A Supramolecular Synthon Containing Two Five-coordinate (Octaethylporphinato)Iron(III) Hemes

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Analysis of structures and solid state resonance Raman spectra of a group of 5-coordinate high-spin iron(III) heme malaria pigment model systems led to the conclusion that supramolecular interactions play an integral role in the resonant Raman excitonic enhancement observed when applying near-infrared excitation wavelengths in β-hematin (malaria pigment)[1]. A distinguishing feature of β-hematin which led to more supramolecular interactions compared to the other model systems was the O-atoms in the propionic acid residues on β-hematin. A strategy to improve the OEP model systems was to use axial ligands containing O-atoms, and indeed a better malaria pigment model complex, (picrato)-(octaethylporphyrinato)Fe(III), has been prepared[2]. Two additional similar complexes have now been prepared: (2-hydroxy-3,5-dinitrobenzoato)[3] and (4-methyl-2,6-dinitrophenolato)(octaethylporphinato)Fe(III).

In analyzing these structures we discovered a new highly concerted group of intermolecular C—H···π and C—H···O interactions forming a supramolecular motif. There are six and eight C—H···O intermolecular interactions in the picrato dimer and the μ_2-dimer structures, respectively. In addition there are six intermolecular C—H···π interactions in each of the two dimer structures, 12 and 14 total concerted interactions, respectively. The third complex in this series, (4-methyl-2,6-dinitrophenolato)(OEP)Fe(III), has six intermolecular C—H···π interactions (the placement of the rings limits such C—H···π interactions to no more than eight possible). This dimer has a whopping 20 intermolecular C—H···O interactions, making a total of 26 concerted interactions and firmly establishing this intriguing motif as another new supramolecular synthon. This synthon, together with the 3D packing/stacking dominated by porphyrin-porphyrin C—H···π interactions supplemented by axial ligand-porphyrin hydrogen bonding interactions may help explain the similarity of the resonant Raman excitonic enhancement noted previously for β-hematin and the picrato model system.

References:
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