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Metal Halide and Pseudohalide Complexes in Dimethyl Sulfoxide Solution. II. The Crystal Structure of Bisdimethyl Sulfoxide Silver(I) Perchlorate

NILS-OLOF BJÖRK and ANDERS CASSEL

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

The crystal structure of $Ag[(CH_3)_2SO]_2ClO_4$ has been determined from three-dimensional, photographic X-ray intensity data and refined from data collected with a four-circle diffractometer. The space group is $P2_1/n$ with $Z=4$ and the unit cell dimensions $a=10.336(1)$ Å, $b=18.188(2)$ Å, $c=6.523(1)$ Å and $\beta=98.56(1)°$. The structure is built up by infinite chains of silver atoms joined by double-bridging dimethyl sulfoxide oxygens. Each silver is also coordinated to a perchlorate ion, in which the oxygens are affected by great thermal motions. The coordination polyhedron of silver can be described as a distorted trigonal bipyramide, with Ag—O distances ranging between 2.36 and 2.74 Å.

This series of investigations mainly deals with metal complexes in solutions of dimethyl sulfoxide (DMSO). However, the structure determination of some crystallized metal dimethyl sulfoxide solvates are planned as they give important information about the coordination properties of the metal ions. With due caution, the structures which most plausibly exist in solution may also be inferred from these investigations. In this paper the structure of $Ag(DMSO)_2ClO_4$ is reported.

EXPERIMENTAL

Preparation and analysis. The preparation and analysis of $Ag(DMSO)_2ClO_4$ have been described elsewhere.[1] The compound was dissolved in acetone and colourless needles were obtained at room-temperature on slow evaporation of excess solvent.

Single crystal work. The compound is decomposed by traces of moisture. The needles are generally twinned and sufficiently good single crystals could not be obtained directly.

From large twinned crystals, however, single crystals of irregular shape were cut out and mounted in capillaries. A crystal, mounted along the c-axis, was used in recording preliminary Weissenberg data (Cu$K\alpha$, 1053 independent reflexions, visually estimated). Another crystal was used for collecting intensity data on a computer-controlled four-circle diffractometer of type CAD-4, using graphite-monochromatized Mo$K\alpha$ radiation ($\lambda=0.71069$ Å). Intensity data were recorded at a take-off angle of 5°. The $\omega-2\theta$ scan technique was used, with a scan interval $\Delta\omega=(0.7+0.5\tan\theta)°$. A fast prescan was used in order to determine the scan speed at which a predetermined minimum number of counts (3000) for each reflexion was received. The recording time was limited to 3 min. The intensities of 2780 reflexions were measured in the range $3°<\theta<27°$. Of these, 841 were below background, while 613 had intensities $I<3\sigma(I)$, where $\sigma(I)$ is the standard deviation of the intensity based on counting statistics. In all, 1454 reflexions were therefore discarded. After every 50th reflexion the intensities of three control reflexions were measured. A decrease of their intensities were found during the course of data collection. All intensities were therefore scaled with a first-order polynomial determined by least-squares. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. No correction for absorption was made [μ(Mo$K\alpha$) = 22.0 cm^{-1}].

Unit cell and space group. $Ag(DMSO)_2ClO_4$ crystallizes in the monoclinic system. Preliminary cell parameters and systematically absent reflexions were obtained from oscillation and Weissenberg photographs. From the systematically absent reflexions $h0l$: $h+l=2n+1$ and $0k0$: $k=2n+1$ the only possible space group is $P2_1/n$. The cell parameters were refined from Guinier-Hägg powder diffraction data by the method of least-squares. The density was deter-

Table 1. Crystal data for $Ag[(CH_3)_2SO]_2ClO_4$.

Space group $P2_1/n$

$a = 10.336(1)$ Å, $b = 18.188(2)$ Å, $c = 6.523(1)$ Å, $\beta = 98.56(1)°$, $V = 1213$ Å^3, $Z = 4$, $M = 363.6$, $D_m = 1.99$ g cm^{-3}, $D_x = 1.99$ g cm^{-3}, $\mu(MoK\alpha) = 22.0$ cm^{-1}.

Table 2a. Final fractional coordinates, multiplied by 10^4, and isotropic thermal parameters. Estimated standard deviations are given in parentheses. The occupancy numbers of the oxygen atoms are 1.0 for O(4), and 0.5 for O(3), O(5)–O(8).

Atom	x	y	z	B (Å^2) [a]
Ag	5737(1)	5261(1)	2647(1)	
S(1)	2604(3)	5867(2)	0588(5)	
S(2)	5535(3)	3417(2)	4073(5)	
O(1)	6143(7)	4411(4)	0080(11)	
O(2)	5365(9)	4185(4)	4846(11)	
O(3)	7508(23)	6098(19)	2351(51)	
O(4)	9671(17)	6369(9)	2423(33)	
O(5)	7998(30)	7055(24)	2884(89)	
O(6)	8198(45)	5774(14)	4085(48)	
O(7)	8629(37)	7014(19)	4543(57)	
O(8)	8859(42)	6366(36)	5404(43)	
Cl	8594(3)	6412(2)	3376(5)	4.4(1)
C(1)	1932(14)	5089(8)	1810(21)	5.7(3)
C(2)	8545(15)	4078(8)	1735(22)	6.5(3)
C(3)	4099(14)	3236(8)	2223(22)	6.5(3)
C(4)	4774(14)	7175(8)	3873(20)	5.8(3)

[a] For β_{ij}, *cf.* Table 2b.

mined from the loss of weight in benzene. Some crystal data are given in Table 1.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The positions of the silver, sulfur, chlorine, and DMSO oxygen atoms were determined by conventional methods, the calculations based on the Weissenberg data.

For the refinement counter intensities for 1326 non-zero reflexions were available. The positional and thermal parameters of the silver, sulfur, chlorine, and DMSO oxygen atoms obtained above were used as preliminary parameters. The resulting discrepancy factor $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0.095. From a subsequent three-dimensional difference synthesis six oxygen atom positions around the chlorine atom could be found.

With the positional and thermal parameters of silver, chlorine, carbon, and the DMSO-oxygens obtained in the last least-squares calculations, a further refinement was performed, where the only quantities varied were the scale factor, the positional and thermal parameters of the perchlorate oxygens and their occupancy numbers. The resulting R-value was 0.054. No oxygen atom gave converging occupancy numbers, but the values of five of them were approximately 0.5 and of the sixth 0.8. It was thus not possible to locate all perchlorate oxygen atoms in the structure. An additional calculation was made where the occupancy numbers were fixed to 0.5 for

Table 2b. Vibrational parameters, multiplied by 10^5, for silver, sulfur and oxygen. The expression used for the anisotropic thermal parameters is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	129(1)	35(0)	202(2)	−8(1)	37(1)	0(1)
S(1)	83(3)	33(1)	278(8)	6(2)	39(4)	−10(2)
S(2)	120(4)	24(1)	256(8)	4(2)	45(4)	−9(2)
O(1)	75(8)	48(3)	234(19)	13(4)	25(10)	−1(6)
O(2)	207(13)	24(2)	248(21)	4(5)	86(14)	−9(6)
O(3)	133(26)	118(18)	780(114)	−73(18)	−77(45)	−190(38)
O(4)	379(31)	77(7)	1775(127)	−6(12)	689(57)	−26(24)
O(5)	160(41)	130(23)	1789(286)	59(25)	291(92)	345(72)
O(6)	661(96)	51(11)	532(99)	−124(27)	196(84)	37(26)
O(7)	302(60)	74(15)	590(115)	−16(25)	94(69)	−158(39)
O(8)	399(74)	208(39)	363(99)	25(47)	−273(69)	−1(50)

five and to 1.0 for the sixth, and the isotropic temperature factors replaced by anisotropic ones. The resulting conventional R-value was 0.052 and the weighted R_w-value, defined by $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{\frac{1}{2}}$, 0.066. The quantity minimized was $w_i(|F_o| - |F_c|)^2$, with $w_i^{-1} = \sigma^2(|F_o|) + a|F_o|^2 + b$, where $a = 0.0015$ and $b = 2.0$ were used in the last refinement. The average values of $w_i(|F_o| - |F_c|)^2$ were nearly constant in different $|F_o|$ and sin θ intervals. A final difference electron density map gave no peaks larger than 2 e Å^{-3}. Scattering factors for neutral silver were taken from Cromer *et al.*[2] and for neutral sulfur, oxygen, chlorine, and carbon from Hanson *et al.*[3]

The final positional and thermal parameters are given in Table 2a, b. A table of observed and calculated structure factors can be obtained from the authors on request. All calculations were made on the Univac 1108 computer in Lund and short accounts of the program system have been given.[4,5]

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Stereoscopic views of the structure of $Ag(DMSO)_2ClO_4$ are given in Figs. 1 and 2. Selected interatomic distances and angles are presented in Table 3. The structure may be described as built up by infinite chains of the same formula, running along the c-axis. The silver atoms are joined by doubly bridging DMSO oxygens. Each silver is also coordinated to a perchlorate ion. Only weak interactions exist between the chains.

The coordination of silver. Silver is surrounded by six oxygen atom positions at distances 2.35 – 2.74 Å. Four of these refer to the DMSO oxygens and two to the perchlorate oxygens.

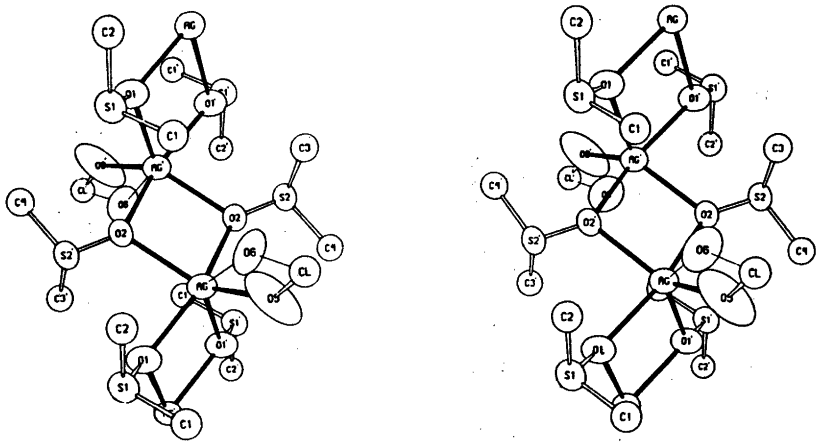


Fig. 1. Stereo view of the silver-oxygen coordination in one infinite chain. For notation, see Table 3a. The oxygen atoms O(4), O(5), O(7) and O(8) are omitted.

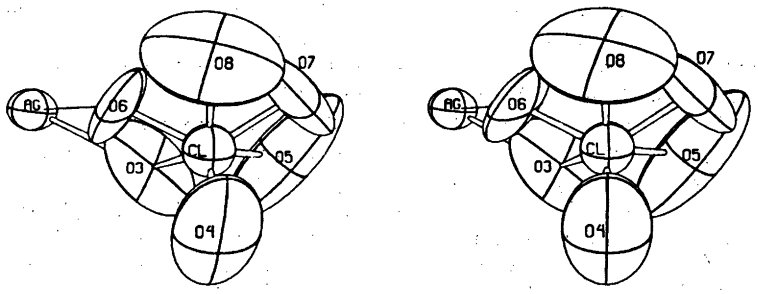


Fig. 2. Stereo view of the perchlorate-silver interaction.

Table 3. Selected interatomic distances (Å) and angles (°). Standard deviations are given in parentheses. For notations, see Figs. 1, 2 and Table 2a. An atom denoted with a prime is related to the unprimed through $\bar{1}$.

The coordination of silver

Ag–O(1)	2.362(7)	O(1)–Ag–O(6)	102.2(7)
–O(1′)	2.504(7)	O(1′)–Ag–O(2)	89.2(3)
–O(2)	2.354(8)	O(1′)–Ag–O(2′)	115.3(3)
–O(2′)	2.489(7)	O(1′)–Ag–O(3)	108.1(8)
–O(3)	2.411(29)	O(1′)–Ag–O(6)	138.1(7)
–O(6)	2.741(43)	O(2)–Ag–O(2′)	78.7(3)
		O(2)–Ag–O(3)	103.7(8)
O(1)–Ag–O(1′)	81.6(3)	O(2)–Ag–O(6)	97.9(7)
O(1)–Ag–O(2)	158.1(3)	O(2′)–Ag–O(3)	136.6(8)
O(1)–Ag–O(2′)	87.3(3)	O(2′)–Ag–O(6)	106.6(6)
O(1)–Ag–O(3)	98.0(8)	O(3)–Ag–O(6)	30(1)

The DMSO molecules

S(1)–O(1)	1.514(8)	O(1)–S(1)–C(1)	105.5(6)
–C(1)	1.812(14)	O(1)–S(1)–C(2)	105.4(6)
–C(2)	1.783(15)	C(1)–S(1)–C(2)	99.6(7)
S(2)–O(2)	1.504(7)	O(2)–S(2)–C(3)	105.6(6)
–C(3)	1.799(15)	O(2)–S(2)–C(4)	105.4(5)
–C(4)	1.784(14)	C(3)–S(2)–C(4)	99.8(7)

The perchlorate ion

Cl–O(3)	1.34(3)	O(4)–Cl–O(5)	109(2)
–O(4)	1.36(2)	O(4)–Cl–O(6)	115(2)
–O(5)	1.34(4)	O(4)–Cl–O(7)	111(2)
–O(6)	1.34(3)	O(4)–Cl–O(8)	113(2)
–O(7)	1.33(4)	O(5)–Cl–O(6)	133(3)
–O(8)	1.31(3)	O(5)–Cl–O(7)	52(3)
O(3)–Cl–O(4)	115(2)	O(5)–Cl–O(8)	108(4)
O(3)–Cl–O(5)	86(2)	O(6)–Cl–O(7)	120(2)
O(3)–Cl–O(6)	62(2)	O(6)–Cl–O(8)	68(3)
O(3)–Cl–O(7)	126(2)	O(7)–Cl–O(8)	60(3)
O(3)–Cl–O(8)	120(3)		

Silver-silver

Ag–Ag 3.685(2) and 3.746(2)

The occupancy numbers of the coordinating perchlorate oxygens O(3) and O(6) are 0.5 and the angle O(3)–Cl–O(6) is 62°. The two positions cannot be occupied simultaneously.

The coordination polyhedron can be described as a distorted trigonal bipyramide, with the two shortest silver oxygen bonds Ag–O(1) (2.36 Å) and Ag–O(2) (2.35 Å) as the axis. The angle O(1)–Ag–O(2) which should ideally be 180° is in fact 158.1°. The silver-oxygen distances of the equatorial plane are 2.49 and 2.50 Å for the DMSO oxygens and either 2.41 or 2.74 Å for the perchlorate oxygen; Table 3 and Fig. 1. Only five of the silver-oxygen distances are within the limits of the sums of covalent and ionic radii, 2.18 and 2.66 Å, respectively.[8] Distances larger than 2.66 Å do not imply bonds between the atoms, but up to 2.90 Å weak interactions may well exist.[7–9]

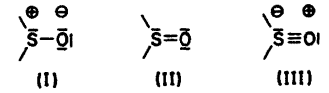
Similar approximately linear O–Ag–O fragments with short silver-oxygen distances are reported in the structures of $NH_2CH_2COOH.AgNO_3$,[10] $(AgC_2F_3O_2)_2C_6H_6$[11] and Ag_2SO_3.[12] In these structures the two short silver oxygen distances and the angle O–Ag–O are 2.22(2), 2.25(2) Å, 163.1(7)°; 2.22, 2.28 Å, 161.6° and 2.23(2), 2.30(3) Å, 155.1(9)°, respectively.

In aprotic solvents like acetone and nitroethane, silver is reported to be surrounded by four DMSO molecules.[13] In pure DMSO, the same coordination is likely to occur.

The perchlorate ion. The six oxygen positions O(3) to O(8) belong to the perchlorate ion. One of them, O(4), is given an occupancy number of 1.0 while the others are assigned 0.5. The distances Cl – O are all between 1.31 and 1.36 Å. In cases where oxygen atoms of the perchlorate ion are bonded to silver atoms, Cl – O(bonded) distances in the range 1.41(1) – 1.49(2) Å are reported.[7,8,14] On the other hand, for uncoordinated perchlorate oxygens distances between 1.22(3) and 1.52(2) Å are found.[7–9,14–16] The great deviations in these distances must be caused by the fact that there is no adequate way of describing the thermal motions of the oxygen atoms. Neither a spherical nor an ellipsoidal approximation of the electron density is satisfactory. In the present structure the perchlorate ion can be described as rotating around the Cl – O(4) axis. A similar model has been applied earlier.[16,17] The positions O(3) and O(6) with occupancy numbers 0.5 may be preferred positions but no acceptable tetrahedron can be derived using them as starting points because it is not possible to use the O(5) position in any tetrahedron involving O(3) or O(6), Fig. 2.

Many types of disordered perchlorate structures are known. In $AgClO_4.3$dioxane,[18] the ClO_4^--group is supposed to rotate completely around the chlorine position. Strong disorder also occurs in $(C_6H_6)_3CClO_4$.[15] As expected, perchlorate oxygens involved in bonding are often in fixed positions, while uncoordinated ones are disordered.[8,14] The present result seems to indicate, however, that the opposite also may occur, *viz.* a non-coordinated oxygen is fixed, while coordinated ones do rotate.

The DMSO molecules. The electronic structure of the S – O bond may be represented as a hybrid of the canonical forms (I), (II) and (III):



(I) (II) (III)

The structure of pure DMSO is most closely described by (II).[19] In the gas phase the S – O distance is 1.48 Å.[19] Coordination *via* oxygen means increased contribution of (I) which causes a decrease of the bond order. Conversely if coordination *via* sulfur occurs, the contribution of (III) would increase. The S – O distances found here, 1.50 and 1.51 Å, are lengthened relative to pure DMSO, as expected. They also agree well with values reported for other metal-DMSO complexes with oxygen coordination, *viz.* $La(NO_3)_3(DMSO)_4$,[20] 1.50(3) Å; $SnCl_4$-$(DMSO)_2$,[21] 1.51 and 1.54 Å and $FeCl_3(DMSO)_2$,[22] 1.541(6) Å. In cases where metal-sulfur coordination occurs the distances S – O found are, as expected, generally shorter, *viz.* $PdCl_2$-$(DMSO)_2$,[23] 1.475(5) Å; $Pd(NO_3)_2(DMSO)_2$,[24] 1.463(7) Å, and $C_{15}H_{13}OIrCl_2(DMSO)_2$,[25] 1.44 and 1.47 Å.

For DMSO, coordination *via* oxygen is far more common than coordination *via* sulfur.[19] The latter occurs only with very soft acceptors, such as the platinum metals in the compounds just mentioned. As silver(I) is also quite a soft acceptor the oxygen coordination in its DMSO solvate is certainly unexpected, the more so as sulfur coordination occurs in such a compound as silver(I) sulfite.[12] It should be noted, however, that also silver-oxygen coordination occurs in this compound.

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