

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, $[\text{Ph}_3\text{PH}]^+[\text{OsBr}_6]^{2-}$ [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

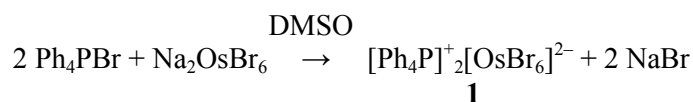
Bond	<i>d</i> , Å	Angle	<i>ω</i> , deg
Os(1)–Br(1 ¹)	2.4985(2)	Br(1 ¹)Os(1)Br1	180.0
Os(1)–Br(1)	2.4986(2)	Br(2)Os(1)Br1	91.620(8)
Os(1)–Br(2)	2.4752(2)	Br(2 ¹)Os(1)Br1	88.380(8)
Os(1)–Br(3)	2.5019(3)	C(1)P(1)C31	106.23(11)
Os(1)–Br(3 ¹)	2.5020(3)	C(1)P(1)C11	109.65(11)
P(1)–C(1)	1.798(2)	C(31)P(1)C11	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).

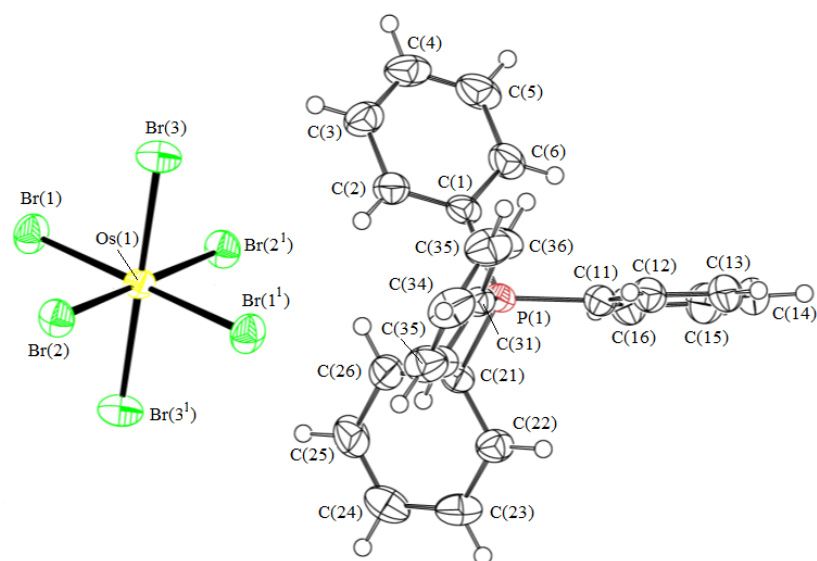


Fig. 1. Structure of complex 1

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).

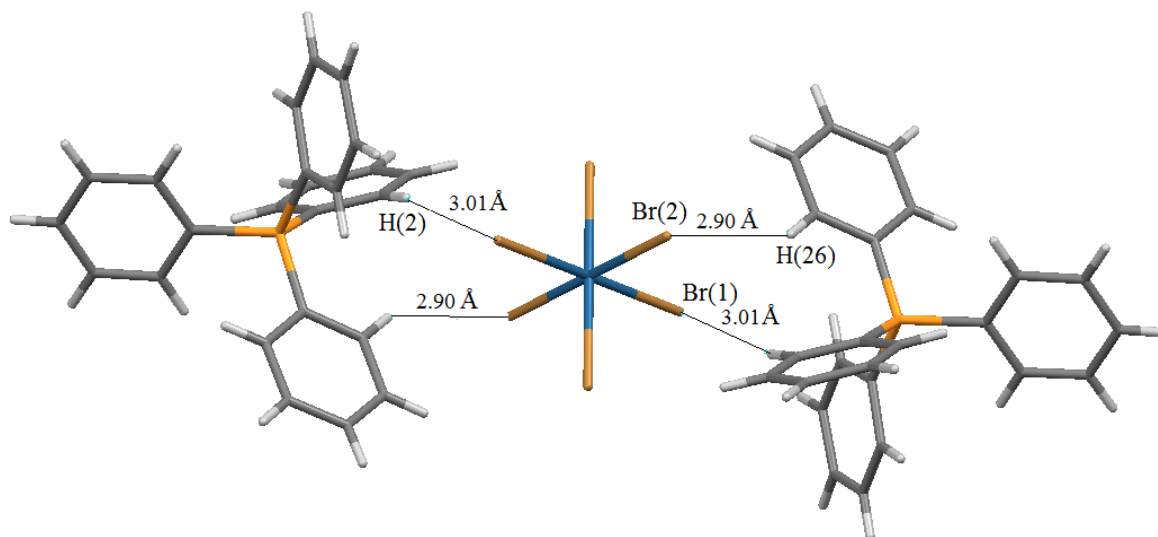


Fig. 2. The system of hydrogen bonds in the crystal of complex 1

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.

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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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