Letters

Electrochemical behaviour of $[Fe_6M_2S_8(SR)_9]^{3-}$ (M = Mo or W) and the roles of molybdenum and tungsten in nitrogenases

REPORTS of the isolation[1] and properties[2,3] of the Fe–Mo cofactor of nitrogenase and the structural inferences obtained from extended *X*-ray absorption fine structure (EXAFS) studies of this molybdenum centre have prompted much synthetic work in pursuit of this entity. Currently, Fe_3MoS_4 cubane-like cluster compounds[4,5] represent the best synthetic analogues for the molybdenum centre of nitrogenase. In these complexes, Mo is six-co-ordinate where Fe is four-co-ordinate and, in the majority of complexes so far reported, the three ligands attached to the Mo and external to the cube bridge to an identical molybdenum centre. Corresponding systems containing Fe_3WS_4 clusters have also been prepared. Comparisons between these Fe_3MoS_4 and Fe_3WS_4 systems are of interest, not least because W, although incorporated[6] into the FeMo protein of nitrogenase in place of Mo, apparently does not lead[7] to a functional enzyme.

The crystal structures of $[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$ and $[NEt_4]_3[Fe_6W_2S_8(SEt)_9]$ show that, if Fe_3MoS_4 clusters are valid structural analogues for the immediate molybdenum environment in nitrogenase, there are no steric impediments to W being incorporated into such a site.[8] Compounds containing Fe_3MS_4 (M = Mo or W) cubane-like clusters manifest a rich redox behaviour. However, there are only small differences in the corresponding redox potentials for $[Fe_6M_2S_8(SEt)_9]^{3-}$ (M = Mo or W) complexes and, phenomenologically, the electrochemical behaviour of these systems is similar to that expected for two Fe_4S_4 cubane-like clusters, linked together with a small amount of inter-cluster coupling.

Earlier,[8] we reported a distinction between the electrochemical behaviour of $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ and $[Fe_6W_2S_8(SEt)_9]^{3-}$ in dimethyl sulphoxide; for the former, the 3–/4– and 4–/5– couples show good electrochemical reversibility whereas for the latter, these couples appeared to be irreversible. Herein we would like to draw attention to the observation[9] that, in MeCN solution, *both* these couples of the $[Fe_6M_2S_8(SEt)_9]^{3-}$ systems show good electrochemical reversibility and, with reference to this solvent dependence and other information available to date, make some observations concerning the participation by Mo, but not W, in functional nitrogenases.

(i) It seems unlikely that Mo is required to extend the range of redox states accessible to the Fe–Mo cofactor, or the redox potential at which this cofactor operates beyond values attainable by an Fe–S centre. Furthermore, the redox behaviour of this cofactor is expected to show little variation upon substitution of W for Mo.

(ii) Since Mo (or W) atoms are capable of binding more ligands than an Fe atom external to the cluster, it is possible that Mo binds the dinitrogen molecule, and its partially reduced products, in a position suitable for reduction.

(iii) The failure of W to produce a functional nitrogenase may originate from the sensitivity of this atom in a (reduced) Fe–W–S cluster towards attack (perhaps at one or more thiolate ligation sites) by oxygen-donor ligands. This may alter the electron-transfer characteristics of the cluster and/or the suitability of this centre for the reduction of dinitrogen.

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