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The Heterotrimetallic Linear Complex Tetraethylammonium Dibromo-2κ^2*Br*-tetra-μ-sulfido-1:2κ^4*S*;1:3κ^4*S*-bis(triphenylphosphine-3κ*P*)-2-iron-3-silver-1-tungsten, $[Et_4N][Br_2FeS_2WS_2Ag(PPh_3)_2]$

PING LIN, QUN HUANG, TIANLU SHENG AND XINTAO WU*

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

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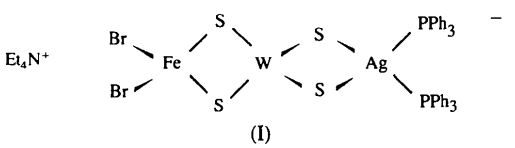
Abstract

The structure of the title complex, $(C_8H_{20}N)[AgFeWS_4Br_2(C_{18}H_{15}P)_2]$, can be simply described as linear with three types of metal atoms distributed along a line. Each metal atom is approximately tetrahedrally coordinated.

Comment

Syntheses of heterotrimetallic compounds are still challenging (Richter & Vahrenkamp, 1978; Gheller *et al.*, 1984; Planalp & Vahrenkamp, 1987). Recently, a few heterotrimetallic complexes have been designedly synthesized in our laboratory, such as the butterfly-like complexes $[Et_4N][(PPh_3)_2AgOMS_3CuCN]$ and the linear complexes $[Et_4N][Cl_2FeS_2MS_2M'(PPh_3)_2]$ and $[Et_4N][(PPh_3)_2AgS_2MS_2CuCN]$ (M = Mo, W; M' = Cu, Ag) (Du, Zhu, Chen, Wu & Lu, 1992*a*,*b*; Zhu, Du, Chen & Wu, 1992; Sheng, Du & Wu, 1993*a*,*b*). The structure of $[Et_4N][Br_2FeS_2WS_2Ag(PPh_3)_2]$, (I), was studied as a supplementary member of the family of heterotrimetallic linear complexes $\{FeS_2MS_2M'\}$ (M = Mo, W; M' = Cu, Ag).



(I)

The Ag···W···Fe angle of 177.04 (3)° suggests that the arrangement of the three metal atoms is essentially linear. The Ws_2Ag and WS_2Fe fragments are planar, forming a dihedral angle of 90.07 (5)° between their planes; *i.e.* these two fragments are almost perpendicular to each other. The W atom is coordinated by four μ_2-S atoms with approximate tetrahedral geometry [106.79 (9)–113.12 (9)°]. However, two μ_2-S and two Br atoms about the Fe atom are arranged with slightly distorted tetrahedral geometry [102.06 (9)–112.6 (1)°], and two μ_2-S and two P atoms about the Ag atom with severely distorted tetrahedral geometry [88.56 (7)–118.27 (7)°]. One reason for the distortions of the tetrahedral geometries about Fe and Ag is the differences in the M—S bond lengths [mean W—S, Ag—S and Fe—S lengths 2.210 (2), 2.616 (2) and 2.304 (3) Å, respectively]; the longer Ag—S distance results in a smaller S—Ag—S angle. The W—Ag and W—Fe distances are 3.0788 (7) and 2.779 (1) Å, respectively, which are similar to the corresponding values found in $[Et_4N][Cl_2FeS_2WS_2Ag(PPh_3)_2]$ [3.076 (1) and 2.786 (2) Å, respectively]. The title complex and $[Et_4N][Cl_2FeS_2WS_2Ag(PPh_3)_2]$ are isomorphic.

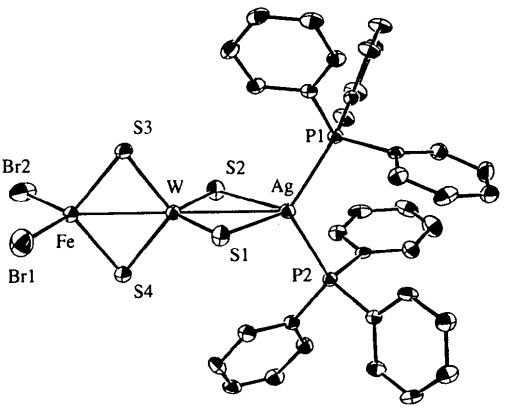


Fig. 1. Structure of the anion showing 20% probability displacement ellipsoids. C atoms are unlabelled for clarity.

Experimental

The complex was synthesized under nitrogen atmosphere by reaction of $[Et_4N][S_2WS_2FeBr_2]$ and $Ag(PPh_3)_3I$ (molar ratio 1:1) in CH_3CN and CH_2Cl_2, and crystallized by slow diffusion of Et_2O into the filtrate.

Crystal data

$(C_8H_{20}N)[AgFeWS_4Br_2(C_{18}H_{15}P)_2]$
M_r = 1290.48
Triclinic
$P\bar{1}$
a = 13.527 (4) Å
b = 15.592 (5) Å
c = 12.429 (6) Å
α = 104.91 (3)°
β = 94.72 (3)°
γ = 101.19 (2)°
V = 2460.8 Å^3
Z = 2
D_x = 1.74 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 3–12.5°
μ = 4.93 mm^{-1}
T = 296 K
Rectangular
0.80 × 0.60 × 0.30 mm
Dark red

Data collection

Rigaku AFC-5*R* diffractometer
ω scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.28, T_{max} = 1.00
9054 measured reflections
8647 independent reflections
6474 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.034
θ_{max} = 25°
$h = 0 \rightarrow 16$
$k = -19 \rightarrow 19$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 300 reflections
intensity decay: 0.9%

Refinement

Refinement on *F*
R = 0.044
wR = 0.053
S = 1.44
6474 reflections
460 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.020F_o)^2 + 1]$
$(\Delta/\sigma)_{max}$ = 0.01
$\Delta\rho_{max}$ = 1.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 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 (Å²)*

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	*y*	*z*	B_{eq}
W	−0.23284 (3)	0.09054 (2)	−0.22847 (3)	3.159 (6)
Ag	−0.22811 (4)	0.28859 (4)	−0.22923 (5)	3.41 (1)
Fe	−0.2266 (1)	−0.08540 (7)	−0.2229 (1)	4.07 (3)
Br1	−0.1063 (1)	−0.11942 (9)	−0.1021 (1)	9.41 (4)
Br2	−0.3411 (1)	−0.21917 (9)	−0.3317 (1)	8.12 (3)
S1	−0.1200 (2)	0.2083 (1)	−0.1227 (2)	4.45 (5)
S2	−0.3447 (2)	0.1272 (2)	−0.3364 (2)	4.71 (5)
S3	−0.1523 (2)	−0.0030 (1)	−0.3362 (2)	4.37 (5)
S4	−0.3126 (2)	0.0137 (2)	−0.1195 (2)	5.13 (6)
P1	−0.1318 (1)	0.3581 (1)	−0.3592 (2)	2.90 (4)
P2	−0.3391 (2)	0.3756 (1)	−0.1174 (2)	3.14 (4)
N	0.7369 (6)	0.0056 (5)	0.2685 (6)	4.8 (2)
C11	0.633 (1)	0.0099 (8)	0.220 (1)	7.7 (3)
C12	0.584 (1)	0.077 (1)	0.301 (1)	10.7 (4)
C21	0.736 (1)	−0.0180 (8)	0.378 (1)	7.6 (3)
C22	0.663 (1)	−0.1074 (9)	0.374 (1)	9.2 (4)
C31	0.771 (1)	−0.0655 (8)	0.179 (1)	7.4 (3)
C32	0.875 (1)	−0.079 (1)	0.210 (1)	10.8 (4)
C41	0.811 (1)	0.0975 (9)	0.293 (1)	8.4 (3)
C42	0.821 (1)	0.133 (1)	0.188 (1)	10.8 (4)
C111	−0.2064 (5)	0.3551 (5)	−0.4896 (6)	3.0 (2)
C112	−0.3115 (6)	0.3329 (6)	−0.4975 (7)	4.9 (2)
C113	−0.3715 (7)	0.3316 (7)	−0.5946 (8)	5.6 (3)
C114	−0.3282 (7)	0.3511 (6)	−0.6821 (7)	4.9 (2)
C115	−0.2250 (7)	0.3723 (7)	−0.6760 (7)	5.5 (2)
C116	−0.1643 (6)	0.3737 (6)	−0.5816 (7)	4.7 (2)
C121	−0.0788 (5)	0.4784 (5)	−0.2927 (6)	3.0 (2)
C122	−0.0009 (6)	0.5036 (6)	−0.2003 (7)	4.2 (2)
C123	0.0333 (7)	0.5933 (7)	−0.1396 (8)	5.0 (2)
C124	−0.0102 (8)	0.6586 (6)	−0.1643 (7)	5.1 (2)
C125	−0.0875 (9)	0.6361 (6)	−0.2525 (8)	6.0 (3)
C126	−0.1209 (7)	0.5453 (5)	−0.3169 (6)	4.5 (2)
C131	−0.0243 (5)	0.3119 (5)	−0.4064 (6)	2.9 (2)
C132	0.0643 (6)	0.3623 (6)	−0.4303 (7)	3.9 (2)
C133	0.1390 (6)	0.3196 (6)	−0.4720 (7)	4.6 (2)
C134	0.1283 (6)	0.2277 (6)	−0.4884 (7)	4.7 (2)
C135	0.0417 (7)	0.1769 (6)	−0.4641 (7)	4.8 (2)
C136	−0.0335 (6)	0.2186 (5)	−0.4229 (7)	3.8 (2)
C211	−0.2815 (6)	0.4799 (5)	−0.0050 (6)	3.2 (2)
C212	−0.3155 (6)	0.5005 (6)	0.0994 (7)	4.0 (2)
C213	−0.2692 (7)	0.5802 (7)	0.1797 (7)	4.8 (2)
C214	−0.1912 (7)	0.6399 (6)	0.1579 (7)	4.8 (2)
C215	−0.1567 (7)	0.6208 (6)	0.0559 (7)	4.9 (2)
C216	−0.2008 (7)	0.5403 (6)	−0.0245 (6)	4.5 (2)
C221	−0.4200 (6)	0.4120 (5)	−0.2155 (6)	3.3 (2)
C222	−0.4094 (7)	0.5001 (6)	−0.2184 (7)	4.3 (2)
C223	−0.4649 (8)	0.5229 (7)	−0.3009 (8)	6.1 (3)
C224	−0.5346 (7)	0.4575 (7)	−0.3787 (7)	5.8 (2)
C225	−0.5482 (6)	0.3667 (7)	−0.3770 (7)	5.3 (2)
C226	−0.4896 (6)	0.3439 (6)	−0.2962 (7)	4.4 (2)
C231	−0.4292 (6)	0.3093 (5)	−0.0529 (6)	3.4 (2)
C232	−0.5263 (7)	0.3267 (6)	−0.0354 (7)	4.5 (2)
C233	−0.5906 (7)	0.2740 (6)	0.0167 (8)	5.0 (2)
C234	−0.5606 (8)	0.2057 (6)	0.0509 (7)	5.4 (2)
C235	−0.4682 (8)	0.1876 (6)	0.0336 (7)	5.5 (2)
C236	−0.4023 (6)	0.2387 (6)	−0.0166 (7)	4.3 (2)

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

W···Ag	3.0788 (7)	Ag—S2	2.643 (2)
W···Fe	2.779 (1)	Ag—P1	2.486 (3)
W—S1	2.184 (2)	Ag—P2	2.488 (2)
W—S2	2.193 (2)	Fe—Br1	2.351 (2)
W—S3	2.227 (2)	Fe—Br2	2.351 (2)
W—S4	2.237 (2)	Fe—S3	2.304 (3)
Ag—S1	2.589 (2)	Fe—S4	2.305 (3)
Ag···W···Fe	177.04 (3)	P1—Ag—P2	118.27 (7)
S1—W—S2	113.12 (9)	Br1—Fe—Br2	110.68 (8)
S1—W—S3	108.65 (9)	Br1—Fe—S3	112.6 (1)
S1—W—S4	109.3 (1)	Br1—Fe—S4	109.9 (1)
S2—W—S3	109.0 (1)	Br2—Fe—S3	110.71 (8)
S2—W—S4	109.8 (2)	Br2—Fe—S4	110.6 (1)
S3—W—S4	106.79 (9)	S3—Fe—S4	102.06 (9)
S1—Ag—S2	88.56 (7)	W—S1—Ag	79.85 (8)
S1—Ag—P1	112.06 (8)	W—S2—Ag	78.48 (7)
S1—Ag—P2	115.98 (8)	W—S3—Fe	75.65 (8)
S2—Ag—P1	111.46 (8)	W—S4—Fe	75.43 (8)
S2—Ag—P2	106.22 (8)		

H atoms were theoretically added and not refined.

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*. Molecular graphics: *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 29–31

The Polymeric Cluster Compound $[(tmenH_2).(W_2Ag_2S_8).(tmen).(H_2O)]_n$ (tmen = *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine)

QUN HUANG, XINTAO WU,* TIANLU SHENG AND QUANMING WANG

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

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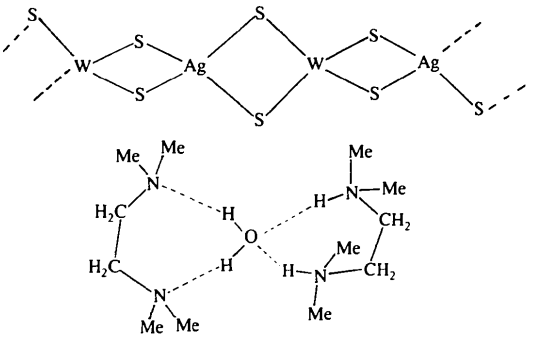
Abstract

The structure of the $(W_2Ag_2S_8)^{2-}$ anion of the title cluster compound, *catena*-poly[*N*,*N*,*N*′,*N*′-tetramethylethylenediammonium bis(tungsten-di-μ-sulfido-silver-di-μ-sulfido) *N*,*N*,*N*′,*N*′-tetramethylethylenediamine hydrate], $\{(C_6H_{18}N_2)[W_2Ag_2S_8].(C_6H_{16}N_2).H_2O\}_n$, can be described as a polymeric chain consisting of extended $>AgS_2W<$ fragments. In the chain, which has disordered W and Ag atoms, neighbouring fragments of this kind are alternately nearly perpendicular to each other. Water molecules are connected to the $tmenH_2^{2+}$ cations and tmen molecules through hydrogen bonding.

Comment

A few polymeric compounds containing different metals have been reported (Nicholson, Flood, Garner & Clegg, 1983; Müller, Jaegermann & Hellmann, 1983; Pruss, Snyder & Stacy, 1993). However, only some structures of such compounds have been characterized by single-crystal X-ray diffraction analyses (Müller, Dartmann, Romer, Clegg & Sheldrick, 1981; Lang, Li, Bao & Xin, 1993). The structure of the title compound, (I), was investigated as a new member of this type.



(I)

*ORTEP*II (Johnson, 1976) drawings of a portion of the anionic chain and of the hydrogen-bonding structure are shown in Fig. 1. The W and Ag atoms are disordered, so the chemical composition may be represented as $[(tmenH_2).(M_4S_8).(tmen).(H_2O)]_n$ (M = 0.50W + 0.50 Ag and tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine). The anion has a polymeric chain structure, which is propagated by inversion symmetry, with extended rhombic networks of $>MS_2M<$ being alternately nearly perpendicular to each other [dihedral angles of 87.9 (2) and 91.6 (2)°]. Each M atom displays distorted tetrahedral coordination with four μ_2-S atoms. As a result of the disorder, the average value [2.350 (10) Å] of the M—S bond lengths is larger than reported W—μ_2-S lengths [2.191 (5)–2.224 (6) Å] and smaller than reported Ag—μ_2-S lengths

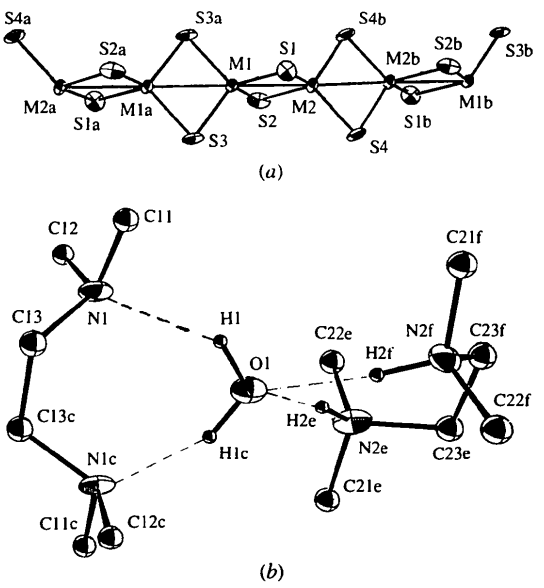


Fig. 1. (*a*) Structure of a portion of the anionic chain showing 20% probability displacement ellipsoids. (*b*) Diagram of the hydrogen-bonding pattern showing 20% probability displacement ellipsoids.