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A Triangular $[\text{Mo}_3\text{S}_7]^{4+}$ Complex: Tris-(diethyldithiocarbamato- S,S')tris(μ_2 - η^2 -disulfido)(μ_3 -sulfido)trimolybdenum(IV)-(3 Mo—Mo) Diethyldithiocarbamate

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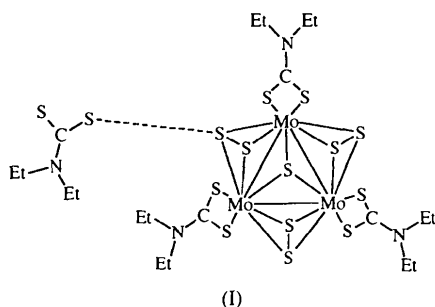
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Abstract

In the cluster cation of the title compound, $[\text{Mo}_3\text{S}_7(\text{Et}_2\text{NCS}_2)_3](\text{Et}_2\text{NCS}_2)$, three Mo atoms form an approximately equilateral triangle, with Mo—Mo distances ranging from 2.7140 (5) to 2.7277 (5) Å, and Mo—Mo—Mo angles of *ca* 60°. The triangle is capped by the μ_3 -S atom, and each Mo—Mo bond is bridged by a disulfido group in μ_2 - η^2 mode. Diethyldithiocarbamate ligands (Et_2dtc) are chelated to the Mo atoms with an average S—Mo—S bite angle of 69.98 (1)°. There is a weak S...S interaction between the cluster cation and the anion (Et_2dtc^-).

Comment

Compounds containing the $[\text{Mo}_3\text{S}_7]^{4+}$ core have been studied extensively (Müller *et al.*, 1979; Keck *et al.*, 1981). Fedin, Sokolov, Virovets *et al.* (1991) have synthesized the title compound, (I), using $(\text{Et}_4\text{N})_2\text{Mo}_3\text{S}_7\text{Br}$ as the starting material, but the crystal structure of the compound has not yet been reported.



The structure of complex (I) consists of an $[\text{Mo}_3\text{S}_7(\text{Et}_2\text{dtc})_3]^+$ cation and an Et_2dtc^- anion (Fig. 1). The cluster cation contains an Mo_3 triangle capped by a μ_3 -S atom, with Mo—Mo distances and Mo—Mo—Mo bond angles ranging from 2.7140 (5) to 2.7277 (5) Å

and from 59.68 (1) to 60.18 (1)°, respectively. There are three parallel planes in the Mo_3S_7 core: the Mo_3 plane, S1/S3/S5 and S2/S4/S6, with a maximum dihedral angle of 1.34 (3)°. In the three S_2 groups, the equatorial S2, S4 and S6 atoms, and the axial S1, S3 and S5 atoms, deviate from the Mo_3 plane by not more than 0.17 Å for the former, and by not less than 1.63 Å for the latter. The Mo_3S_7 core of the cation has idealized C_{3v} symmetry, with a C_3 axis passing through the μ_3 -S atom, and this symmetry also includes the NCS_2 groups of three Et_2dtc^- ligands. All these structural features of the $[\text{Mo}_3\text{S}_7]^{4+}$ core are very similar to those of other complexes reported with an $[\text{M}_3\text{X}_7]^{n+}$ core, for instance, $M = \text{Mo}$ or W , $X = \text{S}$ or Se , $n = 4$ (Shang *et al.*, 1984; Lu *et al.*, 1994; Fedin, Sokolov, Geras'ko *et al.*, 1991; Fedin, Sokolov, Virovets *et al.*, 1991; Hegetchweiler *et al.*, 1991; Zimmermann *et al.*, 1991) or $M = \text{V}$, $X = \text{S}$, $n = 2$ (Yang *et al.*, 1993; Dean *et al.*, 1993).

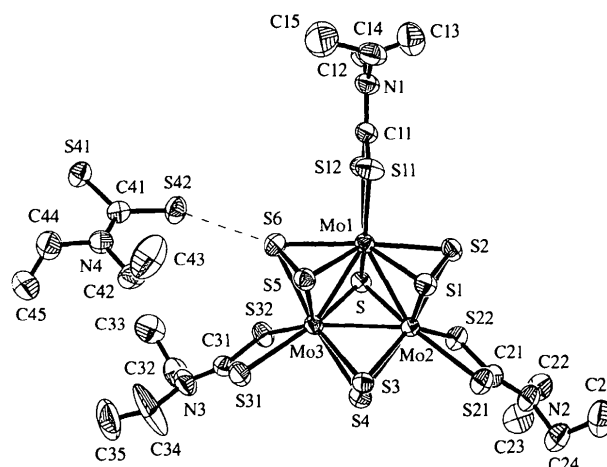


Fig. 1. ORTEP (Johnson, 1976) plot of the molecular structure of $[\text{Mo}_3\text{S}_7(\text{Et}_2\text{dtc})_3](\text{Et}_2\text{dtc})$, showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

All the $[\text{Mo}_3\text{S}_7]^{4+}$ cores of these complexes, including (I), exhibit almost the same structural parameters: (i) Mo—Mo distances in the range 2.700–2.782 Å and Mo—Mo—Mo bond angles of *ca* 60°; (ii) Mo— μ_3 -S bond distances in the range 2.336–2.386 Å; (iii) Mo— S_{eq} distances in the range 2.406–2.416 Å and Mo— S_{ax} distances of 2.487–2.511 Å; (iv) $\text{S}_{\text{eq}}-\text{S}_{\text{ax}}$ distances in the range 2.021–2.069 Å.

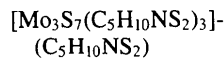
Compared with the selenium analogue, $[\text{Mo}_3\text{Se}_7(\text{Et}_2\text{dtc})_3](\text{Et}_2\text{dtc})$, (II) (Fedin, Sokolov, Geras'ko *et al.*, 1991), complex (I) has an obviously smaller $[\text{Mo}_3\text{S}_7]$ core than the $[\text{Mo}_3\text{Se}_7]$ core of (II). Specifically, all the bond distances in the cluster core of (I) are shorter than those of (II). Examples are: the average Mo—Mo distance [(I) 2.723; (II) 2.778 Å], Mo— μ_3 -X [(I) $X = \text{S}$, 2.386 Å; (II) $X = \text{Se}$, 2.498 Å], Mo— X_{ax} [(I) 2.490; (II) 2.617 Å] and Mo— X_{eq} [(I) 2.406; (II)

2.532 Å]. However, the average Mo—S_{dtc} distance, and the S_{dtc}—Mo—S_{dtc} bite angle [(I) 2.504 Å and 69.98°; (II) 2.505 Å and 69.4°] are almost in agreement. In addition, similar to the weak Se···S_{anion} bonding found in complex (II), an interaction between the S_{dtc} atom in the Et₂dtc[−] anion and the S atom in the cation of (I) has also been observed, with an S42···S6 separation of 3.543 (2) Å.

Experimental

The title compound was obtained as red-brown prismatic crystals, in an attempt to prepare Mo/Ag/S heterometallic cluster compounds. To a mixture of (NH₄)₂MoS₄ (0.26 g, 1 mmol), Ag(PPh₃)₂Cl (1.336 g, 2 mmol), Na(Et₂dtc) (0.69 g, 4 mmol) and Et₄NCl (0.40 g, 3 mmol) was added 30 ml of MeCN. The suspension was stirred for 24 h at room temperature and then filtered. The volume of the dark-red filtrate was reduced to 20 ml, and crystals formed over a period of two months.

Crystal data



M_r = 1105.35

Triclinic

P $\bar{1}$

a = 10.8058 (3) Å

b = 11.1736 (3) Å

c = 16.7577 (5) Å

α = 93.700 (1)°

β = 90.732 (1)°

γ = 100.238 (1)°

V = 1986.35 (10) Å³

Z = 2

D_x = 1.848 Mg m^{−3}

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6424 reflections

θ = 1.86–23.25°

μ = 1.743 mm^{−1}

T = 293 (2) K

Prism

0.40 × 0.30 × 0.12 mm

Red-brown

Data collection

Siemens SMART
diffractometer

ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

T_{min} = 0.563, *T_{max}* = 0.811

7717 measured reflections

5436 independent reflections

5084 reflections with

I > 2 σ (*I*)

R_{int} = 0.037

θ_{\max} = 23.25°

h = −11 → 11

k = −12 → 9

l = −18 → 18

Refinement

Refinement on *F*²

R(*F*) = 0.030

wR(*F*²) = 0.082

S = 0.802

5436 reflections

388 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 6.4177P]$

where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.017

$\Delta\rho_{\max} = 0.541 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.542 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mo1—S	2.3845 (11)	Mo2—S4	2.4970 (12)
Mo1—S5	2.3961 (11)	Mo2—S21	2.5126 (12)
Mo1—S1	2.4184 (11)	Mo2—Mo3	2.7277 (5)
Mo1—S2	2.4703 (11)	Mo3—S	2.3850 (11)
Mo1—S12	2.4991 (11)	Mo3—S5	2.3957 (11)
Mo1—S11	2.5078 (12)	Mo3—S3	2.4167 (11)
Mo1—S6	2.5096 (12)	Mo3—S32	2.4813 (12)
Mo1—Mo2	2.7140 (5)	Mo3—S4	2.4954 (12)
Mo1—Mo3	2.7268 (5)	Mo3—S6	2.5059 (12)
Mo2—S	2.3873 (11)	Mo3—S31	2.5319 (12)
Mo2—S1	2.4033 (11)	S1—S2	2.112 (2)
Mo2—S3	2.4060 (11)	S3—S4	2.068 (2)
Mo2—S2	2.4645 (11)	S5—S6	2.037 (2)
Mo2—S22	2.4926 (12)		
S12—Mo1—S11	70.08 (4)	Mo3—S—Mo2	69.72 (3)
Mo2—Mo1—Mo3	60.177 (13)	Mo2—S1—Mo1	68.51 (3)
S22—Mo2—S21	70.06 (4)	Mo2—S2—Mo1	66.73 (3)
Mo1—Mo2—Mo3	60.144 (13)	Mo2—S3—Mo3	68.89 (3)
S32—Mo3—S31	69.80 (4)	Mo3—S4—Mo2	66.24 (3)
Mo1—Mo3—Mo2	59.679 (13)	Mo3—S5—Mo1	69.37 (3)
Mo1—S—Mo3	69.74 (3)	Mo3—S6—Mo1	65.87 (3)
Mo1—S—Mo2	69.33 (3)		

Twofold disorder was refined for C35. Highly anisotropic displacement parameters for this atom and for C34 show that the model is only approximate.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1994a). Data reduction: SHELXTL (Siemens, 1994b). Program(s) used to solve structure: SHELXTL. Program(s) used to refine structure: SHELXTL. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1227). Services for accessing these data are described at the back of the journal.

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Octakis(dimethyl sulfoxide-*O*)-gadolinium(III) Hexacyanoferrate(III)

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Abstract

In $[\text{Gd}(\text{C}_2\text{H}_6\text{OS})_8][\text{Fe}(\text{CN})_6]$, the central atom of the $[\text{Gd}(\text{C}_2\text{H}_6\text{OS})_8]^{3+}$ complex cation occupies a twofold axis, while in the $[\text{Fe}(\text{CN})_6]^{3-}$ anion, it is positioned on a centre of inversion. Gd—O bond lengths vary between 2.374 (5) and 2.417 (5) Å, but the Fe—C distances of 1.943 (8)–1.952 (8) Å are equal, within experimental error.

Comment

It is well known that hexacyanometallates can be successfully used as building blocks for constructing bimetallic assemblies which exhibit spontaneous magnetization. Two types of compounds have been prepared: (i) Prussian analogues, $A_kB(\text{CN})_6$, where *A* and *B* are either two transition metals or rare-earth ions (Verdaguer, 1996; Khan, 1995; Hulliger *et al.*, 1976), and (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ combined with transition metal complexes (Salah el Fallah *et al.*, 1996). In an attempt to prepare compounds of the latter type, a Gd^{III} complex of the Schiff base which is formed through the 2:1 condensation reaction of 2-pyridinecarboxaldehyde and ethylenediamine was combined with the $[\text{Fe}(\text{CN})_6]^{3-}$ ion. It is noteworthy that, in the reaction conditions used, the Schiff base ligand and the water molecules coordinated to the Gd^{III} atom were replaced by dimethyl sulfoxide (DMSO) molecules, and well developed yellow crystals of the compound $[\text{Gd}(\text{DMSO})_8][\text{Fe}(\text{CN})_6]$, (I), were formed after five days. We report here the structure of this last compound, which consists of discrete $[\text{Gd}(\text{DMSO})_8]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions. The Gd^{III} atom occupies a twofold axis, while the Fe^{III} atom is positioned on a centre of inversion.

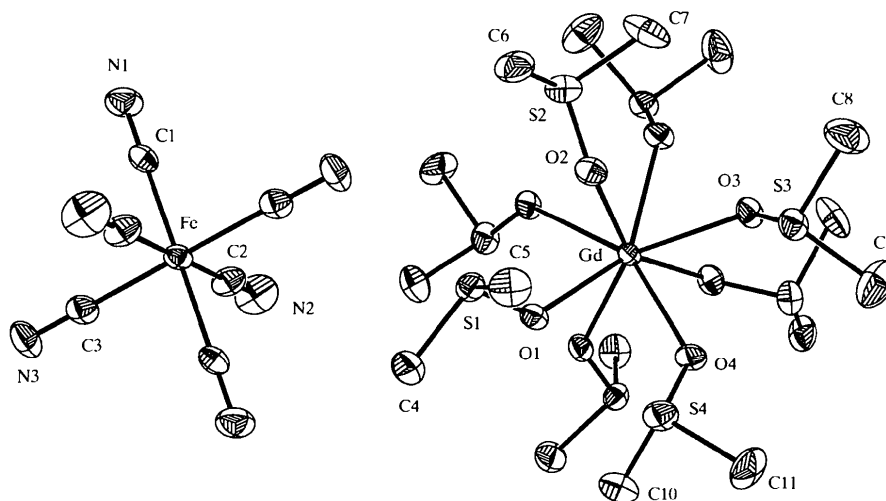
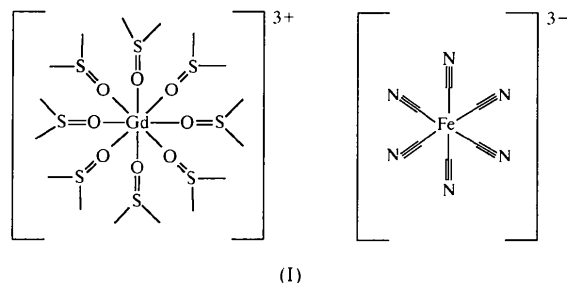


Fig. 1. View of $[\text{Gd}(\text{DMSO})_8][\text{Fe}(\text{CN})_6]$, showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.