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**Air-stable, Electron Deficient Fe(II) Catalytic Porphyrins. Characterization and Molecular Structures of a Rare High Spin Fe(II) Hexacoordinated Porphyrin and a Low Spin Analogue**

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Beamline(s): X7B

**Introduction:** Cytochromes P450 are a class of monooxygenase enzymes that catalyze hydroxylations and epoxidations in vivo and mediate drug metabolism. Multiple redox stages of the iron porphyrin prosthetic group have been identified in the catalytic cycle of cytochrome P450 including high and low spin Fe(II) and Fe(III), as well as higher oxidation states [1]. The roles of cytochrome P450 have led to intense efforts to mimic the enzymatic catalysis [2]. We have recently synthesized a series of electron-deficient porphyrins with one to eight  $\beta$ -pernitro peripheral substituents (**1**) that exhibit a wide range of redox potentials [3] and catalytic behavior and have reported the first molecular structures of Fe(II) porphyrins ligated by two axial alcohols (**1**·(PrOH)<sub>2</sub>) that contain the rare, hexacoordinated high spin Fe(II) state. In addition, we have characterized the same porphyrin with axial water ligands, **1**·(H<sub>2</sub>O)<sub>2</sub> [4].

**Methods and Materials:** Datasets for single crystals of **1** with propanol (**1**·(PrOH)<sub>2</sub>) and water (**1**·(H<sub>2</sub>O)<sub>2</sub>) as axial ligands were collected at 100K by the rotation method using a MAR345 image plate detector. The data were processed and merged with Denzo/Scalepack [5] and the structures were solved and refined with the SHELXTL package [6].

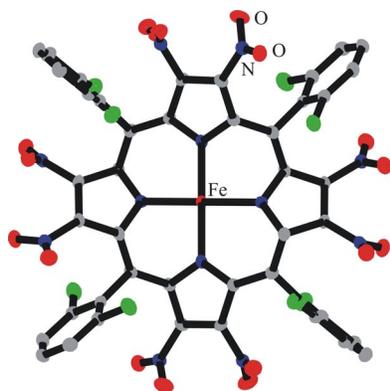
**Results:** The structural formula of **1** is shown in Figure 1 and edge-on views of **1**·(PrOH)<sub>2</sub> and **1**·(H<sub>2</sub>O)<sub>2</sub> that exemplify their conformations are presented in Figure 2.

**Conclusions:** The very different conformations of **1**·(PrOH)<sub>2</sub> and **1**·(H<sub>2</sub>O)<sub>2</sub> illustrate the acute sensitivity and interplay between axial ligands, spins states and conformations of Fe porphyrins.

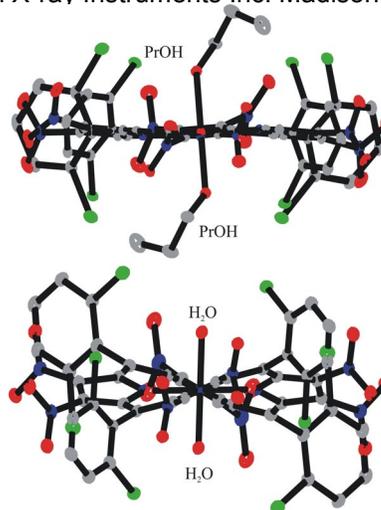
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**References:**

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**Figure 1.** Structural formula of **1** which contains eight  $\beta$ -pernitro groups at the periphery.



**Figure 2.** Edge-on views of the molecular structures of **1**·(PrOH)<sub>2</sub> and **1**·(H<sub>2</sub>O)<sub>2</sub>. Fe-N distances in **1**·(PrOH)<sub>2</sub> are diagnostic of high spin Fe(II) and the macrocycle is planar; those in **1**·(H<sub>2</sub>O)<sub>2</sub> are much shorter, indicative of low spin Fe(II) and the molecule is ruffled.