Synthesis, structural and magnetic characterisation of iron(II/III), cobalt(II) and copper(II) cluster complexes of the polytopic ligand: N-(2-pyridyl)-3-carboxypropanamide†

Mark E. Russell,a Chris S. Hawes,a,b Alan Ferguson,a Matthew I. J. Polson,a Nicholas F. Chilton,b Boujemaa Moubaraki,b Keith S. Murrayb and Paul E. Kruger*a

Herein we describe the synthesis, structural and magnetic characterisation of three transition metal cluster complexes that feature the polytopic ligand N-(2-pyridyl)-3-carboxypropanamide (H2L):

[Fe3IIIFe2II(HL)6(O)(H2O)3][ClO4]5·3MeCN·4H2O, 1, [Co8(HL)8(O)(OH)4(MeOH)3(H2O)]·[ClO4]3·5MeOH·2H2O, 2, and [Cu6(Lox)4(MeOH)(H2O)3]·MeOH, 3. Complex 1 is a mixed valence penta-nuclear iron cluster containing the archetypal {Fe3IIIO} triangular basic carboxylate cluster at its core, with two Fe(II) ions above and below the core coordinated to three bidentate pyridyl-amide groups. The structure of the octanuclear Co(II) complex, 2, is based upon a central Co4 square with the remaining four Co(II) centres at the ‘wing-tips’ of the complex. The cluster core is replete with bridging oxide, hydroxide and carboxylate groups. Cluster 3 contains an oxidised derivative of the ligand, Lox, generated in situ through hydroxylation of an α-carbon atom. This hexanuclear cluster has a ‘barrel-like’ core and contains Cu(II) ions in both square planar and square-based pyramidal geometries. Bridging between Cu(II) centres is furnished by alkoxide and carboxylate groups. Magnetic studies on 1–3 reveal dominant antiferromagnetic interactions for 1 and 2, leading to small non-zero spin ground states, while 3 shows ferromagnetic exchange between the Cu(II) centres to give an S = 3 spin ground state.

Introduction

The pyridyl, amide and carboxylate functional groups are commonly used ligand donor sets in coordination chemistry as they offer a broad range of potential coordination modes to metal ions from across the periodic table.1 While the monodentate pyridyl group is limited in the way it might coordinate to a metal ion, the amide and carboxylate functionalities offer a vast array of coordination capacity ranging from mono- and multi-dentate modes to bridging multiple metal ions in the formation of clusters and polymers. Carboxylate ligands have been used as key building blocks in supramolecular chemistry due to the many potential binding modes available to the carboxylate group.2 These various binding modes are observed often within metallo-clusters that may range in size from two to an impressive eighty-four metal ions.3 Many of these carboxylate containing cluster-complexes behave as single-molecule magnets (SMMs).4 In these rapidly evolving areas of research, the search for new polydentate ligands is an ongoing challenge. This has led increasingly to the design of ligands containing multiple functional groups that are capable of binding several metal ions.5 In this respect, the N-(2-pyridyl)-3-carboxypropanamide ligand, H2L, is an excellent candidate for the synthesis of new polynuclear transition metal complexes.

†Electronic supplementary information (ESI) available: 1H NMR spectrum and single crystal X-ray diffraction data for H2L; hydrogen bonding diagrams and bonding parameters for H2L; magnetisation isotherms for 1–3. CCDC 939536–939538. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51301g

Fig. 1 Structure of the ligand H2L with the labelling scheme used for 1H and 13C NMR spectroscopy shown.
Previous work with $\text{H}_2\text{L}$ is limited and has been concerned primarily with its potential biological activity or medicinal application and in the formation of hydrogels. A few studies have reported the spectral characterisation of mononuclear Cu(n) and Ni(n) complexes of $\text{H}_2\text{L}$, although no solid-state structures of these species are known. Only one structurally characterised coordination compound has been reported: a discrete mono-nuclear complex, $\text{[MnHL(phen)]ClO}_4\cdot1.25\text{H}_2\text{O}$, where HL coordinates via a chelating carboxylate group to Mn(n) with 1,10-phenanthroline (phen) present as a co-ligand. Surprised by the dearth of structural reports featuring $\text{H}_2\text{L}$, and driven by the recognition of its potentially potent coordination capabilities, we began an investigation into its coordination chemistry, the recognition of its potentially potent coordination capabilities, we began an investigation into its coordination chemistry using di $\text{H}_2\text{L}$, with the samples (Quantum Design Squid magnetometer, MPMS 5, at a dc field of 0 T, with the samples ($\text{C}, \text{H}, \text{N})$ were conducted at Campbell Microanalytical dispersed in a Vaseline mull to prevent torquing effects. Elemental analyses (C, H, N) were conducted at Campbell Microanalytical Laboratories, Dunedin.

The magnetic susceptibility measurements were measured using a Quantum Design Squid magnetometer, MPMS 5, at a dc field of 1 T, with the samples (ca. 20 mg) contained in gelatin capsules held at the centre of a drinking straw that was fixed to the end of the sample rod. Ligand diamagnetic corrections were obtained using Pascal’s constants. Magnetization isotherms were measured using the same instrument under dc fields of 0 to 5 T at temperatures 2, 3, 4, 5.5, 10, 20 K with samples 1 and 2 dispersed in a Vaseline mull to prevent torquing effects.

The structural analysis at 120 K was performed on a Agilent dual wavelength SuperNova with monochromated Cu-Kα ($\lambda = 1.5418 \text{ Å}$) (1 and 3) or Mo-Kα ($\lambda = 0.71073 \text{ Å}$) (2) radiation. CrystAlisPro $^9$ was used for the data collection and data processing. The structure was solved using direct methods with SHELX$^{10}$ and refined on Olex2$^{11}$ using all data by full matrix least-squares procedures with SHELXL-97.$^{12}$ Multi-scan absorption correction using SCALE3 ABSPACK.$^{13}$ CCDC numbers: 939536 (1); 939537 (2); 939538 (3).

**Synthesis of $\text{N}(2$-pyridyl)$-3$-carboxypropanamidine, $\text{H}_2\text{L}$**

This synthesis was adapted from the method of Godina and co-workers.$^{14}$ Full details and spectroscopic data are reported here for the first time. Succinic anhydride (2.73 g, 2.73 × 10$^{-2}$ mol) and 2-aminopyridine (2.57 g, 2.73 × 10$^{-2}$ mol) were dissolved in ethyl acetate (150 ml) and heated at reflux temperature for 24 hours to produce a white solid, which was isolated by filtration, washed with hot ethyl acetate (50 ml) and air dried. Recrystallisation from methanol by slow evaporation afforded colourless needle crystals suitable for a single crystal X-ray diffraction study. Yield 2.08 g, 39%; mp. 180–182 °C (lit. 181–182 °C)$^{14}$ HRMS-ESI m/z (MeOH): Found: 195.0766; $\text{C}_5\text{H}_7\text{N}_2\text{O}_4$ requires: 195.0764 [M + H$^+$]; $\delta_{\text{H}}$ (500 MHz, CD$_2$OD): 2.66 (2H, t, $J = 6.1$ Hz, $\text{H}_2$), 7.27 (2H, t, $J = 6.1$ Hz, 12.7 Hz, $\text{H}_4$), 7.08 (1H, at, $J = 6.1$ Hz, 1.0 Hz, $\text{H}_3$), 7.74 (1H, at, $J = 8.1$ Hz, 1.0 Hz, $\text{H}_5$), 8.06 (1H, d, $J = 8.1$ Hz, $\text{H}_4$), 8.26 (6H, d, $J = 6.1$ Hz, 1.0 Hz, $\text{H}_6$); $\delta_{\text{C}}$ (125 MHz, CD$_2$OD): 28 (C$_2$), 31 (C$_3$), 114 (C$_4$), 119 (C$_5$), 138 (C$_6$), 148 (C$_1$), 152 (C$_7$), 172 (C$_8$), 175 (C$_9$); $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3320 br, 3260 br, 3071 m, 2475 m, 1696 s br, 1590 m, 1438 s, 1357 s, 1313 m, 1248 s, 1168 s, 1006 s, 963 m, 916 w, 845 m, 784 s, 745 m, 634 s.

**Synthesis and characterisation of the pentanuclear complex:** $\text{[Fe}_3\text{O}_2\text{O}(\text{H}_2\text{O})_2\text{ClO}_4\cdot3\text{MeCN}-\text{H}_2\text{O}, \text{1}}$

To a MeCN solution (30 ml) of $\text{H}_2\text{L}$ (0.13 g, 0.67 mmol) was added Fe(ClO$_4$)$_2$·6H$_2$O (0.25 g, 0.67 mmol) followed by the dropwise addition of a 10% Et$_3$N solution (MeCN, 1 ml). The mixture was stirred for 12 h at 40 °C. Orange plate crystals suitable for a single crystal X-ray diffraction study were isolated after 1 week following the slow evaporation of the reaction mixture. A sample for analysis was dried in vacuo overnight to generate the partially desolvated phase of 1 as its monohydrate. Yield: 52 mg, 21%. Found: C, 32.20; H, 3.38; N, 8.08%; $C_{10}H_{14}O_6Fe_2N_2O_3$ requires: 32.20; H, 3.38; N, 8.32%; $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3320 br, 3260 br, 3071 m, 2475 m, 1696 s br, 1590 m, 1438 s, 1357 s, 1313 m, 1248 s, 1168 s, 1006 s, 963 m, 916 w, 845 m, 784 s, 745 m, 634 s.

**Synthesis and characterisation of the octanuclear complex:** $\text{[Co}_8(\text{HL})_8(\text{OH})_4(\text{H}_2\text{O})_3]\text{[ClO}_4\cdot3\text{MeOH}-2\text{H}_2\text{O}, \text{2}}$

To a MeOH solution (30 ml) of $\text{H}_2\text{L}$ (0.13 g, 0.67 mmol) was added Co(ClO$_4$)$_2$·6H$_2$O (0.245 g, 0.67 mmol) followed by the dropwise addition of a 10% Et$_3$N solution (MeCN, 1 ml). The mixture was stirred for 12 h at 40 °C. Pink block crystals suitable for a single crystal X-ray diffraction study were isolated after 1 week following the slow evaporation of the reaction mixture. A sample for analysis was dried in vacuo overnight to generate the desolvated phase of 2. Yield: 23 mg, 10%. Found: C, 34.50; H, 3.38; N, 9.18%; $C_{18}H_{40}O_6Fe_2N_10$ requires: C, 34.89; H, 3.66; N 9.05%; $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3318 w br, 1677 s, 1602 m, 1518 m, 1540 s, 1479 s, 1438 s, 1413 s, 1321 s, 1295 s, 1095 s, 884 m, 788 s, 628 m.

**Synthesis and characterisation of the hexanuclear complex:** $\text{[Cu}_6\text{O}_2\text{(OH)}_4(\text{MeOH})_3(\text{H}_2\text{O})_3]\text{[ClO}_4\cdot3\text{MeOH}, \text{3}}$

To a MeOH solution (30 ml) of $\text{H}_2\text{L}$ (0.13 g, 0.67 mmol) was added Cu(OAc)$_2$·H$_2$O (0.133 g, 0.67 mmol) followed by the dropwise addition of a 10% Et$_3$N solution (MeOH, 1 ml). Pink block-like crystals suitable for a single crystal X-ray diffraction study were isolated after 2 weeks following the slow evaporation of the reaction mixture. A sample for analysis was dried in vacuo overnight to generate the desolvated hexanuclear complex.
Yield: 16 mg, 11%. Found: C, 33.80; H, 2.97; N, 8.63%; C_{16}H_{34}Cu_{6}N_{8}O_{19} requires: C, 34.19; H, 2.71; N 8.87%; 
ν_{max/cm}^{-1} (KBr): 3340 w br, 2831 s, 1569 s, 1480 s, 1455 s, 1389 s, 1297 s, 1196 s, 1091 s, 1042 m, 886 s, 773 s, 746 m, 587 s, 581 m, 527 m.

Results and discussion

The ligand, H_{3}L, was synthesised through the condensation of succinic anhydride with 2-aminopyridine which, following recrystallisation from MeOH, produced colourless crystals. The IR spectrum of H_{3}L displays broad absorbance around 3300 cm\(^{-1}\) consistent with the presence of an amide (NH) and a stronger absorbance at around 2475 cm\(^{-1}\), indicating the formation of a hydrogen bond between pyridyl and carboxyl groups. The strong broad peak at 1696 cm\(^{-1}\) can be attributed to C=O of free carboxylic groups and C=O of both amide and hydrogen bonded carboxylic acid groups, respectively. These spectroscopic features are consistent with the interactions observed within the solid state structure as determined through X-ray crystallography (ESI†).

Complexes 1–3 were obtained by adding M(II) salts to either MeCN or MeOH solutions of H_{3}L in a 1:1 stoichiometry, followed by the addition of Et_{3}N base, and allowing the resultant solutions to evaporate slowly at ambient temperature. Although isolated with modest yields, multiple crystalline batches were cropped from the mother liquor on further standing. The crystals of 1–3 were of sufficient quality to enable a single crystal X-ray diffraction study to be carried out from which their structures were determined unambiguously.

X-ray crystal structure of 1

The atomic numbering scheme and atom connectivity for 1 are shown in Fig. 2. The structure was refined in the monoclinic P2_{1}/c space group and crystallographic data are detailed in Table 1. Complex 1 is a pentanuclear mixed valence iron cluster and displays unusual core geometry. Fe(II/III) oxidation states were assigned on the basis of bond valence sum calculations (ESI†), considering the bond lengths and charge balance for the cluster. At the centre of the complex resides the archetypal \{Fe_{7}O_{3}\} triangular basic carboxylate cluster. The coordination sphere around the Fe(III) ions is comprised of the six carboxylate groups of the ligand tail, which bind in a typical 1,3-bridging mode. The distorted octahedral geometry about each Fe(III) is completed by a central µ_{3}-xo-ligand and a coordinated water molecule. This \{Fe_{7}O_{3}\} unit is common in iron-oxo chemistry and has served as a building block for many higher nuclearity clusters.\(^{15}\) At the periphery of the complex, above and below the triangular cluster, are two Fe(II) centres with pseudo-octahedral geometry. Coordination about these peripheral metal centres is furnished by three pyridyl nitrogen atoms and three amido oxygen atoms from three chelating HL\(^{-}\) ligands to yield an N_{3}O_{3} donor set.

The separation between the peripheral Fe(II) centres and the central cluster Fe(III) atoms ranges from 5.932(1) to 6.348(1) Å; intra-triangular cluster separations range from 3.269(1) to 3.304(1) Å and the distance between peripheral Fe(II) centres is 11.535 Å through the central cluster. These Fe(II) ions are offset from the centre of the triangular cluster toward the Fe2–Fe3 axis i.e. they are not positioned directly above/below the central µ_{3}-xo-ligand, O1A. Interestingly, the tris-chelated nature of the HL\(^{-}\) ligands bestows handedness upon the terminal metal ions, which is \Delta and \Lambda about Fe4 and Fe5, respectively. The cluster is therefore a cluster-mesocate; related to the cluster helicates which differ from 1 in that they contain peripheral metal centres that possess the same handedness.\(^{16}\) To the best of our knowledge this is only the second example of a cluster-mesocate to be structurally characterised.\(^{17}\)

X-ray crystal structure of 2

The atomic numbering scheme and atom connectivity for 2 are shown in Fig. 3. The structure was refined in the monoclinic C2/c space group and crystallographic data are detailed in Table 1. Compound 2 consists of an octanuclear Co(u) cluster that is built around a {Co_{4}OH} square assembly, with the four remaining Co(u) centres forming the ‘wing-tips’ of the complex. The Co(u) centres in the {Co_{4}OH} unit (Co2, Co2′, Co3, Co3′) display a distorted octahedral geometry composed of two µ_{3}-O (O1H and O2H), one µ_{2}-OH (O1A) and three carboxylate O atoms (O3, O5 and O11 for Co2; O2, O6 and O8 for Co3). The octahedral geometry of the remaining Co(u) ions (Co1, Co1’, Co4, Co4’) is also distorted. Co4 and Co4’ are bound by one µ_{1}-OH (O1H), two carboxylate O atoms (O9 and O6), one amido O atom (O4), a pyridyl N atom (N3) and a coordinated MeOH molecule (O14). Co1 and Co1’ also possess a similar donor set: one µ_{1}-OH (O2H), two carboxylate O atoms (O3 and O12), one amido O atom (O1), a pyridyl N atom (N1); however, the coordinated MeOH molecule (O19) is present with only 25% occupancy with the remaining occupancy filled by a coordinated water molecule.

The HL\(^{-}\) ligand is present in two distinct binding modes. Firstly, in the µ_{3}-η^{2}:η^{1}:η^{1}:η\(^{0}\) mode the ligand chelates to one Co(u) centre at the wing-tip of the complex through the pyridyl N and amido O atoms, while the carboxylate group bridges three Co(u) ions: two from the central core and one from the
wing-tip. Secondly, the $\eta^1:\eta^1:\eta^0:\eta^0$ bonding mode is unbound at the pyridyl end and links a central Co(II) with a wing-tip Co(II) through the 1,3-bridging mode of the carboxylate group. The unbound pyridyl ring is stabilised by both intra- and inter-molecular interactions. Hydrogen bond interactions between the pyridyl nitrogen atom and a $\mu_3$-OH ligand (N5 to O2H and N7 to O1H) and from the adjacent amido NH to a carboxylate O atom (N6 to O11 and N8 to O8) act to stabilise the flexible unbound arm of the ligand. The pyridyl ring is stabilised further by offset intermolecular face-to-face $\pi \cdots \pi$ interaction (N5–C23 to N3–C14 = 3.475(13) Å, N5–C23 to N3”–C14” = 3.664(14), N7–C32 to N1–C5 = 3.454(13) Å and N7–C32 to N7”–C32” = 3.452(14) Å).

### X-ray crystal structure of 3

The partial atomic numbering scheme and atom connectivity for 3 are shown in Fig. 4. The structure was solved and refined in the monoclinic $C2/c$ space group and the crystallographic data are detailed in Table 1. The data identifies a hexanuclear Cu(II) complex and reveals that an $in situ$ oxidation of the ligand has taken place $via$ hydroxylation of the α-carbon atom adjacent to the amide carboxyl group, Fig. 4. Hydroxylation of this kind, although not common, is not without precedent and has been shown to proceed through metal directed oxidation involving molecular oxygen. When the reaction was performed under oxygen free conditions, and the solution left to stand under an inert atmosphere in an ‘open’ vial for several weeks, crystals of 3 failed to form. This is consistent with molecular oxygen being responsible for the hydroxylation, as no precaution was made to exclude water, and is in agreement with the previously proposed mechanism. The resultant ligand is in its triply deprotonated state and the [Cu : L] ratio

### Table 1: X-ray crystallography data for 1, 2 and 3

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature/K</td>
<td>120(1)</td>
<td>120(1)</td>
<td>120(1)</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C$<em>{60}$H$</em>{77}$Cl$<em>{5}$Fe$</em>{5}$N$<em>{15}$O$</em>{46}$</td>
<td>C$<em>{79.5}$H$</em>{113}$Cl$<em>{3}$Co$</em>{8}$N$<em>{16}$O$</em>{52}$</td>
<td>C$<em>{38}$H$</em>{42}$Cu$<em>{6}$N$</em>{8}$O$_{21}$</td>
</tr>
<tr>
<td>Formula mass</td>
<td>2200.82</td>
<td>2702.65</td>
<td>1328.04</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>16.2556(2)</td>
<td>25.9059(4)</td>
<td>41.7229(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>22.8571(4)</td>
<td>14.9866(2)</td>
<td>13.7165(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>25.5874(4)</td>
<td>27.3422(4)</td>
<td>15.3592(3)</td>
</tr>
<tr>
<td>α/°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β/°</td>
<td>102.0441(15)</td>
<td>91.2539(15)</td>
<td>91.5503(18)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å$^3$</td>
<td>9297.9(2)</td>
<td>10 612.8(3)</td>
<td>8786.7(3)</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
<td>$C2/c$</td>
<td>$C2/c$</td>
</tr>
</tbody>
</table>

* $R_1 = \sum |F_o| - |F_c|/\sum |F_o|$, $wR_2 = (\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)])^{1/2}$. 

Fig. 3 Molecular structure and partial atom labelling scheme for 2 (top) and the coordination core of 2 showing the potential pathways for magnetic exchange between the Co(II) centres (bottom). Hydrogen atoms and solvent molecules of crystallisation omitted for clarity.
of 6:4 generates a neutral hexanuclear cluster that is best described as having a distorted ‘barrel-like’ topology.

Two square planar Cu(II) centres (Cu2 and Cu5) reside at the ends of the barrel, while four square-pyramidal Cu(n) ions (Cu1, Cu3, Cu4 and Cu6) occupy its sides. Square planar Cu2 and Cu5 are each bound by two amido nitrogen atoms (N11 and N16 for Cu2; N9 and N10 for Cu5) and two alkoxy oxygen atoms (O1 and O2 for Cu2; O6 and O7 for Cu5) from two different ligands to form two N,O-chelate rings around each Cu centre (four ligands in total). Each of the pyridyl rings adjacent to the coordinated amido groups are rotated by ca. 50° to the amido-alkoxy chelate ring plane and coordinate to square-pyramidal Cu(n) ions (Cu1, Cu3, Cu4 and Cu6). The basal plane of the square pyramidal Cu-centres is comprised of a pyridyl nitrogen atom, a bridging alkoxy oxygen atom and two bridging carboxylate oxygen atoms with either a coordinated water molecule (Cu1, Cu4 and Cu6) or methanol molecule (Cu3) located at the apex of the pyramid. The bridging and linking between each Cu-ion in 3 is such that the square or basal planes of the coordination spheres around adjacent Cu-centres subtend angles to each other between ca. 98–102° for the twelve angles formed by the six intersecting planes around the barrel.

Each hexanuclear complex is linked to four neighbouring clusters through eight hydrogen bond interactions that involve each amido oxygen atom and the neighbouring coordinated solvent molecules bound to the square-pyramidal Cu(n) ions. These connections create a 2D sheet in the crystallographic bc plane. Weak offset face-to-face π–π interactions between each pyridyl ring and its adjacent symmetry related partner (ring centroid-centroid distances range from 3.416(1)–3.763(1) Å) link the cluster to a further three neighbouring clusters along the crystallographic a-axis. The shortest intermolecular metal-metal separation is between Cu5 and Cu5′ at 3.683(1).

**Magnetic properties**

The bulk magnetic properties of 1–3 were probed *via* variable temperature, DC and AC susceptibility measurements on polycrystalline samples. For 1 the $\chi_M T$ value at 300 K is 10.1 cm$^3$ mol$^{-1}$ K, which is in good agreement with the expected value of $\sim$10.5 cm$^3$ mol$^{-1}$ K for a basic carboxylate {Fe$_3$O} ($S = 5/2$ trimer) plus two non-coupled high-spin Fe(n) $S = 2$ centres, Fig. 5. As the temperature is lowered the $\chi_M T$ product decreases gradually to reach ~7 cm$^3$ mol$^{-1}$ K at ca. 25 K, followed by a more rapid decrease to 1.9 cm$^3$ mol$^{-1}$ K at 2 K. This behaviour is consistent with dominant antiferromagnetic interactions within the cluster, while the sharp decrease at low temperature is due to zero-field splitting (ZFS).

The magnetization ($M$) was measured as a function of the applied field at various temperatures (ESI†). It is clear the magnetisation curves are far from saturated. Even at 2 K and 5 T, the $M$ vs. $H$ curve is not saturated, but equal to 5.2$\mu_B$, consistent with a small non-zero spin ground state for 1. The general shapes are indicative of antiferromagnetically coupled Fe(n) sites together with the two high-spin Fe(n) sites that have their contributing $M$ values reduced because of spin–orbit coupling and orbital degeneracy effects. Antiferromagnetic coupling in Fe(n)-oxo complexes is common, however, larger complexes containing {Fe$_3$O} building blocks have been shown to display large non-zero spin ground states.21

The $\chi_M T$ value of 2 at 300 K is 18 cm$^3$ mol$^{-1}$ K, which is consistent with eight uncoupled spin-only $S = 3/2$ Co(n) centres with $g = 2.19$. The $\chi_M T$ product decreases gradually as the temperature is lowered to reach 0.8 cm$^3$ mol$^{-1}$ K at 2 K, Fig. 5. This indicates antiferromagnetic exchange coupling between the metal centres. Changing the field in the range 2–70 K gave the same $\chi_M T$ value, thus magnetisable impurities and Zeeman depopulation effects appear to be absent. The magnetisation isotherms were measured using dc fields of 0 to 5 T and temperatures of 2 to 20 K (ESI†). The $M$ values do not saturate and the values at 2 and 3 K at 5 T are similar, 2$\mu_B$. These plots suggest the spin ground state is not zero and the low $M$ value at 2 K and 5 T confirms antiferromagnetic coupling probably also influenced by spin–orbit coupling of the parent.

---

**Fig. 4** Molecular structure and partial atomic numbering scheme for 3 (top); the coordination core of 3 showing the potential pathways for magnetic exchange (middle) and the structure of the hydroxylated ligand generated *in situ* (bottom). Hydrogen atoms and solvent of crystallisation removed for clarity.
bridging µ4-OH moiety and the Co(II) ions display trigonal ferromagnetically coupled system.

and no SMM behaviour was observed, as expected for an anti- showing that no slow relaxation of magnetisation occurred and no SMM behaviour was observed, as expected for an anti-ferromagnetically coupled system.

This journal is © The Royal Society of Chemistry 2013

Dalton Transactions Paper

$^{4}T_{1g}$ Single-ion states. Measurements of out-of-phase ac susceptibilities, $\chi''$, for 2 in the range 2–10 K, gave zero values thus showing that no slow relaxation of magnetisation occurred and no SMM behaviour was observed, as expected for an anti-ferromagnetically coupled system.

Modelling Co(n) systems in any situation is extremely difficult due to the strong orbital moment and important crystal field effects. This case with eight such octahedral Co(n) ions is at present much too complicated to make any attempt at quantifying the magnetic data. A previously reported Co(n) complex has a similar core to 2, however, it does not contain a bridging µ1-OH moiety and the Co(n) ions display trigonal bipyramidal geometry compared to the pseudo octahedral geometry observed in complex 2.22 Despite these differences both complexes display similar magnetic behaviour, with antiferromagnetic interactions dominating. Whilst Co(n)-based clusters often display antiferro-magnetic exchange interactions,23 there are several examples where ferromagnetic interactions lead to the observation of SMM behaviour.24

The $\chi_{M}T$ value of 3 at 300 K is 2.5 cm$^3$ mol$^{-1}$ K, which is in good agreement with the expected value for six uncoupled $S = 1/2$ Cu(n) centres with $g = 2.10$, Fig. 6. As the temperature is decreased towards 50 K, $\chi_{M}T$ increases gradually to 3.3 cm$^3$ mol$^{-1}$ K. Then below 50 K there is a more rapid increase in $\chi_{M}T$ to a maximum of 6.1 cm$^3$ mol$^{-1}$ K at 4 K, before finally decreasing to 4.9 cm$^3$ mol$^{-1}$ K at 2 K. Such behaviour is indicative of ferromagnetic exchange coupling with an $S = 3$ ground spin state. The magnetisation isotherms confirm this behaviour with the 2 K data saturating at $M = 6N\beta$ as expected for an isolated $S = 3$ ground state (ESI$^\dagger$). Simultaneous fitting of the susceptibility and magnetisation data was performed with the program PHI,25 using the exchange spin Hamiltonian $-2J_{1}(\hat{S}_{1}\cdot\hat{S}_{2} + \hat{S}_{2}\cdot\hat{S}_{3} + \hat{S}_{3}\cdot\hat{S}_{4} + \hat{S}_{4}\cdot\hat{S}_{5} + \hat{S}_{5}\cdot\hat{S}_{6}) - 2J_{2}(\hat{S}_{1}\cdot\hat{S}_{6} + \hat{S}_{6}\cdot\hat{S}_{7} + \hat{S}_{7}\cdot\hat{S}_{8} + \hat{S}_{8}\cdot\hat{S}_{9})$. The $J_{1}$ pathways involve {OR(1,3-NCN)} bridging while the $J_{2}$ pathways involve {anti-1,3-OCO} bridging. This two $J$ model reproduced the data extremely well and led to a fit of the magnetic properties giving $J_{1} = 15.1$ cm$^{-1}$, $J_{2} = 5.18$ cm$^{-1}$ and $g = 2.10$, Fig. 6. It is more common to observe antiferromagnetic exchange interactions in polynuclear Cu(n) complexes.26 Complex 3 is one of the few examples of a Cu(n) cluster displaying ferromagnetic interactions, leading to a spin ground state of $S > 1$.27 Possible reasons for ferromagnetic coupling occurring include the Cu–OR–Cu bridging angles being low, in the range 102–104º, with Cu–Cu separations of ~3.04 Å, and, or combined with, the equatorial planes of individual Cu centres (having Cu(d$_{x^2-y^2}$) magnetic orbitals) being orthogonal to those observed for neighbouring centres as one traverses the barrel-shaped cluster; vide supra (Fig. 4). The Cu-N-C-N-Cu bridges, from the 2-pyridyl-amido ligand moieties, are not well known for their magnetic exchange features and these might also contribute to ferromagnetic coupling.

Conclusions

This study has identified for the first time some of the potential coordination capability possessed by the polytopic ligand $N$’-(2-pyridyl)-3-carboxy-propanamide, $\text{H}_{3}\text{L}$. Reaction of $\text{H}_{3}\text{L}$ with either Fe(n), 1, Co(n), 2, or Cu(n), 3, led to the formation of three new transition metal cluster complexes possessing different and novel core geometries which were structurally and magnetically characterised. Pentanuclear complex 1 and
octa-nuclear 2 show non-dominant antiferromagnetic interaction that leads to small non-zero spin ground states, whereas hexa-nuclear 3 displays ferromagnetic interaction between the Cu(n) centres yielding an $S = 3$ spin ground state. Interestingly, an in situ oxidation of $H_2L$ occurred during the synthesis of 3 via the hydroxylation of the $\alpha$-carbon adjacent to the amide carbonyl group to form $L_{ox}^{3-}$. $H_2L$ and its oxidised derivative $H_3L_{ox}$ are extremely flexible in the nature of their binding to the metal centres, which is highlighted by the presence of four distinct binding modes across the three complexes, Fig. 7. In complexes 1 and 2, the ligand is mono-deprotonated and binds via the pyridyl group and the amido-O atom with the carboxylate group in various bridging modes. However, in complex 3 coordination involves the pyridyl group, and now the amido-N atom (which is deprotonated) and an O-atom from the hydroxy group in combination with a bridging carboxylate group.

The results presented here suggest that $H_2L$ has great potential in the synthesis of new polynuclear complexes containing paramagnetic metal ions and we are currently extending this family of complexes to include different metals from across the transition and lanthanide metal ion series and will report upon these examples in the future.

Acknowledgements

The authors thank the University of Canterbury (College of Science Scholarship to CSH), the Royal Society of New Zealand Marsden Fund (PEK), the MacDiarmid Institute for Advanced Materials and Nanotechnology (PEK) and the Australian Research Council (KSM) for financial support. We also thank Dr Anthea Lees (UC) for helpful discussions.

Notes and references


Dalton Transactions


