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Co–Co and Co–Fe cyano-bridged pentanuclear clusters based on a methylpyrazinyl-diamine tetradentate ligand: spin crossover and metal substitution effects†

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A pentanuclear Co^{II}–Co^{III} cluster complex has been developed by a solvothermal synthesis. Its highly stable metal-mixed iron–cobalt derivatives display robust spin crossover ($T_{1/2}$ = 268 K) controlled by the degree of substitution.

The design of switchable molecular materials is a highly active topic, aiming at developing a new generation of materials with diverse applications. Spin crossover (SCO) systems are among the most promising candidates showing different tunable properties related to the transition between high-spin (HS) and low-spin (LS) states triggered by heat, pressure, magnetic field or light irradiation.[1–6] They are envisaged for numerous applications due to their switchable physical and chemical properties: thermochromic elements,[7] displays,[8] protective elements,[9] electronic[10,11] and mechanical[12] components, microwave switches,[13] chemical sensors,[14] switchable catalysts,[15] pressure sensors,[16] *etc.*

The design of a SCO compound displaying functionally attractive transition properties constitutes a considerable task in synthetic coordination chemistry. As an important bridge between mononuclear complexes and extended solids, discrete polynuclear SCO clusters offer an opportunity to deepen the knowledge about the origin of cooperativity between spin centres. However, polynuclear examples, particularly those with more than two potential SCO centers,[17–25] are very rare due to inherent difficulties in designing appropriate multidentate or bridging ligands that can provide the favourable ligand field strength for spin transitions. The cyanide ion represents an excellent bridging ligand for the assembly of polynuclear transition metal complexes. Several grid-type Fe_4 complexes,[26–31] a heptanuclear $\{Fe^{II}[(CN)Fe^{III}]_6\}$ complex[32] and a pentadecanuclear $\{Fe_9[Re(CN)_8]_6\}$ spherical cluster[33] have been reported to exhibit SCO at iron centres which are coordinated by the nitrogen end of cyanide. Dunbar *et al.* reported a series of interesting trigonal pyramidal complexes $[Fe^{II}(L)_2]_3[M'(CN)_6]_2$ (L = 3,4,7,8-tetramethyl-1,10-phenanthroline) which showed thermally and light induced SCO when M′ = Fe^{III} or Co^{III}.[34,35]

Recently, we have been interested in constructing SCO complexes of the $FeL(NCX)_2$ type (X = S, Se, BH_3) using pyridine–amine based tetradentate ligands.[36–38] In order to enhance the transition temperature and extend the structure into higher-nuclearity, we designed a new tetradentate ligand, *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyrazinylmethyl)-1,2-ethanediamine ($^{2Me}L_{pz}$). We obtained a new family of cyanide-bridged trigonal bipyramidal pentanuclear clusters by a solvothermal reaction: $[Co^{II}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ (**1**) and Fe^{II} doped complexes $[Fe^{II}{}_xCo^{II}{}_{3-x}(^{2Me}L_{pz})_3][Co^{III}(CN)_6]_2$ (x = 2.1 (**2**), 1.5 (**3**) and 0.9 (**4**)).

The $[Co^{II}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ cluster complex was synthesized from $CoCl_2·6H_2O$, $^{2Me}L_{pz}$ ligand and $NaNCBH_3$ in EtOH–MeCN medium. Cyanide was *in situ* released from $NCBH_3^-$, and Co^{II} was oxidized to Co^{III}. We attempted to obtain Fe_5 analogues since Fe^{II} is known for its spin-crossover behaviour in an N_6 environment. However, using the Fe^{II} salt instead under the same or modified experimental conditions didn't give the expected product. Alternatively, heteronuclear complexes were elaborated to partially substitute the metal. Thus, we got **2–4** with a different degree of substitution. The Fe and Co contents in **2–4** were determined by inductively coupled plasma atomic emission spectroscopy.

In order to determine the valence of the metal ions as well the nature of transition (spin crossover or charge transfer induced spin transition) in Fe^{II} doped complexes, the ^{57}Fe

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Mössbauer spectra of **2** were recorded at 77 K, 200 K and 303 K. As shown in Fig. 1, the spectrum at 77 K consists of a unique quadrupole doublet with an isomer shift of δ = 0.456(7) mm s^{-1} and a quadrupole splitting of ΔE_Q = 0.257(15) mm s^{-1}. These parameters are characteristic of LS Fe^{II} thus confirming that the iron ions take only the divalent metal sites while the trivalent sites are always occupied by Co^{III} ions. Upon warming to 200 K, a new doublet with δ = 0.83(7) mm s^{-1} and a quadrupole splitting of ΔE_Q = 1.86(14) mm s^{-1} appear and account for 12(7)% of the total area, which is attributed to the HS Fe^{II}. Upon further warming to 303 K, the contribution of the HS doublet increases to 40(10)%, indicating a continuous conversion at this temperature.

X-ray studies were carried out for the single crystals of **1** and **2**. A comparison of these two structures and the four powder X-ray diffraction patterns (Fig. S1†) indicates that all complexes are isostructural (substitution to the given degree does not affect the structure) and they crystallize in the chiral space group *R*32. The overall architectures (Fig. 2) are comparable to those reported by Dunbar *et al.*,[34,35] Oshio *et al.*[39] and Murray *et al.*[40] However, what they used are all bidentate ligands while our work shows that a tetradentate ligand could be an alternative choice. These compounds are composed of $[M^{II}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ pentanuclear clusters with a trigonal bipyramidal metal topology, in which $[Co^{III}(CN)_6]^-$ anions occupy the apical positions and M^{II} ions occupy the equatorial sites. Each Co^{III} ion is located in a distorted octahedral environment, coordinated by six carbon atoms from six cyanide ligands. Three of these cyanide ligands act as bridges, linking the M^{II} ions by the nitrogen end. Each M^{II} ion is coordinated by two cyanides and one tetradentate ligand, adopting an MN$_6$ coordination geometry. The tetradentate ligand was found to be disordered over two positions (Fig. S2†).

The Co^{III}–C bond lengths (average distance in **1** at 100 K: 1.89 Å; in **2** at 298 K: 1.87 Å and at 100 K: 1.89 Å) are in accordance with the literature values of Co$^{III}_{LS}$–CN compounds.[30,35,41,42] The average Co–N bond length (2.13 Å) of the metal ions in the equatorial plane in **1** indicates that Co^{II} is in the HS state. In comparison, the corresponding average M^{II}–N bond length in **2** decreases from 2.12 Å at 298 K to 2.06 Å at 100 K, due to the shrinkage of the Fe^{II}–N polyhedron upon the change of spin state. 43% of the Fe^{II} ions were estimated to undergo SCO at 298 K, assuming that a complete transition would have a bond length change of 0.2 Å × 0.7 (0.2 Å is the usual change of bond length for Fe^{II} SCO complexes[2] and 0.7 is the occupancy of Fe^{II}). This is in good accordance with the Mössbauer result (100% Fe$^{II}_{LS}$ at 77 K and ~60% Fe$^{II}_{LS}$ at 303 K).

Solid-state infrared (IR) spectra were recorded for **1–4** at room temperature (Fig. S3†). They exhibit two C≡N stretching bands at 2128 and 2168 cm^{-1}; the one at the lower-frequency corresponds to the terminal CN$^-$ groups and the one at the higher frequency corresponds to the cyanide ligands in the M^{II}–N≡C–Co^{III} bridging mode. These values are comparable with a similar complex reported by Dunbar *et al.*[34,35] IR reveals that the complexes can accumulate some water guest molecules (guest accessible voids are available), but they are very easily lost by the crystals (see IR and TGA in the ESI†).

Magnetic susceptibility measurements were carried out on dehydrated crystalline samples **1–4** with an applied magnetic field of 1000 Oe. As shown in Fig. 3a, the $\chi_M T$ value of **1** at 400 K is 8.20 cm^3 K mol^{-1}, which corresponds to three uncoupled HS Co^{II} centres with a *g* value of 2.4. As the temperature decreases, $\chi_M T$ decreases gradually at first and then more rapidly to reach a value of 4.78 cm^3 K mol^{-1} at 8 K because of spin orbit coupling and zero-field splitting. The $\chi_M T$

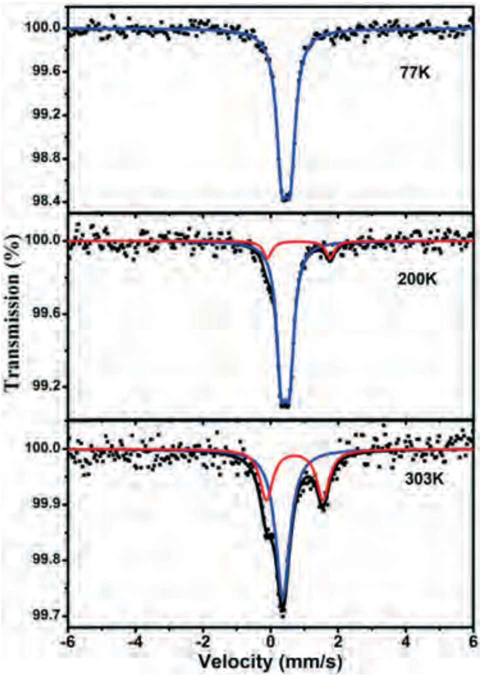

Fig. 1 ^{57}Fe Mössbauer spectra of **2** recorded at 77 K (up), 200 K (middle) and 303 K (down). The spectra are deconvoluted into HS (red line) and LS (blue line) sites.

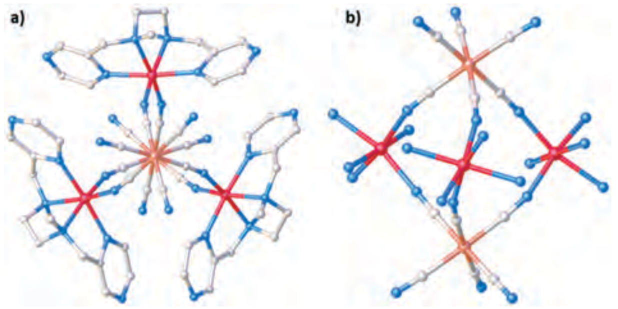

Fig. 2 Crystal structure of **1**: a) top view (along the axis of the bipyramid) of the pentanuclear cluster; b) side view of the pentanuclear core showing the organization and the coordination environment of the metal ions. Color code: red, Co^{II}; orange, Co^{III}; blue, N; gray, C. Hydrogen atoms and one site of the disordered tetradentate ligand have been omitted for clarity.

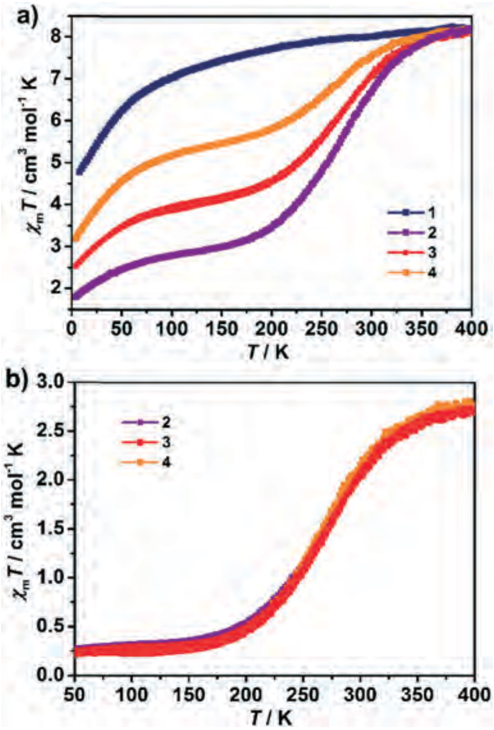

Fig. 3 a) Thermal variation of $\chi_M T$ as a function of T for **1**–**4** at a scan rate of 2 K min^{-1}. b) Comparison of the SCO curves of **2**–**4**, obtained by subtracting the contribution of Co^{II} ions and then divided by the respective number of Fe^{II} ions.

value of **2** at 400 K is 8.21 cm^3 K mol^{-1} and decreases significantly upon cooling to 2.91 cm^3 K mol^{-1} at 150 K due to the conversion from the HS to LS states of the Fe^{II} ions. The drop in $\chi_M T$ below 70 K is probably due to the zero-field-splitting and spin–orbit coupling effect of the HS Co^{II} component. No hysteresis was observed in the subsequent warming mode. The SCO behaviour can be reproduced in the subsequent cooling and heating cycles and even after a heat treatment at 450 K for 30 minutes (Fig. S6 and S7†). The variation of $\chi_M T$ upon temperature change for complexes **3** and **4** is quite similar to that of **2**, confirming that the ligand field strength imposed by the tetradentate ligand together with CN$^-$ can provide the appropriate ligand field for the Fe^{II} sites, although it is not strong enough to induce the spin state change for the Co^{II} sites. In order to get a more intuitive SCO curve of the Fe^{II} sites, the contribution of the HS Co^{II} ions was subtracted and the $\chi_M T$ values were divided by the respective number of Fe^{II} ions, resulting in a curve corresponding to one Fe^{II} unit (Fig. 3b). The comparison of the conversion behaviour of **2**–**4** clearly indicates that the doping content of Fe^{II} has no effect either on the temperature or on the completeness of the crossover. The $\chi_M T$ values below 150 K are in good agreement with the Mössbauer result, suggesting that almost all Fe^{II} ions are in the LS state. The $\chi_M T$ value per Fe^{II} is saturated at 400 K, with a value of 2.77 cm^3 K mol^{-1} indicating that the conversion is practically complete.

This series of Co–Fe clusters exhibits similar gradual SCO property as the example reported by Dunbar *et al.*,[34] where they used tetramethyl substituted phenanthroline as a ligand. In their case, the transition up to 300 K was incomplete. The Co_3Fe_2 cyano-bridged cluster reported by Oshio *et al.* shows a charge transfer induced spin transition instead, with the Co ion located in the N_6 coordination sphere.[39] In contrast to our previously reported mononuclear complexes based on similar tetradentate ligands, which show a sharp switch between the HS Fe^{II} and LS Fe^{II} states,[37,38] the gradual nature in the present case indicates limited Fe^{II}–Fe^{II} communication due to weak intermolecular interactions.

In conclusion, we have obtained a pentanuclear [Co$^{II}_2$Co$^{III}_3$] cluster based on a tetradentate ligand under solvothermal conditions. The magnetic susceptibility study showed a paramagnetic behaviour attributed to three uncoupled high spin Co^{II} ions in the equatorial plane. By doping with Fe^{II}, we successfully obtained three switchable heteronuclear clusters with different Fe^{II}/Co^{II} ratios. The number of centres displaying SCO can be efficiently controlled by the degree of doping, while the transition temperature is not affected. Such robust spin-crossover systems with non-hysteretic gradual spin conversions are prospective materials for the active parts of thermochromic elements, especially considering that their SCO covers a wide temperature range including room temperature.

Conflicts of interest

There are no conflicts to declare.

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