
Downloaded from
https://kar.kent.ac.uk/71482/ The University of Kent's Academic Repository KAR

The version of record is available from
https://doi.org/10.1039/C8CE01901K

This document version
Author's Accepted Manuscript

DOI for this version

Licence for this version
UNSPECIFIED

Additional information

Versions of research works

Versions of Record
If this version is the version of record, it is the same as the published version available on the publisher's web site. Cite as the published version.

Author Accepted Manuscripts
If this document is identified as the Author Accepted Manuscript it is the version after peer review but before type setting, copy editing or publisher branding. Cite as Surname, Initial. (Year) 'Title of article'. To be published in Title of Journal, Volume and issue numbers [peer-reviewed accepted version]. Available at: DOI or URL (Accessed: date).

Enquiries
If you have questions about this document contact ResearchSupport@kent.ac.uk. Please include the URL of the record in KAR. If you believe that your, or a third party's rights have been compromised through this document please see our Take Down policy (available from https://www.kent.ac.uk/guides/kar-the-kent-academic-repository#policies).
Low Dimensional and Frustrated Antiferromagnetic Interactions in Transition Metal Chloride Complexes with Simple Amine Ligands

James E. Chalmers, a Anant Kumar Srivastava,a Richard J. C. Dixey,a Krrishna Sivakumarana and Paul J. Sainesb

This study reports the facile synthesis, crystal structures and magnetic properties of five new Mn, Co and Cu complexes with chloride and simple amine ligands. The four hydrazinium complexes are discrete in nature while the O-methylhydroxylamine phase contains edge-sharing chains bridged by chloride ligands. Investigation of the magnetic properties of these materials reveals that two of these materials, Co(NH₂·NH₃)₂(H₂O)₂Cl₂ and Cu(NH₂·OCH₃)₂Cl₂, exhibit interesting antiferromagnetic properties arising from their low dimensional structures. Co(NH₂·NH₃)₂(H₂O)₂Cl₂ appears to exhibit significant 2D magnetic frustration while the magnetic susceptibilities of Cu(NH₂·OCH₃)₂Cl₂ are well fitted by a one-dimensional chain model. The relationship between the strength of the magnetic coupling observed in these materials and their likely exchange pathways are also discussed.

1. Introduction

Low-dimensional magnets have attracted sustained interest for their ability to host unconventional physics, as reflected by the award of the 2016 Nobel prize to Haldane for his theoretical work in this area.1 2 This includes magnetic chains, which can support spinon quasi-particles that fractionalize electrons by carrying their spin but not charge.3 Magnetic sheets, on the other hand, provide the basis for triangular and Kagome arrangements of cations whose conflicting antiferromagnetic interactions cannot be mutually satisfied.3 This gives rise to magnetic frustration, resulting in exotic states. Experimentally achieving systems with strong magnetic coupling in one or two dimensions remains difficult, particularly in close packed oxides that have traditionally attracted the most attention in the field of magnetism as even canonical systems, e.g. Ca₃Co₂O₆,4 typically have significant residual coupling between their low dimensional units. Systems incorporating organic building blocks that act as spacers between inorganic chains and sheets built from magnetic cations have, however, been shown to be a successful way of achieving phases which host a variety of isolated magnetic chains, ladders and sheets.5 8

Much of the interest in magnetic systems built from combining organic and inorganic building blocks centres on coordination frameworks, including dense metal-organic frameworks (MOFs) where organic linkers connect neighbouring metal centres mediating magnetic coupling between these.5 9 Conversely in other compounds, such as the versatile A₂MX₆ (where A is typically a monovalent N-containing organic cation, M is a divalent transition metal and X is a halide) family, magnetic coupling between discrete transition metal complexes is mediated through short X…X contacts under 4 Å with the organic building block simply acting as a spacer and not coordinating to the transition metal.10 11 In light of the significant interest in these distinct groups of compounds, it is interesting to explore what new low dimensional magnetic architectures can be achieved by compounds related to the A₂MX₆ phases, with regards to having short X…X contacts capable of facilitating magnetic coupling but with organic components that prefer to coordinate to one transition metal rather than act simply in a space filling role. Hydrazine and O-methylhydroxylamine are two of the simplest amines with a tendency to coordinate to a transition metal centre, but only two complexes containing both these and halide ligands have been reported thus far, neither of whose magnetic properties have been explored.12

In this paper, we report five new complexes with O-methylhydroxylamine or hydrazinium molecules coordinated to octahedral Mn, Co and Cu magnetic centres with short Cl…Cl contacts between them. The hydrazinium containing compounds are discrete complexes with magnetic coupling mediated by short Cl…Cl contacts while edge-sharing chains in the methylhydroxylamine phase are anticipated to dominate magnetic coupling. Magnetic property measurements for the four phases made in pure form show that all feature antiferromagnetic coupling. Co(NH₂·NH₃)₂(H₂O)₂Cl₂ and Cu(NH₂·OCH₃)₂Cl₂ are particularly interesting since the former shows clear evidence of strong magnetic frustration while the
later has magnetic properties that resemble a spin ½ 1D chain. This highlights the potential of these and related phases as hosts for low dimensional and frustrated magnetism.

2. Experimental Method

The four hydrazinium phases were made by slow evaporation of 20 mL solutions of MnCl₂·4H₂O (Acros Organics, 99+ %) or CoCl₂·6H₂O (Acros Organics, analytical grade) and NH₄NHCl (Acros Organics, 98 %) over the course of 1-2 weeks at ambient temperature with quantitative yield. The solvent used was a 10:1 mixture of methanol:water, unless otherwise noted. Attempts to make Cu containing phases using CuCl₂·2H₂O (Sigma-Aldrich, ACS reagent 99%) were also made but were unsuccessful, leading to only physical mixtures of the reagents. Co(NH₄NH₃)₂(H₂O)₂Cl₆, hereafter known as Hyd₂CoCl₄, was made from the evaporation of a 0.091 M NH₄NHCl and 0.046 M CoCl₂·6H₂O solution, resulting in the formation of pink blade crystals suitable for X-ray diffraction. Colourless block crystals of (NH₄NH₃)₃Mn(NH₂NH₂)Cl₆ referred to as Hyd₃MnCl₆, were made from the evaporation of a methanol solution containing 0.050 M NH₄NH₂Cl and 0.017 M MnCl₂·4H₂O. Colourless block crystals of Mn(NH₄NH₃)₂(H₂O)₂Cl₆, known as Hyd₂MnCl₆, were made by evaporation of a 0.091 M NH₄NH₂Cl and 0.091 M MnCl₂·4H₂O solution. A sample of (NH₄)₂Mn₃(NH₂NH₂)₃(H₂O)₂Cl₁₆, Hyd₃M₃MnCl₁₆, suitable for structural determination was made by evaporation of a 0.091 M NH₄NH₂Cl and 0.027 M MnCl₂·4H₂O solution, although a purer sample, which was used for bulk analysis, was obtained using 0.092 M NH₄NH₂Cl and 0.027 M MnCl₂·4H₂O. In contrast, Cu(NH₄OH)Cl₂, referred to as MHA₃CuCl₅, was initially made by layering 8 mL of a 0.050 M methanol solution of CuCl₂·2H₂O over 8 mL of a 0.213 M Na(HCO₃)₂ and (NH₄)₂OCl₂ solution in methanol:water (~12:1) leading to observing diffraction quality blue needle single crystals after a week. A larger sample for bulk property measurements was made by the same method by using 0.677 M Na(HCO₃)₂ and 0.427 M (NH₄)₂OCl₂ methanol:water (~6:1) solution and 0.100 M CuCl₂·2H₂O solution in methanol, giving a good yield of 74.3 %. Similar reactions using MnCl₂·4H₂O lead to Mn₂N₂(HCO₃)₂ formation.¹³

Structure determinations were carried out using a Rigaku Oxford Diffraction Supernova equipped with MoKa and Cu Ka microfocus sources (50 kV, 0.8 mA) with multi-layered focusing optics and an Atlas S2 CCD detector. Samples were held on MiTeGen microloops and, where needed, samples were cooled using an Oxford Cryosystems cryostream. Data were integrated and absorption corrections performed using CrysAlis Pro software suite version 171.38.14 and the structure solved using direct methods in SHELXT¹⁵ and least-square refinements carried out using SHELXL-2014/7¹⁶ via the Olex² graphical user interface¹⁷ (see Table 1 for crystallographic details). Displacement parameters of non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were typically located geometrically with displacement parameters constrained to 1.2 times the Ueq of the parent atoms (1.5 times for methyl groups and water molecules). Hydrogen bonding networks between discrete complexes are briefly discussed in the ESI.

Table 1: Crystallographic data for the structures determined in this work by single crystal X-ray diffraction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hyd₂CoCl₄</th>
<th>Hyd₃MnCl₆</th>
<th>Hyd₂MnCl₆</th>
<th>Hyd₃M₃MnCl₁₆</th>
<th>MHA₃CuCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>CoCl₂·H₂O</td>
<td>MnCl₂·H₂O</td>
<td>MnCl₂·H₂O</td>
<td>Mn₃Cl₆·H₄O₂</td>
<td>CuCl₂·H₂O</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>302.88</td>
<td>331.37</td>
<td>230.38</td>
<td>1098.65</td>
<td>228.56</td>
</tr>
<tr>
<td>T (K)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
<td>293(2)</td>
</tr>
<tr>
<td>λ (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>1.54184</td>
<td>1.54184</td>
<td>1.54184</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space Group</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P2₁/n</td>
<td>P1</td>
<td>P1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.9880(6)</td>
<td>8.9779(4)</td>
<td>5.54110(10)</td>
<td>7.5839(3)</td>
<td>3.7868(6)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>5.7019(5)</td>
<td>10.9705(4)</td>
<td>13.9707(3)</td>
<td>9.1752(4)</td>
<td>5.6827(9)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.3808(8)</td>
<td>11.7726(5)</td>
<td>9.9630(3)</td>
<td>15.0656(6)</td>
<td>8.7079(11)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>97.745(7)</td>
<td>94.423(4)</td>
<td>92.648(2)</td>
<td>84.447(3)</td>
<td>98.561(13)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>513.63(7)</td>
<td>1156.05(9)</td>
<td>770.44(3)</td>
<td>1010.83(7)</td>
<td>182.30(5)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>ρ̅ (g cm⁻³)</td>
<td>1.958</td>
<td>1.904</td>
<td>1.986</td>
<td>1.805</td>
<td>2.082</td>
</tr>
<tr>
<td>χ (cm⁻³)</td>
<td>2.677</td>
<td>2.262</td>
<td>22.989</td>
<td>17.584</td>
<td>10.472</td>
</tr>
<tr>
<td>meq/unique</td>
<td>[Rint = 0.0311]</td>
<td>[Rint = 0.0237]</td>
<td>[Rint = 0.0258]</td>
<td>[Rint = 0.0292]</td>
<td>[Rint = 0.0491]</td>
</tr>
<tr>
<td>Parameters refined</td>
<td>54</td>
<td>114</td>
<td>76</td>
<td>217</td>
<td>44</td>
</tr>
<tr>
<td>R₁, wR (all)</td>
<td>0.0429, 0.0602</td>
<td>0.0403, 0.0801</td>
<td>0.0297, 0.0688</td>
<td>0.0341, 0.0818</td>
<td>0.0331, 0.0844</td>
</tr>
<tr>
<td>R₁, wR (obs)</td>
<td>0.0311, 0.0548</td>
<td>0.0323, 0.0757</td>
<td>0.0270, 0.0660</td>
<td>0.0316, 0.0795</td>
<td>0.0314, 0.0806</td>
</tr>
<tr>
<td>Goodness of Fit</td>
<td>1.050</td>
<td>1.044</td>
<td>1.065</td>
<td>1.050</td>
<td>1.096</td>
</tr>
</tbody>
</table>
Sample phase purity was established by powder X-ray diffraction using either a Rigaku MiniFlex utilising Cu Kα radiation (40 kV, 15 mA) and a D/tek Ultra detector. Patterns were held in a plastic sample holder with a 10 mm well, due to these products often reacting with other holders to which they are exposed for a prolonged time, with data typically collected over a range of 5-60° 2θ. The data obtained were subsequently fitted using the Le Bail method in the program Rietica,14 which indicated that the bulk samples were consistent with the crystal structures of the phases determined by single crystal X-ray diffraction and were either single phase or contained trace quantities of this phase (see Fig. S1-4). Hyd3MnCl3 was an exception to this and always contained significant quantities of unidentified phases that prevented further characterisation of this compound. Elemental microanalysis, performed at the London Metropolitan University, confirmed the purity of the four other samples. Hyd3CoCl4 was found to be 4.61 % H and 18.40 % N c.f. to 4.66 % H and 18.38 % expected. HydMnCl3 consisted of 3.86 % H and 11.98 % N c.f. 3.94 % H and 12.16 % N expected. Hyd2MnCl4 was determined to be 5.03 % H and 25.36 % N c.f. 4.95 % H and 25.50 % N. MHA2CuCl2 was found to be 10.36 % C, 4.35 % H and 12.01 % N c.f. 10.51 % C, 4.41 % H and 12.26 % N expected.

Magnetic properties of the four phases prepared in high purity were analysed by a Quantum Design MPMS 5 magnetometer using a 7 T superconducting magnet. Samples were placed in gelatin capsules inside a pierced straw with a uniform diamagnetic background. Thermal stabilities of the same samples were analysed using a NETZSCH 409 PG/PC TG with simultaneous DSC capabilities. The sample was held in an alumina crucible under flowing air and typically heated at a rate of 10°/minute to 800 °C, with the exception of MHA2CuCl2 where a heating rate of 5°/minute was used due to the high exothermic nature of its initial decomposition. Infrared spectra were collected over a range of 4000-500 cm⁻¹ using a Shimadzu IRAfinity-1S Fourier transform spectrometer equipped with an attenuated total reflection stage (see ESI for spectra, Fig. S5-8, and their assignments); measurements were averaged over a total of 16 scans.

3. Results and Discussion

3.1 Crystal Structures

Hyd3CoCl4 adopts P2₁/c monoclinic symmetry with discrete octahedral Co complexes. The asymmetric unit of Hyd3CoCl4 contains one Co atom, on an inversion centre, an H₂O and a NH₄NH₂ ligand and two Cl atoms, one of which is coordinated to the Co (see Fig. S9). The Co atoms are coordinated to N atoms from two hydrazinium cations, two oxygen atoms from water molecules and two chloride anions, with like atoms bound in a trans-fashion. The bond valence sum of Co is 1.94, consistent with a divalent cation.19 The relatively regular octahedral Co cations are connected by Cl…Cl contacts (3.7413(11) Å) into a layer with Co in a diamond-like arrangement (see Fig. 1). The space between these layers is occupied by an undulating layer of Cl anions, with nearest intralayer and interlayer Cl…Cl contacts of 3.827(4) and 3.8191(10) Å. Neighbouring Co cations in a diamond all have the same Co-Cl…Cl-Co contacts with a likely magnetic exchange pathway of 8.5522(15) Å and a dihedral angle of 127.49(2)°. It should, however, be noted that the distance separating the closest two Co cation on opposite sides of the diamond are shorter than those bridged by the Cl…Cl contacts (c.f. 5.7016(5) to 6.3642(4) Å). All Cl…Cl contacts between layers involve three Cl atoms so coupling between layers must be far weaker; the nearest-neighbour Co-Co distance between layers is also much longer (c.f. 7.9862(6) to 5.7017(5) Å).

![Fig. 1: Crystal structure of Hyd3CoCl4 showing a) the structure of an individual layer and b) the arrangement of neighbouring layers. The Co octahedra are shown in dark blue and Cl, C, N, O and H atoms are shown as dark green, black, light blue, red and light pink spheres, respectively. Nearest neighbour Cl…Cl contacts within a layer are shown as dashed lines. The Co centres in one diamond are highlighted in Fig. 1a by red dashed lines and the nearest neighbours through space highlighted by a lavender dashed line](Image)
Hyd$_3$MnCl$_5$ adopts $P2_1/n$ monoclinic symmetry and consists of relatively regular discrete octahedral complexes. The asymmetric unit contains one Mn atom, five Cl atoms, one complete NH$_3$NH$_2$ ligand and two complete uncoordinated NH$_3$H$^+$ cations (see Fig. S10). The Mn atom is coordinated to five Cl atoms and one NH$_3$NH$_2$ ligand and has a bond valence sum of 1.95, consistent with Mn$^{2+}$. The shortest Cl...Cl contacts, of 3.718(6) Å, between molecular complexes connect these into chains that run roughly along the [01T] axis, while modestly longer Cl...Cl contacts, 3.879(2) to 3.918(2) Å connect complexes within the ob plane into an approximately square lattice, completing a three dimensional network (see Fig. 2).

The bond valence sums of the Mn cations are 1.85 and 2.02 for Mn1 and Mn2, respectively, broadly consistent with Mn$^{2+}$. The structure of Hyd$_3$Mn$_3$Cl$_{16}$ can be viewed as layers of regular octahedral Mn complexes stacked along the c-axis that only contain Mn1 or Mn2 atoms, with the following sequence: Mn1Mn2Mn2Mn1 (see Fig. 4). While the octahedral Mn2 centres in neighbouring layers are stacked on top of each other, Mn1Cl$_6$ octahedra are shifted by about half a unit cell along both the a- and b-axis compared to the octahedral Mn2 centres in the layers above and below it. NH$_3$H$^+$ cations and Cl$^-$ anions occupy space between the octahedral Mn2 centres in a layer. Short Cl...Cl contacts (3.712(7) and 3.798(9) Å) connect Mn1 atoms to Mn2 atoms in the layer above and below, forming rhombohedra that are linked to each other by their corners (see Fig. S14 for more details of Cl...Cl contact distances). The only other Cl...Cl contacts of comparable length (3.775(3) Å) are between these free Cl$^-$ anions and Cl$^-$ atoms coordinated to Mn2. Longer Cl...Cl links crosslink the neighbouring rhombohedra (3.946(11) Å) and Mn2 cations are connected by Cl...Cl interactions of similar lengths both within (3.946(11) Å) and between the layers (3.980(6) Å). The shortest potential magnetic coupling pathways alternate within the rhombohedra with distances of 8.809(9) Å and 8.902(11) Å distances and dihedral angles of 69.40(2) and 127.353(15)$^\circ$. The exchange pathways associated with the other Cl...Cl contacts mentioned above are between 8.951(13) and 9.024(6) Å long with generally have smaller dihedral angles, between 27.30(3) and 84.15(2)$^\circ$.

**Fig. 3:** Crystal structure of HydMnCl$_3$ showing the two sets of zig-zag Mn–Cl⋯Cl: Mn chains with the closest Cl⋯Cl contacts shown as green dashed lines and the Cl⋯Cl contacts in the other chain shown in blue. The Mn octahedra are shown in pink and all other colours are the same as in Fig. 1.
Unlike the other phases in this article \( \text{MHA}_2\text{CuCl}_2 \), which adopts \( P\bar{T} \) triclinic symmetry, contains 1D chains of Cu connected by Cl atoms. The asymmetric unit of \( \text{MHA}_2\text{CuCl}_2 \) features one Cu atom, on a special position with half the site multiplicity of the general position, one O-MHA ligand and one Cl ligand (see Fig. S15). The Cu cations are coordinated to the N atoms of two O-MHA ligands, in a trans-fashion, and four Cl ligands; the Jahn-Teller distortion significantly elongates two of the Cu-Cl bonds (c.f. 2.312(20) Å to 2.866(19) Å). The bond valence sum of the Cu cation is 2.06, consistent with a divalent Cu cation. The octahedral Cu are arranged in edge-sharing chains bridged by Cl ligands with close Cl...Cl contacts (3.820(19) Å) between chains connecting these into a layer, which are well separated from each other by the bulk of the O-MHA ligand that interdigitate between layers (see Fig. 5). With regards to potential magnetic coupling within the chains the Jahn-Teller axis of the Cu alternates so that the intrachain super-exchange bridges all involve a long and a short Cu-Cl bond, leading to a super-exchange distance of 5.18(3) Å and a Cu-Cu bond angle of 93.38(4)°. The magnetic coupling between chains in a layer is likely to be facilitated through Cu-Cl...Cl-Cu pathways, which are 8.44(3) Å and a dihedral angle of 180°. Between the layers only through-space interactions are possible, which are likely to be very weak due to the 8.7078(11) Å nearest neighbour distances between Cu in neighbouring planes, which are also far longer than nearest neighbour Cu distances within the layers (3.787(6) Å and 5.6824(9) Å, respectively).

3.2 Thermal Stability

Thermogravimetric analysis indicated that \( \text{Hyd}_2\text{CoCl}_4 \) is stable in air until 80 °C where mass corresponding to the two water molecules is lost in an endothermic process (see Fig. S16). Further mass loss is then observed between 165 °C and 360 °C, with the product at this stage likely CoCl\(_2\) based on the residual mass; this stage of the decomposition appears to be a two stage process with the first half endothermic and the second half exothermic. This may suggest that chloride is lost first and then NH\(_2\)NH\(_2\) molecules during the second stage of the process since decomposition of the later is highly exothermic. The final stage of decomposition takes place between 470 and 660 °C via a mildly exothermic process, with the final mass of the residue confirmed by powder X-ray diffraction to be Co\(_2\)O\(_4\).

\( \text{Hyd} \text{O} \text{MnCl}_3 \) appears to be stable to only 50 °C above which mass broadly corresponding to losing its water molecules occurs in an endothermic process (see Fig. S17). This anhydrous phase is then stable until 275 °C above which weight is lost in two stages which finishes at 700 °C; the final product from this decomposition process has been identified to be a mixture of Mn\(_3\)O\(_4\) and Mn\(_2\)O\(_3\) by powder X-ray diffraction.

\( \text{Hyd}_2 \text{Mn}_2\text{Cl}_{16} \) initially decomposes between 60 and 100 °C in an endothermic process consistent with the loss of the water molecules (see Fig. S18). This anhydrous phase is then stable to 170 °C above which mass is lost continually up to 625 °C, where residual mass is consistent with the formation of Mn\(_3\)O\(_4\), confirmed by powder X-ray diffraction. There is a clear change in slope of weight loss between a rapid decrease to a much more gradual decrease at around 360 °C, with the process below this being high exothermic and only mildly so above this temperature.

\( \text{MHA}_2\text{CuCl}_2 \) is stable up to 100 °C in air where it undergoes a highly exothermic decomposition in a single rapid step that is...
complete by 150 °C and involves loosing mass equivalent to the organic ligands (see Fig. S19). Almost continuous mass loss is observed above this temperature up to 500 °C via mildly exothermic processes, yielding a final product confirmed by powder X-ray diffraction to be CuO.

### 3.3 Magnetic Properties

Magnetic susceptibility measurements ($\chi$) of Hyd$_2$CoCl$_4$ obtained in an applied field of 1000 Oe increase gradually on cooling with field cooled (FC) measurements and zero field cooled (ZFC) measurements not diverging, indicating the phase remains paramagnetic down to 1.8 K (see Fig. 6). $\chi$ can be fit between 75-300 K using Curie-Weiss law yielding a Curie-Weiss temperature, $\Theta_{CW}$, of -18.75 K, indicating moderate antiferromagnetic coupling, and an effective magnetic moment of 4.95 $\mu_B$; this is within the range of typical values exhibited by octahedral Co$^{2+}$ and is consistent with the orbital angular momentum not being fully quenched.\(^{20}\) At 300 K, $\chi T$ is 2.89 emu K mol$^{-1}$ Oe$^{-1}$; this gradually decreases to 100 K before falling rapidly below this to 1.75 emu K mol$^{-1}$ Oe$^{-1}$ around 5 K (see Fig. S20), consistent with significant antiferromagnetic coupling at low temperature. While isothermal magnetisation measurements at 1.8 K are also consistent with paramagnetic behaviour, increasingly linearly at low applied fields before saturating near 24 kOe, the value of 2.2 $\mu_B$ per magnetic centre observed at 50 kOe is around half the value typically expected for Co$^{2+}$ (see Fig. S21). This is likely the result of significant local antiferromagnetic interactions in this phase at low temperature despite long-range magnetic order being suppressed by magnetic frustration. This is consistent with a frustration index $|\theta_{CW}/\theta_N|$, where $\theta_N$ is the Néel temperature, of at least 11.2. The cause of this magnetic frustration is unclear as antiferromagnetic interactions within the diamondoid layers of Co atoms are not frustrated if only nearest neighbours coupled through Co-Cl...Cl-Co bridges are considered, which are anticipated to be the dominant magnetic coupling pathways in this compound. Geometrically the most likely source of magnetic frustration is competition between antiferromagnetic coupling through Co-Cl...Cl-Co bridges in the diamond and between nearest neighbouring Co cations in space, which are formally on the opposite sides of the diamond. While the later are far enough apart in space, 5.7016(5) Å, that direct exchange seems unlikely the magnetic coupling between these may be facilitated by Co-Cl...Cl-Co contacts (a total exchange pathway of 12.2932(18) Å) or coupling via a Co-Cl...O-Co pathway (with a total exchange pathway of 7.860(6) Å).

$\chi$ measurements of MHA$_2$CuCl$_2$ feature a broad cusp, indicating the emergence of antiferromagnetic order below 29 K, with the width of this feature suggestive of low dimensional magnetic order (see Fig. 7). Below 5 K the magnetic susceptibility decreases at an increasing rate, suggesting the possibility of another magnetic transition. Tiny increases in magnetic susceptibility below 2.5 K may be indicative of a small paramagnetic impurity. $\chi$ measurements obtained in an applied field of 1000 Oe can be fit over the range of 70-300 K using Curie-Weiss law, yielding a Curie-Weiss temperature of -28.3 K, consistent with moderate antiferromagnetic coupling, and an effective magnetic moment of 1.77 $\mu_B$ close to the...
expected spin-only value of 1.73 μB expected for Cu²⁺ (see Fig. S26). A plot of χT indicates a value of 0.36 emu K mol⁻¹ Oe⁻¹, close to that expected for isolated Cu²⁺ centres and that this drops rapidly below 100 K approaching zero at 1.8 K, consistent with the emergence of antiferromagnetic interactions (see Fig. S27). Isothermal magnetisation measurements at 1.8 K, 2.8 K and 10 K are very similar with slow linear increases in magnetisation observed to just over 0.04 μB per Cu²⁺ under an applied field of 50 kOe, consistent with antiferromagnetic order (see Fig. S28).

![Graph](image)

**Fig. 7: Evolution of χ versus temperature from 1000 Oe ZFC (hollow symbol) and FC (filled symbol) measurements with a red line showing a spin ½ Heisenberg chain fit to the FC data.**

Given the anticipation that the magnetic interactions within the chains in MHA₃CuCl should be dominant we attempted to fit the evolution of χ with temperature with the well-known Bonner-Fisher approximation for a spin ½ Heisenberg chain, which takes the formism:

\[ \chi = \frac{N_s g^2 \mu_B^2}{k_B T} \times \frac{0.25 + 0.074975x + 0.075236x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3} \]

where \( x = |J|/k_B T \). Excellent fits to both ZFC and FC data collected at 1000 Oe above 10 K were obtained yielding values within two standard deviations of each other; with those to the FC data giving \( g = 2.0547(15) \) and \( J/k_B = 45.26(8) \) K (see Fig. 7). This suggests that MHA₃CuCl is predominantly a 1D antiferromagnet, although as indicated, for example, by our previous paper on 1D formate frameworks this does not exclude the presence of significant interchain coupling, particularly through the Cl...Cl close contacts in the plane.

It is difficult to compare the magnetic behaviour of four compounds with significant differences in topologies and containing distinct magnetic cations. The different strengths of the magnetic interactions, as measured by ΘCW, however can be rationalised with regards to the length of the likely exchange pathways in these compounds. MHA₃CuCl₂, which appears to predominantly have coupling within its edge-sharing chains has the highest ΘCW. This is followed by Hyd₃CoCl₄, which is connected within a layer by relatively short 8.552(15) Å Co-Cl...Co pathway. Both Hyd₃MnCl₃ and Hyd₃µ₃Mn₃Cl₆ have much lower ΘCW, and while their precise topology undoubtedly play a significant role in this, it is notable that these compound require Mn-Cl...Cl-Mn contacts of 8.708(4) and 8.809 (9) Å to connect the octahedral centres into extended units, with the later having the weaker ΘCW of the two. Comparison to a number of previously reported compounds with coupling mediated by Cl...Cl contacts into an extended unit, most typically chains in AMCl₄ (where A is an organic cation and B is typically Cu) type compounds, suggests that for magnetic order to emerge above 1.8 K typically the Cl...Cl contact must be less than 3.9 Å. This is consistent with the emergence of magnetic order in MHA₃CuCl₂ and Hyd₃CoCl₄ while the lack of magnetic order from Hyd₃MnCl₃ and Hyd₃µ₃Mn₃Cl₆ despite Cl...Cl contacts in this range may be a result of the precise architectures of these compounds, including the specific bond and dihedral angles, which are also known to have a significant effect on magnetic coupling.

**Conclusions**

This study has reported the synthesis, crystal structures and magnetic properties of five octahedral Mn, Co and Cu complexes with simple amine ligands. Despite adopting a wide variety of crystal structures they all exhibit close Cl...Cl contacts, which in the majority of cases are the principle source of magnetic coupling. The four compounds whose magnetic properties are measured all show antiferromagnetic interactions. While in Hyd₃MnCl₃ and Hyd₃µ₃Mn₃Cl₆ these are relatively weak Hyd₃CoCl₄ and MHA₃CuCl₂ exhibit significant magnetic coupling. There is no indication of magnetic order emerging in Hyd₃CoCl₄ above 1.8 K indicating that this compound is likely highly magnetically frustrated, with an analysis of its crystal structure showing this is likely restricted to the diamonoid layers of Co cations. In contrast MHA₃CuCl₂ exhibits magnetic susceptibility measurements which are well fitted by a 1D spin ½ Heisenberg antiferromagnetic model, with this coupling likely facilitated by Cl bridges that link octahedra in an edge-sharing fashion.

**Conflicts of interest**

There are no conflicts of interest to declare.

**Acknowledgements**

The authors would like to thank EPSRC for funding as part of grant EP/R011524/1. One of us (RJCD) would like to thank for the University of Kent for funding via a Vice-Chancellors PhD studentship.

**References**
ARTICLE


