

STUDIES OF CHEMICAL MODELING OF NITROGENASE CATALYSIS — LIGAND-ASSISTED SELF-ASSEMBLY OF FEMO-CO MODEL COMPOUNDS*

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A great number of polynuclear Fe-M-S (M=Mo, W or V) clusters have been obtained by "spontaneous self-assembly" procedures, that employs simple reactants and the $[MS_4]^{2-}$ anions as a soluble source of Mo, W or V sulfides. However, the reaction mechanistic implication is still unknown and the synthesis of most of novel cubane-like clusters remains impossible. For the attempted synthesis of FeMo-cofactor^[1] and its analogs in this endeavor, a systematic study has been made on the effects of a variety of Lewis-basic ligands on self-assembling procedures.

The synthetic method is based essentially upon the following strategy: with the aid of certain suitably chosen bidentate and monodentate Lewis bases which inhibit or promote *in vitro* nitrogenase activity as neutral ligands, labile-ligand-assisted assembling of $(NR_4)MoS_4 \cdot (FeCl_2)_2$ linear trinuclear compound with an excess of $FeCl_2$ in DMF is carried out at room temperature, and followed the course of reaction by *in situ* electronic absorption measurement.

It was found that, only the characteristic electronic absorption peaks of the linear trinuclear complex were the absorption in $Mo_4^{2-} \cdot 8FeCl_2 \cdot DMF$ ($C_{Mo} > 10^{-3} M$) without the addition of any extraneous labile ligands at the beginning of the reaction. Regarding the behaviors of bidentate Lewis base ligands, the addition of $Ph_2PCH_2CH_2PPh_2$ to the system could bring about practically complete disappearance of the electronic absorption peaks of the linear trinuclear cluster in a few hours, resulting in a feature-less electronic absorption curve, similar to that of FeMo-co or a monocubane $MoFe_3S_4L_n$ cluster. Whereas the addition of $Ph_2PCH_2CH_2PPh_2$ presented a striking contrast, it shows little effect on the characteristic absorption peaks of trinuclear complex. In a subsequent series of experiments, the addition of nitrogenase inhibitor *o*-phthalaldehyde ($C_6H_4-1,2-(CHO)_2$) can slowly bring about almost complete disappearance of the linear complex in 24~36 h, while the addition of pyrocatechol shows practically no effect, in contrast.

It might be possible for the bi-phosphorus of dppe to coordination on the cationic Mo (not Fe, because the $dppe : Mo : Fe \approx 1 : 1 : 8$) of the trinuclear complex, to form a stable pentacyclic ring and assume temporarily a hexa- or hepta-coordination cubane structure. While the tetra-atomic between Mo and $Ph_2PCH_2CH_2PPh_2$ is hardly taken shape. The strong tendency towards the formation of monocubane cluster complexes and successful synthesis in labile-ligand-assisted self assembly reactions in the project will be reported and compared.

Reference

- [1] J. Kim and D. C. Rees, *Science*, 1992, **257**, 1677.

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