Supramolecular C–H···π and C–H···O interactions in a new synthon relevant to malaria pigment model systems

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Metalloporphyrin complexes occur in many biochemical systems prompting considerable study of related model compounds, perhaps none more so than the heme model systems. Previous work from our group has presented analysis of structures and solid state resonance Raman spectra of a group of five-coordinate high-spin iron(III) heme complexes, work that 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]. The larger number of supramolecular interactions for β-hematin compared to the other model systems was attributed to the O-atoms in the propionic acid residues on β-hematin. Thus, a strategy to improve the OEP model systems was to use axial ligands containing a number of O-atoms, specifically nitro and/or carboxylate groups. A better malaria pigment model complex, (picrato)(OEP)Fe(III), has been prepared and reported [2]. Two additional similar O-phenolato complexes have now been prepared as part of our study of 5-coordinate high-spin ferric heme model compounds of malaria pigment: (2-hydroxy-3,5-dinitrobenzoato)(OEP)Fe(III) [3] and (4-methyl-2,6-dinitrophenolato)-(OEP)Fe(III).

Our analysis of these structures revealed the expected abundance of C—H···O interactions. These, together with the normal C—H···π interactions, form a newly highly concerted group of intermolecular interactions forming a supramolecular motif. There are six and eight C—H···O intermolecular interactions in the picrato-dimer and the benzato-dimer structures, respectively. In addition there are six intermolecular C—H···π interactions in each of the two dimer structures, i.e. 12 and 14 total concerted interactions, respectively. The third complex in this series, (4-methyl-2,6-dinitrophenolato)(OEP)Fe(III) (see Fig. 1), also 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 3-D packing/stacking dominated by C—H···π porphyrin-porphyrin 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 [2].

Figure 1. ORTEP illustration of the (4-methyl)-2,6-dinitrophenolato(OEP)Fe(III) complex showing the supramolecular dimeric unit. The two porphyrin planes are related by an inversion center and are parallel in this complex. C—H···π interactions are not indicated.