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# Synthesis and Structure of Osmium Complexes: $[Ph_4Sb]_2^+[OsCl_6]^{2-}$, and $[p\text{-}Tol_4Sb]_2^+[OsCl_6]^{2-}$

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**Abstract**—The reaction of sodium hexachloroosmate with tetraphenyl- or tetra(*para*-tolyl)stibonium chloride in dimethyl sulfoxide gave the complexes $[Ph_4Sb]_2[OsCl_6]$ (**I**) and $[p\text{-}Tol_4Sb]_2[OsCl_6]$ (**II**). According to X-ray diffraction data, the CSbC angles in the tetrahedral cations $[Ph_4Sb]^+$ and $[p\text{-}Tol_4Sb]^+$ are 105.97(17)°–117.98(16)° in **I** and 103.1(3)°–118.0(2)° in **II**; the Sb–C bond lengths vary in the ranges of 2.090(4)–2.104(4) Å (**I**) and 2.086(6)–2.107(7) Å (**II**). In the octahedral anions $[OsCl_6]^{2-}$, the Os–Cl bond lengths are 2.3364(10)–2.3435(12) Å (**I**) and 2.3159(16)–2.3361(19) Å (**II**) (CIF files CCDC no. 1000137 (**I**), 1010809 (**II**)).

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## INTRODUCTION

As follows from published data, the reaction of tetraorganylphosphonium or -stibonium halide with halogen complexes of platinum [1], palladium [2], rhodium [3], ruthenium [4], or iridium [5, 6] in dimethyl sulfoxide is usually accompanied by ligand exchange in the anion.

It was found that in a dimethyl sulfoxide solution, hexachloroosmates undergo reactions involving replacement of the inner-sphere chloride ions by solvent molecules with simultaneous reduction of osmium(IV) to osmium(III) and osmium(II) [7].

This study is devoted to reactions of tetraarylstibonium chlorides with sodium hexachloroosmate dihydrate in dimethyl sulfoxide and determination of the structures of the obtained complexes.

## EXPERIMENTAL

**Synthesis of $[Ph_4Sb]_2^+[OsCl_6]^{2-}$ (I).** A mixture of tetraphenylstibonium chloride (0.058 g, 0.12 mmol) and sodium hexachloroosmate(IV) dihydrate (0.030 g, 0.06 mmol) was dissolved with stirring in 2 mL of dimethyl sulfoxide. Slow evaporation of the solvent down to 0.5 mL resulted in the formation of green crystals, which were filtered off and dried. The yield of complex **I** was 0.044 g (56%); $T_m$ = 210°C (dec.).

IR (ν, $cm^{-1}$): 3050, 1573, 1478, 1435, 1334, 1309, 1191, 1164, 1065, 1017, 994, 734, 689, 612, 456, 442.

For $C_{48}H_{40}Cl_6Sb_2Os$

| | | |
|---|---|---|
| anal. calcd., %: | C, 45.62; | H, 3.17. |
| Found, %: | C, 45.47; | H, 3.24. |

**$[p\text{-}Tol_4Sb]^+[OsCl_6]^{2-}$ (II)** was synthesized by the same procedure as described for **I**. The yield of green crystals was 69%. $T_m$ = 200°C (dec.).

IR (ν, $cm^{-1}$): 3049, 2918, 1612, 1588, 1492, 1442, 1395, 1314, 1211, 1190, 1122, 1066, 1038, 1011, 799, 584, 481.

For $C_{56}H_{56}Cl_6Sb_2Os$

| | | |
|---|---|---|
| anal. calcd., %: | C, 48.88; | H, 4.07. |
| Found, %: | C, 48.62; | H, 4.18. |

IR spectra were recorded on a Bruker Tensor 27 IR spectrometer for KBr pellets.

**X-ray diffraction** analysis of the crystals of **I** and **II** was carried out on a D8 Quest Bruker diffractometer (Mo$K_\alpha$ radiation, λ = 0.71073 Å, graphite monochromator). SMART and SAINT-Plus software were used for data collection and editing, refinement of unit cell parameters, and applying absorption corrections [8]. All calculations for structure solution and refinement were carried out using SHELXL/PC [9] and OLEX2 [10] software. The structures of **I** and **II** were solved by direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen

**Table 1.** Crystallographic data and X-ray diffraction experiments and structure refinement details for **I** and **II**

| Parameter | Value | |
|---|---|---|
| | **I** | **II** |
| $M$ | 631.60 | 1375.41 |
| $T$, K | 296(2) | 296(2) |
| System | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| $a$, Å | 10.1404(8) | 11.9321(6) |
| $b$, Å | 10.1952(8) | 43.8014(19) |
| $c$, Å | 12.4006(10) | 12.2747(6) |
| α, deg. | 99.500(2) | 90.00 |
| β, deg. | 94.282(2) | 118.4460(10) |
| γ, deg. | 113.383(2) | 90.00 |
| $V$, Å$^3$ | 1146.59(16) | 5640.7(5) |
| $Z$ | 2 | 4 |
| ρ(calcd.), g/cm$^3$ | 1.829 | 1.620 |
| μ, mm$^{-1}$ | 4.316 | 3.516 |
| $F$(000) | 608.0 | 2688.0 |
| Crystal size, mm | 1.3 × 1.13 × 0.86 | 0.26 × 0.18 × 0.07 |
| Range of θ, deg | 5.96–52.96 | 5.98–52.78 |
| Ranges of reflection indices | $-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$ | $-14 \leqslant h \leqslant 14$, $-54 \leqslant k \leqslant 54$, $-15 \leqslant l \leqslant 15$ |
| Number of measured reflections | 43392 | 73428 |
| Number of unique reflections ($R_{int}$) | 4718 (0.0558) | 11496 (0.0586) |
| Number of parameters refined | 260 | 594 |
| GOOF | 1.077 | 1.055 |
| $R$-factors for $F^2 > 2\sigma(F^2)$ | $R_1 = 0.0308$, $wR_2 = 0.0830$ | $R_1 = 0.0555$, $wR_2 = 0.1154$ |
| $R$-factors for all reflections | $R_1 = 0.0324$, $wR_2 = 0.0851$ | $R_1 = 0.0846$, $wR_2 = 0.1288$ |
| Residual electron density (min/max), $e$/Å$^3$ | 1.11/–1.99 | 4.17/–2.13 |

atoms. The selected crystal characteristics and refinement details for structures **I** and **II** are summarized in Table 1; selected bond lengths and bond angles are presented in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC № 1000137 (**I**), 1010809 (**II**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

We found that dissolution of sodium hexachloroosmate(IV) dihydrate and tetraphenyl- or tetra-*para*-tolylstibonium chloride (molar ratio 1 : 2) in dimethyl sulfoxide followed by slow evaporation of the solvent results in precipitation of air-stable green crystals of complexes **I** and **II**:

$$2Ar_4SbCl + Na_2OsCl_6 \cdot 2H_2O \xrightarrow{DMSO} [Ar_4Sb]_2^+[OsCl_6]^{2-} + 2NaCl + 2H_2O,$$

Ar = Ph (**I**), *p*-Tol (**II**).

According to X-ray diffraction data, the crystals of complexes **I** and **II** consist of tetraarylstibonium cations and hexachloroosmate anions (Fig. 1). In **II**, there are two types of crystallographically independent cations with slightly different geometric parameters.

The antimony atoms in the cations have a distorted tetrahedral coordination, the CSbC angles varying in the ranges of 105.91(16)–118.13(15) (**I**) and 106.0(3)°–114.6(3)°, 103.1(3)°–118.0(2)° (**II**). The Sb–C distances in **I** and **II** are 2.092(4)–2.105(4)) and 2.092(7)–2.104(6), 2.086(6)–2.107(7) Å, respectively. The bond angles and bond lengths in **I** and **II** are close

**Table 2.** Selected bond lengths and bond angles in structures in structures **I*** and **II**

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| | | **I** | |
| Os(1)–Cl(1) | 2.3458(10) | Cl(2)Os(1)Cl(1*A*) | 88.93(4) |
| Os(1)–Cl(2) | 2.3361(10) | C(31)Sb(1)C(1) | 111.64(16) |
| Os(1)–Cl(3) | 2.3437(11) | C(31)Sb(1)C(21) | 118.13(15) |
| Sb(1)–C(1) | 2.105(4) | C(31)Sb(1)C(11) | 106.65(16) |
| Sb(1)–C(31) | 2.092(4) | C(21)Sb(1)C(1) | 107.52(16) |
| Sb(1)–C(21) | 2.096(4) | C(11)Sb(1)C(1) | 105.91(16) |
| Sb(1)–C(11) | 2.095(4) | C(11)Sb(1)C(21) | 106.20(15) |
| C(1)–C(6) | 1.375(7) | | |
| | | **II** | |
| Sb(1)–C(31) | 2.103(6) | C(31)Sb(1)C(21) | 110.7(2) |
| Sb(1)–C(11) | 2.095(7) | C(11)Sb(1)C(31) | 107.8(2) |
| Sb(1)–C(1) | 2.092(7) | C(11)Sb(1)C(21) | 106.0(3) |
| Sb(1)–C(21) | 2.104(6) | C(1)Sb(1)C(31) | 106.9(3) |
| Sb(2)–C(41) | 2.102(6) | C(1)Sb(1)C(11) | 110.8(3) |
| Sb(2)–C(51) | 2.107(7) | C(1)Sb(1)C(21) | 114.6(3) |
| Sb(2)–C(61) | 2.100(7) | C(41)Sb(2)C(51) | 103.1(3) |
| Sb(2)–C(71) | 2.086(6) | C(61)Sb(2)C(41) | 118.0(2) |
| Os(1)–Cl(2) | 2.3361(19) | C(61)Sb(2)C(51) | 106.9(3) |
| Os(1)–Cl(4) | 2.3159(16) | C(71)Sb(2)C(41) | 112.5(2) |
| Os(1)–Cl(3) | 2.331(2) | C(71)Sb(2)C(51) | 104.8(2) |
| Os(1)–Cl(6) | 2.3370(17) | C(71)Sb(2)C(61) | 110.4(2) |
| Os(1)–Cl(1) | 2.344(2) | Cl(2)Os(1)Cl(6) | 90.36(7) |
| Os(1)–Cl(5) | 2.333(2) | Cl(2)Os(1)Cl(1) | 178.00(7) |
| C(41)–C(42) | 1.351(9) | Cl(4)Os(1)Cl(2) | 90.04(7) |
| C(41)–C(46) | 1.361(12) | Cl(4)Os(1)Cl(3) | 178.81(10) |
| C(51)–C(56) | 1.369(10) | Cl(4)Os(1)Cl(6) | 90.90(6) |
| C(51)–C(52) | 1.378(10) | Cl(4)Os(1)Cl(1) | 89.35(7) |
| C(31)–C(36) | 1.384(10) | Cl(4)Os(1)Cl(5) | 89.50(8) |
| C(31)–C(32) | 1.378(9) | Cl(3)Os(1)Cl(2) | 91.13(9) |
| C(35)–C(36) | 1.372(8) | Cl(3)Os(1)Cl(6) | 89.32(8) |
| C(35)–C(34) | 1.388(10) | Cl(3)Os(1)Cl(1) | 89.50(9) |
| C(11)–C(12) | 1.382(9) | Cl(3)Os(1)Cl(5) | 90.29(9) |
| C(11)–C(16) | 1.374(10) | Cl(6)Os(1)Cl(1) | 87.75(7) |
| C(1)–C(2) | 1.384(10) | Cl(5)Os(1)Cl(2) | 88.91(8) |
| C(56)–C(55) | 1.399(11) | Cl(5)Os(1)Cl(6) | 179.16(8) |
| C(71)–C(72) | 1.368(9) | Cl(5)Os(1)Cl(1) | 92.98(8) |

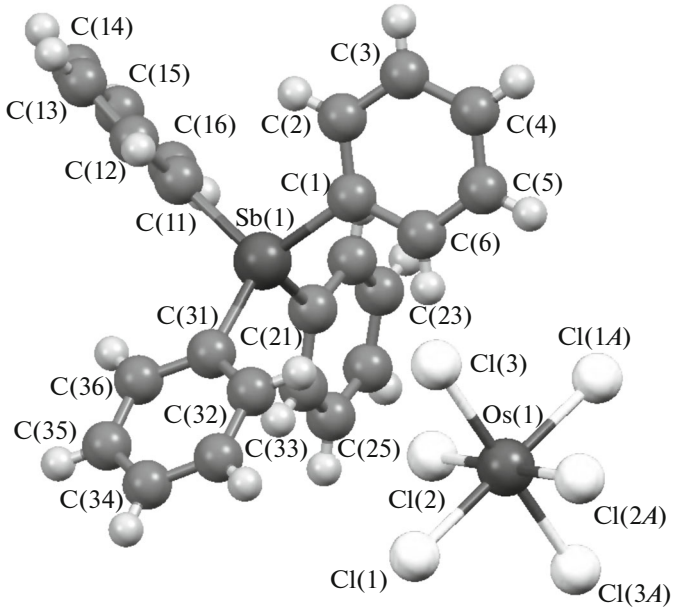
* Symmetry codes: (a) $-x$, $1-y$, $1-z$.

to those observed in tetraarylstibonium cations and other ionic compounds of antimony [11].

Whereas in the centrosymmetric anion $[OsCl_6]^{2-}$ of compound **I**, the ClOsCl *cis*-angles are 88.93(4)°–91.07(4)°, i.e., they are close to ideal 90°, in the anion of compound **II**, the *trans*- (178.00(7)°–179.16(8)°) and *cis*-ClOsCl angles (87.75(7)°–90.90(6)°) vary to a greater extent. The variation of the Os–Cl distances in **I** 2.3361(10)–2.3458(10) Å) is also less pronounced than in **II** (2.3159(16)–2.344(2) Å).

The structural organization in the crystals of **I** and **II** is caused by weak hydrogen bonds. The cations and anion in **I** are combined into polymer chains by a system of Cl···H–C hydrogen bonds

(a)




(b)

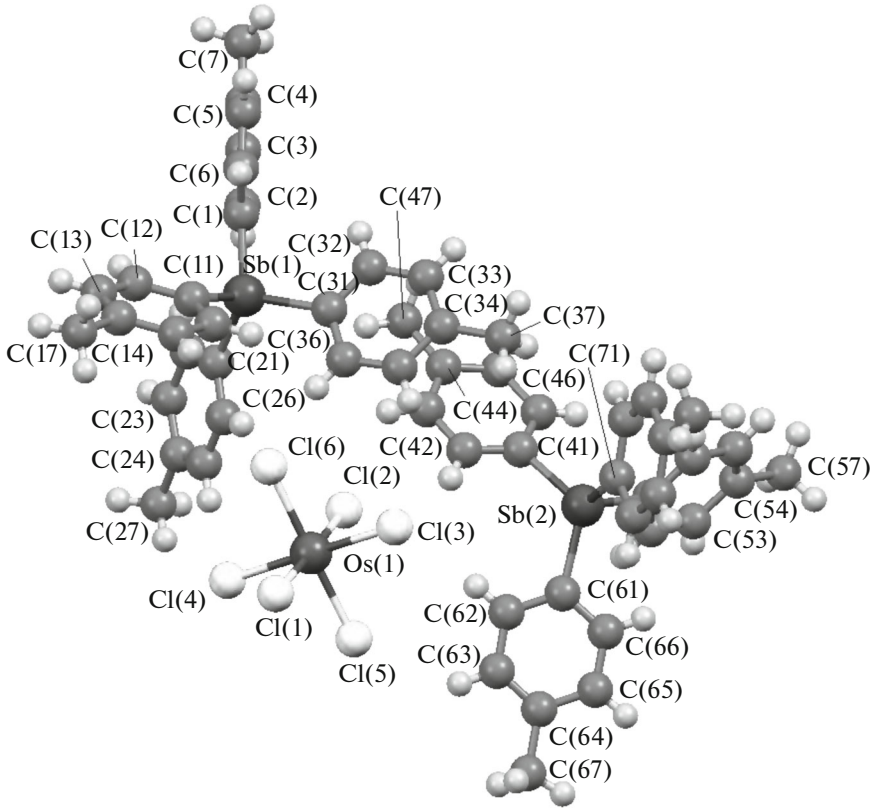



**Fig. 1.** Molecular structures of compounds (a) **I**, (b) **II**.

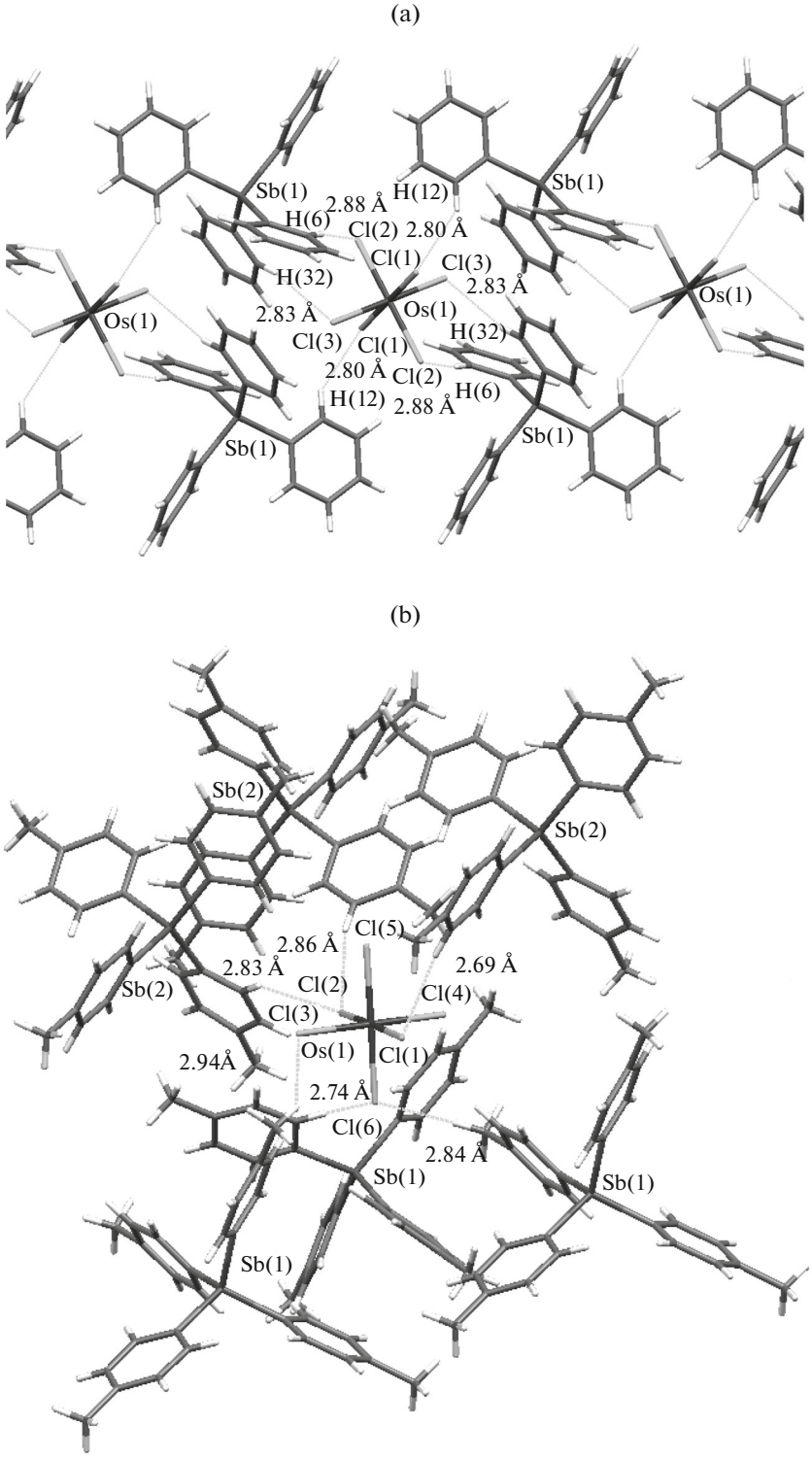



**Fig. 2.** Hydrogen bonds in the crystals of complexes (a) **I**, (b) **II**.

formed by chlorine atoms and the *ortho*-hydrogen atoms of the phenyl groups (Cl···H 2.80–2.88 Å). Each anion has four cations in the local environment (Fig. 2a).

In the crystal of **II**, apart from the Cl···H–C hydrogen bonds involving *ortho*- and *meta*-hydrogen atoms of the tolyl groups (Cl···H 2.69–2.86 Å), there are also close contacts with the hydrogen atoms of the methyl

groups (Cl···H 2.84–2.94 Å), and each anion is surrounded by six cations (Fig. 2b).

Thus, in the sodium hexachloroosmate – tetraarylstibonium chloride–dimethyl sulfoxide, the $[OsCl_6]^{2-}$ anions are kinetically inert and do not undergo ligand exchange. When the complexes are formed, the solvent molecules do not enter the coordination sphere of the tetraarylstibonium cation and do not participate in the formation of the crystal lattice.

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