MS080.P07

Eight-coordinate iron(III) within coordination complex containing pre-organized ligand H$_2$PDA

Behnaz Ramezanpour[1], Masoud Mirzaei[1]
[1]*Ferdowsi University Of Mashhad, Mashhad, Iran, Islamic Rep.*
E-mail: Behnaz.ramezanpour@gmail.com

The chemistry of high coordination numbers (CNs) of transition metal complexes has been of interest because unusual CNs are observed in certain metallobiomolecules and are also design targets for open-framework catalytic inorganic materials. Investigations of inorganic chemistry demonstrates that CNs of four, five, and six are conventional for first-row transition metals, whereas CNs of three, seven and eight are rarely observed.

Multidentate macrocyclic or rigid ligands enforce a particular structure on a metal complex. Pre-organized ligand does not change its conformation upon complexation to a metal ion. An example of such highly pre-organized ligands is the non-macrocyclic ligand that based on the rigid phenanthroline backbone with donor groups at the 2- and 9- positions (1,10-phenanthroline-2,9-dicarboxylic acid, hereafter H2 PDA).

Based on a Cambridge Structural Database (CSD version 5.37) analysis, we found only two octacoordinated coordination complexes bearing iron(II) and iron(III) ions with N,O-donors ligands which are proven by X-ray structure determination. Here, we introduce the pre-organized N,O-donor ligand of H2PDA and then discuss on the uncommon eight-coordinated iron complex. It should be pointed out that this observation is only accessible when this ligand to be used under solvothermal conditions. The PDA2- ligand is very useful in constructing stable complexes that the phenanthroline rings and carboxylate groups can grasp the metal ions tightly. The complex was crystallizes in the orthorhombic space group Ibam, the structure was reported: a = 9.989(2) Å, b = 15.122(3) Å, c = 19.566 (4) Å, α=β=γ=90°, V= 2955.5 (10) Å3, Z= 4, R=0.04, WR2= 0.1267. As it has been shown in Figure1, central metal ion is coordinated by four nitrogen atoms of two phenanthroline units and four oxygen atoms of two carboxylato groups. Therefore H2PDA acts as a tetradentate ligand and the lattice is composed of eight-coordinated complex. In this crystal, different non-covalent interactions such as π-π stacking and hydrogen bonding play important roles in the construction of extended networks in the crystal system. In this study we synthesized a novel complex, the structure was characterized by IR spectroscopy, X-ray diffraction methods and the elemental analysis was performed to check the purity of the compound. The observed structure may open up new window for the design of future materials with desirable topologies and encourages further research in this area.

Considering four equal bond lengths around of the Iron with oxygen atoms and on the base of previous studies with Miao, Y.-L. et al. there is a possibility for existence of hydronium ion instead of water molecule in the crystal structure. As a result, Iron has a formal charge of three at present complex. Further measurement seems necessary which will enclose.

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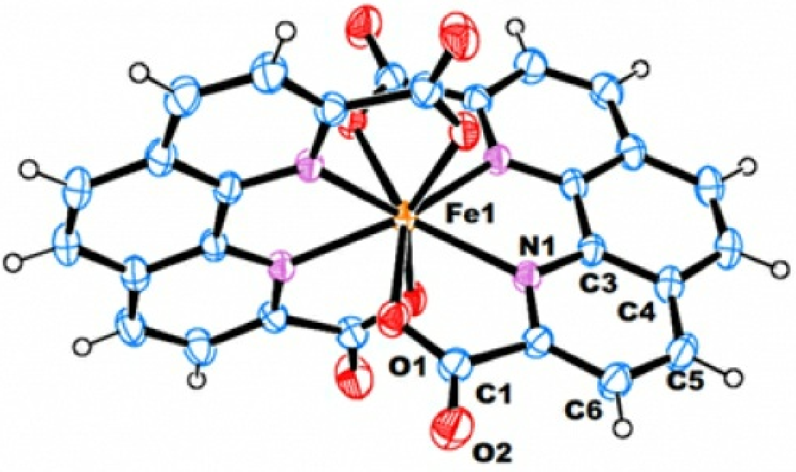

Fig.1 A view of the $(H_3O)[Fe(PDA)_2]\cdot 2CH_3CN$ complex

Keywords: Eight-coordinate, H2PDA, Pre-organization