Hydrothermal Synthesis, Structure, and Magnetism of $[Co_2(OH)\{1,2,3\text{-}(O_2C)_3C_6H_3\}(H_2O)]\cdot H_2O$ and $[Co_2(OH)\{1,2,3\text{-}(O_2C)_3C_6H_3\}]$: Magnetic Δ-Chains with Mixed Cobalt Geometries**

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Solvo- and hydrothermal syntheses have been used for many years to prepare oxide-based materials such as zeolites and phosphates.[1] The use of these techniques for synthesizing coordination compounds with extended structures is also receiving increasing interest.[2] Many of the coordination solids thus prepared have small and simple repeat units which come together to build complex symmetrical forms, and this makes these materials particularly esthetically pleasing. Incorporation of the structure-directing organic moiety into the extended structure offers the possibility of producing composite materials, an area of current interest in materials research. A guiding principle of our work is the attempt to express some aspect of the templating ligand's character in the product. For instance, we previously demonstrated the ability of benzene-1,3,5-tricarboxylate to impose threefold symmetry on a three-dimensional metal–ligand array.[2j] We now present the results of reactions with benzene-1,2,3-tricarboxylic acid. This ligand possesses polar and nonpolar regions, a property which we wish to exploit in the preparation of bulk materials which mirror this structural feature. By studying the effect of structure on function we hope to "engineer" specific properties into materials by the action of structure-directing ligands. Of particular interest to us is the exploration of magnetostructural correlations in these types of compound. Our methodology allows us to create a number of hitherto rare, but theoretically important, spin topologies,[3] and here we report on the formation and properties of two compounds built on the Δ-chain structure. Lattices in which the spin carriers lie at the vertices of triangles are of interest because they provide examples of spin-frustrated materials when antiferromagnetic coupling is present. Of the possible chain-like arrangements of triangles, the Δ-chain (Figure 1 a) is of particular theoretical interest,[4] as it represents a section of the two-dimensional spin-frustrated Kagomé lattice[5] and provides a rare example of a topologically frustrated one-dimensional system which, in the absence of interchain couplings, cannot show magnetically ordered states.[6] Here, in addition, the topological frustration should cause a large degeneracy in the ground state manifold, and at low temperatures unusual quantum spin liquid phases may be found. Whilst the Δ-chain topology has been the subject of extensive theoretical investigation prior to this work, only one real example[4d,e] was known.

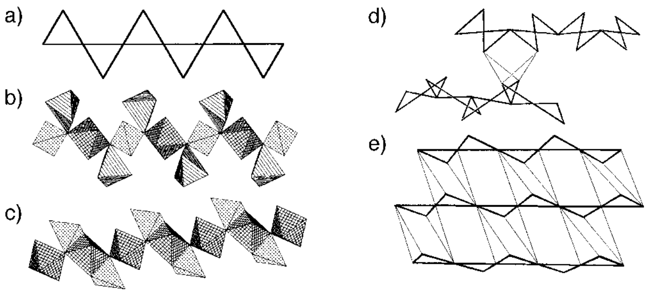

Figure 1. a) The idealized Δ-chain topology with a metal atom at each vertex. Polyhedral representation of a portion of a chain in b) **1** and c) **2**; octahedra are cross-hatched, trigonal bipyramids are striped, and tetrahedra have dotted faces. Topology of the superexchange-mediated magnetic lattice in d) **1** and e) **2**; a magnetic ion resides on each vertex, bold lines represent single-atom bridges, and narrow lines represent three-atom bridges.

The hydrothermal reaction of $CoCl_2\cdot 6H_2O$ with 1,2,3-benzenetricarboxylic acid hydrate and NaOH in the approximate ratio 2:1:4 at temperatures between 200 and 220 °C produces a mixture of dark bluish purple prismatic crystals of **1** and thin purple plates of **2**. The synthesis can be optimized to produce predominantly one compound or the other, so that single-phase material is obtained following purification. The X-ray crystal structures[7] of **1** and **2** show them to have simple and closely related formulas, but extremely complex and entirely different structures. For **1** the asymmetric unit (Figure 2) consists of one ligand, three metal atoms, a μ_3-OH group, and a terminal coordinated water molecule, as well as two (fractional occupancy) lattice water molecules. The material is built on a framework consisting of strips of corner-sharing $Co_3(\mu_3\text{-}OH)$ triangles which have the Δ-chain topology (Figure 1 b). Octahedral and tetrahedral cobalt sites alternate along the backbone of the chain, and pendant trigonal-bipyramidal cobalt sites are attached at each bridging hydroxide. The metal hydroxide strips run along the crystallographic *a* and *b* axes, and no atoms are shared between orthogonal chains. Co1 (octahedral) and Co2 (tetrahedral) have only minor deviations from idealized symmetry, whilst the geometry around Co3 is rather distorted; the two apical atoms are arranged in a nearly linear fashion, but there is significant distortion of the equatorial ligands. Bond lengths and angles for the cobalt ions and the ligand are all normal (Figure 2). Each oxygen atom of the ligand is coordinated to only one metal atom; O1, O2, and O3 are bonded to cobalt atoms which are part of one chain, while O4, O5, and O6 are bonded to an orthogonal chain. Two sites within the channels are occupied by water molecules (O9 and O10). The ligands do indeed arrange themselves so as to produce polar regions surrounding the cobalt hydroxide strips and nonpolar regions surrounding channels (Figure 3). There is no interaction between lattice water molecules and the bridging hydroxide

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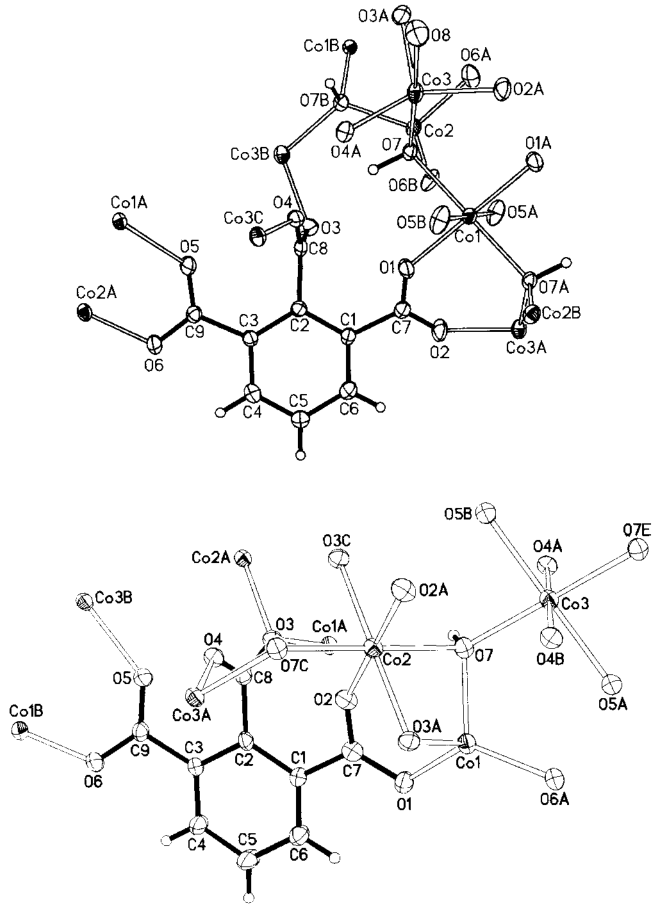

Figure 2. View of the ligand–metal environment in **1** (top) and **2** (bottom).

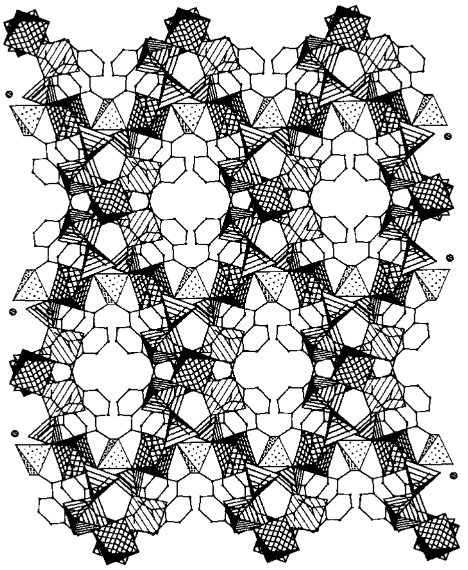

Figure 3. View down the crystallographic *a* axis of the packing in **1** showing the linking of polyhedra by the carboxylate ligands. Shading of polyhedra is as for Figure 1.

as we have observed in similar materials.[21] The individual Δ-chains are linked to their four orthogonal nearest neighbors by OCO bridges between trigonal-bipyramidal cobalt ions. Two adjacent ions in one chain are both connected to two similar ions on neighboring chains to give a pseudotetrahedral linkage (Figure 1d). Thus, an infinite three-dimensional lattice is created in which the metal ions form a relative of the pyrochlore[8] structure, another topology in which topological spin frustration is possible.[9]

$[Co_2(OH)\{1,2,3\text{-}(O_2C)_3C_6H_3\}(H_2O)]\cdot H_2O$ **1**

$[Co_2(OH)\{1,2,3\text{-}(O_2C)_3C_6H_3\}]$ **2**

The structure of **2** is also based on the Δ-chain structure in which the chains have backbones consisting of two crystallographically independent octahedral cobalt ions. Pendant tetrahedral cobalt ions are attached by μ_3-OH groups (Figure 1c) and also to Co2 through a 1,1-bridging carboxylate. The conformation of the ligand and the arrangement of metal atoms around it in **2** is similar to that in **1** (Figure 2). The asymmetric unit contains one complete ligand in which five out of six oxygen atoms are nonbridging and bonded to only one metal center, while O3 bridges two metal atoms. Bond lengths and angles in **2** are all normal. The $Co_3(OH)$ unit shows greater distortion than that in **1**, and the Co1–Co2 edge, which is triply bridged, is significantly shorter (2.906(2) vs. 3.419(2) and 3.666(1) Å). The ligand straddles adjacent chains and holds them together with 1,3-bridging carboxylate groups to form infinite layers (Figure 4). This forms further triangles that link individual Δ-chains to their two adjacent equivalents (Figure 1e). The cobalt atoms and the polar half of the ligand lie in the interior of the layer sandwiched between the nonpolar ligand regions. The ligands are arranged in such a way that the surface of the layers undulate. The grooves of adjacent layers fit quite tightly together, although we assume there are only weak interlayer interactions resulting from the nonpolar nature of the surfaces. The platelike shape of the crystals and their brittle character are good evidence for this.

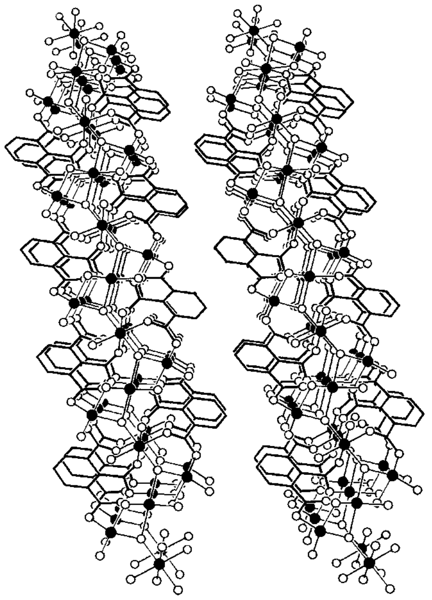

Figure 4. View down the crystallographic *b* axis showing the packing of layers in **2**.

Compounds **1** and **2** have similar nearest-neighbor interactions, but the 1,3-carboxylate bridges which link the next-nearest neighbors generate entirely different lattices, and therefore different superexchange topologies. Furthermore the triangles forming the chains in the two compounds deviate from equilateral by different amounts. At a simplistic level this might be expected to lead to different ratios between the three exchange interactions corresponding to the triangle's edges. For an idealized frustrated arrangement these should be equal, and deviation from equality is likely to lead to suppression of the frustration. A further complication is the possibility of orbital contributions to the susceptibility from the octahedral sites, particularly as the two compounds contain different proportions of sites with this geometry.

The magnetic susceptibility curve for **1** (Figure 5) resembles that expected for a simple paramagnet with the addition of a shoulder at approximately 4 K. Between 50 and 300 K, **1** obeys the Curie–Weiss law, and the values of $C = 5.61\ \mathrm{cm^3\,mol^{-1}\,K}$ and $\theta = -57$ K correspond to a high-temperature moment of 6.70 μ_B per unit. As expected, this is slightly higher than the spin-only value resulting from the orbital contribution from the single octahedral Co^{II} ion in the formula unit. Plotting the product χT against T is also very informative. Down to 20 K this value decreases, confirming that the dominant exchange is antiferromagnetic; however, following a local minimum at 20 K, the value increases up to a local maximum at 5 K, before again decreasing. This is exactly the behavior predicted[4d,e] for a Δ-chain. The Weiss constant is significantly larger than others we have measured for Co^{II} compounds which show long-range ordering at higher temperatures.[2g] It is therefore significant that no sharp transition indicative of long-range order is observed, as this suggests that either spin frustration or a one-dimensional character as a result of weak interchain interactions may be important in **1**.

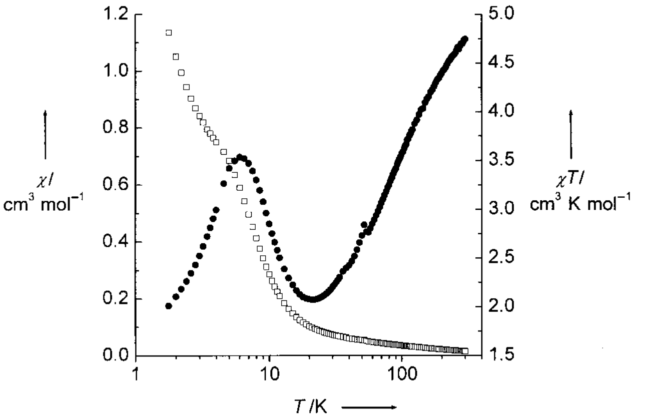

Figure 5. Plot of the susceptibility χ (□) and χT (●) for **1** derived from field cooled measurements at 100 G.

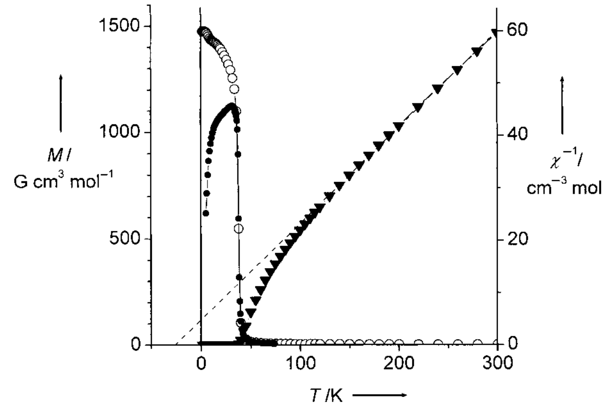

Figure 6. Graph of field cooled magnetization (□), zero-field cooled magnetization (●), and inverse susceptibility $1/\chi$ (▼) for **2** in a field of 100 G.

The magnetization of **2** shows a dramatic phase transition at approximately 40 K to a state with spontaneous magnetization (Figure 6). The sample obeys the Curie–Weiss law in the high-temperature paramagnetic regime, and fitting between 120 and 300 K yields values of $C = 5.44\ \mathrm{cm^3\,mol^{-1}\,K}$ and $\theta = -27$ K, characteristic of an overall antiferromagnetic interaction. The plot of χT shows a broad local minimum at approximately 110 K. The combination of antiferromagnetic interactions and a large spontaneous magnetization indicated that the material is a ferrimagnet. This was confirmed by ac susceptibility measurements (Figure 7), in which the imaginary, "out-of-phase" component χ'' becomes nonzero below T_c.[10] Hysteresis measurements (Figure 8) in this ferrimagnetic state gave a saturation magnetization of 9700 G cm^3 mol^{-1} and revealed coercive fields of 250 and 1800 G at 25

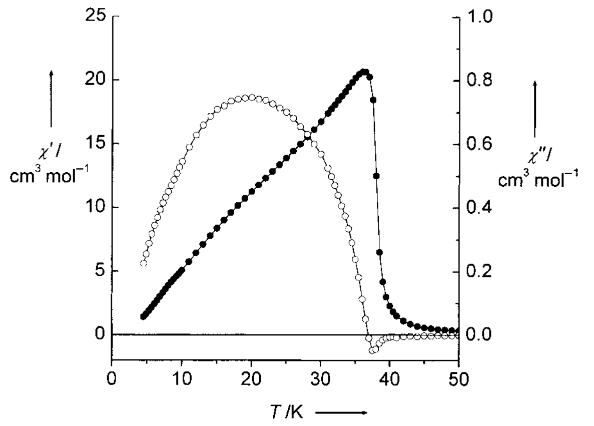

Figure 7. Real χ' (●) and imaginary χ'' (○) components of the ac susceptibility of **2**.

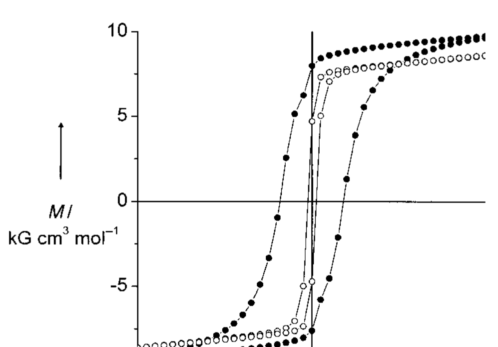

Figure 8. Hysteresis curve for **2** between ±10 kG at 5 K (●) and 25 K (○).

and 5 K, respectively. The saturation magnetization appears to correspond to between 1/4 and 1/3 of that expected for a parallel (ferromagnetic) arrangement of spins. This suggests a complicated ground-state spin configuration.

It is remarkable that materials with such similar building blocks, that is, metal hydroxide chains, and arrangement of metal ions around the ligand, can have such different structures. In investigating the reactivity of this ligand we hoped to find that it would encourage the formation of low-dimensional structures, and this proved correct; both compounds contain one-dimensional metal–oxygen chains, and compound **2** has an overall two-dimensional structure. Both structures are made up of arrays of Δ-chains. In the case of **1** this gives rise to a completely new three-dimensional spin-frustrated topology with no magnetic ordering down to 2 K. Compound **2** also displays complex and unusual magnetism. In both cases we would ascribe the complexity of structure and magnetism to the presence of relatively low symmetry molecular components.

Experimental Section

1: In a typical experiment, 1,2,3-benzenetricarboxylic acid hydrate (0.110 g, 0.52 mmol) was dissolved in a solution of NaOH (0.085 g, 2.13 mmol) in H_2O (6 mL), and the resulting solution added to a solution of $CoCl_2 \cdot 6H_2O$ (0.250 g, 1.05 mmol) in 2 mL of water. The blue mixture was placed in a 23-mL Teflon-lined autoclave and heated at 220 °C for 16 h. The autoclave was cooled over a period of 4 h, and the product, which was a mixture of dark purple crystals of **1** and an approximately equal amount of **2**, was collected by filtration, washed with water, and dried in air. Pure product was obtained by manual separation. Final yield of **1**: 35 mg, 19 % based on Co (total yield of crude product: 75 mg). Elemental analysis (%) calcd for $C_9H_8O_9Co_2$: C 28.60, H 2.13; found: C 28.65 H, 1.76.

2: The same procedure as for the preparation of compound **1** was followed, except that the autoclave was heated to 200 °C for 40 h. Yield: 90 mg, 52 % based on Co. Elemental analysis (%) calcd for $C_9H_4O_7Co_2$: C 31.58, H 1.14; found: C 30.57, H 1.14.

Magnetization studies were performed with a Quantum Design MPMS SQUID magnetometer. The sample magnetizations were corrected for the intrinsic diamagnetic contributions by using Pascal's constants;[11] $\chi_{dia} = -147 \times 10^{-6}\,cm^3\,mol^{-1}$ for **1** and $-121 \times 10^{-6}\,cm^3\,mol^{-1}$ for **2**.

Field cooled magnetization measurements on **1** were performed with applied fields of 10 and 100 G between 2 and 300 K. For **2**, field cooled magnetization measurements were recorded in a field of 100 G between 2 and 300 K. Subsequent field cooled and zero-field cooled measurements were recorded for the ordered phase, as well as hysteresis measurements at 5 and 25 K between -10000 and $+10000$ G. Dynamic ac susceptibility measurements were made between 4.5 and 50 K with a 1 G oscillating field (125 Hz) and no offset field.

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[7] Crystal data for **1**: $C_9H_8O_9Co_2$, purple parallelepiped, $0.20 \times 0.08 \times 0.08\,mm^3$, tetragonal, $I4_1/a$, $a = 12.900(2)$, $c = 27.728(4)$ Å, $V = 4614(1)$ Å^3, $Z = 16$, $\rho_{calcd} = 2.177\,g\,cm^{-3}$, $2\theta_{max} = 59.5°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 2.920\,mm^{-1}$ (no absorption correction was applied), $T = 293$ K, Rigaku RAXIS-II area detector. Data were integrated and scaled, and Lorentz and polarization corrections applied using the HKL 1.9.0 package. 7204 reflections were recorded of which 1951 were unique ($R_{int} = 0.0868$) and 1476 had $F > 4\sigma(F)$. The structure was solved by direct methods (SHELXTL-PLUS), the hydrogen atoms on the ligand and the hydroxide were placed in idealized positions, all other atoms were refined anisotropically by full-matrix least-squares methods on F^2 to give $R1 = 0.0415$ (4σ data), $wR2 = 0.1043$, $S = 0.993$ (all data), max./min. residual electron density: $0.60/-1.26$ e Å^{-3}. Crystal data for **2**: $C_9H_4O_7Co_2$, purple plate, $0.18 \times 0.12 \times 0.01\,mm^3$, triclinic, $P\bar{1}$, $a = 5.510(1)$, $b = 7.368(2)$, $c = 12.376(3)$ Å, $\alpha = 80.11(3)$, $\beta = 88.04(2)$, $\gamma = 70.75(1)°$, $V = 467.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.431\,g\,cm^{-3}$, $2\theta_{max} = 50.5°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 3.576\,mm^{-1}$ (no absorption correction was applied), $T = 293$ K. Data reduction as above. 2353 reflections, of which 1415 were unique ($R_{int} = 0.0921$) and 1227 had $F > 4\sigma(F)$. Solution and refinement as above, $R1 = 0.0538$ (4σ data), $wR2 = 0.1758$, $S = 1.102$ (all data), max./min. residual electron density: $0.585/-0.538$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147449 (**1**) and CCDC-147450 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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