inorganic compounds

A spin-frustrated cobalt(II) carbonate pyrochlore network

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The crystal structure of the cobalt(II) carbonate-based compound cobalt(II) dicarbonate trisodium chloride, $Co(CO_3)_2Na_3Cl$, grown from a water–ethanol mixture, exhibits a three-dimensional network of corner-sharing $\{Co_4(\mu_3\text{-}CO_3)_4\}$ tetrahedral building blocks, in which the Co^{II} centres define a pyrochlore lattice and reside in a slightly distorted octahedral $Co(O–CO_2)_6$ environment. The space outside the hexagonal framework defined by these interlinked groups is occupied by Na^+ and Cl^- ions. Antiferromagnetic coupling between adjacent Co^{II} centres, mediated by carbonate bridges, results in geometric spin frustration which is typical for pyrochlore networks. The Co and Cl atoms reside on the special position $\bar{3}$, one Na atom on position 2 and a carbonate C atom on position 3.

Figure 1
The unit-cell of the title compound, emphasizing the CoO_6 coordination polyhedra as transparent octahedra (blue in the electronic version of the paper; also Co light blue, O red, C black, Na dark green and Cl light green).

compounds in which magnetic transition metal cations are linked by comparatively simple and hydrogen-free inorganic bridging ligands (Fielden & Kögerler, 2009). We herein demonstrate that, under solvothermal conditions (433 K), small anions such as carbonate can compete with chelating ligands (here, 1,10-phenanthroline) to yield a three-dimensional cobalt(II) carbonate framework structure, the voids of which are filled with Na^+ and Cl^- ions (Fig. 1). Single crystals of the resulting compound, $Co(CO_3)_2Na_3Cl$, were grown from

Comment

Geometrically frustrated magnetic materials continue to be a important topic in magnetism, their study motivated by the multitude of magnetic phenomena they exhibit, ranging from spin-glass behaviour to phase transitions and quantum fluctuations (Ramirez, 1994; Greendan, 2001). Competing antiferromagnetic exchange interactions between localized spin centres can be realized within several classes of compound. Typically, extended (one- to three-dimensional) polymeric spin structures are at the heart of such studies, for example, planar Kagomé lattices of regular triangles and hexagons (Schweika et al., 2007). Interest in spin frustration has also spawned efforts to recreate these phenomena in molecular (quasi zero-dimensional) systems (Kögerler et al., 2010). Next to spin-frustrated magnetic molecules, our interest concerns purely inorganic coordination networks that contain no hydrogen. These can thus be subjected to neutron diffraction studies, in order to study the magnetic phenomena associated with spin frustration, without the need for prior deuteration. In this context, we found that the presence of multidentate ligands can indeed induce the formation of network
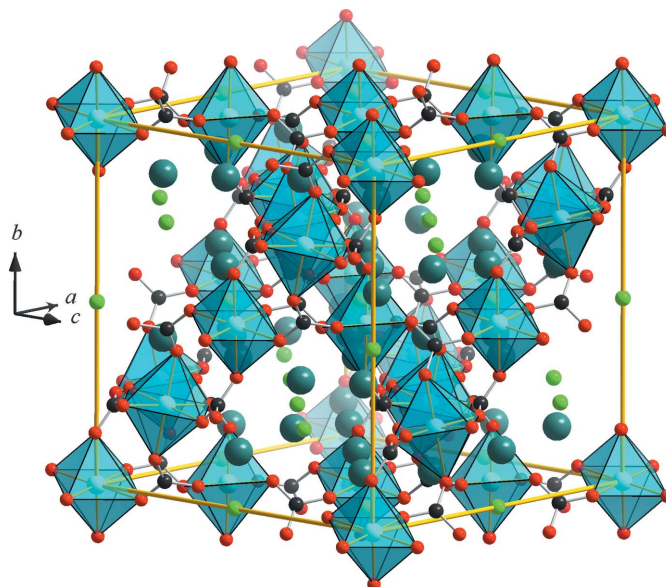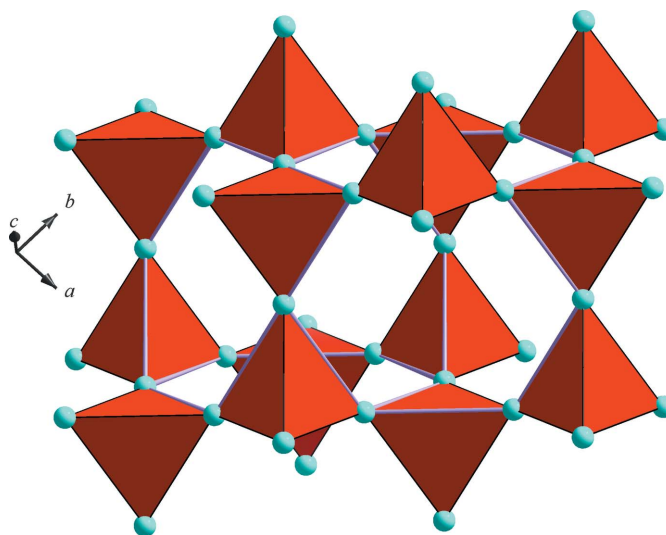

Figure 2
A section of the pyrochlore lattice assembled from Co_4 tetrahedra. The regular hexagons around which the tetrahedra are arranged are emphasized by thick light-coloured lines (purple in the electronic version of the paper).
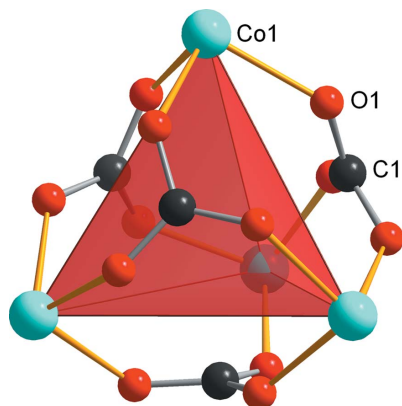
Figure 3
The structure of a $\{Co_4(CO_3)_4\}$ tetrahedron, the building block of the pyrochlore sublattice of the title compound.

a water–ethanol mixture and characterized at 123 K, showing that they crystallize in the cubic space group $Fd\overline{3}$.

Importantly for the magnetochemistry, the octahedrally coordinated Co^{II} centres are orbitally degenerate and thus exhibit large single-ion anisotropy. The Co^{II} centres define a cubic pyrochlore lattice of corner-sharing regular Co_4 tetrahedra arranged around hexagons, forming interconnected stacks of Kagomé layers (Fig. 2).

The Co^{II} centres reside in slightly distorted octahedral CoO_6 coordination environments (Table 1), with symmetry-equivalent Co—O bond lengths of 2.0950 (9) Å, but with O—Co—O bond angles alternating between 86.08 (3) and 93.92 (3)°. The nearest-neighbour Co···Co distances (*i.e.* the edge lengths of the Co_4 tetrahedra) are 4.9483 (2) Å. Each carbonate group coordinates to, and bridges, three Co sites and the carbonate planes are coplanar with the respective faces of the Co_4 tetrahedra, with an interplanar distance of 1.2256 (19) Å (Fig. 3).

Preliminary low-field magnetic susceptibility studies of $Co(CO_3)_2Na_3Cl$ reveal pronounced ligand-field and spin-orbit coupling effects, assessed using the simulation package *CONDON 2.0* (Speldrich *et al.*, 2011), as well as dominant antiferromagnetic coupling between the Co^{II} spin centres. Here, nearest-neighbour antiferromagnetic coupling, mediated by bridging carbonate anions [Co—O—C bond angles = 132.07 (9)°], results in a highly geometrically frustrated material (Bramwell & Harris, 1998). Preliminary susceptibility data for the title compound also indicate a gradual spin-glass transition between 3.0 and 4.5 K, where the fluctuating disorder required for the spin-glass state is supposed to stem from dynamic disorder of the Na^+ and Cl^- sublattice.

Experimental

A mixture of $CoCl_2 \cdot 6H_2O$ (5.9 g, 0.025 mol), 1,10-phenanthroline (10.0 g, 0.05 mol), Na_2CO_3 (2.5 g, 0.025 mol), ethanol (72 ml) and water (6 ml) was stirred in air for 10 min and then transferred to a 110 ml PTFE-lined autoclave, which was heated to 433 K for 96 h, followed by cooling to room temperature at a rate of 5 K h^{-1}. The

resulting pink polycrystalline product was washed with a large amount of ethanol/water (yield 3.0 g, 42% based on Co). Crystals suitable for single-crystal diffraction analysis were taken directly from the precipitate. Elemental analysis calculated (found): Na 24.4 (24.8), Co 20.8 (22.3), Cl 12.4% (12.1%); Na and Co were determined by ICP–OES and chloride by ion-exchange chromatography). IR (KBr pellet, ν, 4000–370 cm^{-1}): 3506 (*m*), 3387 (*m*), 2947 (*w*), 2854 (*m*), 2625 (*w*), 2509 (*m*), 1435 (*s*), 1414 (*s*), 872 (*s*), 708 (*m*).

Crystal data

Table 1
Selected bond angles (°).

C1—O1—Co1	132.07 (9)	O1—C1—O1^{ii}	119.966 (6)
O1—C1—O1^i	119.972 (6)	O1^i—C1—O1^{ii}	119.969 (6)

Symmetry codes: (i) $z - \frac{1}{2}, -x + \frac{3}{4}, -y + \frac{5}{4}$; (ii) $-y + \frac{3}{4}, -z + \frac{5}{4}, x + \frac{1}{2}$.

The positions of almost all atoms were found by direct methods, the remainder being located *via* iterative cycles of least-squares refinement and difference Fourier synthesis.

Data collection: *APEX2* (Bruker, 2010); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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