

Ligand Substitution Reactions of Iron–Molybdenum–Sulphur Cubane-like Cluster Dimers; Selective Halide Incorporation

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Summary The complexes $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ (where R = Et, $\text{CH}_2\text{CH}_2\text{OH}$, or CH_2Ph) react with PhCOX (where X = Cl or Br) to form the corresponding $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_3\text{-X}_6]^{3-}$ complex in good yield; ^1H n.m.r. spectral studies indicate that selective substitution of the thiolato-groups attached to the iron atoms has been achieved, with the bridging region remaining essentially unchanged.

THE structure of the molybdenum site of the nitrogenase enzymes continues to attract much attention. A possible interpretation of EXAFS data¹ for the iron–molybdenum cofactor of *A. vinelandii* nitrogenase is the presence of an $\{\text{Fe}_3\text{MoS}_4\}$ cubane-like cluster as a constituent of this unit. Analyses² of the extracted cofactor apparently indicate the absence of any liganded amino acid or thiolato-groups. The complexes $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ (where R = alkyl or aryl),³⁻⁷

containing two $\{\text{Fe}_3\text{MoS}_4\}$ cubane-like clusters bridged by three μ_2 -thiolato-groups, are presently among the best available synthetic analogues of the molybdenum site of nitrogenase. However, to date no derivative of these systems with non-thiolato ligands has been reported. Using the approach⁸ which has yielded $[\text{Fe}_4\text{S}_4\text{X}_4]^{2-}$ (X = halide) complexes, we have investigated the possibility of substituting the thiolato-groups of $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ complexes by halide atoms. In this way we have sought to extend the chemical reactivity of this novel group of cluster compounds, for which complete exchange of one set of thiolato-groups by another has already been demonstrated.⁴

Pure crystalline samples of $[\text{NMe}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8\text{Cl}_6(\text{SPh})_3]$, $[\text{NEt}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8\text{Cl}_6(\text{SR})_3]$ (where R = Et, PhCH_2 , or HOCH_2CH_2), and $[\text{NEt}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8\text{Br}_6(\text{SEt})_3]$ were obtained in 40–60% yield by the following routes.

Treatment of a solution of $[\text{NR}'_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SEt})_9]$ in acetonitrile with an excess of benzoyl chloride (*ca.* 20 equiv.) produced a rapid disappearance of the golden brown coloration to give a paler brown solution. After a minimum reaction time of *ca.* 1 h at room temperature, the product was precipitated by addition of an excess of diethyl ether and recrystallised as black well-formed crystals from MeCN or MeCN-EtOH. $[\text{NEt}_4]_3[\text{Fe}_6\text{Mo}_2\text{S}_8\text{Br}_6(\text{SEt})_3]$ was obtained in a similar fashion using PhCOBr . The corresponding chloro derivatives of the R = CH_2Ph or $\text{CH}_2\text{CH}_2\text{OH}$ complexes were obtained by ligand exchange⁴ of $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SEt})_9]^{3-}$ with PhCH_2SH or $\text{HOCH}_2\text{CH}_2\text{SH}$, respectively, followed by treatment (of the isolated material) with PhCOCl as described above.

The retention of the $\text{Fe}_6\text{Mo}_2\text{S}_8$ framework and the three μ_2 -thiolato-groups in these anions was confirmed, initially by analytical data, then by ^1H n.m.r. spectroscopy and

differential pulse polarography.⁹ The latter displayed the closely-spaced two, one-electron reductions characteristic of $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ complexes.^{3,9} Each ^1H n.m.r. spectrum was particularly diagnostic, when compared with that of the corresponding $[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ complex, since the resonances characteristic of the terminal groups were absent whereas those of the bridging groups were present, albeit slightly shifted.

Having achieved clean substitutions of the terminal thiolato-groups, substitution of the bridging thiolato-groups was sought. A larger excess (up to 30 equiv.) of the benzoyl halide was used and the reactants maintained at temperatures up to 50 °C for 16 h. However, no indications were obtained for any further halide substitution. This failure to achieve complete substitution of the μ_2 -thiolato-groups contrasts with the ready replacement of both terminal and bridging alkyl thiolato-groups by other alkyl thiols under mild conditions.⁴ Furthermore, the substitutions achieved have led to a neat discrimination between the terminal and bridging thiolato-groups, in the sense opposite to that achieved in the isolation of $[\text{Fe}_6\text{M}_2\text{S}_8(\text{SPh})_9(\text{OMe})_2]^-$ (M = Mo or W).¹⁰ These $[\text{Fe}_6\text{Mo}_2\text{S}_8\text{X}_6(\text{SR})_3]^{3-}$ complexes should be useful intermediates for the synthesis of other derivatives of these cubane-like cluster dimers. The demonstration that $\{\text{Fe}_3\text{MoS}_4\}$ cores can be obtained without thiol-groups co-ordinated to the iron atoms, lends support to the idea² that the extracted iron-molybdenum-sulphur cofactor of nitrogenase could contain such a group even though thiolato-groups are apparently absent.

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