Advanced Study of Switchable Spin Crossover Compounds

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Chapter 10: Conclusions

The motivation of this work was to explore the possibility of using synthetic derivatives of the ligand 3-bpp to obtain novel Fe(II) compounds with the potential to display SCO behaviour. This would constitute a new approach in the context of this family of systems. The design of the derivatives was driven by the aim to successfully crystallise the systems, so that the interpretation of the magnetic properties could be supported with structural evidence. To this end, two new ligands have been prepared based on 3-bpp, by employing bis-β-diketones as a point of entry to be able to change the groups appended to the polypyrazolyl core. With these chelating species, 15 iron-based compounds have been crystallised and studied, adding significantly to the family of 3-bpp compounds found in the literature. The number of crystal structures resolved has allowed an extensive study of the interactions that help form the lattice and influence the magnetic properties of the compounds. The promise of these ligands more generally in coordination chemistry was demonstrated by the synthesis of a series of compounds based on other 1st row transition metal ions.

The strategy of appending additional aromatic rings and hydrogen bonding donors to the central 3-bpp moiety has aided the formation of crystal lattices that display a variety of intermolecular interactions. These were sought due to their role as the principle mediators of elastic interactions in SCO systems, helping to improve levels of cooperativity. The preferred packing motif in the compounds obtained is that of the “terpyridine embrace”, which is predicated on face-to-face interactions between flat aromatic rings. Despite the flexibility of the novel polypyrazolyl ligands, the presence of extended aromatic wings is sufficient to encourage the crystallisation of the compounds in this motif. In many of the compounds obtained, the interplay between lattice components such as the anions or the solvent molecules and the ligand-containing cations has caused interruptions to the regularity of the terpyridine embrace. The stability of this assembly was seen to be superceded by that of a dinuclear complex when the anions employed were more strongly coordinating than perchlorate, tetrafluoroborate, or triflate.

The structural study was also supported by the use of Hirshfeld surface analysis, which is a relatively new approach in SCO research. The packing effects that result from the combination of the lattice entities in the terpyridine embrace have been shown to distort

the shape of the cations and deform the coordination sphere around the Fe(II) cation, as observed through Continuous Symmetry Measures (CSMs) and other structural parameters. This effect was particularly pronounced in the systems containing the bulkier ligand H_2L1. This distortion is proposed as the root of the absence of SCO behaviour in many of the compounds.

However, in the H_4L-based compound **1**, the array of intermolecular contacts induced by the ligand was crucial to achieve the required cooperativity for the thermal SCO process to take place with hysteresis. The magneto-structural relationship proved to be more complicated, and the crystallographic disorder was revealed to be coupled with the spin state: the transition is accompanied by ordering within the lattice. The effect of this coupling was to make the hysteresis loop asymmetric, with the disorder→order transition concomitant with a less abrupt HS→LS transition. Iso-thermal relaxation experiments allowed the real hysteresis loop to be traced.

The photo-physical properties of meta-stable states of **1** were demonstrated to be distinct to those of the thermally-obtained meta-stable states. This was shown by a variety of techniques, but the discrepancy in the iso-thermal relaxation kinetics pointed to the formation of different phases depending on the method used to trap the compound. This could be confirmed by the crystal structures available for both the thermally-trapped meta-stable state and the LIESST state. The LIESST state was shown to possess lower structural disorder, contributing to its simpler relaxation kinetics with respect to the thermally-trapped structure. DSC was used to show that there were two events occurring separately when the thermally-trapped phase relaxed to the LS state, and the combination of all of this experimental evidence allowed the proposal of a two-step model to account for its relaxation. According to this model, the thermally-trapped system first orders to a phase closer in nature to the LIESST phase, and then relaxes to the LS state. Re-interpretation of the experimental kinetic data confirmed the validity of this model. Using Raman spectroscopy, the SCO process in **1** could be induced by laser irradiation within the hysteresis loop, and also proved to be reversibly induced by applying pressure to the compound.

The sensitivity of 3-bpp-based system's magnetic behaviour to the degree of hydration of the sample was also observed here for compound **7**. An ageing process, which saw the crystallinity of the compound degrade with time, accompanied by the absorption of atmospheric water and partial loss of lattice solvent molecules, led to an increase in the cooperativity associated with the transition.

The work described in this thesis provides a platform to devise further derivatives of 3-bpp, which is still a relatively unexploited approach to the synthesis of SCO compounds, especially when compared to the regio-isomer 1-bpp. An article published by Halcrow and co-workers during the preparation of this thesis functionalised the remaining nitrogen atom of the pyrazolyl rings in 3-bpp.[1] This approach, with progressively bulkier substituents of varied electronic effects, yielded a group of compounds that were devoid of SCO. That paper, together with the results of the studies here, leave the functionalisation of the *para*- position of the central pyridyl ring of 3-bpp as a potential avenue for future work in this area.

1. T. D. Roberts, M. A. Little, L. J. K. Cook, S. A. Barrett, F. Tuna and M. A. Halcrow, *Polyhedron*, 2013, DOI: 10.1016/j.poly.2013.1001.1057.

Appendix: List of Publications

A1. G. A. Craig, L. A. Barrios, J. S. Costa, O. Roubeau, E. Ruiz, S. J.Teat, C. C. Wilson, L. Thomas, G. Aromí "Synthesis of a novel heptacoordinated Fe(III) dinuclear complex: experimental and theoretical study of the magnetic properties" *Dalton Trans.*, **39**, 4874-4881, 2010.

A2. G. A. Craig, J. S. Costa, O. Roubeau, S. J. Teat, G. Aromí "Coupled Crystallographic Order-Disorder and Spin State in a Bistable Molecule: Multiple Transition Dynamics" *Chem. Eur. J.*, **17**, 3120-3127, 2011.

A3. J. S. Costa, G. A. Craig, L. A. Barrios, O. Roubeau, E. Ruiz, S. Gomez-Coca, S. J. Teat, G. Aromí "The Use of a Bis(phenylpyrazolyl)pyridyl Ligand to Prepare [Mn_4] and [Mn_{10}] Cage Complexes" *Chem. Eur. J.*, **17**, 4960-4963, 2011.

A4. G. A. Craig, J. S. Costa, D. Aguilà, L. A. Barrios, O. Roubeau, S. J. Teat, G. Aromí "Molecular [Co(III)Co(II)] x 2 assemblies of a new bis-phenol/pyrazolyl ligand" *New J. Chem.*, **35**, 1202-1204, 2011.

A5. J. S. Costa, L. A. Barrios, G. A. Craig, S. J. Teat, F. Luis, O. Roubeau, M. Evangelisti, A. Camón, G. Aromí "A molecular [Mn_{14}] coordination cluster featuring two slowly relaxing nanomagnets" *Chem. Commun.*, **48**, 1413-1415, 2012.

A6. G. A. Craig, J. S. Costa, O. Roubeau, S. J. Teat, G. Aromí "Local coordination geometry and spin state in novel Fe(II) complexes with 3-bpp type ligands as controlled by packing forces and structural correlations" *Chem.-Eur. J.*, **18**, 11703-11715, 2012.

A7. G. A. Craig, J. S. Costa, O. Roubeau, S. J. Teat, G. Aromí "A Novel Fe(II) Spin Crossover Complex Becomes Increasingly Cooperative with Ageing"; *Eur. J. Inorg. Chem.*, 745-752, 2013.

A8. G. A. Craig, O. Roubeau, J. Ribas-Ariño, S. J. Teat, G. Aromí "Two Isosceles Coordination [Ni3] Triangles Strongly Interacting via Hydrogen Bonds" *Polyhedron*, **52**, 1369-1374, 2013.

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