ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, **50**, 1435

Received 25th May 2013,
Accepted 10th December 2013

DOI: 10.1039/c3cc43922d

www.rsc.org/chemcomm

Hysteretic spin crossover in iron(II) complexes of a new pyridine–triazole–pyrazine ligand is tuned by choice of NCE co-ligand†

Ross W. Hogue, Reece G. Miller, Nicholas G. White, Humphrey L. C. Feltham, Guy N. L. Jameson and Sally Brooker*

A family of three new mononuclear complexes of the general form [Fe(L^{pz})$_2$(NCE)$_2$] has been prepared (L^{pz} = 4-*p*-tolyl-3-(2-pyrazinyl)-5-(2-pyridyl)-1,2,4-triazole; E = S, Se, BH$_3$). All three exhibit spin crossover, in two cases with hysteresis, with $T_{1/2}$ being predictably tuned by varying the coordinated anion.

The ability of first-row transition metal complexes to undergo spin crossover (SCO) between the high spin (HS) and low spin (LS) states is well-documented.[1,2] Driven by scientific curiosity and the potential uses of these complexes as nanotechnological components (either sensors or displays[3–10]) we, and many others, have been attempting to rationally design SCO complexes with tuneable properties. Rapidly growing numbers of SCO-active complexes have been prepared, particularly those containing iron(II), but the ability to achieve and tune SCO deliberately, rather than relying on serendipity is still rare.[11,12] Within those complexes that do display SCO behaviour, the advantageous property of *hysteresis*, *i.e.* a memory effect, is rarer still.

One class of ligand that has been used to deliberately prepare SCO-active iron(II) complexes is the 4-substituted-3,5-di(2-pyridyl)-triazole (**Rdpt**) family (Fig. 1).[13] Compounds of the form [Fe(**Rdpt**)$_2$X$_2$] (where X is a *trans*-coordinated anion) give SCO for a number of R-substituents including NH$_2$,[14–19] 4-tolyl (**ptdpt**, Fig. 1),[20] pyrrolyl[21] and hexadecyl.[22] Notably, when R = NH$_2$, tuneable SCO is observed where the $T_{1/2}$ (temperature at which there is a 1 : 1 HS : LS ratio) can be altered by varying the ligand field strength of the anion X (X = NCS, NCSe, N(CN)$_2$, and the radical anion of tetracyanoquinodimethane).[14–16]

We were interested to see if a new ligand incorporating pyrazine in place of one of the pyridine rings in **Rdpt** would lead to enhanced SCO properties of the resulting iron(II) complexes. Pyrazine is a better π-acceptor and poorer σ-donor than pyridine,[23] so *if coordinated* it is expected to stabilise the LS state of iron(II),[23,24] *i.e.* raise the $T_{1/2}$ of any SCO event. Regardless of whether the pyrazine coordinates or not, the packing interactions, another vitally important factor in SCO,[25–27] will also be modified. We were also keen to probe whether the SCO behaviour of iron(II) complexes of this new ligand could be further tuned by varying the coordinated anions.

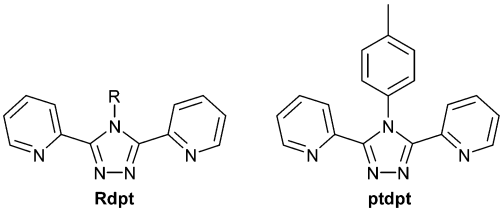

Fig. 1 **Rdpt** ligands used to prepare SCO-active complexes of iron(II), including **ptdpt**, the dipyridyl analogue of the ligand used in this work.

The novel ligand L^{pz} is, to the best of our knowledge, the first example of a pyrazine-containing analogue of an **Rdpt** ligand,[28] and was prepared according to our general method[29] as shown in Scheme 1. Briefly, the tolyl-substituted thioamide was activated by alkylation and then condensed with pyrazine-2-carbohydrazide, giving L^{pz} in 64% yield over two steps. The ligand was characterised by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, elemental analysis and X-ray crystallography (Fig. S3, see ESI† for experimental details and NMR spectra of the new compounds; CCDC 937363–937365).

Reaction of two equivalents of L^{pz} with [Fe(py)$_4$(NCS)$_2$] or [Fe(py)$_4$(NCSe)$_2$] in methanol causes precipitation of the complexes [Fe(L^{pz})$_2$(NCS)$_2$] and [Fe(L^{pz})$_2$(NCSe)$_2$] as analytically clean powders with colours ranging from pale pink to red. Two distinct polymorphs of [Fe(L^{pz})$_2$(NCSe)$_2$] were obtained: pink polymorph (**A**) showed hysteretic SCO (see later) whereas pale pink polymorph (**B**) was HS from 300–4 K (Fig. S8, ESI†). These two polymorphs also gave distinctly different powder X-ray diffraction patterns (Fig. S5, ESI†). The reaction of L^{pz} with [Fe(py)$_4$(NCBH$_3$)$_2$] in methanol did not lead to precipitation of any solid, and so analytically clean [Fe(L^{pz})$_2$(NCBH$_3$)$_2$] was instead obtained, as a red powder, by conducting the reaction in CHCl$_3$/CH$_3$OH and subjecting the reaction

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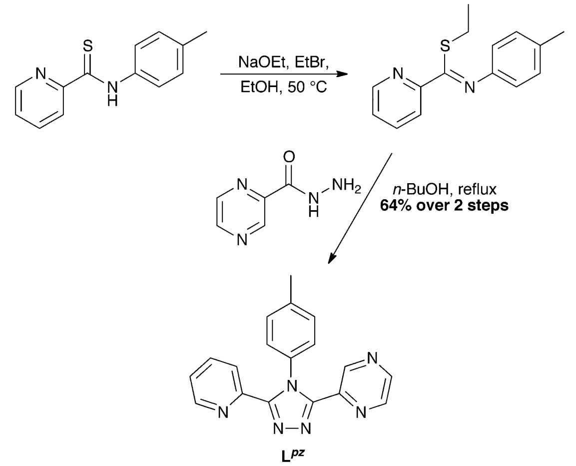
Department of Chemistry and MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Otago, PO Box 56, Dunedin, 9054, New Zealand. E-mail: sbrooker@chemistry.otago.ac.nz; Fax: +64 3 4797906; Tel: +64 3 4797919

† Electronic supplementary information (ESI) available: Synthetic details, NMR spectra, instrumentation, plus additional structural, magnetic and Mössbauer information and diagrams. CCDC 937363–937365. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43922d



Scheme 1 Synthesis of the novel pyridine–triazole–pyrazine ligand $\mathbf{L}^{pz}$.

mixture to diethyl ether vapour diffusion. As well as elemental analysis, the three complexes were also characterised by IR spectroscopy: analysis of the C≡N stretching modes of the NCE anions suggests that all complexes are HS at room temperature[20,22,30] and have *trans*-coordinated anions.[31] High resolution ESI mass spectrometry also supported the proposed formulation, with molecular ions of the form $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCE})]^+$ being observed for all complexes. Diethyl ether vapour diffusion into a methanol solution of a $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCSe})_2]$ reaction mixture that had been taken to dryness gave a few solventless single crystals, allowing determination of the solid state structure of polymorph **B** of the complex at 100 K[32] and 260 K, by single crystal X-ray crystallography (Fig. 2). Careful analysis (see ESI†) clearly showed that in polymorph **B** the iron(II) centre is coordinated to the pyridine, not pyrazine, ring. The bond lengths and angles are fully consistent with HS iron(II) at both temperatures, in contrast to polymorph **A**, which undergoes SCO (see later), demonstrating once again the critical effect of the polymorph on the observed SCO behaviour.[33]

The temperature dependence of the magnetic susceptibility of each of the four powder samples of the solvent-free complexes was examined between 4 and 300 K (Fig. 3; for polymorph **B** see Fig. S8, ESI†). At 300 K, the effective magnetic moments range from 5.0 to 5.6 BM, consistent with fully HS iron(II) in all four samples. On cooling,

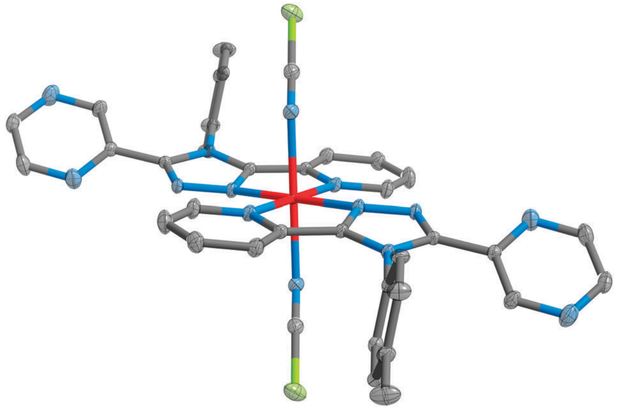


Fig. 2 Solid state structure of polymorph **B** of $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCSe})_2]$ at 100 K. Hydrogen atoms are omitted for clarity, thermal ellipsoids are drawn at 50% probability.

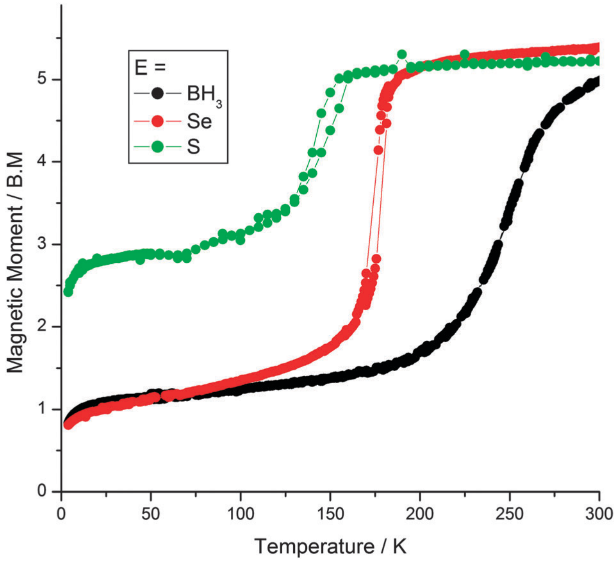


Fig. 3 Plots of μ_{eff} *vs.* temperature for $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCS})_2]$, polymorph **A** of $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCSe})_2]$ and $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCBH}_3)_2]$, measuring continuously at the following scan rates: between 300–50 K at 5 K min^{-1}, 50–10 K at 2 K min^{-1}, 10–4 K at 1 K min^{-1}.

the magnetic moment of the three SCO active complexes drops, such that at 50 K, the moments are 1.1, 1.1 and 2.8 BM for E = BH_3, Se (polymorph **A**) and S, respectively. Examining the magnetic properties in both cooling and warming modes revealed that *all three complexes undergo SCO and two of these are hysteretic, albeit with modest loop widths* (of 5 and 7 K at a scan rate of 5 K min^{-1}, see ref. 34 and 35).

The complex $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCS})_2]$ undergoes an incomplete SCO, with a μ_{eff} of 2.8 BM and χT of 0.98 cm^3 kmol^{-1} at 50 K indicative of approximately three quarters of the iron(II) centres undergoing SCO. The SCO is hysteretic, with $T_{1/2}\downarrow$ = 142 K, and $T_{1/2}\uparrow$ = 149 K[36] (a hysteresis loop width of 7 K). $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCSe})_2]$ has a μ_{eff} of 1.1 BM and χT of 0.15 cm^3 kmol^{-1} at 50 K, consistent with all of the iron(II) centres undergoing reversible hysteretic SCO (Fig. S5 and S6, ESI†). As expected, the NCSe anions exert a stronger ligand field than NCS and so the SCO temperatures are increased, to $T_{1/2}\downarrow$ = 172 K and $T_{1/2}\uparrow$ = 177 K (a 5 K hysteresis loop). Likewise $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCBH}_3)_2]$ has a μ_{eff} of just 1.1 BM and χT of 0.15 cm^3 kmol^{-1} at 50 K, consistent with all of the iron(II) centres undergoing SCO (see Mössbauer spectrum, later). The NCBH_3 anions exert a stronger field than NCS or NCSe and so the SCO temperature increases further, to $T_{1/2}$ = 247 K.

Variable temperature ^{57}Fe Mössbauer spectroscopy was also used to probe the oxidation and spin states of the iron complexes (Fig. 4; Fig. S9 and S10, Tables S2 and S3, ESI†). The Mössbauer parameters of all three complexes (Tables S2 and S3, Fig. S9 and S10, ESI†) are nearly identical to related complexes.[21,22] There is a general decrease in the isomer shift of the LS species in the order NCS > NCSe > NCBH_3 and the reverse order for the HS species, as has been seen previously.[30] The Mössbauer spectra confirm that the NCS coordinated complex is fully HS at 250 K and that at ∼5 K three quarters of the iron(II) has undergone SCO to the LS state (Fig. 4 and Table S2, ESI†), similarly, the NCSe complex is mostly HS at 250 K but has undergone SCO to be almost completely LS at ∼5 K (Fig. S9 and Table S3, ESI†). Spectra taken near the SCO event (at 150 K and 170 K

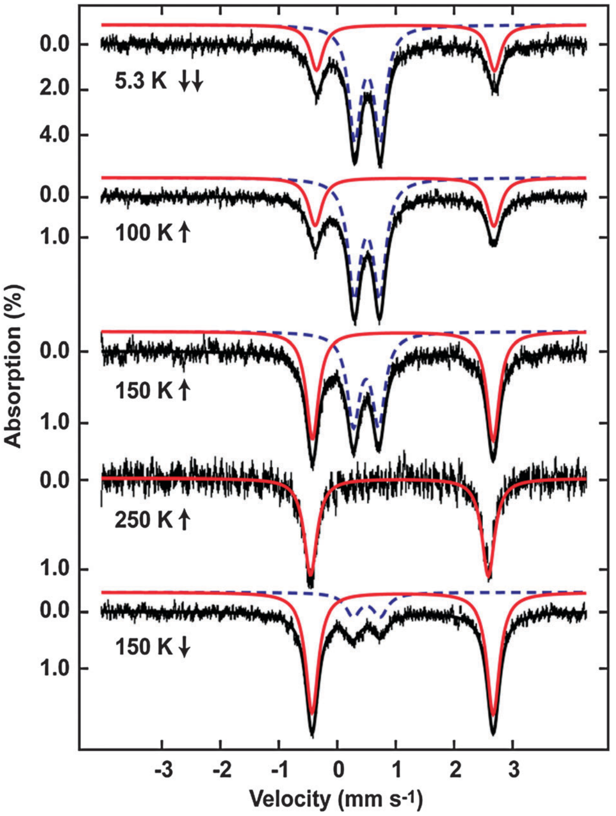


Fig. 4 ^{57}Fe Mössbauer spectra of $[\mathrm{Fe}(\mathbf{L}^{pz})_2(\mathrm{NCS})_2]$ measured at variable temperatures with an applied field of 47 mT parallel to the γ-rays. The sample was initially quench cooled in liquid nitrogen before being cooled to 5.3 K in the spectrometer. Slow warming (∼1 K min^{-1}) to 100 K then 150 K and 250 K produced the spectra shown. The sample was then slowly cooled back to 150 K, confirming the presence of a hysteresis. The spectra are deconvoluted into high spin (red solid line) and low spin (blue dashed line).

for E = S and Se; Fig. 4 and Fig. S9, ESI†) differ depending on whether they were measured upon cooling or warming, confirming the hysteretic nature of the SCO event. The low Lamb–Mössbauer factor of the $\mathrm{NCBH_3}$ complex at high temperatures precluded measurement at higher temperatures but the data (Fig. S10, ESI†) do confirm that, in contrast to the other two complexes, this E = $\mathrm{BH_3}$ sample is fully LS at 5.6 K. All results are in good agreement with the magnetic data.

In summary, we report a family of iron(II) complexes of the new pyrazine-containing ligand $\mathbf{L}^{pz}$. Unusually, SCO events are observed for *all three complexes*, with *hysteresis* observed in two of these cases, and the crossover temperatures can be *predictably tuned* by varying the coordinated anion. Further work investigating the intricacies of this and related systems is currently underway.

We thank the University of Otago and the Marsden Fund (RSNZ) for supporting this research, the MacDiarmid Institute for the Mössbauer spectrometer and magnetometers, Dr S. Chong (Callaghan Innovation) for his help, and Dr J. L. Tallon (Callaghan Innovation) for advice.

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