

neutral didentate and two mononegative ligands (usually thiocyanate)[1,2].

Using a single tetradentate ligand [3] we present variable temperature results on [(tpa)Fe(NCS)₂] (tpa = tris(pyridine-2-ylmethyl)amine) crystallised with a variety of solvents. The variation in solvent with the concomitant change in the hydrogen bonding significantly affects the position of the HS ↔ LS crossover. Furthermore we report on our initial results from determining the structures of photoinduced metastable HS states.

[1] Money V. A., Elhaik J., Radosavljevic Evans I., Halcrow M. A., Howard J. A. K., *J. Chem. Soc., Dalton Trans.*, 2004, 65. [2] Marchivie M., Guionneau P., Howard J. A. K., Goeta A. E., Chastanet G., Létard J-F, Chasseau D., *J. Am. Chem. Soc.*, 2002, **124**, 194-195. [3] Højland F., Toftlund H., Yde-Andersen S., *Acta Chem. Scand.*, 1983, **A37**, 251-257.

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Synthetic and Structural Studies on Photoactivated Complexes

Teresa L. Savarese, Paul R. Raithby, Andrew L. Johnson, *Department of Chemistry, University of Bath, United Kingdom.* E-mail: T.L.Savarese@bath.ac.uk

Photocrystallography[1] is the technique for determining the structure of molecules in their excited state. Single crystal X-ray diffraction studies have been carried out on a number of complexes that have metastable or microsecond lifetimes[2]. These are very challenging experiments and it is difficult to maximise the level of excitation without destroying the crystal. In order to overcome these difficulties we are investigating several new strategies.

We are developing methods of studying metastable and excited state structures using X-ray **powder diffraction**. This relies on significant structural changes in the molecules such as isomerism, and in the initial investigations we are studying the linkage isomerism of [Ru(SO₂)(NH₃)₄L][X_n] (L=Cl, X=Cl, n=1; L=H₂O, X=MeC₆H₄SO₂, n=2) where the coordination mode of the SO₂ changes from μ₁-S to μ₂-S-O under illumination by a bright white light source. The μ₂-S-O isomer is metastable at temperatures below 120K.

In a related series of synthetic studies, we are co-crystallizing the ruthenium complexes with cyclodextrin molecules, so that the cations may be held in the cyclodextrin pocket. Then if photocrystallographic studies are carried out on these systems, higher levels of excitation may be observed because the SO₂ group will be free to isomerise shielded from the rest of the crystal structure by the cyclodextrin cage.

[1] Coppens P., Ma B., Gerlits O., Zhang Y., Kulshrestha P., *Cryst. Eng. Comm.*, 2002, **4**, 1. [2] Novozhilova I.V., Volkov A.V., Coppens P., *J. Am. Chem. Soc.*, 2003, **125**(4), 1079-1087.

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Charge Density Study of Photo-Excited State in Spin Crossover Complex

Kenichi Kato^{a,b}, Yutaka Moritomo^{a,b,c}, Masaki Takata^{a,b}, Akio Nakamoto^d, Norimichi Kojima^d, ^aJASRI/SPring-8. ^bCREST/JST. ^cDepartment of Applied Physics, Nagoya University. ^dGraduate School of Arts and Sciences, University of Tokyo, Japan. E-mail: katok@spring8.or.jp

The spin crossover complexes are widely recognized for the temperature and photo-induced transitions from low-spin (LS: S=0) to high-spin (HS: S=2) state of the Fe²⁺ ions. By the photo-excitation at low temperature the HS state is trapped even after the photo-irradiation. This phenomenon is called Light Induced Excited Spin State Trapping (LIESST). Here we have found the photo-excited state in [Fe(ptz)₆](BF₄)₂ [1] and Fe(phen)₂(NCS)₂, at 92K. At this temperature the LIESST phenomenon is not observed. The experimental and analytical methods used are as follows.

The powder diffraction data of the complexes were measured at 92K under 532nm CW laser irradiation by using Large Debye-

Scherrer Camera installed at BL02B2, SPring-8. An imaging plate was used as a detector to collect whole powder patterns simultaneously. The N₂ gas flow type system was combined with the laser system for the low-temperature measurements. As a result, the volume ratio of the photo-excited phase reached to approximately 90%. The charge density obtained by using the MEM/Rietveld method revealed the distinguished difference between the photo and temperature-induced HS state in the Fe-N bonding nature. In the talk, the detail including the LIESST phase will be presented.

[1] Moritomo Y., et al., *J. Phys. Soc. Jpn.*, 2002, **71**, 2609.

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Thermal and Light-Induced Polymorphism in Fe(II) Spin Crossover Materials

Amber L. Thompson^a, Andrés E. Goeta^a, Ana Galet^c, José A. Real^b, M. Carmen Muñoz^c, ^aDepartment of Chemistry, University of Durham, U.K. ^bDepartament de Química Inorgànica, Universitat de València, Spain. ^cDepartament de Física Aplicada, Universitat Politècnica de València, Spain. E-mail: A.L.Thompson@durham.ac.uk

In certain Fe(II) complexes, the energy difference between the high spin (HS) and low spin (LS) state is of the order of k_bT . In these materials it is possible to induce a spin crossover (SCO) by a change of temperature, application of pressure and more interesting for potential applications, by light irradiation [1].

Materials such as Fe[H₂BPz₂]₂L (Pz = pyrazol L = 2,2'-bipyridine (1) or 1,10-phenanthroline (2)) have been shown to exhibit Light-Induced Excited Spin-State Trapping (LIESST) when irradiated at low temperature [2]. In 2, the thermal SCO is coupled with a structural change from C2/c to P1, which is retained on irradiation, giving a new high spin structure [3].

Another SCO material, the coordination polymer {Fe(Bpe)₂[Ag(CN)₂]₂} (3) exhibits an incomplete SCO transition [4], the structural consequences which include an effect complementary to the "Thermal and Light-Induced Polymorphism" seen in 2.

[1] Kahn, Kröber, Jay, *Adv. Mater.*, 1992, **4**(11), 718. [2] a) Real, Muñoz, Faus, Solans, *Inorg. Chem.*, 1997, **36**, 3008; b) Moliner, et al., *J. Phys. Chem. B*, 2002, **106**, 4276. [3] Thompson, Goeta, Real, Galet, Muñoz, *Chem. Commun.*, 2004, 1390. [4] Niel, Muñoz, Galet, Gaspar, Levchenko, Real, *Chem. Eur. J.*, 2002, **8**(11), 2446.

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