Direct Incorporation of Ferric Ion in Porphyrinogen Core: Tetrakiscyclohexylferricporphyrinogen Anion with Different Conformers

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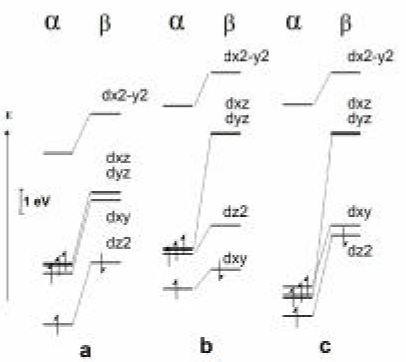
Direct synthesis of $[Et_4N]$ $[L”e^{III}]$ **1** has been achieved by introducing stiochiometric amount of anhydrous ferric chloride into a solution of lithium salt of tetrakiscyclohexylporphyrinogen (L”). X-ray structure analysis of **1** revealed that Fe(III) has been incorporated into this porphyrinogen core. Its room temperature magnetic moment in the solid state has been found to be 4.3BM at 298K (3.8BM at 6K). Its magnetic moment value in solution changed to S=5/2 yielding μ_{eff}=6.0BM. This change in spin state of S = 3/2 (in solid) to S = 5/2 (in solution) is a general phenomenon observed in all characterizedFe(III) porphyrinogen systems. Space filling model of **1** showed no room for solvent coordination, which could have been responsible for altering the energy of dx2-y2 orbital resulting in the change in spin state. Recrystallization of **1** in DCM in the presence of pyridine retained the molecular structure of **1** with the presence of pyridine in the lattice to yield **2**. The conformational orientation of the molecules in **2** differed in comparison to that found in **1**. In the asymmetric unit of **2** the orientation of two molecules differed each other and with that of the molecule present in **1**. A DFT calculation (Fig, a,b.c) of these conformers showed interesting perturbation in molecular orbital energy level. The relative energy levels of all d –orbital changes drastically in three conformers highlighting the influence of disposition of peripheral ligand (flipping of cyclohexyl ring). The electrostatic surface potential of all the three conformers differ suggesting the possibility of solvent interaction with **1** which may affect the conformation of the molecule in such a way to lower the energy of d_{x2-y2} orbital resulting in the change in spin state in solution. Oxidation of **1** by iodine led to the oxidation of L” with the formation of a new complex with $\{Fe^{II}\text{-}I\}$ moiety (Fig.2).



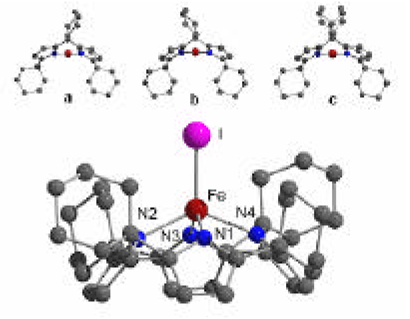


Fig.2