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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, $[Fe_6Mo_2S_8(SC_6H_5)_9]^{3-}$, which has been prepared and isolated as its $[(n\text{-}C_4H_9)_4N]^+$ salt. *Anal.*: Calcd. for $C_{102}H_{153}N_3Fe_6Mo_2S_{17}$: 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 $[Fe_4S_4(SC_6H_5)_4]^{2-}$ 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 $[Fe_4S_4(SCH_2C_6H_5)_4]^{2-}$ [9]. No e.s.r. activity is manifest at room temperature.

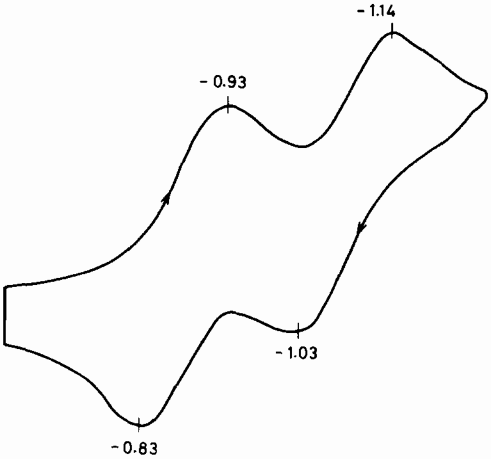

Figure 1. Cyclic voltammogram recorded for $[(n\text{-}C_4H_9)_4N]_3[Fe_6Mo_2S_8(SC_6H_5)_9]$ (0.01 *M*) in DMF containing $[(n\text{-}C_4H_9)_4N][ClO_4]$ (0.1 *M*).

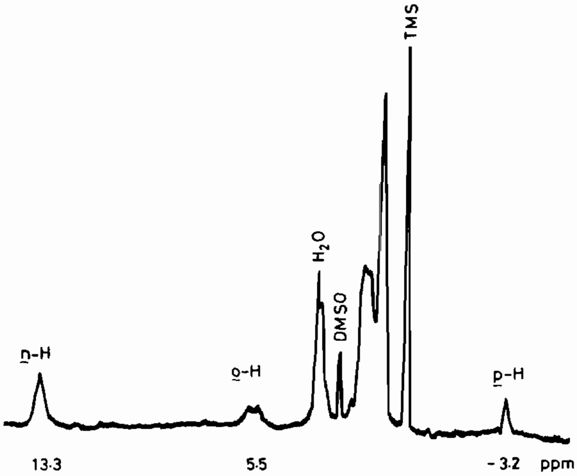

Figure 2. ^1H n.m.r. spectrum (90 MHz) of $[(n\text{-}C_4H_9)_4N]_3[Fe_6Mo_2S_8(SC_6H_5)_9]$ in DMSO-d_6 at 35 °C.

Other physical properties obtained for this $Mo_2Fe_6S_8$ unit differ significantly from those characteristic [2] of $[Fe_4S_4(SR)_4]^{2-}$ centres. Cyclic voltammetric studies for an 0.01 M solution in DMF, with $[(n\text{-}C_4H_9)_4N][ClO_4)$ as the background electrolyte, have identified two reversible reductions (Figure 1) at –0.87 and –1.08V (*vs.* Ag/AgCl electrode), with no further reductions being observed to –1.80V ($[Fe_4S_4(SC_6H_5)_4]^{2-}$ shows similar features at –0.90 and –1.68V under these conditions. The ^1H n.m.r. spectrum of $[(n\text{-}C_4H_9)_4N]_3[Fe_6Mo_2S_8(SC_6H_5)_9]$, dissolved in DMSO-$d_6$ at 35 °C shows (Figure 2), in addition to peaks characteristic of $[(n\text{-}C_4H_9)_4N]^+$, resonances at 13.3, 5.5 and –3.2 ppm relative to TMS as an internal reference. These are assigned, respectively

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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 $[Fe_4S_4(SC_6H_5)_4]^{2-}$, 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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