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Stereochemistry for engineering spin crossover: structures and magnetic properties of a homochiral *vs.* racemic [Fe(N₃O₂)(CN)₂] complex⁺

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The Schiff-base condensation of the $R_{,R}$ -(+)-diamine (2a) with 2,6diacetyl pyridine in the presence of Fe^{II} affords the macrocyclic complex [Fe(dpN₃O₂)(CN)₂] (3a) (dp = diphenyl) with ligand centred chirality comprising of a 1:1 mixture of LS 6- and HS 7-coordinate Fe^{II} centres. Variable temperature magnetic susceptibility and Mössbauer studies reveal that (3a) undergoes an incomplete thermal SCO transition with a $T_{1/2}$ = 250 K as well as a LIESST effect. In contrast its racemic counterpart (3c) comprises of mostly LS Fe^{II} and exhibits no LIESST properties.

The first spin crossover (SCO) complex was discovered by Cambi *et al.* in the 1930's.¹ In the years that followed the development of the field of coordination chemistry provided insight into this behaviour which more than eighty years later has developed into a research intensive field. The large proportion of SCO complexes reported to-date incorporate octahedral Fe^{II} centres that switch between high-spin (HS) and low-spin (LS) states *via* the application of temperature, pressure or light. During the SCO transition, the majority of these complexes undergo very subtle changes in their molecular geometries and/or shapes, a topic that has been extensively reviewed by Halcrow.²

Scientists are currently exploring new applications for SCO compounds that include display and memory storage devices, temperature sensitive MRI contrast agents, as well as switchable liquid crystals, SCO nanoparticles and pressure sensors.^{1,3} In recent years, it has been proposed that optical activity could also be used to monitor the spin-state switching in these materials affording an alternative readout process to conventional achiral optical recording media.⁴ In this context, a breakthrough in the field was made when Ohkoshi et al. reported that the magnetic properties of a chiral three dimensional [Fe(CN)₆]⁴⁻ complex displayed alternate optical switching between the crystallographic and magnetic contributions to the second-harmonic generation, opening up new and exciting applications for chiral SCO complexes as magneto-optical memory and optoelectronic devices.⁵ Despite these advances, examples of chiral SCO complexes are quite rare.⁶ The majority of chiral SCO complexes reported to-date have been obtained via spontaneous resolution i.e. fortuitous crystallisation of crystals of both Λ and Δ configuration rather than generation of a racemate.^{5,7} or *via* a self-assembly process, together with an auxiliary chiral building block.^{6a} Here we report an alternative strategy in which we employ chiral centres on the ligand framework in order to enforce formation of a chiral SCO complex with full control over the stereochemistry of the bulk material. Specifically we introduce chirality into the backbone of the parent $[Fe(N_3O_2)CN)_2]$ SCO complex 1, first reported by Nelson in the 1970's.⁸ Complex 1 remains the only known example of an Fe^{II} SCO system for which the solid state phase transition involves a significant change in the coordination geometry of the Fe^{II} centre² and has also been shown to undergo light induced excited state spin trapping or LIESST, with a long lived excited state.9 In more recent years this macrocycle has been exploited for the self-assembly of diverse structural topologies that include magnetic chains and networks.¹⁰ Surprisingly no synthetic derivatives have been studied to-date, most likely due to the lack of commercial availability of suitably substituted diamine precursors. As part of our approach we have invested considerable effort in the preparation and characterization of two chiral diamines 2a and 2b as the precursors to the novel Schiff-base (N_3O_2) macrocyclic complexes 3a and 3b, Fig. 1.11

The two new chiral diamines 2a and 2b were prepared in five steps from commercially available (R,R)-(+)- or (S,S)-(-)-hydrobenzoin 4 following the strategy presented in

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[†]Electronic supplementary information (ESI) available: Experimental, X-ray crystallographic, Magnetic, Mössbauer and XRD data. CCDC 1025310 and 1025311. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00357a

Fig. 1 Molecular structure of the parent macrocycle $[Fe(N_3O_2)(CN)_2]$ (1); the chiral diamine (2) and the chiral macrocycle $[Fe(dpN_3O_2)(CN)_2]$, where dp = diphenyl (3).



Scheme 1 Reagents and Conditions: (i) NaH, THF allyl bromide, reflux; (ii) OsO₄, NalO₄ THF-H₂O (iii) NaBH₄, DCM-NaOH (iv) phthalimide, triphenylphosphine, di-iso-propylazodicarboxylate, THF, 4 days, (v) hydrazine monohydrate, EtOH, reflux.

Scheme 1. In the first step, hydrobenzoin was reacted with allyl bromide to afford the diene 5 as pale yellow oil in 73% yield. Oxidation of 5 with $OsO_4/NaIO_4$ afforded the dialdehyde 6 which was then reduced *in situ* with NaBH₄ to yield the corresponding diol 7 that was isolated as a yellow oil in 84% yield. Reaction of 7 with phthalimide, triphenylphosphine and di-isopropylazodicarboxylate gave the bis-phthalimide 8 that after hydrazinolysis afforded the diamine 2 as a white solid in 78% yield. Full experimental details for 2 and its synthetic intermediates are presented in S-1 of the ESI.[†]

The metal-templated Schiff-base condensation of 2a and 2b with 2,6-diacetyl pyridine afforded the new chiral complexes 3a (R,R) and **3b** (S,S) as dark blue solids in 59% yield.⁸ The racemate 4c was prepared from a 1:1 mixture of 2a and 2b in 56% yield following the same strategy. The opposite chiralities of 3a and 3b were confirmed by CD spectroscopy where as expected, the racemic complex 3c showed no CD spectrum (S-2, ESI⁺). Magnetic susceptibility studies on 3a reveal that at 370 K, the $\chi_{\rm M}T$ value (2.78 cm³ K mol⁻¹) is less than that expected for 100% HS Fe^{II} (3.3 cm³ K mol⁻¹, g = 2.1), reflecting an incomplete SCO transition. Upon cooling, a smooth decrease in $\chi_{\rm M}T$ is observed down to 50 K where it remains constant before decreasing again to 0.43 cm³ K mol⁻¹ at 10 K which can be attributed to the zero field splitting of the remaining HS fraction. In contrast to the parent macrocycle 1, no thermal hysteresis was observed.



Fig. 2 Left, temperature dependence of the $\chi_M T$ product for **3a**. Right, VT ⁵⁷Fe Mössbauer spectra of **3a** (red line), simulated HS component (green line) and LS component (blue line).

Variable temperature ⁵⁷Fe Mössbauer spectroscopy studies of **3a** show a dominant quadrupole doublet at 293 K for the HS Fe^{II} complex (green line, Fig. 2), but on cooling the narrower quadrupole doublet (blue line, Fig. 2), corresponding to the LS Fe^{II} complex increases in intensity. At 5 K both HS and LS forms of the complex are still present, consistent with the magnetic data. A determination of the percentage of Fe^{II} sites as a function of temperature (Fig. 2) based on both Mössbauer and magnetic data reveals $T_{1/2} = 250$ K, *i.e.* at 250 K the complex comprises a 1:1 mixture of HS and LS complexes with 25% HS at 5 K and 61% HS at room temperature (see also S-5, ESI†). In contrast, VT magnetic susceptibility and Mössbauer studies on racemic **3c** are consistent with a predominantly LS complex of which less than 10% undergoes a SCO transition (S-5, ESI†).

Photomagnetic studies of **3a** reveal a LS to HS conversion could be obtained by illuminating the sample with green light $(\lambda = 514 \text{ nm})$ at 10 K. After photo-excitation for 10 hours, $\chi_M T$ doubled to a value of 0.86 cm³ K mol⁻¹. A subsequent slow increase of the sample temperature revealed that the $\chi_M T$ plot remained almost constant up to 40 K, when it decreases slightly and remains more or less constant up to 125 K, the temperature at which the curve merges with the thermal spin transition recorded in the dark (Fig. 2, left, open circles). The photoconversion is estimated to be *ca.* 18% (S-4, ESI†). In contrast, photomagnetic studies on **3c** under the same conditions reveal no such LIESST behaviour.

Suitable single crystals of **3a** were obtained *via* slow diffusion of diethyl ether into an acetonitrile solution of **3a**. At 250 K, **3a** crystallizes in the chiral space group P_{2_1} , with two independent molecules (**A** and **B**) in the unit cell (Fig. 3). Interestingly, the two crystallographically independent macrocycles **A** and **B** possess different coordination geometries. For **A**, the three nitrogen atoms N(1), N(2) and N(3) and the O(2) atom from the macrocycle coordinate the Fe^{II} cation in the equatorial plane with the second Fe(1)–O(1) distance (3.097(5) Å) longer than the sum of the van der Waals radii. Two axial cyanide ligands complete a distorted octahedron around the Fe^{II} cation (Fig. 3, left), reminiscent of the structure of the LS form of the parent complex **1**.¹²

In contrast, for **B**, three nitrogen atoms N(6), N(7) and N(8) and two oxygen atoms O(3) and O(4) coordinate the Fe^{II} cation



Fig. 3 ORTEP plot of the two independent molecules A and B in complex 3a with partial labelling scheme. Atomic displacement parameters are plotted at 50%. Solvent molecules are omitted for clarity. Crystallographic data for 3a is available as $(S-3, ESI^{\dagger})$.

in the equatorial plane and the two cyanide groups complete a pentagonal bipyramidal geometry that closely resembles the HS structure of the parent complex 1.9,13 These observations are consistent with the 1:1 mixture of HS and LS Fe^{II} centres obtained from Mössbauer and magnetic measurements at 250 K. The coordination geometries of A and B were further examined by calculating their continuous shape measures (CSMs)¹⁴ which reveal that A is best described as 6-coordinate, but the large CSM value of 3.06 confirms that the octahedron is significantly distorted. In contrast, **B** is close to ideal D_{5h} symmetry, reflected in the small CSM value of 0.33. At 100 K, the P21 space group is retained, but there are subtle changes to the molecular structure; whilst A remains 6-coordinate with no significant changes in the CSM value, the coordination geometry of B undergoes more marked changes, with both the Fe-O bond lengths increasing by 0.1 and 0.15 Å and the Fe-N and Fe-CN bond lengths decreasing by 0.02-0.27 and 0.12 Å respectively, affording a more distorted D_{5h} polyhedron with a CSM of 0.99. This structural change, in which both O atoms move away from the metal centre, appears to be an alternative strategy for this macrocycle to stabilize the LS complex, not previously observed. In contrast, the first order SCO transition in the parent macrocycle 1, is accompanied by a dramatic change in coordination geometry from 7 to 6 due to a reversible Fe-O bond break.¹² The difference in the two mechanisms to achieve a LS configuration is attributed to the larger steric effects of the phenyl substituents at the stereogenic centres of 3; a large displacement of the O atom positions (as for 1) would lead to significant motion of the phenyl groups leading to considerable strain and disruption in the crystal lattice. Notably, on warming above 250 K, crystals of 3a collapse suggesting the transition of molecule A from LS to HS requires a major reorganisation of the crystal lattice. Furthermore, the breadth of the SCO transition in 3a reflects a lack of cooperativity in the solid. A close examination of the crystal packing reveals that molecules of 3a are packed in a head-to-tail arrangement along the c-axis of the unit cell (Fig. 4). In contrast to 1, the axial cyanide ligands of 3a do not participate in short intermolecular H-bonding interactions. A table summar-



Fig. 4 View down the *c*-axis of the unit cell. Showing the head-to-tail arrangement of macrocycles in **3a**. H-atoms are omitted for clarity.

izing the hydrogen bonding interactions in the crystal packing at both 250 and 100 K is presented in the S-3 of the ESI.[†] Although there are subtle changes to these intermolecular interactions during the SCO propagation, the D…A contacts are in the range of 3.389(15)-3.541(15) at 250 K and 3.221(16)-3.522(15) at 100 K, much longer than those reported in the crystal structure of **1** affording much weaker cooperativity in the crystal lattice leading to the observed gradual spin crossover transition in **3a** with no hysteresis.

Small single crystals of the *S*,*S* enantiomer **3b** measured at 100 K afforded an identical unit cell to that of **3a** confirming that the two enantiomers are isostructural (S-3. ESI[†]). No single crystals of **3c** have been grown to-date but VT powder data clearly reveal changes in the intensities, but no changes to the positions of the peaks in the powder patterns on cooling, (Fig. 5, left), consistent with a second order phase transition where subtle changes of atomic positions indicate some of the molecules are undergoing a SCO. Moreover the PXRD pattern of **3c** at 250 K is different from that simulated from the single crystal data for the chiral complex **3a**, confirming that the molecule crystallises in a different unit cell and space group (Fig. 5, right).

In conclusion, we have reported a new strategy for the preparation of an Fe^{II} SCO macrocycle employing a chiral ligand that enables full control over the stereochemistry of the final complex. This is the first study where the SCO properties of a chiral and racemic complex are compared side-by-side. To



Fig. 5 Left, VT PXRD for the racemic complex 3c; right, comparison of experimental PXRD data for 3c (blue) vs. simulated PXRD for chiral 3a (red).

Communication

the best of our knowledge this methodology has not previously been reported and therefore constitutes the first proof-ofconcept work in this area. In essence we show that crystal structures of chiral complexes that crystallize in polar space groups can be quite different from their racemic counterparts which have a marked impact on their magnetic behaviour. These stark differences augers well for the development of new families of magneto-optical materials, in contrast to the most common previously reported methodology which employs the spontaneous (i.e. entirely fortuitous) resolution of a chiral material during the crystallization process which affords chiral single crystals for study, but the bulk material remains a racemic mixture, comprising a 50: 50-mix of 'left-handed' and 'right handed' crystals. Although the magnetic properties of 3a are modest, it is the first chiral mononuclear Fe^{II} complex to display a LIESST. The phenyl substituents shed more light on the correlation between the structural changes and SCO properties within this unique N₃O₂ system where a 7- to 6-coordination change is not the only pathway for this macrocycle. Interestingly, the coordination equilibria between a 7- and 5-coordinate Fe^{II} N5 complex was recently demonstrated by spectroscopic studies in solution, but has yet to be observed in a single crystal.¹⁵ Work is currently in progress to study and prepare new chiral Fe^{II} N₃O₂ derivatives and employ them as building blocks for the self-assembly of cyanide bridged clusters, chains and networks with magneto-optical and/or ferroelectric properties. This work was financially supported by NSERC-DG, CFI, CRC, ORF, ERA and Brock University.

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