



Experiment title: Determination of the structure of the meta-stable high spin state of an iron(II) spin crossover complex and its evolution at low temperature.		Experiment number: CH-1030
Beamline: ID11	Date of experiment: from: 2/6/2001 to: 5/6/2001	Date of report: 6/10/2001
Shifts: 9	Local contact(s): Ann Terry and Gavin Vaughan	<i>Received at ESRF:</i>
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The aim of these experiments was to use single crystal X-ray diffraction to determine the structure of the light induced meta-stable states of some iron(II) spin crossover complexes. We have recently obtained very high quality data for both the high spin and low spin forms of $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ using SR single crystal diffraction at Daresbury on station 9.8, and there are data in the literature for the high and low spin states of $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$.

During our visit to the ESRF in June 2001 the experiments suffered from some severe data acquisition and data integration problems, with the result that we were only able to collect good quality, analyzable data on the final day. In addition to the data acquisition problems, the cryostat available only had a base temperature of *ca.* 35 K, which whilst cold enough to demonstrate the principle of the experiment was not sufficient to ensure complete conversion to the meta-stable state. Despite these setbacks, we were able to demonstrate that SR single crystal diffraction was able to identify the structural changes.

A summary of the data collected and analyzed is given in the table below. In particular we were able to show that at 300 K the crystallinity of the sample reduced with time, indicating some form of photochemical change, not entirely surprisingly based on our previous L-edge XAFS experiments.¹ This effect was not observed at 293 K on station 9.8 at Daresbury highlighting the difference in flux between the two sources. At 100 K (using a different crystal) the data were in excellent agreement with our previous Daresbury data. When the crystal was cooled to the minimum temperature (*ca.* 30–35 K) and irradiated with white light, there was a clear change in the diffraction pattern, associated with a lengthening of the Fe-N bonds in the first coordination sphere of *ca.* 0.02 Å. Whilst this change is characteristic of a change from low- to high-spin, it is considerably smaller than expected from the difference of the *hs* and *ls* states (*ca.* 0.19 Å) and is almost certainly due to the temperature not being low enough to stabilise the meta-stable *hs* state. Our EXAFS experiments indicate that at lower temperatures (*ca.* 10 K) there is complete conversion. When the same crystal was illuminated only with green light, there is a very slight shortening of the Fe-N bonds which again might indicate that the temperature is not low enough as a slight reduction in photon flux lowers the proportion of *hs* molecules present. We have demonstrated previously using iron(III) dithiocarbamate

complexes that single crystal diffraction yields an average of the two spin states, whilst EXAFS can give bond lengths for both states.² In addition to the work on $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ we also tried to obtain data for $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$, for which there is single crystal data in the *hs* and *ls* states,³ but not for the meta-stable *hs* state, but unfortunately, these crystals were too small to give data of sufficient quality.

Therefore, we believe that we have been able to demonstrate the proof of the principle, but in order to obtain high quality data need to repeat the experiments at lower temperatures.

Comparison of 9.8 and ESRF single crystal SR X-ray data for $\text{Fe}(\text{phen})_2(\text{NCSe})_2$

	DL (9.8)	ESRF (ID11)	DL (9.8)	ESRF (ID11)	ESRF (ID11)	ESRF (ID11)
	293 K	300 K	100 K	100 K	<i>ca.</i> 35 K white light	<i>ca.</i> 35 K Green only
Fe-N	2.080(3)	Slow loss of	1.933(2)	1.9297(29)	1.9473(40)	1.9395(44)
Fe-N	2.187(2)	crystallinity	1.971(2)	1.9722(29)	1.9873(39)	1.9772(41)
Fe-N	2.188(2)	with time	1.992(2)	1.9801(31)	1.9980(41)	1.9874(44)

References

¹ D. Collison, C. D. Garner, C. M. McGrath, J. F. W. Mosselmans, M. D. Roper, J. M. W. Seddon, E. Sinn, N. A. Young, *J. Chem. Soc., Dalton Trans.*, 1997, 4371.

² C. M. McGrath, C. J. O'Connor, C. Sangregorio, J. M. W. Seddon, E. Sinn, F. E. Sowrey and N. A. Young, *Inorg. Chem. Comm.*, 1999, **2**, 536.

³ B. Gallois, J. A. Real, C. Hauw, J. Zarembowitch, *Inorg. Chem.*, 1990, **29**, 1152; T. Granier, B. Gallois, J. Gaultier, J. A. Real, J. Zarembowitch, *Inorg. Chem.*, 1993, **32**, 5305.