

Thiol Exchange Reactions of Iron–Molybdenum–Sulphur Clusters; Preparation and X-Ray Crystal Structure of $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_9]$, a Water Soluble Iron–Molybdenum–Sulphur Cluster

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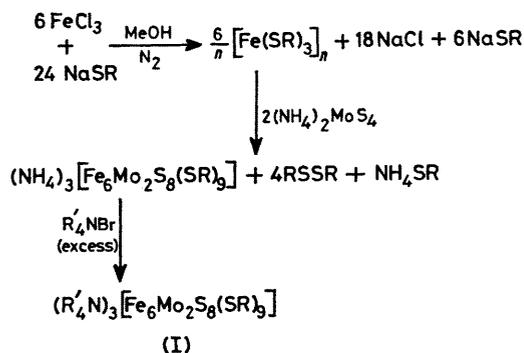
Summary Complete thiolato-ligand exchange has been demonstrated for $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ (R = alkyl) complexes and used to prepare the water-soluble 2-hydroxyethanethiolato-derivative which has been structurally characterised as its $[\text{Et}_4\text{N}]^+$ salt; the complex is stable in buffered aqueous solution, in the presence of an excess of 2-hydroxyethanethiol, and in the absence of dioxygen.

RECENTLY we have reported the isolation¹ and characterisation² of $[\text{Bu}_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SPh})_9]$. A similar compound, $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SEt})_9]$, has been prepared by Holm *et al.*³ Compounds containing Fe_3MoS_4 'cubes' are of particular interest since they contain the molybdenum in an environment which closely resembles that suggested for this atom in nitrogenase enzymes and their FeMo-cofactor.⁴

We have, therefore, been interested in developing the chemistry of compounds containing Fe_3MoS_4 species.

We have used the reaction sequence shown in the Scheme to prepare a range of compounds of type (I). Exchange of alkylthiolato-groups of $[\text{Fe}_6\text{S}_4(\text{SR})_4]^{2-}$ complexes under mild conditions is readily accomplished⁵ and we wished to ascertain if this would occur for the corresponding iron-molybdenum complexes. Treatment of (I) (R = R' = Et) with an excess of 2-hydroxyethanethiol in MeCN at ambient temperatures and removal of liberated ethanethiol *in vacuo* effects conversion into the corresponding type (I) (R = $\text{HOCH}_2\text{CH}_2\text{S}$; R' = Et) complex. Thus both the terminal and the bridging alkylthiolato-groups of $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ complexes are accessible for and susceptible to exchange reactions.

Analytically pure† samples of $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_9] \cdot \text{Me}_2\text{CO}$ containing well formed, needle-like crystals suitable for X-ray crystallographic studies, were obtained by recrystallisation from MeCN– Me_2CO solutions. *Crystal data*: $M = 1925.9$, hexagonal, $a = 17.001(7)$, $c = 16.381(9)$ Å, $U = 4100.5$ Å³, $D_m = 1.56$, $D_c = 1.57$ g cm⁻³, space group $P6_3/m$, $Z = 2$. Single-crystal X-ray diffraction data were collected on a G.E. XRD5 diffractometer using zirconium-filtered Mo- K_α radiation, with the stationary-crystal-stationary-counter method, a 4° take off angle, and a counting time of 10 s. 647 reflections were considered observed ($2\theta < 40^\circ$) and used in the subsequent solution and refinement of the crystal structure. The structure was solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least-squares methods using the 'Shel-X-76' system⁶ of programs. At the current stage of refinement $R = 0.09$, with



SCHEME

† Satisfactory C, H, Fe, Mo, N, and S analyses were obtained for this compound.

Mo, Fe, and S atoms having anisotropic and C and O atoms having isotropic thermal parameters.

A representation of the structure of the anion which has crystallographically imposed $3/m$ ($= \bar{6}$) symmetry, is illustrated in Figure 1† which also gives selected interatomic

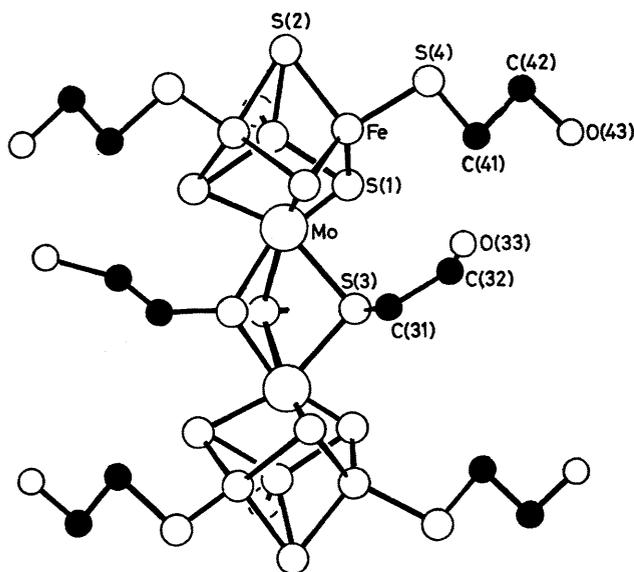


FIGURE 1. The structure of the $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_9]^{3-}$ ion. Unique atoms are numbered. Only one of the two possible positions for C(32) and O(33) are included. Three $-\text{CH}_2\text{CH}_2\text{OH}$ groups bonded to sulphur atoms at the rear of the molecule have been omitted for clarity. Selected mean interatomic dimensions (\AA) and angles ($^\circ$) are: Fe-S(1), 2.28(2); Fe-S(2), 2.25(2); Fe-S(4), 2.25(1); Mo-S(1), 2.39(2); Mo-S(3), 2.55(2); Fe...Fe, 2.72(1); Fe...Mo, 2.75(1); and Mo...Mo, 3.64(1); \angle S(1)-Fe-S(1), 109.4(6); \angle S(1)-Fe-S(2), 103.4(6); \angle S(1)-Fe-S(4), 116.0(7); \angle S(2)-Fe-S(4), 107.0(7); \angle S(1)-Mo-S(1), 102.3(5); \angle S(1)-Mo-S(3), 89.9(8); and \angle S(3)-Mo-S(3), 74.6(7).

dimensions within the anion. The overall molecular structure closely resembles that established for $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_6\text{H}_5)_9]^{3-}$ (II)² and $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_2\text{H}_5)_9]^{3-}$ (III).³ Indeed the compound is crystallographically isomorphous with the $[\text{Et}_4\text{N}]^+$ salt of the latter. The similarities also extend to most of the interatomic dimensions but we note that the Mo...Mo separation of 3.64(1) \AA is very similar to that [3.685(3) \AA] in (II) but is significantly larger than that [3.306(3) \AA] in (III). This is consistent with the presence of three bridging μ -thiolato-groups in the title compound§ and (II), whereas (III) contains one sulphido- and two thiolato-groups bridging across the molybdenum centres. The $-\text{CH}_2\text{OH}$ groups of the bridging μ -thiolato-groups are disordered either side of the mirror plane. There are also signs of disorder in the cation and the solvent acetone molecule is disordered about an imposed three-fold axis.

† The atomic co-ordinates of this structure 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 the communication.

§ These bridging sulphur atoms have almost spherical thermal parameters in contrast with the highly anisotropic ones found in (III) because of the disorder around the crystallographic three-fold axis.

There are short contacts between $-\text{OH}$ groups of the thiolato-ligands attached to the iron atoms; $-\text{OH}$ groups from six different dimers form an approximate hexagon (Figure 2) around 0,0,0 so that each of these groups is hydrogen-bonded to two others [$\text{O}\cdots\text{O} = 2.75 \text{\AA}$].

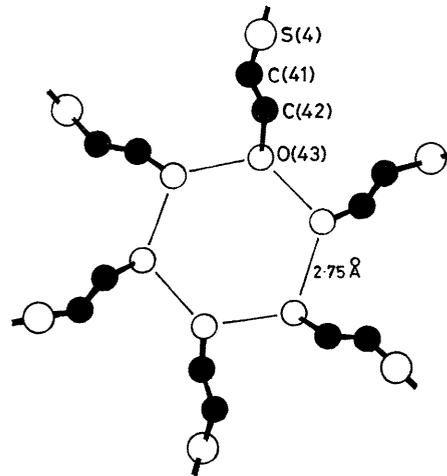


FIGURE 2. Proposed hydrogen-bonding (thin lines) for six (Fe)- $\text{SCH}_2\text{CH}_2\text{OH}$ groups about (0,0,0), a site with $\bar{3}$ symmetry.

The title compound exhibits absorption maxima in Me_2SO solution at 284 ($\epsilon = 63.2 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 389 nm ($\epsilon = 41.2 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) and in water, containing 50 mmol l^{-1} tris buffer (pH 8.5) and an excess of 2-hydroxyethanethiol, at 277 ($\epsilon = 67.0 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) and 371 nm ($\epsilon = 40.1 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$) (Figure 3).

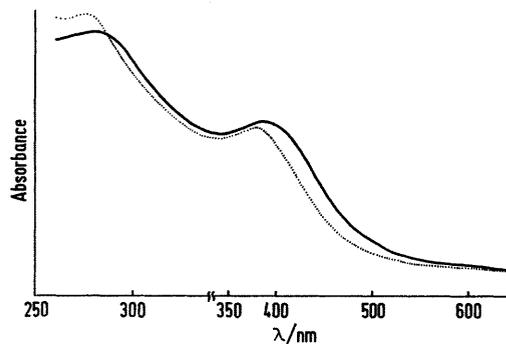


FIGURE 3. Absorption spectra of $[\text{Et}_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SCH}_2\text{CH}_2\text{OH})_9]$ in Me_2SO (—) and aqueous tris buffer (pH 8.5) containing additional 2-hydroxyethanethiol (.....).

The 2-hydroxyethanethiolato-complex is the first water-soluble Fe_3MoS_4 derivative reported thus far, this solubility doubtless being assisted by hydrogen-bonding between the solvent and the hydroxy groups of the ligands.

This solution behaviour should be of a considerable value for the evaluation of these clusters as models of naturally occurring redox centres.

Preliminary Mössbauer studies have been completed⁷ for the title compound and $[\text{Bu}^n_4]_3[\text{Fe}_6\text{Mo}_8\text{S}_8(\text{SPh})_9]$; the isomer shifts are consistent with all of the iron atoms being equivalent and in an oxidation state of *ca.* + 2.5.

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⁶ 'Shel-X 76' system of programs, G. M. Sheldrick, 1976.

⁷ C. E. Johnson and J. D. Rush, personal communication.