



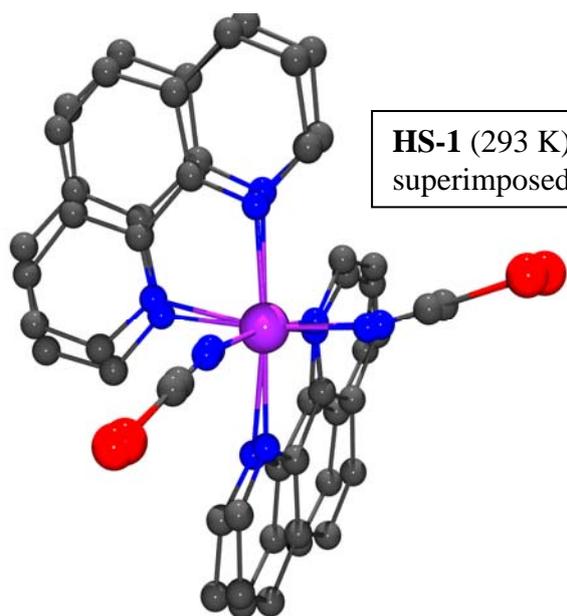
	Experiment title: Continuation of a study of the meta-stable high spin states of some iron(II) complexes.	Experiment number: CH-1237
Beamline: ID11	Date of experiment: from: 26/1/2002 to: 29/1/2002	Date of report: 23/2/2010
Shifts: 9	Local contact(s): Gavin Vaughan	<i>Received at ESRF:</i>
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Report:

This work was part of a larger programme of research using X-ray diffraction and absorption spectroscopic techniques to study spin crossover in Fe(II) and Fe(III) complexes. This particular series experiments followed on from a preliminary study (CH-1030) where there was insufficient cooling capacity and was a very successful application of extreme low temperature X-ray diffraction to the study of meta-stable photochemically generated species. This has resulted in a high quality publication [1] which has been well cited.

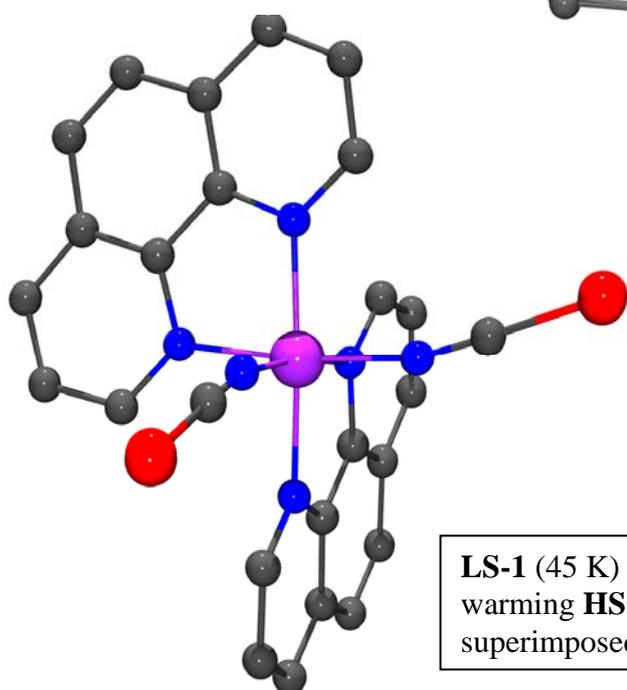
The data obtained at ID 11 using the Oxford Diffraction HeliJet cryostat allowed for the first synchrotron radiation single crystal diffraction structural data to be obtained for $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ in its LIESST (light induced excited spin state trapping) metastable high-spin state at *ca.* 25 K. The room temperature high-spin; 100K, low-spin data had been obtained previously at Daresbury SRS and ID11 of the ESRF. The space group for all of the spin states was found to be P_{bcn} . On cooling from the high-spin state (**HS-1**) at 292 K through the spin crossover at about 235 K to the low-spin state at 100 K (**LS-1**) the iron coordination environment changed to a more regular octahedral geometry and the Fe-N bond lengths decreased by 0.216 and 0.196 Å (Fe-N(phen)) and 0.147 Å (Fe-N(CSe)). When the low-spin state was illuminated with visible light at about 26 K, the structure of this LIESST induced metastable high-spin state (**HS-2**) was very similar to that of **HS-1** with regards to the Fe-phen bond lengths, but there were some differences in the bond lengths in the Fe - NCSe unit between **HS-1** and **HS-2**. When **HS-2** was warmed in the dark to 50 K, the resultant low-spin state (**LS-2**) had an essentially identical structure to **LS-1**. In all spin states, all of the shortest

intermolecular contacts (in terms of van der Waals radii) involved the NCSe ligand, which may be important in describing the cooperativity in the solid state.



HS-1 (293 K) and LIESST induced
HS-2 (25 K) superimposed.

The image shows a ball-and-stick model of the [Fe(phen)₂(NCSe)₂] complex. The iron atom is represented by a purple sphere, the phenanthroline ligand by grey spheres, and the two NCSe ligands by blue and red spheres. The structure is shown in two superimposed states: HS-1 (high spin, 293 K) and HS-2 (high spin, 25 K, LIESST induced). The phenanthroline ligand is shown in a semi-transparent grey style to reveal the iron and NCSe atoms. The two NCSe ligands are shown in red and blue, with the iron atom coordinated to the nitrogen atoms.



[1] *Structural study of the thermal and photochemical spin states in the spin crossover complex [Fe(phen)₂(NCSe)₂]*, E. J. MacLean, C. M. McGrath, C. J. O'Connor, C. Sangregorio, J. M. W. Seddon, E. Sinn, F. E. Sowrey, S. L. Teat, A. E. Terry, G. B. M. Vaughan, and N. A. Young, *Chem.-Eur. J.*, 2003, **9**, 5314.