H., Williams J.M. Structure of a New Iodobismuthate: Tetra(*n*-butyl)ammonium 1,2;1,2;1,2;2,3;2,3;2,3-hexa-μ-iodo-1,1,1,3,3,3-hexaiodotribismuthate (III) (3:1) *Acta Crystallographica Section C*, 1990, vol. 46, no 8, pp. 1547–1549. DOI: 10.1107/S0108270190003006
2. Carmalt C.J., Farrugia L.J., Norman N.C. Structural Studies on some Iodoantimonate and Iodobismuthate Anions *Zeitschrift für anorganische und allgemeine Chemie*, 1995, vol. 621, no. 47, pp. 47–56. DOI: 10.1002/zaac.19956210110
3. Mallick D., Sarker K.K., Saha R., Mondal T.K., Sinha C. Intercalated Iodobismuthate in the Layers of Azoimidazoles. Structure, Photochromism and DFT Computation *Polyhedron*, 2013, vol. 54, pp. 147–157. DOI:10.1016/j.poly.2013.01.061
4. Sharutin V.V., Egorova I.V., Klepikov N.N., Boyarkina E.A., Sharutina O.K. Synthesis and Structure of Bismuth Complexes [Ph₃MeP]₆⁺ [Bi₃Br₃]₃³⁻ [Bi₂I₆Br₃]₃³⁻·H₂O₂, [Ph₃EtP]₃⁺ [Bi₂I₉]₃³⁻, [Ph₃MeP]₃⁺ [Bi₃I₁₂]₃³⁻, [Ph₃(*iso*-Pr)P]₃⁺ [Bi₃I₁₂]₃³⁻·2Me₂C=O, and [Ph₄Bi]₃⁺ [Bi₅I₁₈]₃³⁻ *Russian Journal of Inorganic Chemistry*, 2009, vol. 54, no. 1, pp. 52–68. DOI: 10.1134/S0036023609010124
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341.
8. Batsanov S.S. Atomnyye Radiusy Jelementov. *Zhurn. neorgan. himii. [Russian Journal of Inorganic Chemistry]*, 1991, vol. 36, no. 12, pp. 3015–3037.

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**СИНТЕЗ И СТРОЕНИЕ КОМПЛЕКСОВ ВИСМУТА
[p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P, Sb**

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Взаимодействием эквимольных количеств иодидов тетра-*n*-толилфосфония и тетра-*n*-толилстибония с трииодидом висмута в 2-этоксигэтанолу получены комплексы [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P (I), Sb (II). Проведен рентгеноструктурный анализ I и II. В катионах координация атомов фосфора и сурьмы тетраэдрическая (углы CPC 107.3(3)°–113.4(4)° (I), CSbC 105.4(3)°–113.7(3)° (II); связи P–C 1.761(9)–1.815(7) Å (I), Sb–C 2.085(8)–2.099(8) Å (II). В трехъядерных анионах [Bi₃I₁₂]³⁻ концевые фрагменты BiI₃ (Bi–I_{терм} 2.8714(5)–2.9181(5) Å (I) 2.8867(5)–2.9248(6) Å (II)) связаны с центральным атомом висмута посредством шести μ₂-мостиковых атомов иода (Bi–I_{мост} 3.0454(6)–3.3891(6) Å (I) 3.0595(4)–3.3694(6) Å (II)).

Ключевые слова: трииодид висмута, комплексы висмута [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅, E=P, Sb, синтез, строение.

Литература

1. Structure of a New Iodobismuthate: Tetra(*n*-butyl)ammonium 1,2;1,2;1,2;2,3;2,3;2,3-hexa-μ-iodo-1,1,1,3,3,3-hexaiodotribismuthate (III) (3:1) / U. Geiser, E. Wade, H.H. Wang, J.M. Williams // *Acta Crystallographica Section C*, 1990. – V. 46, № 8. – P. 1547–1549.
2. Carmalt, C.J. Structural Studies on some Iodoantimonate and Iodobismuthate Anions / C.J. Carmalt, L.J. Farrugia, N.C. Norman // *Zeitschrift für anorganische und allgemeine Chemie*. – 1995. – V. 621, № 47. – P. 47–56.
3. Intercalated Iodobismuthate in the Layers of Azoimidazoles. Structure, Photochromism and DFT Computation / D. Mallick, K.K. Sarker, R. Saha, T.K. Mondal et al. // *Polyhedron*. – 2013. – V. 54, P. 147–157.
4. Synthesis and Structure of Bismuth Complexes [Ph₃MeP]₆⁺ [BiI₃Br₃]³⁻ [Bi₂I₆Br₃]³⁻ · H₂O₂, [Ph₃EtP]₃⁺ [Bi₂I₉]³⁻, [Ph₃MeP]₃⁺ [Bi₃I₁₂]³⁻, [Ph₃(*iso*-Pr)P]₃⁺ [Bi₃I₁₂]³⁻ · 2Me₂C=O, and [Ph₄Bi]₃⁺ [Bi₅I₁₈]³⁻ / V.V. Sharutin, I.V. Egorova, N.N. Klepikov, E.A. Boyarkina et al // *Russian Journal of Inorganic Chemistry*. – 2009. – V. 54, № 1. – P. 52–68.
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. OLEX2: a Complete Structure Solution, Refinement and Analysis Program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // *J. Appl. Cryst.* – 2009. – V. 42. – P. 339–341.
8. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // *Журн. неорган. химии*. – 1991. – Т. 36. – № 12. – С. 3015–3037.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Synthesis and structure of bismuth complexes [p-Tol₄E]⁺₃[Bi₃I₁₂]³⁻·HOCH₂CH₂OC₂H₅ E=P, Sb / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin et al. // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 44–51. DOI: 10.14529/chem150406

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SYNTHESIS OF POLYACRYL THICKENERS BY RADICAL PRECIPITATION POLYMERIZATION

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Lightly cross-linked polymer thickeners on the basis of acrylic and methacrylic acid have been synthesized with the use of radical precipitation polymerization. The influence of introducing hydrophobic units, cross-linking degree, the nature of neutralizing agents, neutralization degree of acidic units, and other factors upon thickening properties of obtained polymers in water, as well as water mixtures with glycerol or propylene glycol, has been determined.

Keywords: acrylic acid, methacrylic acid, alkyl (meth)acrylates, radical polymerization, lightly cross-linked polymers, thickeners, water, glycerol, glycols.

Introduction

Polyacrylic thickeners, obtained on the basis of acrylic acid (AA) and methacrylic acid (MAA) are widely used as modifiers of rheological properties for aqueous systems in textile industry [1], as well as for water-glycol de-icing fluids (DIF) of type IV, which are designed for preflight treatment of aircrafts in winter conditions [2]. In accordance with the conditions of use, such thickeners should achieve the necessary thickening degree of solutions at their minimal content in mixtures, also they should exhibit the optimal change of viscosity at various tensions and temperatures. This is accomplished by varying the composition of polymers and their molar mass, by choosing the neutralizing agent, changing the neutralization degree of acidic units and other factors [3]. At present the lightly cross-linked hydrophobically modified polymers of AA and MAA, containing the units of higher alkyl acrylates or alkyl methacrylates, are the most widely used thickeners of acryl type. Interaction of hydrophobic alkyl fragments of such macromolecules in aqueous solutions enhances their thickening property [4, 5]. At that the degree of cross-linking, the molar mass of the polymer and the content of hydrophobic units should ensure retention of the polymer solubility in the used systems at all operating conditions. Quite often the hydrophobically modified polyacryl thickeners are synthesized with the use of radical precipitation polymerization in the medium of hydrophobic organic solvents [6, 7]. By way of trial-and-error selection of the solvent and the synthesis conditions it is possible to achieve precipitation of the polymers exhibiting the necessary set of properties in water and water-glycol solutions.

The aim of the present study is the synthesis by precipitations polymerization of thickeners on the basis of AA and MAA, differing in composition, cross-linking degree, the nature of neutralizing agents, and neutralization degree of acidic units, as well as evaluation of thickening properties of obtained polymers in aqueous solutions and in the systems water – propylene glycol (PG) and water – glycerol.

Experimental

Reagents that were used in the study: AA, n-butyl acrylate (BA) by "SIBUR-neftekhim", MAA, lauryl methacrylate (LMA), acrylamide (AAM), triethylene glycol dimethacrylate (TGM-3), and ethylene glycol dimethacrylate (DMEG) by "Aldrich".

Copolymerization of MAA and BA was carried out in cyclohexane, heptane, or benzene at various monomer ratios and their total concentration ($\Sigma[M]_0$) equaling 12 % m/m, in the presence of lauroyl pe-

roxide (1.0% mol of $\Sigma[M]_0$) as the initiator and DMEG (0.6 % mol of $\Sigma[M]_0$) as the cross-linking agent, at boiling temperature of the reaction mixture. The time of synthesis equaled 3 h. Homopolymerization of AA or its copolymerization with LMA (mole ratio 99.5 : 0.5), AAm or BA (mole ratio 95.0 : 5.0) was carried out at the total monomer concentration 13 % m/m in ethyl acetate medium, in the presence of 2,2'-azobis-(2,4-dimethylvaleronitrile) (0.1–0.2 % mol of $\Sigma[M]_0$) as the initiator and TGM or DMEG (0.2–0.5% mol of $\Sigma[M]_0$) as the cross-linking agent, at temperature 70 °C and synthesis time 2 h. After the synthesis the precipitated polymers were filtered and dried at reduced pressure and temperature 50–60 °C to constant mass. Then the weighed samples of the polymers were dissolved at intensive stirring in the aqueous solution of the neutralizing agent (in order to reach the predetermined neutralization degree of acidic units) or in the mixtures glycerol – water (60 : 40 % m/m), propylene glycol (PG) – water (50 : 50 % m/m), followed by neutralization with the concentrated aqueous solution of sodium hydroxide to pH 7-8.

Kinematic viscosity of the solutions of copolymers MAA–BA in DMFA (0.25 % m/m) and neutralized copolymers MAA–BA in aqueous solutions (0.2 % m/m) was determined, respectively, in viscosimeter VPZh-1 with capillar diameter 2.10 mm, and VPZh-2 with capillar diameter 0.73 mm at temperature 20 °C. Relative viscosity (η_{rel}) was determined according to the formula:

$$\eta_{rel} = \tau_p / \tau_x,$$

where τ_p and τ_x are flow times of solutions with a thickener and without a thickener, respectively, s.

Dynamic viscosity of the solutions of (co)polymers AA in the mixtures water – glycol and water – glycerol was measured in the apparatus Brookfield DV-II+Pro, furnished with the small-sample adapter and spindle #31 in Brookfield classification, at temperature 20 °C and various rotation speeds of the spindle.

Results and Discussion

Thickeners on the basis of hydrophobically modified polymethacrylic acid are mostly used for aqueous systems, therefore the synthesized copolymers MAA–BA have been tested in aqueous solutions. To choose the conditions of the synthesis, comparative experiments have been carried out in three nonpolar hydrocarbon solvents: heptane, cyclohexane, and benzene. The listed solvents are close to each other in polarity, that is, the solubility of the formed copolymers in them should differ insignificantly. However, the chain transfer constants C_s for these solvents differ, they equal $1.7 \cdot 10^{-4}$ for heptane, $0.1 \cdot 10^{-4}$ for cyclohexane, $0.075 \cdot 10^{-4}$ for benzene. Viscosity values of 0.2 % copolymer solutions in DMFA equal 1.5, 1.8, and 2.0 for the polymers obtained in heptane, cyclohexane, and benzene, respectively, at the same amounts of the monomer, the cross-linking agent, and the initiator. Thus, it has been shown that the molar mass of macromolecules increases with decrease of C_s value, exactly as expected. In the course of experimental study it has been also shown that the use of benzene as the medium for the reaction leads to decrease of the polymer yield. In addition, benzene is more toxic than heptane and cyclohexane. Therefore, cyclohexane has been chosen for further experiments. One of the key parameters, that influence the efficiency of the thickening polyacryl polymers, is the ratio of hydrophilic acidic units and the hydrophobic units of alkyl (meth)acrylates. The optimal value of this ratio depends on the nature of hydrophilic and hydrophobic units in copolymers, it should be selected individually for each system under investigation.

To choose the optimal ratio in the case of thickening aqueous solutions with MAA–BA copolymers the series of syntheses in cyclohexane medium has been carried out at various initial ratios of the acidic monomer and the esteric one, at

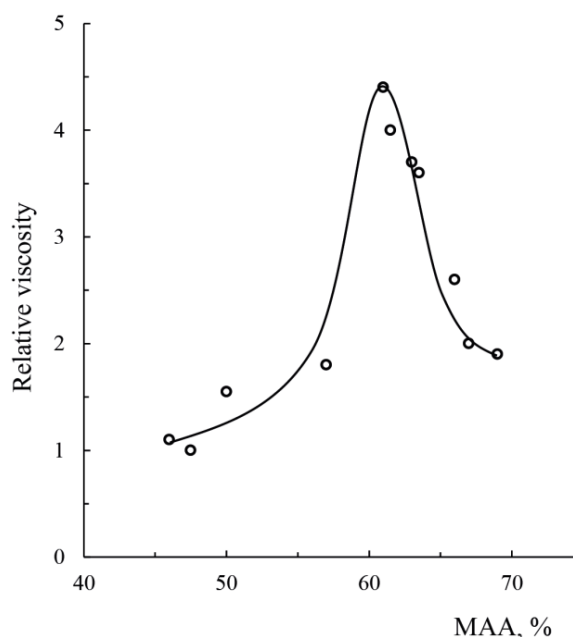


Fig. 1. Relative viscosity of the solutions of MAA–BA copolymers in DMFA as the function of the acidic unit content in them

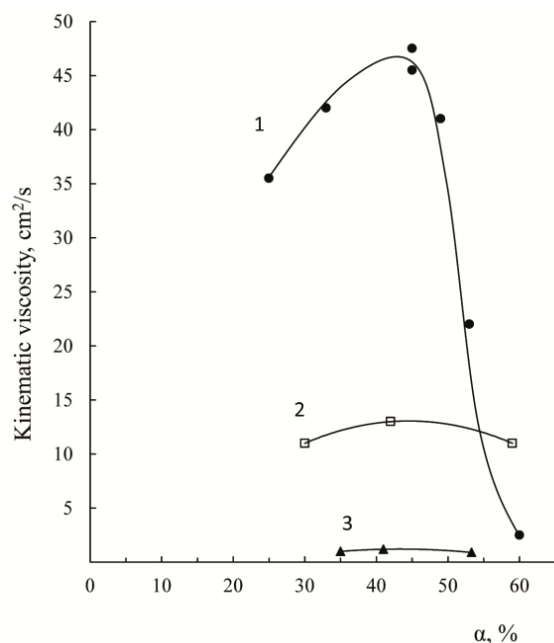


Fig. 2. Kinematic viscosity of the MAA–BA copolymers as the function of the acidic unit content and the degree of neutralization (α) by diethylamine. MAA : BA = 63:37 (1); 80:20 (2); 90:10 (3)

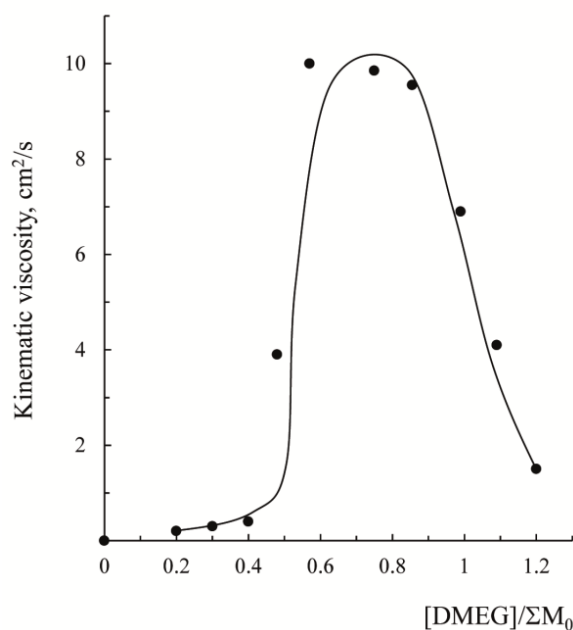


Fig. 3. Kinematic viscosity of the aqueous solutions of MAA–BA copolymers as the function of DMEG content in the initial monomer mixture

constant content of the cross-linking agent, namely, DMEG (0.6 % mol of $\Sigma[M]_0$). The obtained samples of the copolymers differ in the acidic unit content, which varies from 45 to 70 %. Figure 1 shows the influence of the acidic unit content on the viscosity of 0.2 % polymer solutions in DMFA. The maximal viscosity value, corresponding to the acidic unit content 62–64 %, is observed on the resultant curve. The relationship between the thickening property of polymers and the degree of acidic unit neutralization, represented in Fig. 2, supports the greater thickening property of copolymers containing 63 % MAA units.

Because of this, in the following experiments with the MAA–BA copolymer the influence of other factors has been evaluated at the ratio of monomer units 63:37.

An important factor, which influences the viscosity characteristics of the polymers, is the cross-linking degree that depends on content of the introduced cross-linking agent. Due to experimental study of DMEG content variation in the monomer mixture (Fig. 3) it has been established that the relationship between the thickening property of the MAA–BA copolymer and the initial DMEG content exhibits a clearly defined maximum.

Special consideration must be given to the steep rise of the thickening property at increasing DMEG concentration from 0.4 to 0.5 % mol. of the total concentration of main monomers ($\Sigma[M]_0$), as well as the steep decline of this property after increasing DMEG concentration from 0.9 to 1.0–1.2 % mol of $\Sigma[M]_0$. Observational data point at the interval of the optimal cross-linking degree for macromolecules, in order to achieve the greatest viscosity of their solutions (that is, the formation of macromolecular coils occupying the greatest volume in a solution).

The neutralization degree of acidic groups and the nature of neutralizing agent have a dramatic effect on the viscosity of aqueous solutions. Fig. 4 shows the kinematic viscosity values depending on the neutralization degree of acidic groups and the kind of the base used to neutralize the cross-linked copolymer obtained from MAA–BA (63 : 37). The following bases have been used: monoethanolamine, diethylamine, and NaOH. From the represented data it is apparent that viscosity of aqueous solutions significantly increases at the neutralization degree of acidic groups equaling 30–40 %, after which it just as significantly decreases. Besides, the position of the viscosity maximum and the intensity of thickening depend on the nature of a neutralizing agent, especially in the range 20–40 % neutralization degree.

On the basis of the obtained data complex the recommended conditions for the synthesis of MAA–BA copolymer thickeners, to be used in aqueous systems, have been chosen: the solvent is cyclohexane, the ratio MAA : BA = 67:33, the initial total concentration of monomers equals 12 % m/m, the initiator concentration (lauroyl peroxide) is 1.0 % mol, the cross-linking agent (DMEG) is present in the amount

0.6 % mol (of $\Sigma[M]_0$). The neutralizing agent and the neutralization degree of acidic units should be chosen individually for each application object.

Other type of polyacryl thickeners, studied in the present paper, has been the lightly cross-linked water-soluble polymers of acrylic acid. In view of the abovementioned literature data, the thickening properties of the polymers on the AA basis were determined in low-freezing aqueous solutions of glycerol and PG, in order to evaluate the possibilities of using such polymers to produce DIF of type IV. The important property of such DIFs is their decreasing viscosity, when an aircraft gathers speed during takeoff, which facilitates the removal of DIF from the hull surface.

That's why the main criteria for comparison of various thickeners are achievement of the optimal level of dynamic viscosity and the degree of its decreasing under mechanical load.

First of all the study has concerned the influence of the type and concentration of the cross-linking agent on the thickening properties of AA homopolymers, obtained by precipitation polymerization in ethyl acetate. As indicated by Table 1, the homopolymer obtained without any cross-linking agent shows a low thickening degree (200 mPa·s) even at its high concentration in the solution, namely, 1.0 % m/m. Low viscosity persists also for the solutions on the basis of the AA homopolymer obtained at insignificant (0.06 % mol of $\Sigma[M]_0$) concentration of the cross-linking agent, which is TGM-3. The observed data point at low molecular masses of the synthesized thickeners. However, with increasing TGM-3 concentration at the synthesis stage up to 0.3 % mol of $\Sigma[M]_0$, the formed polymer has high thickening ability, and the dynamic viscosity of the thickening agent solutions in the media water-glycerol and water-PG equals 7600 and 6700 mPa·s, respectively. Further increase of cross-linking content in the polymer makes it insoluble in the mentioned systems (Table 1, no. 3). As an alternative cross-linking agent, DMEG has been tested, but in this case the obtained polymers have lower thickening ability compared to the samples linked by TGM-3.

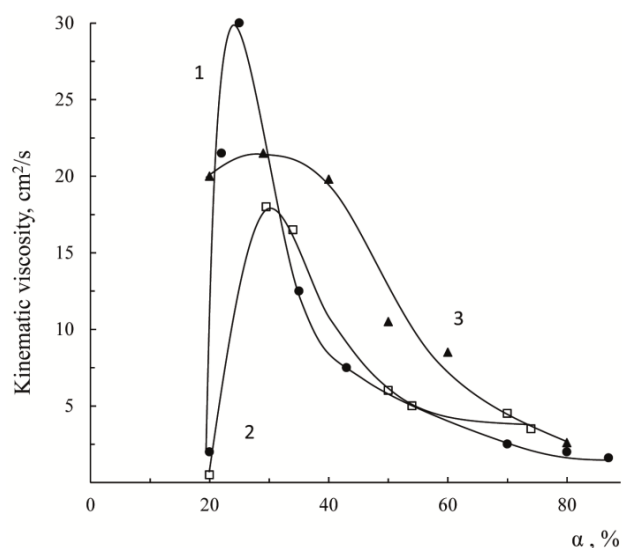


Fig. 4. Kinematic viscosity of the MAA-BA copolymer (63:37) as the function of the neutralization degree of acidic units by monoethanolamine (1), diethylamine (2), and NaOH (3)

Table 1

Synthesis conditions and characteristics of solutions of the polymer thickeners on the basis of acrylic acid

No.	Comonomer (% mol)	Cross-linking agent (% mol of $\Sigma[M]_0$)	Solvent for synthesis	Solvent for testing SPL	C, % m/m	Dynamic viscosity*, mPa·s
1	–	–	Ethyl acetate	Glycerol – water	1.0	200
2	–	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	7600
				PG – water	0.9	6700
3	–	TGM-3 (0.50)	Ethyl acetate	Glycerol – water	0.4	insoluble
4	–	DMEG (0.30)	Ethyl acetate	Glycerol – water	0.4	7000
				PG – water	0.9	5000
5	AAm (5.0)	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	900
				PG – water	0.9	200
6	BA (5.0)	TGM-3 (0.30)	Ethyl acetate	Glycerol – water	0.4	6500
				PG – water	0.9	4000
7	LMA (0.5)	TGM-3 (0.20)	Ethyl acetate	Glycerol – water	0.4	5500
				PG – water	0.9	7700

* 0,3 rpm, pH 7.7–8.0.

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The next stage has centered on studying the properties of AA copolymers, linked by TGM-3 and containing additional hydrophobic or hydrophilic fragments. As hydrophobic comonomers at polymerization, butyl acrylate (BA) and lauryl methacrylate (LMA) have been used, while acrylamide (AAm) has been used as the hydrophilic one. The data collected in Table 1, obtained after the testing the abovementioned copolymers in the mixtures water-glycerol and water-PG, show that they are characterized by lower values of dynamic viscosity compared to the linked AA homopolymer. It is particularly remarkable that, as a whole, the obtained laboratory samples thicken the aqueous solutions of glycerol better than the aqueous solutions of PG. This may be explained by better dissolving capacity of the mixture glycerol–water in relation to the obtained polymers, which leads to increasing the size of macromolecular coils in solutions. The given fact points at the preference of using aqueous solutions of glycerol with the thickeners of this type.

Note that for the solutions of almost all obtained polymers (except those with the viscosity value lower than 1000 mPa·s) the pseudo-plastic flow curve under load is typical (Fig. 5).

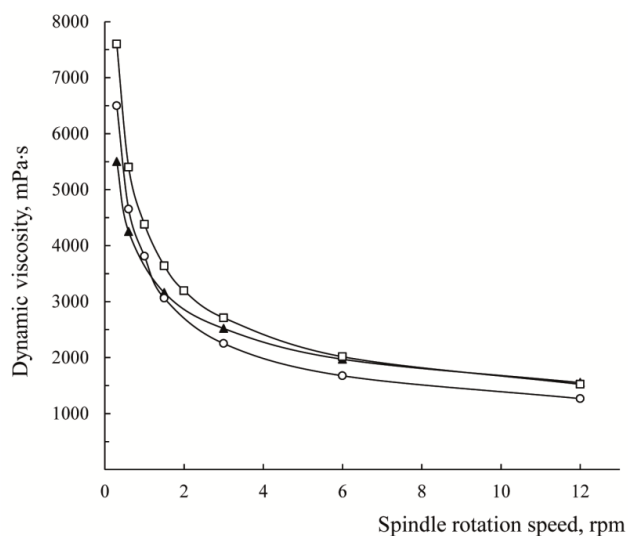


Fig. 5. Dynamic viscosity of water-glycerol solutions of the synthesized thickeners as the function of the spindle rotation speed. Copolymer composition; mass percentage of polymers in the mixture, %; thickener content in the polymer, % mol: (▲) AA:LMA (99.5:0.5), 0.4 %, 0.2 %; (■) AA, 0.4 %, 0.3 %; (○) AA:BA (95.0:5.0), 0.4 %, 0.3 %

In order to evaluate this effect quantitatively, the degree of pseudo-plasticity has been determined as the ratio of the dynamic viscosity of a solution at the spindle rotation speed 0.3 rpm to the dynamic viscosity of the same solution at the spindle rotation speed 1.5 rpm. Comparative analysis has shown that the pseudo-plasticity effect is the most pronounced for solutions on the basis of the cross-linked AA homopolymer (Table 1, no. 2). The average value of the pseudo-plasticity degree of this polymer, both in the mixture water–glycerol and in the mixture water–PG, equals 2.15; while other thickeners do not reach 2.0 of this value.

Thus, under the chosen experimental conditions the AA homopolymer with the optimal cross-linking degree is found to be the most efficient potential thickener for antifreezing compositions intended for producing DIF of type IV, since its solutions are distinguished by the greatest viscosity and the pseudo-plasticity degree compared to solutions of other investigated thickeners.

Conclusion

Lightly cross-linked polymer thickeners on the basis of acrylic and methacrylic acid have been synthesized with the use of radical precipitation polymerization. For MAA–BA copolymers the influence of cross-linking degree, content of acidic units, the nature of the neutralizing agent, neutralization degree of acidic units upon thickening properties in aqueous solutions has been determined. For cross-linked AA homopolymers fine prospects to be of use as thickeners for DIF of type IV on the basis of water–glycerol solutions have been shown.

Acknowledgments

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References

1. Tselms R.N. *Sozdanie kompozitsiy na osnove akrilovykh sopolimerov dlya protsessov pechata-niya tekstil'nykh materialov pigmentami i aktivnymi krasitelyami. Dis. kand. tekhn. nauk* [Preparation of Compositions on the Basis of Acryl Copolymers for Printing Textile Materials by Pigments and Active Dyes. Cand. sci. diss.]. St. Petersburg, 2010. 161 p.
2. Abdala A.A. [Solution Rheology of Hydrophobically Modified Associative Polymers: Solvent Quality and Hydrophobic Interactions]. *J. Rheol.*, 2003, vol. 47, pp. 497–511. DOI: 10.1122/1.1545076
3. Wang Y., Hudson N.E., Pethrick R.A., Schaschke C.J. [Poly(acrylic acid)–Poly(vinyl pyrrolidone)–Thickened Water/Glycol De-icing Fluids]. *Cold Regions Science and Technology*, 2014, vol. 101, pp. 24–30. DOI: 10.1016/j.coldregions.2014.01.006.
4. Tian Q. Xbo-Ztai Tang, Dong-Qing Zhuang, Yun-Xiang Zhang. [Synthesis of Hydrophobically Modified Poly (acrylic acid) Gels and Interaction of the Gels with Cationic/Anionic Surfactants]. *Chinese Journal of Chemistry*, 2010, vol. 20, pp. 1088–1096. DOI: 10.1002/cjoc.20020201030
5. Zhuang D.-Q., Chen J., Da A.-H., Zhang Y.-X., Dieing R., Ma L., Haeussling L. [Hydrophobically Modified Polyelectrolytes II: Synthesis and Characterization of Poly(acrylic acid-co-alkyl acrylate)]. *Polym. Advan. Technol.*, 2001, vol. 12, pp. 616–625. DOI: 10.1002/pat.79
6. Zhang H. [Controlled/“living” Radical Precipitation Polymerization: a Versatile Polymerization Technique for Advanced Functional Polymers]. *European Polymer Journal*, 2013, vol. 49, pp. 579–600. DOI: 10.1016/j.eurpolymj. 2012.12.016
7. Bunyakana C., Hunkeler D. [Precipitation Polymerization of Acrylic Acid in Toluene. I: Synthesis, Characterization and Kinetics]. *Polymer*, 1999, vol. 40, pp. 6213–6224. DOI: 10.1016/S0032-3861(98)00836-2

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СИНТЕЗ ПОЛИАКРИЛОВЫХ ЗАГУСТИТЕЛЕЙ МЕТОДОМ ОСАДИТЕЛЬНОЙ РАДИКАЛЬНОЙ ПОЛИМЕРИЗАЦИИ

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Методом радикальной осадительной полимеризации синтезированы слабосшитые полимерные загустители на основе акриловой и метакриловой кислот. Определено влияние введения гидрофобных звеньев, степени сшивки, природы нейтрализующего агента, степени нейтрализации кислотных звеньев и других факторов на загущающие свойства полученных полимеров в воде, а также смесях воды с глицерином или пропиленгликолем.

Ключевые слова: акриловая кислота, метакриловая кислота, алкил(мет)акрилаты, радикальная полимеризация, слабосшитые полимеры, загустители, вода, глицерин, гликоли.

Литература

1. Целмс, Р.Н. Создание композиций на основе акриловых сополимеров для процессов печатания текстильных материалов пигментами и активными красителями: дис. ... канд. техн. наук / Р.Н. Целмс. – СПб., 2010. – 161 с.
2. Abdala, A.A. Solution Rheology of Hydrophobically Modified Associative Polymers: Solvent Quality and Hydrophobic Interactions / A.A. Abdala // *J. Rheol.* – 2003. – V. 47. – P. 497–511.
3. Poly(acrylic acid) – Poly(vinyl pyrrolidone) – Thickened Water/Glycol De-icing Fluids / Y. Wang, N.E. Hudson, R.A. Pethrick, C.J. Schaschke // *Cold Regions Science and Technology.* – 2014. – V. 101. – P. 24–30.
4. Synthesis of hydrophobically modified poly(acrylic acid) gels and Interaction of the gels with cationic/anionic surfactants / Q. Tian, X.-Z. Tang, D.-Q. Zhuang, Y.-X. Zhang // *Chinese Journal of Chemistry.* – 2010. – V. 20. – P. 1088–1096.
5. Hydrophobically modified polyelectrolytes II: synthesis and characterization of poly(acrylic acid-co-alkyl acrylate) / D.-Q. Zhuang, J. Chen, A.-H. Da et al. // *Polym. Advan. Technol.* – 2001. – V. 12. – P. 616–625.
6. Zhang, H. Controlled/“living” radical precipitation polymerization: a versatile polymerization technique for advanced functional polymers / H. Zhang // *European Polymer Journal.* – 2013. – V. 49. – P. 579–600.
7. Bunyakana, C. Precipitation polymerization of acrylic acid in toluene. I: synthesis, characterization and kinetics / C. Bunyakana, D. Hunkeler // *Polymer.* – 1999. – V. 40. – P. 6213–6224.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Kazantsev, O.A. Synthesis of polyacryl thickeners by radical precipitation polymerization / O.A. Kazantsev, M.S. Rumyantsev, M.V. Savinova et al. // *Вестник ЮУрГУ. Серия «Химия».* – 2015. – Т. 7, № 4. – С. 52–58. DOI: 10.14529/chem150407

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INFLUENCE OF SYNTHESIS CONDITIONS ON COMPOSITION OF ALKYL (METH)ACRYLATE – VINYL ALKYL ETHER COPOLIMERS

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Synthesis of methyl methacrylate copolymers with vinyl butyl ether has been carried out from the monomer mixture by compensate polymerization method. Analysis of their composition has shown that, respectively, either a conversion nonuniform copolymer is formed with methyl methacrylate units for the most part, or a copolymer nearing equimolar composition. By the example of monomer couple butyl acrylate–vinyl alkyl ether it has been shown that in order to get the structurally uniform copolymer, it is possible to use both classical radical initiators and binary alkylborane–oxygen initiators.

Keywords: methyl methacrylate, butyl acrylate, vinyl butyl ether, vinyl isobutyl ether, radical initiation, azobisisobutyronitrile, amine complex, triethylborane, tri-n-butylborane, copolymer composition.

Introduction

Synthesis of new copolymers under radical initiation conditions is a promising direction in chemistry of high-molecular compounds. Modification of polymer properties using the development of copolymer synthesis without additives, with radical initiators of various types, is still an urgent problem [1, 2]. In particular, fractional introduction of one of the monomers into the reaction sphere makes it possible to obtain copolymers whose composition is unlike those from the monomer mixture, with correspondingly new properties. Thus, such a method, used for copolymerization of some alkyl (meth)acrylates (AMA) with vinyl alkyl ethers, leads to structurally uniform copolymers. The results have been obtained by the example of monomer couples, including butyl acrylate (BA), the mixtures of esters formed by methacrylic acid and higher alcohols of C₈–C₁₀ fractions (CMA-1) and C₁₂–C₁₈ fractions (CMA-2) with vinyl butyl ether (VBE), vinyl isobutyl ether (ViBE) [3-6].

The aim of the present study is the comparative analysis of the composition of methyl methacrylate (MMA) copolymers with vinyl alkyl ethers (VAE) in synthesis from monomer mixture by compensate polymerization method, as well as of various initiators used to obtain BA–VBE copolymers of equimolar composition.

Experimental

Commercial reagents were used throughout.

In order to synthesize copolymers in ampoules the exact amounts of monomers and initiator were placed into glass ampoules, freed from oxygen by freezing the reaction mixture in liquid nitrogen and pumping out to residual pressure < 1.3 Pa. The ampoules were glass-sealed, then polymerization was carried out at strictly determined temperature. For that an ampoule was placed into a thermostat for pre-set time, after which the ampoule was taken out and frozen in liquid nitrogen to stop polymerization. The copolymer was isolated by recrystallization from solution [4]. Monomer conversion was gravimetrically determined.

The synthesis of copolymers by compensate polymerization method. The synthesis was performed in a four-necked flask with a reflux condenser, a paddle-type agitator, a thermocouple, and an outlet for reagent injection, placed in a thermostat. An exactly weighed sample of less reactive monomer was placed into the flask, the mixture was brought to boil while stirring. Through the outlet for reagent injection a solution of exactly weighed sample of azobisisobutyronitrile (BIN) was measured in doses with

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the use of a dropping funnel. After preset synthesis time the flask was cooled in water bath (40 °C). Unreacted monomers were pumped out at low pressure (to 0.5 mm of mercury). Under vacuumization conditions the polymer was dried in the flask to constant weight at $T = 20\text{--}25$ °C.

In the case of using triethylborane- (TEB) or tri-*n*-butylborane (TNB) – oxygen, the commercial complex trialkylborane hexamethylenediamine was placed into the reactor, and organoelemental component was isolated by measuring in doses the equimolar amount of methacrylic acid together with the reactive monomer.

IR spectra of the synthesized copolymers were recorded on the Fourier-transform IR spectrometer Shimadzu FTIR-8400S in KBr cuvettes with pathlength 0.26 mm in chloroform solution. The range of wavenumbers was $5500\text{--}550$ cm^{-1} , determination error did not exceed ± 0.05 cm^{-1} . The copolymer composition was determined with the use of calibrating curve by characteristic peak area. The analytical bands were the following: the band at 1727 cm^{-1} for carbonyl group (acrylate fraction); the band at 1100 cm^{-1} for C–O–C group of ether (VAE fraction).

^1H NMR spectra were recorded on the Agilent DD2 400 spectrometer (solutions in CDCl_3), at operating frequency 400 MHz. Chemical shifts are given in ppm in relation to the solvent residual signal (chloroform: 7.26 ppm). All spectra are recorded at temperature 25 °C.

Results and Discussion

In accordance with the purpose in hand the samples of MMA and VBE copolymers were obtained from the monomer mixture (Table 1) and by compensate polymerization (Table 2), the composition analysis was performed by IR- and NMR-spectroscopy.

It can be seen from the data in Table 1 that the copolymer synthesis from the monomer mixture of the following composition: 60 mol % MMA and 40 mol % VBE leads to formation of samples composed by MMA units for the most part, their fraction insignificantly decreases with conversion. Similar results were previously obtained by the example of the monomer couple BA–ViBE. The obtained results are obviously explained by relative reactivities of comonomers, whose values equal $r_{\text{MMA}} = 10\text{--}11$, $r_{\text{VBE}} \sim 0$ [7, 8]: high reactivity of the growing MMA radical with respect to its monomer leads to formation of the macromolecule containing but small amount of VBE units. Though with conversion buildup the content of BVE fragments in the polymer insignificantly increases (rows 3, 4).

Table 1
Characteristics of the copolymers obtained from the monomer mixture of the composition:
60 mol % MMA, 40 mol % VBE, initiator BIN (0.1 mol %). Temperature 60 °C

No.	Time, h	Conversion, %	Content of MMA units, mol %, according to ^1H NMR data
1	2	15	98
2	4	27	96
3	6	57	–
4	8	55	94
5	10	62	94

Table 2
Data on composition of MMA–VBE copolymers obtained by compensate polymerization method at general monomer ratio 1:4 in the presence of BIN (0.1 mol %) at boiling VBE

No.	MMA dosing time, min	Yield in reactive monomer, %	Content of MMA units, mol %, according to data	
			IR	^1H NMR
1	20	44	58	56
2	40	51	53	53
3	53	62	56	57
4	80	78	59	57
5	180	92	54	53

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Such coordination is possible for AMA and acrylonitrile [11]. As coordination proceeds on the basis of the growth radical, formed by the reactive monomer, consequently, copolymer composition should be determined only by the way of synthesis.

Table 4

Data on composition of the copolymers BA-VAE obtained by compensate polymerization method in a total proportion of the monomers 1:4 in the presence of trialkylboranes at reflux of VBE

No.	Initiator	VAE	BA dosing time, min	Yield in reactive monomer, %	Content of BA units, mol %, according to IR data
1	BIN*	VBE	20–30	~100	51–52
2	TEB			56–66	51–52
3	TNB			18–20	48–50
4	BIN	ViBE	40	~100	65–70
5	TEB			50–51	59–60
6	TNB			30	65–66

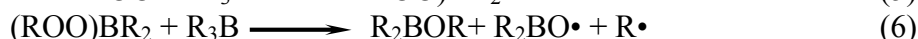
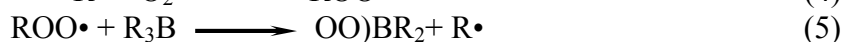
* data [4].

Based upon the data in Table 4, the composition of the copolymer BA-VAE, obtained at initiation by BIN, compared to trialkylboranes TEB and TNB, which form initiating radicals after oxidizing by atmospheric oxygen [9], left in small proportion in boiling VAE, is almost the same. For the copolymer BA-ViBE, synthesized in the presence of trialkylboranes (rows 5, 6), the content of acrylate is somewhat less than for it at initiation by BIN (row 4). Note that the use of organoelemental initiator leads to decrease of the copolymer yield. This is obviously correlated to the characteristic features of polymerization initiation in the presence of trialkylboranes [9]: at introduction of trialkylborane the oxygen in the reaction mixture is rapidly consumed. Autooxidation begins with homolytic S_{R2} substitution by oxygen of an alkyl radical in trialkylborane (scheme (3)). The formed alkyl radical interacts with the next oxygen molecule, yielding peroxy radical (scheme (4)), which can further react with original trialkylborane (scheme (5)), continuing the chain reaction (6). Then monoalkylperoxyborane reacts with oxygen to produce dialkylperoxyborane (scheme (7)) or with original trialkylborane (scheme (8)). In the latter case the product is dialkylalkoxyborane $(RO)BR_2$, capable of further reaction with oxygen, eventually forming trialkylborate $B(OR)_3$ (scheme (9)) [9]:

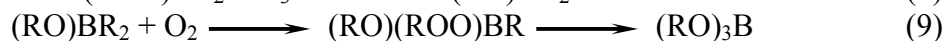
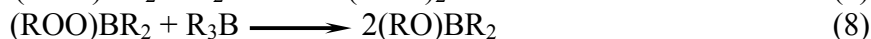
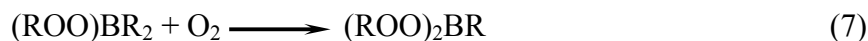
Initiation:



Chain growth:



Following reactions:



Except the abovementioned reactions, other processes are possible. Conversion level for autooxidation of trialkylboranes depends on the ratio of borane and oxygen. Apparently, under the conditions of compensate copolymerization, the results of which have been shown in Table 4, the specific features are such that it is impossible to obtain the copolymer with quantitative yield in acrylate. Though the copolymer composition stays almost equimolar, independently on the used initiator.

Thus, the investigation on the influence of the synthesis conditions for copolymers of AMA with VAE upon their composition, by the example of several monomer couples, has allowed detecting that the method of monomer introduction into the reaction mixture influences the process significantly, and that the nature of initiator causes but a slight change in the copolymer composition; the use of organoelemental initiator leads to decrease in copolymer yield.

Conclusions

1. Copolymers of methyl methacrylate with vinyl butyl ether have been synthesized from the monomer mixture and by compensate polymerization method. The analysis of their composition has shown that in the first case the gradient copolymer is formed, nonuniform in conversion, with methyl methacrylate units for the most part; when acrylate is dosed uniformly, the copolymer of almost equimolar composition is obtained.

2. It has been shown that in order to obtain the structurally uniform copolymer from the monomer couple butyl acrylate–vinyl alkyl ether it is possible to use both classical radical initiators, e.g. BIN, and binary alkylborane–oxygen initiators. At that the copolymer conversion decreases if trialkylboranes are used for initiation.

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References

1. Matyjaszewski K., Davis T.P. *Spravochnik radikal'noy polimerizatsii* [Handbook of Radical Polymerization]. West Sussex: Wiley & Sons, 2002. 936 p.
2. Moad G., Solomon D.H. *Khimiya radikal'noy polimerizatsii* [The Chemistry of Radical Polymerization]. Elsevier, 2006. 639 p.
3. Semenycheva L.L., Bogatova E.I., Vins V.V. [Copolymers of Butyl Acrylate with Vinyl Alkyl Ethers as Thickening Additives to Oils]. *Rus. J. Appl. Chem.*, 2008, vol. 81, pp. 1638–1641. DOI: 10.1134/S1070427208090310
4. Semenycheva L.L., Vins V.V., Bogatova E.I., Malysheva E.V., Khoroshen'kov G.V., Zavyalova E.A., Shavyrin A.S., Moikin A.A. [A New Procedure for Preparing Butyl Acrylate–Vinyl n-Butyl Ether Copolymer as Effective Thickening Additive to Oils]. *Rus. J. Appl. Chem.*, 2009, vol. 82, pp. 1644–1647. DOI: 10.1134/S1070427209090249
5. Geraskina E.V., Matkivskaya Yu.O., Chukhmanov E.P., Moikin A.A., Semenycheva L.L. [Viscosity Modifiers Based on Vinyl Isobutyl Ether Copolymers for Lubricating Oils]. *Rus. J. Appl. Chem.*, 2014, vol. 87, no 11, pp. 1649–1653. DOI: 10.1134/S1070427214110135
6. Semenycheva L.L., Geraskina E.V., Kazantsev O.A., Sivokhin A.P., Moikin A.A. [Influence of the Molecular Weight on the Properties of Alkyl Methacrylate–Vinyl Butyl Ether Copolymers as Thickening Additives to Petroleum Oils]. *Rus. J. Appl. Chem.*, 2014, vol. 87, no 2, pp. 224–229. DOI: 10.1134/S1070427214020177
7. Khomutov A.M. [Reactivity of Vinyl Ethers in Copolymerization]. *Polym. Sci. U.S.S.R.*, 1964, vol. 5, iss. 2, pp. 181–187. DOI: 10.1016/0032-3950(64)90402-2
8. Arakelov G.G., Badalyan V.E., Khachatryan S.S. [Vinyl Ethers. Review. Information Series, "Polymerization Plastics"]. Moscow, NIITEHIM Publ., 1979. 28 p.
9. Zaremski M.Yu., Garina E.S., Gurskii M.E., Bubnov Yu.N. [Organoboranes–Atmospheric Oxygen Systems as Unconventional Initiators of Radical Polymerization]. *Polymer Science. Series B.*, 2013, vol. 55, no. 5–6, pp. 304–326. DOI: 10.1134/S1560090413050072.
10. Dodonov V.A., Galkin R.V., Starostina T.I., Malysheva Y.B., Kuropatov V.A. Azobis(isobutyronitrile)–Tri-n-butylborane Radical-Producing System in Methyl Methacrylate Polymerization. *Doklady Chemistry*, 2015, vol. 463, no. 1, pp. 174–177. DOI: 10.1134/S0012500815070034.
11. Dodonov V.A., Grishin D.F., Aksenova I.N. [Electrophilicity of Propagating Macroradicals as a Rate-Determining Factor in Coordination-Radical Polymerization of Acrylic Monomers]. *Polymer science. Series B*, 1993, vol. 35, no. 12, pp. 2070–2072.

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**ВЛИЯНИЕ УСЛОВИЙ СИНТЕЗА НА СОСТАВ СОПОЛИМЕРОВ
АЛКИЛ(МЕТ)АКРИЛАТ-ВИНИЛАЛКИЛОВЫЙ ЭФИР**

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Проведен синтез сополимеров метилметакрилата с винилбутиловым эфиром из мономерной смеси и компенсационным способом. Анализ их состава показал, что происходит образование, соответственно, неоднородного по конверсии сополимера с преимущественным содержанием звеньев метилметакрилата и сополимера близкого к эквимольному составу. На примере мономерной пары бутилакрилат-винилалкиловый эфир показано, что для получения композиционно однородного сополимера могут быть использованы как классические радикальные инициаторы, так и бинарные инициаторы боралкид-кислород.

Ключевые слова: метилметакрилат, бутилакрилат, винилбутиловый эфир, винилизобутиловый эфир, радикальное иницирование, динитрил азоизомаляной кислоты, аминный комплекс, триэтилбор, три-*n*-бутилбор, состав сополимера.

Литература

1. Matyjaszewski, K. Handbook of Radical Polymerization / K. Matyjaszewski, T.P. Davis. – West Sussex: Wiley & Sons, 2002. – 936 p.
2. Moad, G. The Chemistry of Radical Polymerization / G. Moad, D.H. Solomon. – Elsevier, 2006. – 639 p.
3. Семенычева, Л.Л. Соплимеры бутилакрилата с виниловыми эфирами как загущающие присадки к маслам / Л.Л. Семенычева, Е.И. Богатова, В.В. Винс // Журнал прикладной химии. – 2008. – Т. 81. – С. 1536–1566.
4. A New Procedure for Preparing Butyl Acrylate–Vinyl *n*-Butyl Ether Copolymer as Effective Thickening Additive to Oils / L.L. Semenycheva, V.V. Vins, E.I. Bogatova et al. // Russian Journal of Applied Chemistry. – 2009. – V. 82. – P. 1644–1647.
5. Модификаторы вязкости на основе сополимеров винилизобутилового эфира для смазочных масел / Е.В. Гераськина, Ю.О. Маткивская, Е.П. Чухманов и др. // Журнал прикладной химии. – 2014. – Т. 87. – С. 1609–1614.
6. Влияние молекулярной массы на свойства сополимеров винилбутилового эфира и алкил(мет)акрилатов как загущающих присадок к нефтяным маслам / Л.Л. Семенычева, Е.В. Гераськина, О.А. Казанцев и др. // Журнал прикладной химии. – 2014. – Т. 87, № 2. – С. 244–249.
7. Khomutov, A.M. Reactivity of vinyl ethers in copolymerization / A.M. Khomutov // Polym. Sci. U.S.S.R. – 1964. – V. 5, № 2. – P. 181–187.
8. Аракелов, Г.Г. Простые виниловые эфиры / Г.Г. Аракелов, В.Е. Бадалян, С.С. Хачатрян. – М.: НИИТЭХИМ. – 28. – (Обзор. инф серия «Полимеризационные пластмассы»)
9. Organoboranes-atmospheric oxygen systems as unconventional initiators of radical polymerization / M.Yu. Zaremski, E.S. Garina, M.E. Gurskii, Yu.N. Bubnov // Polymer Science. Series B. – 2013. – V. 55, № 5–6. – P. 304–326.
10. Додонов В.А., Галкин Р.В., Старостина Т.И., Куропатов В.А., Малышева Ю.Б. Радикальная система динитрил азоизомаляной кислоты – три-*n*-бутилборан в полимеризации метилметакрилата // Доклады Академии наук. – 2015. – Т. 463, № 2. – С. 168–171. DOI: 10.7868/S0869565215200116
11. Dodonov, V.A. Electrophilicity of Propagating Macroradicals as a Rate-Determining Factor in Coordination-Radical Polymerization of Acrylic Monomers / V.A. Dodonov, D.F. Grishin, I.N. Aksenova // Polymer science. Series B. – 1993. – V. 35, № 12. – P. 2070–2072.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

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REACTION OF 3-AMINOPROPYLTRIETHOXY-SILANE WITH TRIPHENYLPHOSPHATE

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Interaction of 3-aminopropyltriethoxysilane RNH_2 [$\text{R} = (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2$] with triphenylphosphate $(\text{PhO})_3\text{P}=\text{O}$ proceeds at temperature 180–200 °C and leads to formation of quaternary ammonium salt of phenylphosphoric acid $[\text{PhOP}(\text{O})\text{O}_2]^{2-}[\text{PhH}_2\text{NR}]^{2+}$, which turns into liquid silicon-containing oligoamidophosphates $\text{RNH}[\text{P}(\text{O})(\text{OPh})\text{NR}]_n\text{P}(\text{O})(\text{OPh})\text{NHR}$ and phenol at high temperature. The latter transesterifies the original 3-aminopropyltriethoxysilane and the obtained products. With the use of high-temperature vacuum rectification liquid oligomers and the solid cross-linked polymer have been isolated. Heating of the solid polymer up to 1000 °C in inert atmosphere results in the amorphous phase, containing SiO_2 and NPO. The reactions of 3-aminopropyltriethoxysilane with triphenylphosphate and trimethylphosphate have been compared.

Keywords: 3-aminopropyltriethoxysilane, triphenylphosphate, trimethylphosphate, oligomers, thermal transformations.

Introduction

Molecules of triethoxysilylpropylamidophosphates $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NRP}(\text{O})\text{X}_2$ ($\text{R} = \text{H}$, Al ; $\text{X} = \text{OR}$, NR_2) contain the easily hydrolyzed group $(\text{EtO})_3\text{Si}$ and the amidophosphate fragment $\text{NRP}(\text{O})\text{X}_2$, which can form coordination compounds with d- and f-elements. Ability of sol-gel polymerization and forming coordination compounds offers a way to obtain metal-containing gels, films [1], transparent glasses [2] on their basis. Target syntheses of such compounds are based on the reaction of 3-aminopropyltriethoxysilane $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (APTES) with the derivatives of phosphorous oxychloride $\text{ClP}(\text{O})\text{X}_2$ ($\text{X} = \text{OPh}$, NR_2). Organic bases (triethylamine, pyridine) are used as acceptors of the evolving hydrogen chloride. Voluminous precipitates of triethylamine or pyridine hydrochlorides, produced in this reaction, badly thicken the reaction mixtures and demand great amounts of solvents, which need to be carefully dewatered, as the initial compounds and the products are hydrolytically unstable. In this context finding a more convenient method of obtaining alkoxy-silyl derivatives of amidophosphates seems an urgent problem. The alternative way of synthesis involves the reaction of two industrial products: APTES and triorganophosphates $(\text{RO})_3\text{P}=\text{O}$, which can lead to substitution of RO groups at the phosphorus atom and production of alcohol. Nevertheless, in recently performed study [3] it has been shown that interaction of APTES with trimethylphosphate $(\text{MeO})_3\text{P}=\text{O}$ (TMP) leads to release of ethyl (not methyl) alcohol in the first stage and production of organophosphosilicates. Replacement of methyl groups in triorganophosphate by phenyl ones has led to cardinal change of the process direction, so that release of phenol and production of silicon-containing amidophosphate oligomers has been observed. In the present paper the results in investigating APTES interaction with triphenylphosphate $(\text{PhO})_3\text{P}=\text{O}$ (TPP) are described, the comparison of the related reactions is carried out, and the explanation of possible causes for different behavior of two structurally similar compounds $(\text{PhO})_3\text{P}=\text{O}$ and $(\text{MeO})_3\text{P}=\text{O}$ is suggested.

Experimental

IR spectra were recorded on the Fourier-transform IR spectrometer "FSM-1201". Liquid and resinous substances were spread in a film between KBr plates. In order to record solid samples a mineral oil suspension was prepared. Both ^1H and ^{31}P NMR spectra of the samples dissolved in CDCl_3 were recorded on the "Bruker Avance DPX-200" spectrometer, operating frequency equaled 200 and 80 MHz for ^1H and ^{31}P , respectively; internal standard for ^1H was Me_4Si , for ^{31}P it was 85 % H_3PO_4 . X-ray phase analysis was performed on "DRON-3M" diffractometer ($\text{CuK}\alpha$ -emission) with the graphite monochromator on the diffracted beam. Thermogravimetric analysis was performed on the "Perkin Elmer Pyris 6

TGA" apparatus. Heating of the 50 mg sample was carried out at the rate 5 deg per min from 40 to 1000 °C in nitrogen atmosphere. Mass spectra were obtained on the chromato-mass spectrometer "Trace GC Ultra" with mass analyzer "Polaris Q" (capillary chromatographic column NR-5MS, 30 m × 0.25 mm, thickness of stationary phase film 0.25 µm; injector temperature 250 °C; helium as the carrier gas; flow rate 1.5 mL per min; programmed temperature rise from 40 to 250 °C; mass analyzer with the ion trap; energy of ionizing electrons 70 eV; temperature of ion source 300 °C; the range of detected masses 40–400). Total ion current chromatograms were recorded. The analyzed mixture was dissolved in CH₂Cl₂. The sample volume equaled 1 µL. Interpretation of mass spectra was carried out with the use of NIST MS Search 20 database.

APTES (Slavgorod PA "Altaikhimprom") was rectified under vacuum in the column 1×50 cm, filled by nichrome wire coils. TPP was recrystallized from heated toluene before use.

APTES was analyzed on the gas chromatograph "Tsvet-530" in the stainless steel column 0.3×200 cm, filled by solid support Chromaton-N-AW-DMCS with 5 % liquid phase XC-2-1; thermal conductivity detector; helium as the carrier gas; temperature of the column thermostat 160 °C, temperature of the detector and vaporizer thermostat 220 °C. Content of isomeric 2-aminopropyltriethoxysilane equaled 1.2 %. To analyze liquid fractions, obtained after distillation of oligomers under vacuum, the column 0.3×200 cm was used, filled by solid support Chromaton-N-AW with 5 % liquid phase SE-30; thermal conductivity detector; helium as the carrier gas; temperature of the column thermostat 200 °C, temperature of the detector and vaporizer thermostat 250 °C.

Reaction of APTES with TPP. APTES and TPP in molar ratio 1:1, 2:1 or 3:1 (Table 1) were placed at room temperature into a round-bottom flask with a stirrer and a reflux condenser.

Table 1

The reaction products of APTES with TPP

№	Quantity APTES, g (×10 ² mol)	Quantity TPP, g (×10 ² mol)	Weight of the collected liquid fractions, g (mas. %) (b. p., 0.05 mm Hg)			Weight of fixed residue, g (mas. %)
			1 (50-100°C)	2 (100-180°C)	3 (180-250°C)	
I	9.52 (4.30)	14.00 (4.30)	3.06 (13)	10.58 (45)	4.70 (20)	5.18 (24)
II	9.52 (4.30)	7.00 (2.15)	1.65 (10)	8.93 (54)	2.48 (15)	3.46 (21)
III	9.52 (4.30)	4.70 (1.45)	1.14 (8)	8.68 (61)	1.71 (12)	2.70 (19)

The reaction mixture was heated in an oil bath up to 200 °C, then it was constantly stirred at this temperature for 8-10 h. After TPP was melted at 40-50 °C, the mixture became homogeneous, its viscosity increased. On completion of the process the viscous yellow liquids were obtained. Color intensity and viscosity decreased with increasing APTES content. The obtained products were distilled under vacuum in glass ampoules with attached side outlets. The ampoules were slowly heated up to 300 °C at the pressure 0.05 torr in a cylinder furnace with controlled output, and were kept at these conditions for 2 h. The temperature was registered with the use of a thermometer placed in the furnace. In Table 1 the distillation temperature intervals for corresponding fractions are shown, as well as the masses calculated in proportion to the initial amounts of reactants. All collected liquids were transparent and practically colorless, except fraction I-3 of yellowish color. The first fraction was condensed in the trap, cooled by liquid nitrogen, two others were collected into the side outlet and then detached. At 250 °C the mixture of oligomers began foaming. On completion of distillation and cooling to room temperature the formed yellowish foams were easily broken with a glass rod, turning into powders, insoluble in water and organic solvents.

All liquid fractions were analyzed by gas-liquid chromatography and chromato-mass spectrometry. In consequence of high-boiling components of the second and, especially, the third fraction transition into the gas phase and separation in the chromatographic column were hampered. The greater part of oligomeric products were not recorded by the given methods. In mass spectra phenol, APTES and several isomeric products, containing fragments of silicon alkoxides NHCH₂CH₂CH₂Si(OEt)_x(OPh)_{3-x}, were determined unambiguously. Those compounds were contained in all distilled liquids, but the ratio was different. The first fraction included phenol with no more than 5 % admixtures of APTES derivatives. It was also demonstrated by IR spectroscopy data and the fact that the liquid, collected in the trap, har-

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dened at room temperature (phenol m.p. 41 °C). The second fraction contained scarcely any phenol, while the third one was again enriched by phenol due to decomposition of the solid product.

Thermal decomposition of the solid product of APTES–TPP reaction. The weighed sample 1.0–1.5 g of the powder was placed in an ampoule, connected with a pump through a trap, kept under vacuum for 30 min and heated for 4 h at 400–420 °C. At that temperature the powder color changed from yellow to dark brown. In the side outlet, cooled by liquid nitrogen, gaseous products of pyrolysis were collected. The walls of the trap and the cold part of the apparatus were covered by white deposit. After cooling to room temperature the ampoule outlet was detached, the darkened powder was weighed. The loss of mass equaled 30–35 %. The gaseous decomposition products were refrozen through a connector under vacuum into an ampoule with a silicone stopper for chromato-mass spectrometry analysis. Those gases, representing not less than 70 % from the mass loss in the given stage, were the mixture of isomeric unsaturated hydrocarbons C₃–C₆. The white deposit from the outlet walls was dissolved in methylene chloride and also analyzed with the use of chromato-mass spectrometer. It consisted of phenol c 10 % admixture of elemental phosphorus P₄.

After thermal treatment of the powder under vacuum the subsequent heating was carried out under nitrogen flow. The weighed samples 0.1–0.2 g of the powder obtained in the previous stage were placed in quartz boats 7×100 mm into a wide horizontal quartz tube, and nitrogen was blown through it for 1 h. Then they were heated in electric furnace at 600, 800, and 1000 °C, were allowed to stand for 5 h and cooled to room temperature. At 600 and 800 °C black powders were obtained, the loss of mass in those stages equaled not more than 5 %. Pyrolysis at 1000 °C led to formation of greyish sintered samples, the mass decreased by 40–50 %. In all those cases at the beginning of heating yellow-brown vapors were carried from the hot zone, with increasing temperature they carbonized.

In a similar way heating was carried out for the powder, obtained in the reaction of APTES with TPP, under oxygen flow at 1000 °C. The loss of mass equaled 45 %, practically colorless sintered material with greyish inclusions was obtained.

Results and Discussion

The reaction of APTES with TPP proceeds slowly only at heating up to 180–200 °C. Excess of APTES and short-term (3 h) heating at 150 °C does not result in interaction. In order to achieve higher conversion degree, it is necessary to heat at 180–200 °C during 10 h. The reaction mixture looks like a low-viscous liquid of pale yellow color. Phenol and ethyl alcohol have been found among low-boiling products by gas-liquid chromatography and IR spectroscopy.

Fig. 1 (curve 1) shows the IR spectrum of the products obtained after evaporation of alcohol and phenol under vacuum. The characteristic feature of the spectrum is the wide absorption band of high intensity, in the range from 3070 to 2200 cm⁻¹, consisting of stretching vibrations of N–H bond in cation PhH₂N⁺, together with superposition of less intensive absorption bands of stretching vibrations of C–H bonds of phenyl (3063, 3043 cm⁻¹) and alkyl (2978, 2930, 2980 cm⁻¹) groups. Deformation vibrations of N–H are represented as the shoulder 1620 cm⁻¹. Presence of phenoxy groups (PhOP, PhOSi) is proved by the series of intensive bands caused by stretching (1595, 1493 cm⁻¹) and out-of-plane deformation (691 cm⁻¹) vibrations of the bonds C=C and C–H (shoulder 810 cm⁻¹ and band 759 cm⁻¹ of the doublet 759, 772 cm⁻¹) [4]. The groups SiOEt are characterized by the series of bands 1161, 1094, 961 и 772 cm⁻¹ [5]. The doublet 1246, 1212 cm⁻¹ is related to vibrations of C–O and P–O bonds, respectively [6]. Widening of the band ν(C–O) is caused by the simultaneous presence of groups POPh, SiOPh, SiOEt. Two bands of medium intensity 1452 and 1392 cm⁻¹ are related to deformation vibrations of C–H bonds in –CH₂– and –CH₃ groups.

The IR spectroscopy data attest the presence in the reaction mixture of amine phenylphosphate salts Ia,b; which are formed through transfer of one or two phenyl groups from TPP to APTES nitrogen atom. Triethoxysilyl groups of these compounds are transesterified by phenol, produced in the reaction (Scheme 1, reaction 5). Diamine phenylphosphate salt Ib can be obtained both at the interaction of Ia with APTES (Scheme 1, reaction 2) and as the result of Ia disproportionation (reaction 3), which is specific to organophosphoric acids (RO)₂P(O)OH and their derivatives [7]. Phenol evolving suggests that Ia, b transform into phenyldiamidophosphate II, which then condenses into oligomeric amidophosphates III. Their identification becomes possible after distillation of the reaction mixture under vacuum at maximum underpressure and at temperature as high as 300 °C. At that amine salts Ia,b move into the vapor phase and are distilled only in a

minimal amount, which is attested by the IR spectroscopy data (Fig. 1, curves 3, 4). High temperature promotes reactions 4–6 and distillation of oligomers III. By and large their chemical nature is identical to 3-triethoxysilylpropylamidophosphate $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHP}(\text{O})(\text{OPh})_2$ (IV), that we have synthesized earlier [1].

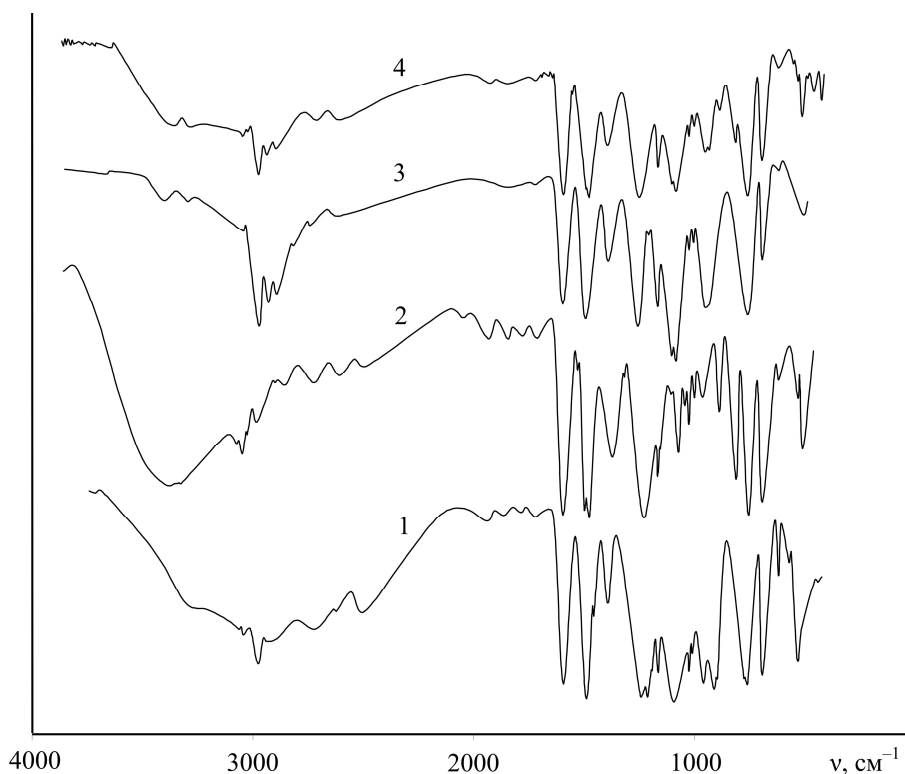
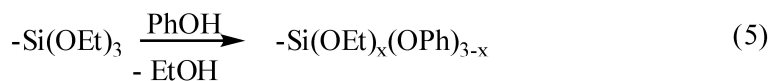
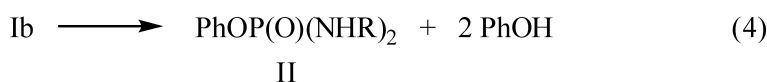
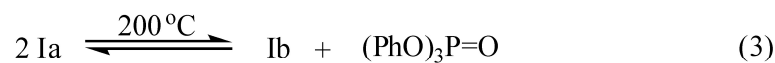
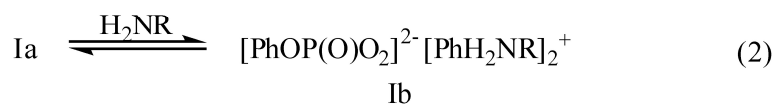
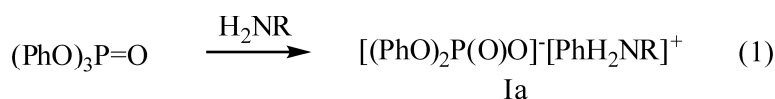


Fig. 1. FTIR spectra of the reaction products of equimolar quantities of APTES with TPP: 1 – a reaction mixture after removal of a great bulk of ethanol and phenol; 2 – fraction I-1; 3 – fraction I-2, 4 – fraction I-3 (liquid films)



III



Scheme 1

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Fig. 1 represents IR spectra of three fractions separated in the result of distillation of the reaction mixture APTES : TPP = 1 : 1. The first fraction (curve 2) constitutes the mixture of phenol with APTES. In two high-boiling fractions (curves 3 and 4) accumulation of PhO groups takes place, at that they are bonded not only to the phosphorus atom, but also to the silicon atom. The consequence is the intensity decrease of the most characteristic band ($1083\text{--}1103\text{ cm}^{-1}$) of $\text{Si}(\text{OEt})_3$ fragment vibrations in relation to the stretching vibration band of C–O bonds (1246 cm^{-1}).

The intensity of bands $\nu(\text{C-H})$ of phenoxy radicals ($3066, 3040\text{ cm}^{-1}$) in relation to $\nu(\text{C-H})$ of aliphatic radicals increases significantly. The most high-boiling fraction contains the greater part of the product completely transesterified by phenol and the unreacted TPP. The character of the spectrum in the range $3500\text{--}3100\text{ cm}^{-1}$ attests that the band $\nu(\text{N-H})$ in oligomers is of low intensity. The observed wide band of medium intensity at 3300 cm^{-1} corresponds to stretching vibrations of the phenol hydroxyl group, which is admixed to all the fractions.

The possibility of transesterification has been examined by the example of phenol reaction with APTES. Heating of their equimolar mixture at $180\text{--}190\text{ }^\circ\text{C}$ for 3 h has led to consumption of initial reactants and to formation of one main high-boiling compound (according to gas-liquid chromatography data), which constitutes 3-aminopropyldiethoxyphenoxysilane.

Thus, the reactions represented in scheme 1 include not only the initial APTES, but also its transesterified derivatives. Their formation is most probable when reaction proceeds with an excess of APTES.

The ^1H NMR spectroscopy data also suggest increasing the content of phenoxy radicals in high-boiling oligomers obtained by high-temperature vacuum rectification. Comparison of the ^1H NMR spectra for the reaction mixture APTES : TPP = 2 : 1 before distillation, as well as the second and third fractions, to the spectrum of the model compound amidophosphate IV, shows the following results. In the amidophosphate IV spectrum there are three groups of lines with equal intensity: $0.47\text{--}0.55, 1.49\text{--}1.56, 2.97\text{--}3.03\text{ ppm}$, that characterize three methylene fragments between the atoms of silicon and nitrogen $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$. Ethoxy substituents are represented by the intensive triplet at 1.12 ppm (CH_3) and the quadruplet 3.74 ppm (CH_2). The proton resonance of phenoxy groups at the phosphorus atom appears as the multiplet in the range $7.08\text{--}7.25\text{ ppm}$. Formation of SiOPh fragments in the reaction mixture leads to significant complication of the ^1H NMR spectrum. First of all, two new multiplets appear, which are positioned to the right of the similar group of lines belonging to the PhOP fragment. The triplet of the methyl fragment and the quadruplet of the methylene fragment of ethoxy groups transform into multiplets owing to appearance of the mixed (ethoxy)(phenoxy)silyl groups $\text{Si}(\text{OEt})_x(\text{OPh})_{3-x}$. Three groups of lines of the fragment $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$ in compound I are supplemented by the multiplet $0.97\text{--}1.07\text{ ppm}$, which is related to the methylene fragment $-\text{CH}_2-\text{Si}(\text{OEt})_x(\text{OPh})_{3-x}$ (influence of electron-accepting PhO groups, transmitted by the silicon atom). In the spectra of distilled fractions these differences are strengthened. Even greater increase of the proton resonance intensity for phenyl groups, bonded to the silicon atom, takes place, and proportional decrease of intensity for bands related to ethoxysilyl substituents. In the most high-boiling fraction the content of SiOEt groups becomes minimal, which follows from very low intensity of signals at $1.1\text{--}1.3\text{ ppm}$. Appearance of two resonances at 5.47 and 5.55 ppm is observed in the second fraction, they are probably related to the hydrogen atoms of the terminal amidophosphate groups $-\text{P}(\text{O})-\text{NH}-$. They are not located in the third the most high-boiling fraction. According to scheme 1, in the reaction mixture without rectification quaternary ammonium base $\text{PhH}_2\text{N}^+-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OR})_3$ should be present. It is known [8] that the resonances of the methylene fragment N^+-CH_2 in the compounds of such kind are located near 3.7 ppm , that is, they are superimposed by the signals of SiOCH_2 group. Indirect confirmation of amine salt existence follows from the intensive widening and splitting of the multiplet band related to the central methylene group. The new band with the center at 1.77 ppm appears because of electron-accepting influence of the group $\text{PhH}_2\text{N}^+-\text{CH}_2-$. In the second fraction quaternary amine salt is practically absent, and the proton resonances of the central methylene fragment appear as one widened band with the center at 1.68 ppm . In the third fraction accumulation of electronegative groups $\text{Si}(\text{OPh})_3$ [compared to $\text{Si}(\text{OEt})_3$] once again leads to widening and splitting of this band. Overintensity of the multiplet $2.5\text{--}2.8\text{ ppm}$, belonging to the fragment $-\text{CH}_2-\text{N}$, engages our attention. Presumably other organic amines, besides the silicon-containing one, are present in the mixture; they are produced as the result of its high-temperature treatment both during the synthesis process itself and during its rectification.

The changes of ^1H NMR spectrum for the reaction mixture APTES : TPP = 1 : 1 and the fractions isolated from it are similar to the above, as a whole. The ^1H and ^{31}P NMR spectroscopy data demonstrate that the greater part of TPP remains unreacted, whereas APTES is consumed comparatively fast and to the fullest extent. The presence of unreacted TPP attests that reactions 1–4 (scheme 1), leading to compounds Ib and II with the ratio Si : P = 2 : 1, proceed easier than the following condensation and formation of oligomers III (reaction 6), in which the ratio Si : P approaches one. The transesterification of triethoxysilyl groups by phenol proceeds with efficiency, the appearance of ethylphosphate fragments can be observed. In the spectra of 2- and 3-fractions there are the signals of the group $\text{CH}_3\text{-CH}_2\text{-OP(O)}$ protons at 1.3 ppm (multiplet) and 4.3 ppm (triplet).

The differences in the ^1H NMR spectra changes for the products of the APTES–TPP reaction, carried out at the ratio 3:1, are determined by the greater rate of phenol consumption for the use in transesterification of APTES that is in excess. The formed phenoxyated organosilicon amines are of less reactivity concerning TPP. Because of this in excess conditions the initial APTES reacts first of all, while the evolving phenol is expelled from the process mostly in the form of phenoxyated APTES derivative. Thus, the rate of oligoamidophosphate phenoxylation decreases, if there is an excess of organosilicon amine in the reaction.

Association of phenol with amidophosphate groups does not allow to separate it by rectification completely. Effective decrease of its concentration in oligomers is reached by treatment of APTES–TPP reaction products by hexamethyldisilazane at heating. Ammonia evolves intensively and phenoxytrimethylsilane forms, which has been isolated, purified by rectification and identified by gas-liquid chromatography and IR spectroscopy [9].

Additional information about the composition of the liquid products is provided by ^{31}P NMR spectroscopy data. Table 2 presents the relative intensity of the signals for oligomers before distillation and in two high-boiling fractions. The signal $\delta = -10$ ppm is contained in the spectra of all the products. In the spectra of distilled fractions the second signal appears $\delta = -11$ ppm. It is also present in the spectrum of the product of APTES : TPP = 1:1 before distillation.

Table 2
Relative intensity of signals in ^{31}P NMR spectra of oligomers obtained in reaction APTES with TPP

Oligomers		Relative intensity of signals		
		$\delta = -10$ ppm	$\delta = -11$ ppm	$\delta = -16.5$ ppm
I	Before distillation	1.0	0.1	0.03
	Fraction I-2	1.0	0.8	0.6
	Fraction I-3	1.0	1.9	0.3
II	Before distillation	1.0	–	–
	Fraction II-2	1.0	0.5	–
	Fraction II-3	1.0	0.7	–
III	Before distillation	1.0	–	–
	Fraction III-2	1.0	0.1	–
	Fraction III-3	1.0	0.2	–

Only in the latter and in two fractions obtained from it the signal $\delta = -16.5$ ppm is observed, it is related to the unreacted TPP. The relative intensity of the signal $\delta = -11$ ppm is maximal at the ratio APTES : TPP = 1:1, it decreases with increasing APTES content. Furthermore, its contribution is always greater in the most high-boiling fraction. On the basis of qualitative patterns concerning correlation between the chemical shifts of ^{31}P nuclei and the nature of substituents in various phosphorus–nitrogen compounds [10, 11], the signal $\delta = -10$ ppm can be correlated with the phosphorus atoms in $-\text{NHP(O)(OPh)}-$ groups, which the signal $\delta = -11$ ppm with those in $-\text{NRP(O)(OPh)}-$ groups.

The data presented in Table 2 involve the following conclusions.

When the reaction is carried out at ratio 1:1, not all TPP reacts. The APTES excess leads to its complete consumption.

In the process of high-temperature vacuum rectification oligomers with formula III (Scheme 1) are accumulated. Their content decreases at dilution of the initial mixture by 3-aminopropyltriethoxysilane. The latter circumstance is connected to the lower phenoxylation degree of oligomers, and, consequently, to the significantly lower temperatures necessary for completion of rectification process. If organosili-

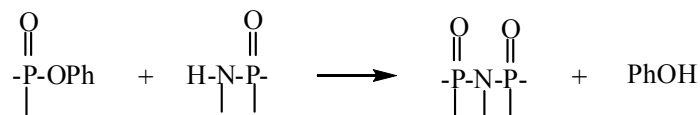
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con amine is in excess, the evolving phenol is largely consumed for the APTES phenoxylation, during rectification process it is distilled in the form of its derivatives. The formed amidophosphate oligomers contain smaller amount of $\text{Si}(\text{OEt})_x(\text{OPh})_{3-x}$ groups. As a consequence, in the process of vacuum rectification they move into the vapor phase and are distilled away at relatively low temperature (under 250°C), which is nevertheless sufficient to start the condensation process described by equation 6 in Scheme 1. High temperatures (up to 300°C) are necessary to distil maximally phenoxyolated oligomers that are produced in the reaction of APTES : TPP = 1:1. In this connection they contain greater amount of condensed oligomers, that is also expressed in their greater viscosity.

In addition to three main signals (-10 , -11 , -16.5 ppm) in the ^{31}P NMR spectra of the isolated fractions there is a series of low-intensive signals, attesting to complication of the mixture composition during the process of high-temperature rectification ($(250\text{--}300^\circ\text{C} / 0.05 \text{ torr})$). The formed admixtures are not recorded in the original products before distillation. The complication of the composition during the rectification process is observed to a lesser extent for the products of the reaction with reactant ratio 2:1; it is absent for the products of the process with the reactant ratio 3:1. The observed pattern is connected to decreasing temperature during rectification of the products for the reactions, carried out with an excess of APTES. The low-intensive signals, recorded by ^{31}P NMR method, are related to the mixed structures, in which fragments $-\text{OP}(\text{O})(\text{OPh})\text{O}-$, $-\text{OP}(\text{O})(\text{OPh})\text{NR}-$, $-\text{OP}(\text{O})(\text{OPh})\text{NH}-$, and $-\text{OP}(\text{O})(\text{OPh})\text{OSi}(\text{OR})_2-$ alternate.

After the liquid products have been distilled away under vacuum, at the temperature increasing up to 300°C the yellow-brown foam is left in the apparatus; it is easily broken with a glass rod into a powder that is insoluble in water and organic solvents. The mass of the powder equals up to 24 % of the mass of the reaction mixture taken for distillation. The nature of the solid product of the APTES–TPP reaction has been established by thermogravimetric analysis, IR spectroscopy, chromato-mass spectrometry, X-ray phase analysis, and elemental analysis.

Fig. 2 presents the thermogravimetric curves of the obtained powder. The main loss of mass takes place in the temperature range $400\text{--}450^\circ\text{C}$. The products of thermal decomposition, according to chromato-mass spectrometry data, are the mixture of gaseous unsaturated hydrocarbons $\text{C}_3\text{--}\text{C}_6$, phenol and elemental phosphorus. Hydrocarbons form as the result of decomposition of the fragments $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$. Phenol evolves at condensation of phenylphosphate and amidophosphate groups.



Phosphorus is the product of high-temperature reduction of amidophosphate derivatives by carbon components [12]. The next stage of the mass loss at temperature higher than 450°C is related to increasing reduction efficiency of the phosphorus derivatives and removing it in the form of P_4 , possibly also as NPO [13]. Besides thermogravimetric analysis the powder has been thermally treated in stages at 400 , 600 , 800 , and 1000°C in an argon atmosphere, in order to establish the nature of the thermal decomposition products. The powder color have changed from yellow to dark brown (400°C), black (600 and 800°C), and grayish white (1000°C). Transition from the intermediate black (caused by amorphous carbon) to the final pale color of the pyrolysis products (SiO_2 and NPO) is in accordance with the reduction of phosphates by carbon, known from the literature [12]. All ignited samples are amorphous. The change of IR spectra at thermal transformation, shown in Fig. 3, fits the processes described above.

In the IR spectrum of the original product (Fig. 3, curve 1) the bands of phenyl groups are observed: stretching vibrations C–H (shoulder at 3070 cm^{-1}), planar stretching vibrations (1594 , 1489 cm^{-1}) and out-of-plane deformation vibrations of the bonds C=C (690 cm^{-1}) and C–H (768 cm^{-1}). Likewise, the spectrum includes the bands of stretching vibrations (wide absorption $3500\text{--}3200 \text{ cm}^{-1}$) and deformation vibrations (1628 cm^{-1}) of the bond N–H. In the range $1250\text{--}900 \text{ cm}^{-1}$ badly defined bands are concentrated, they correspond to the fragments P(O)N (1212 cm^{-1}) and SiOR (1073 , 1026 , 921 cm^{-1}). In the IR spectra of all heated samples absorption of PhO and EtO groups is absent. With increasing temperature the intensity of the bands related to vibrations of the bond N–H decreases.

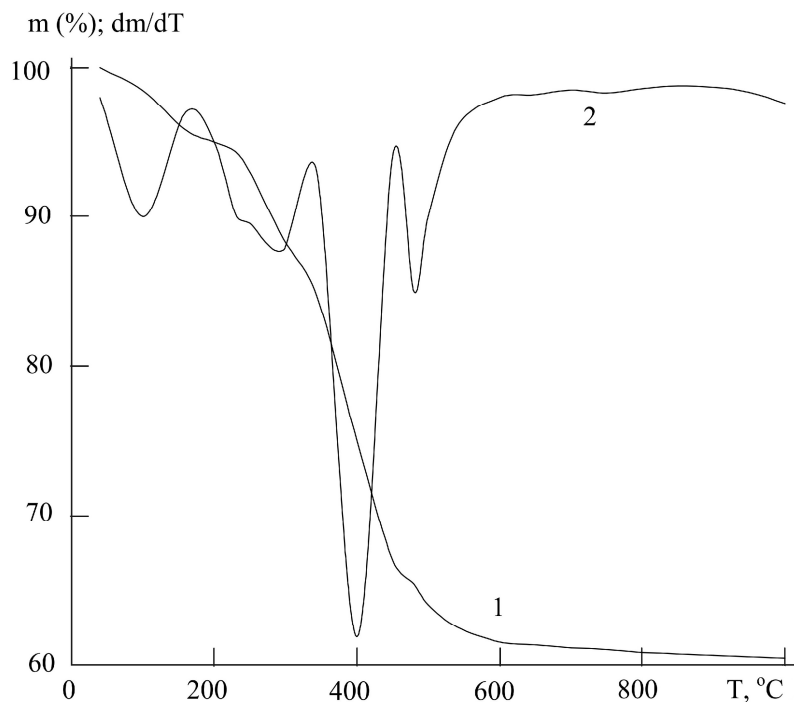


Fig. 2. Integral (1) and differential (2) curves of the solid product of reaction APTES with TPP

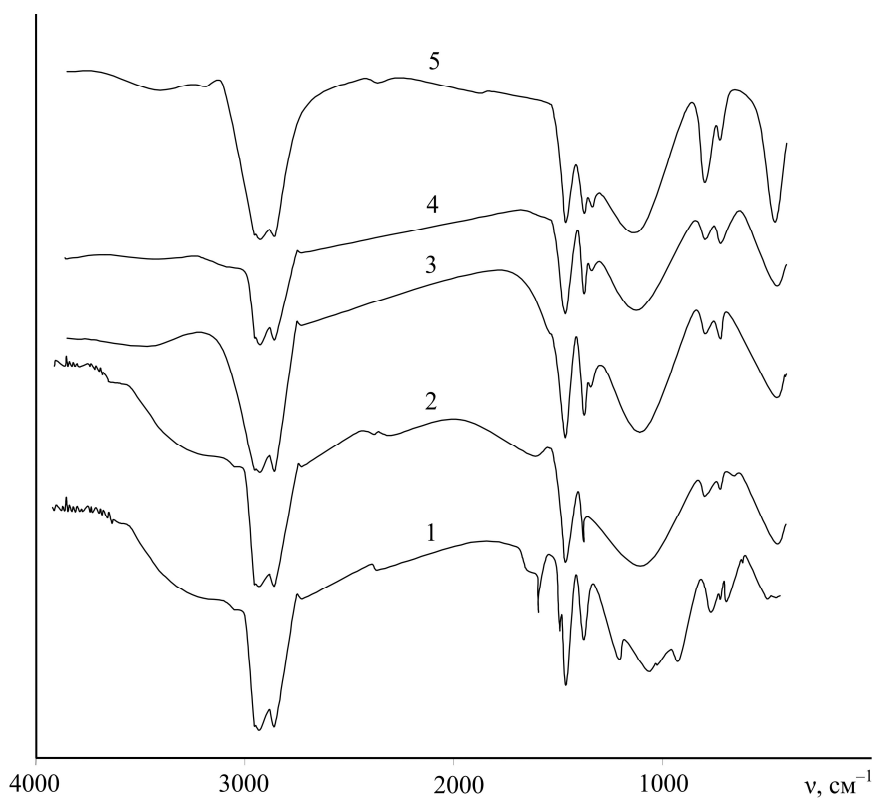


Fig. 3. Transformation of FTIR spectrum of the solid product of reaction APTES with TPP on heating: 1 – the initial sample, 2 – 400 °C, 3 – 600 °C, 4 – 800 °C, 5 – 1000 °C (suspensions in Nujol)

The IR spectrum of the sample, thermally treated at 1000 °C in argon, matches the superposition of the amorphous SiO₂ and NPO spectra (Fig. 3, curve 5). Even at 400 °C the well-defined, though low-intensity, band of symmetrical stretching vibrations of the fragment SiOSi appears at 800 cm⁻¹. Its intensity sharply increases after thermal treatment at 1000 °C. The band of symmetrical stretching vibra-

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tions of SiOSi at 465 cm^{-1} appears also at $400\text{ }^{\circ}\text{C}$. It is widened and highly intensive. Heating at $1000\text{ }^{\circ}\text{C}$ causes decrease in width and further increase in intensity.

The IR spectrum of amorphous silica, according to data [14, 15], includes 6 absorption bands: deformation vibrations of the absorbed water H–O–H 1635 cm^{-1} ; stretching vibrations of the bond Si–O in Si–OH groups 1214 cm^{-1} ; LO-mode of asymmetrical stretching vibrations of the fragment Si–O–Si 1100 cm^{-1} ; TO-mode of asymmetrical stretching vibrations of the fragment Si–O–Si 970 cm^{-1} ; symmetrical stretching vibrations of Si–O–Si 805 cm^{-1} ; symmetrical deformation vibrations Si–O–Si 470 cm^{-1} . The band 1100 cm^{-1} is the most intensive. All the bands except 1214 cm^{-1} are usually well-defined.

It is known [16] that in the IR spectrum of amorphous phosphorus oxynitride three wide absorption bands are present: at $1500 - 1250$, $1150 - 900$, and $450 - 550\text{ cm}^{-1}$ with centers at 1350 , 1000 , and 500 cm^{-1} .

The resultant spectrum (Fig. 3, curve 5) resembles the spectrum of amorphous silica to a great extent. The differences, that are explained by the presence of the amorphous phase NPO, are expressed in widening of the most intensive band 1100 cm^{-1} . The intensity of the band related to symmetrical deformation vibrations of SiOSi at 470 cm^{-1} is enlarged compared to pure silica, with the sacrifice of the respective band $450 - 550\text{ cm}^{-1}$, which is the most intensive in the spectrum of phosphorus oxynitride. Vibrations of the bond P=O are represented by absorption at 1337 cm^{-1} . The final product (Fig. 3, curve 5) is weakly hydrated, which is corroborated by the low-intensive band of stretching vibrations of the bond O–H at 3442 cm^{-1} . Markedly lower component of NPO compared to SiO_2 , registered by IR spectroscopy, is the consequence of significant loss of phosphorus at pyrolysis. The intermediate and final spectra, presented in Fig. 3, do not correlate to the spectra of phosphosilicates [17, 18], which could in principle have been produced at thermal decomposition of the solid product of the APTES–TPP reaction.

Annealing the solid product of the APTES–TPP reaction under oxygen flow, as expected, has led to formation of the mixture of crystal and amorphous phosphosilicates. X-ray phase analysis (Fig. 4) has shown that the annealed sample represents the mixture of three crystal modifications: hexagonal $\text{Si}_5\text{O}(\text{PO}_4)_6$, monoclinic and cubical SiP_2O_7 ; it also includes noticeable amount of amorphized component.

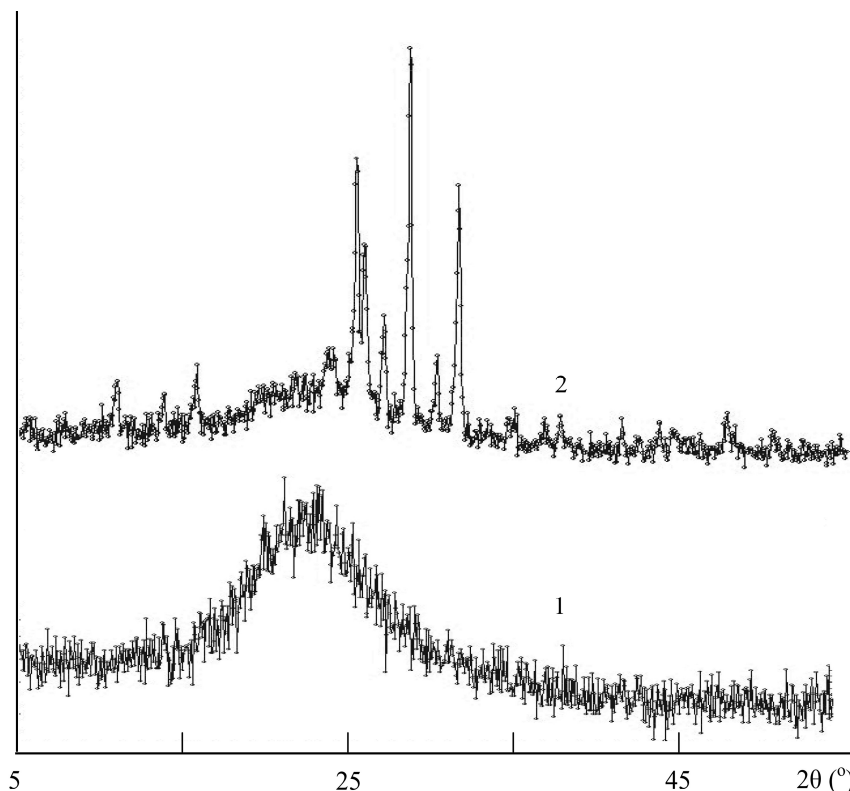


Fig. 4. X-ray patterns of the reaction product of APTES with TPP thermally treated on $1000\text{ }^{\circ}\text{C}$ in argon (1) and in oxygen (2)

The elemental analysis data for the solid products of the APTES–TPP reaction, heated under vacuum at 300 °C, are shown in Table 3.

The element analysis of solid residue from reaction APTES with TPP

Table 3

Starting proportion of APTES:TPP	Content of elements, mas. %				
	C	H	N	P	Si
1:1	24.43	4.24	4.37		
2:1	23.56	5.21	4.00	15.24	12.59
3:1	23.29	5.43	4.12		

It follows that the composition of the products changes but insignificantly with the ratio of initial reactants. It should be mentioned that in the powder obtained at the ratio APTES : TPP = 1:1 the content of carbon is somewhat greater, while the content of hydrogen is lower. The ratio Si : P is still 1:1, in spite of the fact that APTES has been taken in excess. Based upon the data of elemental and X-ray phase analysis, as well as the IR spectroscopy data, the obtained product can be described as the cross-linked polymer, containing structural fragments $OP(O)N(CH_2)_3Si(OEt)O$, $P(O)OO$, $Si(OEt)_2O$, $Si(OEt)(OPh)O$ to the ratio 1 : 0.6 : 0.5 : 0.1.

The factual findings are in agreement with the data in the literature [7, 19, 20] about thermal transformations of amidophosphates.

Thus, the interaction between APTES and TPP proceeds only at high temperature and leads to producing phenol, ethyl alcohol and liquid amidophosphate oligomers. Phenol is consumed in transesterification of triethoxysilyl groups to a large extent. In the process of high-temperature vacuum rectification of the oligomers the solid insoluble cross-linked polymer is formed, which is structurally more or less related to the liquid products. Thermal decomposition of the cross-linked polymer (400–1000 °C) in the inert atmosphere gives the amorphous mixture composed of silicon dioxide and phosphorus oxynitride.

The APTES–TPP reaction paths and the properties of the obtained products are cardinally different from the data found earlier by us [3], concerning the similar reaction between APTES and trimethylphosphate. The interaction of APTES with TMP and TPP begins with the transfer of organic radical (Me or Ph) from the group POR to the nitrogen atom of organosilicon amine and formation of the amine salt of dimethyl- or diphenylphosphoric acid, which disproportionates into the salt of methyl-(phenyl)phosphoric acid. In the course of the APTES–TMP reaction the acid-base properties of the mixture change from basic (because of APTES) to neutral to acidic, which is explained by formation of free methylphosphoric acids $(MeO)_2P(O)OH$ and $MeOP(O)(OH)_2$. In the APTES–TPP reaction the basic medium, due to the presence of organosilicon amine, is still weakly basic to the end of the reaction. This indicated the absence of free phenylphosphoric acids $(PhO)_2P(O)OH$ and $PhOP(O)(OH)_2$ in the reaction mixture. To summarize, the key point that distinguishes two similar processes (APTES–TMP and APTES–TPP) is the presence of free methylphosphoric acids in the first case and the absence of phenylphosphoric acids in the second case. Methylphosphoric acids interact with APTES and its methylated derivative according to the reaction path of substitution of OEt group at the silicon atom and the formation of methylphosphosiloxane, which easily polymerizes at medium (100–120 °C) temperature. Owing to the absence of free phenylphosphoric acids, the similar reaction with $Si(OEt)_3$ group cannot be realized, as a consequence, the amine salt of phenylphosphoric acid transformation into diamidophosphate and phenol becomes preferential.

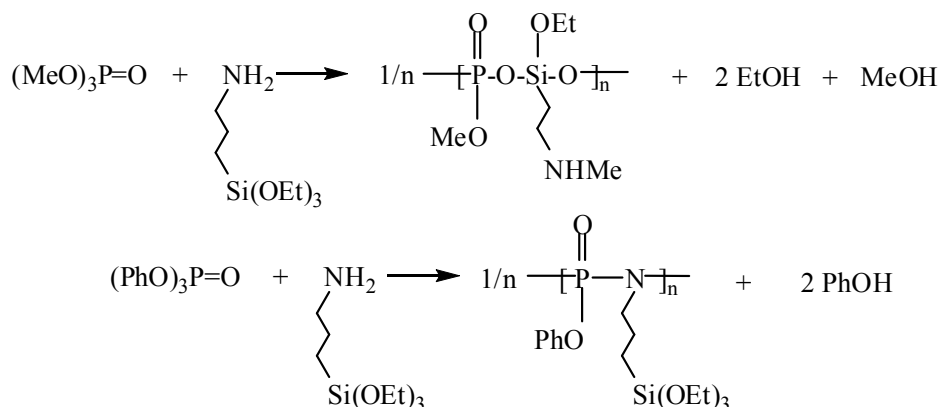
Scheme 2 shows the main directions of the APTES reactions with TMP and TPP (without going into detail).

Different nature of the obtained compounds predetermines their following thermal transformations. Polymethylphosphosiloxane, containing the structural fragments Si–O–P, produces crystalline phosphosilicates, which polyamidophosphate, containing the P–N groups, gives the mixture of amorphous SiO_2 and NPO.

Previously in papers [21–23] it has been shown that the mixture of oligomers, obtained as the result of the APTES–TPP reaction, can be used in the capacity of fast-cured lacquer, forming colorless transparent photo- and heat-resistant coatings. The results of the present study make it possible to evaluate

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the chemical composition of the coatings generated from organophosphorus-silicon oligomers after high-temperature treatment.



Scheme 2

Acknowledgements

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References

1. Semenov V.V., Cherepennikova N.F., Klapshina L.G., Bushuk B.A., Bushuk S.B., Douglas W.E. Organosilicon Amidophosphates and Their Eu and Er Complexes in Solutions and Films: Spectral and Luminescence Properties. *Rus. J. Coord. Chem.*, 2005, vol. 31, no. 7, pp. 521–529. DOI: 10.1007/s11173-005-0130-2
2. Khimich N.N., Zub Yu.L., Koptelova L.A., Mashchenko T.S., Troshina E.P., Voronkov M.G. Synthesis and Optical Properties of Nanohybrids in the System Constituted by Silica and Lanthanide Phosphoramidate Complexes. *Rus. J. Appl. Chem.*, 2006, vol. 79, iss. 11, pp. 1769–1774. DOI: 10.1134/S1070427206110061
3. Klement'eva S.V., Cherepennikova N.F., Semenov V.V., Kirillov A.I., Lopatin M.A., Kuznetsova O.V., Kurskiy Yu.A., Zaytsev A.A., Klapshina L.G., Domrachev G.A., Duglas V.E. Synthesis and thermal transformations of polyphosphosiloxane based on trimethyl phosphate and (3-aminopropyl)triethoxysilane. *Russian Chemical Bulletin*, 2007, vol. 56, no. 11, pp. 2214–2224.
4. Silverstein R., Bassler G., Morrill T. *Spektrometricheskaya identifikatsiya organicheskikh soedineniy (perevod s angliyskogo Mal'tsev A.A.)* [Spectroscopic Identification of Organic Compounds]. Moscow, Mir Publ, 1977. 590 p.
5. Newton W.E., Rochow E.G. Vibrational Spectra of Some Trialkoxysilane. *J. Chem. Soc. Ser. A.*, 1970, no. 16, pp. 2664.
6. Shagidullin R.R., Chernova A.V., Vinogradova V.S., Mukhametov F.S. *Atlas IK spektrov fosfororganicheskikh soedineniy (interpretirovannye spektrogrammy)* [Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)]. Moscow, Nauka Publ., 1984. 336 p.
7. Nifant'ev E.E. *Khimiya fosfororganicheskikh soedineniy* [Chemistry of Organophosphorus Compounds] Moscow, Moscow St. Univ. Publ., 1971. 352 p.
8. Pretsch E., Clerc Th., Seibl J., Simon W. Tables of Spectral Data for Structure Determination of Organic Compounds. Berlin: Springer Verlag, 1989, 75 p.
9. Wilson G.R., Smith A.G., Ferris F.C. Preparation, Properties and Infrared Spectra of 2,6-Disubstituted Phenoxysilanes. *J. Org. Chem.*, 1959, vol. 24, no. 11, pp. 1717.
10. Nielsen M.L., Pustinger J.V. Phosphorus – 31 Nuclear Magnetic Resonance Studies of Phosphorus – Nitrogen Compounds. *J. Phys. Chem.*, 1964, vol. 68, no. 1, pp. 152–158.

11. Samitov Yu.V., Zykova T.V. *Khimiya i primeneniye fosfororganicheskikh soedineniy. Trudy tret'ey konferentsii* [Chemistry and Application of Organophosphorus Compounds. Papers of the Third Conference]. Moscow, Nauka Publ., 1972, pp. 49–74.
12. Markovskiy L.Ya., Orshanskiy D.L., Pryanishnikov V.P. *Khimicheskaya elektrotermiya* [Chemical Electrothermy]. L.: Goskhimizdat Publ., 1952. 408 p.
13. Averbukh T.G., Bakina N.P., Alpatova L.V. [Thermal Decomposition of Phosphoryl Amide]. *Vysokomolekulyarnye soedineniya* [Polymer Science], 1966, vol. 8, no. 10, pp. 1754–1757. (in Russ.)
14. Shibata N., Horiguchi M., Edakiro T. Raman Spectra of Binary High-silica Glasses and Fibers Containing GeO₂, P₂O₅ and B₂O₃. *Journal of Non-Crystalline Solids*, 1981, vol. 45, no. 1, pp. 115–126. DOI: 10.1016/0022-3093(81)90096-X
15. Bertoluzza A., Fagnano C., Morelli M.A., Gottardi V., Guglielmi M. Raman and Infrared Spectra on Silica Gel Evolving Toward Glass. *J. Non-Cryst. Solids.*, 1982, vol. 48, no. 1, pp. 117–128. DOI: 10.1016/0022-3093(82)90250-2
16. Miller T.N., Vitola A.A. *Neorganicheskie soedineniya fosfora s azotom* [Inorganic Compounds of Phosphorus with Nitrogen]. Riga, Zinatne Publ., 1986. 208 p.
17. Voronkov M.G. *Kremnekislorodnye soedineniya nemetallov. Proizvodnye azota i fosfora* [Silicon Oxygen Compounds of Nonmetals. Derivatives of Nitrogen and Phosphorus]. Novosibirsk, Nauka Publ., 1988. 365 p.
18. Massiot P., Centeno M.A., Carrizosa I., Odriozola J.A. Thermal Evolution of Sol-gel-obtained Phosphosilicate Solids (SiPO). *J. Non-Cryst. Solids.*, 2001, vol. 292, no 1–3, pp. 158–166.
19. Dishon B. Trimeric Phosphonitrilic Dibutyl and Dimethyl Ester. *J. Am. Chem. Soc.*, 1949, vol. 71, no. 6, pp. 2251–2253.
20. Steger E., Mildner E. Infrarotspektroskopische Untersuchungen zur Bildung von Phosphornitroxid aus Phosphorsauuretriamid und zu seiner hydrolytischen Zersetzung. *Z. Anorg. Allgem. Chem.*, 1964, B. 332. № 5–6. – P. 314–316.
21. Semenov V.V., Ladilina E.Yu., Lyubova T.S. *Bystrootverzhdaemyy termostoykiy lak i sposob ego polucheniya* [Fast (cured) Heat-Resistant Lacquer and Preparation Method Thereof]. Patent RF, no. 2418024, 2011.
22. Semenov V.V. Fast Cured Heat Resistant Coatings Based on Phosphorus-containing Organosilicon Varnish. *Rus. J. Appl. Chem.*, 2013, vol. 86, no. 11, pp. 1779–1784. DOI: 10.1134/S1070427213110244
23. Semenov V.V. [Coatings on the Basis of Phosphorus-containing Organosilicon Varnish and Organosilicon Perylene Pigment]. *Lakokrasochnie Materialy i ikh Primeneniye* [Russian Coatings Journal], 2011, no. 8, pp. 34. (in Russ.)

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РЕАКЦИЯ 3-АМИНОПРОПИЛТРИЭТОКСИСИЛАНА С ТРИФЕНИЛФОСФАТОМ

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Взаимодействие 3-аминопропилтриэтоксисилана RNH_2 [$\text{R} = (\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2$] с трифенилфосфатом $(\text{PhO})_3\text{P}=\text{O}$ протекает при температуре 180–200 °С и приводит к образованию четвертичной аминной соли фенилфосфорной кислоты $[\text{PhOP}(\text{O})\text{O}_2]^{2-} [\text{PhH}_2\text{NR}]^{2+}$, которая в условиях высокой температуры превращается в жидкие крем-

нийсодержащие олигоамидофосфаты $\text{RNH}[\text{P}(\text{O})(\text{OPh})\text{NR}]_n\text{P}(\text{O})(\text{OPh})\text{NHR}$ и фенол. Последний переэтерифицирует исходный 3-аминопропилтриэтоксисилан и получающиеся продукты. Методом высокотемпературной вакуумной ректификации выделены жидкие олигомеры и сшитый твердый полимер. Нагревание твердого полимера до $1000\text{ }^\circ\text{C}$ в инертной атмосфере дает аморфную фазу, состоящую из SiO_2 и NPO . Проведено сравнение реакций 3-аминопропилтриэтоксисилана с трифенилфосфатом и с триметилфосфатом.

Ключевые слова: 3-аминопропилтриэтоксисилан, трифенилфосфат, триметилфосфат, олигомеры, термические превращения.

Литература

1. Спектрально-люминесцентные свойства кремнийорганических амидофосфатов и их комплексов с европием и эрбием в растворах и в пленках / В.В. Семенов, Н.Ф. Черепенникова, Л.Г. Клапшина и др. // Координационная химия. – 2005. – Т. 31, № 7. – С. 550–558.
2. Синтез и оптические свойства наногрибидов в системе кремнезем-триамидофосфатные комплексы лантаноидов / Н.Н. Химич, Ю.Л. Зуб, Л.А. Коптелова и др. // Журнал прикладной химии – 2006. – V. 79, № 11. – P. 1769–1774. DOI: 10.1134/S1070427206110061
3. Синтез и термические превращения полифос-фосилоксана на основе триметилфосфата и 3-аминопропилтриэтоксисилана / С.В. Клементьева, Н.Ф. Черепенникова, В.В. Семенов и др. // Изв. АН. Серия химическая – 2007. – № 11. – С. 2138–2148.
4. Сильверстейн, Р. Спектроскопическая идентификация органических соединений (перевод с английского Мальцев А.А.) / Р. Сильверстейн, Г. Басслер, Т. Моррил. – М.: Мир, 1977. – 590 с.
5. Newton, W.E. Vibrational spectra of some trialkoxysilane / W.E. Newton, E.G. Rochow // J. Chem. Soc. Ser. A. – 1970. – № 16. – P. 2664.
6. Атлас ИК-спектров фосфорорганических соединений: (интерпретированные спектрограммы) / Р.Р. Шагидуллин, А.В. Чернова, В.С. Виноградова, Ф.С. Мухаметов. – М.: Наука, 1984. – 334 с.
7. Нифантьев, Э.Е. Химия фосфорорганических соединений / Э.Е. Нифантьев. – М.: Изд-во МГУ, 1971. – 352 с.
8. Tables of Spectral Data for Structure Determination of Organic Compounds / E. Pretsch, Clerc Th., J. Seibl, W. Simon. – Berlin: Springer Verlag, 1989. – P. 75.
9. Wilson, G.R. Preparation, Properties and Infrared Spectra of 2,6-Disubstituted Phenoxyxilanes / G.R. Wilson, A.G. Smith, F.C. Ferris // J. Org. Chem. – 1959. – V. 24, № 11. – P. 1717.
10. Nielsen, M.L. Phosphorus – 31 nuclear magnetic resonance studies of phosphorus – nitrogen compounds / M.L. Nielsen, J.V. Pustinger // J. Phys. Chem. – 1964. – V. 68, № 1. – P. 152–158.
11. Самитов, Ю.В. Химия и применение фосфорорганических соединений. Труды третьей конференции / Ю.В. Самитов, Т.В. Зыкова. – М.: Наука, 1972. – С. 49–74.
12. Марковский, Л.Я. Химическая электротермия / Л.Я. Марковский, Д.Л. Оршанский, В.П. Прянишников. – Л.: Госхимиздат, 1952. – 408 с.
13. Авербух, Т.Д. Термическое разложение фосфориламида / Т.Г. Авербух, Н.П. Бакина, Л.В. Алпатова // Высокомолекулярные соединения – 1966. – Т. 8. – № 10. – С. 1754–1757.
14. Shibata, N. Raman Spectra of Binary High-silica Glasses and Fibers Containing GeO_2 , P_2O_5 and B_2O_3 / N. Shibata, M. Horigudhi, T. Edahiro // Journal of Non-Crystalline Solids – 1981. – V. 45. № 1. – P. 115–126.
15. Bertoluzza, A. Raman and Infrared Spectra on Silica Gel Evolving Toward Glass / A. Bertoluzza, C. Fagnano, M.A. Morelli, V. Gottardi, M. Guglielmi // Journal of Non-Crystalline Solids. – 1982. – V. 48. – № 1. – P. 117.
16. Миллер, Т.Н. Неорганические соединения фосфора с азотом / Т.Н. Миллер, А.А. Витола. – Рига: Зинатне, 1986. – 208 с.
17. Воронков, М.Г. Кремнекислородные соединения неметаллов. Производные азота и фосфора: монография / М.Г. Воронков. – Новосибирск: Наука, 1988. – 365 с.
18. Thermal Evolution of Sol-gel-obtained Phosphosilicate Solids (SiPO) / P. Massiot, M.A. Centeno, I. Carrizosa, J.A. Odriozola // J. Non-Cryst. Solids. – 2001. – V. 292, № 1–3. – P. 158–166.
19. Dishon, B. Trimeric phosphonitric dibutyl and dimethyl ester / B. Dishon // J. Am. Chem. Soc. – 1949. – V. 71, № 6. – P. 2251–2253.

20. Steger, E. Infrarotspektroskopische Untersuchungen zur Bildung von Phosphornitroxid aus Phosphorsäuretriimid und zu seiner hydrolytischen Zersetzung / E. Steger, E. Mildner // *Z. Anorg. Allgem. Chem.* – 1964. – В. 332, № 5–6. – Р. 314–316.

21. Пат. 2418024 Российская Федерация, МПК C09D 183/08, C08G 77/30. Быстроотверждаемый термостойкий лак и способ его получения / В.В. Семенов, Е.Ю. Ладилина, Т.С. Любова; патентообладатель Учреждение Российской академии наук Институт металлоорганической химии им. Г.А. Разуваева РАН (RU). – № 2418024; заявл. 10.11.2009; опубл. 10.05.2011. – 14 с.

22. Семенов, В.В. Быстроотверждаемое термостойкое покрытие на основе фосфорсодержащего кремнийорганического лака / В.В. Семенов // *Журнал прикладной химии.* – 2013. – Т. 86, № 11. – С. 1831–1836.

23. Семенов, В.В. Покрытия на основе фосфорсодержащего кремнийорганического лака и кремнийорганического периленового красителя / В.В. Семенов // *Лакокрасочные материалы и их применение.* – 2011. – № 8. – С. 34.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Semenov, V.V. Reaction of 3-aminopropyltriethoxysilane with triphenylphosphate / V.V. Semenov // *Вестник ЮУрГУ. Серия «Химия».* – 2015. – Т. 7, № 4. – С. 66–79. DOI: 10.14529/chem150409

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SYNTHESIS AND STRUCTURE OF IRIDIUM COMPLEX [Ph₄Sb(DMSO)]⁺[IrCl₄(DMSO)₂]⁻

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Iridium complex [Ph₄Sb(DMSO)]⁺[IrCl₄(DMSO)₂]⁻ (**1**) has been synthesized by interaction of tetraphenylstibonium chloride with sodium hexachloroiridate(III) in water. From X-ray diffraction analysis data, two types of crystallographically independent cations [Ph₄Sb(DMSO)]⁺ and anions [IrCl₄(DMSO)₂]⁻ exist in the crystal. The antimony atoms in cations have distorted trigonal-bipyramidal surroundings with *O*-dimethyl sulphoxide ligand in axial position (equatorial angles CSbC 113.6(2)°–121.2(2)°, axial angles CSbO 178.33(18)°, 176.47(18)°, bond lengths Sb–C_{eq} 2.106(6)–2.119(6) Å, Sb–C_{ax} 2.126(6), 2.130(6) Å, Sb–O 2.545(4), 2.465(4) Å). In mononuclear octahedral anions the equatorial positions are occupied by chlorine atoms (angles ClIrCl-*trans* 178.69(7)°–179.56(7)°, SIrS-*trans* 178.35(7)°, 175.88(7)°; dimethyl sulfoxide ligands are coordinated with iridium atoms through sulfur atoms (Ir–S 2.2958(16)–2.3148(17) Å), bond lengths Ir–Cl vary in the range 2.3407(19)–2.3681(17) Å. The structural organization in the crystal is determined by interionic hydrogen bonds (H···Cl 2.80–2.94 Å and H···O 2.56–2.71 Å).

Keywords: tetraphenylstibonium chloride, sodium hexachloroiridate(III), dimethyl sulfoxide, (dimethylsulfoxido)tetraphenylstibonium bis(dimethylsulfoxido)tetrachloroiridate(III), synthesis, X-ray diffraction analysis, structure.

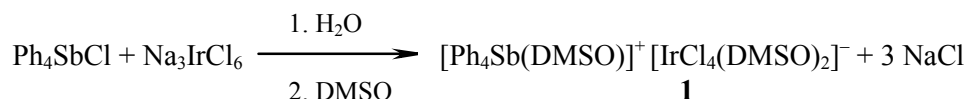
Introduction

Ionic complex compounds of iridium with anions of the type [IrHal₄(S–DMSO)₂]⁻ are described in the literature as single examples [1–4]. Note that both organic cations and tetraorganylphosphonium cations [4] can act as counterions in the crystals of these compounds, at this the structural organization of iridium complexes is determined by the presence of solvent molecules in their structure. In the present paper the synthesis of (dimethylsulfoxido)tetraphenylstibonium bis(dimethylsulfoxido)tetrachloroiridate (III), the characteristic features of its structure are examined.

Results and Discussion

In order to synthesize new iridium complexes we studied the reactions of tetraphenylstibonium chloride with sodium hexachloroiridate(III) in aqueous solution.

It has been found that after addition of sodium hexachloroiridate(III) in water to the aqueous solution of tetraphenylstibonium chloride in equimolar amount, followed by solvent evaporation and recrystallization of the solid precipitate from dimethyl sulfoxide, yellow crystals are formed; it is (dimethylsulfoxido)tetraphenylstibonium bis(dimethylsulfoxido)tetrachloroiridate(III) [Ph₄Sb]⁺[IrCl₄(DMSO)₂]⁻ (**1**):



According to X-ray diffraction analysis, two types of crystallographically independent cations [Ph₄Sb(DMSO)]⁺ and anions [IrCl₄(DMSO)₂]⁻ coexist in the crystal. The antimony atoms in cations have distorted trigonal-bipyramidal surroundings with *O*-dimethyl sulphoxide ligand in axial position (equatorial angles CSbC 113.6(2)°–121.2(2)°, axial angles CSbO 178.33(18)°, 176.47(18)°, bond lengths Sb–C_{eq} 2.106(6)–2.119(6) Å, Sb–C_{ax} 2.126(6), 2.130(6) Å, Sb–O 2.545(4), 2.465(4) Å) (Fig. 1).

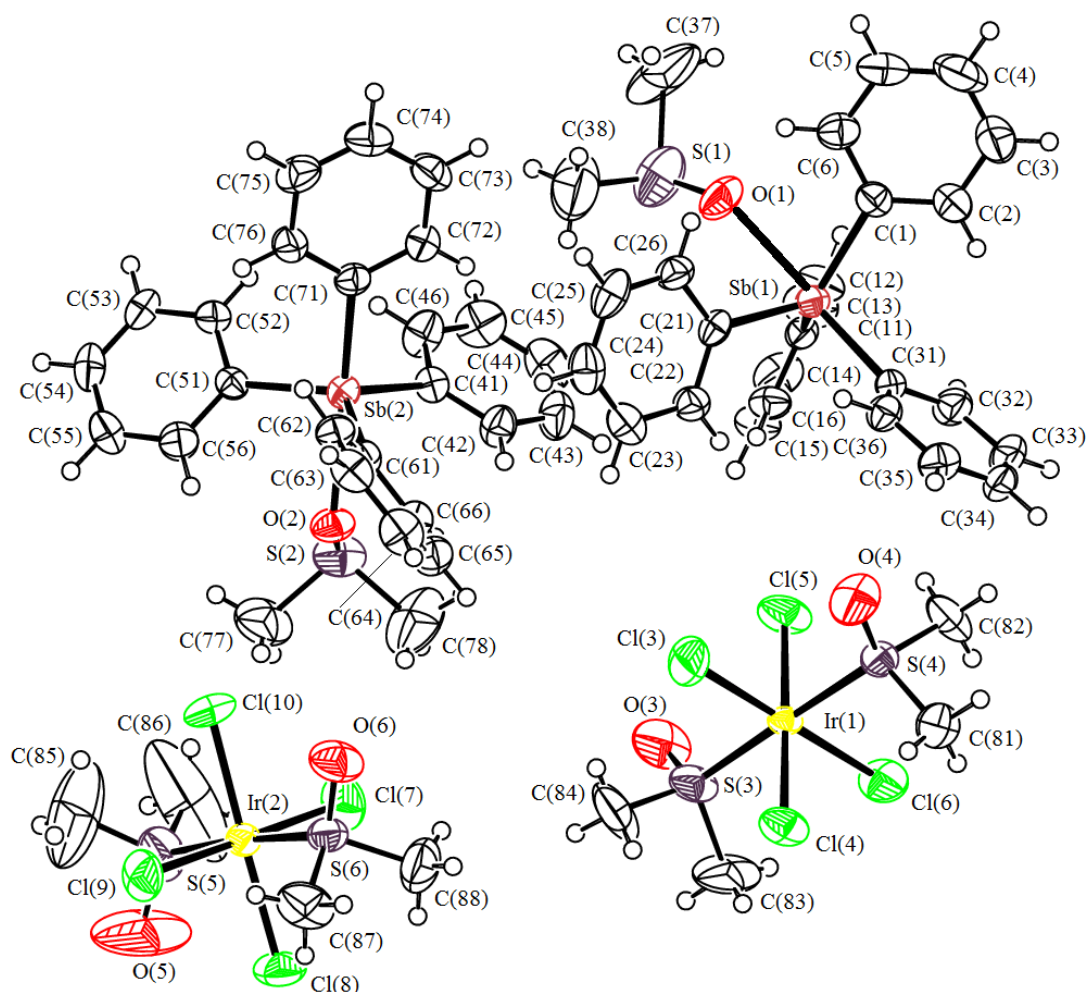


Fig. 1. The structure of compound 1

In mononuclear octahedral anions the equatorial positions are occupied by chlorine atoms (angles ClIrCl-*trans* 178.69(7)°–179.56(7)°, SiRS-*trans* 178.35(7)°, 175.88(7)°; dimethyl sulfoxide ligands are coordinated with iridium atoms through sulfur atoms (Ir–S 2.2958(16)–2.3148(17) Å), bond lengths Ir–Cl vary in the range 2.3407(19)–2.3681(17) Å. The structural organization in the crystal is determined by interionic hydrogen bonds (H···Cl 2.80–2.94 Å and H···O 2.56–2.71 Å), the strongest ones are shown in Fig. 2. Cations and anions are packed in stacks oriented along crystallographic axis *a*.

X-ray diffraction analysis of the complex **1** crystal was performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_α-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [5]. All calculations for structure determination and refinement were performed using the SHELXL/PC programs [6]. The structure **1** was determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for structure **1** are listed in Table 1, the selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1048264; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

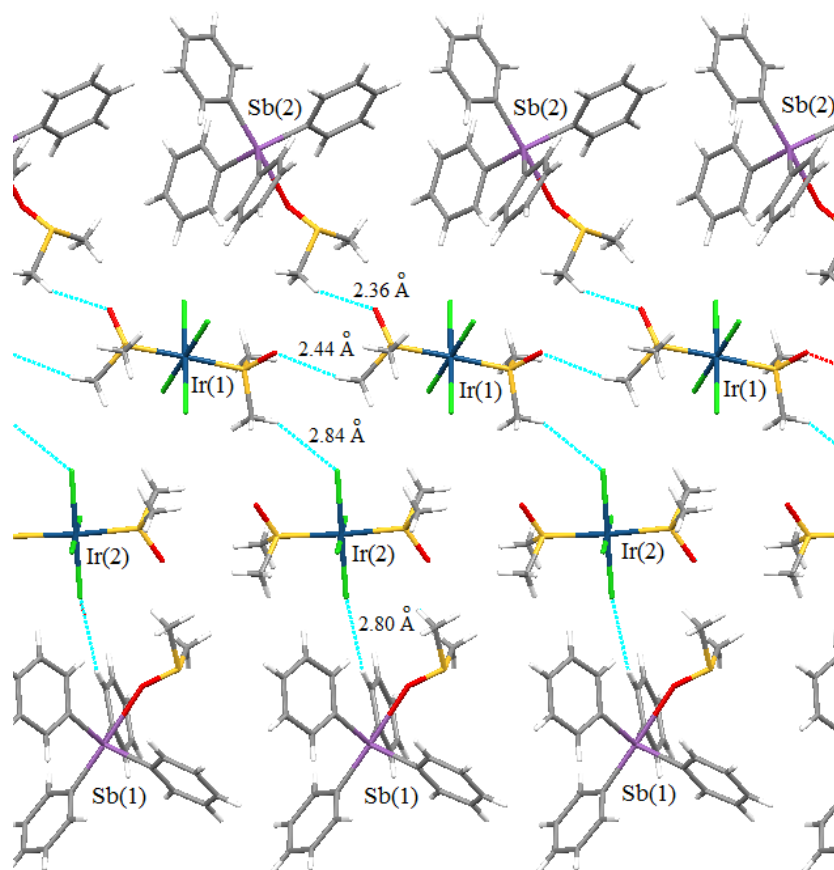


Fig. 2. Interionic bonds in the crystal of compound 1

Crystallographic data and the experimental and structure refinement parameters for compound 1

Table 1

Parameter	Value
Empirical formula	$C_{60}O_6S_6Cl_8Sb_2Ir_2H_{76}$
Formula weight	1997.07
T , K	296(2)
Crystal system	Triclinic
Space group	P-1
a , Å	9.5963(6)
b , Å	19.2090(14)
c , Å	19.5688(14)
α , deg	91.109(3)
β , deg	90.549(2)
γ , deg	90.095(3)
V , Å ³	3606.4(4)
Z	2
ρ (calcd.), g/cm ³	1.839
μ , mm ⁻¹	4.935
$F(000)$	1944.0
Crystal size, mm	0.11 × 0.18 × 0.24
2 θ Range of data collection, deg	5.98 – 41.32°
Range of refraction indices	$-9 \leq h \leq 9, -19 \leq k \leq 19, -19 \leq l \leq 19$
Measured reflections	67394
Independent reflections	7363
R_{int}	0.0325

Table 1 (end)

Parameter	Value
Refinement variables	769
GOOF	1.026
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0237$, $wR_2 = 0.0533$
R factors for all reflections	$R_1 = 0.0286$, $wR_2 = 0.0560$
Residual electron density (min/max), e/Å ³	1.12/-0.93

Table 2

Selected bond lengths and bond angles in the structure of compound 1

Bond	<i>d</i> , Å	Angle	ω, deg
Ir(1)–S(3)	2.2958(16)	S(3)Ir(1)S(4)	178.35(7)
Ir(1)–S(4)	2.3002(15)	S(3)Ir(1)Cl(3)	90.09(8)
Ir(1)–Cl(3)	2.3407(19)	S(3)Ir(1)Cl(4)	87.48(6)
Ir(1)–Cl(4)	2.3529(16)	S(3)Ir(1)Cl(5)	92.21(6)
Ir(1)–Cl(5)	2.3500(17)	S(3)Ir(1)Cl(6)	90.33(7)
Ir(1)–Cl(6)	2.3681(17)	S(4)Ir(1)Cl(3)	91.55(7)
Ir(2)–S(5)	2.311(2)	S(4)Ir(1)Cl(4)	92.71(6)
Ir(2)–S(6)	2.3148(17)	S(4)Ir(1)Cl(5)	87.62(6)
Ir(2)–Cl(7)	2.3493(18)	S(4)Ir(1)Cl(6)	88.03(6)
Ir(2)–Cl(8)	2.3498(17)	Cl(3)Ir(1)Cl(4)	90.30(8)
Ir(2)–Cl(9)	2.3546(17)	Cl(3)Ir(1)Cl(5)	88.89(8)
Ir(2)–Cl(10)	2.3396(17)	Cl(3)Ir(1)Cl(6)	179.56(7)
Sb(1)–O(1)	2.545(4)	Cl(4)Ir(1)Cl(6)	89.60(7)
Sb(1)–C(1)	2.117(6)	Cl(5)Ir(1)Cl(4)	179.14(7)
Sb(1)–C(11)	2.106(6)	Cl(5)Ir(1)Cl(6)	91.20(8)
Sb(1)–C(21)	2.106(6)	S(5)Ir(2)S(6)	175.88(7)
Sb(1)–C(31)	2.126(6)	S(5)Ir(2)Cl(10)	91.53(8)
Sb(2)–O(2)	2.465(4)	Cl(7)Ir(2)Cl(9)	179.22(7)
Sb(2)–C(51)	2.106(6)	Cl(10)Ir(2)Cl(8)	178.69(7)
Sb(2)–C(71)	2.130(6)	Cl(10)Ir(2)Cl(9)	90.30(8)
Sb(2)–C(41)	2.111(6)	C(1)Sb(1)O(1)	77.93(19)
Sb(2)–C(61)	2.119(6)	C(1)Sb(1)C(31)	100.4(2)
O(4)–S(4)	1.459(5)	C(11)Sb(1)O(1)	78.92(18)
O(6)–S(6)	1.464(5)	C(11)Sb(1)C(1)	116.7(2)
S(1)–O(1)	1.457(5)	C(11)Sb(1)C(21)	113.6(2)
S(1)–C(38)	1.739(10)	C(11)Sb(1)C(31)	102.2(2)
S(1)–C(37)	1.785(11)	C(21)Sb(1)O(1)	80.45(19)
S(2)–O(2)	1.517(4)	C(21)Sb(1)C(1)	119.2(2)
S(2)–C(77)	1.763(8)	C(21)Sb(1)C(31)	100.2(2)
S(2)–C(78)	1.753(9)	C(31)Sb(1)O(1)	178.33(18)
S(3)–O(3)	1.450(5)	C(51)Sb(2)O(2)	82.50(18)
S(3)–C(84)	1.779(9)	C(51)Sb(2)C(71)	98.7(2)
S(3)–C(83)	1.758(8)	C(51)Sb(2)C(41)	114.4(2)
S(4)–C(81)	1.764(6)	C(51)Sb(2)C(61)	121.2(2)
S(4)–C(82)	1.769(7)	C(71)Sb(2)O(2)	176.47(18)
S(5)–C(86)	1.676(11)	C(41)Sb(2)O(2)	83.41(18)
S(5)–O(5)	1.477(6)	C(41)Sb(2)C(71)	99.0(2)
S(5)–C(85)	1.678(11)	C(41)Sb(2)C(61)	117.3(2)
S(6)–C(88)	1.765(7)	C(61)Sb(2)O(2)	77.58(18)
S(6)–C(87)	1.770(7)	C(61)Sb(2)C(71)	99.0(2)

Conclusion

The structure of iridium complex $[\text{Ph}_4\text{Sb}(\text{DMSO})]^+[\text{IrCl}_4(\text{DMSO})_2]^-$, obtained from tetraphenylstibonium chloride and sodium hexachloroiridate (III) in water, followed by recrystallization from dimethyl sulfoxide, has been established by X-ray diffraction analysis.

References

1. Haddad Y.M.Y., Henbest H.B., Trocha-Grimshaw J. Aspects of Catalysis. Part II. Dimethyl Sulphoxide Complexes of Iridium(III) Including Hydrides. *Journal of the Chemical Society, Perkin Transactions 1*, 1974, pp. 592–595.
2. Messori L., Marcon G., Orioli P., Fontani M., Zanello P., Bergamoc A., Savac G., Murad P. Molecular Structure, Solution Chemistry and Biological Properties of the Novel $[\text{ImH}][\text{trans-IrCl}_4(\text{Im})(\text{DMSO})]$, (I) and of the Orange Form of 4 $[(\text{DMSO})_2\text{H}][\text{trans-IrCl}_4(\text{DMSO})_2]$, (II). *Journal of Inorganic Biochemistry*, 2003, vol. 95, iss. 1, pp. 37–46.
3. Albertí F.M., Fiol J.J., García-Raso A., Torres M., Terrón A., Barceló-Oliver M., Prieto M.J., Moreno V., Molins E. Ruthenium(III) and Iridium(III) Complexes with Nicotine. *Polyhedron*, 2010, vol. 29, iss. 1, pp. 34–41. DOI: 10.1016/j.poly.2009.05.082
4. Sharutin V.V., Sharutina O.K., Senchurin V.S., Somov N.V. [Synthesis and Structure of Iridium Complexes $[\text{Ph}_3\text{PR}][\text{trans-IrCl}_4(\text{DMSO})_2]$. *Russian Journal of General Chemistry*, 2015, vol. 85, no. 3, pp. 634–639. DOI: 10.1134/S1070363215030184
5. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. – Bruker AXS Inc. – 1998. – Madison, Wisconsin, USA.
6. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. – Bruker AXS Inc. – 1998. – Madison, Wisconsin, USA.

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СИНТЕЗ И СТРОЕНИЕ КОМПЛЕКСА ИРИДИЯ $[\text{Ph}_4\text{Sb}(\text{DMSO})]^+[\text{IrCl}_4(\text{DMSO})_2]^-$

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Взаимодействием хлорида тетрафенилстибония с гексахлороиридатом(III) натрия в воде синтезирован комплекс иридия $[\text{Ph}_4\text{Sb}(\text{DMSO})]^+[\text{IrCl}_4(\text{DMSO})_2]^-$ (1). По данным РСА в кристалле присутствуют по два типа кристаллографически независимых катионов $[\text{Ph}_4\text{Sb}(\text{DMSO})]^+$ и анионов $[\text{IrCl}_4(\text{DMSO})_2]^-$. Атомы сурьмы в катионах имеют искаженное тригонально-бипирамидальное окружение с аксиально расположенным *O*-диметилсульфоксидным лигандом, (экваториальные углы CSbC 113.6(2)°–121.2(2)°, аксиальные углы CSbO 178.33(18)°, 176.47(18)°, длины связей $\text{Sb}-\text{C}_{\text{эkv}}$ 2.106(6)–2.119(6) Å, $\text{Sb}-\text{C}_{\text{акс}}$ 2.126(6), 2.130(6) Å, $\text{Sb}-\text{O}$ 2.545(4), 2.465(4) Å). В моноядерных октаэдрических анионах экваториальные положения занимают атомы хлора (углы ClIrCl-транс 178.69(7)°–179.56(7)°, ClIrS-транс 178.35(7)°, 175.88(7)°; диметилсульфоксидные лиганды координируются с атомами Ir посредством атомов серы (Ir-S 2.2958(16)–2.3148(17) Å), длины связей $\text{Ir}-\text{Cl}$ изменяются в интервалах 2.3407(19)–2.3681(17) Å. Структурная организация в кристалле обусловлена межмолекулярными водородными связями ($\text{H}\cdots\text{Cl}$ 2.80–2.94 Å и $\text{H}\cdots\text{O}$ 2.56–2.71 Å).

Ключевые слова: хлорид тетрафенилстибония, гексахлороиридат(III) натрия, диметилсульфоксид, бис(диметилсульфоксидо)тетрахлороиридат(III) (диметилсульфоксидо)тетрафенилстибония, синтез, рентгеноструктурный анализ, строение.

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SYNTHESIS AND STRUCTURE OF TRI- AND TETRAPHENYLANTIMONY AROXIDES: Ph₃Sb[OC₆H₃(Br₂-2,6)(Me-4)]₂ AND Ph₄SbOC₆H₃Br₂-2,6, Me-4

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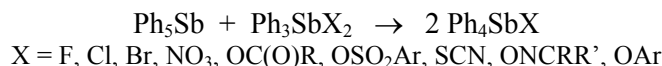
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Interaction of pentaphenylantimony with 2,6-dibromo,4-methylphenol or with *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**) leads to formation of 2,6-dibromo,4-methylphenoxytetraphenylantimony (**2**). In molecules of compounds **1** and **2** the antimony atoms have distorted trigonal-bipyramidal coordination with the oxygen atoms in axial positions (OSbO 179.20(15)° (**1**), OSbC 179.7(9)° (**2**)). The bond lengths Sb–C and Sb–O equal 2.090(5), 2.101(5), 2.110(5) and 2.088(4), 2.088(4) Å (**1**), 2.11(2), 2.11(2), 2.11(2), 2.17(3) and 2.234(18), 2.234(18) Å (**2**), respectively.

Keywords: pentaphenylantimony, triphenylantimony, 2,6-dibromo,4-methylphenol, *tert*-butyl hydroperoxide, *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony, (2,6-dibromo,4-methylphenoxy)tetraphenylantimony, molecular structure, X-ray diffraction analysis.

Introduction

It is known that redistribution of organic radicals between pentaphenylantimony and symmetrical derivatives of antimony with the general formula Ph₃SbX₂ leads to formation of the single organoantimony compound with the general formula Ph₄SbX, yielding up to 99 % [1–6].



This reaction is of universal character, since it is valid for compounds containing substituents (X) of various nature, but for tetraphenylantimony aroxides it has been demonstrated by one example only [5].

In the course of research on characteristic features of ligand redistribution we have studied the reactions of pentaphenylantimony with *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (**1**) and 2,6-dibromo,4-methylphenol. The structures of the products have been established by X-ray diffraction analysis.

Experimental

Synthesis of *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (1**).** The mixture of 0.353 g (1.00 mmol) triphenylantimony, 0.532 g (2.00 mmol) 2,6-dibromo,4-methylphenol and 0.129 g 70% solution of *tert*-butyl hydroperoxide in 10 mL ether stood for 18 h at 24 °C. After slow evaporation of the solvent, large crystals **1** with melting point 214 °C were formed to yield 0.786 g (89%). Found, %: C 43.37; H 2.99. Calculated for C₃₂H₂₅O₂Br₄Sb, %: C 43.49; H 2.83.

Interaction of pentaphenylantimony with *bis*(2,6-dibromo,4-methylphenoxy) triphenylantimony. The mixture of 0.250 g (0.50 mmol) pentaphenylantimony, 0.441 g (0.50 mmol) *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony and 2 mL toluene in glass ampoule was heated in boiling water bath for 1 hour. The progress of the reaction was controlled by thin-layer chromatography. The solution was decanted from the crystals, and the solvent was evaporated. Formation of large crystals **2** with decomposition temperature 224 °C was observed. IR spectrum (ν, cm⁻¹): 3048, 2917, 2361, 2342, 1577, 1447, 1434, 1302, 1291, 1240, 1176, 1069, 1020, 996, 849, 799, 730, 692, 570, 563, 491, 467, 458, 447. Found, %: C 54.43; H 3.71. Calculated for C₃₁H₂₅OBr₂Sb, %: C 53.54, H 3.60.

Interaction of pentaphenylantimony with 2,6-dibromo,4-methylphenol. The mixture of 0.25 g (0.49 mmol) pentaphenylantimony, 0.131 g (0.49 mmol) 2,6-dibromo-4-methylphenol and 2 mL toluene

in glass ampoule was heated in boiling water bath for 1 hour. The solution was decanted from the crystals, the solvent was evaporated. Colorless crystals with decomposition temperature 224 °C were formed to yield 0.274 g (80%). IR spectrum is identical to the IR spectrum of the compound obtained by the abovementioned procedure.

IR spectra were recorded on the Fourier-transform spectrometer Bruker Tensor 27 in KBr pellets.

The X-ray diffraction analyses of crystals **1** and **2** were performed on the Bruker D8 Quest diffractometer (Mo K_{α} -emission, $\lambda = 0.71073$ Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [7]. All calculations for structure determination and refinement were performed using the SHELXL/PC [8] and OLEX2 programs [9]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for the structures are listed in Table 1, the selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1043497, 1009712; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic data and the experimental and structure refinement parameters for compounds **1**, **2**

Parameter	Value	
	1	2
Empirical formula	C ₃₂ H ₂₅ O ₂ Br ₄ Sb	C ₃₁ H ₂₅ OBr ₂ Sb
Formula weight	882.91	695.08
<i>T</i> , K	273.15	273.15
Crystal system	triclinic	orthorhombic
Space group	P-1	Pnma
<i>a</i> , Å	10.1942(6)	16.3869(9)
<i>b</i> , Å	11.0622(6)	11.6579(6)
<i>c</i> , Å	15.3136(8)	14.5305(7)
α , deg	87.547(3)	90.00
β , deg	78.460(3)	90.00
γ , deg	69.703(3)	90.00
<i>V</i> , Å ³	1586.28(15)	2775.9(2)
<i>Z</i>	2	4
ρ (calcd.), g/cm ³	1.848	1.663
μ , mm ⁻¹	5.934	3.894
<i>F</i> (000)	848.0	1360.0
Crystal size, mm	0.35 × 0.18 × 0.09	0.68 × 0.45 × 0.43
2 θ Range of data collection, deg	5.56 – 53.02°	6.08 – 52.9°
Range of refraction indices	–12 ≤ <i>h</i> ≤ 12, –13 ≤ <i>k</i> ≤ 13, –19 ≤ <i>l</i> ≤ 19	–20 ≤ <i>h</i> ≤ 20, –14 ≤ <i>k</i> ≤ 14, –18 ≤ <i>l</i> ≤ 18
Measured reflections	31896	67786
Independent reflections	6504	2998
<i>R</i> _{int}	0.0801	0.0474
Refinement variables	354	184
<i>GOOF</i>	1.018	1.050
<i>R</i> factors for $F^2 > 2\sigma(F^2)$	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.1073	<i>R</i> ₁ = 0.0324, <i>wR</i> ₂ = 0.0785
<i>R</i> factors for all reflections	<i>R</i> ₁ = 0.0857, <i>wR</i> ₂ = 0.1236	<i>R</i> ₁ = 0.0419, <i>wR</i> ₂ = 0.0881
Residual electron density (min/max), e/Å ³	1.35/–0.91	0.60/–0.83

Selected bond lengths and bond angles in the structure of compounds 1, 2

Bond	<i>d</i> , Å	Angle	ω , deg
1			
Sb(1)–O(1)	2.088(4)	O(1)Sb(1)O(2)	179.20(15)
Sb(1)–O(2)	2.089(4)	O(1)Sb(1)C(1)	89.6(2)
Sb(1)–C(1)	2.110(5)	O(1)Sb(1)C(11)	89.39(18)
Sb(1)–C(11)	2.101(5)	O(1)Sb(1)C(21)	92.17(19)
Sb(1)–C(21)	2.090(5)	O(2)Sb(1)C(1)	89.6(2)
Br(1)–C(32)	1.892(6)	O(2)Sb(1)C(11)	91.17(19)
Br(2)–C(36)	1.892(6)	O(2)Sb(1)C(21)	88.0(2)
Br(3)–C(46)	1.886(7)	C(11)Sb(1)C(1)	121.3(2)
Br(4)–C(42)	1.894(6)	C(21)Sb(1)C(1)	116.9(2)
O(1)–C(31)	1.338(7)	C(21)Sb(1)C(11)	121.8(2)
O(2)–C(41)	1.339(7)	C(31)O(1)Sb(1)	130.1(3)
Sb(1)···Br(4)	3.914(4)	C(41)O(2)Sb(1)	130.3(3)
Sb(1)···Br(2)	3.984(4)	C(2)C(1)Sb(1)	119.2(4)
2			
Sb(1)–O(1)	2.234(18)	C(1)Sb(1)O1	179.7(9)
Sb(1)–C(1)	2.17(3)	C(31)Sb(1)O1	85.0(6)
Sb(1)–C(31 ¹)	2.11(2)	C(31)Sb(1)C1	95.2(7)
Sb(1)–C(31)	2.11(2)	C(31)Sb(1)C21	122.7(6)
Sb(1)–C(21)	2.11(3)	C(31 ¹)Sb(1)C21	122.7(6)
Br(1)–C(12)	1.90(2)	C(21)Sb(1)O1	84.2(9)
O(1)–C(11)	1.31(3)	C(21)Sb(1)C1	95.4(11)

Symmetry operations: ¹+x, 1/2–y, +z

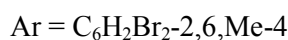
Results and Discussion

The way of synthesis of antimony compounds with the general formula Ph_4SbX by ligand redistribution reaction is particularly attractive due to easy isolation and high yield of the target product, the amount of which reaches two moles for one mole of initial pentaphenylantimony amount. The similar reaction with the use of pentaphenylantimony and triphenylantimony dioxides was previously studied on the single example of tetraphenylantimony 4-nitrophenoxide [5].

It has been suggested that this disproportionation reaction proceeds through formation of the intermediate labile complex of ionic structure with tetraphenylstibonium cation and an anion containing two electronegative groups X, apart from four phenyl ligands. The following transition of electronegative group X to tetraphenylstibonium cation is accompanied by formation of the target product Ar_4SbX . It is obvious that aryl compounds of antimony easily enter into disproportionation reactions with groups X, whose electronegativity is high enough.

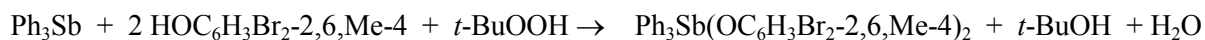
We have studied the possibility of radical redistribution reaction between pentaphenylantimony and *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony (1).

The reaction was carried out in toluene solution (1 h, 100 °C). The progress of the reaction was controlled by thin-layer chromatography (Silufol UV-254, *o*-xylene as eluent). The reaction was considered completed after the disappearance of the spot peculiar to pentaphenylantimony. It has been established that the interaction between the abovementioned reactants proceeds with formation of (2,6-dibromo,4-methylphenoxy)tetraphenylantimony (2).



Tetraphenylantimony aroxide 2, obtained by the radical redistribution reaction, was identical in its characteristics (melting point, IR spectrum) to the compound synthesized from pentaphenylantimony and 2,6-dibromo,4-methylphenol.

The parent antimony compound **1** was obtained by triphenylantimony oxidation with the use of *tert*-butyl hydroperoxide in the presence of 2,6-dibromo,4-methylphenol, according to the procedure described in [6]:



From the X-ray analysis data it follows that in molecule **1** the antimony atoms have distorted trigonal-bipyramidal coordination with aroxyl ligands in axial positions (Fig. 1).

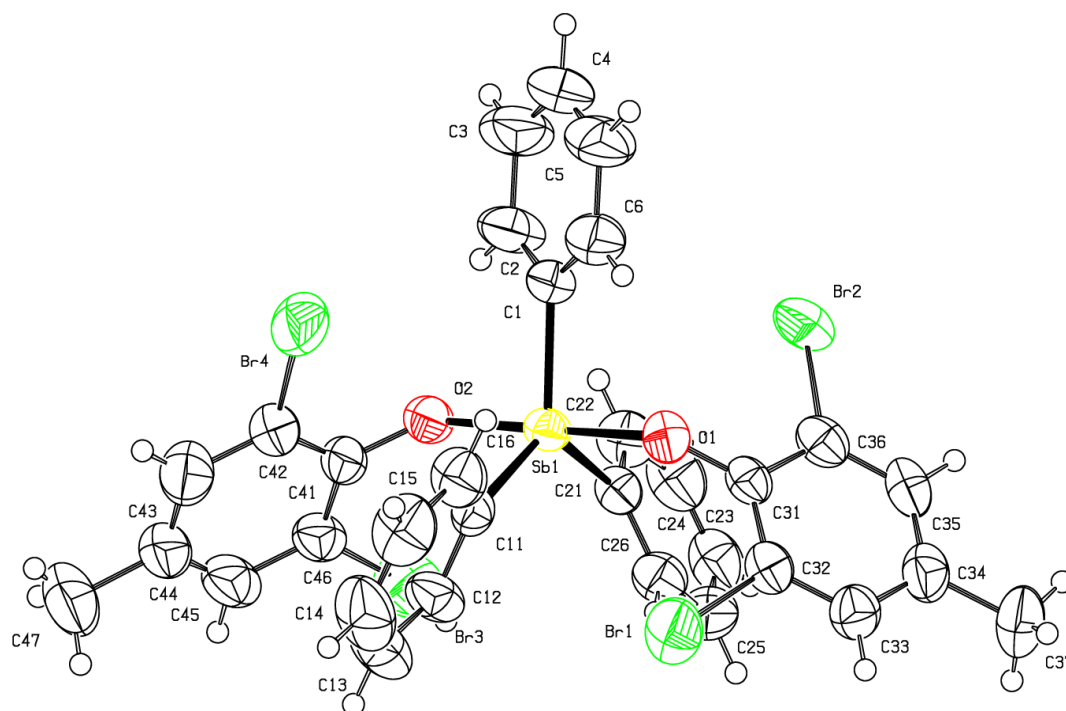


Fig. 1. The structure of compound **1**

The axial angle OSbO measures $179.20(15)^\circ$, the sum of angles CSbC in equatorial plane equals 360° . The angles between axial and equatorial bonds OSbC vary in the range $88.0(2)\text{--}92.17(19)^\circ$. The lengths of equatorial bonds Sb–C ($2.090(5)$, $2.101(5)$, $2.110(5)$ Å) exceed the values of axial distances Sb–O ($2.088(4)$, $2.089(4)$ Å) and the sum of antimony and oxygen covalent radii (2.07 Å [10]). In **1** the close intermolecular contacts between the central atom and one of bromine atoms of aroxyl ligand are observed (Sb \cdots Br(2) $3.984(6)$, Sb \cdots Br(4) $3.914(6)$ Å, while the sum of Van der Waals radii of antimony and bromine is 4.15 Å [10]). The structural organization of the crystal is formed with the participation of weak hydrogen bonds of the type H \cdots O (2.61 Å) and H \cdots Br ($3.02\text{--}3.03$ Å).

Geometrical characteristics of compound **2** (Fig. 2) differ from those found in **1**, obviously because of the presence of different ligands in axial positions.

For example, the axial angle OSbC equals $179.7(9)^\circ$, while the sum of angles CSbC in equatorial plane (357.5°) differs from the ideal value of 360° . The lengths of equatorial bonds Sb–C ($2.11(2)$, $2.11(2)$, $2.11(3)$ Å) are less than the values of axial distances Sb–O ($2.234(18)$ Å) and Sb–C ($2.17(3)$ Å). Intra- and intermolecular interactions H \cdots Br in crystal **2** are nonexistent, though the structure-forming contacts H \cdots O (2.53 Å) are stronger than in **1**.

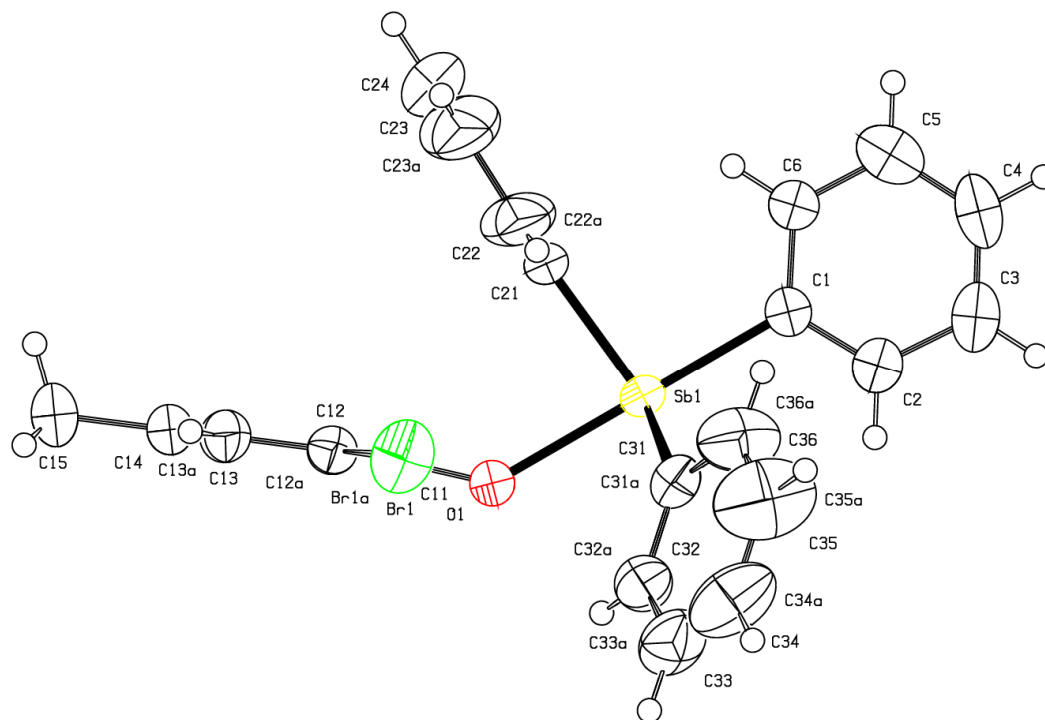


Fig. 2. The structure of compound 2

Conclusions

To summarize, the ligand redistribution reaction with participation of pentaphenylantimony and *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony, leading to formation of (2,6-dibromo,4-methylphenoxy)tetraphenylantimony, confirms the general character of the abovementioned reaction. In the molecules of *bis*(2,6-dibromo,4-methylphenoxy)triphenylantimony and (2,6-dibromo,4-methylphenoxy)tetraphenylantimony the antimony atoms have distorted trigonal-bipyramidal coordination with aroxyl ligands in axial positions. The compound 1 is characterized by short axial bonds Sb–O (2.088(4), 2.089(4) Å), intramolecular contacts Sb⋯Br (3.914(6), 3.984(6) Å).

References

1. Sharutin V.V., Senchurin V.S., Sharutina O.K., Pakusina A.P., Panova L.P. [Synthesis Method of Tetraphenylstibonium Salts with the General Formula Ph₄SbX [X=Cl, Br, OC(O)Ph, SCN]. *Russian Journal of General Chemistry*, 1996, vol. 66, no. 10, pp. 1755–1756. (in Russ.)
2. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetra- and Triphenylantimony Sulfoxides]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, pp. 1438–1442.
3. Sharutin V.V., Sharutina O.K., Pakusina A.P., Belskii V.K. [Reactions of Pentaarylantimony with Triarylantimony Diacylates]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, pp. 1538–1543.
4. Sharutin V.V., Sharutina O.K., Molokova O.V., Etenko E.N., Krivolapov D.B., Gubaydul-lin A.T., Litvinov I.A. [Synthesis and Structure of Tetra- and Triarylantimony Oximates]. *Russian Journal of General Chemistry*, 2001, vol. 71, no. 8, pp. 1243–1247. DOI:10.1023/A:1013220911661
5. Sharutin V.V., Sharutina O.K., Osipov P.E., Subacheva O.V. [New Method for Preparing Aroxy-tetraaryl Derivatives of Antimony]. *Russian Journal of General Chemistry*, 2001, vol. 71, no. 6, pp. 983–984. DOI:10.1023/A:1012368510207
6. Sharutin V.V., Senchurin V.S. *Imennye reaktsii v khimii elementoorganicheskikh soedineniy* [Name Reactions in Chemistry of Organoelemental Compounds]. Chelyabinsk, South Ural St. Univ. Publ., 2011. 426 p. (in Russ.)
7. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.

8. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341.
10. Batsanov S.S. [Atomic radiuses of the elements]. *Russian Journal of Inorganic Chemistry*, 1991, vol. 36, no. 12, pp. 3015–3037. (in Russ.)

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СИНТЕЗ И СТРОЕНИЕ АРОКСИДОВ ТРИ- И ТЕТРАФЕНИЛСУРЬМЫ: $Ph_3Sb[OC_6H_3(Br_{2-2,6})(Me-4)]_2$ И $Ph_4SbOC_6H_3Br_{2-2,6}, Me-4$

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Взаимодействием пентафенилсурьмы с 2,6-дибром,4-метилфенолом или с бис(2,6-дибром,4-метилфенокси)трифенилсурьмой (1) получена 2,6-дибром,4-метилфенокси-тетрафенилсурьма (2). В молекулах 1 и 2 атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомами кислорода в аксиальных положениях ($OSbO$ 179.20(15)° (1), $OSbC$ 179.7(9)° (2)). Длины связей $Sb-C$ и $Sb-O$ составляют 2.090(5), 2.101(5), 2.110(5) и 2.088(4), 2.088(4) Å (1), 2.11(2), 2.11(2), 2.11(2), 2.17(3) и 2.234(18), 2.234(18) Å (2) соответственно.

Ключевые слова: пентафенилсурьма, трифенилсурьма, 2,6-дибром,4-метилфенол, третбутилгидропероксид, бис(2,6-дибром,4-метилфенокси)три-фенилсурьма, (2,6-дибром, 4-метилфенокси)тетрафенилсурьма, молекулярная структура, рентгено-структурный анализ.

Литература

1. Способ получения солей тетрафенилстибония общей формулы Ph_4SbX [$X=Cl, Br, OC(O)Ph, SCN$] / В.В. Шарутин, В.С. Сенчурин, О.К. Шарутина и др. // Журн. общ. химии. – 1996. – Т. 66, № 10. – С. 1755–1756.
2. Сульфонаты тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова, В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67, № 9. – С. 1531–1535.
3. Реакции пентаарилсурьмы с диацилатами триарилсурьмы / В.В. Шарутин, О.К. Шарутина, А.П. Пакусина В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67. – № 9. – С. 1536–1541.
4. Шарутин, В.В. Синтез и строение оксиматов тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, О.В. Молокова и др. // Журн. общ. химии. – 2001. – Т. 71, № 8. – С. 1317–1321.
5. Новый метод синтеза арокситетраарильных соединений сурьмы / В.В. Шарутин, О.К. Шарутина, П.Е. Осипов, О.В. Субачева // Журн. общ. химии. – 2001. – Т. 71, № 6. – С. 1045–1046.
6. Шарутин, В.В. Именные реакции в химии элементоорганических соединений: справочник / В.В. Шарутин, В.С. Сенчурин. – Челябинск: Издательский центр ЮУрГУ, 2011. – 427 с.
7. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
8. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
9. OLEX2: a Complete Structure Solution, Refinement and Analysis Program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.
10. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // Журн. неорган. химии. – 1991. – Т. 36. – № 12. – С. 3015–3037.

Organometallic chemistry

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SYNTHESIS AND STRUCTURE OF TRI(META-TOLYL)ANTIMONY BIS(BENZENESULFONATE)

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Tri(*meta*-tolyl)antimony bis(benzenesulfonate) *m*-Tol₃Sb(OSO₂C₆H₅)₂ (**1**) has been synthesized by interaction of tri(*meta*-tolyl)antimony with benzenesulfonic acid in the presence of *tert*-butyl hydroperoxide (mole ratio 1:2:1) in ether solution. Antimony atoms in **1** have trigonal-bipyramidal coordination with arenesulfonate substituents in axial positions (OSbO 171.05(11)°, CSbC 116.21(19)°, 117.38(18)°, 126.40(15)°). The Sb–C and Sb–O distances equal 2.091(4), 2.098(4), 2.115(4) и 2.105(2), 2.116(3) Å. Intermolecular contact (Sb⋯O 3.421(3) Å) occurs between the central atom and the oxygen atom of sulfonate group.

Keywords: tri(*meta*-tolyl)antimony, benzenesulfonic acid, *tert*-butyl hydroperoxide, molecular structure, X-ray diffraction analysis.

Introduction

In the course of research on the synthesis and structure of quinquevalent antimony arenesulfonates [1–4] we have studied the reaction of tri(*meta*-tolyl)antimony with benzenesulfonic acid in the presence of *tert*-butyl hydroperoxide in ether. The structure of the obtained product has been established by X-ray diffraction analysis.

Experimental

Tri(*meta*-tolyl)antimony bis(benzenesulfonate) synthesis. The mixture of 0.250 g (0.63 mmol) tri(*meta*-tolyl)antimony, 0.200 g (1.26 mmol) benzenesulfonic acid and 0.057 g 70% aqueous solution of *tert*-butyl hydroperoxide in 10 mL ether stood for 24 h at room temperature. The obtained crystals were recrystallized from toluene. The yield is 0.386 g (86%) of colorless crystals **1** with decomposition temperature 152 °C. Found, %: C 55.23, H 4.34. Calculated for C₃₃H₃₁O₆S₂Sb, %: C 55.87, H 4.37. IR spectrum, (ν, cm⁻¹): 1320, 1140, 1140 (SO₂).

IR spectra were recorded on the Fourier-transform spectrometer Bruker Tensor 27 in KBr pellets.

The X-ray diffraction analyses of crystal **1** were performed on the Bruker D8 Quest diffractometer (Mo K_α-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [5]. All calculations for structure determination and refinement were performed using the SHELXL/PC [6] and OLEX2 programs [7]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for the structures are listed in Table 1, the selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1057589, deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Table 1

Crystallographic data and the experimental and structure refinement parameters for compound **1**

Parameter	Value
Empirical formula	C ₃₃ H ₃₁ O ₆ S ₂ Sb
Formula weight	709.45
<i>T</i> , K	296
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> , Å	14.4831(6)

Parameter	Value
b , Å	12.7730(5)
c , Å	17.7157(7)
α , deg	90.00
β , deg	99.4680(10)
γ , deg	90.00
V , Å ³	3232.6(2)
Z	4
ρ (calcd.), g/cm ³	1.458
μ , mm ⁻¹	1.024
$F(000)$	1440.0
Crystal size, mm	0.68 × 0.38 × 0.26
2 θ Range of data collection, deg	6.54 – 51.4°
Range of refraction indices	-17 ≤ h ≤ 17, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Measured reflections	40302
Independent reflections	6147
R_{int}	0.0288
Refinement variables	382
$GOOF$	1.081
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0387$, $wR_2 = 0.0866$
R factors for all reflections	$R_1 = 0.0513$, $wR_2 = 0.0973$
Residual electron density (min/max), e/Å ³	0.80/-0.49

Table 2

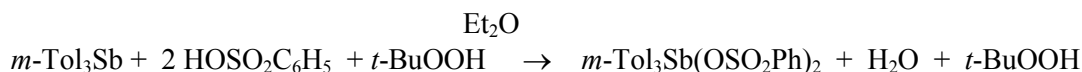
Selected bond lengths and bond angles in the structure of compound 1

Bond	d , Å	Angle	ω , deg
Sb(1)–O(1)	2.116(3)	C(11)Sb(1)O(1)	94.96(14)
Sb(1)–C(11)	2.091(4)	C(11)Sb(1)C(1)	117.38(18)
Sb(1)–C(1)	2.098(4)	C(11)Sb(1)O(4)	93.68(14)
Sb(1)–O(4)	2.105(2)	C(11)Sb(1)C(21)	116.21(19)
Sb(1)–C(21)	2.115(4)	C(1)Sb(1)O(1)	85.33(13)
S(1)–O(1)	1.499(3)	C(1)Sb(1)O(4)	92.74(12)
S(1)–O(2)	1.402(4)	C(1)Sb(1)C(21)	126.40(15)
S(1)–O(3)	1.407(4)	O(4)Sb(1)O(1)	171.05(11)
S(1)–C(31)	1.772(4)	O(4)Sb(1)C(21)	85.13(14)
S(2)–O(5)	1.411(3)	C(21)Sb(1)O(1)	88.98(15)
S(2)–O(6)	1.425(3)	O(1)S(1)C(31)	100.53(19)
S(2)–O(4)	1.523(3)	O(2)S(1)O(1)	109.9(2)
S(2)–C(41)	1.765(4)	O(2)S(1)O(3)	118.3(3)
C(11)–C(12)	1.371(7)	O(2)S(1)C(31)	108.9(2)
C(11)–C(16)	1.377(7)	O(3)S(1)O(1)	109.1(2)
C(12)–C(13)	1.393(8)	O(3)S(1)C(31)	108.7(2)
C(13)–C(14)	1.394(14)	O(5)S(2)O(6)	118.2(2)
C(13)–C(17)	1.489(12)	O(5)S(2)O(4)	107.14(18)
C(14)–C(15)	1.339(14)	O(5)S(2)C(41)	108.9(2)
C(15)–C(16)	1.391(9)	O(6)S(2)O(4)	109.74(17)
C(31)–C(32)	1.362(6)	O(6)S(2)C(41)	108.1(2)
C(31)–C(36)	1.367(7)	O(4)S(2)C(41)	103.88(17)

Results and Discussion

It is known that oxidation of tri(*meta*-tolyl)antimony by hydrogen peroxide in the presence of benzenesulfonic acid leads to formation of tri(*meta*-tolyl)antimony bis(benzenesulfonate) with 72% yield [4].

We have established that the oxidative addition reaction with the use of tri(*meta*-tolyl)antimony, benzenesulfonic acid and *tert*-butyl hydroperoxide leads to formation of the target product with 86% yield:



Note that compound **1**, obtained by this reaction, has higher melting point (152 °C), than that according to the procedure with the use of hydrogen peroxide (145 °C [4]).

From the X-ray analysis data it follows that the antimony atoms in tri(*meta*-tolyl)antimony bis(benzenesulfonate) have trigonal-bipyramidal coordination with arenesulfonate substituents in axial positions (Fig. 1).

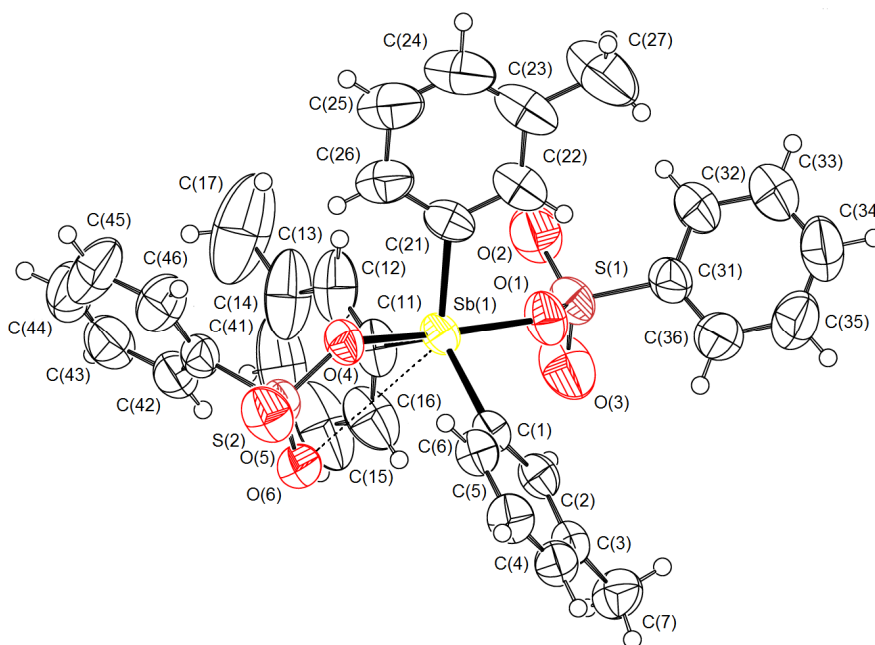


Fig. 1. The structure of compound **1**

The value of axial angle OSbO equals 171.05(11)°, the angles between equatorial phenyl substituents are unequal: 116.21(19)°, 117.38(18)°, 126.40(15)° (Table 2). Their sum (359.99°) is practically consistent with the theoretical value. This fact testifies that the antimony atoms and three carbon atoms, bonded to them, are coplanar. The distances Sb–C equal 2.091(4), 2.098(4), 2.115(4) Å, the bonds Sb–O (2.105(2), 2.116(3) Å) are of covalent character.

As viewed from the maximal equatorial angle CSbC the close intermolecular contact between the central atom and the oxygen atom O(6) of the sulfonate group is observed (Sb···O 3.421(3) Å), which is less than the sum of Van der Waals radii of antimony and oxygen atoms (3.7 Å [8]). The structural organization of the crystal is formed with the participation of weak hydrogen bonds of the type O···H (2.525, 2.650 Å).

Conclusions

Thus, tri(*meta*-tolyl)antimony is oxidized by *tert*-butyl hydroperoxide in the presence of benzenesulfonic acid in ether to obtain tri(*meta*-tolyl)antimony bis(benzenesulfonate). In its molecule one sulfonate group is characterized by monodentate bonding type, the other one is of bidentate type.

References

1. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetraphenylstibonium Arenesulfonates. Synthesis and Structure]. *Russian Journal of Coordination Chemistry*, 1997, vol. 23, no. 7, pp. 513–519. (in Russ.)
2. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetra- and Triphenylantimony Sulfonates]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, 1438–1442.
3. Sharutin V.V., Sharutina O.K., Panova L.P., Platonova T.P., Pakusina A.P., Bel'skii V.K. [Synthesis and Structure of Tri-*p*-Tolylantimony Ditosylate]. *Russian Journal of General Chemistry*, 2002, vol. 72, iss. 2, pp. 229–231. DOI: 10.1023/A:1015469517544
4. Sharutin V.V., Sharutina O.K., Platonova T.P., Pakusina A.P., Panova L.P., Fukin G.K., Zakharov L.N. [Synthesis and Structure of Triarylantimony Bis(arenesulfonates)]. *Russian Journal of General Chemistry*, 2003, vol. 73, iss. 3, pp. 354–357. DOI: 10.1023/A:1024945617228
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341. DOI: 10.1107/S0021889808042726.
8. Batsanov S.S. [Atomic Radiuses of the Elements]. *Russian Journal of Inorganic Chemistry*, 1991, vol. 36, no. 12, pp. 3015–3037. (in Russ.)

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СИНТЕЗ И СТРОЕНИЕ БИС(БЕНЗОЛСУЛЬФОНАТА) ТРИ(МЕТА-ТОЛИЛ)СУРЬМЫ

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Взаимодействием три(*meta*-толил)сурьмы с бензолсульфоновой кислотой в присутствии *трет*бутилгидропероксида (1:2:1 мольн.) в растворе эфира синтезирован бис(бензолсульфонат) три(*meta*-толил)сурьмы (*m*-Tol₃Sb(OSO₂C₆H₅)₂) (1). Атомы сурьмы в **1** имеют тригонально-бипирамидальную координацию с аренсульфонатными заместителями в аксиальных положениях (OSbO 171,05(11)°, CSbC 116,21(19)°, 117,38(18)°, 126,40(15)°). Расстояния Sb–C и Sb–O равны 2,091(4), 2,098(4), 2,115(4) и 2,105(2), 2,116(3) Å. Между центральным атомом и атомом кислорода сульфонатной группы имеет место внутримолекулярный контакт (Sb···O 3.421(3) Å).

Ключевые слова: три(*meta*-толил)сурьма, бензолсульфоновая кислота, *трет*-бутилгидропероксид, молекулярная структура, рентгеноструктурный анализ.

Литература

1. Аренсульфонаты тетрафенилстибония. Синтез и строение / В.В. Шарутин, О.К. Шарутина, Л.П. Панова и др. // Журнал коорд. химии. – 1997. – Т. 23, № 7. – С. 513–519.

2. Сульфонаты тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова, В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67, № 9. – С. 1531–1535.
3. Синтез и строение дитозилата три-*n*-толилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова и др. // Журн. общ. химии. – 2002. – Т. 72, Вып. 2. – С. 249–251.
4. Синтез и строение бис(аренсульфонатов) триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Т.П. Платонова и др. // Журн. общ. химии. – 2003. – Т. 73, Вып. 3. – С. 380–384.
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.
8. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // Журн. неорган. химии. – 1991. – Т. 36, Вып. 12. – С. 3015–3037.

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ОБРАЗЕЦ ЦИТИРОВАНИЯ

Sharutin, V.V. Synthesis and structure of tri(meta-tolyl)antimony bis(benzenesulfonate) / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 93–97. DOI: 10.14529/chem150412

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SYNTHESIS AND STRUCTURE OF GOLD COMPLEXES [*p*-Tol₄Sb][*p*-TolAuCl₃] AND [*p*-Tol₄Sb][AuCl₄]

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Gold complexes [*p*-Tol₄Sb]⁺[*p*-TolAuCl₃]⁻ (**1**) and [*p*-Tol₄Sb]⁺[AuCl₄]⁻ (**2**) have been synthesized by interaction of tetra-*para*-tolylstibonium chloride and aurichlorohydric acid tetrahydrate in acetone. In **1** the tetra-*para*-tolylstibonium cations are tetrahedral (Sb-C 2.091(7)-2.097(6) Å, CSbC 106.1(3)^o-112.7(3)^o), the [*p*-TolAuCl₃]⁻ anions have square-planar structure (Au-Cl 2.286(2)-2.389(2) Å, Au-C 2.028(7) Å, ClAuCl 89.92(9)^o, 92.42(9)^o, 176.68(8)^o, CAuCl 88.27(18)^o, 89.57(18)^o, 175.59(19)^o). In crystal **2** the geometrical characteristics of cations (Sb-C 2.076(7)-2.097(9), CSbC 106.5(3)^o-111.5(4)^o) and [AuCl₄]⁻ square-planar anions (Au-Cl 2.248(3)-2.278(3) Å, ClAuCl 89.17(9)^o-90.74(13)^o, 177.24(16)^o, 177.61(13)^o) are similar to those in **1**.

Keywords: synthesis, structure, gold compounds, X-ray diffraction analysis.

Introduction

Synthesis and structure of complex compounds of gold, containing [AuHal₄]⁻ anions in their composition, were mentioned in the literature [1-5]. In the present paper the synthesis and structure of gold complexes [*p*-Tol₄Sb][AuCl₄] and [*p*-Tol₄Sb][*p*-TolAuCl₃] are described.

Experimental

Synthesis of [*p*-Tol₄Sb]⁺[*p*-TolAuCl₃]⁻ (1**).** Tetra-*para*-tolylantimony chloride 0.250 g (0.48 mmol) and aurichlorohydric acid tetrahydrate 0.197 g (0.48 mmol) were dissolved in 10 mL acetone, then 5 mL toluene was added. The solution was left to stand for 12 h at 20 °C. After evaporation of the solvent 0.287 g (68%) of tetra-*para*-tolylantimony *para*-tolyltrichloroaurate was obtained (mp 156 °C). IR spectrum (ν, cm⁻¹): 484, 587, 800, 1007, 1072, 1194, 1305, 1401, 1492, 1588, 1627, 1905, 2926. Found, %: C 47.38, H 4.03. Calculated for C₃₅H₃₅AuCl₃, %: C 47.72, H 3.98.

Synthesis of [*p*-Tol₄Sb]⁺[AuCl₄]⁻ (2**).** a) The mixture of tetra-*para*-tolylantimony chloride 0.137 g (0.26 mmol) and aurichlorohydric acid tetrahydrate 0.108 g (0.26 mmol) in 10 mL acetone stood for 24 h at room temperature. The solvent was evaporated. The yield is 0.205 g (95%) of tetra-*para*-tolylantimony tetra-*para*-chloroaurate with decomposition temperature 148–150 °C. IR spectrum (ν, cm⁻¹): 483, 529, 585, 633, 697, 809, 1101, 1040, 1066, 1123, 1190, 1212, 1313, 1396, 1444, 1493, 1589, 1708, 2863, 2918, 2953, 3045. Found, %: C 40.52, H 3.49. Calculated for C₂₈H₂₈SbAuCl₄, %: C 40.75, H 3.40.

b) The mixture of penta-*para*-tolylantimony 0.181 g (0.31 mmol) and aurichloric acid tetrahydrate 0.129 g (0.31 mmol) in 10 mL acetone stood for 24 h at room temperature. The solvent was evaporated. The yield is 0.232 g (90%) of pale yellow tetra-*para*-tolylantimony tetrachloroaurate, the melting point and IR spectrum coincide with tetra-*para*-tolylantimony tetrachloroaurate obtained according to method a. Found: %: C 40.54, H 3.52. Calculated for C₂₈H₂₈SbAuCl₄, %: C 40.75, H 3.40.

IR spectra were recorded on the Bruker Tensor 27 in KBr pellets.

The X-ray diffraction analyses of crystals **1** and **2** were performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_α-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the *SMART* and *SAINTE-Plus* programs [6]. All calculations for structure determination and refinement were performed using the *SHELXL/PC* programs [7]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms.

The main crystallographic data and refinement results for the structures are listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1000139 for **1**, CCDC 1000140 for **2**; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

Table 1
Crystallographic data, the experimental and structure refinement parameters for compounds **1**, **2**

Parameter	Value	
	1	2
<i>M</i>	880.70	825.02
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
<i>a</i> , Å	12.748(5)	12.7962(5)
<i>b</i> , Å	14.941(5)	14.8701(5)
<i>c</i> , Å	18.19 8(10)	16.1167(5)
α, град	90.00	90.00
β, град	102.87(4)	101.8270(10)
γ, град	90.00	90.00
<i>V</i> , Å ³	3379(3)	3001.59(18)
<i>Z</i>	4	4
ρ(calcd.), г/см ³	1.731	1.826
μ, мм ⁻¹	5.395	6.153
<i>F</i> (000)	1704.0	1576.0
Crystal size, mm	0.54 × 0.36 × 0.34	0.99 × 0.61 × 0.5
2θ Range of data collection, deg	4.48 – 62.1°	6.16 – 60.1°
Range of refraction indices	-18 ≤ h ≤ 18, -16 ≤ k ≤ 21, -25 ≤ l ≤ 26	-17 ≤ h ≤ 13, -20 ≤ k ≤ 7, -22 ≤ l ≤ 20
Measured reflections	38599	7733
Independent reflections	10659 (<i>R</i> _{int} = 0.0819)	5051 (<i>R</i> _{int} = 0.0298)
Refinement variables	366	311
GOOF	1.011	0.993
<i>R</i> -factors for <i>F</i> ² > 2σ(<i>F</i> ²)	<i>R</i> ₁ = 0.0653, <i>wR</i> ₂ = 0.1145	<i>R</i> ₁ = 0.0416, <i>wR</i> ₂ = 0.0913
<i>R</i> -factors for all reflections	<i>R</i> ₁ = 0.1352, <i>wR</i> ₂ = 0.1342	<i>R</i> ₁ = 0.1046, <i>wR</i> ₂ = 0.1137
Residual electron density (min/max), e/Å ³	2.06/-0.82	0.55/-0.85

Table 2
Selected bond lengths (*d*) and bond angles (ω) in the structures of compounds **1**, **2**

Bond <i>d</i> , Å		Angle ω, deg	
1			
Au(1)–Cl(1)	2.286(2)	Cl(1)Au(1)Cl(2)	176.68(8)
Au(1)–Cl(2)	2.292(2)	C(41)Au(1)Cl(3)	175.59(19)
Au(1)–Cl(3)	2.389(2)	C(1)Sb(1)C1(1)	110.6(3)
Au(1)–C(41)	2.028(7)	C(1)Sb(1)C(21)	106.1(3)
Sb(1)–C(1)	2.094(6)	C(21)Sb(1)C(11)	112.7(3)
Sb(1)–C(11)	2.097(6)	C(31)Sb(1)C(1)	111.3(3)
Sb(1)–C(21)	2.095(7)	C(31)Sb(1)C(11)	108.1(3)
Sb(1)–C(31)	2.091(7)	C(31)Sb(1)C(21)	108.0(3)
2			
Au(1)–Cl(1)	2.266(3)	Cl(1)Au(1)Cl(2)	90.74(13)
Au(1)–Cl(2)	2.269(3)	Cl(1)Au(1)Cl(3)	89.58(13)
Au(1)–Cl(3)	2.278(3)	Cl(2)Au(1)Cl(3)	177.61(13)
Au(1)–Cl(4)	2.248(3)	Cl(4)Au(1)Cl(1)	177.24(16)

Bond <i>d</i> , Å		Angle ω , deg	
Sb(1)–C(1)	2.076(9)	Cl(4)Au(1)Cl(2)	89.17(13)
Sb(1)–C(11)	2.095(8)	Cl(4)Au(1)Cl(3)	90.62(13)
Sb(1)–C(31)	2.097(9)	C(1)Sb(1)C(1)	109.5(3)
Sb(1)–C(21)	2.086(8)	C(1)Sb(1)C(31)	111.5(4)
C(1)–C(2)	1.391(13)	C(1)Sb(1)C(21)	109.4(3)
C(1)–C(7)	1.370(12)	C(11)Sb(1)C(31)	106.5(3)
C(2)–C(3)	1.375(16)	C(21)Sb(1)C(11)	111.2(3)
C(4)–C(5)	1.501(16)	C(21)Sb(1)C(31)	108.6(4)

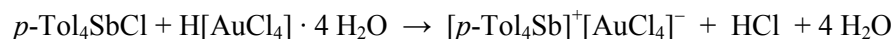
Results and Discussion

It is known that the product of pentaphenylantimony reaction with aurichlorohydric acid (hydrogen tetrachloroaurate (III)) at 20 °C in acetone is tetraphenylantimony tetrachloroaurate, separated from the reaction mixture with 84 % yield [2].

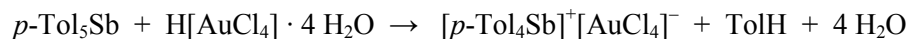
We have found that in similar conditions the interaction of aurichlorohydric acid, obtained by dissolving jewelry gold in aqua regis, with tetra-*para*-tolylantimony chloride runs with formation of tetra-*para*-tolylantimony *para*-tolyltrichloroaurate (1):



If chemically pure aurichlorohydric acid is used, such an unusual transmetalation reaction between antimony and gold compounds is not observed. In this case the formation of tetra-*para*-tolylantimony tetrachloroaurate (2) occurs:



Complex 2 has also been obtained from penta-*para*-tolylantimony and aurichlorohydric acid:



It is obvious that the presence of impurities in the initial jewelry gold and, consequentially, in the used acid affects the direction of the chemical reaction between aurichlorohydric acid and tetra-*para*-tolylantimony chloride.

According to the X-ray analysis data, the crystal of complex 1 consists of tetra-*para*-tolylstibonium tetrahedral cations and $[p\text{-TolAuCl}_3]^-$ square-planar anions (Fig. 1).

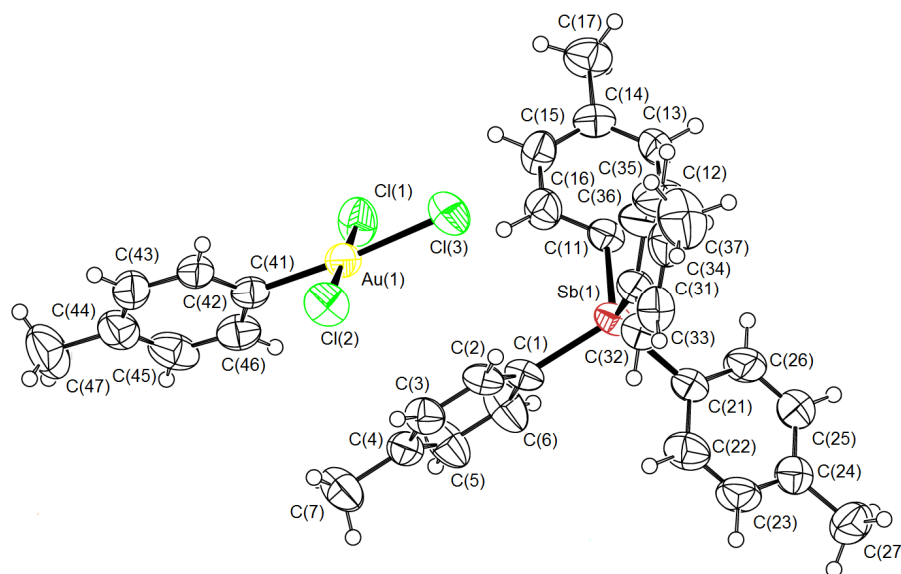


Fig. 1. The structure of the molecule of compound 1

In crystal **1** tetra-*para*-tolylstibonium tetrahedral cations (Sb–C 2.091(7)–2.097(6) Å, CSbC 106.1(3)°–112.7(3)°) are present, as well as [*p*-TolAuCl₃][–] anions of square-planar structure (Au–Cl 2.286(2)–2.389(2) Å, Au–C 2.028(7) Å, ClAuCl 89.92(9)°, 92.42(9)°, 176.68(8)°, CAuCl 88.27(18)°, 89.57(18)°, 175.59(19)°). In crystal **2** the geometric characteristics of cations (Sb–C 2.076(7)–2.097(9), CSbC 106.5(3)°–111.5(4)°) and [AuCl₄][–] square-planar anions (Au–Cl 2.248(3)–2.278(3) Å, ClAuCl 89.17(9)°–90.74(13)°, 177.24(16)°, 177.61(13)°) (Fig. 2, Table 2) are similar to those found in **1**.

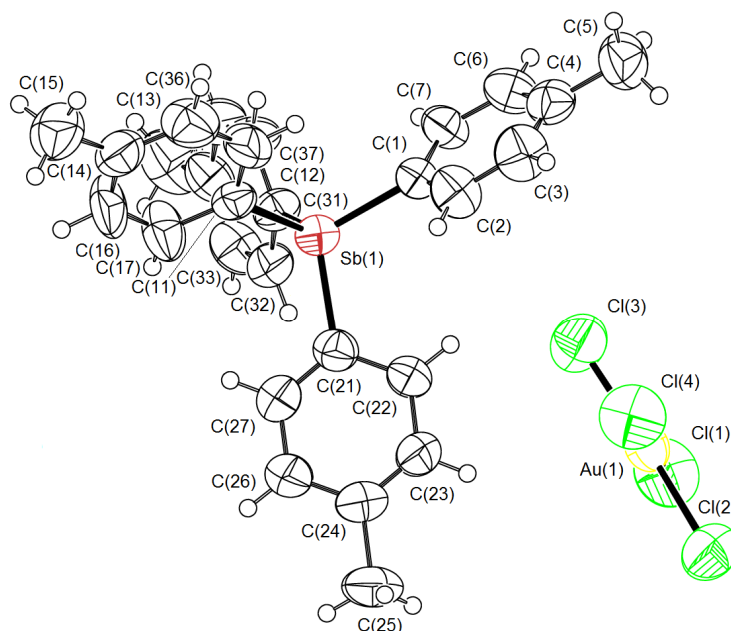


Fig. 2. The structure of complex **2**

The structural organization in crystals I and II is caused by weak interionic hydrogen bonds. At that in I the single interionic contact is observed: *ortho*-H_{Ph}(16)⋯Cl(1) (2.92 Å). In complex II each anion is bonded with four cations through Cl⋯H bonds, formed with the use of all four chlorine atoms and *ortho*-, *meta*- and methyl hydrogen atoms of tolyl substituents (2.81–2.88 Å) (Fig. 3).

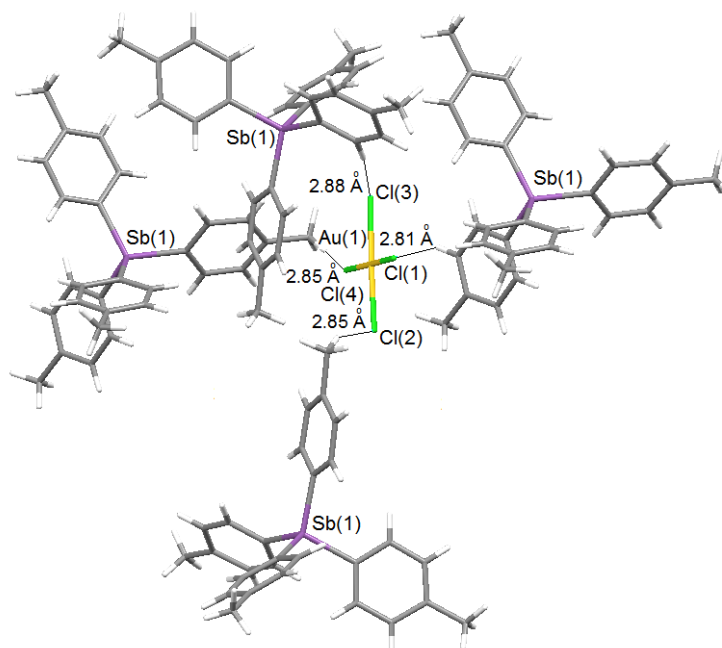


Fig. 3. Interionic hydrogen bonds in the crystal of complex **2**

Conclusions

Thus, the ionic complexes of gold with tetra-*para*-stibonium tetrahedral cation and $[p\text{-TolAuCl}_3]^-$ and $[\text{AuCl}_4]^-$ square-planar anions have been synthesized and structurally described for the first time. The first example of transmetalation reaction with the use of antimony and gold compounds has been described.

References

1. Sharutin V.V., Senchurin V.S., Fastovets O.A., Pakurina A.P., Sharutina O.K. [Synthesis and Structure of Mixed-ligand Complex Compounds of Antimony $[\text{Et}_2\text{NH}_2]_4^+$ $[\text{SbCl}_2\text{Hal}_4]^{3-}$ $[\text{Cl}]^{1-}$ (Hal = I, Br) and Gold $[\text{Ph}_3\text{PMe}]_2^+$ $[\text{AuCl}_2\text{Br}_2]^{1-}$ $[\text{AuHal}_2]^{1-}$ (Hal = Cl, Br)]. *Russian Journal Butlerov Communication*, 2007, vol. 11, no. 2, pp. 43–48. (in Russ.)
2. Sharutin V.V., Senchurin V.S., Fastovets O.A., Pakurina A.P., Sharutina O.K. [Tetrafenylantimony(V) Gexachloroplatinate, Tetrachloroaurate, and Gexachlorostannate $[\text{Ph}_4\text{Sb}]_2^+$ $[\text{PtCl}_6]^{2-}$, $[\text{Ph}_4\text{Sb}]^+$ $[\text{AuCl}_4]^-$, $[\text{Ph}_4\text{Sb}]_2^+$ $[\text{SnCl}_6]^{2-}$: Synthesis and Crystal Structures]. *Russian Journal of Coordination Chemistry*, 2008, vol. 34, no. 5, pp. 367–373. DOI: 10.1134/S1070328408050096
3. Sharutin V.V., Senchurin V.S., Sharutina O.K., Vinokurova L.N. [Synthesis and Crystal Structure of Tetrachloroaurate butyltrifenyolphosphonium $[\text{Ph}_3\text{BuP}]^+$ $[\text{AuCl}_4]^-$]. *Russian Journal Butlerov Communication*, 2011, vol. 27, no. 16, pp. 68–71. (in Russ.)
4. Sharutin V.V., Sharutina O.K., Senchurin V.S. [Synthesis and Crystal structure of acetyltriphénylphosphonium tetrachloroaurate $[\text{Ph}_3\text{PCH}_2\text{C}(\text{O})\text{CH}_3]^+$ $[\text{AuCl}_4]^-$]. *Russian Journal Butlerov Communication*, 2014, vol. 38, no. 5, pp. 151–154. (in Russ.)
5. Cambridge Crystallographic Data Center. 2015 (deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).
6. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., 1998, Madison, Wisconsin, USA.
7. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., 1998, Madison, Wisconsin, USA.
8. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341. DOI:10.1107/S0021889808042726.

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СИНТЕЗ И СТРУКТУРА КОМПЛЕКСОВ ЗОЛОТА [*p*-Tol₄Sb][*p*-TolAuCl₃] AND [*p*-Tol₄Sb][AuCl₄]

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Взаимодействием хлорида тетра-*пара*-толилстибония с тетрагидратом золотохлористоводородной кислоты в ацетоне синтезированы комплексы золота $[\text{p-Tol}_4\text{Sb}]^+[\text{p-TolAuCl}_3]^-$ (**1**) и $[\text{p-Tol}_4\text{Sb}]^+[\text{AuCl}_4]^-$ (**2**). В **1** катионы тетра-*пара*-толилстибония тетраэдрические (Sb-C 2.091(7)-2.097(6) Å, CSbC 106.1(3)^o-112.7(3)^o), анионы $[\text{p-TolAuCl}_3]^-$ имеют плоскоквадратное строение (Au-Cl 2.286(2)-2.389(2) Å, Au-C 2.028(7) Å, ClAuCl 89.92(9)^o, 92.42(9)^o, 176.68(8)^o, SAuCl 88.27(18)^o, 89.57(18)^o, 175.59(19)^o). В кристалле **2** геометрические характеристики катионов (Sb-C 2.076(7)-2.097(9), CSbC 106.5(3)^o-111.5(4)^o) и плоскоквадратных анионов $[\text{AuCl}_4]^-$ (Au-Cl 2.248(3)-2.278(3) Å, ClAuCl 89.17(9)^o-90.74(13)^o, 177.24(16)^o, 177.61(13)^o) близки к найденным в **1**.

Ключевые слова: синтез, строение, соединения золота, строение, рентгеноструктурный анализ.

Литература

1. Синтез и строение смешаннолигандных комплексных соединений сурьмы [Et₂NH₂]₄⁺[SbCl₂Hal₄]³⁻[Cl]¹⁻ (Hal = I, Br) и золота [Ph₃PMe]₂⁺[AuCl₂Br₂]¹⁻[AuHal₂]¹⁻ (Hal = Cl, Br) / В.В. Шарутин, В.С. Сенчурин, О.А. Фастовец и др. // Бутлеровские сообщения. – 2007. – Т. 11, № 2. – С. 43–48.
2. Синтез и кристаллические структуры гексахлороплатината, тетрахлоороурата и гексахлороостанната тетрафенилсурьмы (V) [Ph₄Sb]₂⁺[PtCl₆]²⁻, [Ph₄Sb]⁺[AuCl₄]⁻, [Ph₄Sb]₂⁺[SnCl₆]²⁻ / В.В. Шарутин, В.С. Сенчурин, О.А. Фастовец и др. // Коорд. химия. – 2008. – Т. 34, № 5. – С. 373–379.
3. Синтез и кристаллическая структура тетрахлоороурата бутилтрифенилфосфония [Ph₃BuP]⁺[AuCl₄]⁻ / В.В. Шарутин, В.С. Сенчурин, О.К. Шарутина, Л.Н. Винокурова // Бутлеровские сообщения. – 2011. – Т. 27, № 16. – С. 68–71.
4. Шарутин, В.В. Синтез и кристаллическая структура тетрахлоороурата ацетонилтрифенилфосфония [Ph₃PCH₂C(O)CH₃]⁺[AuCl₄]⁻ / В.В. Шарутин, О.К. Шарутина, В.С. Сенчурин // Бутлеровские сообщения. – 2014. – Т. 38, № 5. – С. 151–154.
5. Cambridge Crystallographic Data Center. – 2015. – <http://deposit@ccdc.cam.ac.uk> / <http://www.ccdc.cam.ac.uk>.
6. SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. – Madison (Wisconsin, USA): Bruker AXS Inc., 1998.
7. SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. – Madison (Wisconsin, USA): Bruker AXS Inc., 1998.
8. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.

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