

Bis[tris(diisobutyldithiocarbamato)- μ_3 -sulfido-tri- μ_2 -disulfido-trimolybdenum(IV)] sulfide tetrahydrofuran monosolvate

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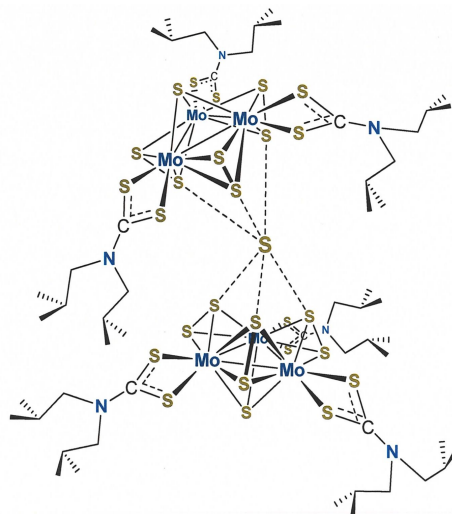
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The title compound, $[\text{Mo}_3(\text{C}_9\text{H}_{18}\text{NS}_2)_3(\text{S}_2)_3\text{S}]_2\text{S}$, crystallizes on a general position in the monoclinic space group $P2_1/n$ (No. 14). The cationic $[\text{Mo}_3\text{S}_7(\text{S}_2\text{C}-\text{N}^i\text{Bu}_2)_3]^+$ fragments are joined by a monosulfide dianion that forms close $\text{S}\cdots\text{S}$ contacts to each of the disulfide ligands on the side of the Mo_3 plane opposite the μ_3^{2-} ligand. The two Mo_3 planes are inclined at an angle of $40.637(15)^\circ$, which gives the assembly an open clamshell-like appearance. One $\mu_6\text{-S}^{2-}\cdots\text{S}_2^{2-}$ contact, at $2.4849(14)\text{ \AA}$, is appreciably shorter than the remaining five, which are in the range $2.7252(13)$ – $2.8077(14)\text{ \AA}$.

1. Chemical context

Triangular molybdenum sulfide clusters of the form $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CNR}_2)_3]^+\text{I}^-$ (R = alkyl group) function as precatalysts for an H_2 evolving system under both photolytic and electrolytic conditions with H_2O serving as source of protons (Fontenot *et al.*, 2019). In the photolysis system, rapid mass spectrometry assays in the first moments of irradiation reveal the loss of atomic sulfur from the bridging S_2^{2-} ligands to form monosulfido bridges and an $[\text{Mo}_3\text{S}_4]^{4+}$ core prior to the onset of H_2 evolution. In a bulk electrolysis of $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]^+\text{I}^-$ in the presence of H_2O , the Faradaic efficiency is observed to be only about 37%. Because the same system and set of conditions reduced methyl viologen with much higher Faradaic efficiency, it is probable the the extruded elemental sulfur is competing for reducing equivalents.



As a means of developing further insight into this system, we undertook a preparative scale reduction of $[\text{Mo}_3\text{S}_7(\text{S}_2-$

$\text{CN}^i\text{Bu}_2)_3]^+ \text{I}^-$ using the prototypical outer-sphere reductant Cp_2Co . While the initial reaction was marked by a darkening in color, the work-up and subsequent crystallization identified yellow $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$ as the dominant isolable species. The presence of the sulfido counter-anion, which forms close $\text{S} \cdots \text{S}$ contacts with the axial S atoms of the bridging disulfide ligands of two different $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]^+$ clusters, confirms the diversion of electrons to free S^0 in competition with H^+ reduction in the bulk electrolysis. In this article, we detail the structural features of $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$, (I).

2. Structural commentary

The $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$ structure comprises two $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]^+$ cations between which is ensconced an S^{2-} counter-anion (S27). The asymmetric joining of the two Mo_3 clusters, as if by a hinge at S27, produces a half-opened clamshell-like appearance to the compound (Fig. 1). The angle at which these two Mo_3 planes are disposed is $40.637(15)^\circ$ with a distance of 6.88 \AA between the centroids of the two Mo_3 triangles.

A general observation in the structures of $[\text{Mo}_3\text{E}_7(\text{S}_2\text{CNR}_2)_3]^+$ ($\text{E} = \text{S}$ or Se ; $\text{R} = \text{alkyl group}$) complexes is that soft monoatomic counter-anions situate themselves at the ‘underside’ of the cluster cation opposite to the unique $\mu_3\text{-E}$ ligand and in close proximity to the ‘axial’ chalcogen atom of the bridging dichalcogenide (Fig. 2) (Zimmermann *et al.*, 1991; Fedin *et al.*, 1992; Il’inchuk *et al.*, 2002; Lu *et al.*, 1993).

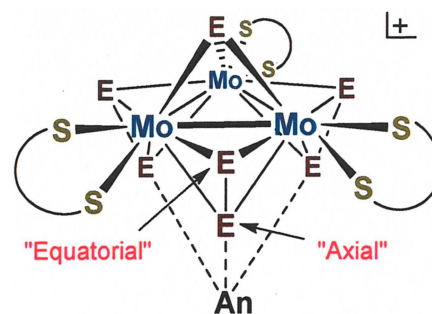


Figure 2
Illustration of the structural distinction between axial and equatorial sulfur atoms of the $\mu\text{-S}_2^{2-}$ ligands in $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CNR}_2)_3]^+$ structures, with anion position in proximity to the axial S atoms.

These anion $\cdots \text{E}_{\text{ax}}$ contacts are typically less than the sum of the van der Waals radii, a fact attributed to an electrophilic character of the E_{ax} atom and the felicitous nature of the ‘soft-soft’ $\text{E}_{\text{ax}} \cdots \text{anion}$ interaction. In $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$, the $\text{S27} \cdots \text{S}_{\text{ax}}$ interatomic distances partition into two sets: the $\text{S27} - \text{S3}$ distance at $2.4849(14) \text{ \AA}$ and the remaining five, which are in the range $2.7252(13) - 2.8077(14) \text{ \AA}$, all of which are substantially less than twice the crystallographic radius for sulfur (3.6 \AA ; Batsanov, 2001) and therefore indicative of appreciable covalency to the interactions. The markedly stronger interaction of S27 with the $\text{S3} - \text{S4}$ disulfide ligand is

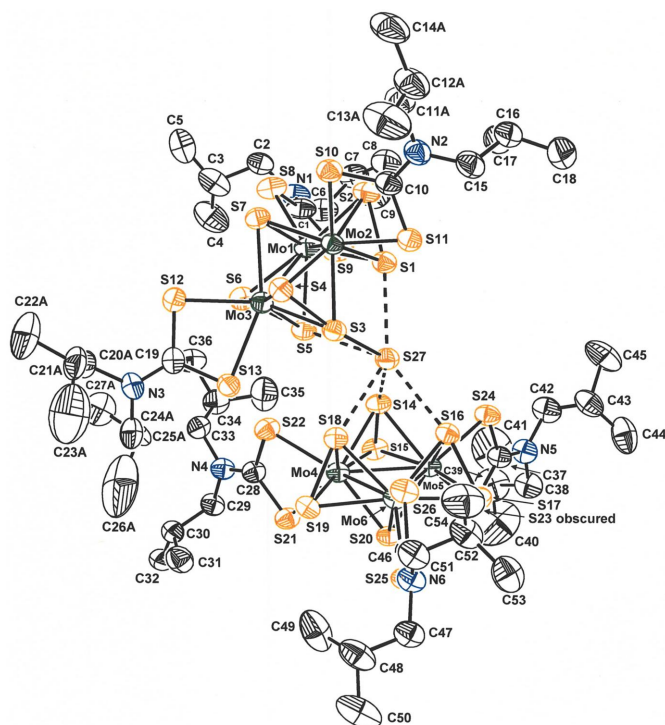


Figure 1
Displacement ellipsoid plot (50% probability level) of $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$ with complete atom labeling. For greater clarity, all H atoms and one of the two disordered parts of each disordered isobutyl group are removed.

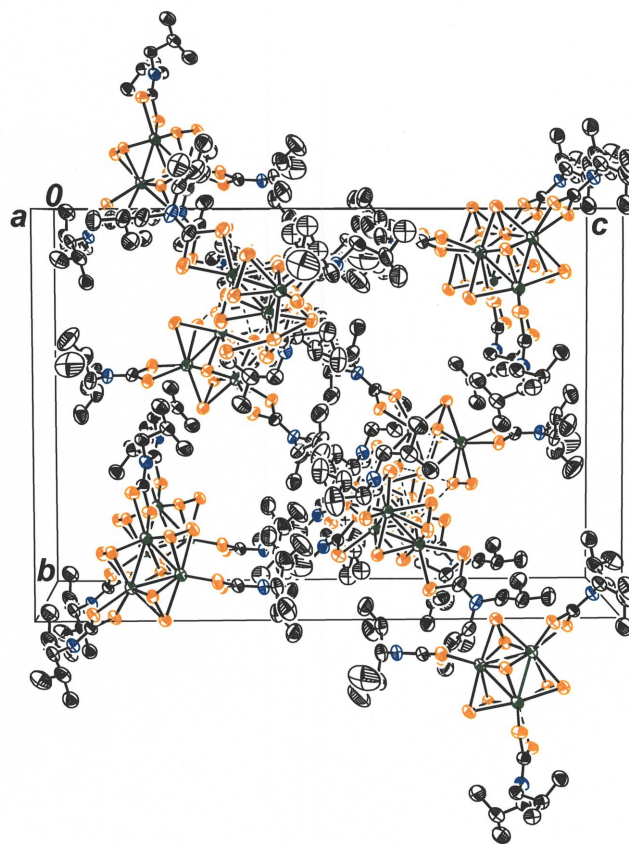


Figure 3
Packing arrangement for $[\text{Mo}_3\text{S}_7(\text{S}_2\text{CN}^i\text{Bu}_2)_3]_2(\mu_6\text{-S})$ viewed down the a axis of the unit cell. Displacement ellipsoids are presented at the 50% probability level, and all H atoms are omitted for clarity.

Table 1
Experimental details.

Crystal data	
Chemical formula	[Mo ₃ (C ₉ H ₁₈ NS ₂) ₃ (S ₂) ₃ S] ₂ S
<i>M_r</i>	2282.72
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.1699 (7), 21.1139 (10), 30.0046 (14)
β (°)	91.576 (2)
<i>V</i> (Å ³)	10240.0 (8)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	11.24
Crystal size (mm)	0.36 × 0.27 × 0.12
Data collection	
Diffractometer	Bruker D8 QUEST PHOTON 3
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.120, 0.355
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	332865, 20942, 18768
<i>R</i> _{int}	0.054
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.627
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.038, 0.089, 1.15
No. of reflections	20942
No. of parameters	967
No. of restraints	492
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.55, -0.67

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

manifested in the S3–S4 distance being significantly longer [2.2414 (13) Å] than the remaining S–S distances in the μ -S₂²⁻ ligands, which range from 2.0671 (13)–2.1198 (13) Å and average as 2.0857 (6) Å. This comparative elongation of the S3–S4 bond length is consistent with the proposal, as advanced in a review of the structural chemistry of [M₃X₇]⁴⁺ and [M₃X₄]⁴⁺ (*M* = Mo, W; *X* = O, S, Se) clusters (Virovets & Podberezkaya, 1993), that the sulfide counter-anion (S27) infuses electron density into the S3–S4 σ^* orbital by overlap with one of its electron lone pairs.

The packing arrangement for [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S) places the assembly into columnar stacks along the *a* axis of the cell (Fig. 3). The *isobutyl* substituents of the ^{*i*}Bu₂NCS₂⁻ ligands project into the spacings between these columns and likely play a decisive role in guiding the formation of this pattern by virtue of favorable dispersion-type attractive forces.

3. Database survey

The first reported observation of the [Mo₃E₇(S₂CNR₂)₃]₂(μ ₆-E) (*E* = S or Se) structure type was a serendipitous formation of [Mo₃S₇(S₂CNET₂)₃]₂(μ ₆-S) by substitution of the oxyquinolate (oxq) ligands in [Mo₃S₇(oxq)₃]⁺ with a slight excess of Na⁺Et₂NCS₂⁻ in wet DMSO, the presumed source of the bridging S²⁻ ligand being the excess Et₂NCS₂⁻ anion *via* hydrolysis (Meienberger *et al.*, 1993). Here, the assembly crystallized in *Ab*a2 (No. 41) upon a crystallographic *C*₂ axis

that was coincident with the μ ₆-S²⁻ ligand. The angle formed by the two Mo₃ planes was 33.37° in [Mo₃S₇(S₂CNET₂)₃]₂(μ ₆-S), somewhat smaller than the analogous value in [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S), but the Mo₃···Mo₃ centroid-to-centroid distance was 7.00 Å, slightly greater than the 6.88 Å assessed for [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S). Notably, the μ ₆-S²⁻···S_{ax} distances spanned a much more narrow range of 2.70 (1)–2.72 (1) Å than seen in [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S), possibly because the latter's more sterically encumbering *isobutyl* groups have hindered close, symmetric approach to the S²⁻ bridge.

Another structure of the type with an all selenium inorganic core, [Mo₃Se₇(S₂CNET₂)₃]₂(μ ₆-Se), was obtained by the oxidative addition of Et₂NC(S)S-SC(S)NET₂ and Se⁰ to Mo(CO)₆ and crystallized as an isomorph of [Mo₃S₇(S₂CNET₂)₃]₂(μ ₆-S) with a similar unit cell in the same space group (Almond, *et al.*, 2000). Although larger in magnitude than the corresponding values in [Mo₃S₇(S₂CNET₂)₃]₂(μ ₆-S), the spread in Se_{ax}··· μ ₆-Se²⁻ interatomic distances was still narrow compared to the range of analogous values in [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S). A pseudopolymorph of [Mo₃Se₇(S₂CNET₂)₃]₂(μ ₆-Se) with interstitial 1,2-dichlorobenzene revealed a similar range in Se_{ax}··· μ ₆-Se distances as seen for the structure without solvent (Brakefield *et al.*, 2020). The tungsten analogue, [W₃Se₇(S₂CNET₂)₃]₂(μ ₆-Se), prepared similarly from W(CO)₆ (Almond *et al.*, 2000), has also been described and is the only other example of the structure type.

4. Synthesis and crystallization

A solution of [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂I (0.049 g, 0.0039 mmol) in tetrahydrofuran (THF) was cooled to 195 K in the cold well of a glove-box. Upon cooling, a solution of cobaltocene in THF (0.0183 g, 0.0968 mol) was added dropwise to the stirring solution. This reaction mixture was stirred at 243 K for 30 min and then was removed from the cold well and warmed to room temperature with continued stirring. Upon attaining room temperature, the solution was filtered through Celite, and the volatiles were removed under reduced pressure. The oily residue was then dissolved in 20% THF in hexanes and passed through a 3 cm pad of silica in a glass pipette. All volatiles were then removed under reduced pressure to yield a dark-orange–brown oil. Crystals suitable for X-ray diffraction were grown by layering a concentrated THF solution with hexanes and maintaining the layered mixture at 243 K. Yield: 70%. ¹H NMR (300 MHz; δ , ppm in CDCl₃): 3.59 (*dd*, *J* = 24 Hz, 7.5 Hz, 2H, *CH*₂), 2.22 (*m*, 1H, *CH*), 0.95 (*d*, *J* = 6.6 Hz, 6H, *CH*₃).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. An initial solution for [Mo₃S₇(S₂CN^{*i*}Bu₂)₃]₂(μ ₆-S) was obtained by direct methods and revealed the positions of most of the non-H atoms except for some peripheral C atoms of the *isobutyl* groups. Subsequent cycles of least-squares refinement revealed several *isobutyl* groups that suffered a static disorder over two posi-

tions. This disorder was treated with a split atom model that attained a best fit distribution in each case. All non-H atoms were refined anisotropically, but the disordered C atoms were treated with SIMU and RIGU restraints. All H atoms were refined isotropically as riding atoms with displacement parameters 1.2–1.5 times those of the C atoms to which they were attached. In the final difference maps, two positions occupied by disordered solvent molecules were identified. These severely disordered solvent molecules, which presented an electron density attributable to 367 electrons in a solvent-accessible volume of 1692 Å³ per unit cell, have been masked using the SQUEEZE routine (Spek, 2015) in *PLATON* (Spek, 2020).

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