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ELECTRONIC AND MAGNETIC PROPERTIES OF SYNTHETIC ANALOGS FOR THE M AND P CLUSTERS OF NITROGENASE

Spectroscopic results (Mössbauer, EPR [1] and EXAFS [2]) for the Fe-Mo protein of nitrogenase have led to a structural model according to which the 30 ± 2 iron atoms of the protein are distributed into two cluster types labelled M and P respectively. The M cluster consists of two identical centers (cofactor centers) each containing six Fe atoms and one Mo atom in a configuration which, in the native state, is EPR active with $S = 3/2$. A cubane formation containing four Fe and four S atoms has been proposed for the P cluster type. Two inequivalent sites have been assigned for the Fe atoms with an occupation ratio of 3:1.

We present in this communication Mössbauer and magnetic susceptibility studies of two groups of synthetic analogs for the M and P clusters respectively.

Two binuclear (Fe-Mo) and two trinuclear (Fe-Mo-Fe and Mo-Fe-Mo) complexes with sulfur bridges between the metal centers have been studied and compared with the electronic structure and magnetic properties of the Fe-Mo cofactor of nitrogenase. The isomer shift of these complexes indicates that the MoS_4^{2-} moiety withdraws electronic charge from the Fe(II) ions resulting in their partial oxidation. This ability of the MoS_4^{2-} ligand may well represent a characteristic feature of the Fe-Mo-S aggregates of nitrogenase. Intramolecular antiferromagnetic interactions are present in the trinuclear complex $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ leading to a spin $S = 0$ ground state. On the other hand, the trinuclear anion $[S_2MoS_2FeS_2MoS_2]^{3-}$, which may be described with formal valences of Fe and Mo either (I) and (V) or (III) and (IV) respectively, has a resultant spin $S = 3/2$.

A number of 4Fe-4S cubane clusters with mixed terminal ligands have been investigated as possible models for the other major Fe-component of the Mo-Fe protein of nitrogenase, the «P-clusters». The latter exhibit unique spectral properties which have been attributed to significant differences in the ligation of their Fe_4S_4 cores [3]. An extensive charge delocalization prevails in the Fe_4S_4 cores of the cubanes with monodentate asymmetric ligands resulting in four essentially indistinguishable Fe sites with a formal oxidation state of $+2.5$. The introduction of one bidentate terminal ligand results in a differentiation of the corresponding iron site from the remaining three, leading to the 3:1 ratio similar to the P-clusters of nitrogenase. The present results indicate clearly that a differentiation of sites within the Fe_4S_4 core can be achieved with a change in their coordination number without an increase in the charge (core reduction) or charge localization within the core.

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SL12 — TU

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RESONANCE RAMAN SPECTROSCOPY OF IRON-SULFUR PROTEINS

Resonance Raman (RR) spectroscopy allows a very selective and sensitive structural probing of chromophores in biological systems, whatever their physical state. Its application to [Fe-S] proteins has made significant progress in the last few years. Characteristic spectra are now available for [1Fe], [2Fe-2S], [3Fe-xS] and [4Fe-4S] sites in rubredoxins and ferredoxins. Thus, RR spectroscopy can be used for the unambiguous identification of [Fe-S] clusters.

Furthermore, RR spectroscopy can afford detailed structural information which is not accessible to other techniques. By measuring the frequency shifts occuring upon $^{32}S \rightarrow {}^{34}S$ or $^{76}Se \rightarrow {}^{82}Se$ isotopic substitutions on core chalcogenide atoms, and the depolarization ratios of the RR bands, it is in general possible to discriminate the vibrational modes of the inorganic core (Fe-S*) from those involving the cysteine ligands (Fe-Scys), and to determine the symmetry species of the RR active modes. The symmetry point group of the [Fe-S] cluster may therefrom be inferred, *i.e.* the configuration of the active site may be determined with accuracy. Relevant investigations involving [4Fe-4X] and [2Fe-2X] (X = S,Se) proteins will be presented and discussed.

A given type of [Fe-S] cluster may assume slightly different structures depending on which polypeptide chain accomodates it. Recent studies have shown RR spectroscopy to be exceptionnally efficient in detecting such differences, particularly in the cases of [2Fe-2S] and [3Fe-xS] proteins. In some instances spectral differences can be assigned to structural differences involving a given subset of Fe-S bo ds of the active site.

Investigations on simple [Fe-S] proteins such as those outlined above are opening the way to similar studies of more complex proteins.