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Preparation and Structure of Acetonyltriphenylphosphonium Bis(dimethylsulfoxido)tetrachlororuthenate(III)

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Abstract—The $[Ph_3PCH_2C(O)CH_3]^+[RuCl_4(DMSO)_2]^-$ complex has been prepared via interaction of potassium hexachlororuthenate(IV) with acetonyltriphenylphosphonium chloride in the dimethylsulfoxide–ethanol mixture in the presence of hydrochloric acid. The product structure has been confirmed by X-ray diffraction studies.

Keywords: hexachlororuthenate(IV), acetonyltriphenylphosphonium, bis(dimethylsulfoxido)tetrachlororuthenate(III), X-ray diffraction analysis

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Structure of ruthenium(III) complexes containing the $[RuCl_4(DMSO)_2$-*trans*$]^-$ anion has been studied earlier; such complexes are generally prepared from ruthenium(III) chloride [1–7].

Herein we describe preparation of ruthenium(III) complex from the complex salt of ruthenium(IV). It was found that interaction of potassium hexachlororuthenate(IV) and acetonyltriphenylphosphonium chloride in the dimethylsulfoxide–ethanol mixture in the presence of hydrochloric acid gave acetonyltriphenylphosphonium *trans*-bis(dimethylsulfoxido)tetrachlororuthenate(III) (**I**). Noteworthily, the target product was not formed in the absence of ethanol.

$$[Ph_3PCH_2C(O)CH_3]Cl + K_2RuCl_6 \xrightarrow[HCl]{DMSO–EtOH} [Ph_3PCH_2C(O)CH_3]^+[RuCl_4(DMSO)_2]^-.$$

It is known that coordination of dimethylsulfoxide with metal via the oxygen atom results in the decreased frequency of S=O stretching band in the IR spectrum (by 60–70 cm^{-1} as compared with the band position for the free dimethylsulfoxide, 1055 cm^{-1}), whereas the coordination via sulfur shifts the band towards higher frequencies by 60–100 cm^{-1} [8]. IR spectrum of complex **I** contained the S=O stretching band at 1104 cm^{-1}, pointing at the DMSO coordination with ruthenium via the sulfur atom. The presence of Ru–S bonds in complex **I** was further confirmed by the strong IR absorption band at 413 cm^{-1} [7].

According to the X-ray diffraction analysis (Table 1), coordination polyhedron of phosphorus in cation of complex **I** was a distorted tetrahedron with the C–P–C bond angles ranging from 104.64(13)° to 113.53(13)°, close to the theoretical value (Fig. 1).

The $P–C_{Ph}$ bonds in the prepared complex [1.794(3)–1.800(3) Å] were somewhat shorter than the $P–C_{Alk}$ ones [1.807(3) Å] (Table 2). Dimethylsulfoxide molecules in the $[RuCl_4(DMSO)_2$-*trans*$]^-$ octahedral anion were *trans*-located and coordinated with ruthenium atom via sulfur. The values of S–Ru–S [178.51(3)°] and *trans*-Cl–Ru–Cl [176.35(4) and 177.93(4)°] bond angles evidenced about the somewhat distorted octahedral configuration of the anion. The Ru–Cl [2.3365(8)–2.3590(8) Å] and Ru–S [2.3497(7), 2.3631(7) Å] bond lengths were close to those in the complexes with similar chlorine-containing anions [2.337(2)–2.357(3) and 2.335(3)–2.356(3) Å] [1–5]. The crystal structure was formed by weak hydrogen bonds between the cations and the anions (C–H···Cl 2.66–2.82 Å; $C–H\cdots O_{DMSO}$ 2.52 and 2.62 Å) (Fig. 2).

To conclude, the ionic complex of Ru(III) with phosphonium cation and Ru-containing octahedral anion was prepared for the first time from potassium hexachlororuthenate(IV).

Table 1. Crystallographic data of complex **I**; data collection and structure refinement parameters

Parameter	Value	Parameter	Value
Formula	$C_{25}H_{32}O_3PCl_4S_2Ru$	μ, mm^{-1}	1.092
M	718.47	*F*(000)	1460.0
Crystal system	Monoclinic	Crystal size, mm	0.40×0.35×0.33
Space group	$P2_1/c$	θ range, deg	5.88–52.8
a, Å	13.6121(9)	Indexes range	$-17 \le h \le 17$, $-10 \le k \le 10$, $-34 \le l \le 34$
b, Å	8.0717(6)	Reflections collected	75666
c, Å	27.7256(19)	Independent reflections	6147
α, deg	90.00	R_{int}	0.0257
β, deg	98.352(2)	Refinement parameters	330
γ, deg	90.00	GOOF	1.155
V, $Å^3$	3014.0(4)	*R* factors over $F^2 > 2\sigma(F^2)$	R_1 0.0314, wR_2 0.0743
Z	4	*R* factors over all reflections	R_1 0.0340, wR_2 0.0757
d_{calc}, g/cm^3	1.583	Residual electron density (min/max), $e/Å^3$	0.71/–0.55

EXPERIMENTAL

IR spectrum was recorded using a Bruker Tensor 27 spectrophotometer (KBr pellets, 4000–400 cm^{-1}).

X-ray diffraction studies were performed using a D8 Quest Bruker diffractometer (MoK_α radiation, λ = 0.71073 Å, graphitic monochromator) at 296±2 K. Data collection and processing, unit cell parameters refinement, and correction for absorption were performed using SMART and SAINT-Plus software [9]. Structure elucidation and refinement was performed taking advantage of SHELXL/PC [10] and

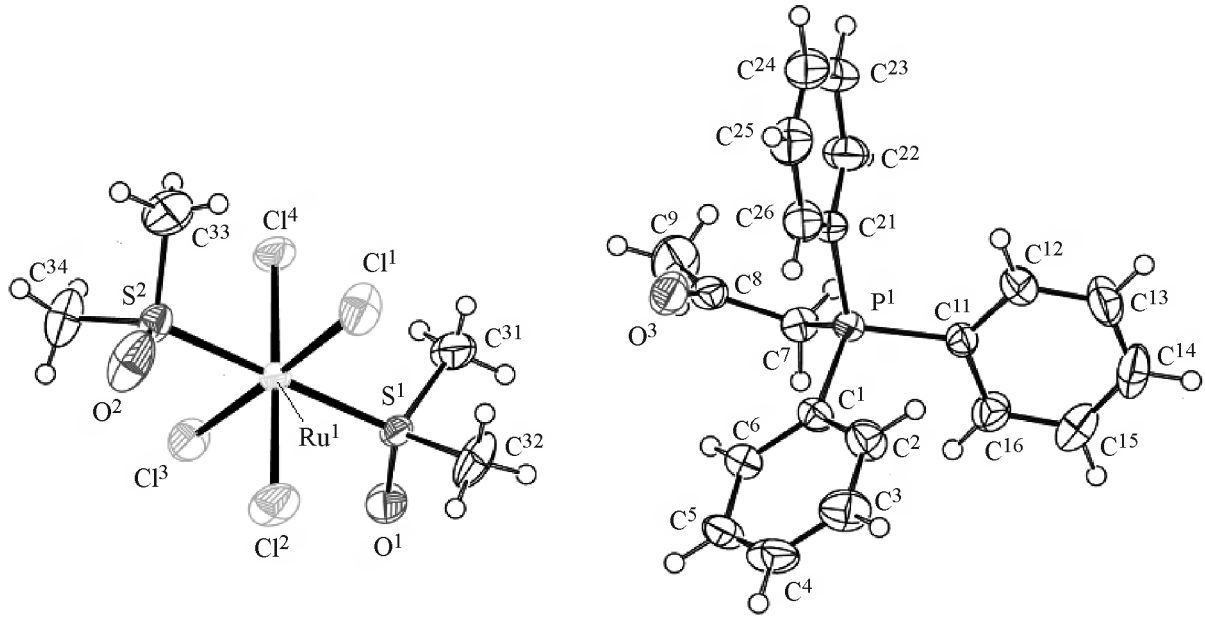

Fig. 1. General view of complex **I** molecule.

Table 2. Bond lengths and angles in molecule of complex **I**

Angle	*d*, Å	Angle	ω, deg
$Ru^1–S^1$	2.3497(7)	$S^1Ru^1Cl^1$	90.76(3)
$Ru^1–S^2$	2.3631(7)	$S^1Ru^1Cl^4$	92.80(3)
$Ru^1–Cl^1$	2.3590(8)	$S^1Ru^1S^2$	178.51(3)
$Ru^1–Cl^2$	2.3365(8)	$Cl^3Ru^1S^1$	90.35(3)
$Ru^1–Cl^3$	2.3372(8)	$Cl^3Ru^1Cl^1$	177.93(4)
$Ru^1–Cl^4$	2.3562(8)	$Cl^3Ru^1Cl^4$	87.61(3)
$S^1–O^1$	1.470(2)	$Cl^3Ru^1S^2$	90.96(3)
$S^1–C^{31}$	1.778(3)	$Cl^2Ru^1S^1$	85.71(3)
$S^1–C^{32}$	1.771(3)	$Cl^2Ru^1Cl^3$	89.06(4)
$S^2–O^2$	1.471(2)	$Cl^2Ru^1Cl^1$	92.76(4)
$S^2–C^{34}$	1.771(4)	$Cl^2Ru^1Cl^4$	176.35(4)
$S^2–C^{33}$	1.787(4)	$Cl^2Ru^1S^2$	93.60(3)
$P^1–C^{11}$	1.800(3)	$Cl^1Ru^1S^2$	87.95(3)
$P^1–C^1$	1.792(3)	$Cl^4Ru^1Cl^1$	90.59(4)
$P^1–C^{21}$	1.794(3)	$Cl^4Ru^1S^2$	87.97(3)
$P^1–C^7$	1.807(3)	$O^1S^1Ru^1$	118.41(9)
$O^3–C^8$	1.208(4)	$O^1S^1C^{31}$	106.95(17)

OLEX2 [11] software. The structure was solved via direct method and refined via least squares method in the anisotropic approximation for non-hydrogen atoms. Basic crystallographic parameters of the structure are listed in Table 1, basic bond lengths and angles are given in Table 2.

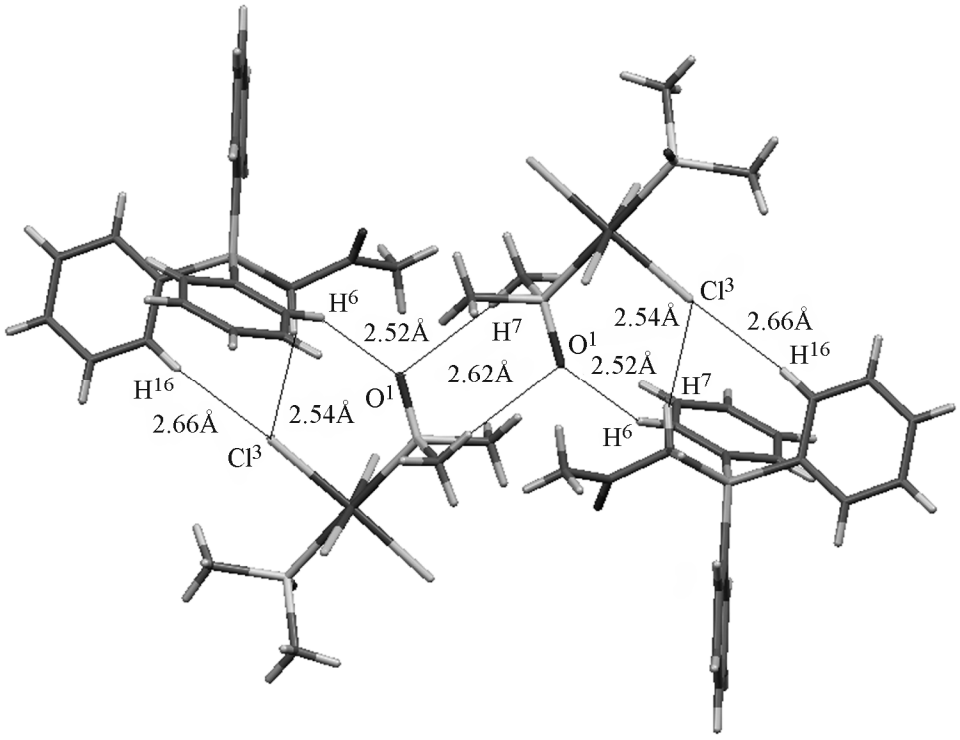

Fig. 2. Hydrogen bonds in the crystal of complex **I**.

Complete tables of atom coordinates, bond lengths and bond angles were deposited at the Cambridge Crystallographic Data Center (CCDC 1026060).

Acetonyltriphenylphosphonium *trans*-bis(dimethylsulfoxido)tetrachlororuthenate(III) (I). A mixture of 0.014 g (0.038 mmol) of acetonyltriphenylphosphonium chloride and 0.015 g (0.038 mmol) of potassium hexachlororuthenate(IV) were dissolved in 2.0 mL of dimethylsulfoxide upon stirring, and 2.0 mL of hydrochloric acid (36%) and 0.5 mL of ethanol were added. The solution was slowly evaporated to about 1 mL; 0.014 g (52%) of cherry crystals were formed, decomp. at 194°C. IR spectrum, ν, cm^{-1}: 3071, 3016, 2901, 2836, 1711, 1631, 1589, 1487, 1440, 1403, 1378, 1355, 1309, 1295, 1200, 1155, 1113, 1104, 994, 968, 935, 829, 804, 783, 752, 720, 691, 508, 492, 450, 435, 413. Found, %: C 41.67; H 4.51. $C_{25}H_{32}O_3S_2PCl_4Ru$. Calculated, %: C 41.78; H 4.46.

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