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Tetraphenylantimony Perrhenate and Tetraphenylantimony Chlorate: Syntheses and Structures

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Abstract—The reaction of tetraphenylantimony chloride with sodium perrhenate or potassium chlorate yields tetraphenylantimony perrhenate (**I**) and tetraphenylantimony chlorate (**II**), respectively. Complex **I** was also synthesized from pentaphenylantimony and triphenylantimony diperrhenate in toluene. According to X-ray diffraction, crystals **I** and **II** consist of almost regular tetrahedral tetraphenylstibonium cations (CSbC, 109.4(2)°–109.5(7)° in **I** and 109.1(1)°–109.6(1)° in **II**) and $[ReO_4]^-$ (OreO, 107.6(3)°–113.3(5)°) and $[ClO_3]^-$ (OClO, 96.3(9)°, 116.4(5)°) anions, respectively. The average Sb–C bond lengths (2.094(3) Å in **I**, 2.097(2) Å in **II**) are close to the sum of the covalent radii of the Sb and C atoms. The average distances Re–O in complex **I** (1.672(4) Å) and Cl–O in complex **II** (1.315 Å) correspond to multiple bonds.

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It is known that pentavalent antimony compounds with the general formula Ph_4SbX (X = Cl, Br, NO_3, OSO_2R, OAr, OC(O)R, ONCRR', RC(O)CHC(O)R') can be synthesized by the substitution reaction from tetraphenylantimony halide and alkali metal salts, or from pentaphenylantimony and an acid HX, or by the ligand redistribution reaction from pentaphenylantimony and symmetric antimony derivatives Ph_3SbX_2 [1–7]. In compounds of this type, the coordination of the antimony atoms changes from an almost regular tetrahedron [8–10] to an octahedron [11–15], passing through the trigonal-bipyramidal state [16–22]. It should be noted that the residues of inorganic and organic OH-acids are more often prone to the formation of covalent polar bonds with the antimony atom. The tetrahedral coordination of the antimony atom is observed in ionic molecules. The contribution of the ionic component to the character of the Sb–X bond is determined by the nature of the X ligand, in particular, by its ability to delocalize the negative charge. In the case of efficient delocalization, the stable X^- anion and $[Ph_4Sb]^+$ cation are formed, and the bond in Ph_4SbX is ionic. Tetraphenylantimony perchlorate [8], hydrogen sulfate [9], and 2,5-dimethylbenzenesulfonate [10] can serve as examples of the compounds with the ionic bond. The relative arrangement of the cation and anion in crystals of these compounds and the distortion of their configuration compared to the ideal one are determined by the influence of the factors that provide the minimum of the crystal lattice energy as a whole. It is not always possible to estimate beforehand the contribution of the ionic component to the character of the Sb–X bond, because the use of the pK_a value of the corresponding acid is incorrect for this estimate. For instance, the geometric parameters of molecules of tetraphenylantimony hydrogen phthalate [23], hydrogen maleinate [20], and nitrate [24] with the polar covalent Sb–O bond have similar values, although it is known that the dissociation constants of the corresponding acids differ strongly.

The purpose of this work is to synthesize tetraphenylantimony perrhenate (**I**), and tetraphenylantimony chlorate (**II**) and to determine their structures.

EXPERIMENTAL

Synthesis of complex I. (a) A mixture of pentaphenylantimony (0.50 g, 0.99 mmol), triphenylantimony diperrhenate (0.65 g, 0.99 mmol), and benzene (20 mL) was heated in a glass evacuated ampule for 1 h at 90°C. The solvent was removed. The residue was recrystallized from a benzene–hexane (3 : 1) mixture. Colorless crystals of compound **I** with mp = 298°C (decomp.) were obtained (0.90 g, 78%). IR (cm^{-1}): 3062 m, 3031 w, 1650 w, 1573 w, 1478 vs, 1433 vs, 1388 m, 1338 vs, 1309 s, 1162 s, 1065 vs, 1019 s, 994 vs, 924 vs, 906 vs, 853 m, 739 vs, 690 vs, 610 m, 452 vs, 434 vs.

For $C_{24}H_{20}O_4ReSb$, anal. calcd. (%): C, 42.35; H, 2.94.

Found (%): C, 41.84; H, 2.54.

(b) A solution of sodium perrhenate (0.58 g, 2.15 mmol) in water (10 mL) was added to a solution of tetraphenylantimony chloride (1.00 g, 2.15 mmol) in water (20 mL). The precipitate formed was dried and recrystallized from acetone. Colorless crystals of compound **I** with T_m = 298°C (decomp.) were obtained in 68% yield (1.00 g).

Table 1. Crystallographic data and details of the X-ray experiment and refinement for structures **I** and **II**

Characteristic	Value	
	I	**II**
FW	680.35	513.60
T, K	100(2)	295(2)
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$
a, Å	12.8306(3)	12.5675(3)
c, Å	6.5938(2)	6.8006(2)
V, Å^3	1085.50(5)	1074.10(5)
Z	2	2
ρ_{calcd}, g/cm^3	2.082	1.588
μ_{Mo}, mm^{-1}	6.843	1.431
F(000)	644	512
Shape (crystal size, mm)	Prism ($0.15 \times 0.20 \times 0.15$)	Prism ($0.78 \times 0.24 \times 0.24$)
θ, deg	3.18 – 29.92	2.29 – 37.51
Index ranges	$-17 \le h \le 17$, $-17 \le k \le 17$, $-9 \le l \le 9$	$-21 \le h \le 19$, $-19 \le k \le 21$, $-5 \le l \le 11$
All reflections	5647	6640
Independent reflections;	1484 ($R_{int} = 0.0210$)	2642 ($R_{int} = 0.0190$)
Reflections with $I > 2\sigma(I)$	1291	2299
Number of refined parameters	68	68
GOOF	0.781	1.111
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0150$, $wR_2 = 0.0359$	$R_1 = 0.0271$, $wR_2 = 0.0641$
R factors for all reflections	$R_1 = 0.0153$, $wR_2 = 0.0360$	$R_1 = 0.0607$, $wR_2 = 0.0953$
Extinction coefficient	Not determined	0.00012(8)
Residual electron density (min/max), e/Å^3	–0.814/0.896	–0.555/1.096

Synthesis of complex II. A mixture of tetraphenylantimony chloride (1.00 g, 2.15 mmol) and potassium chloride (0.30 g, 2.45 mmol) in water (20 mL) was kept for 24 h at 12°C. The solvent was removed. Transparent needle-like crystals with T_m = 228°C (decomp.) were obtained by recrystallization from acetone (0.98 g, 89%). IR (cm^{-1}): 3055 m, 2641 w, 2332 w, 2135 m, 2087 m, 1966 m, 1890 m, 1817 m, 1769 w, 1729 w, 1653 m, 1572 s, 1480 vs, 1436 vs, 1335 vs, 1303 s, 1190 s, 1070 s, 965 s, 845 vs, 736 vs, 688 vs, 596 vs, 451 s, 435 vs.

For $C_{24}H_{20}ClO_3Sb$ anal. calcd. (%): C, 56.14; H, 3.89.

Found (%): C, 55.84; H, 3.21.

The IR spectra of compounds I and II were recorded on an FSM 1201 FT-IR spectrophotometer as KBr pellets.

X-ray crystallographic analysis of compounds I and II was carried out from single crystals with natural faceting on Bruker AXS Smart Apex and Bruker-Nonius X8Apex diffractometers, respectively. The structures were solved by direct methods and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The positions of the hydrogen atoms were calculated geometrically and included in the refinement as riding on their bonded atoms. The data were collected and edited and the unit cell parameters were refined using the SADABS [25], SMART, and SAINT *Plus* [26] programs. All calculations for structure determination and refinement were performed with the SHELXTL/PC program package [27].

Selected crystallographic data and results for the refinement of structures **I** and **II** are presented in Table 1. The coordinates and temperature factors of atoms are given in Table 2. Selected bond lengths and bond angles are listed in Table 3.

Table 2. Atomic coordinates of atoms ($\times 10^4$) and isotropic equivalent temperature parameters ($\times 10^3$) in structures **I** and **II**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I		
Sb(1)	5000	0	7500	13(1)
Re(1)	5000	–5000	5000	20(1)
C(1)	5780(2)	–1080(2)	9336(4)	18(1)
C(2)	6565(2)	–737(3)	10630(4)	23(1)
C(3)	7066(3)	–1452(3)	11874(5)	29(1)
C(4)	6769(3)	–2491(3)	11857(5)	29(1)
C(5)	5982(3)	–2827(2)	10561(5)	25(1)
C(6)	5489(2)	–2126(2)	9277(5)	20(1)
O(1)	5027(5)	–3911(5)	6393(10)	123(2)
		II		
Sb(1)	0	0	0	29.14(5)
C(1)	0.07609(16)	–0.11264(15)	0.1787(3)	34.1(3)
C(2)	0.04347(19)	–0.21785(19)	0.1777(4)	45.5(4)
C(3)	0.0905(3)	–0.2891(2)	0.3070(5)	60.4(7)
C(4)	0.1693(3)	–0.2552(3)	0.4315(5)	66.3(9)
C(5)	0.2039(3)	–0.1522(3)	0.4282(5)	69.5(10)
C(6)	0.1570(3)	–0.0785(2)	0.3024(4)	53.8(6)
Cl(1)	0.0000	0.5000	0.7500	102.0(8)
O(1)*	–0.0768(7)	0.5132(8)	0.6210(12)	205(5)

* The site occupancy factor is 0.75.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in structures **I** and **II**

Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–C(1)	2.094(3)	C(1)#1Sb(1)C(1)	109.52(7)
Re(1)–O(1)	1.672(4)	C(1)#2SbC(1)	109.38(15)
		O(1)Re(1)O(1)#3	107.6(3)
C(1)–C(2)	1.392(4)	O(1)Re(1)O(1)#4	113.3(5)
C(1)–C(6)	1.394(4)		
C(2)–C(3)	1.389(4)		
C(3)–C(4)	1.387(4)		

Symmetry codes: #1) $-x + 1/2, y + 1/2, -z + 3/2$; #2) $-x + 1, -y, z$; #3) $x - 1, -y, -z + 1$; #4) $-x + 1, -y - 1, z$.

Bond	*d*, Å	Angle	ω, deg
		II	
Sb(1)–C(1)	2.097(2)	C(1)#1Sb(1)C(1)	109.64(5)
Cl(1)–O(1)	1.315(6)	C(1)#2Sb(1)C(1)	109.13(10)
C(1)–C(2)	1.384(3)	O(1)Cl(1)O(1)#3	116.4(5)
C(1)–C(6)	1.388(3)	O(1)Cl(1)O(1)#4	96.3(9)
C(2)–C(3)	1.388(4)		
C(3)–C(4)	1.371(6)		

Symmetry codes: #1) $-x, y, -z$; #2) $-x, -y, z$; #3) $-x + 1/2, y - 1/2, -z + 3/2$; #4) $-x, -y + 1, z$.

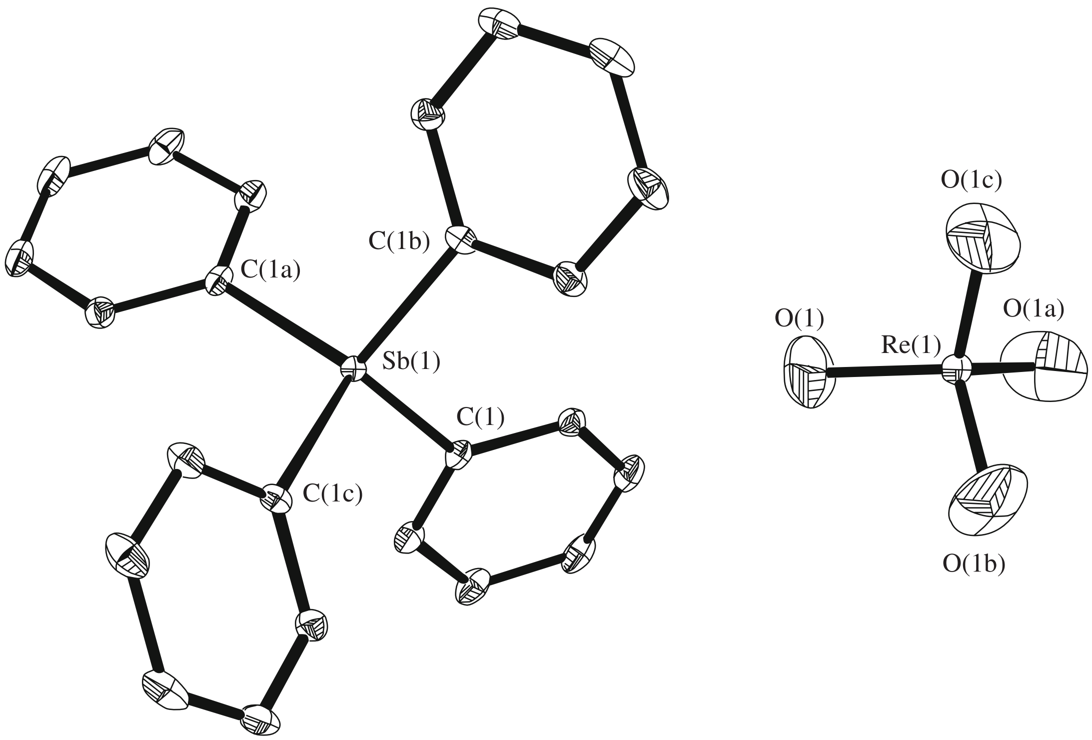

Fig. 1. Structures of the cation and anion in compound **I**.

RESULTS AND DISCUSSION

Complexes **I** and **II** are uncolored crystalline substances that are stable in air and soluble in aromatic hydrocarbons and polar organic solvents. They were synthesized from tetraphenylantimony chloride and the corresponding sodium or potassium salts

$$Ph_4SbCl + NaReO_4 \longrightarrow [Ph_4Sb][ReO_4],$$

$$Ph_4SbCl + KClO_3 \longrightarrow [Ph_4Sb][ClO_3].$$

The reactions occur in an aqueous solution almost instantly.

Tetraphenylantimony perrhenate (**I**) was also synthesized by the ligand redistribution reaction from pentaphenylantimony and tetraphenylantimony diperrhenate:

$$Ph_5Sb + Ph_3Sb(ReO_4)_2 \longrightarrow 2[Ph_4Sb][ReO_4].$$

The reaction mixture in a benzene solution should be heated (90°C, 1 h) for the reaction to be completed.

According to the X-ray diffraction data, complexes **I** and **II** have ionic structures. The antimony atoms in the tetraphenylantimony cations of compounds **I** (Fig. 1) and **II** (Fig. 2) have an almost undistorted tetrahedral coordination. The CSbC angles are 109.4(2)° and 109.5(7)° in complex **I** and 109.1(1)° and 109.6(1)° in complex **II**, whereas the Sb–C bond lengths are 2.094(3) Å in complex **I** and 2.097(2) Å in complex **II**. The cation geometry in complexes **I** and **II** is similar to that found in tetraphenylantimony perchlorate (**III**) (CSbC 109.44(8)° and 109.49(8)°, Sb–C 2.095(2) Å [8]).

In the $[ReO_4]^-$ anion of structure **I**, the rhenium atom has the expected insignificantly distorted tetrahedral coordination (the OReO angles are 107.6(3)° and 113.3(5)°). The Re–O distance (1.672(4) Å) corresponds to a multiple bond. In tetramethylantimony perrhenate (**IV**), the OReO angles vary in a range of 106.73(3)°–111.13(5)°, and the Re–O bond lengths are 1.710(4)–1.755(4) Å [28]. Crystal **I** contains short contacts between the hydrogen atoms in the *ortho* position of the phenyl substituent and the oxygen atoms of the perrhenate anion (O(1)···H(6A) 2.38 Å), as well as the C···H contacts between the hydrogen and carbon atoms in the *meta* positions of the phenyl substituents of the adjacent cations (C(5)···H(3A) 2.86 Å). Crystal **IV** also exhibits many intermolecular hydrogen bonds O···H–C (O···H 2.39–2.53 Å). In addition, the antimony atom in the $[Me_4Sb]^+$ cation of structure **IV** is sterically unhindered, which allows this atom to contact with three anions (Sb···O 3.094, 3.135, and 3.153 Å, whereas the sum of the van der Waals radii of Sb and O is 3.70 Å [29]). Each anion has three short contacts O···Sb. Evidently, the listed intermolecular interactions result in an elongation of the Re–O bonds in compound **IV** compared to similar bonds in compound **I** and in a notice-

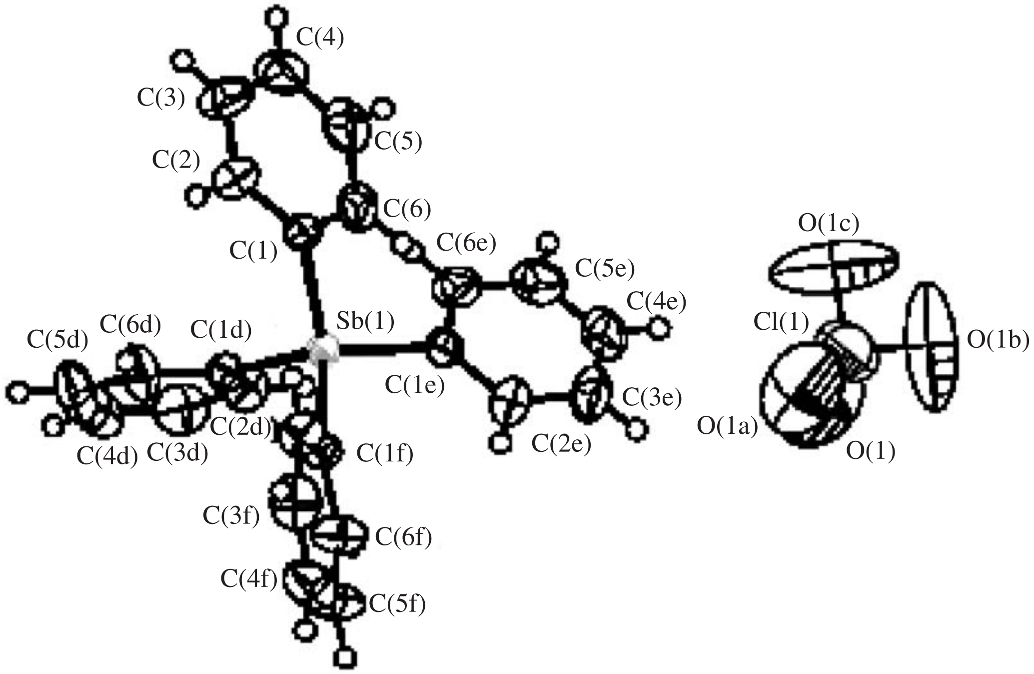

Fig. 2. Structures of the cation and anion in compound **II**.

able distortion of the SbC_4 tetrahedron in the cation of structure **IV**.

It is known that the chlorate anion $[ClO_3]^-$ has the structure of a trigonal pyramid, where the Cl–O bond length ranges from 1.452 to 1.507 Å and the OClO angle is 106° [30]. The $[ClO_3]^-$ anion in structure **II** was found to be disordered over four equiprobably occupied positions of the oxygen atoms (75% each, the chlorine atom being in the special position). The OClO angles are 96.3(9)° and 116.4(5)°, and the Cl–O distance (1.315(6) Å) corresponds to a multiple chlorine–oxygen bond. In the $[ClO_4]^-$ perchlorate anion of complex **III**, the OClO angles are 108.6(4)° and 111.3(2)°, and the Cl–O bond (1.361(5) Å), as should be expected, is longer than that in complex **II**.

Crystals **II** and **IV** are isostructural. The unit cell is body-centered: the cations are arranged at the vertices and in the center of the tetragonal cell, and the anions are located at the rectangular faces A and B with the antimony and chlorine atoms in special positions (symmetry S_4) (Fig. 3). In crystal **I**, the $[ReO_4]^-$ anions are arranged in the center and at the vertices of the unit cell, and the cations occupy positions at the faces of the cell (Fig. 4).

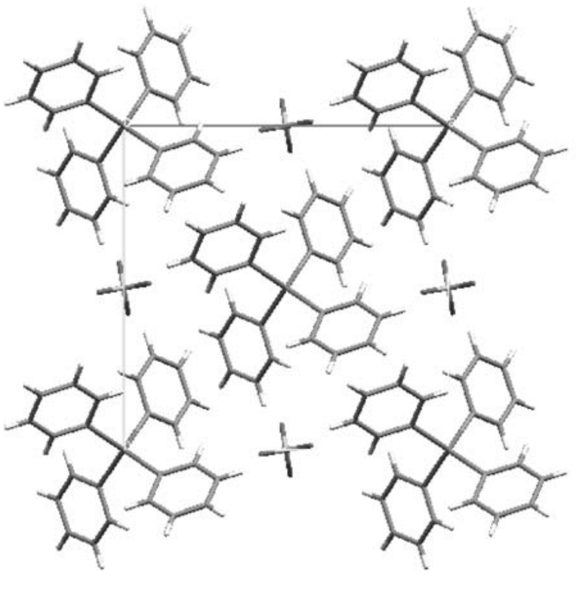

Fig. 3. Packing of the cations and anions in the crystal structure of complex **II** (projection along the *c* axis).

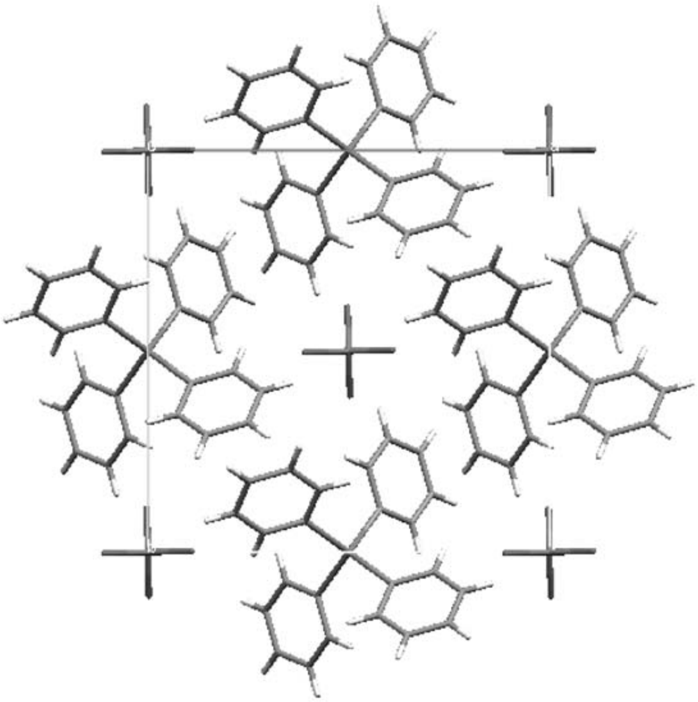

Fig. 4. Packing of the cations and anions in the crystal structure of complex **I** (projection along the *c* axis).

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REFERENCES

1. V. V. Sharutin, A. P. Pakusina, I. V. Egorova, et al., Koord. Khim. **28** (12), 883 (2002).
2. V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, et al., Koord. Khim. **31** (2), 117 (2005).
3. V. V. Sharutin, V. S. Senchurin, O. K. Sharutina, et al., Zh. Obshch. Khim. **66** (10), 1755 (1996).
4. V. V. Sharutin, O. K. Sharutina, L. P. Panova, and V. K. Bel'skii, Zh. Obshch. Khim. **67** (9), 1531 (1997).
5. V. V. Sharutin, O. K. Sharutina, P. E. Osipov, et al., Zh. Obshch. Khim. **70** (6), 931 (2000).
6. V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, et al., Zh. Obshch. Khim. **67** (9), 1536 (1997).
7. V. V. Sharutin, O. K. Sharutina, O. V. Molokova, et al., Zh. Obshch. Khim. **70** (12), 1990 (2000).
8. G. Ferguson, C. Glidewell, D. Lloyd, and S. Metcalfe, J. Chem. Soc., Perkin Trans. II, 731 (1988).
9. V. V. Sharutin, A. P. Pakusina, I. V. Egorova, et al., Zh. Obshch. Khim. **73** (4), 569 (2003).
10. V. V. Sharutin, O. K. Sharutina, L. P. Panova, and V. K. Bel'skii, Koord. Khim. **23** (7), 513 (1997).
11. V. V. Sharutin, O. K. Sharutina, O. P. Zadachina, et al., Zh. Obshch. Khim. **70** (10), 1672 (2000).
12. V. V. Sharutin, O. K. Sharutina, O. P. Zadachina, et al., Koord. Khim. **29** (1), 8 (2003).
13. A. V. Ivanov, A. P. Pakusina, M. A. Ivanov, et al., Dokl. Akad. Nauk **401** (5), 643 (2005).
14. V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, et al., Zh. Obshch. Khim. **72** (9), 1465 (2002).
15. V. V. Sharutin, O. K. Sharutina, T. P. Platonova, et al., Koord. Khim. **29** (1), 13 (2003).
16. V. V. Zhidkov, V. V. Sharutin, V. K. Bel'skii, and N. S. Magomedova, Zh. Obshch. Khim. **65** (2), 251 (1995).
17. V. V. Sharutin, V. V. Zhidkov, D. V. Muslin, et al., Izv. Akad. Nauk, Ser. Khim., No. 5, 958 (1995).
18. V. V. Sharutin, O. K. Sharutina, P. E. Osipov, et al., Zh. Obshch. Khim. **67** (9), 1528 (1997).
19. S. P. Bone and D. B. Sowerby, J. Chem. Res., Synop., No. 3, 82 (1979).

20. S. P. Bone and D. B. Sowerby, Phosphorus, Sulfur, Silicon Relat. Elem. **45** (1–2), 23 (1989).
21. O. K. Sharutina, V. V. Sharutin, V. S. Senchurin, et al., Izv. Akad. Nauk, Ser. Khim., No. 1, 194 (1996).
22. V. V. Sharutin, O. K. Sharutina, A. P. Pakusina, and V. K. Belsky, J. Organomet. Chem. **536** (1), 87 (1997).
23. V. V. Sharutin, O. K. Sharutina, I. G. Mel'nikova, et al., Izv. Akad. Nauk, Ser. Khim., No. 8, 2082 (1996).
24. V. V. Sharutin, O. K. Sharutina, L. P. Panova, et al., Zh. Obshch. Khim. **72** (1), 45 (2002).
25. G. M. Sheldrick, *SADABS. Program for Empirical X-ray Absorption Correction* (Bruker-Nonius, 1990–2004).
26. *SMART and SAINT-Plus, Versions 5.0: Data Collection and Processing Software for the SMART Sistem* (Bruker, Madison, 1998).
27. G. M. Sheldrick, *SHELXTL/PC, Versions 6.12: Structure Determination Software Suite* (Bruker, Madison, 2000).
28. P. K. Burkert, M. Grommelt, T. Pietrass, et al., Z. Naturforsch. B **45**, 725 (1990).
29. S. S. Batsanov, Zh. Neorg. Khim. **36** (12), 3015 (1991).
30. *Chemical Encyclopedia*, Ed. by N. S. Zefirov (Bol'shaya Ros. Entsiklopediya, Moscow, 1999), Vol. 5, p. 284 [in Russian].