ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 12, pp. 779–782. © Pleiades Publishing, Ltd., 2016.
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Synthesis and Structure of the Rhodium Complex $[p\text{-Tol}_4Sb(DMSO\text{-}O)]_2^+[trans\text{-}RhBr_4(DMSO\text{-}S)_2]^-[cis\text{-}RhBr_4(DMSO\text{-}S)_2]^-$

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Received January 25, 2016

Abstract—The complex $[p\text{-(Tol)}_4Sb(DMSO\text{-}O)]_2^+[trans\text{-}RhBr_4(DMSO\text{-}S)_2]^-[cis\text{-}RhBr_4(DMSO\text{-}S)_2]^-$ (CIF file CCDC no. 1415243) was synthesized by the reaction of sodium hexabromorhodate with tetra(*para*-tolyl)stibonium bromide in DMSO and studied by X-ray diffraction. The antimony atoms in two types of crystallographically independent $[p\text{-Tol}_4Sb(DMSO\text{-}O)]^+$ cations have a distorted trigonal-bipyramidal coordination with axially arranged DMSO oxygen atoms (Sb–C, 2.088(9)–2.135(10) Å; Sb···O, 2.641(10), 2.690(10) Å). In the octahedral $[trans\text{-}RhBr_4(DMSO\text{-}S)_2]^-$ and $[cis\text{-}RhBr_4(DMSO\text{-}S)_2]^-$ anions, the dimethyl sulfoxide ligands are coordinated to the metal via the sulfur atoms. The Rh–S distances are longer in the *trans*-isomer (2.333(2), 2.339(2) Å) than in the *cis*-isomer (2.303(3), 2.318(4) Å).

Keywords: *trans*-bis(dimethyl sulfoxido)tetrabromorhodate, *cis*-bis(dimethyl sulfoxido)tetrabromorhodate, (dimethyl sulfoxido)tetraphenylstibonium, complex, synthesis, structure

DOI: 10.1134/S1070328416120058

INTRODUCTION

The rhodium(III) chloro dimethyl sulfoxide complexes $[RhCl_x(DMSO)_{6-x}]_{3-x}$ ($x = 1$–4) exist as two or more isomers, which differ by both the geometry and the dimethyl sulfoxide (DMSO) coordination mode [1]. It is of interest that the number of DMSO molecules attached to Rh(III) via a sulfur atom in these complexes does not exceed two. The subsequent increase in the number of ligands leads to increasing number of O-coordinated molecules, and the DMSO-O ligand preferably occurs in the *trans*-position to DMSO-S [2–4].

The synthesis, structure, and properties of the ionic rhodium chloride complexes like $[Cat]^+[RhCl_4(DMSO)_2]^-$ (Cat = K^+, R_4N^+, R_3S^+, etc.) were described in [5–10]. A specific feature of these structures is the presence of $[RhCl_4(DMSO)_2]^-$ anions with *cis*- and *trans*-positions of dimethyl sulfoxide ligands.

Rhodium(III) bromodimethyl sulfoxide complexes have been less studied [11, 12]. The only structurally characterized rhodium bromide complex, $[Ph_3MeP]^+[trans\text{-}RhBr_4(DMSO\text{-}S)_2]^-$, has *trans*-arranged dimethyl sulfoxide groups coordinated to rhodium via sulfur [12].

Here we synthesized and structurally characterized the first rhodium(III) bromo dimethyl sulfoxide complex, $[p\text{-Tol}_4Sb(DMSO\text{-}O)]_2^+[trans\text{-}RhBr_4(DMSO\text{-}S)_2]^-[cis\text{-}RhBr_4(DMSO\text{-}S)_2]^-$ (**I**), containing isomeric anions with *trans*- and *cis*-coordinated ligands.

EXPERIMENTAL

Synthesis of I. A mixture of tetra-*para*-tolylstibonium bromide (0.043 g, 0.08 mmol) and sodium hexabromorhodate(III) (0.050 g, 0.08 mmol) was dissolved with stirring in 2 mL of DMSO. The solution was concentrated to give red-brown crystals, which were collected on a filter and dried. The yield of complex **I** was 0.054 g (62%). $T_{dec.} = 155$°C.

IR (ν, cm^{-1}): 3010, 2989, 2912, 1589, 1492, 1444, 1394, 1313, 1211, 1190, 1129, 1066, 1015, 956, 801, 714, 677, 580, 484, 419.

For $C_{34}H_{46}O_3S_3Br_4RhSb$		
anal. calcd., %:	C, 35.72;	H, 4.03.
Found, %:	C, 35.54;	H, 4.11.

The IR spectrum was measured on a Bruker Tensor 27 IR spectrometer for a KBr pellet.

Single crystal X-ray diffraction study of **I** was performed on a D8 Quest Bruker diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator). The SMART and SAINT-Plus software packages were used for data collection and editing, refinement of unit

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

Parameter	Value
M	1143.19
T, K	296(2)
System	Monoclinic
Space group	$P2_1$
a, Å	9.5564(3)
b, Å	19.2473(6)
c, Å	22.9300(8)
β, deg	98.7980(10)
V, Å^3	4168.0(2)
Z	4
ρ_{calcd}, g/cm^3	1.822
μ, mm^{-1}	5.060
F(000)	2232.0
Crystal size, mm	0.21 × 0.08 × 0.08
θ range, deg	2.897–26.372
Ranges of reflection indices	$-11 \le h \le 11$, $-24 \le k \le 24$, $-28 \le l \le 28$
Collected reflections	117592
Unique reflections	16978
Number of refinement parameters	867
GOOF	1.009
R-factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0406$, $wR_2 = 0.0803$
R-factors for all reflections	$R_1 = 0.0703$, $wR_2 = 0.0907$
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	−0.691/1.064

cell parameters, and application of absorption corrections [13]. All calculations for structure solution and refinement were performed using SHELXL/PC software [14]. The structure of **I** was determined by direct methods and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms. The key crystallographic data and structure refinement details for **I** are summarized in Table 1, and selected bond lengths and bond angles are given in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (no. 1415243; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In most cases, rhodium(III) dimethyl sulfoxide complexes are prepared from hydrated rhodium(III) chloride [1]. We synthesized complex **I** from equimolar amounts of sodium hexabromorhodate and tetra-*para*-tolylstibonium bromide in dimethyl sulfoxide:

$$(p\text{-Tol})_4SbBr + Na_3RhBr_6 \xrightarrow{DMSO} \mathbf{I} + 3NaBr.$$

Stirring of the reactants in DMSO resulted in a change in the solution color to red-brown. As the solvent evaporated, the product precipitated as red-brown crystals.

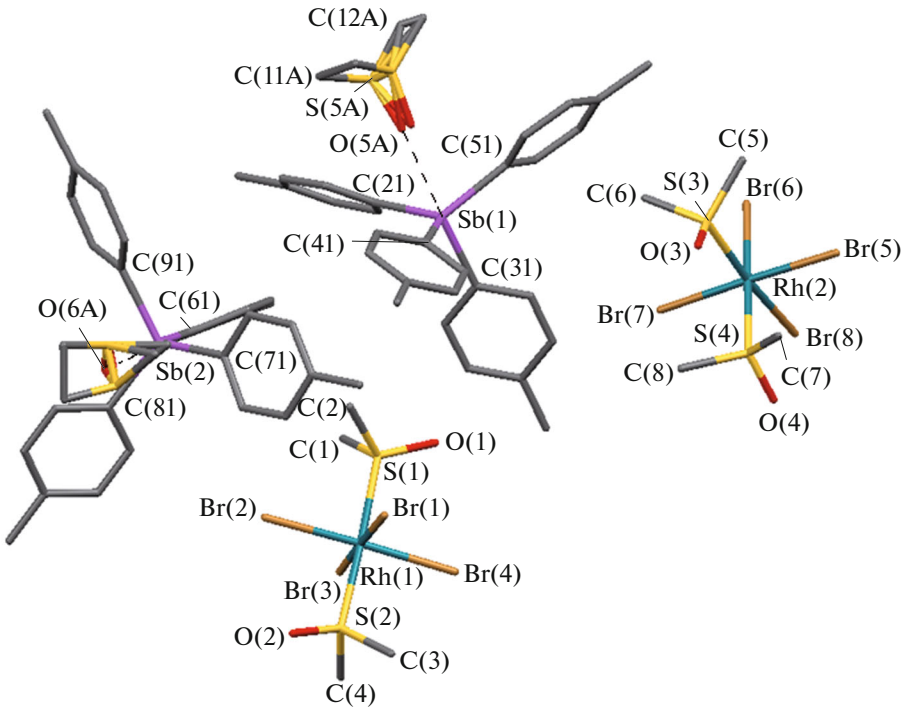
According to X-ray diffraction data, the crystal of complex **I** (figure) comprises two crystallographically independent $[(p\text{-Tol})_4Sb(DMSO\text{-}O)]^+$ cations in which the antimony atoms have a distorted trigonal-bipyramidal coordination, being bound to DMSO molecules disordered over two positions.

The DMSO molecule coordinated to antimony via oxygen occupies the pseudo-axial position. The C(31)Sb(1)O(5A) angles are 177.5(2)° (C(61)Sb(2)O(6A) 179.1(3)°; hereinafter, the values for the Sb(2) cation are given in parentheses). The sum of the CSb(1)C angles in the pseudo-equatorial plane is 348.0(3)° (348.3(3)°). The axial C(31)–Sb(1) bond of 2.134(10) (2.134(10) Å) is longer than the equatorial Sb(1)–C bonds: 2.093(9), 2.112(9), and 2.123(8) (2.088(10), 2.098(8), and 2.102(8) Å). The Sb(1)···O(5A) distance is 2.690(9) (2.641(10) Å).

In the isomeric octahedral anions, [*trans*-$RhBr_4(DMSO\text{-}S)_2]^-$ and [*cis*-$RhBr_4(DMSO\text{-}S)_2]^-$, the DMSO molecules are coordinated to rhodium via sulfur. The bond angles are 87.69(7)°–92.83(4)° at the Rh(1) atom and 85.85(10)°–95.99(14)° at Rh(2); the largest angle is S(3)Rh(2)S(4). The average Rh(1)–Br and Rh(2)–Br bonds (2.4855(14) Å and 2.4820(16) Å) are somewhat shorter in **I** than in $[Ph_3MeP]^+$[*trans*-$RhBr_4(DMSO\text{-}S)_2]^-$ (2.4882(7) Å) [12]. The Rh(1)–S distances (2.333(2), 2.339(2) Å) in **I** are close to those found in $[Ph_3MeP]^+$[*trans*-$RhBr_4(DMSO\text{-}S)_2]^-$

Table 2. Selected bond lengths (*d*) and bond angles (ω) in structure **I**

Bond	*d*, Å	Angle	ω, deg
C(51)–Sb(1)	2.112(9)	C(21)Sb(1)C(51)	119.1(3)
C(31)–Sb(1)	2.134(10)	C(41)Sb(1)C(51)	113.1(3)
C(41)–Sb(1)	2.093(9)	C(21)Sb(1)C(41)	115.8(4)
C(21)–Sb(1)	2.123(8)	O(5A)Sb(1)C(31)	177.5(2)
O(5A)···Sb(1)	2.690(9)	C(71)Sb(2)C(91)	113.8(4)
C(61)–Sb(2)	2.134(10)	C(81)Sb(2)C(91)	116.8(4)
C(71)–Sb(2)	2.098(8)	C(71)Sb(2)C(81)	117.7(3)
C(81)–Sb(2)	2.102(8)	O(6A)Sb(2)C(61)	179.1(3)
C(91)–Sb(2)	2.088(10)	S(2)Rh(1)S(1)	175.34(10)
O(6A)···Sb(2)	2.641(10)	Br(1)Rh(1)Br(3)	178.29(5)
S(1)–Rh(1)	2.339(2)	Br(4)Rh(1)Br(2)	177.18(5)
S(2)–Rh(1)	2.333(2)	S(2)Rh(1)Br(1)	87.69(7)
S(3)–Rh(2)	2.303(3)	S(2)Rh(1)Br(2)	89.35(7)
S(4)–Rh(2)	2.318(4)	S(2)Rh(1)Br(3)	92.71(7)
Br(1)–Rh(1)	2.4789(12)	S(2)Rh(1)Br(4)	90.21(7)
Br(2)–Rh(1)	2.4928(13)	Br(1)Rh(1)Br(2)	92.83(4)
Br(3)–Rh(1)	2.4853(14)	Br(1)Rh(1)Br(4)	89.94(4)
Br(4)–Rh(1)	2.4849(14)	Br(3)Rh(1)Br(2)	88.84(4)
Br(5)–Rh(2)	2.4819(16)	Br(4)Rh(1)Br(3)	88.41(4)
Br(6)–Rh(2)	2.4961(19)	S(3)Rh(2)Br(8)	173.31(11)
Br(7)–Rh(2)	2.4779(14)	S(4)Rh(2)Br(6)	177.85(11)
Br(8)–Rh(2)	2.4723(15)	S(3)Rh(2)S(4)	95.99(14)
O(1)–S(1)	1.474(8)	S(3)Rh(2)Br(5)	89.41(10)
O(2)–S(2)	1.436(8)	S(3)Rh(2)Br(6)	85.85(10)
O(3)–S(3)	1.425(9)	S(3)Rh(2)Br(7)	92.06(10)
O(4)–S(4)	1.408(12)	S(4)Rh(2)Br(5)	88.68(11)



Structure of complex **I**.

and are longer than the Rh(2)–S distances (2.303(3), 2.318(4) Å).

The shortening of the Rh–S bonds in the *cis*-isomeric $[RhCl_4(DMSO\text{-}S)_2]$ anions compared with the *trans*-isomers was attributed [9] to higher thermodynamic stability of the *cis*-isomers.

The structural organization of crystal **I** is formed by intermolecular hydrogen bonds O···H (2.30–2.60), S···H (2.79–2.86), and Br···H (2.79–3.05 Å).

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Translated by Z. Svitanko