O7—Ca2—O7'	126.6 (2)	O5'—Ca2—N3	156.1 (2)
O5—Ca2—N3	66.8 (2)	O7'—Ca2—N3	124.1 (2)
O7—Ca2—N3	88.1 (1)	N3—Ca2—N3'	108.3 (2)
O5'—Ca2—N4	87.2 (2)	O5'—Ca2—N4'	124.9 (1)
O7—Ca2—N4'	157.7 (1)	O7—Ca2—N4	66.7 (1)
N3—Ca2—N4	69.6 (2)	N3'—Ca2—N4	70.1 (2)
N4'—Ca2—N4	107.9 (2)	O9—Ca3—O8"	88.2 (2)
O9—Ca3—O11	153.5 (2)	O8"—Ca3—O11	96.6 (2)
O9—Ca3—O10	100.2 (2)	O8"—Ca3—O10	158.4 (2)
O11—Ca3—O10	84.8 (2)	O9—Ca3—O2	125.7 (2)
O8"—Ca3—O2	83.4 (2)	O11—Ca3—O2	80.8 (2)
O10—Ca3—O2	75.5 (2)	O9—Ca3—O8	80.3 (2)
O8"—Ca3—O8	68.8 (2)	O11—Ca3—O8	77.3 (2)
O10—Ca3—O8	132.1 (2)	O2—Ca3—O8	142.0 (2)
O9—Ca3—O1	74.4 (1)	O8"—Ca3—O1	88.2 (1)
O11—Ca3—O1	131.6 (2)	O10—Ca3—O1	75.1 (1)
O2—Ca3—O1	51.9 (1)	O8—Ca3—O1	146.2 (1)
O9—Ca3—O7	73.7 (1)	O8"—Ca3—O7	118.8 (2)
O11—Ca3—O7	81.2 (2)	O10—Ca3—O7	82.7 (1)
O2—Ca3—O7	152.8 (1)	O8—Ca3—O7	51.0 (1)
O1—Ca3—O7	136.8 (1)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

Table 3. *Contact distances (Å)*

O9···O5'	2.77 (1)	O10···O3'	2.81 (1)
O11···O13"	2.82 (1)	O11···O19'	2.92 (1)
O12···O20'	3.07 (2)	O13···O4'	2.74 (1)
O13···O6	2.77 (1)	O13···O17	2.59 (1)
O14···O4'	2.81 (1)	O14···O15'''	2.78 (1)
O14···O19'''	2.58 (1)	O15···O2'	2.79 (1)
O15···O17"	2.80 (1)	O16···O6'	2.75 (1)
O16···O19'	2.72 (1)	O17···O18'''	2.58 (1)
O17···O20'	2.69 (1)	O18···O19'	2.75 (1)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (iii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $-x, 1 - y, -z$; (v) $x, 1 - y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Unfortunately, the crystal was lost due to icing with approximately 500 reflections to collect; consequently no azimuthal data were collected. C-bound H atoms were placed in idealized positions [C—H = 0.96 Å, U(H) = 0.08 Å^2(fixed)] and all O-bound H atoms, except for those of O12 and O20, were located in a difference Fourier map. H atom parameters were not refined. The H atoms bound to O12 and O20 were not included in the list of atomic coordinates.

Data collection: *P3* (Siemens, 1982*a*). Data reduction: *XTAPE* (Siemens, 1982*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1990).

The Siemens *R3m/E* X-ray diffractometer and crystallographic computing system at Colorado State University were purchased with funds provided by the US National Science Foundation.

References

Clarke, E. T. & Martell, A. (1991). *Inorg. Chim. Acta*, **190**, 27–36.
Dale, J. (1980). *Isr. J. Chem.* **20**, 3–11.
Desreux, J. (1980). *Inorg. Chem.* **19**, 1319–1324.
Groth, P. G. (1983). *Acta Chem. Scand. Ser. A*, **37**, 283–291.
Hay, R. W. & Norman, P. R. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1441–1445.

Reibenspies, J. H. (1992). *Acta Cryst.* C48, 1717–1718.
Reibenspies, J. H. & Anderson, O. P. (1990). *Acta Cryst.* C46, 163–164.
Sheldrick, G. M. (1986). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1982*a*). *P3.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1982*b*). *XTAPE.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1990). *XP.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spirlet, M., Rebizant, J., Desreux, J. & Loncin, M. (1984). *Inorg. Chem.* **23**, 359–363.
Vishwanath, C. K., Shamala, N., Easwaran, K. R. K. & Vijayan, M. (1983). *Acta Cryst.* C39, 1640–1643.

The Polymeric Cluster Complex {[(CH3CH2)3NH][WAgS4].(DMF)}n

Qun Huang, Xintao Wu,* Quanming Wang and Tianlu Sheng

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China
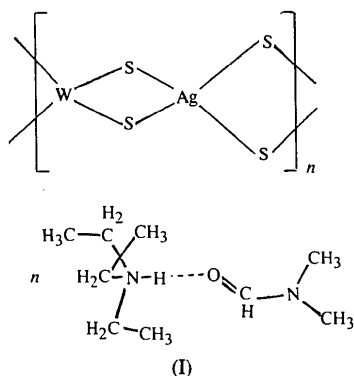
Abstract

The structure of the anion in *catena*-poly[triethylammonium [tungsten-di-μ-sulfido-silver-di-μ-sulfido] N,N'-dimethylformamide solvate], $\{(C_6H_{16}N)[WAgS_4].(C_3H_7NO)\}_n$, can be viewed as a polymeric chain composed of extended fragments of AgS_2W, which are alternately almost perpendicular to each other. Each metal atom displays approximate tetrahedral coordination with four μ-S atoms. Hydrogen-bond interactions exist between the DMF molecule and the $[(CH_3CH_2)_3NH]^+$ cation.

Comment

Early in 1983, Müller and co-workers proposed the polymeric structure of $[(C_6H_5)_4P][AgMoS_4]$ from the strong absorption in the Mo—S absorption bands in its resonance Raman spectrum (Müller, Jaegermann & Hellmann, 1983; Müller & Hellmann, 1985). The crystal structure of this kind of complex, however, was not reported until 1993 (Lang, Li, Bao & Xin, 1993). The

(I)

Fig. 2. Packing diagram viewed down the b axis. H atoms are omitted for clarity.

structure of the title compound, (I), is described as an addition to this family.

A portion of the anion chain and of the hydrogen-bonding structure and the packing diagram of the unit cell are shown in Figs. 1 and 2. The anion chain, which is propagated by cell translation along the crystallographic a axis and runs parallel to the a axis, is composed of extended rhombic networks of AgS₂W; neighbouring rhombi in the chain are alternately almost perpendicular to each other [dihedral angle 91.0(2)°]. Metal atoms are approximately tetrahedrally coordinated by four μ-S atoms with the coordination angles varying from 91.5(4) to 123.0(4)°. The average W—S, Ag—S and W—Ag distances are 2.202(9), 2.546(11) and 2.983(6) Å, respectively, which are comparable with the corresponding values found in (PPh₃)₃[Ag₂WS₄].0.8CH₂Cl₂ [2.207(6), 2.528(6) and 2.971(2) Å, respectively (Müller, Bögger & Koniger-Ahlborn, 1979)]. As shown in Fig. 1(b), hydrogen-bond interactions exist between the O atom of the DMF molecule and the N atom of the [(CH₃CH₂)₃NH]⁺ cation; the O···H1—N2 distance and angle are 2.78(3) Å and 178(3)°, respectively.

Experimental

The complex was synthesized by the reaction of ammonium tetrathiotungstate, silver nitrate and triethylamine (1:2:1) in DMF and CH₃CN, and crystallized by allowing the filtrate to stand in the air for several days. The orange crystals are stable in air.

Crystal data

(C₆H₁₆N)[WAgS₄].C₃H₇NO	Mo $K\alpha$ radiation
$M_r = 595.27$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 20
Cc	reflections
$a = 5.964(3)$ Å	$\theta = 3{-}13.8°$
$b = 27.04(2)$ Å	$\mu = 7.91$ mm⁻¹
$c = 11.376(6)$ Å	$T = 293$ K
$\beta = 94.42(5)°$	Rectangle
$V = 1829(3)$ Å³	$0.50 \times 0.20 \times 0.10$ mm
$Z = 4$	Orange
$D_r = 2.16$ Mg m⁻³	

Data collection

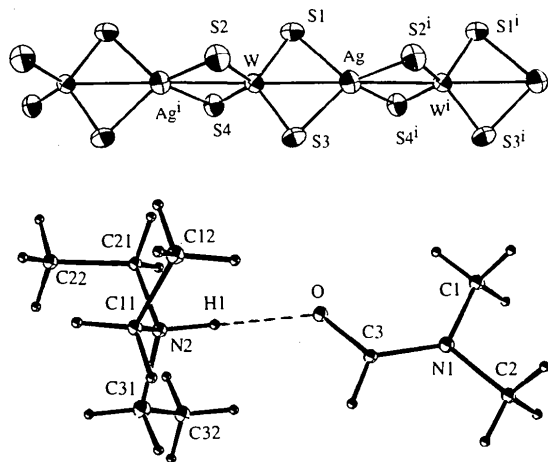|	
Rigaku AFC-5R diffractometer	1044 observed reflections
	$[I > 3\sigma(I)]$
$\omega/2\theta$ scans	$\theta_{max} = 25.0°$
Absorption correction:	$h = 0 \rightarrow 7$
refined from ΔF	$k = 0 \rightarrow 32$
(*DIFABS*; Walker &	$l = -13 \rightarrow 13$
Stuart, 1983)	3 standard reflections
$T_{min} = 0.839$, $T_{max} =$	monitored every 250
1.000	reflections
1656 measured reflections	intensity decay: 0.6%
1656 independent reflections	

Fig. 1. (a) Structure of a portion of the anion chain showing 50% probability displacement ellipsoids. (b) Diagram of the hydrogen-bonding structure. H atoms are unlabelled except for H1.
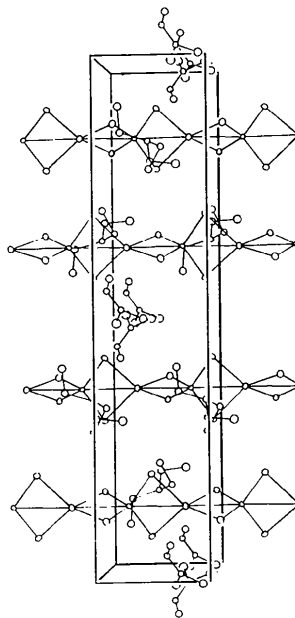
Refinement

Refinement on F
$R = 0.0448$
$wR = 0.0498$
$S = 1.11$
1044 reflections
101 parameters
H-atom parameters not
  refined
$w = 1/[\sigma^2(F) + (0.02F)^2 + 1 - F]$

$(\Delta/\sigma)_{max} = 0.014$
$\Delta\rho_{max} = 1.19 \text{ e Å}^{-3}$ (ghost of Ag atom)
$\Delta\rho_{min} = -0.46 \text{ e Å}^{-3}$
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
W	0.7486	−0.13864 (4)	0.2506	0.0343 (2)
Ag	0.2464 (7)	−0.13737 (9)	0.2446 (4)	0.0570 (5)
S1	0.554 (1)	−0.0772 (3)	0.3179 (9)	0.062 (3)
S2	0.984 (1)	−0.1635 (3)	0.3986 (7)	0.050 (2)
S3	0.536 (1)	−0.2018 (3)	0.1944 (8)	0.056 (2)
S4	0.922 (1)	−0.1133 (4)	0.0965 (7)	0.058 (2)
O	0.325 (3)	−0.0746 (9)	0.829 (2)	0.067 (6)
N1	0.253 (4)	−0.0170 (9)	0.964 (2)	0.048 (6)
N2	0.552 (4)	−0.157 (1)	0.751 (2)	0.052 (7)
C1	0.313 (7)	0.008 (2)	1.075 (4)	0.10 (1)
C2	0.051 (7)	0.000 (2)	0.904 (4)	0.09 (1)
C3	0.368 (5)	−0.053 (1)	0.923 (3)	0.049 (8)
C11	0.796 (5)	−0.141 (1)	0.734 (3)	0.068 (9)
C12	0.801 (6)	−0.092 (2)	0.658 (3)	0.08 (1)
C21	0.547 (6)	−0.194 (1)	0.851 (3)	0.07 (1)
C22	0.322 (7)	−0.198 (2)	0.889 (4)	0.10 (1)
C31	0.419 (5)	−0.170 (1)	0.643 (3)	0.057 (9)
C32	0.519 (6)	−0.215 (1)	0.581 (3)	0.07 (1)

Table 2. *Selected geometric parameters (Å, $°$)*

W—Ag	2.991 (6)	W—S4	2.211 (9)
W—Ag^i	2.975 (6)	Ag—S1	2.545 (11)
W—S1	2.196 (9)	Ag—S2^{ii}	2.539 (11)
W—S2	2.211 (8)	Ag—S3	2.550 (10)
W—S3	2.192 (9)	Ag—S4^{ii}	2.552 (11)
Ag—W—Ag^i	177.1 (2)	S1—Ag—S3	91.5 (4)
S1—W—S2	106.6 (4)	S1—Ag—S4^{ii}	123.0 (4)
S1—W—S3	112.5 (3)	S2^{ii}—Ag—S3	115.4 (4)
S1—W—S4	109.5 (4)	S2^{ii}—Ag—S4^{ii}	92.8 (3)
S2—W—S3	107.7 (4)	S3—Ag—S4^{ii}	121.3 (4)
S2—W—S4	113.0 (3)	W—S1—Ag	77.8 (3)
S3—W—S4	107.7 (4)	W—S2—Ag^i	77.2 (3)
W—Ag—W^{ii}	177.1 (2)	W—S3—Ag	77.8 (3)
S1—Ag—S2^{ii}	114.9 (4)	W—S4—Ag^i	77.0 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $x − 1, y, z$.

The structure and its enantiomorph were refined by full-matrix least-square methods; the absolute configuration was assigned to the enantiomorph that gave the better of the two sets of agreement factors (R, wR and S). H atoms were all located theoretically and not refined. Structure solution and refinement were carried out on a Compaq PROLINEA 4/50 computer.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DE1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lang, J.-P., Li, J.-G., Bao, S. & Xin, X.-Q. (1993). *Polyhedron*, **12**, 801–806.
Molecular Structure Corporation (1988). *CONTROL. An Automatic Package for Rigaku AFC Single-Crystal Diffractometers*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Müller, A., Bögger, H. & Koniger-Ahlborn, E. (1979). *Z. Naturforsch. Teil B*, **34**, 1698–1702.
Müller, A. & Hellmann, W. (1985). *Spectrochim. Acta Part A*, **41**, 359–366.
Müller, A., Jaegermann, W. & Hellmann, W. (1983). *J. Mol. Struct.* **100**, 559–570.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

trans-[Mo(CO)4{P(OMe)3}2]

Neil R. Champness, Alison M. Hopkins and Gillian Reid*

Department of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, England. E-mail: gr@soton.ac.uk

Abstract

Crystals of *trans*-tetracarbonylbis(trimethyl phosphite)molybdenum(0) contain discrete [Mo(C$_3$H$_9$O$_3$P)$_2$(CO)$_4$] molecules whose metal atoms occupy crystallographic inversion centres. Valency angles at the Mo atom deviate from ideal octahedral values by no more than 3.3 (1)°. Mo–ligand bond lengths are normal, with an Mo—P distance of 2.4256 (8) and Mo—C distances of 2.041 (3) and 2.037 (4) Å.

Comment

The title complex, *trans*-tetracarbonylbis(trimethyl phosphite)molybdenum(0), (I), has been prepared previously in a mixture of [Mo(CO)$_{6-n}${P(OMe)$_3$}$_n$] ($n =$