

A Molybdenum Derivative of a Four-Iron Ferredoxin Type Centre

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The biological importance of four-iron ferredoxin centres is well recognised [1] and the detection and investigation of such units has been aided considerably by the synthesis and characterisation of their chemical analogues [2]. In contrast, much has still to be defined concerning the environment about, and function of, molybdenum in the various enzymes for which it is an essential constituent [3]. Certain of these molybdoenzymes, the nitrogenases, xanthine and aldehyde oxidases, and some nitrate reductases contain ferredoxin centres. The concept of a molybdenum-containing co-factor, common to different molybdoenzymes, derives from genetic arguments [4] and receives considerable support from the biochemical studies of Nason and Ketchum [5, 6]. The first definitive isolation of such a co-factor was achieved by Shah and Brill [7] who obtained an iron–molybdenum co-factor from the Fe–Mo protein of the nitrogenase of *Azotobacter vinelandii*. Analyses of this unit suggested that it contains iron, molybdenum and acid-labile sulphur in the ratios 8:1:6. EXAFS studies [8] have suggested that the molybdenum is attached to several sulphur atoms in this co-factor and in nitrogenase: a conclusion which is compatible with the e.s.r. signals observed for the molybdenum centres of other molybdoenzymes [3].

Therefore, we have been interested in developing the chemistry of molybdenum–iron–sulphur compounds. Here we report one such species, $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_6\text{H}_5)_9]^{3-}$, which has been prepared and isolated as its $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salt. *Anal.*: Calcd. for $\text{C}_{102}\text{H}_{153}\text{N}_3\text{Fe}_6\text{Mo}_2\text{S}_{17}$: C 49.1; H 6.2; N 1.7; Fe 13.5; Mo 7.7; S 21.9%. Found C 49.1; H 6.2; N 1.7; Fe 13.7; Mo 7.6; S 22.0%.

This air-sensitive, microcrystalline material, m.p. 216–217 °C (dec.) resembles $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{2-}$ salts [2] in appearance and the uv/vis comprises intense absorptions above 275 nm, 'tailing' to lower energy, upon which features at 350 and 450 nm are apparent. The room temperature magnetic moment per Fe_6Mo_2 unit is 4.1 ± 0.1 BM, which is the same as that reported for $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{C}_6\text{H}_5)_4]^{2-}$ [9]. No e.s.r. activity is manifest at room temperature.

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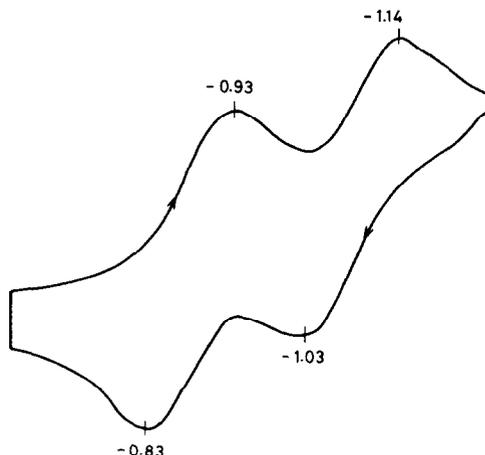


Figure 1. Cyclic voltammogram recorded for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_6\text{H}_5)_9]$ (0.01 M) in DMF containing $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{ClO}_4]$ (0.1 M).

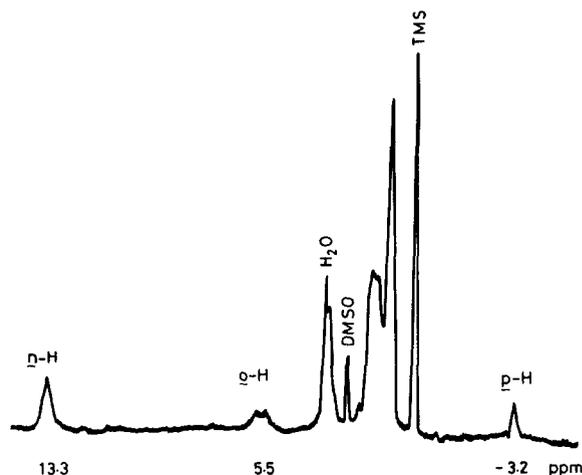


Figure 2. ^1H n.m.r. spectrum (90 MHz) of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_6\text{H}_5)_9]$ in DMSO-d_6 at 35 °C.

Other physical properties obtained for this $\text{Mo}_2\text{-Fe}_6\text{S}_8$ unit differ significantly from those characteristic [2] of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ centres. Cyclic voltammetric studies for an 0.01 M solution in DMF, with $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{ClO}_4]$ as the background electrolyte, have identified two reversible reductions (Figure 1) at -0.87 and -1.08 V (vs. Ag/AgCl electrode), with no further reductions being observed to -1.80 V ($[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{2-}$ shows similar features at -0.90 and -1.68 V under these conditions. The ^1H n.m.r. spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SC}_6\text{H}_5)_9]$, dissolved in DMSO-d_6 at 35 °C shows (Figure 2), in addition to peaks characteristic of $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$, resonances at 13.3, 5.5 and -3.2 ppm relative to TMS as an internal reference. These are assigned, respectively

to the *meta*, *ortho*, and *para* hydrogens of the phenyl rings. Not only are the positions of these resonances at significantly different positions to those observed [10] for $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{2-}$, but also their temperature dependence is opposite to that typical [10] of four-iron ferredoxin centres. As the temperature is increased from 25 to 90 °C, the separation between these peaks *decreases*, so that at 90 °C the resonances occur at 12.7, 5.2 and -1.5 ppm. Thus, the antiferromagnetic coupling which typifies four-iron centres [10] would not appear to be occurring here.

Although the molybdenum-iron-sulphur complex reported here retains certain features typical of four-iron ferredoxin centres, the association of a molybdenum atom would seem to have significantly affected the basic electronic structure of the iron-sulphur core.

Acknowledgments

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