Spin Transitions

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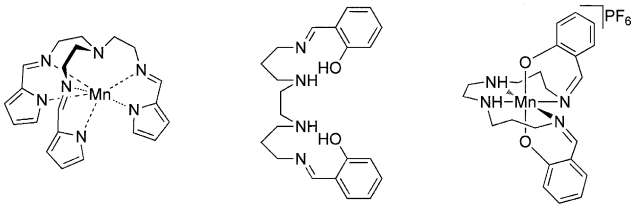
Cooperative Spin Transition in a Mononuclear Manganese(III) Complex**

*Paulo N. Martinho, Brendan Gildea, Michelle M. Harris, Tibebe Lemma, Anil D. Naik, Helge Müller-Bunz, Tia E. Keyes, Yann Garcia, and Grace G. Morgan**

Spin-crossover (SCO) molecules are a class of compounds that show promise for application in memory devices.[1] A hysteretic transition pathway is essential in promoting a memory effect, and considerable efforts have been expended to develop systems with wide hysteresis loops close to room temperature. These efforts were led by Kahn et al., who published the first SCO Fe^{II} complex with a RT hysteretic loop.[2] Many more examples have since appeared,[3] which are mostly polymeric Fe^{II} complexes with triazole[4–6] or pyrazine ligands[4,7] or mononuclear Fe^{II} complexes with N-heterocyclic ligands,[8] but several hysteretic Fe^{III} [9] and Co^{II} [10] complexes are also known. In 2008, Weber et al. described a 70 K RT hysteresis for a mononuclear Fe^{II} complex, demonstrating the potential of intermolecular interactions to promote effective cooperativity and sharp transitions.[11] Bousseksou, McGarvey, et al. have shown how pulsed light can be used to switch the spin state on the hysteresis loop of [Fe(pyrazine){$Pt(CN)_4$}], underscoring the very real possibility of harnessing SCO into a data storage device.[12]

In contrast to Fe and Co, there are few examples of SCO in Mn^{III}.[13,14] Mn^{III} is a particularly interesting candidate for SCO as it has a pronounced Jahn–Teller (JT) effect in the high-spin (HS) state. The paucity of SCO data on this ion limits generalizations about how the JT distortion will affect coupling of the SCO to the lattice, but it may result in different profiles to those observed to date with Fe^{II} and Fe^{III}. Indeed the original [$Mn(pyrol)_3$tren] SCO complex[13] has an unusual double transition profile, which prompted several experimental[15] and theoretical studies.[15a,16] We have shown the importance of ligand flexibility in promoting Mn^{III} SCO where population of $d_{x^2-y^2}$ on switching to HS requires elasticity in the xy plane.[14a–d] This is readily achievable with L1 and its derivatives, which have an appropriately tuned N_4O_2 ligand field and the necessary equatorial flexibility. To date, this system has promoted gradual SCO profiles[14a–d,f] but we now report the first example of a Mn^{III} compound with an abrupt complete thermal spin transition and opening of an 8 K hysteresis window in [MnL1]PF_6 (**1**). The perchlorate salt [MnL1]ClO_4 has previously been reported as being HS.[17]



[$Mn(pyrol)_3$tren] L1 [MnL1]PF_6 (**1**)

Magnetic data of a crystalline sample of (**1**) were recorded in cooling and warming modes between 300–10 K (Figure 1).

At room temperature, $\chi_m T = 2.79\ cm^3 mol^{-1} K$ ($S = 2$) with $g = 1.93$, which persists on cooling to 132 K when it drops sharply to $\chi_m T = 1.25\ cm^3 mol^{-1} K$ over a 4 K range with critical temperature $T_c^{\downarrow} = 130$ K. There is a further decrease to $\chi_m T = 1.09\ cm^3 mol^{-1} K$, with $g = 2.08$ by 100 K, that is, full conversion to S = 1, followed by a drop below 25 K owing to spin–orbit coupling. On warming, a similarly abrupt transition is observed but with $T_c^{\uparrow} = 138$ K, resulting in a thermal magnetic hysteresis loop of 8 K centered at 134 K, which is much wider than for the [$Mn(pyrol)_3$tren] complex with the same type of magnetometer (1.6 K loop).[15d] The crossover profile was sensitive to particle size, as revealed by temperature-cycling experiments on a second crystalline sample. These also exhibited an 8 K-wide hysteretic transition with identical $\chi_m T$ values in the HS and LS regimes and no fatigue over three cycles of heating/cooling (Supporting Information, Figure S2), but the transition was centered at a slightly lower temperature (closer to 132 K). An abrupt transition was also

[*] Dr. P. N. Martinho, B. Gildea, M. M. Harris, Dr. H. Müller-Bunz, Dr. G. G. Morgan
School of Chemistry & Chemical Biology, University College Dublin
Belfield, Dublin 4 (Ireland)
E-mail: grace.morgan@ucd.ie
Dr. A. D. Naik, Prof. Dr. Y. Garcia
Institute of Condensed Matter and Nanosciences, MOST-Inorganic Chemistry, Université Catholique de Louvain (Belgium)
Dr. T. Lemma, Prof. T. E. Keyes
School of Chemical Sciences, Dublin City University (Ireland)

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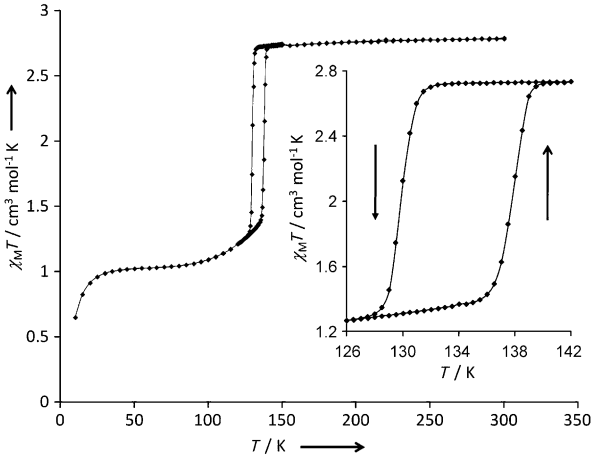

Figure 1. Plot of $\chi_m T$ versus T for [MnL1]PF_6 (**1**) in warming (↑) and cooling (↓) modes between 10–300 K.

observed on the second sample after grinding, which also persisted without fatigue over three cycles of heating/cooling (Supporting Information, Figure S3). In the ground sample, the transition was centered close to 134 K, with some variation of the profile and $\chi_m T$ values at the temperature extremes indicating that the transition is sensitive to particle size as observed elsewhere.[18]

Calorimetry between 98–300 K, Figure 2, revealed an exothermic peak at $T_{max}{}^{\downarrow} = 127(4)$ K, corresponding to a first-order phase transition, and an endothermic peak at $T_{max}{}^{\uparrow} =$

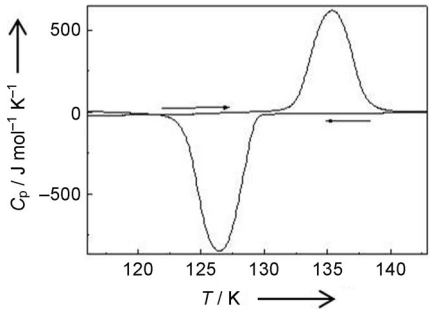

Figure 2. Plot of heat capacity versus T for [MnL1]PF_6, (**1**), in warming (→) and cooling (←) modes between 98–300 K.

135(4) K, delineating a hysteretic loop of 8 K in full agreement with the magnetic data.

The associated enthalpy and entropy values of $\Delta H = 2.72(1)$ kJ mol^{-1} and $\Delta S = 20.9(1)$ J mol^{-1} K^{-1} are higher than those for [Mn(pyrol)$_3$tren],[15a] and fully confirm the cooperative character of the spin transition. For Mn^{III} the electronic contribution to the SCO entropy variation is $\Delta S_{el} = R\ln(5/3) = 4.24$ J mol^{-1} K^{-1},[19] and considering a JT contribution to the quintet state of $\Delta S_{JT} = R\ln 3$,[16a] the vibrational contribution to the entropy change,[20] can be evaluated as $\Delta S_{vib} = 7.56(1)$ J mol^{-1} K^{-1}.

Variable-temperature Raman spectroscopy was used to characterize the vibrational characteristics of (**1**) in the HS

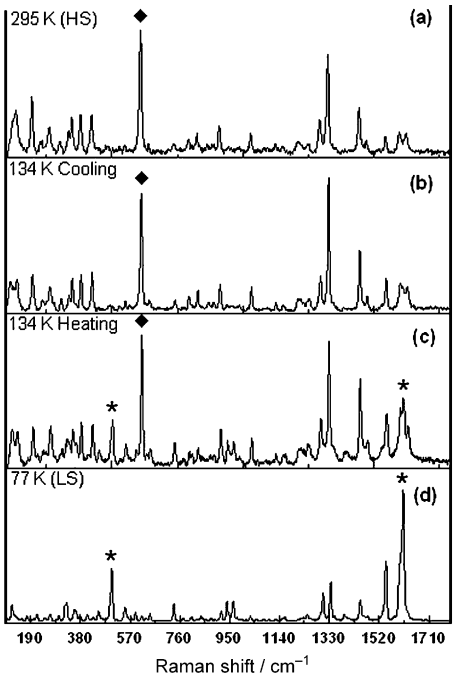

Figure 3. Raman spectra in a) fully HS (295 K) and d) fully LS (77 K) electronic states and in both b) HS and c) LS states at $T = 134$ K for [MnL1]PF_6 (**1**). Modes associated with the HS (◆) and LS (⋆) states are marked.

and LS regimes, particularly in the hysteretic region (Figure 3). The Mn^{III} ion is coordinated by pairs of *cis* imine and amine nitrogens and two *trans* phenolate oxygen donors (Figure 4), and the low-wavenumber region (100–1000 cm^{-1}) contains many of the Mn–N and Mn–O modes as well as these

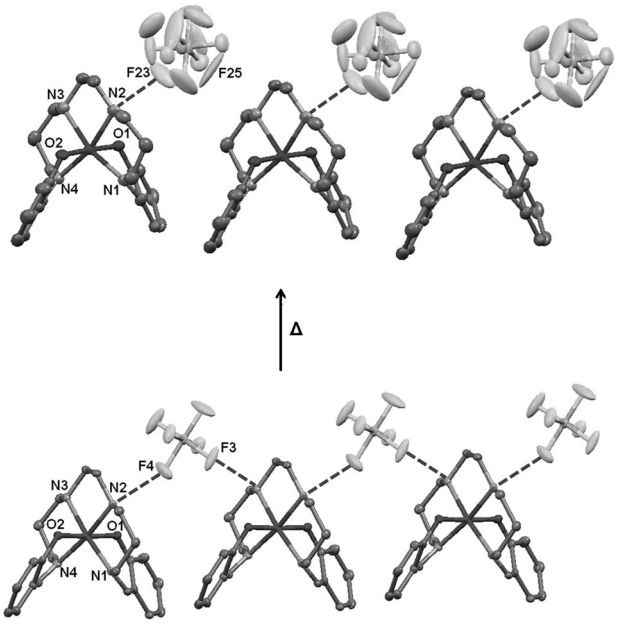

Figure 4. View of the 1D chain formed by hydrogen-bonding between $[MnL1]^+$ cations and PF_6^- anions at 100 K (bottom) showing how this is broken at 142 K (top) by disorder in the PF_6^- anions at higher temperature.

mixed with ligand-centered modes.[21] The region between 1000–2000 cm^{-1} is largely associated with ligand-based vibrational modes. Comparison of the room temperature and 77 K data (Supporting Information, Figure S4) reveal extensive changes to the spectroscopy during spin transition. A number of key modes, exclusive to the LS and HS states are clearly identifiable including the intense HS mode at 610 nm attributed to O-Mn-O symmetric and ring-stretch vibrations, and the LS feature at 503 nm which is assigned to skeletal C=N, N-Mn-N, and ring-breathing modes. Spectra were recorded in cooling/warming modes within the hysteresis loop where the bistability at 134 K is clearly apparent. The HS spectrum at RT (Figure 3a) matches that obtained on cooling to 134 K (Figure 3b), but the 134 K spectrum collected on warming from 77 K (Figure 3c) is predominantly LS (⋆) with some HS markers (◆) as expected from the $\chi_m T$ value of 1.25 $cm^3 mol^{-1} K$ obtained in warming mode (Figure 1), which indicates a small fraction of HS sites at this temperature.

The abrupt nature of the transition and the wide hysteresis window suggests significant cooperativity for the transition, and this was probed by single-crystal diffraction. Compound **1** crystallizes in chiral space group $P2_12_12_1$, and at all temperatures the asymmetric unit comprises one $[MnL1]^+$ cation and one PF_6^- anion (Figure 4), with four asymmetric units in the unit cell. As in previously reported complexes with related ligands,[14a–d,f] local geometry around Mn is pseudo-octahedral with *trans*-O donors and pairs of *cis*-imine and *cis*-amine nitrogens. At 100 K, bond lengths are short (Table 1), reflecting the LS t_{2g}^4 population,[14a] and on warming to 142 K the equatorial rather than axial bond lengths increase, as observed in related complexes. The HS structure is also significantly more distorted with Σ[22] = 54.51° (142 K) compared to 28.91° (100 K) and an even larger difference in the trigonal distortion value Θ[22] which increases from 70.86° (100 K) to 163.71° (142 K). The degree of distortion is significantly greater than that reported for the $[Mn(pyrol)_3tren]$ complex (LS: $\Sigma = 64°$, $\Theta = 199°$; HS: $\Sigma = 71°$, $\Theta = 239°$)[15c] and may contribute to the cooperative nature of the spin transition. Temperature cycling of the unit cell parameters established that hysteresis could also be observed on the single-crystal determinations, although here estimation of the temperature at the crystal surface was more difficult in the open nitrogen stream. The offset was estimated to be 6–8 K, and hysteresis was observed when the temperature was set to 126 K where both LS and HS structures could be measured (Table 1; see the Supporting Information for full details).

Table 1: Representative bond lengths [Å] and distortion parameters [°] for (**1**) at various temperatures.

	100 K LS	126 K↑[a] LS[b]	126 K↓[a] HS	142 K HS
Mn–O1	1.8773(14)	1.8763(15)	1.8702(12)	1.8745(19)
Mn–O2	1.8836(14)	1.8783(16)	1.8723(12)	1.873(2)
Mn–N4	1.9899(17)	1.9971(18)	2.0834(15)	2.086(2)
Mn–N1	2.0008(16)	2.0123(18)	2.0900(14)	2.098(2)
Mn–N2	2.0552(17)	2.0635(18)	2.1800(17)	2.182(3)
Mn–N3	2.0677(17)	2.0827(19)	2.2135(17)	2.210(3)
Σ [°]	28.91	31.97	53.89	54.51
θ [°]	70.86	79.06	162.42	163.71
N3–F3/25	3.01(2)	3.01(3)	3.17(7)	3.16(2)
N2–F4/23	2.98(3)	2.99(3)	2.97(6)	3.00(1)

[a] Temperature set to 126 K corresponds to T = 132-134 K at crystal surface; see the Supporting Information for full details. [b] Data for spin state in the low-temperature plateau within the hysteresis window, which includes a small HS fraction ($\chi_m T$ = 1.25 $cm^3 mol^{-1} K$), reflected here by slightly longer bond lengths and higher distortion values than for the fully LS form at 100 K ($\chi_m T$ = 1.09 $cm^3 mol^{-1} K$).

An important aspect of the structural study was to analyse the intermolecular interactions to ascertain their contribution to the hysteresis. The important interaction is the hydrogen bonding between fluorine atoms of the PF_6^- anion to NH groups on the complexes, which is temperature-dependent and related to the degree of disorder in the PF_6^- anion. This is well-ordered at 100 K but disordered over two positions at 142 K (Figure 4).

At low temperature, the NH hydrogen atoms on the cation each form a hydrogen bond to the adjacent PF_6^- anion, resulting in well-ordered 1D chains of LS molecules (Figure 4). On warming, the increase in disorder of the PF_6^- groups causes one hydrogen bond to break, thereby disconnecting the cations in the 1D chains, and the system abruptly switches to HS.

Oakley has reported examples of S- and Se-based organic radicals, which also effectively spin-cross by thermally switching between low T diamagnetic dimers and high T paramagnetic monomers, opening wide (100 K) RT-centered hysteresis windows.[23] The H-bond making and breaking observed for **1** is reminiscent of the Oakley diamagnetic–paramagnetic radical transition with its in-built cooperativity owing to the major adjustment in orientation of the heterocyclic radicals. Anion or solvent order–disorder in transition-metal SCO has been previously reported to affect crossover profiles in Fe^{II} [8b,24] although not in breaking a 1D chain. An anion or solvent order–disorder transition can also be disconnected from a spin transition, and this is manifest by the two events occurring over different temperature ranges.[25,26] In **1**, the order–disorder is coupled to the spin transition and so two ΔS_{vib} contributions, ΔS_{vib}(intra) and ΔS_{vib}(latt), should be considered, the latter comprising the order–disorder transition. In **1**, the order–disorder transition in the anion is clearly coupled to the hydrogen-bonding and thus the connectivity of the spin-active d^4 ions. The unique combination of temperature dependent anion order–disorder, which disrupts the hydrogen bonding chain, together with the anisotropic JT distortion that results on warming, result in a highly cooperative SCO for Mn^{III}. The critical design element required to realise spin switching in this and related Mn^{III} complexes[14a–d] appears to be the ligand field generated by an imine/amine/phenolate N_4O_2 donor set arranged with 323 methylene connectivity. This ligand system opens up an important route to modulation of SCO profile and switching temperature in Mn^{III} by tuning the electronic and steric properties of the ligand (phenolate substitution pattern) and by crystal engineering (choice of anion and crystallizing solvent). Such systems warrant further study, and our investigations into related Mn^{III} complexes continue to try and

understand the unique features of SCO associated with the d^4 configuration and to establish the design criteria required to promote RT spin switching.

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