

## Thermal and light induced polymorphism in iron(II) spin crossover compounds†

Amber L. Thompson,<sup>a</sup> Andrés E. Goeta,<sup>\*a</sup> José A. Real,<sup>\*b</sup> Ana Galet<sup>c</sup> and M. Carmen Muñoz<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE.

E-mail: A.E.Goeta@durham.ac.uk; Fax: +44 191 384 4737; Tel: +44 191 334 2102

<sup>b</sup> Institut de Ciència Molecular/Departament de Química Inorgànica, Universitat de València, Doctor Moliner 50, Burjassot, Spain. E-mail: jose.a.real@uv.es

<sup>c</sup> Departament de Física Aplicada, Universitat Politècnica de València, Camino de Vera s/n, 46071, Valencia, Spain

Received (in Cambridge, UK) 3rd March 2004, Accepted 14th April 2004

First published as an Advance Article on the web 14th May 2004

The spin crossover complexes {Fe[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>2</sub>L} ([H<sub>2</sub>B(pz)<sub>2</sub>]<sup>−</sup> = dihydrobis(pyrazolyl)borate, L = 2,2'-bipyridine (**1**), bipy and 1,10-phenanthroline, phen (**2**)) undergo both thermal and light induced spin crossover, but the structure of the low spin and light induced high spin states for **2** are different from that of the thermally induced high spin state and from those of **1**.

The ability of spin crossover (SC) materials to change their magnetic, structural and optical properties stimulated by pressure or temperature, has led to increasing interest in their potential use in technological applications such as molecular switches, data displays, data storage devices and more recently as intelligent contrast agents for Magnetic Resonance Imaging.<sup>1</sup> The discovery that at low temperature it is sometimes possible to photo-excite SC materials into a metastable high spin state<sup>2</sup> has enabled the study of high and low spin complexes without the added complication of thermal effects. This Light Induced Excited Spin-State Trapping (LIESST) has also engendered significant interest in the optical properties of these materials.

While structural studies of thermally induced high and low spin complexes (HS and LS) are increasingly common, structure determinations of the metastable high spin state (MHS) are still very rare with only a handful reported in the literature.<sup>3</sup> In addition, to date, all structural studies on metastable light induced states have been carried out on materials where the LS, HS and MHS states are isostructural. Here we present the first structural study of a spin crossover complex, which exhibits thermal and light induced polymorphism.

Both {Fe[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>2</sub>bipy} (**1**) and {Fe[H<sub>2</sub>B(pz)<sub>2</sub>]<sub>2</sub>phen} (**2**) undergo thermally induced SC (with characteristic temperatures of  $T_{1/2} \approx 160$  K) as well as light-induced SC.<sup>4</sup> The thermal transition in **2** is more cooperative than in **1** though, as shown by the more abrupt transition that takes place with hysteresis. Structural data have been reported previously for **1** above and below the SC transition, however, until now it had only been possible to collect data on **2** in the HS state as the crystal suffers structural damage on cooling through the transition. This problem was avoided by embedding the crystal in epoxy resin that remained flexible when immediately quench cooled.

Single crystal diffraction data‡ have been recorded for **1** at 200 K, 120 K, 30 K and at 30 K after irradiation with a red laser ( $\lambda = 633$  nm). The structure of the HS and LS states agree with the published data, where the structure is monoclinic ( $C2/c$ ), with the molecule astride the two-fold rotation axis, which passes through the centre of the iron atom and between the rings of the bipy ligand. On cooling through the transition, there is a decrease in the average Fe–N bond length and the volume of the FeN<sub>6</sub> octahedron (Table 1), which is consistent with those seen previously for this and other SC compounds. After irradiation, the unit cell volume, average Fe–N distance and octahedral volume increase to values that

suggest there has been close to 100% conversion to the MHS state, as seen from the magnetism.

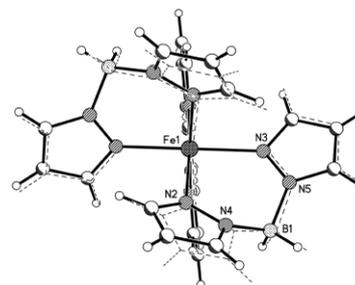
Single crystal diffraction data§ have also been recorded for **2** at 200 K, 100 K, 30 K and at 30 K after irradiation. The crystal was found to be in the  $C2/c$  monoclinic space group at 200 K (HS, same as in **1**), but to undergo a loss of symmetry to a related, primitive structure ( $P\bar{1}$ ), with unit cell volume approximately half that of the high spin structure. This loss of lattice symmetry also leads to the loss of the  $C_2$  molecular symmetry and this dramatic structural change explains the structural damage that previously led to difficulties in collecting data. The Fe–N bond lengths for **2** at 200 K and 100 K, clearly indicate a spin crossover transition coupled with the structural change (Table 1).

There is no further structural change on cooling **2** to 30 K. However, irradiation of **2** at 30 K leads to an increase in the unit cell volume from 1192.9(4) Å<sup>3</sup> to 1231.0(13) Å<sup>3</sup> (3.2%), and a corresponding increase in the octahedral volume from 10.53(2) Å<sup>3</sup> to 13.44(3) Å<sup>3</sup> indicates a high degree of conversion in agreement with that seen from the magnetic data.<sup>4</sup> Thus, the MHS state generated by irradiation with light has produced a second high spin polymorph, without the  $C_2$  symmetry seen in the first. An overlay of the two HS molecules shows the conformational difference between the polymorphs (Fig. 1).

**Table 1** Unit cell volumes, average Fe–N distances and octahedral volumes for **1** and **2**.

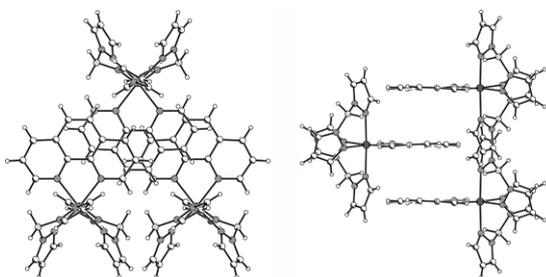
	Temperature	Unit cell volume	Fe–N Distance <sup>a</sup>	Octahedral volume <sup>a</sup>
<b>1</b>	200 K	2441.5(4) Å <sup>3</sup>	2.183(1) Å	13.67(2) Å <sup>3</sup>
	120 K	2334.5(2) Å <sup>3</sup>	2.004(9) Å	10.65(2) Å <sup>3</sup>
	30 K	2327.2(3) Å <sup>3</sup>	2.007(8) Å	10.69(2) Å <sup>3</sup>
	30 K-Irr <sup>b</sup>	2398.4(2) Å <sup>3</sup>	2.187(2) Å	13.74(2) Å <sup>3</sup>
<b>2</b>	200 K	2504.4(4) Å <sup>3</sup>	2.180(1) Å	13.63(2) Å <sup>3</sup>
	100 K	1198.1(2) Å <sup>3</sup>	1.998(6) Å	10.56(2) Å <sup>3</sup>
	30 K	1192.9(4) Å <sup>3</sup>	1.996(9) Å	10.53(2) Å <sup>3</sup>
	30 K-Irr <sup>b</sup>	1231.0(13) Å <sup>3</sup>	2.171(8) Å	13.44(3) Å <sup>3</sup>

<sup>a</sup> Calculated using IVTON.<sup>5</sup> <sup>b</sup> After irradiation at 30 K with red light ( $\lambda = 633$  nm).



**Fig. 1** Overlay of the two high spin polymorphs of **2**, showing the loss of  $C_2$  molecular symmetry. The light induced state is shown with a broken line.

† Electronic supplementary information (ESI) available: complete crystallographic information. See <http://www.rsc.org/suppdata/cc/b4/403179b/>



**Fig. 2**  $\pi$ - $\pi$  interactions in **2** at 200 K, showing the overlapping ligands (left) and the stacking (right).

In addition to the loss of molecular symmetry, there is also a change in the crystal packing. The  $C2/c$  structures of **1** and **2** form stacks held together with  $\pi$ - $\pi$  interactions between the interdigitating bipy/phen ligands (Fig. 2). At 200 K, the phen-phen distance is 3.886(6) Å, which on cooling to 100 K, splits into two shorter, non-equivalent distances (3.657(9) Å and 3.528(9) Å). Between 100 K and 30 K, these distances contract (to 3.640(7) Å and 3.507(7) Å). While in **1** the bipy-bipy distance is 0.06 Å shorter for the MHS state than for the thermal HS state, the light induced expansion in **2** is highly asymmetric. In **2**, one phen-phen distance remains unchanged (3.638(10) Å) and the second expands by approximately 0.3 Å to 3.813(11) Å. This peculiar behaviour suggests that the light induced high spin polymorph is relatively unstable and only occurs because there is insufficient energy (supplied by the laser or available as thermal energy) to enable the structure to undergo a symmetry change to the preferred  $C2/c$  structure. This also explains why the relaxation temperatures ( $T_{\text{LIESST}}$ ),<sup>6</sup> as observed from the magnetic data, for the MHS states for **1** and **2** are 52 K and 44 K respectively. This is unusual because the thermal transition for **2** on cooling begins at a slightly lower temperature than that for **1**, and in general, higher temperature thermal SC transitions yield lower temperature relaxations for the LIESST state. The thermal HS state for **2** is marginally more stable than that for **1**, suggesting that the light induced MHS state for **2** should also be more stable, and consequently the relaxation from the MHS state should take place at a higher temperature for **2** than for **1**. The light induced polymorphic behaviour of **2** explains why this is not the case, and in practice the  $C2/c$  MHS state of **1** is more stable than the triclinic light induced high spin polymorph of **2**.

The authors would like to thank The Royal Society for a Study Visit and a Joint Project award, the EPSRC for a postgraduate fellowship (ALT), the Universitat Politècnica de València for a predoctoral fellowship (AG), and Ministerio Español de Ciencia y Tecnología for financial assistance of the (MCM & JAR, project BQU 2001-2928).

## Notes and references

‡ The crystals of **1** were synthesised as discussed previously in the literature.<sup>4</sup> A typical red crystal was chosen  $0.20 \times 0.10 \times 0.07$  mm, mounted in fluoropolyether oil on a hair and quench cooled to 200 K using an Oxford Cryosystems Cryostream 600 series open flow  $N_2$  cooling device.<sup>7</sup> Using a Bruker SMART-CCD 1000 area detector diffractometer, with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å), several sets of  $\omega$ -scans ( $0.3^\circ/\text{frames}$ ) at different  $\phi$  settings were collected. On completion, the crystal was cooled to 120 K at  $240 \text{ K h}^{-1}$ , where the data collection was repeated. The crystal was then warmed to 200 K at  $180 \text{ K h}^{-1}$  then to 290 K at  $360 \text{ K h}^{-1}$  where the crystal was removed. The Cryostream was then replaced with an Oxford Cryosystems HeliX open flow helium cryostat,<sup>8</sup> and the crystal was cooled to 30 K in stages. At 30 K a hemisphere of data was collected ( $\omega$ -scans,  $0.9^\circ/\text{frames}$ ), after which the crystal was irradiated for approximately 30 min with a 25 mW red laser ( $\lambda = 633$  nm) after which data were collected as at 200 K and 120 K. Cell parameters were determined and refined using the SMART software<sup>9</sup> and raw frame data were integrated using the SAINT program.<sup>10</sup> The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using SHELXTL software<sup>11</sup> (crystal data are listed below). Reflection intensities

were corrected for absorption effects by numerical integration based on measurements and indexing of the crystal faces (using SHELXTL software). Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located in the difference map and refined with isotropic displacement parameters. *Single Crystal Data:*  $C_{22}H_{24}B_2FeN_{10}$ ,  $M_r = 505.98$ , monoclinic,  $C2/c$ ,  $Z = 4$ . 30 K -  $a = 16.1106(11)$ ,  $b = 14.5909(10)$ ,  $c = 10.8281(8)$  Å,  $\beta = 113.895(3)^\circ$ ,  $V = 2327.2(3)$  Å<sup>3</sup>, Data/restraints/parameters - 2662/0/207,  $R_{\text{int}} = 0.0606$ , Final  $R_1 = 0.0491$ ,  $wR_2 = 0.0823$  ( $I > 2\sigma(I)$ ). 30 K-Irr -  $a = 16.0350(9)$ ,  $b = 14.9377(9)$ ,  $c = 11.0470(7)$  Å,  $\beta = 114.986(2)^\circ$ ,  $V = 2398.4(2)$  Å<sup>3</sup>, Data/restraints/parameters - 2700/0/207,  $R_{\text{int}} = 0.0629$ , Final  $R_1 = 0.0630$ ,  $wR_2 = 0.0969$  ( $I > 2\sigma(I)$ ).  $\Delta\rho_{\text{min,max}} < \pm 1 \text{ e.}\text{Å}^{-3}$  in all cases.

§ The crystals of **2** were synthesised as discussed previously in the literature.<sup>4</sup> A typical red crystal was chosen ( $0.28 \times 0.10 \times 0.02$  mm), mounted in epoxy resin (Araldite®) on a hair and quench cooled to 200 K using an Oxford Cryosystems Cryostream 600 series open flow  $N_2$  cooling device.<sup>8</sup> Using a Bruker SMART-CCD 6000 area detector diffractometer, with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å), data were collected as for **1**. On completion, the crystal was cooled to 100 K at  $360 \text{ K h}^{-1}$ , where the data collection was repeated. A second red crystal ( $0.15 \times 0.12 \times 0.08$  mm) was selected, mounted (as before), and quenched to 200 K using an Oxford Cryosystems HeliX.<sup>7</sup> Cell parameters recorded using a Bruker ProteumM diffractometer with Bede Microsource® (Mo- $K\alpha$  radiation,  $\lambda = 0.71073$  Å), agreed with those seen previously at 200 K, so the crystal was cooled to 30 K at  $360 \text{ K h}^{-1}$ , where a hemisphere was collected (as before). On completion, the crystal was irradiated for approximately 2 min with a 25 mW red laser ( $\lambda = 633$  nm) after which another hemisphere was collected. The data treatment was carried out as for **1**, except that hydrogen atoms were positioned geometrically and refined using a riding model. *Single Crystal Data:*  $C_{22}H_{24}B_2FeN_{10}$ ,  $M_r = 505.98$ . 200 K - monoclinic,  $C2/c$ ,  $a = 17.3607(16)$ ,  $b = 16.0397(14)$ ,  $c = 10.5614(9)$  Å,  $\beta = 121.617(4)^\circ$ ,  $V = 2504.4(4)$  Å<sup>3</sup>, Data/restraints/parameters - 3370/0/216,  $R_{\text{int}} = 0.0485$ , Final  $R_1 = 0.0461$ ,  $wR_2 = 0.0888$  ( $I > 2\sigma(I)$ ). 100 K - triclinic,  $P1$ ,  $a = 11.6730(13)$ ,  $b = 11.0458(13)$ ,  $c = 10.5651(12)$  Å,  $\alpha = 69.520(3)^\circ$ ,  $\beta = 109.777(3)^\circ$ ,  $\gamma = 93.368(3)^\circ$ ,  $V = 1198.1(2)$  Å<sup>3</sup>, (the related larger cell:  $a = 16.5354(14)$ ,  $b = 15.5923(13)$ ,  $c = 10.5651(12)$  Å,  $\alpha = 89.688(4)^\circ$ ,  $\beta = 118.202(3)^\circ$ ,  $\gamma = 93.168(3)^\circ$ ,  $V = 2396.2(3)$  Å<sup>3</sup>) Data/restraints/parameters - 6409/0/403,  $R_{\text{int}} = 0.0539$ , Final  $R_1 = 0.0628$ ,  $wR_2 = 0.1296$  ( $I > 2\sigma(I)$ ). 30 K - triclinic,  $P1$ ,  $a = 16.655(2)$ ,  $b = 11.0156(19)$ ,  $c = 10.5664(8)$  Å,  $\alpha = 69.492(3)^\circ$ ,  $\beta = 109.755(3)^\circ$ ,  $\gamma = 93.280(3)^\circ$ ,  $V = 1192.9(4)$  Å<sup>3</sup>, Data/restraints/parameters - 5832/0/407,  $R_{\text{int}} = 0.0546$ , Final  $R_1 = 0.0545$ ,  $wR_2 = 0.0894$  ( $I > 2\sigma(I)$ ). 30 K-Irr - triclinic,  $P1$ ,  $a = 10.727(7)$ ,  $b = 12.415(8)$ ,  $c = 10.712(6)$  Å,  $\alpha = 67.473(15)^\circ$ ,  $\beta = 110.377(15)^\circ$ ,  $\gamma = 93.505(11)^\circ$ ,  $V = 1231.0(13)$  Å<sup>3</sup>, Data/restraints/parameters - 5369/0/350,  $R_{\text{int}} = 0.0302$ , Final  $R_1 = 0.0798$ ,  $wR_2 = 0.1620$  ( $I > 2\sigma(I)$ ).  $\Delta\rho_{\text{min,max}} < \pm 1.2 \text{ e.}\text{Å}^{-3}$  in all cases. All structures have been deposited with the CCDC (Nos 233281-233288). See <http://www.rsc.org/suppdata/cc/b4/b403179b/> for crystallographic data in .cif or other electronic format.

- O. Kahn, J. Kröber and C. Jay, *Adv. Mater.*, 1992, **4**(11), 718; O. Kahn and C. J. Martinez, *Science*, 1998, **279**, 44; O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993.
- S. Decurtins, P. Gütlich, K. M. Hasselbach, H. Spiering and A. Hauser, *Inorg. Chem.*, 1985, **24**, 2174.
- J. Kusz, H. Spiering and P. Gütlich, *J. Appl. Cryst.*, 2001, **34**, 229; M. Marchivie, P. Guionneau, J. A. K. Howard, G. Chastanet, J.-F. Létard, A. E. Goeta and D. Chasseau, *J. Am. Chem. Soc.*, 2002, **124**, 194; V. A. Money, I. R. Evans, M. A. Halcrow, A. E. Goeta and J. A. K. Howard, *Chem. Commun.*, 2003, 158.
- J. A. Real, M. C. Muñoz, J. Faus and X. Solans, *Inorg. Chem.*, 1997, **36**, 3008; N. Moliner, L. Salmon, L. Capes, M. C. Muñoz, J.-F. Létard, A. Bouseksou, J.-P. Tuchagues, J. J. McGarvey, A. C. Dennis, M. Castro, R. Burriel and J. A. Real, *J. Phys. Chem. B*, 2002, **106**, 4276.
- T. Balić-Zunić and I. Vicković, *J. Appl. Cryst.*, 1996, **29**, 305.
- J.-F. Létard, L. Capes, G. Chastanet, N. Moliner, S. Létard, J.-A. Real and O. Kahn, *Chem. Phys. Lett.*, 1999, 115.
- J. Cosier and A. M. Glazer, *J. Appl. Cryst.*, 1986, **19**, 105.
- A. E. Goeta, L. K. Thompson, C. L. Sheppard, S. S. Tandon, C. W. Lehmann, J. Cosier, C. Webster and J. A. K. Howard, *Acta Cryst.*, 1999, **C55**, 1243; Oxford Cryosystems Newsletter, Issue 2, August 2003.
- SMART-NT, Data Collection Software, Version 5.0; Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1999.
- SAINT-NT, Data Reduction Software, Version 5.0., Bruker Analytical Instruments Inc., Madison, Wisconsin, USA, 1999.
- SHELXTL, Structure Refinement and Solution Software, Version 5.1., Bruker Analytical Instruments Inc., Madison, Wisconsin, USA, 1999.