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Synthesis and Structure of the Rhodium Complex $[Ph_3MeP][RhBr_4(DMSO)_2$-*trans*]

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Abstract—The ionic complex, methyltriphenylphosphonium(I) *trans*-bis(dimethylsulfoxido)tetrabromorhodiate, was prepared by the reaction of sodium hexabromorhodiate with methyltriphenylphosphonium bromide in dimethyl sulfoxide and studied by X-ray diffraction. The phosphorus atom in the $[Ph_3MeP]^+$ cation has an almost undistorted tetragonal coordination (the CPC angles are 108.3(2)°–110.5(2)°, the P–C bonds are 1.779(6)–1.798(4) Å). In the octahedral complex anion $[RhBr_4(DMSO)_2$-*trans*$]^-$, the dimethyl sulfoxide ligands are coordinated by the sulfur atoms (Rh–S, 2.344(1), 2.336(1); Rh–Br, 2.4839(7)–2.4934(7) Å; SRhS, 179.56(7)°; *trans*-BrRhBr, 179.30(3)°, 179.56(7)°) (CIF file CCDC no. 978748).

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INTRODUCTION

The synthesis, structure, and the properties of the rhodium chloride complexes $[Kat][RhCl_4(DMSO)_2]$ (Cat = K^+, R_4N^+, R_3S^+, etc.) were described previously [1–6]. A characteristic feature of these structures is the presence of $[RhCl_4(DMSO)_2]^-$ anions with *cis*- and *trans*-positions of the dimethyl sulfoxide ligands.

Here we report the fist synthesis and X-ray diffraction study for methyltriphenylphosphonium *trans*-bis(dimethylsulfoxido)tetrabromorhodiate (**I**).

EXPERIMENTAL

Synthesis of $[Ph_3MeP]^+[RhBr_4(DMSO)_2$-*trans*$]^-$ (I). A mixture of methyltriphenylphosphonium bromide (0.022 g, 0.06 mmol) and sodium hexabromorhodiate (0.040 g, 0.06 mmol) was dissolved with stirring in dimethyl sulfoxide (2 mL). After solvent evaporation, red-brown crystals formed. The yield of complex **I** was 0.046 g (87%); the complex decomposes at 191°C.

For $C_{23}H_{30}O_2S_2PBr_4Rh$		
anal. calcd., %:	C, 32.27;	H, 3.51.
Found, %:	C, 32.21;	H, 3.63.

IR (ν, cm^{-1}): 3056, 3008, 2978, 2911, 1586, 1438, 1403, 1303, 1288, 1128, 1109, 1018, 997, 899, 877, 788, 738, 719, 685, 512, 503, 472, 420.

The IR spectrum was measured on a BrukerTensor 27 IR spectrometer in KBr pellets.

X-ray diffraction study of the crystal of **I** was carried out on a D8 Quest Bruker diffractometer (MoK_α-radiation, $\lambda = 0.71073$ Å, graphite monochromator). Data collection and editing and refinement of unit cell parameters were performed and absorption corrections were applied by the programs SMART and SAINT-Plus [7]. All calculations for the structure solution and refinement were performed by SHELXL/PC package [8]. The structure of **I** was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement details for **I** are presented in Table 1 and selected bond lengths and bond angles are in Table 2.

Full tables of atom coordinates, bond lengths, and bond angles are deposited at the Cambridge Crystallographic Data Centre (No. 978748; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Complex **I** was synthesized from sodium hexabromorhodiate and methyltriphenylphosphonium bromide in dimethyl sulfoxide.

$$Ph_3MePBr + Na_3RhBr_6$$
$$\xrightarrow{DMSO} [Ph_3MeP]^+[RhBr_4(DMSO)_2\text{-}\mathit{trans}]^- + 3NaBr.$$

Stirring of equimolar amounts of the starting reactants in dimethyl sulfoxide resulted in a change in the solution color to red-brown; evaporation of the solvent gave the target product in 87% yield.

According to X-ray diffraction data, the phosphorus atom in $[Ph_3MeP]^+$ has a slightly distorted tetragonal coordination (the CPC angles are 108.3(2)°–110.5(2)°, Fig. 1). The P–C bond lengths (1.779(6)–1.798(4) Å) also differ insignificantly and do not

Table 1. Crystallographic data and X-ray experiment and structure refinement details for **I**

Parameter	Value
Formula	$C_{23}H_{30}O_2PS_2Br_4Rh$
M	856.11
T, K	296(2)
System	Triclinic
Space group	$P\bar{1}$
a, Å	8.4894(3)
b, Å	9.1120(3)
c, Å	11.2647(4)
α, deg	70.811(1)
β, deg	81.396(1)
γ, deg	63.548(1)
V, Å^3	736.81(4)
Z	1
ρ_{calcd}, g/cm^3	1.929
μ, mm^{-1}	6.218
F(000)	416
Crystal size, mm	0.30 × 0.20 × 0.08
Data collection range over θ, deg	3.288–26.082
Ranges of reflection indices	$-10 \le h \le 10$, $-11 \le k \le 11$, $-13 \le l \le 13$
The number of measured reflections	18259
The number of independent reflections	5490
The number of refinement parameters	299
GOOF	1.043
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0179$, $wR_2 = 0.0408$
R factors for all reflections	$R_1 = 0.0198$, $wR_2 = 0.0415$
Residual electron density (min/max), e/Å^3	−0.338/0.31

Table 2. Selected bond lengths and bond angles in structure **I**

Bond	d, Å	Bond	d, Å
Rh(1)–S(1)	2.3439(13)	P(1)–C(11)	1.798(4)
Rh(1)–S(2)	2.3365(13)	P(1)–C(17)	1.791(4)
Rh(1)–Br(1)	2.4914(7)	S(1)–C(1)	1.774(7)
Rh(1)–Br(2)	2.4839(7)	S(1)–C(2)	1.787(6)
Rh(1)–Br(3)	2.4934(7)	S(2)–C(3)	1.775(7)
Rh(1)–Br(4)	2.4841(7)	S(2)–C(4)	1.779(7)
P(1)–C(23)	1.791(4)	S(2)–O(1)	1.468(4)
P(1)–C(5)	1.779(6)	S(1)–O(2)	1.468(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
S(2)Rh(1)S(1)	179.56(7)	S(1)Rh(1)Br(1)	88.82(4)
Br(2)Rh(1)Br(4)	179.30(3)	S(2)Rh(1)Br(3)	89.10(4)
Br(1)Rh(1)Br(3)	179.89(4)	S(1)Rh(1)Br(3)	91.24(4)
Br(2)Rh(1)Br(1)	91.30(2)	O(1)S(2)C(3)	106.7(3)
Br(4)Rh(1)Br(1)	89.40(3)	O(2)S(1)C(1)	106.9(3)
Br(2)Rh(1)Br(3)	88.61(2)	C(5)P(1)C(17)	110.0(2)
Br(4)Rh(1)Br(3)	90.69(2)	C(5)P(1)C(23)	109.8(3)
S(2)Rh(1)Br(2)	92.04(4)	C(17)P(1)C(23)	108.3(2)
S(1)Rh(1)Br(2)	87.69(4)	C(5)P(1)C(11)	110.5(2)
S(2)Rh(1)Br(4)	87.95(4)	C(17)P(1)C(11)	108.32(18)
S(1)Rh(1)Br(4)	92.32(4)	C(23)P(1)C(11)	110.0(2)
S(2)Rh(1)Br(1)	90.84(4)		

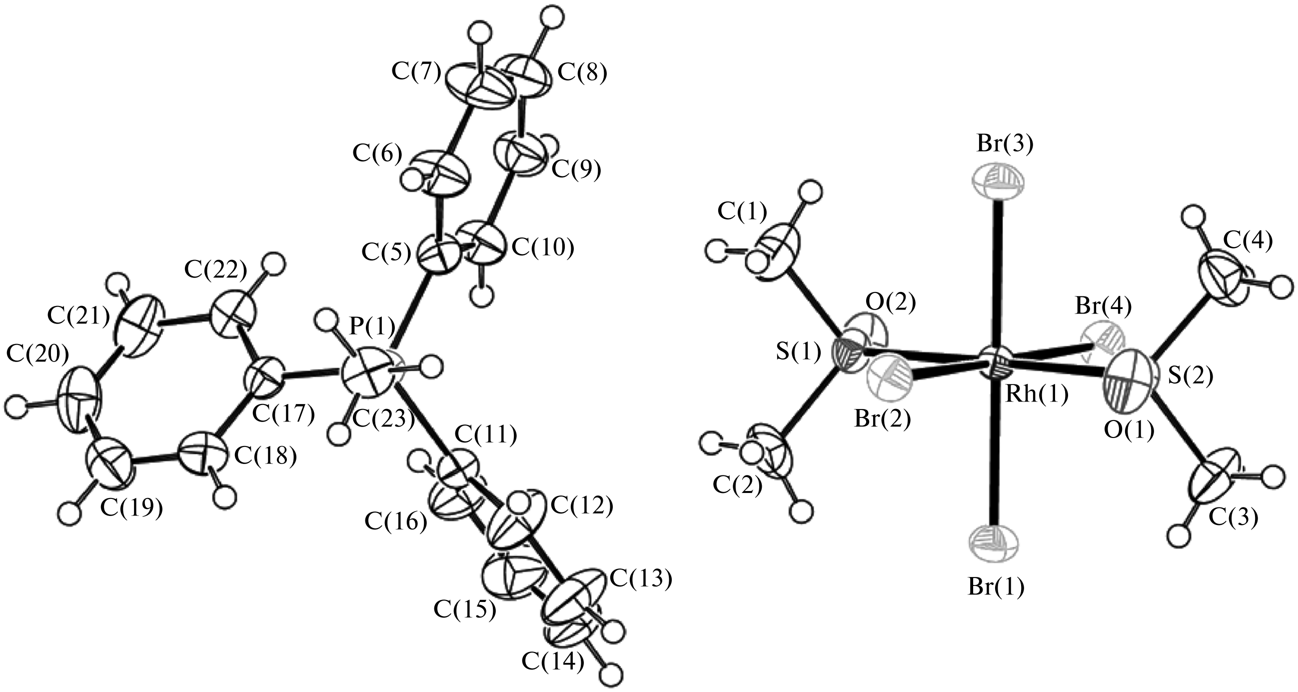

Fig. 1. Structure of complex **I**.

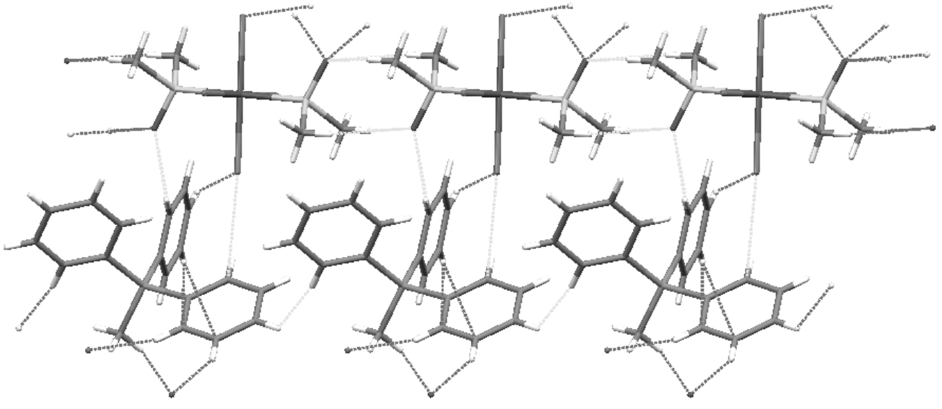

Fig. 2. Cation and anion interaction system in the crystal of **I**.

depend on the radical nature. In the $[RhBr_4(DMSO)_2$-*trans*$]^-$ complex anion, the DMSO molecules that occupy *trans*-positions are coordinated to rhodium through the sulfur atom. The SRhS angle of 179.56(7)° and the BrRhBr angles of 179.30(3)° and 179.56(7)° attest to virtually perfect octahedral configuration of the anion.

The Rh–Br bond lengths are 2.4839(7)–2.4934(7) Å. The Rh–S distances in **I** (2.344(1), 2.336(1) Å) are close to the values found for complexes with chloro-containing anions $[RhCl_4(DMSO)_2$-*trans*$]^-$ (2.318(1)–2.336(1) Å) [1–4, 6], whereas in the anions with *cis*-arrangement of the ligands, the corresponding Rh–S distances are much shorter (2.256(1)–2.294(1) Å) [1, 5].

The structural organization of the crystal of **I** is formed by intermolecular hydrogen bonds. The anions are combined into polymeric chains by a system of hydrogen bonds formed by dimethyl sulfoxide ligands: O···H(Me) (O···H 2.59–2.66 Å) (Fig. 2). The chain of cations is linked to two neighboring anion chains by the hydrogen bonds O···H(Ph) and O···H(Me) 2.41–2.70 Å and Br···H(Ph) 2.90, 2.92 Å.

Thus, a complex with the phosphonium cation and Rh,Br-containing anion in which the S-coordinated DMSO molecules occupy *trans*-positions was synthesized and studied by X-ray diffraction for the first time.

The strength of Rh—S binding does not depend on the halogen nature in the anion but is determined by the position of the dimethyl sulfoxide ligand. The crystal of $[Ph_3MeP]^+[RhBr_4(DMSO)_2\text{-}trans]^-$ is formed through intermolecular hydrogen bonds.

REFERENCES

1. Abbasi, A., Geranmayeh, S., Skripkin, M.Y., and Eriksson, L., *Dalton Trans.*, 2012, vol. 41, p. 850.
2. Calligaris, M. and Faleschini, P., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, vol. 51, p. 588.
3. Gamage, S.N., Morris, R.H., Rettig, S.J., et al., *Chem. Commun.*, 1987, p. 894.
4. James, B.R., Morris, R.H., Einstein, F.W.B., and Willis, A., *Chem. Commun.*, 1980, p. 31.
5. Alessio, E., Santi, A.S., Faleschini, P., et al., *Dalton Trans.*, 1994, no. 13, p. 1849.
6. Gamage, S.N., James, B.R., Rettig, S.J., and Trotter, J., *Can. J. Chem.*, 1988, vol. 66, p. 1123.
7. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System,* Madison (WI, USA): Bruker AXS Inc., 1998.
8. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,* Madison (WI, USA): Bruker AXS Inc., 1998.

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