

**Preparation and X-Ray Crystal Structure of $[\text{S}_2\text{MoS}_2\text{Mo}(\text{NNMe}_2)_2(\text{PPh}_3)]$,
a Binuclear Molybdenum Hydrazido(2-)-complex containing
Co-ordinated Tetrathiomolybdate**

By JONATHAN R. DILWORTH*

(ARC Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ)

and JON A. ZUBIETA

(Department of Chemistry, State University of New York at Albany, Albany, NY 12222)

Summary Reaction of $[\text{MCl}(\text{NNMe}_2)_2(\text{PPh}_3)_2]\text{Cl}$ ($\text{M} = \text{Mo}$ or W) with $[\text{Bu}^n_4\text{N}]_2[\text{M}'\text{S}_4]$ ($\text{M}' = \text{Mo}$, W) gives the complexes $[\text{S}_2\text{M}'\text{S}_2\text{M}(\text{NNMe}_2)_2(\text{PPh}_3)]$; an X-ray crystal structure of the dinuclear complex with $\text{M} = \text{M}' = \text{Mo}$ shows the molybdenum atoms to have distorted tetrahedral and trigonal bipyramidal geometries.

Complex (1) crystallises from acetonitrile as monoclinic crystals, space group Cc , $a = 15.301(3)$, $b = 10.266(4)$, $c = 18.339(3)$ Å, $\beta = 90.03(1)^\circ$, $U = 2880.68$ Å³, $Z = 4$. The structure solution was based on 2512 reflections with

RECENT EXAFS studies of both nitrogenase and the iron-molybdenum co-factor suggest that the molybdenum is ligated by sulphur.¹ Moreover, it seems probable that the sulphur is predominantly sulphide in character, functioning in part to bridge to one or more adjacent iron atoms. Hydrazido(2-)-species are intermediates in the protonation of co-ordinated dinitrogen to ammonia on molybdenum, and we here report our initial efforts to synthesise hydrazido(2-)-complexes with μ -sulphido-ligands. The title complex is both the first tetrathiomolybdate derivative with multiply bonded nitrogen ligands and the first binuclear bis[hydrazido(2-)-]complex.

The hydrazido(2-)-complex $[\text{MoCl}(\text{NNMe}_2)_2(\text{PPh}_3)_2]\text{Cl}^2$ reacts with $[\text{Bu}^n_4\text{N}]_2[\text{MoS}_4]$ in acetonitrile at room temperature to produce dark green dichroic crystals of $[\text{S}_2\text{MoS}_2\text{Mo}(\text{NNMe}_2)_2(\text{PPh}_3)]$ (1). The analogous product (2) formed from $[\text{WS}_4]^{2-}$ is dark red. Similarly, reactions of $[\text{WCl}(\text{NNMe}_2)_2(\text{PPh}_3)_2]\text{Cl}^2$ with $[\text{Bu}^n_4\text{N}]_2[\text{M}'\text{S}_4]$ yield $[\text{S}_2\text{M}'\text{S}_2\text{W}(\text{NNMe}_2)_2(\text{PPh}_3)]$. The u.v. spectrum of (1) in dimethylformamide solution shows bands at 610(1030), 520(4300), 480(6500), 356(6300), and 290(8500) nm (molar absorptivities in parentheses). The ¹H n.m.r. spectrum in CD₂Cl₂ showed a singlet at δ 1.45 assigned to equivalent hydrazido methyl groups.

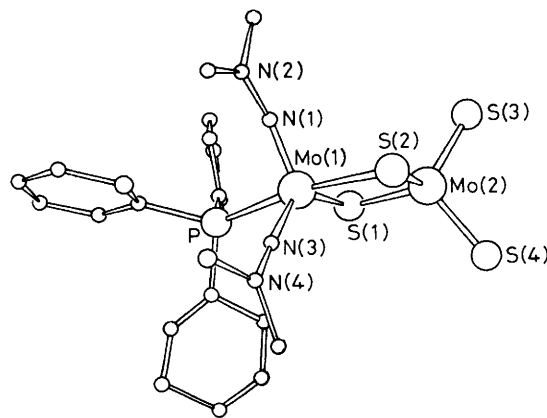


FIGURE. ORTEP representation of the molecular geometry of $[\text{S}_2\text{MoS}_2\text{Mo}(\text{N}_2\text{Me}_2)_2\text{PPh}_3]$. Some relevant bond lengths and interatomic distances (Å) and angles ($^\circ$) are: Mo(1) Mo(2) 3.006(3); Mo(1)-S(1) 2.397(8); Mo(1)-S(2) 2.517(11); Mo(1)-N(1) 1.78(3); Mo(1)-N(3) 1.85(3); Mo(1)-P 2.468(10); Mo(2)-S(1) 2.244(10); Mo(2)-S(2) 2.235(10); Mo(2)-S(3) 2.153(10); Mo(2)-S(4) 2.139(11); N(1)-N(2) 1.30(4); N(3)-N(4) 1.27(4); \angle S(1)-Mo(1)-S(2) 94.1(3); S(1)-Mo(1)-N(1) 117.3(11); S(1)-Mo(1)-N(3) 129.9(11); S(2)-Mo(1)-P 170.7(4); N(1)-Mo(1)-N(3) 112.6(15); S(1)-Mo(2)-S(2) 106.9(4); S(1)-Mo(2)-S(3) 108.6(4); S(1)-Mo(2)-S(4) 108.7(4); S(2)-Mo(2)-S(3) 110.9(5); S(2)-Mo(2)-S(4) 110.9(4); S(3)-Mo(2)-S(4) 110.7(5); Mo(1)-N(1)-N(2) 165.0(30); Mo(1)-N(3)-N(4) 178.2(30).

$I_{\text{obs}} > 3.0\sigma(I)$. The two Mo atom positions were determined from a Patterson map, and non-hydrogen atoms were located from the subsequent difference Fourier synthesis. The current value for R is 0.098.†

The structure (Figure) is unusual in the trigonal bipyramidal geometry exhibited by Mo(1). To date only tetrahedral and square-pyramidal geometries have been reported for tetrathiomolybdate co-ordinated metal ions. The hydrazido(2-)-ligands are essentially equivalent with comparable Mo-N and N-N distances and both Mo-N-N systems are linear or nearly so.³ This is in contrast to the complex $[\text{MoCl}(\text{NNMe}_2)_2(\text{PPh}_3)_2]^+$ where there are considerable differences in the bond lengths and angles within the hydrazido(2-)-ligands.² The bridging sulphido-atom S(1) completes the equatorial plane. The differences in the Mo(1)-S(1) and Mo(1)-S(2) bond lengths reflect their occupancy of the equatorial and axial positions about Mo(1) respectively. The average Mo(2)-terminal sulphide distance of 2.14(5) Å

lies within the range for other tetrathiomolybdate derivatives,⁴ as does the average Mo(2)-bridging sulphide distance of 2.24(1) Å.

Complex (1) reacts rapidly with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ to give a deep red-purple solution with u.v. bands at 512, 570, 408, and 360 nm. An analogous product containing three different metal ions is obtained from complex (2) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and these Fe^{II} -cluster species are currently being characterised. The complexes $[\text{MCl}(\text{NNMe}_2)_2(\text{PPh}_3)_2]$ ($\text{M} = \text{Mo}, \text{W}$) do not react with $[\text{Cl}_2\text{FeS}_2\text{MoS}_2]^{2-}$ ⁵ to give the same products, indicating that the sequence of addition of metal ions is important in the construction of these asymmetric clusters.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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