Synthesis and Structure of the Platinum Complexes [Bu₄N]⁺[PtBr₅(DMSO)]⁻, [Ph₄P]⁺[PtBr₅(DMSO)]⁻, and [Ph₃(*n*-Am)P]⁺[PtBr₅(DMSO)]⁻

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Abstract—The complexes $[Bu_4N]_2^+ [PtBr_6]^{2-}$ (I), $[Ph_4P]_2^+ [PtBr_6]^{2-}$ (II), and $[Ph_3(n-Am)P]_2^+ [PtBr_6]^{2-}$ (III) are synthesized by the reactions of tetrabutylammonium bromide, tetraphenylphosphonium bromide, and triphenyl(*n*-amyl)-tetraphenylphosphonium bromide, respectively, with potassium hexabromoplatinate (mole ratio 2 : 1). After recrystallization from dimethyl sulfoxide, complexes I, II, and III transform into $[Bu_4N]^+ [PtBr_5(DMSO)]^-$ (IV), $[Ph_4P]^+ [PtBr_5(DMSO)]^-$ (V), and $[Ph_3(n-Am)P]^+ [PtBr_5(DMSO)]^-$ (VI). According to the X-ray diffraction data, the cations of complexes IV—VI have a slightly distorted tetrahedral structure. The N–C and P–C bond lengths are 1.492(7)–1.533(6) and 1.782(10)–1.805(10) Å, respectively. The platinum atoms in the mononuclear anions are hexacoordinated. The dimethyl sulfoxide ligands are coordinated with the Pt atom through the sulfur atom (Pt–S 2.3280(18)–2.3389(11) Å). The Pt–Br bond lengths are 2.4330(6)–2.4724(6) Å.

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In continuation of the study of the reactions of inorganic platinum salts with onium compounds of the 15 Group elements [1-3], we synthesized tetrabutylammonium, tetraphenylphosphonium, and triphenyl(*n*-amyl)phosphonium hexabromoplatinates by the reaction of potassium hexabromoplatinate with ammonium and phosphonium bromides in water and studied the structures of the products of their reactions with dimethyl sulfoxide.

EXPERIMENTAL

Synthesis of $[Bu_4N]_2^+[PtBr_6]^{2-}$ (I). Potassium hexabromoplatinate (0.15 g, 0.20 mmol) was dissolved on heating in 15 ml of distilled water, and tetrabutylammonium bromide (0.13 g, 0.40 mmol) in water (5 ml) was added to the solution with stirring. A yellow-orange precipitate was formed, filtered off, washed with distilled water, and dried. The yield of complex I was 0.17 g (74%), $T_{decomp} = 240^{\circ}$ C.

IR, v, cm⁻¹: 739, 882, 1030, 1068, 1154, 1169, 1379, 1471, 2872, 2959, 3442.

$For C_{32}H_{72}N_2Br_6Pt$		
anal. calcd., %:	C, 33.13;	Н, 6.21.
Found, %:	C, 33.00;	Н, 6.54.

Synthesis of $[Ph_4P]_2^+[PtBr_6]^{2-}$ (II). Potassium hexabromoplatinate (0.15 g, 0.20 mmol) was dissolved on heating in 15 ml of distilled water, and tetraphenylphosphonium bromide (0.17 g, 0.40 mmol) in water (15 ml) was added to the solution with stirring. A yellow-orange precipitate was formed, filtered off, washed with distilled water, and dried. The yield of complex II was 0.25 g (93%), $T_{decomp} = 255^{\circ}C$.

IR, v, cm⁻¹: 528, 690, 723, 753, 762, 996, 1107, 1165, 1190, 1316, 1435, 1440, 1483, 1584, 3053.

For $C_{48}H_{40}P_2Br_6Pt$		
anal. calcd., %:	C, 42.57;	Н, 2.97.
Found, %:	C, 42.47;	Н, 3.07.

Synthesis of $[Ph_3(n-Am)P]_2^+[PtBr_6]^{2-}$ (III). Potassium hexabromoplatinate (0.15 g, 0.20 mmol) was dissolved on heating in 15 ml of distilled water, and triphenyl(*n*-amyl)phosphonium bromide (0.17 g, 0.40 mmol) in water (15 ml) was added to the solution with stirring. A yellow-orange precipitate was formed, filtered off, washed with distilled water, and dried. The yield of complex III was 0.23 g (86%), $T_{decomp} > 220^{\circ}C$.

IR, v, cm⁻¹: 5077, 534, 692, 724, 749, 997, 1113, 1164, 1188, 1314, 1336, 1437, 1483, 1586, 2359, 2923, 2953, 3055, 3081.

For C46H52P2Br6Pt		
anal. calcd., %:	C, 41.16;	H, 3.88.
Found, %:	C, 39.87;	H, 3.96.

Synthesis of $[Bu_4N]^+[PtBr_5(DMSO)]^-$ (IV). Complex I (0.08 g, 0.07 mmol) was dissolved with stirring in dimethyl sulfoxide (5 ml). A red solution was concentrated, and the red needle-like crystals that formed were filtered off and dried. The yield of complex IV was 0.58 g (92%), $T_{decomp} = 180^{\circ}C$.

IR, v, cm⁻¹: 425, 737, 882, 1025, 1169, 1311, 1381, 1470, 2873, 2961, 3434.

For	C_{10}	$H_{42}N$	OSB	-Pt
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anal. calcd., %:	C, 23.62;	H, 4.59.
Found, %:	C, 23.53;	H, 4.68.

Synthesis of $[Ph_4P]^+[PtBr_5(DMSO)]^-$ (V). Complex II (0.15 g, 0.11 mmol) was dissolved with stirring in dimethyl sulfoxide (5 ml). A red solution was concentrated, and the red crystals that formed were filtered off and dried. The yield of complex V was 0.10 g (91%), $T_{decomp} = 204^{\circ}$ C. IR, v, cm⁻¹: 528, 688, 724, 756, 761, 994, 1026,

IR, v, cm⁻¹: 528, 688, 724, 756, 761, 994, 1026, 1108, 1160, 1167, 1312, 1437, 1482, 1585, 2920, 3006, 3034, 3053, 3077.

For C₂₆H₂₆OPSBr₅Pt

anal. calcd., %:	C, 30.84;	Н, 2.57.
Found, %:	C, 30.59;	H, 2.66.

Synthesis of $[Ph_3(n-Am)P]^+[PtBr_5(DMSO)]^-$ (VI). A mixture of potassium hexabromoplatinate (0.15 g, 0.2 mmol), triphenyl-*n*-amylphosphonium bromide (0.08 g, 0.2 mmol), and dimethyl sulfoxide (5 ml) was stirred at 20°C for 5 min. A red solution was concentrated, and the red crystals that formed were filtered off and dried. The yield of complex VI was 0.18 g (90%), $T_{decomp} = 220^{\circ}$ C.

IR, v, cm⁻¹: 507, 534, 692, 724, 748, 997, 1025, 1113, 1437, 2853, 2871, 2918, 2953, 3055, 3080.

For C₂₅H₃₂OPSBr₅Pt

anal. calcd., %:	C, 29.83;	H, 3.18.
Found, %:	C, 30.03;	H, 3.28.

The IR spectra of complexes I–VI were recorded on a 1201 FTIR spectrometer in KBr pellets.

X-ray diffraction analyses of crystals **IV–VI** were carried out on an Xcalibur, Sapphire3, Gemini S diffractometer (Mo K_{α} radiation, $\lambda = 0.71073$ Å, tube operation mode 50/40 kV/mA, graphite monochromator). An absorption correction was applied numerically by the crystal shape [4]. The structures were

determined by a direct method and refined by the fullmatrix least-squares method in the anisotropic approximation for non-hydrogen atoms (SHELX-97, WinGX) [5, 6]. Positions of hydrogen atoms were determined geometrically by the riding model. The main crystallographic data and results of refinement of structures **IV–VI** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

The full tables of coordinates of atoms and bond lengths and bond angles were deposited with the Cambridge Crystallographic Data Centre (nos. 815004 (**IV**), 815005 (**V**), and 815006 (**VI**); deposit@ccdc. cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The syntheses and structures of the bromine-containing platinum complexes were described for single examples of the mononuclear $[PtBr_6]^{2-}$, binuclear $[Pt_2Br_9]^-$ and trinuclear $[Pt_3Br_{12}]^{2-}$, anions [7].

We found that the reactions of tetrabutylammonium, tetraphenylphosphonium, and triphenylamylphosphonium bromides with potassium hexabromoplatinate at a mole ratio of the reactants of 2 : 1 in water afforded yellow-orange finely crystalline compounds **I**, **II**, and **III** with the Pt-containing anions.

$$2[R_4E]^+Br^- + K_2^+[PtBr_6]^{2-}$$
$$\xrightarrow{H_2O} [R_4E]_2^+[PtBr_6]^{2-} + 2KBr,$$
$$E = N, R = Bu; E = P, R = Ph, n-Am.$$

We found that the dissolution of compounds I-III in dimethyl sulfoxide resulted in ligand exchange in the anion, which was accompanied by a change in the yellow color of the solution to red-brown. The reaction products are the complexes with mixed-ligand anions (IV-VI).

$$[R_4E]_2^+ [PtBr_6]^{2-}$$

$$\xrightarrow{DMSO} [R_4E]^+ [PtBr_5(DMSO)]^- + [R_4E]^+ Br^-,$$

$$E = N, R = Bu; \quad E = P, R = Ph, n-Am.$$

The compounds of this type can be obtained directly from tetraorganylammonium or phosphonium bromide and potassium hexabromoplatinate in dimethyl sulfoxide at a mole ratio of the reactants of 1 : 1:

$$[Ph_{3}(n-Am)P]^{+}Br^{-} + K_{2}^{+}[PtBr_{6}]^{2-}$$
$$\xrightarrow{DMSO} [Ph_{3}(n-Am)P]^{+}[PtBr_{5}(DMSO)]^{-}$$
$$+ 2KBr.$$

The crystals of **IV–VI** are red and soluble in polar organic solvents.

According to the X-ray diffraction data, the cations $[Bu_4N]^+$, $[Ph_4P]^+$, and $[Ph_3(n-Am)P]^+$ of complexes **IV**, **V**, **VI** have a weakly distorted tetrahedral structure. The bond angles CNC and CPC (107.4(3)°-112.7(3)° in **IV**, 105.4(5)°-112.9(6)° in **V**, and 108.1(2)°-

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Table 1	Crystallographic data and e	vperimental and refinement	narameters for the structures	of complexes IV_VI
Table 1.	Crystanographic data and c	Apermental and remement	parameters for the structures	

Davaataa	Value			
Parameter	IV	V	VI	
<i>Т</i> , К	298(2)	298(2)	293(2)	
Crystal system	Monoclinic	Triclinic	Orthorhombic	
Space group	<i>P</i> 2 ₁ /n	$P\overline{1}$	$P 2_1 L_1 2_1$	
a, Å	11.5329(3)	7.9290(4)	11.8019(2)	
b, Å	21.5469(13)	13.3730(8)	12.7545(2)	
<i>c,</i> Å	23.3728(7)	14.5704(7)	20.4615(4)	
α , deg	90	79.092(4)	90	
β, deg	91.289(3)	87.763(4)	90	
γ, deg	90	88.607(4)	90	
<i>V</i> , Å ³	5806.6(4)	1515.66(14)	3080.01(9)	
Ζ	8	2	4	
ρ calcd, g/cm ³	2.092	2.218	2.170	
μ , mm ⁻¹	11.796	11.36	11.179	
<i>F</i> (000)	3464	948	1896	
Crystal size, mm	$0.2975 \times 0.1483 \times 0.1127$	0.4147 imes 0.1858 imes 0.0855	$0.3457 \times 0.2309 \times 0.1327$	
ρ range of data collection, deg	3.46-30.51	3.46-30.51	3.35-30.51	
Ranges of reflection indices	$-16 \le h \le 15$ $-30 \le k \le 29$ $-32 \le 1 \le 33$	$-11 \le h \le 11$ $-19 \le k \le 19$ $-13 \le l \le 20$	$-16 \le h \le 16$ $-18 \le k \le 17$ $-29 \le l \le 22$	
Measured reflections	46450	14644	27364	
Independent reflections	17010 ($R_{\rm int} = 0.0848$)	9131 ($R_{\rm int} = 0.0288$)	9382 ($R_{\rm int} = 0.0498$)	
Reflections with $I > 2\sigma(I)$	5840	5086	6518	
Refinement variables	487	317	307	
Goodness-of-fit	0.67	1.114	0.504	
<i>R</i> factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.042, wR_2 = 0.0625$	$R_1 = 0.0615, wR_2 = 0.1892$	$R_1 = 0.0299, wR_1 = 0.0503$	
<i>R</i> factors on all reflections	$R_1 = 0.1825, wR_2 = 0.0798$	$R_1 = 0.1156, wR_2 = 0.2008$	$R_1 = 0.0555, wR_1 = 0.0574$	
Residual electron density (min/max), $e/Å^3$	-0.766/1.114	-1.926/3.739	-1.06/1.086	
$(\Delta/\rho)_{\rm max}/(\Delta/\rho)_{\rm min}$	0.039/0.002	0.003/0.001	0.003/0	

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SYNTHESIS AND STRUCTURE OF THE PLATINUM COMPLEXES

	Table 2.	Selected bond lengths	(d) and bond angles (ω) in the structures of	compounds IV-VI
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Bond	<i>d,</i> Å	Angle	ω, deg	
]	IV	<u> </u>	
Pt(1)–S(2)	2.3280(18)	Br(5)Pt(2)Br(1)	89.46(2)	
Pt(1)-Br(8)	2.4479(8)	Br(6)Pt(2)Br(1)	177.57(2)	
Pt(1)–Br(2)	2.4531(6)	Br(9)Pt(2)Br(1)	90.45(2)	
Pt(1)-Br(10)	2.4575(6)	Br(4)Pt(2)Br(1)	89.68(3)	
Pt(1)-Br(7)	2.4618(6)	O(2)S(1)C(21)	111.0(4)	
Pt(1)-Br(3)	2.4641(6)	O(2)S(1)C(23)	104.7(3)	
Pt(2)–S(1)	2.3398(18)	C(21)S(1)C(23)	99.8(4)	
Pt(2)-Br(5)	2.4330(6)	O(2)S(1)Pt(2)	115.81(19)	
Pt(2)-Br(6)	2.4543(7)	C(21)S(1)Pt(2)	112.5(3)	
Pt(2)-Br(9)	2.4575(6)	C(23)S(1)Pt(2)	111.5(3)	
Pt(2)-Br(4)	2.4685(8)	O(1)S(2)C(22)	105.3(4)	
Pt(2)-Br(1)	2.4724(6)	O(1)S(2)C(24)	106.5(4)	
	'	V	'	
Pt(1)–S(1)	2.332(3)	S(1)Pt(1)Br(4)	90.52(9)	
Pt(1)-Br(4)	2.4525(13)	S(1)Pt(1)Br(3)	88.59(9)	
Pt(1)-Br(3)	2.4583(15)	Br(4)Pt(1)Br(3)	89.23(6)	
Pt(1)-Br(1)	2.4611(13)	S(1)Pt(1)Br(1)	90.26(9)	
Pt(1)–Br(2)	2.4620(13)	Br(4)Pt(1)Br(1)	179.16(6)	
Pt(1)-Br(5)	2.4625(15)	Br(3)Pt(1)Br(1)	91.08(5)	
VI				
Pt(1)–S(1)	2.3389(11)	S(1)Pt(1)Br(2)	95.11(3)	
Pt(1)-Br(2)	2.4568(5)	S(1)Pt(1)Br(3)	92.02(3)	
Pt(1)-Br(3)	2.4597(5)	Br(2)Pt(1)Br(3)	89.357(19)	
Pt(1)-Br(5)	2.4613(5)	S(1)Pt(1)Br(5)	175.25(3)	
Pt(1)-Br(4)	2.4641(5)	Br(2)Pt(1)Br(5)	88.88(2)	
Pt(1)-Br(1)	2.4657(5)	Br(3)Pt(1)Br(5)	90.582(19)	

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Fig. 1. Structure of complex IV.



Fig. 2. Structure of complex V.







Fig. 4. Ion packing in complexes IV–VI (view along the *z* axis).

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111.2(2)° in (VI) differ slightly from a theoretical value of 109.5°. Crystal IV contains two types of crystallographically independent cations $[Bu_4N]^+$ and two types of crystallographically independent anions $[PtBr_5(DMSO)]^-$.

The platinum atoms in the anions of complexes IV-VI have octahedral coordination. The equatorial plane of the octahedron contains four bromine atoms, and the axial positions are occupied by the bromine atoms and sulfur atoms of dimethyl sulfoxide (Figs. 1-3). The platinum atoms lie rigidly in the equatorial plane PtBr₄, although the axial positions of the octahedron contain ligands different in type and volume: bromine and dimethyl sulfoxide. The Pt-S distances in the anions of complexes IV-VI are shorter than the sum of van der Waals radii of platinum and sulfur (3.5 Å [8]). In IV and VI, the Pt–S bonds are shortened almost equally (2.332(3)-2.340(2) Å) compared to the sum of covalent radii (2.41 Å [8]). On the contrary, the Pt-Br bond lengths (2.4330(6)-2.4724(6) Å) approach in value the sum of covalent radii of the platinum and bromine atoms (2.46 Å [8]). The bond angles $Br_{ax}PtBr_{eq}$ and $SPtBr_{eq}$ differ slightly from a theoretical value of 90°. The axial angles SPtBr_{ax} in the anions of complexes IV, V, and **VI** are equal to 177.05(4)°, 178.94(9)°, 175.25(3)°, respectively.

The packing of cations and anions in complexes **IV**–**VI** is shown in Fig. 4.

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