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A ladder type iron(II) coordination polymer with cooperative spin transition†

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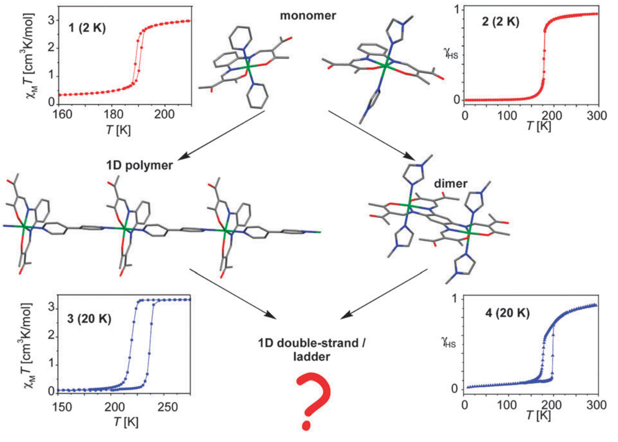
Ladder type 1D coordination polymers were synthesised with the aim to improve the spin crossover properties of the iron(II) complexes following the concepts of crystal engineering. A wide hysteresis loop (34 K) was observed if rigid linkers were used. The first X-ray structure for a 1D iron(II) ladder is reported.

Spin crossover (SCO) complexes are a fascinating class of switchable molecules that continue to attract the interest of several research groups all over the world.[1–3] Reason for the continuing interest in this substance class is the possibility to combine a sensing device (T and/or p, magnetic field,[4] adsorption or desorption of guest molecules[5]), memory and display (colour change) in one compound. This requires bistability (or memory effect) of the material during the spin transition.[6,7] Over the last few years several new concepts were proposed that show that intermolecular interactions in the crystal lattice are necessary to achieve cooperative effects.[2,3,6,8,9] Thus one of the key questions is how such intermolecular contacts can be controlled.

The ideas of crystal engineering can be easily associated with the aims of SCO research, as they have a great deal in common concerning fundamental concepts and strategies. Desiraju defined crystal engineering as "the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties".[10] This includes chemical reactivity as well as optical, magnetic or electronic properties.[11] Purposeful ligand design can be used to increase the intermolecular interactions in the crystal packing,[8,9] but the possibility of crystal engineering of SCO compounds is questioned.[12] Especially the effect of solvent inclusion or polymorphism is difficult to predict.[12] With the following example we will demonstrate that despite this the concepts of crystal engineering can be applied successfully to the design of SCO compounds.

In our group we started using mononuclear iron(II) complexes with Schiff-base like ligands (L1).[13] Typically we observed gradual or abrupt spin transitions (ST), sometimes with small hysteresis loops.[2] The complexes [FeL1(py)$_2$] (**1**) and [FeL1(1-meim)$_2$] (**2**) given on top of Scheme 1 are examples of a cooperative ST (2 K hysteresis). The cooperative interactions are in both cases due to the 2D network of short van der Waals (vdW) contacts.[14] We did use two different strategies to increase the number of short contacts in the crystal packing and by this the hysteresis width. One is the use of rigid bridging axial ligands such as 4,4′-bipyridine (bipy) leading to the 1D coordination polymer [FeL1(bipy)] (**3**).[15] The combination of the rigid axial ligand and several short vdW contacts increases the hysteresis width to about 20 K[15] (bottom, left of Scheme 1). The other possibility is the replacement of L1 by the bitopic ligand L2.[13] Due to the increase in symmetry the dimension of the network of short vdW contacts increases (2D → 3D) leading to a wider hysteresis loop for the dinuclear complex [Fe$_2$L2(1-meim)$_4$] (**4**, 20 K).[16]

Keeping the concepts of crystal engineering in mind, the question arises if it is possible to increase the hysteresis loop width further by a combination of the two above-mentioned approaches. Consequently we started with the synthesis of 1D chain iron(II) complexes of the bitopic ligand L2 with the aim to achieve double strand or ladder structures where the advantages of the two different approaches are combined. The synthesis of a double strand coordination polymer is not as straight forward as for the 1D chain compounds as a wide variety of different side products are thinkable (Scheme 2).



Scheme 1 General strategy for the optimisation of the SCO properties in a crystal engineering like approach.

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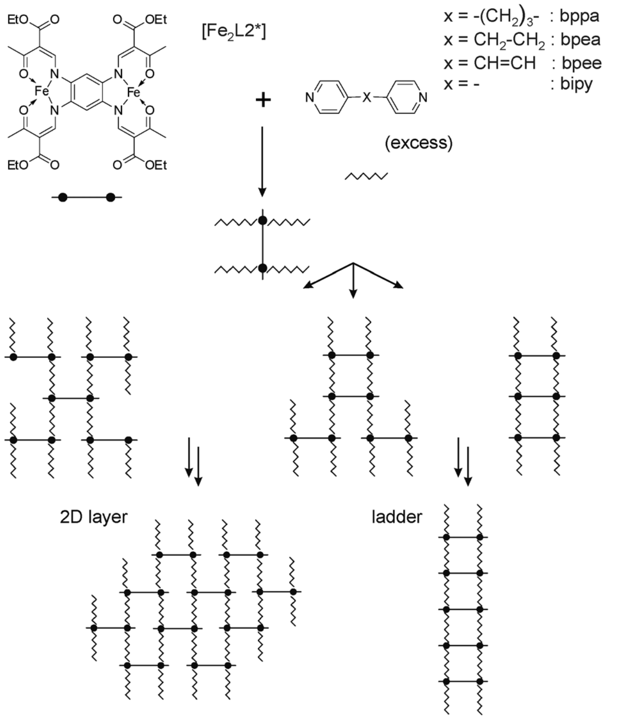

Scheme 2 Potential products and side products for the reaction of a dinuclear iron complex with a bridging axial ligand.

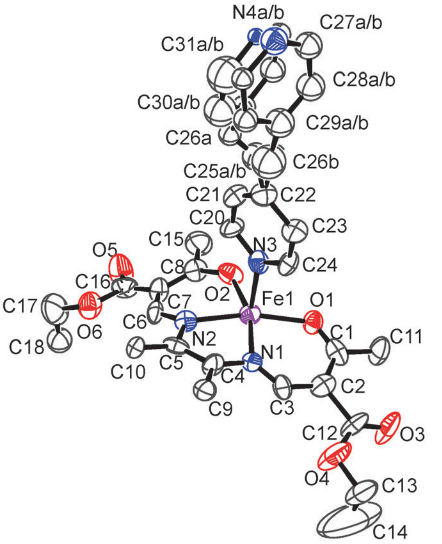

Fig. 1 ORTEP drawing of the asymmetric unit of compound **5** (anisotropic displacement ellipsoids drawn at the 50% probability level). Included solvent and hydrogen atoms omitted for clarity.

Next to various types of incomplete double strands the formation of a 2D network is possible. In the presence of additional monodentate ligands (*e.g.* solvent) the formation of 1D zigzag chains with alternating ligands is also possible. This was recently reported by Kaizaki *et al.* for an iron(II) complex with a steep one-step ST.[17] The situation is complicated because both, product and side products, have a very low solubility. As the SCO properties of the product will be strongly influenced by such variations it was important to determine the optimal reaction conditions.

This task relies strongly on the concepts of supramolecular chemistry, where the desired product is obtained by spontaneous self-assembly.[18] Kinetically labile systems and long reaction times are necessary to allow the system to reach its energetic minimum. The first question to be answered is whether the double strand or the 2D layer is the thermodynamically stable final product. As the composition of the two products is identical (in contrast to the side products that can be easily distinguished this way), great efforts were made to obtain crystals of sufficient quality for X-ray analysis. We succeeded in the synthesis and crystallisation of the ladder compound $[Fe_2L2^*(bpea)_2]\cdot x$MeOH (**5**) (bpea = 1,2-bis(4-pyridyl)ethane)[13] by applying a slow diffusion technique, thus ensuring long reaction times. The crystal data are summarized in Table S1 (ESI†). The quality of the orthorhombic crystals was inferior so we can only speak of a structural motif, nonetheless this motif describes the first structural example of an iron(II) ladder coordination polymer, to the best of our knowledge. In Fig. 1 the asymmetric unit of the complex is displayed. All iron centres are crystallographically equal and clearly in the HS state with bond lengths within the inner coordination sphere of 2.100(9)/2.105(9) Å (Fe–N$_{1/2}$), 2.026(8)/2.034(8) Å (Fe–O$_{1/2}$) and 2.186(5)/2.265(8)/2.279(8) Å (Fe–N$_{3/4a/4b}$) and the O–Fe–O angle of 112.2(2)°.[2] The full bitopic ligand is obtained after applying the twofold crystallographic axis that runs through the atoms C9 and C10. One of the two pyridyl rings of the axial bpea ligand is disordered. As can be seen from Fig. 2, infinite one-dimensional ladder-like chains are formed, with the base vector [1 0 0]. Within the ladders, the backbones of the binuclear ligands (the "rungs of the ladders") are not perpendicular to the axial ligands but include an angle of 75°.

The distance between the two iron centres within the bitopic ligands is 8.2 Å, not much shorter than the distance between the iron centres of two neighbouring ladders (8.5 Å). Thus the formation of a 2D network seems to be thinkable. However, in this case the equatorial ligands cannot be arranged offset as observed in molecular packing at the top of Fig. S2 (ESI†), but they have to align in one line. Such an arrangement with an iron–iron distance of 8.2 Å is not possible due to steric demand of the methyl groups at the outer periphery of the ligand. The ladder structure is the preferred structural motif for this type of complexes. The molecular packing displayed in Fig. S2 (ESI†) reveals that the chains form parallel layers in the *a*–*b*-plane as well as in the *a*–*c*-plane and are staggered in the *b*–*c*-plane.

With the knowledge that the synthesis of ladder structures is possible and this is the preferred structural motif the second question is whether the hysteresis width can be increased further with such a system. The single crystals were not obtained in enough quantity for a magnetic characterisation. For the preparation of bulk material in enough quantity, high reaction temperatures and long reaction times are necessary. From methanol under reflux conditions a material with the composition

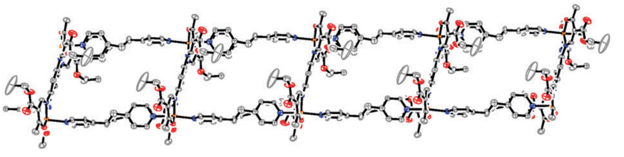

Fig. 2 Excerpt of the infinite 1D ladder structure of compound **5**. Solvent molecules and hydrogen atoms omitted for clarity.

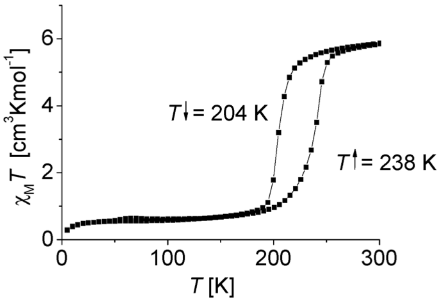

Fig. 3 Plot of the $\chi_M T$ product *versus* T for the compound **6**.

$[Fe_2L2^*(bpea)_3]\cdot MeOH$ is obtained showing a stepwise incomplete spin transition (Fig. S1, ESI†). This is not unexpected as the number of bpea molecules per metal centre clearly indicates the formation of side products (or a mixture of the desired product and side products) and several inequivalent iron centres are thinkable. Toluene as solvent in combination with longer reaction times proved to be more suited and the corresponding complexes with 4,4′bipyridine (bipy), bispyridylethane (bpea), bispyridylethene (bpee) and bispyridylpropane (bppa) were synthesised. SQUID measurements on those samples reveal that the complex with bipy is a pure HS complex over the entire temperature range. The other three complexes show SCO behaviour. However, for the flexible ligands bppa and bpea the ST is gradual and incomplete – this is not unexpected as rigid bridging ligands are needed for an effective communication of cooperative effects within the polymer chain.[19] For the 1D chain compounds of L1 with the flexible ligands incomplete spin transitions that stop at $\gamma_{HS} = 0.5$ were observed frequently.[19] For the rigid ligand bpee we obtained the complex **6** with the composition $[Fe_2L2^*(bpee)_2]\cdot 1.5$ Tol. The results of the magnetic measurements are displayed in Fig. 3.

The room temperature $\chi_M T$ value is 5.9 cm^3 K mol^{-1} in the range expected for binuclear iron(II) complexes with both iron centres almost in the high-spin (HS) state. The $\chi_M T$ value decreases gradually between 300 and 235 K, followed by an abrupt transition to a minimum value of 0.85 cm^3 K mol^{-1} at 185 K. Below 185 K the $\chi_M T$ value remains approximately constant down to 50 K. The $T_{\frac{1}{2},\,\text{down}}$ of this SCO is 205 K. Upon heating, the $\chi_M T$ value is identical to the cooling mode between 50 and 185 K. Above 185 K, the $\chi_M T$ value increases first gradually then rapidly then again gradually to attain the maximum value of 5.90 cm^3 K mol^{-1} at 300 K. The $T_{\frac{1}{2},\,\text{up}}$ is 239 K, resulting in a 34 K wide hysteresis loop that can be repeated several times. In order to evaluate the structural similarities of the crystalline sample **5** and the powder **6**, the X-ray powder patterns of **6** were investigated at room temperature (HS) and 173 K (LS) and compared with the calculated X-ray powder pattern of **5**. The corresponding data are given in Fig. S3 (ESI†) in the 5–45 2Θ range. One has to keep in mind that different linkers were used for the synthesis of the polymers (bpea *vs.* bpee) and different solvents are included in the crystal lattice (methanol *vs.* toluene). Despite this several similarities are observed in the powder pattern of the HS and LS species **5** and **6** (Fig. S3, ESI†), so that the same structural motif can be assumed. Upon spin transition the powder pattern of **6** changes and a different set of reflexes is observed for the LS and the HS state (Fig. S3, ESI†). In agreement with results from SQUID measurements, the spin transition is not complete at 173 K and the HS peaks are not fully vanished.

We succeeded with the synthesis and crystallisation of the first example of an iron(II) 1D coordination polymer with ladder structure. The search for this structural motif was initiated by applying the concepts of crystal engineering to the design of spin crossover materials with wide hysteresis loops. The successful synthesis of a powder sample with a 34 K wide hysteresis loop demonstrates that this approach is worthwhile to be considered further for the design of spin crossover materials.

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Notes and references

1 (*a*) P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2024–2054; (*b*) *Spin Crossover in Transition Metal Compounds I–III*, eds. P. Gütlich and H. Goodwin, Springer Berlin/Heidelberg, 2004, pp. 233–235; (*c*) J.-F. Létard, *J. Mater. Chem.*, 2006, **16**, 2550–2559; (*d*) O. Sato, J. Tao and Y.-Z. Zhang, *Angew. Chem., Int. Ed.*, 2007, **46**, 2152–2187; (*e*) J. A. Kitchen and S. Brooker, *Coord. Chem. Rev.*, 2008, **252**, 2072–2092; (*f*) M. A. Halcrow, *Coord. Chem. Rev.*, 2009, **253**, 2493–2514; (*g*) K. S. Murray, *Aust. J. Chem.*, 2009, **62**, 1081; (*h*) A. Gaspar, M. Seredyuk and P. Gütlich, *J. Mol. Struct.*, 2009, **924–926**, 9–19; (*i*) S. Brooker and J. A. Kitchen, *Dalton Trans.*, 2009, 7331–7340; (*j*) A. B. Koudriavtsev and W. Linert, *J. Struct. Chem.*, 2010, **51**, 335–365; (*k*) H. Naggert, A. Bannwarth, S. Chemnitz, T. von Hofe, E. Quandt and F. Tuczek, *Dalton Trans.*, 2011, 6364; (*l*) C. Gandolfi, C. Moitzi, P. Schurtenberger, G. G. Morgan and M. Albrecht, *J. Am. Chem. Soc.*, 2008, **130**, 14434–14435; (*m*) A. Bousseksou, G. Molnar, L. Salmon and W. Nicolazzi, *Chem. Soc. Rev.*, 2011, **40**, 3313–3335.

2 B. Weber, *Coord. Chem. Rev.*, 2009, **253**, 2432–2449.

3 M. A. Halcrow, *Chem. Soc. Rev.*, 2011, **40**, 4119.

4 A. Bousseksou, K. Boukheddaden, M. Goiran, C. Consejo, M.-L. Boillot and J.-P. Tuchagues, *Phys. Rev. B*, 2002, **65**, 172412.

5 G. J. Halder, *Science*, 2002, **298**, 1762–1765.

6 O. Kahn, *Science*, 1998, **279**, 44–48.

7 (*a*) O. Kahn, C. Jay, J. Krober, R. Claude and F. Groliere, *EP*, 0666561, 1995; (*b*) A. D. Naik, L. Stappers, J. Snauwaert, J. Fransaer and Y. Garcia, *Small*, 2010, **6**, 2842–2846; (*c*) Y. Garcia, V. Ksenofontov, S. Mentior, M. M. Dîrtu, C. Gieck, A. Bhatthacharjee and P. Gütlich, *Chem.–Eur. J.*, 2008, **14**, 3745–3758.

8 J.-F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Chasseau and O. Kahn, *J. Am. Chem. Soc.*, 1997, **119**, 10861–10862.

9 J. A. Real, A. B. Gaspar, V. Niel and M. C. Muñoz, *Coord. Chem. Rev.*, 2003, **236**, 121–141.

10 G. Desiraju, *Crystal engineering. The design of organic solids*, Elsevier, Amsterdam, 1989.

11 G. Desiraju, *J. Chem. Sci.*, 2010, **122**, 667–675.

12 M. Hostettler, K. W. Törnroos, D. Chernyshov, B. Vangdal and H.-B. Bürgi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4589–4594.

13 L1 = [([3,3′]-[1,2-phenylenebis(iminomethylidyne)]bis(2,4-pentanedionato)(2-)]; L2 = [3,3′, 3″, 3‴]-[1,2,4,5-phenylenetetra(iminomethylidyne)]tetra(2,4-pentanedionato)(4-)]; L2* = Tetraethyl-[2,2′,2″,2‴]-[1,2,4,5-phenylenetetra(iminomethylidyne)]tetra(3-oxobutanato)(4-)].

14 B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.-F. Létard, K. Achterhold and F. G. Parak, *Inorg. Chem.*, 2008, **47**, 487–496.

15 B. Weber, R. Tandon and D. Himsl, *Z. Anorg. Allg. Chem.*, 2007, **633**, 1159–1162.

16 B. Weber, E. S. Kaps, J. Obel, K. Achterhold and F. G. Parak, *Inorg. Chem.*, 2008, **47**, 10779–10787.

17 K. Yoneda, K. Adachi, S. Hayami, Y. Maeda, M. Katada, A. Fuyuhiro, S. Kawata and S. Kaizaki, *Chem. Commun.*, 2006, 45–47.

18 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 89–112.

19 W. Bauer, W. Scherer, S. Altmannshofer and B. Weber, *Eur. J. Inorg. Chem.*, 2011, 2803–2818.