

Selected Synthetic Models for the Nitrogenase Enzyme

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Since it was isolated in 1960 [1], there have been many spectroscopic studies performed to determine the structural and electronic properties of the nitrogenase enzyme. Based on the data on the FeMo cofactor of the enzyme, many different model systems have been developed.

The nitrogenase enzyme consists of two components, one of which contains approximately 2 Mo atoms, 28-32 Fe atoms, and 28-32 inorganic sulfides. Component two contains 4 Fe atoms and an equal number of inorganic sulfides [2]. The enzyme is not substrate specific, and is able to reduce alkynes, nitriles, and isonitriles.

EPR studies indicate that the Fe centers in the enzyme couple to give rise to a spin system of $S = 3/2$ [2]. Mossbauer studies indicate that the Fe atoms present have an average oxidation state of 2.67 [3]. Electron-nuclear double resonance (ENDOR) experiments along with more recent Mossbauer studies indicate the the iron atoms are not equivalent and that there may be as many as six different Fe environments present in the FeMo protein [4]. The Mo K-edge EXAFS indicated the presence of sulfur atoms at distances of 2.35 and 2.49 Å, and iron atoms at 2.72 Å from the Mo center [5]. Later studies also revealed the presence of oxygen or nitrogen atoms(s) at a distance of 2.2 Å from the Mo atom [6].

In 1980 Zumft reported that MoS_4^{2-} was released following acid hydrolysis of the FeMo protein. This discovery prompted further investigation of the use of this unit as a ligand. Coucouvanis and McDonald, working independently, found that $[(\text{MoS}_4)_2\text{Fe}]^{3-}$ can be prepared and isolated easily as opposed to $[(\text{MoS}_4)_2\text{Fe}]^{2-}$ [7].



The interesting feature of this complex is that iron exists as Fe^{+1} . Other linear complexes containing the MoS_4^{2-} unit have been prepared [8].

A second class of models consists of capped prismane-type clusters which are prepared from $\text{Fe}_6\text{S}_6\text{X}_6$ prismanes and Mo compounds (Figure 1) [9]. These complexes do not compare favorably with the nitrogenase properties, although the Fe_6S_6 core is similar to that found in natural mineral pentlandites. In a more recent study Holm has prepared $\text{Fe}_7\text{S}_6(\text{PET}_3)_4\text{Cl}_3$ which is a link between prismane and cuboctahedral complexes [10]. Its stoichiometry is closer to that of the nitrogenase cofactor if a molybdenum atom could be incorporated into this complex.

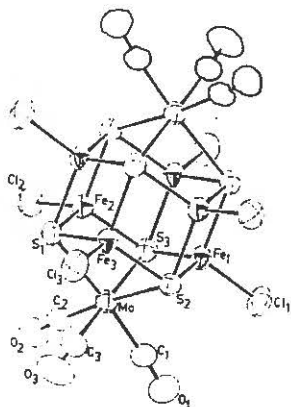


Figure 1
 $[\text{Fe}_6\text{S}_6\text{Cl}_6(\text{Mo}(\text{CO})_2)_2]^{4-}$

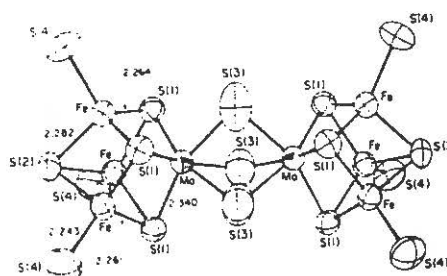
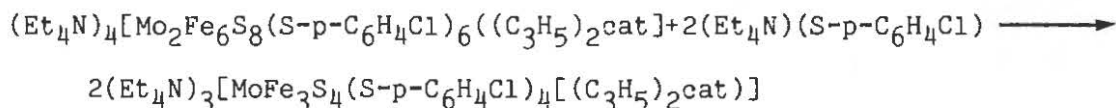


Figure 2
 $[\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SC}_2\text{H}_5)_8]^{3-}$

The last group of models, cubanes, have been studied extensively by Holm [11]. The "spontaneous self-assembly" of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{-2}$ clusters led to an investigation of the corresponding mixed-metal systems. Such condensations give MoFe_3S_4 cubane pairs which are connected via a combination of S^{-2} , RS^- or OMe bridges between two Mo atoms (Figure 2). The double cubanes were only able to exchange terminal ligands on the iron atoms. Later studies showed that double cubanes could be converted to single cubanes through reactions with catechols [12]. Several of the single cubane



complexes are able to bind nitrogenase ligands (N_3^- , PhNHNH_2 , CN^-) to the Mo center [13]. This was the first step to show that these synthetic complexes may indeed have some characteristic properties present in the nitrogenase enzyme. The cubane-type models have bond distances and spectroscopic properties that are similar to those present in the nitrogenase FeMo protein [14].

It should be emphasized that none of the models have the "correct" enzymatic stoichiometry and all three systems fail to interact with dinitrogen or other substrates. Further studies of nitrogenase and its synthetic models are needed to determine why molybdenum is a key element in dinitrogen fixation, if indeed it is, and how it participates chemically in the reduction process.

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