L. V. Shirshova, I. P. Lavrent'ev	UDC 542.91:548.737:541.49:547.279.53:
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The ionic silver complexes $[Me_2S^+CH_2COR]AgX_2^-$, where X is Br or I and R is Me or Ph, in the Ag⁰(AgX)-DMSO-HX-ketone system are synthesized and characterized by the x-ray structural method.

It was established previously that a silver halide and its trimethylsulfonium salts $[Me_3S^+]AgX_2^-$ and $[Me_3S^+]Ag_2X_3^-$ [1] are the products of the oxidative dissolution of silver in the DMSO-HX (where X is Br or I) system. On further study of silver-complex formation in this metal-oxidizing system in the presence of ketones it is observed that carbonyl-containing sulfonium salts of silver halides are the reaction products, the formation of which, similar to those described by Nozaki et al. [2], can be formally represented as the condensation of DMSO with ketones in acid medium in the presence of silver halides:

$$Me_{2}S = 0 + R' - CH_{2} - CO - R \xrightarrow{HAgX_{2}} [Me_{2}S^{+} - CH_{2} - CO - R] AgX_{2}^{-}$$
(1)
(I)-(IV)

where R is CH_3 , X is Br (I); R is CH_3 , X is I (II); R is C_6H_5 , X is Br (III); R is C_6H_5 , X is I (IV); R' is H or CH_3CO .

Complexes (I)-(IV) are identified by elemental analysis and IR spectroscopy (Table 1). Complexes (I)-(III) are studied by x-ray diffraction analysis.

The isostructural compounds (I) and (II) contain a chain of tetrahedral [AgX₄⁻] anions, bonded to each other along an edge in the direction of the shortest parameter c (Fig. 1). The differences in the Ag-X bond lengths in the tetrahedra are small [0.08 Å for Br, 0.05 Å for (I)], but the angular distortions are larger, i.e., up to 20°. The mean Ag-Br distances are larger than the sum of the covalent radii by 10%, as against $\sim 3\%$ for Ag-I. In the sulfur-containing cation the distances and angles are within the usual limits (Table 2), the "acetone" part of the cation being planar. The dihedral angle between the carbon atoms at the base of the sulfur pyramid and the "acetone" part is $\sim 40^{\circ}$. On formation of a cation at the sulfur and oxygen atoms there are two limiting possibilities for the mutual arrangement relative to the C³-C⁴ bond. A cis position is produced in the structure, the fragment C³C⁴O is close to planar, the torsion angle is 7°; and the S...O distances, 2.81 Å (Br)

Compound	vC—S				ðCH₃			vС—Н	
	s	as	ρCH₃	vCCO	8	as	vC=0	s	as
(I), (II)	570 675	765 785	940 1000 1035 1055	1165	1300 1360	1410 1440	1720	2915 2945	299 5 30 20
(III), (IV)	565 635 690	760	935 1005 1050	1190 1220	1305 1330 1375	1415 1445	1680	2910 2940	299 0 30 10 30 20

TABLE 1. IR Spectra of Complexes (I)-(IV), ν , cm⁻¹ [3-5]

*Deceased.

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TABLE 2. Distance and Angles in the Cation $[Me_2S^+CH_2COCH_3]$ in Structures (I) and (II)*

Atom	d,	Å	- Atom	ω, deg		
ALOM .	X=I	X=Br		X=I	X=Br	
$ \begin{array}{c} S-C^{1} \\ S-C^{2} \\ S-C^{3} \\ C^{3}-C^{4} \\ C^{4}-C^{5} \\ C^{4}-O \\ S-O \end{array} $	1,81 1,78 1,82 1,54 1,56 1,22 2,82	1,79 1,80 1,80 1,49 1,51 1,23 2,81	$\begin{array}{c} C^{1}-S-C^{2}\\ C^{1}-S-C^{3}\\ C^{2}-S-C^{3}\\ S-C^{3}-C^{4}\\ C^{3}-C^{4}-C^{5}\\ C^{3}-C^{4}-O\\ C^{5}-C^{4}-O\\ C^{5}-C^{4}-O\\ \end{array}$	$\begin{array}{c} 99.5\\ 103.6\\ 100.6\\ 107.1\\ 111.4\\ 122.5\\ 126.0 \end{array}$	101.5 104.7 99,7 110.0 117,1 120.1 122,8	

*Standard error in distances, 0.02 Å; in angles, 0.5°.



Fig. 1. Projection of the structure [Me₂SCH₂COCH₃]AgX₂ [(I) and (II)] on the *ab* plane.

and 2.82 Å (I), can be considered as due to intramolecular electrostatic interaction, which exceeds steric repulsion in the cis position.

Structure (III) consists of (Fig. 2) the tetrahedral anions $[AgBr_4^-]$, bonded through the common side of the tetrahedron into an endless chain, oriented along the crystal c axis. The Ag...Ag and Ag-Br distances are 3.708 and 2.713-2.725 Å respectively. The distribution of valence angles (94.1-117.8°) indicates a certain elongation of the tetrahedron along the c axis. The singly charged cation $[(CH_3)_2SCH_2COC_6H_5^+]$ is at the same level as the sulfur atoms. The cations in the direction of the c axis are stacked in an antiparallel "stack" devoid of shortened intermolecular contacts. The "stacks" can be combined into "layers," which overstack the "layers" from the chains of anions in the direction of the largest period α . In the cation the acetophenone fragment is planar, and the peripheral S atoms and the C² and C¹ carbon atoms deviate from this plane by 0.43, -0.85, and 0.99 Å, respectively. The S atoms retain their typical pyramidal structure, the pyramid base (C¹, C², and C³) forming an angle of 48° with the acetophenone.

There are several paths for the formation of structures (I)-(IV): condensation [2] or nucleophilic substitution of halogen in halogenosulfonium salts [6]. Reaction (1) also

Anions in Structures (I) and (II)* d, Å ω, deg ω, deg Atom d, Å Atom Ag-Br¹ 2,7342,758Ag-I 2.881Ag-Br¹ Ag-Br² Ağ-I'' 2,887 2,688 Ag-I² 2.835 Ag-Br²' Br¹-Br² 2,711 4,744 -1² 2,862 Ag 122,0 4,940 119,6 102.4 Br1-Br1 4,216 4,436 100,5 Br²-Br²' 112,4 4,487 - 12 4,750 113,0

104,4

103,2

112,1

4,561

4,302

4,656

Br1'-Br2

 $\mathbf{Br^{1}-Br^{2}'}_{\mathbf{Br^{1}'-Br^{2}'}}$

TABLE 3. Interatomic Distances and Valence Angles in [AgX₂⁻]

*The errors in the Ag-X and X-X distances are 0.002 and 0.004 Å, respectively, and in the X-Ag-X angles, 0.1°.

- T2

-I2

4,545

4,545

4,809

105,2

104,6

113.5



Fig. 2. Projection of the structure $[Me_2SCH_2COC_6H_5]AgBr_2$ (III) on the *a*b plane.

occurs on introduction of AgX (product from the oxidative dissolution of silver) into an $Me_2S \cdot I_2$ solution in the appropriate ketone (acetone, acetylacetone, acetophenone). With this as the starting point, it can be assumed that active electrophilic particles, i.e., the products from the interaction of the components of the DMSO-HX system, are involved in formation of (I)-(IV), and are simultaneously active in the oxidative dissolution of silver. Either $[Me_2S^*X]X^-$, or (A) [7] can be active electrophilic particles in the DMSO-HX system.

$$[Me_{2}S^{+}-OH]X^{-}+CH_{3}-CO-R\xrightarrow{AX}_{-H_{2}O}(I)-(IV)$$
(A)
(2)

Excess DMSO relative to HX (DMSO/HX > 5, yield about 87%) creates optimum conditions for synthesis of (I)-(IV), from which it can be concluded that the particle (A), formed when the DMSO is in excess, takes part in formation of (I)-(IV).

The particle (A) is obviously responsible for the interaction of $Me_2S \cdot I_2$ with ketone in the presence of AgX [8, 9],

Atom	d, Å	Atom	ω, deg
$\begin{array}{c} Ag - Br^{1} \\ Ag - Br^{1} \\ Ag - Br^{2} \\ Ag - Br^{2} \\ S - C^{1} \\ S - C^{2} \\ S - C^{3} \\ C^{3} - C^{4} \\ C^{4} - C^{5} \\ C^{5} - C^{6} \\ C^{5} - C^{6} \\ C^{5} - C^{6} \\ C^{7} - C^{8} \\ C^{8} - C^{9} \\ C^{9} - C^{10} \\ O - C^{4} \\ S \dots O \\ Ag \dots Ag \end{array}$	$\begin{array}{c} 2,725(1)\\ 2,717(1)\\ 2,716(1)\\ 2,713(1)\\ 1,798(7)\\ 1,801(7)\\ 1,801(6)\\ 1,512(8)\\ 1,471(8)\\ 1,387(9)\\ 1,374(8)\\ 1,396(10)\\ 1,376(10)\\ 1,353(14)\\ 1,411(12)\\ 1,216(8)\\ 2,789(9)\\ 3,708(2)\\ \end{array}$	$\begin{array}{c} Br^{2'} - Ag - Br^{2} \\ Br^{2'} - Ag - Br^{1'} \\ Br^{2'} - Ag - Br^{1} \\ Br^{2} - Ag - Br^{1} \\ Br^{2} - Ag - Br^{1} \\ Br^{2} - Ag - Br^{1} \\ Br^{1'} - Ag - Br^{1} \\ C^{1} - S - C^{2} \\ C^{4} - S - C^{3} \\ C^{2} - S - C^{3} \\ C^{4} - C^{5} \\ C^{3} - C^{4} - C^{5} \\ C^{3} - C^{4} - C^{5} \\ C^{4} - C^{2} - C^{6} \\ C^{4} - C^{5} - C^{10} \\ C^{5} - C^{4} - C^{9} \\ C^{5} - C^{10} - C^{9} \\ \end{array}$	$\begin{array}{c} 103,3(1)\\ 117,8(1)\\ 114,6(1)\\ 114,6(1)\\ 112,8(1)\\ 114,9(1)\\ 94,1(1)\\ 94,1(1)\\ 101,5(4)\\ 103,9(4)\\ 100,7(3)\\ 109,5(5)\\ 118,8(5)\\ 122,6(5)\\ 118,8(5)\\ 122,6(5)\\ 118,6(5)\\ 122,6(6)\\ 119,4(7)\\ 119,9(8)\\ 120,7(8)\\ 120,7(8)\\ 120,3(7)\\ 119,3(7)\\ \end{array}$

TABLE 4. Interatomic Distances and Valence Angles in Structure (III)

$$\operatorname{Me}_{2} S \cdot I_{2} \rightleftharpoons [\operatorname{Me}_{2} S^{+} I] I^{-} \xrightarrow{\operatorname{H}_{2} O} [\operatorname{Me}_{2} S^{+} - OH] I^{-}$$
(3)

We established that when HI is introduced into the $Me_2S \cdot I_2$ -AgI-acetone system, the complex (II) is not formed.

Silver halides evidently stabilize the intermediate sulfonium cations [6]

$$(A) \xrightarrow{AgX} [Me_2S^+ - OH]AgX_2^-$$
(4)

The special features of reaction (1) for acetylacetone should be noted. In contrast to [2], reaction of acetylacetone with DMSO involves breaking of the C-C bond and splitting off of an acyl fragment. Compounds (I)-(IV) are also formed on dissolution of $[Me_3S^+]AgX_2^-$ or $[Me_3S^+]Ag_2X_3^-$ [1] in the DMSO (excess)-HX-ketone system,

$$[Me_{3}S^{+}]AgX_{2}^{-} + [Me_{2}S^{+} - Y]X^{-} + CH_{3} - CO - R \rightarrow \rightarrow [Me_{2}S^{+} - CH_{2} - CO - R]AgX_{2}^{-} + [Me_{3}S^{+}]X^{-} Y = OH, X.$$
(5)

EXPERIMENTAL

A two-necked flask fitted with a magnetic stirrer and a reflux condenser was used for the tests on silver dissolution. The silver powder was obtained by production of AgI with atomic hydrogen and subsequent repeated purification. Tablets of dimensions $27 \times 8 \times 0.3$ mm were compacted from the powder, obtained under a pressure of 300 kg/cm². The DMSO (chemically pure), HBr (ultrapure), HI (analytical grade), acetone and acetophenone (chemically pure), and acetylacetone (chemically pure) were vacuum distilled.

The IR spectra of the complexes were recorded on a UR-20 instrument, using KBr tablets.

The experimental material for x-ray diffraction analysis of the silver complexes was obtained from single crystals and was analyzed on a model DAR-UM automatic diffractometer, with CuK α irradiation, with additional treatment in the automated DAR-UM-BÉSM-6 system of the Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR [10].

<u>Production of Complex (I)</u>. a) A 0.45-g (4.2 mmoles) quantity of silver was dissolved in a mixture of DMSO (2 ml, 28 mmoles) and HBr (20 ml, 363 mmoles) at 60°C over 3 h; the AgBr [1] that deposited on cooling the solution was filtered off, and 10 ml of acetone was added to the filtrate in portions. Transparent, lamellar crystals were deposited from the the solution after 1 day at \sim 20°C, which were filtered off, washed with a 1:3 mixture of ethanol and ether, and dried. Yield of (I) 0.22 g (14%), mp 133°C. Found: 27.9 Ag, 15.4 C, 2.8 H, 41.2 Br, 8.1% S. AgBr₂C₅H₁₁OS. Calculated: 27.91 Ag, 15.50 C, 2.84 H, 41.34 Br, 8.27% S. b) A 0.15-g (1.4 mmoles) quantity of silver was dissolved over 5 h in a mixture of DMSO (16 ml, 230 mmoles) and HBr (1.3 ml, 24 mmoles) at 60°C. On adding acetone to the solution (15 ml) (or a mixture of acetone and ethanol, 8 and 20 ml, respectively) over 2 days at \sim 20°C, crystals of (I) were deposited. The complex was filtered off, washed with ether, and then with acetone, and dried. Yield of (I) 0.43 g (80%).

c) To a solution containing 0.021 g (0.2 mmole) of silver mixed with 2.6 ml (37 mmoles) of DMSO and 0.2 ml (3.7 mmoles) HBr was added 1.64 ml (16 mmoles) acetylacetone. Crystals of (I) were deposited from the solution obtained after 4 days at room temperature. Yield of (I) 0.069 g (92%).

d) Compound (I) is also formed on dissolution of AgBr in a mixture of DMSO (7.5 ml, 106 mmoles) and HBr (1.2 ml, 22 mmoles), with subsequent crystallization of the complex from acetone or acetylacetone.

e) The compound $[Me_3S]AgBr_2$ (0.038 g, 0.11 mmole) (or $[Me_3S]Ag_2Br_3$) [1] was dissolved in a mixture of DMSO (7.5 ml, 106 mmoles) and HBr (1.2 ml, 22 mmoles). On addition to the solution of a mixture of 8 ml acetone and 20 ml ethanol over 2 days, crystals of (I) were deposited from the solution. Yield of (I) 0.031 g (72%). Complex (I) has good solubility in DMSO, DMF, HBr, and an HBr-DMSO mixture.

<u>Production of Complex (II).</u> a) A quantity of $Me_2S \cdot I_2$ was dissolved in 6 ml of acetone, and to the brown solution was added AgI powder (0.129 g, 0.55 mmole) and a mixture of HI(2 ml) and 10 ml ethanol. After 4 days the transparent yellow crystals that formed were filtered off, washed with acetone, and dried. Yield of (II) 0.22 g (83%), mp 129°C. Found: 22.6 Ag, 11.7 C, 2.25 H, 46.1 I, 6.5% S. $AgI_2C_5H_{11}OS$. Calculated: 22.45 Ag, 12.47 C, 2.29 H, 52.81 I, 6.65% S.

b) A 0.18-g (1.7 mmoles) quantity of silver was dissolved at room temperature in a mixture of DMSO (2 ml, 28 mmoles) and HI (18 ml, 240 mmoles) over 2 days. The brown-black oil-like deposit of $Me_2S \cdot I_2$ [1] formed on 1 day was separated, and to the filtrate was added 25 ml of ethanol heated to 40°C. On slow cooling of the solution, a light yellow powder - the compound $[Me_3S]Ag_2I_3$ - was deposited [1] and filtered off. To the filtrate was added a mixture of ethanol (20 ml) and acetone (8 ml). On slow cooling of the hot solution over 1 day, long acicular crystals were deposited, which were filtered off, washed with aqueous ethanol, and dried. Yield of (II): 0.15 g (19%).

c) The compound $[Me_3S]Ag_2I_3$ [1] was dissolved with heating on a water bath in a mixture of DMSO (1 ml, 14 mmoles) and HI (9 ml, 120 mmoles). To the hot solution was added a mixture of 20 ml ethanol and 8 ml acetone, and the solution was allowed to cool slowly. Crystals of (II) were deposited after 5 days. The compound (II) was soluble in DMSO and DMF.

<u>Production of Complex (III).</u> A 0.012-g (0.11 mmole) quantity of silver was dissolved over 2 h in a mixture of DMSO (1.8 ml, 30 mmoles) and HBr (0.15 ml, 3 mmoles) at 60°C, and to the solution was added a mixture of 2 ml acetophenone and 5 ml of ethanol. Transparent colorless needless were crystallized from the solution after 2 days. The crystals were filtered off, washed with ether and ethanol, and dried. Yield of (III): 0.0394 g (79%), mp 176°C. Found: 24.1 Ag, 35.4 Br, 27.8 C, 2.9 H, and 6.8% S. AgBr₂C₁₀H₁₃OS. Calculated: 24.05 Ag, 35.63 Br, 26.73 C, 2.90 H, 7.13% S. The complex is soluble in DMSO and DMF.

<u>Production of Complex (IV).</u> A 0.134-g (0.57 mmole) quantity of AgI was dissolved in a mixture of DMSO (7.5 ml, 106 mmoles) and HI (1.62 ml, 21.5 mmoles). A mixture of 8.7 ml of acetophenone and 10 ml of ethanol was then added to the solution. Transparent crystals of (IV) were deposited from the solution after 1 day, which were filtered off, washed with ethanol, and dried. Yield of (IV): 0.3 g (97%). The IR spectra of (III) and (IV) were identical.

<u>X-ray Diffraction Analysis.</u> Crystals of (I) $AgBr_2C_5H_{11}OS$, are of laminar form, a = 19.525(6), b = 16.050(8), c = 6.636(4) Å, V = 2079.2(8) Å³, $d_{calc} = 1.05$ g/cm³, Z = 4. Space group Pbca, CuK_{α} radiation, max sin $\theta/\lambda = 0.600$, number of reflections 912, $R_f = 0.064$. Crystals of (II) $AgI_2C_5H_{11}OS$, laminar form, a = 20.350(4), b = 16.366(3), c = 6.944(3) Å, V = 2312.7(8) Å³, $d_{calc} = 1.22$ g/cm³, Z = 4. Space group Pbca, MoK_{α} radiation, max sin $\theta/\lambda = 0.501$, number of reflections 654, $R_f = 0.048$. Interatomic distances and angles, corresponding to full-matrix least-squares anisotropic refinement, are given in Tables 2 and 3. Crystals (III) $AgBr_2C_{10}H_{13}OS$, triclinic, size up to 1 mm, $\alpha = 12.767(7)$, b = 7.807(2), c = 7.077(1) Å; $\alpha = 105.39(2)$, $\beta = 91.15(2)$, $\gamma = 81.05(2)^\circ$, V = 671(1) Å³, d_{calc} = 1.34 g/cm³, Z = 2. Space group PI. The structure was determined by analysis of the Patterson function (Ag and Br atoms), and subsequent electron density syntheses (S, 0, C). Refinement by full-matrix least squares led to an R-factor of 0.057. In the difference synthesis of the electron density, eight of the 13 H atoms were objectively localized. The interatomic distances are given in Table 4.

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Re(III) COMPLEXES IN THE SYNTHESIS OF PLATINUM ACETATE COMPLEXES AND THE STRUCTURE OF [PPh_Pt(OAc)_]?

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Reaction of tetrachlorodiacetatodirhenium dihydrate with triphenylphosphineplatinum (II) triacetatoargentate(I) produces a new binuclear platinum complex with acetate bridges, bis[(μ^2 -acetato)acetatotriphenylphosphine]diplatinum(II). The new complex is characterized by x-ray structural analysis, IR, and PMR spectroscopies. The Re(III) complex in this reaction is not only the source of chloride ions, which are necessary for precipitation of silver, and the acetate acceptor, but also the silver(I) reductant which is oxidized during the reaction to Re(IV).

Binuclear complexes of platinum(II) are of interest as starting compounds for preparation of catalytically active multinuclear systems. In contrast to the well known and structurally characterized palladium complexes with bridging acetate groups, platinum complexes of the type $[LPt(OAc)_2]_2$ (L = PR₃, allyl) have not been prepared. Moreover, their preparation using traditional synthesis methods [1-4] have not succeeded [5, 6]. We studied reaction of PPh₃Pt(OAc)₃Ag with Re₂(OAc)₂X₄·2H₂O (X = C1, Br) in order to discover synthetic routes to binuclear platinum acetate complexes.

EXPERIMENTAL

Solvents were purified by standard methods [7]. $PPh_3Pt(OAc)_3Ag(I)$ was prepared by reaction of AgOAc with $[PPh_3PtCl_2]_2$ in AcOH. $Re_2(OAc)_2X_4$ (X = Cl, Br) was prepared as in [8].

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1739