

Poster Presentation

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Effect of pressure on a mixed valence $Fe^{ii}Fe^{iii}_2$ complex

S. Madsen¹, J. Overgaard¹, B. Iversen¹

¹Aarhus University, Center for Materials Crystallography, Department of Chemistry and iNANO, Denmark

Intramolecular electron transfer (ET) in mixed valence (MV) oxo-centered $[Fe^{ii}Fe^{iii}_2O(\text{carboxylate})_6(\text{ligand})_3]\text{-solvent}$ complexes is highly dependent on temperature, on the nature of the ligands, and on the presence of crystal solvent molecules [1]. Whereas the effects of temperature, crystal solvent, and ligand variation on the details of the ET have been explored thoroughly, the effect of pressure is less well described [2]. The effect of pressure on the ET in MV $Fe_3O(\text{cyanoacetate})_6(\text{water})_3$ has been investigated with single crystal X-ray diffraction and Mössbauer spectroscopy. Previous multi-temperature studies have shown that at room temperature the ET between the three Fe sites is fast and the observed structure of the Fe_3 core is a perfectly equilateral triangle [3]. Cooling the complex below 130 K induces a phase transition as the ET slows down. Below 120 K the Fe_3 core is distorted due to the localization of the itinerant electron on one of the three Fe sites in the triangle (the complex is then in the valence trapped state). The valence trapping is complete within a temperature interval of just 10 K. The abruptness of the transition has been attributed to the extended hydrogen bond network involving water ligands and cyano groups, promoting intermolecular cooperative effects. The high-pressure X-ray diffraction data show that there is a 90° flip of half the cyano groups at 3.5 GPa, which dramatically changes the hydrogen bond network. At a slightly higher pressure, a phase transition is found to occur. The five single crystals investigated all broke into minor fragments at the transition; however triclinic unit cells, similar to the low temperature unit cell, could be indexed from selected spots. Additional evidence that the complex is valence trapped comes from high pressure Mössbauer spectra measured above the phase transition (4 GPa). The relationship between valence trapping and the structural changes will in this work be highlighted using void space and Hirshfeld surface analysis.

[1] S. M. Oh, *J. Am. Chem. Soc.*, 1985, 107, 8009, [2] J. K. McCusker et al., *Inorg. Chem.*, 1991, 30, 1985; S. Scheins et al, *Chem. Eur. J.*, 2013, 19, 195, [3] T. Nakamoto, et al., *Chemistry Letters*, 1993, 1463; T. Nakamoto et al., *Inorg. Chem.*, 1997, 37, 4347

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