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The Polymeric Cluster Compound $[(\text{tmenH}_2) \cdot (\text{W}_2\text{Ag}_2\text{S}_8) \cdot (\text{tmen}) \cdot (\text{H}_2\text{O})]_n$ ($\text{tmen} = N, N, N', N'$ -Tetramethylethylenediamine)

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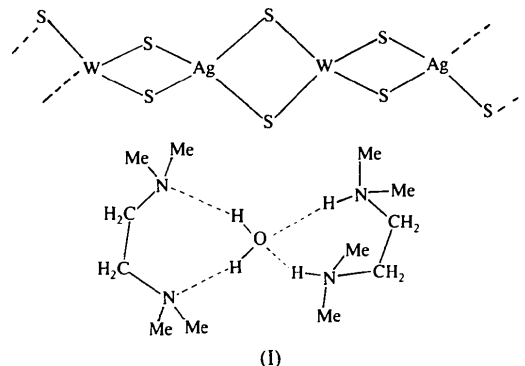
Abstract

The structure of the $(\text{W}_2\text{Ag}_2\text{S}_8)^{2-}$ 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], $\{(\text{C}_6\text{H}_{18}\text{N}_2)[\text{W}_2\text{Ag}_2\text{S}_8] \cdot (\text{C}_6\text{H}_{16}\text{N}_2) \cdot \text{H}_2\text{O}\}_n$, can be described as a polymeric chain consisting of extended $>\text{AgS}_2\text{W}<$ 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^+ 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.



ORTEPII (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 $[(\text{tmenH}_2) \cdot (M_4\text{S}_8) \cdot (\text{tmen}) \cdot (\text{H}_2\text{O})]_n$ ($M = 0.50\text{W} + 0.50\text{Ag}$ and $\text{tmen} = N, N, N', N'$ -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 $91.6(2)^\circ$]. 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

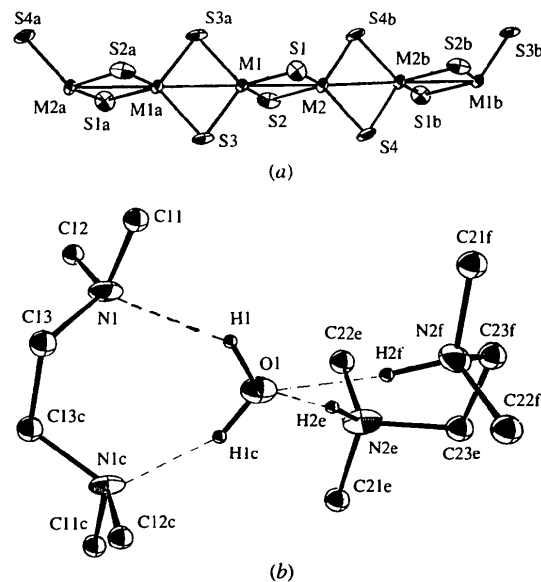


Fig. 1. (a) Structure of a portion of the anionic chain showing 20% probability displacement ellipsoids. (b) Diagram of the hydrogen-bonding pattern showing 20% probability displacement ellipsoids.

[2.475 (6)–2.580 (6) Å] in [(PPh₃)₃Ag₂WS₄].0.8CH₂Cl₂ (Müller, Bögge & Koniger-Ahlborn, 1979). Compared with W···Ag distances in [(PPh₃)₃Ag₂WS₄].0.8CH₂Cl₂ [2.971 (2) Å] and [Ag₄W₂S₈(PMePh₂)₄] [3.002 (2) Å] (Stalick, Siedle, Mighell & Hubbard, 1979), the average M···M distance of 2.946 (2) Å suggests that there is a slight W···Ag interaction in the chain.

The structure determination shows that the water molecule, the tmen molecule and the tmenH₂²⁺ cation lie on twofold axes, and there are hydrogen bonds between O1 and N1 (and N1c), and between O1 and N2e (and N2f): O1—H1···N1 2.85 (3), O1—H1c···N1c 2.85 (3), O1···H2e—N2e 2.82 (3) and O1···H2f—N2f 2.82 (3) Å.

Experimental

The compound was prepared by the reaction of (NH₄)₂WS₄, AgNO₃ and tmen (molar ratio 1:1:2) in H₂O, and recrystallized from DMF. The orange–yellow crystals are stable in air.

Crystal data

(C₆H₁₈N₂)[W₂Ag₂S₈].
(C₆H₁₆N₂).H₂O

M_r = 1092.40

Monoclinic

*C*2/*c*

a = 8.641 (4) Å

b = 21.921 (4) Å

c = 16.298 (4) Å

β = 97.67 (3)°

V = 3059.7 Å³

Z = 4

D_x = 2.37 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 20 reflections

θ = 3–12.5°

μ = 9.45 mm⁻¹

T = 296 K

Rectangular

0.30 × 0.25 × 0.20 mm

Orange–yellow

*R*_{int} = 0.021

θ_{max} = 25°

h = 0 → 10

k = 0 → 26

l = -19 → 19

3 standard reflections

monitored every 300

reflections

intensity decay: 4.2%

Refinement

Refinement on *F*

R = 0.053

wR = 0.054

S = 1.44

1151 reflections

89 parameters

H-atom parameters not

refined

w = 1/[σ²(*F_o*²) + (0.010*F_o*)² + 1]

(Δ/σ)_{max} = 0.33

Δρ_{max} = 1.55 e Å⁻³ (adjacent to metal atoms)

Δρ_{min} = -0.77 e Å⁻³ (adjacent to metal atoms)

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

<i>B</i> _{iso} for C atoms: <i>B</i> _{eq} = (4/3)Σ _{<i>i</i>} Σ _{<i>j</i>} β _{<i>ij</i>} · <i>a_i</i> · <i>a_j</i> for others.				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
M1*	0.4377 (2)	0.43701 (7)	0.4986 (1)	3.70 (3)
M2*	0.3113 (2)	0.31206 (7)	0.4959 (1)	4.12 (3)
S1	0.491 (1)	0.3532 (5)	0.4165 (6)	7.1 (2)
S2	0.254 (1)	0.3964 (5)	0.5766 (6)	7.4 (3)
S3	0.337 (1)	0.5225 (5)	0.4234 (6)	6.7 (2)
S4	0.092 (1)	0.2717 (5)	0.4169 (6)	7.7 (3)
O1	1/2	0.063 (1)	1/4	4.2 (6)
N1	0.348 (2)	0.173 (1)	0.193 (1)	3.9 (5)
N2	0.128 (2)	0.454 (1)	0.196 (1)	4.3 (5)
C11	0.187 (4)	0.167 (1)	0.208 (2)	5.5 (7)
C12	0.342 (4)	0.181 (1)	0.108 (2)	5.3 (7)
C13	0.413 (4)	0.224 (2)	0.244 (2)	6.4 (9)
C21	0.080 (4)	0.446 (1)	0.105 (2)	6.2 (8)
C22	0.303 (4)	0.459 (2)	0.209 (2)	6.8 (9)
C23	0.085 (4)	0.403 (2)	0.246 (2)	7.0 (9)

* Mixed site *M* is defined as 0.50W + 0.50Ag.

Table 2. Selected geometric parameters (Å, °)

M1···M1a'	2.962 (2)	M2···M2b''	2.929 (2)
M1···M2	2.947 (2)	M2—S1	2.331 (9)
M1—S1	2.355 (9)	M2—S2	2.360 (10)
M1—S2	2.340 (9)	M2—S4	2.317 (9)
M1—S3	2.343 (9)	M2—S4b''	2.401 (10)
M1—S3a'	2.354 (9)		
M1a'···M1···M2	179.56 (8)	M1···M2—S2	50.9 (3)
M1a'···M1—S1	129.6 (3)	M1···M2—S4	129.6 (3)
M1a'···M1—S2	128.3 (3)	M1···M2—S4b''	127.1 (2)
M1a'···M1—S3	51.1 (2)	M2b''···M2—S1	131.0 (3)
M1a'···M1—S3a'	50.7 (3)	M2b''···M2—S2	126.7 (3)
M2···M1—S1	50.7 (3)	M2b''···M2—S4	52.9 (3)
M2···M1—S2	51.5 (3)	M2b''···M2—S4b''	50.3 (2)
M2···M1—S3	128.6 (2)	S1—M2—S2	102.3 (4)
M2···M1—S3	129.6 (3)	S1—M2—S4	113.2 (4)
S1—M1—S2	102.1 (4)	S1—M2—S4b''	114.8 (4)
S1—M1—S3	114.5 (3)	S2—M2—S4	113.1 (4)
S1—M1—S3a'	113.0 (3)	S2—M2—S4b''	110.5 (4)
S2—M1—S3	110.9 (3)	S4—M2—S4b''	103.3 (4)
S2—M1—S3a'	115.1 (3)	M1—S1—M2	77.9 (3)
S3—M1—S3a'	101.8 (3)	M1—S2—M2	77.6 (3)
M1···M2···M2b''	176.52 (8)	M1—S3—M1a'	78.3 (3)
M1···M2—S1	51.4 (3)	M2—S4—M2b''	76.7 (3)

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) ½ - *x*, ½ - *y*, 1 - *z*.

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···N1	0.95 (2)	2.04 (2)	2.85 (3)	142 (4)
O1—H1c···N1c'	0.95 (2)	2.04 (2)	2.85 (3)	142 (4)
N2e—H2e···O1''	0.96 (2)	1.88 (3)	2.82 (3)	172 (4)
N2f—H2f···O1'''	0.96 (2)	1.88 (3)	2.82 (3)	172 (4)

Symmetry codes: (i) 1 - *x*, *y*, ½ - *z*; (ii) ½ + *x*, *y* - ½, *z*; (iii) ½ - *x*, *y* - ½, ½ - *z*.

H atoms bonded to C atoms were located theoretically and fixed as riding atoms; those bonded to O1 and N2 atoms were located from difference Fourier syntheses and also fixed as riding atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(1,2-benzenediolato)dimethanol-germanium(IV)

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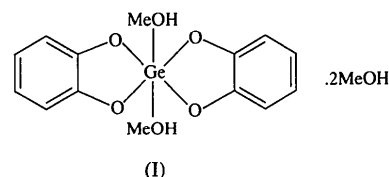
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Abstract

$[\text{Ge}(\text{C}_6\text{H}_4\text{O}_2)_2(\text{CH}_3\text{OH})_2] \cdot 2\text{CH}_3\text{OH}$ was prepared from germanium dioxide and catechol in refluxing H_2O followed by refluxing the crude product in methanol; the product was identified by IR, ^1H NMR, ^{13}C NMR and elemental analysis. The complex has a slightly distorted octahedral structure with two methanol ligands in axial positions and two bidentate deprotonated catechols in equatorial positions. The Ge—O bonds involving the methanol groups are longer than the Ge—O bonds involving the catechol ligands.

Comment

Reports concerned with the structures of germanium complexes indicate that the coordination numbers of the central Ge atom are diverse (Yoder & Zukerman, 1967; Sau & Holmes, 1981; Day, Holmes, Sau & Holmes, 1982; Lazraq, Couret, Declercq, Dubourg, Escudie & Riviere-Bandet, 1990; Cereau, Chuit, Corriu & Reye, 1991). Among these, Yoder & Zukerman (1967) reported that the complex $[\text{Ge}(\text{C}_6\text{H}_4\text{O}_2)_2(\text{C}_5\text{H}_5\text{N})_2]$ has an octahedral structure and Sau & Holmes (1981) showed that the complex $[\text{Ge}(\text{C}_6\text{H}_4\text{O}_2)_2\text{X}]^-$ is square pyramidal. These interesting findings have prompted our investigation of related derivatives with catechol, as a part of a general study of the structures of germanium complexes (Chiang, Lin & Ueng, 1992; Chiang, Wang & Ueng, 1993). Here we report the synthesis and structure of the title compound, (I).



An *ORTEP* diagram (Johnson, 1965) of the molecular structure is shown in Fig. 1. The complex has a slightly distorted octahedral structure with two methanol molecules in axial positions and two bidentate deprotonated catechol moieties in equatorial positions. The Ge atom lies on a crystallographic inversion centre, as found in $[\text{Ge}(\text{H}_2\text{O})_2\{\text{OCH}(\text{C}_6\text{H}_5)\text{COO}\}_2]$ (Sterling, 1967) and $[\text{Ge}(\text{H}_2\text{O})_2(\text{OCH}_2\text{COO})_2]$ (Chiang, Wang & Ueng, 1993). The 12 *cis* angles around the metal are in the range $89.3(1)$ – $90.8(1)^\circ$ and the dihedral angles between two of the three mutually perpendicular planes are $90.06(5)$, $89.25(5)$ and $90.50(5)^\circ$. The Ge—O bond lengths for the methanol group are longer than those for the catechol groups owing to the stronger coordination for the aryloxy ligands. The good planarity of the five-membered chelate rings is indicated by the sum of the

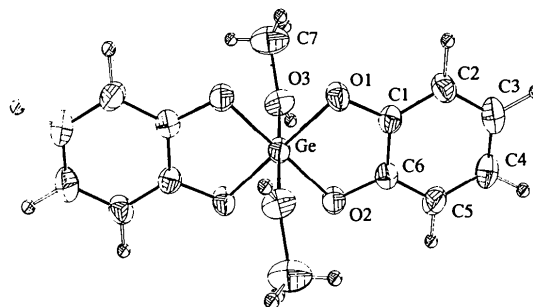


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular structure of $[\text{Ge}(\text{C}_6\text{H}_4\text{O}_2)_2(\text{CH}_3\text{OH})_2]$. Displacement ellipsoids are shown at the 50% probability level.