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Reaction of Pentaphenylphosphorus with Hexachloroplatinic Acid

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Abstract—This work is a continuation of the study of ligand exchange in the synthesis of the platinum complexes in the presence of dialkyl sulfoxides. Tetraphenylphosphonium hexachloroplatinate (**I**) is synthesized by the reaction of pentaphenylphosphorus with hexachloroplatinic acid in acetone. In order to study a possibility of incorporating dimethyl sulfoxide into the coordination sphere of platinum, complex **I** was recrystallized from dimethyl sulfoxide (DMSO). As a result, tetraphenylphosphonium pentachlorodimethyl sulfoxidoplatinate (**II**) is synthesized. The compounds are characterized by IR spectroscopy and X-ray diffraction (XRD) (CIF files CCDC nos. 1865783 (**I**) and 829586 (**II**)). The crystals of complexes **I** and **II** are formed from tetrahedral tetraphenylphosphonium cations and octahedral anions. In the tetraphenylphosphonium cations, the phosphorus atoms have a slightly distorted tetrahedral environment (CPC 107.8(3)°–113.2(3)° (**I**), 105.9(3)°–112.9(3)° (**II**)), and the P–C bond lengths are 1.785(6)–1.805(6) Å (**I**) and 1.783(7)–1.791(6) Å (**II**). The platinum atoms in the anions of complexes **I** and **II** are hexacoordinated. In complex **II**, the DMSO ligand coordinates to the platinum atom via the sulfur atom (2.290(2) Å).

Keywords: pentaphenylphosphorus, hexachloroplatinic acid hydrate, acetone, tetraphenylphosphonium, XRD

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INTRODUCTION

The dephenylation of pentaphenylphosphorus with inorganic acids [1–5], nonmetal oxides [6], carboxylic acids [7, 8], arylsulfonic acids [9], and metal halides [10] affording the tetraphenylphosphonium derivatives [11, 12] is described in rather detail. Tetraorganylphosphonium salts attract attention due to their wide use as solvents and mediators in catalytic processes. Ionic liquids based on tetraorganylphosphonium are stable in basic media because of the absence of an acidic proton and have a high thermal activity [13]. The disinfection properties of tetraorganylphosphonium salts are described [14–17]. Alkyltriphenylphosphonium halides exhibit high antimicrobial and antimycotic activity against strains of the pathogenic microflora: *Pseudomonas aeruginosa*, *Proteus mirabilis*, *Escherichia coli*, *Staphyloccocus aureus*, and *Candida albicans* [17]. The platinum(IV) complexes also found wide use in medicine as antitumor agents and, hence, the synthesis of tetraphenylphosphonium hexahaloplatinates provides broad prospects for their application.

This work is a continuation of our study of the regularities of the ligand exchange in the synthesis of the platinum complexes in the presence of dialkyl sulfoxides. In this work, we showed that the reaction of pentaphenylphosphorus with hexachloroplatinic acid in acetone afforded tetraphenylphosphonium hexachloroplatinate (**I**), the recrystallization of which resulted in the incorporation of DESO into the coordination sphere of platinum to form tetraphenylphosphonium pentachlorodimethyl sulfoxidoplatinate (**II**).

EXPERIMENTAL

All procedures associated with the synthesis of new complexes were carried out in air using acetone. Hexachloroplatinic acid synthesized by a described procedure [18] was used.

The IR spectra of the complexes were recorded on a SHIMADZU IRAffinity-1S FT-IR spectrometer in a range of 4000–400 cm^{-1}. Solid samples were prepared in KBr pellets.

Synthesis of tetraphenylphosphonium hexachloroplatinate(IV) (I). A solution of pentaphenylphosphorus (0.041 g, 0.1 mmol) in acetone (4 mL) was poured to a solution of hexachloroplatinic acid hydrate (0.05 g, 0.1 mmol) in acetone (4 mL). The solution was concentrated to a volume of 0.5 mL, and the formed crystals were filtered and dried. The yield of compound **I** was 0.090 g (83%) (orange crystals, T_m = 179°C (decomp.)).

IR of **I** (ν, cm^{-1}): 3062 ν(C_{Ar}–H), 1481 ν(C_{Ar}), 1436 δ(C–P).

For $C_{48}H_{40}P_2Cl_6Pt$

Anal. calcd., %	C, 53.04	H, 3.68
Found, %	C, 52.89	H, 3.84

Synthesis of tetraphenylphosphonium pentachlorodimethyl sulfoxidoplatinate (II). A weighed sample of complex **I** (0.05 g, 0.046 mmol) was dissolved in DMSO (4 mL). The crystals formed after the evaporation of the solvents. The yield of compound **II** was 0.030 g (81%) (orange crystals, T_m = 194°C).

IR of **II** (ν, cm^{-1}): 3079, 3056 ν(C_{Ar}–H), 1585, 1482 ν(C_{Ar}), 1437 δ(C–P), 1175 ν(S=O).

For $C_{26}H_{26}OSPCl_5Pt$

Anal. calcd., %	C, 39.52	H, 3.29
Found, %	C, 39.22	H, 3.76

XRD of the crystals of compounds **I** and **II** was carried out on a D8 QUEST automated four-circle diffractometer (Bruker, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data were collected and processed, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [19]. All calculations on structure determination and refinement were performed using the SHELXL/PC program [20]. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were refined by the riding model (U_{iso}(H) = 1.2U_{eq}(C)). The crystallographic data and the main refinement parameters are given in Table 1. 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 (CIF files CCDC nos. 1865783 (**I**) and 829586 (**II**); http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of pentaphenylphosphorus with an equimolar amount of hexachloroplatinic acid hydrate in acetone results in the quantitative formation of tetraphenylphosphonium hexachloroplatinate (**I**), which represents orange crystals isolated from the reaction mixture in a yield of 83%

$$2Ph_5P + H_2PtCl_6\cdot 6H_2O \rightarrow \underset{\textbf{(I)}}{[Ph_4P][PtCl_6]} + 2PhH + 6H_2O.$$

The dissolution of compound **I** in DMSO is accompanied by the ligand exchange in the $[PtCl_6]^{2-}$ anion to form tetraphenylphosphonium pentachlorodimethyl sulfoxidoplatinate (**II**) in a yield of 81%

$$[Ph_4P][PtCl_6] \xrightarrow{\text{DMSO}} \underset{\textbf{(II)}}{[Ph_4P][PtCl_5(DMSO)]} + [Ph_4P]Cl.$$

Similar reactions occur when equimolar amounts of hexachloroplatinic acid hydrate and tetraphenylphosphonium chloride interact in a solution of acetonitrile and DMSO [21] or diethyl sulfoxide (DESO) [22]

$$[Ph_4P]Cl + H_2PtCl_6\cdot 6H_2O \xrightarrow{CH_3CN,\ DMSO} [Ph_4P][PtCl_5(DMSO)] + 2HCl + 6H_2O,$$
$$2[Ph_4P]Cl + H_2PtCl_6\cdot 6H_2O \xrightarrow{CH_3CN,\ DESO} [Ph_4P][PtCl_6]\cdot CH_3CN + 2HCl + 6H_2O.$$

The IR spectra of compounds **I** and **II** exhibit absorption bands of the phenyl groups (C–H at 3062 cm^{-1} (**I**) and 3079, 3056 cm^{-1} (**II**); C=C at 1481 cm^{-1} (**I**) and 1585, 1482 cm^{-1} (**II**)) that coincide with the reference values [23]. The IR spectrum of compound **I** exhibits an intense absorption band at 1175 cm^{-1} corresponding to the S=O bond vibrations, which confirms sulfoxide binding via the sulfur atom.

According to the XRD data, the tetraphenylphosphonium cations in the structures of compounds **I** and **II** exist in a slightly distorted tetrahedral configuration (Fig. 1). The CPC bond angles vary in ranges of 107.8(3)°–113.2(3)° for compound **I** and 105.9(3)°–112.9(3)° for compound **II**. The P–C distances are 1.785(6)–1.805(6) Å (**I**) and 1.783(7)–1.791(6) Å (**II**). The platinum atoms in the anions of complexes **I** and **II** are hexacoordinated. In the $[PtCl_6]^{2-}$ octahedral

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
FW	1085.91	789.51
T, K	293.15	293.15
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.205(10)	7.767(4)
b, Å	10.970(15)	13.307(7)
c, Å	12.160(11)	1.256(7)
α, deg	73.65(4)	80.97(4)
β, deg	80.64(3)	88.21(4)
γ, deg	77.48	89.19(4)
V, Å^3	1272(2)	1454(13)
Z	1	2
ρ_{calc}, g/cm^3	1.529	1.811
μ, mm^{-1}	3.188	5.449
F(000)	582.0	770
Measurement range over θ, deg	5.7–52.92	3.49–29.13
Number of measured reflections	27973	12166
Number of independent reflections	5202	7672
Refinement variables	287	317
GOOF	1.028	1.023
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0470$, $wR_2 = 0.1252$	$R_1 = 0.0683$, $wR_2 = 0.1905$
R factors for all reflections	$R_1 = 0.0474$, $wR_2 = 0.1258$	$R_1 = 0.0941$, $wR_2 = 0.1963$
Residual electron density (min/max), e/Å^3	6.33/–1.14	–1.429/4.427

anions in the crystal of compound **I**, the ClPtCl *trans* angles are 180.0° and the *cis* angles (89.12(9)°–0.88(9)°) are close to the ideal value. The Pt–Cl bond lengths in compounds **I** and **II** are close to each other and vary within 2.309(2)–2.326(3) and 2.311(2)–2.336(2) Å, respectively. In the crystal of compound **II**, the octahedral coordination is distorted, since the values of the *trans* angles deviate from a theoretical value of 180°: S(1)PtCl(3) 178.15(8)°, Cl(1)PtCl(4) 178.88(8)°, and Cl(2)PtCl(5) 178.73(9)°. The *cis* angles differ from 90° (SPtCl 88.32(8)°–91.94(8)° and ClPtCl 88.98(10)°–91.08(9)°). The bond between the platinum atom and sulfur atom of the DMSO ligand (Pt–S 2.290(2) Å) is shortened compared to the sum of covalent radii of the indicated atoms (2.31 Å [24]). The parameters of the coordinated DMSO ligand differ from the parameters of the free DMSO molecule. The OSC(8) and OSC(9) angles in complex **II** are 111.7(6)° and 111.2(6)°, respectively, whereas similar angles in the unbound DMSO molecule are 106.7(4)° and 106.8(4)° [24]. The C(8)SC(9) (101.9(6)°) angle differs from its value in the free DMSO molecule

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

Bond	*d*, Å	Bond	*d*, Å
	I		
Pt(1)–Cl(1)	2.309(2)	Pt(1)–Cl(6)	2.327(3)
Pt(1)–Cl(2)	2.326(3)	P(1)–C(11)	1.805(6)
Pt(1)–Cl(3)	2.317(2)	P(1)–C(1)	1.802(6)
Pt(1)–Cl(4)	2.311(2)	P(1)–C(21)	1.784(6)
Pt(1)–Cl(5)	2.315(2)	P(1)–C(31)	1.801(6)
	II		
Pt(1)–Cl(6)	2.311(2)	P(1)–C(14)	1.788(6)
Pt(1)–Cl(3)	2.321(2)	P(1)–C(15)	1.790(7)
Pt(1)–Cl(4)	2.324(2)	Pt(1)–S(1)	2.290(2)
Pt(1)–Cl(1)	2.326(2)	S(1)–O(1)	1.414(8)
Pt(1)–Cl(2)	2.336(2)	S(1)–C(9)	1.763(10)
P(1)–C(17)	1.785(7)	S(1)–C(8)	1.826(12)
P(1)–C(19)	1.786(7)		
Angle	ω, deg	Angle	ω, deg
	I		
Cl(1)Pt(1)Cl(3)	90.88(9)	Cl(6)Pt(1)Cl(2)	89.79(11)
Cl(1)Pt(1)Cl(6)	180.0	Cl(1)Pt(1)Cl(4)	89.12(9)
Cl(1)Pt(1)Cl(2)	90.21(11)	C(31)P(1)C(11)	113.2(3)
Cl(3)Pt(1)Cl(4)	179.999(1)	C(1)P(1)C(11)	107.9(3)
Cl(2)Pt(1)Cl(5)	180.0	C(1)P(1)C(31)	109.1(3)
	II		
C(14)P(1)C(15)	105.9(3)	Cl(3)Pt(1)Cl(2)	88.98(10)
Cl(5)Pt(1)Cl(4)	90.87(9)	S(1)Pt(1)Cl(6)	91.94(8)
Cl(3)Pt(1)Cl(4)	90.03(9)	S(1)Pt(1)Cl(3)	178.15(8)
Cl(5)Pt(1)Cl(1)	88.99(9)	S(1)Pt(1)Cl(4)	90.57(8)
Cl(3)Pt(1)Cl(1)	91.08(9)	S(1)Pt(1)Cl(1)	88.32(8)
Cl(4)Pt(1)Cl(1)	178.88(8)	S(1)Pt(1)Cl(2)	89.28(9)
Cl(5)Pt(1)Cl(2)	178.73(9)		

(97.4°). The S–C(8) and S–C(9) bond lengths (1.824(12), 1.765(10) Å) are consistent with the values in the free molecule (1.771(8), 1.805(11) Å [25]) and the earlier published values (1.775, 1.821 Å) [26]. A comparison of the S–O bond lengths shows differences between the coordinated and free DMSO molecules. In complex **II**, this bond (1.415(8) Å) is substantially shorter than that in the free molecule (1.531 Å).

Hydrogen bonds of the C–H···Cl type (2.81–2.89 Å (**I**), 2.81–2.94 Å (**II**)) are observed in the crystals of complexes **I** and **II**. In compound **I**, each cation has short contacts with three anions. In compound **II**, each cation contacts with four anions. The anions in the crystals of complex **II** are linked with each other via C(8)–H···Cl(3) (2.92 Å) and C(9)–H···Cl(2) (2.79 Å) interactions (Fig. 2).

Thus, tetraphenylphosphonium hexachloroplatinate (**I**) was synthesized by the dephenylation of pentaphenylphosphorus with hexachloroplatinic acid hydrate in acetone. The reaction of compound **I** with

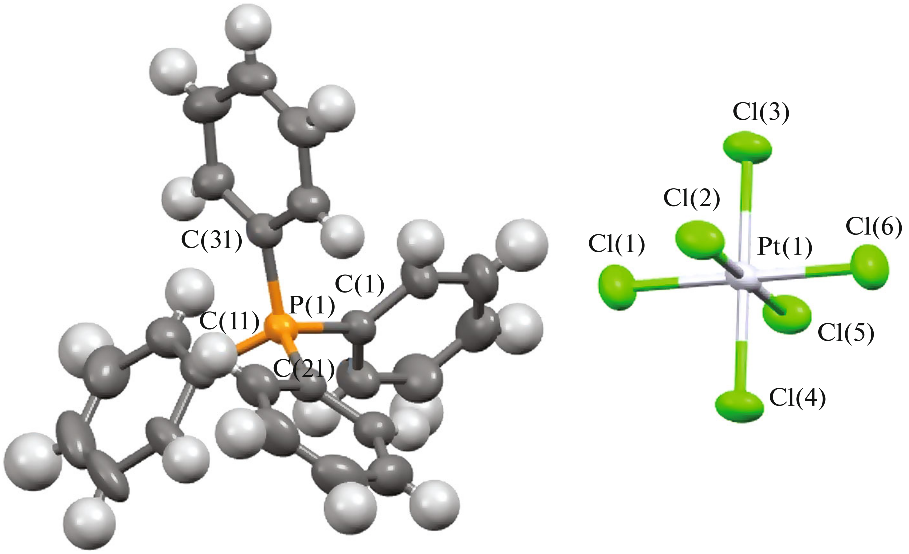

Fig. 1. Structure of complex **I**.

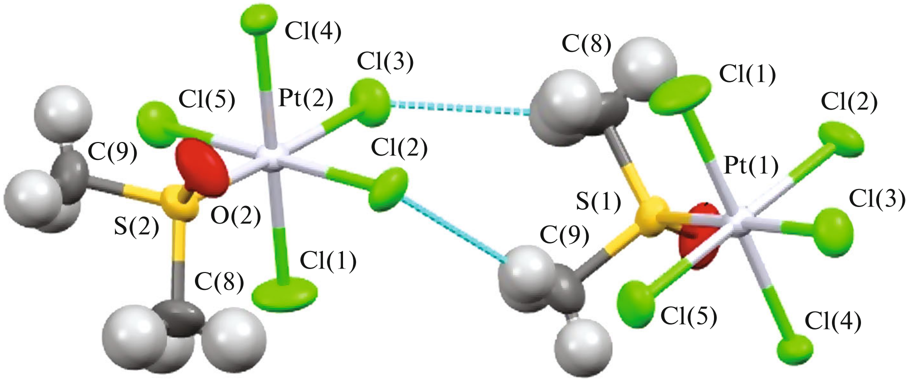

Fig. 2. Hydrogen bonds between the DMSO ligands in the crystal of complex **II**.

DMSO induces the substitution of the chlorine atom in the anion by the DMSO molecule to form the Pt–S bond. Specific features of the synthesized complexes were studied by XRD.

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CONFLICT OF INTEREST

The author declares that she has no conflicts of interest.

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