

**[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>]<sup>4-</sup>: the First Complex with Two MoS<sub>4</sub><sup>2-</sup> Ions Coordinated to a Ferredoxin Type Central Unit**

ACHIM MÜLLER\*, ACHIM HILDEBRAND,  
MICHAEL PENK, HARTMUT BÖGGE

Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld  
1, F.R.G.

ECKHARD BILL and ALFRED TRAUTWEIN

Institut für Physik, Medizinische Universität zu Lübeck,  
D-2400 Lübeck 1, F.R.G.

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Physical studies like EXAFS and <sup>57</sup>Fe Mössbauer spectroscopy have shown the presence of an iron–molybdenum–sulfur cluster in the iron–molybdenum cofactor (FeMoco) of the enzyme nitrogenase [1–3]. Although the structure of this cofactor is still not known its exploration has led to several new Fe–Mo–S and Fe–W–S clusters with ‘linear’ [4–8] or ‘cubane-like’ [9, 10] structure. As part of our studies in this area, we report here the synthesis, structure and physical properties of [NMe<sub>3</sub>CH<sub>2</sub>Ph]<sub>2</sub>[NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>]. It is important to note that MoS<sub>4</sub><sup>2-</sup> is obtained on hydrolysis of the Fe–Mo protein [11].

## Experimental

### Preparation

All operations were performed under an argon atmosphere. Solvents of a p.a. quality were degassed prior to use.

0.12 g (2.1 mmol) NaHS is added to a solution of 0.27 g (0.32 mmol) [PPh<sub>4</sub>][NMe<sub>3</sub>CH<sub>2</sub>Ph][Cl<sub>2</sub>-FeMoS<sub>4</sub>] [12] in a mixture of 30 ml CH<sub>3</sub>CN and 1 ml H<sub>2</sub>O. After stirring for 20 min at room temperature the resulting reddish-brown solution is filtered and 0.2 g [NEt<sub>4</sub>]I in 10 ml CH<sub>3</sub>CN is added to the filtrate. After 2 days (at room temperature) the precipitated black crystals are filtered, washed with 20 ml EtOH and 20 ml Et<sub>2</sub>O and dried *in vacuo*.

*Anal.* Calc. for C<sub>36</sub>H<sub>72</sub>N<sub>4</sub>Fe<sub>2</sub>Mo<sub>2</sub>S<sub>10</sub>: C, 36.48; H, 6.12; N, 4.73; Mo, 16.19; S, 27.05. Found: C, 36.45; H, 6.07; N, 4.68; Mo, 16.44; S, 27.50%.

### Structural Studies

[NMe<sub>3</sub>CH<sub>2</sub>Ph]<sub>2</sub>[NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>] crystallizes in the monoclinic space group P2<sub>1</sub>/c with *a* = 1235.8(6), *b* = 1618.5(8), *c* = 1269.2(6) pm, β = 93.25(4)°; *V* = 2534.5 × 10<sup>6</sup> pm<sup>3</sup>; *Z* = 2; ρ<sub>calc</sub> =

\*Author to whom correspondence should be addressed.

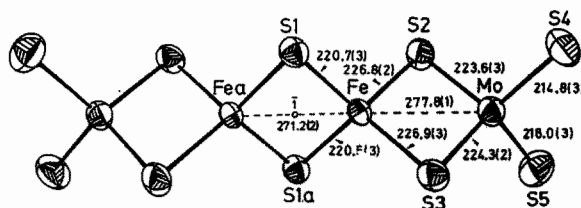


Fig. 1. Structure of [Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>]<sup>4-</sup> in crystals of [NMe<sub>3</sub>CH<sub>2</sub>Ph]<sub>2</sub>[NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>] with bond lengths (pm). Selected bond angles (°): S2–Mo–S4 109.8(1); S4–Mo–S5 110.7(1); S2–Mo–S3 104.9(1); S1–Fe–S2 113.1(1); S1–Fe–S1a 104.1(1); S2–Fe–S3 102.9(1); Mo–S2–Fe 76.2(1); Fe–S1–Fea 75.9(1).

1.60 g cm<sup>-3</sup>; *F*(000) = 1224. Data were collected to 2θ<sub>max</sub> = 50° on a Syntex P2<sub>1</sub> four-circle diffractometer with monochromatized Mo Kα radiation (λ = 71.069 pm, μ = 14.60 cm<sup>-1</sup>) and corrected for absorption by an empirical method. Heavy atom methods were employed for structure solution and all non-hydrogen atoms were located by subsequent least-squares refinements and difference electron density maps. Least-squares refinements using anisotropic thermal parameters for the atoms of the anion and geometrical constraints for the cations (C–H = 96 pm; H–C–H = 109.5° for –Et, –Me, –CH<sub>2</sub>–; C–C = 139.5 pm, C–C–C–H–C–C = 120° for –Ph) converged to *R* = 0.069 and *R<sub>w</sub>* = 0.066 (*R<sub>w</sub>* = (Σ*w*(|*F<sub>o</sub>*| – |*F<sub>c</sub>*|)<sup>2</sup>/Σ*w*|*F<sub>o</sub>*|<sup>2</sup>)<sup>1/2</sup>; 1/*w* = σ<sup>2</sup>*F<sub>o</sub>* + 0.0002*F<sub>o</sub>*<sup>2</sup>) for 2948 independent reflexions (*F<sub>o</sub>* > 3.92 σ(*F<sub>o</sub>*)). See also ‘Supplementary Material’.

## Results and Discussion

The structure of the anion in crystals of [NMe<sub>3</sub>CH<sub>2</sub>Ph]<sub>2</sub>[NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>] including interatomic distances and bond angles is shown in Fig. 1. All four metal atoms in the anion are approximately tetrahedrally coordinated with the two tetrathiomolybdate ions acting as bidentate ligands to the Fe atoms. The anion occupies a center of inversion in the crystal. It has an almost linear arrangement of the four metal atoms with an Fea–Fe–Mo angle of 178.6(1)°. The Fe–S1–Fea–S1a ring is planar according to the center of inversion and the Fe–S2–Mo–S3 ring is also almost planar. The structure corresponds to those of [Fe<sub>2</sub>S<sub>2</sub>(WS<sub>4</sub>)<sub>2</sub>]<sup>4-</sup> [13] and [Fe<sub>2</sub>S<sub>2</sub>(MoO<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]<sup>4-</sup> [14].

The electronic absorption spectrum of [NMe<sub>3</sub>CH<sub>2</sub>Ph]<sub>2</sub>[NEt<sub>4</sub>]<sub>2</sub>[Fe<sub>2</sub>S<sub>2</sub>(MoS<sub>4</sub>)<sub>2</sub>] was measured in reflectance (due to the fast decomposition of the complex in solution). It shows three L–L\* bands comparable to those of the free MoS<sub>4</sub><sup>2-</sup> ion at 355, 402 and 450 nm (only qualitative assignment because of the strong electron delocalisation) and two further significant bands at 515 and 607 nm (Fig. 2).

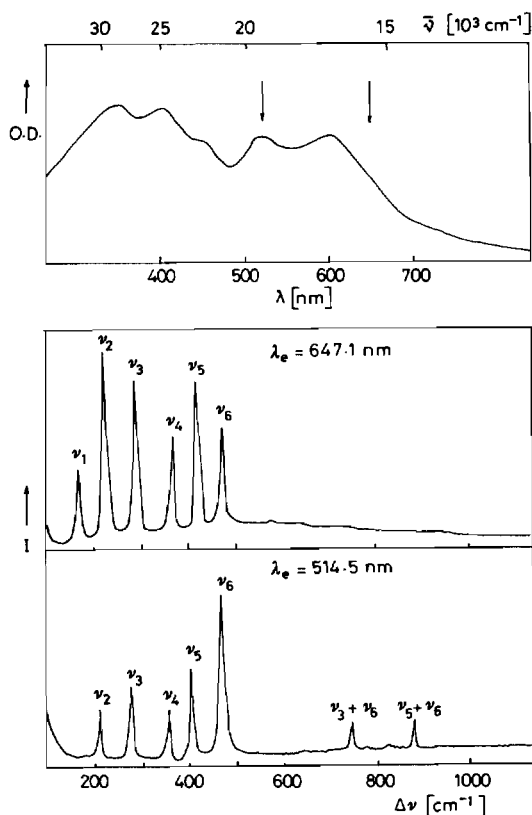


Fig. 2. Reflectance, Raman and resonance Raman spectra of  $[\text{NMe}_3\text{CH}_2\text{Ph}]_2[\text{NEt}_4]_2[\text{Fe}_2\text{S}_2(\text{MoS}_4)_2]$ .  $\nu_1 = \delta(\text{MoS}_4)$  (170);  $\nu_2 = \nu_c(\text{FeS}_2\text{Fe})$  (221);  $\nu_3 = \nu_s(\text{Fe}-\text{S}(\text{Mo}))$  (288);  $\nu_4 = \nu_c(\text{FeS}_2\text{Fe})$  (368);  $\nu_5 = \nu_s(\text{Mo}-\text{S}_{\text{br}})$  (417)\*;  $\nu_6 = \nu_s(\text{Mo}-\text{S}_t)$  (468)\* (\*both are strongly coupled (see text)).

The infrared spectrum of the title complex is very similar to that of  $[\text{Fe}_2\text{S}_2(\text{WS}_4)_2]^{4-}$  [15]. The  $\nu_3(\text{F}_2)$  band of  $\text{MoS}_4^{2-}$  splits into three different bands ( $A_1$ ,  $B_1$ ,  $B_2$ ) due to its local  $C_{2v}$  symmetry (the coupling between the two  $\text{MoS}_4^{2-}$  ligands is negligible, but the coupling between  $\text{Mo}-\text{S}_{\text{br}}$  and  $\text{Mo}-\text{S}_t$  is extreme [16]). It is interesting to note that the highest wave number band of the  $\text{FeS}_2\text{Fe}$  moiety occurs at a lower energy ( $392\text{ cm}^{-1}$ ) compared to that of the analogous ones in  $[\text{Fe}_2\text{S}_2\text{R}_2]^{2-}$  species ( $\text{R} = \text{Cl}, \text{Br}, \text{SPh}$ ) ( $416\text{--}420\text{ cm}^{-1}$ ) [17]. This appears reasonable, because of the reduced  $\{\text{Fe}_2\text{S}_2\}^0$  unit (compared to  $\{\text{Fe}_2\text{S}_2\}^{2+}$ ).

The pre-resonance Raman ( $\lambda_e = 647.1\text{ nm}$ ) and resonance Raman spectrum ( $\lambda_e = 514.5\text{ nm}$ ) of the title complex are displayed in Fig. 2. They demonstrate clearly the existence of strong electronic coupling between the  $\text{Fe}_2\text{S}_2$  unit and the  $\text{MoS}_4^{2-}$  ligands, i.e. the existence of delocalized orbitals spread over the whole complex (see presence of the combination band  $\nu_3 + \nu_6$  in the resonance Raman spectrum with  $\lambda_e = 514.5\text{ nm}$ ; see also ref. 18).

The  $^{57}\text{Fe}$  Mössbauer spectrum of  $[\text{NMe}_3\text{CH}_2\text{Ph}]_2[\text{NEt}_4]_2[\text{Fe}_2\text{S}_2(\text{MoS}_4)_2]$  shows a single doublet

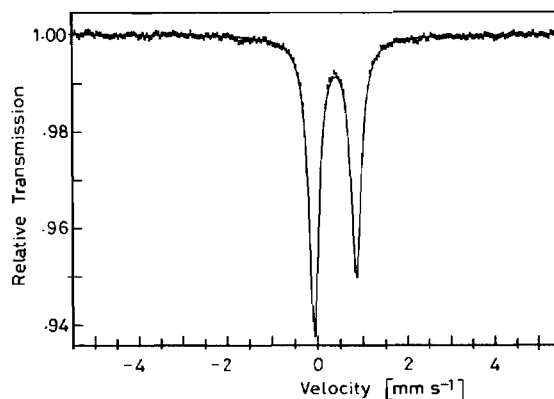


Fig. 3.  $^{57}\text{Fe}$  Mössbauer spectrum of  $[\text{NMe}_3\text{CH}_2\text{Ph}]_2[\text{NEt}_4]_2[\text{Fe}_2\text{S}_2(\text{MoS}_4)_2]$  at 4.2 K. The line asymmetry is due to texture of the sample.

with  $\delta = 0.41\text{ mm/s}$  (versus Fe metal at room temperature) and  $\Delta E_Q = 0.94\text{ mm/s}$  at 4.2 K,  $\delta = 0.40\text{ mm/s}$  and  $\Delta E_Q = 0.94\text{ mm/s}$  at 77 K. The asymmetry of the spectrum depicted in Fig. 3 is due to the texture of the powder sample, which has been checked by a separate Mössbauer measurement with rotated absorber. The empirical, qualitative relationship between the Mössbauer isomer shift and the mean oxidation state  $s$  for clusters containing  $\text{FeS}_4$  sites has been developed by Christou *et al.* [19]. For each iron atom in  $[\text{Fe}_2\text{S}_2(\text{MoS}_4)_2]^{4-}$  it gives a formal value of  $s = +2.4$ , which shows an oxidation state of Fe between Fe(II) and Fe(III). Compared with the formal oxidation state Fe(II) in this complex it indicates the electron delocalisation from Fe to  $\text{MoS}_4^{2-}$ .

The isomer shift is the lowest ever measured for linear Fe–Mo–S complexes. The corresponding tungsten complex  $[\text{Fe}_2\text{S}_2(\text{WS}_4)_2]^{4-}$  yields  $\delta = 0.44\text{ mm/s}$  and  $\Delta E_Q = 1.08\text{ mm/s}$  at 77 K (this value may be converted to the 4.2 K value by adding 0.01–0.02 mm/s accounting for second order Doppler shift). The resulting difference of  $\Delta\delta = 0.04\text{ mm/s}$  between the two complexes indicates the less ferrous nature of iron in  $[\text{Fe}_2\text{S}_2(\text{MoS}_4)_2]^{4-}$  compared to  $[\text{Fe}_2\text{S}_2(\text{WS}_4)_2]^{4-}$  as expected (see ref. 20).

It is remarkable that the  $\{\text{Fe}_2\text{S}_2\}^0$  unit, which has not yet been observed in nature, is stabilized by the thiometallate ligands.

### Supplementary Material

Further details on the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein, Leopoldshafen 2 on quoting the depository number CSD 53074, the names of the authors and the full citation of the journal.

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