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Hydrothermal synthesis and characterization of a new 3D-network containing the versatile *cis*,*cis*-cyclohexane-1,3,5-tricarboxylate

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The hydrothermal synthesis, characterization, single crystal X-ray structures and magnetic properties of three-dimensional coordination polymers, $[M_3(CTC)_2(\mu\text{-}H_2O)_2(H_2O)_2]\cdot 5(H_2O)$ (**1**: M = Co, **2**: M = Ni), employing the flexible *cis*,*cis*-cyclohexane-1,3,5-tricarboxylate (CTC or $C_9H_9O_6^{3-}$) are described. X-Ray crystal structure analyses reveal that **1** and **2** are isostructural. They belong to the triclinic system, $P\bar{1}$: $a = 7.799(2)$, $b = 9.212(1)$, $c = 10.784(2)$ Å, $\alpha = 107.595(3)$, $\beta = 92.877(3)$, $\gamma = 110.248(3)$°, $V = 682.4(2)$ Å^3 and $Z = 2$ for **1**, and $a = 7.694(1)$, $b = 9.210(1)$, $c = 10.764(2)$ Å, $\alpha = 108.598(3)$, $\beta = 92.300(3)$, $\gamma = 109.814(3)$°, $V = 670.6(2)$ Å^3 and $Z = 2$ for **2**. They consist of trinuclear motifs of pseudo-octahedral MO_6 linked through μ-OH_2 and μ-carboxylate to generate one-dimensional chains, which are further bridged by the tricarboxylate to form a non-interpenetrated three-dimensional network. The network possesses extended channels along all three crystallographic axes in which water molecules reside. Each carboxylate group displays a different coordination mode to the metals. The temperature dependence of the magnetic susceptibilities indicates dominant antiferromagnetic interaction within the trimer of the cobalt complex, tending towards a ferrimagnetic alignment at low temperatures, and mostly ferromagnetic interactions for the nickel complex.

Introduction

Recently, there has been considerable interest in synthesizing organic–inorganic hybrid materials having potentially dual or multiple properties.[1] Amongst these are the charge-transfer salts of organic donors, such as the TTF class of compounds, studied in the search for magnetism and superconductivity.[2] The presence of non-linear optical activity and magnetism is also under investigation.[3] The latter two make use of the layered structural nature in the TTF family of compounds and in MPS_3 and bimetallic oxalates for insertion of either paramagnetic ions or optically active components. The organic radicals of the nitronyl nitroxide family have already found applications as magnetic markers in biology and are now being used as functional groups on TTF derivatives[4] in the hope of creating magnetic conductors. Organic dyes intercalated between an inorganic layered framework are used in monitoring water pollution. Combining optical and electrical, optical and magnetic or electrical and magnetic properties has had some success and is currently an active area of chemistry and materials science.[1] However, the combination of structural properties such as porosity with any of these physical properties is rare. It is generally believed that there should be some orbital overlap between the nearest neighbors, whether TTF derivatives or paramagnetic metal ions,[5] to generate a conduction band for electrical conductivity or long-range magnetic orderings. This requirement and the presence of pores are therefore incompatible. Given the long list of applications of porous materials, such as gas sorption, catalysis, drug delivery, purification of solvents, *etc.*,[6] they would even be more powerful agents if, in addition to their pores, they possessed another property such as magnetism. In line with our extensive study of long-range order in low-dimensional cobalt compounds,[7] we have been trying to develop porous-like structures exhibiting long-range magnetic orderings and have found few porous magnets consisting of one-dimensional chains of cobalt. Here, we describe the synthesis, crystal structure, thermogravimetric analysis and the IR and magnetic properties of two new compounds based on paramagnetic transition metal ions and a flexible organic ligand favoring a structure with cavities, $M^{II}_3(CTC)_2(H_2O)_4\cdot 5H_2O$, M = Co or Ni and CTC = cyclohexane-1,3,5-tricarboxylate.

A literature search for complexes of CTC found only two communications based on a complex of zinc, pyridine and dimethylformamide and the other is a hydrated compound of erbium(III).[8] There are no known binary first row divalent transition metal complexes. For BTC (BTC = benzene-1,3,5-tricarboxylate) there are at least ten known examples and many of them possess large cavities.[9] However, so far none of these structurally characterized compounds of BTC has shown any long-range magnetic ordering. There is only one example that exhibits long-range magnetic ordering, but its structure has not been determined. We anticipate CTC to show more diverse coordination polymers because of its flexibility, compared to the rigid BTC, and its two possible isomers (Scheme 1). We have employed the technique of hydrothermal synthesis, which is well suited to the preparation of crystals of synthetic minerals, new inorganic materials and metal-organic framework polymers.[9,10]

Experimental

The syntheses were carried out in home-built, Teflon-lined, cylindrical, stainless steel pressure bombs with a maximum capacity of either 40 or 120 ml. X-Ray powder diffraction data were collected using a flat-plate geometry on a Siemens D-500 with Co-Kα (1.789 Å) radiation at room temperature.

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†The IUPAC name for nitronyl nitroxide is 4,4,5,5-tetramethyl-3-oxido-4,5-dihydro-1*H*-imidazol-3-ium-1-oxyl.

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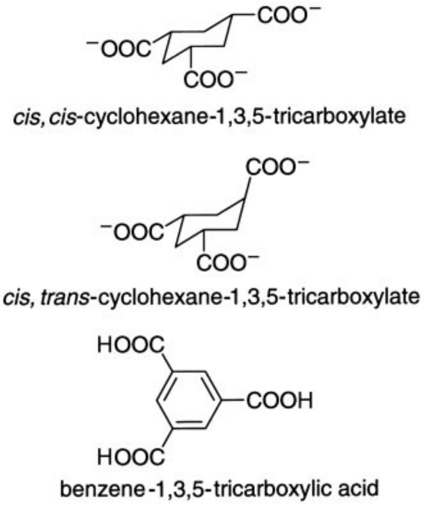

Scheme 1 Possible stereochemistries of cyclohexane-1,3,5-tricarboxylate and benzene-1,3,5-tricarboxylate.

Thermogravimetric analyses (20 to 900 °C) were performed at a rate of 5 °C per minute in a constant flow of air on a SETARAM TGA-DTA system. Infrared spectra were recorded by transmission through fine particles of the compounds dispersed on a KBr plate. UV–Vis spectra were obtained from the compounds dispersed in oil and held between two silica plates by use of a Hitachi U-3000 spectrometer. The temperature and field dependence of the magnetization of the complexes was determined on a Quantum Design MPMS-XL SQUID magnetometer operating in the temperature range 2–300 K and at fields up to 5 T. A Princeton Applied Research Vibrating Sample magnetometer was also used in the temperature range 4–300 K and at fields up to 1.8 T.

All chemicals were purchased from Aldrich or Fluka and used without purification.

Preparation of $[Co_3(CTC)_2(\mu\text{-}H_2O)_2(H_2O)_2]\cdot5(H_2O)$ (1)

$Co(NO_3)_2\cdot6H_2O$ (0.5 g) was dissolved in distilled water (*ca.* 20 ml) and a solution of *cis,cis*-cyclohexane-1,3,5-tricarboxylic acid (0.51 g) and NaOH (0.10 g) in distilled water (*ca.* 20 ml) was added. The mixture was placed in the Teflon liner of an autoclave, sealed and heated to 170 °C for 1 day. It was allowed to cool to room temperature in a water bath. Violet crystals of **1** were harvested by decantation from the clear pink solution. The crystals were washed with water and acetone and dried in air.

Calcd for **1**; $Co_3O_{21}C_{18}H_{36}$: C, 28.25; H, 4.74; found: C, 27.97; H, 4.72%. Infrared: 600s, 705m, 725m, 773s, 894w, 919w, 972w, 1039w, 1140w, 1218w, 1267w, 1281w, 1295w, 1330w, 1353s, 1411vs, 1440sh, 1533sh, 1596vs, 1660sh, 2928w, 2963w, 3340s br cm^{-1}.

Preparation of $[Ni_3(CTC)_2(\mu\text{-}H_2O)_2(H_2O)_2]\cdot5(H_2O)$ (2)

Compound **2** was prepared by a similar procedure to that described above using $Ni(NO_3)_2\cdot6H_2O$ (0.5 g) to yield green crystals of the analogous nickel complex.

Calcd for **2**; $Ni_3O_{21}C_{18}H_{36}$: C, 28.28; H, 4.75; found: C, 28.09; H, 4.67%. Infrared: 600s, 702m, 721m, 770s, 890w, 916w, 967w, 1036w, 1137w, 1218w, 1267w, 1280w, 1292w, 1330w, 1354s, 1411vs, 1440sh, 1533sh, 1592vs, 1662sh, 2928w, 2963w, 3340s br cm^{-1}.

X-Ray crystallography and structure solution

Selected single crystals were glued on the tip of a glass fiber. Diffraction data for the complexes were collected on a Bruker SMART APEX CCD area detector employing the ω-scan mode at room temperature. The diffractometer was supplied with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[11] The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of the coordinated water molecules were located from difference Fourier maps, whereas those of the water molecules in the cavities and those associated with O(9), O(10) and O(11) for complexes **1** and **2** were not located. Toward the end of the refinement of the structure, the thermal ellipsoid of O(11) and the short O–O distance indicated disorder and were finally refined as 50% occupancy at the two sites. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections $[I > 3.00\sigma(I)]$ and n variable parameters. They converged (large parameter shift was σ times its esd) with agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$. No extinction corrections have been applied. Details of crystallographic data are collected in Table 1. CCDC reference numbers 159142 and 159143. See http://www.rsc.org/suppdata/jm/b1/b101531l/ for crystallographic files in .cif or other electronic format.

Results and discussion

Syntheses and structures of 1 and 2

As is the case for the unsaturated benzene-1,3,5-tricarboxylate acid (H_3BTC, trimesic acid),[9] the saturated cyclohexane-1,3,5-tricarboxylic acid (H_3CTC) is able to carry three different charges depending on the pH of the reaction. In most cases the binary complexes of these acids with divalent metals are trivalent and the consequent formulation is $M_3(acid)_2\cdot nH_2O$. The present compounds have the same stoichiometry. It is interesting to note that hydrothermal synthesis provides, in general cases, crystals or powders of the less soluble phases, while metathesis of a dicarboxylic acid, for example, with a divalent transition metal ion in water usually forms soluble complexes, such as the ionic $M(H_2O)_6{}^{2+}(acid)^{2-}$, $[M(H_2O)_4(acid)]_\infty$ chains or $[M(H_2O)_2(acid)]_\infty$ layers.

The X-ray crystal structure analyses of **1** and **2** revealed that the complexes are isomorphous (Table 1) and show the expected lattice contraction on going from divalent cobalt with an ionic radius of 0.89 Å to nickel with 0.83 Å. The crystals belong to the triclinic system, $P\bar{1}$ with $a = 7.799(2)$, $b = 9.212(1)$, $c = 10.784(2)$ Å, $\alpha = 107.595(3)$, $\beta = 92.877(3)$, $\gamma = 110.248(3)°$, $V = 682.4(2)$ Å^3 and $Z = 2$ for **1** and $a = 7.694(1)$, $b = 9.210(1)$, $c = 10.764(2)$ Å, $\alpha = 108.598(3)$, $\beta = 92.300(3)$, $\gamma = 109.814(3)°$, $V = 670.6(2)$ Å^3 and $Z = 2$ for

Table 1 Crystallographic details for compounds **1** and **2**

	1	**2**
Formula	$Co_3O_{21}C_{18}H_{36}$	$Ni_3O_{21}C_{18}H_{36}$
Molecular weight	382.63	382.28
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	7.799(2)	7.694(1)
b/Å	9.212(2)	9.210(1)
c/Å	10.784(2)	10.764(2)
α/°	107.595(3)	108.598(3)
β/°	92.877(3)	92.300(3)
γ/°	110.248(3)	109.814(3)
V/Å^3	682.4(2)	670.6(2)
Z	2	2
D_c/g cm^{-3}	1.862	1.893
μ(Mo-Kα)/cm^{-1}	18.97	21.81
No. of reflections measured	4053	3986
No. of observations $[I > 3.00\sigma(I)]$	2677	2503
R^a (R_w)	0.037 (0.052)	0.045 (0.056)

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$

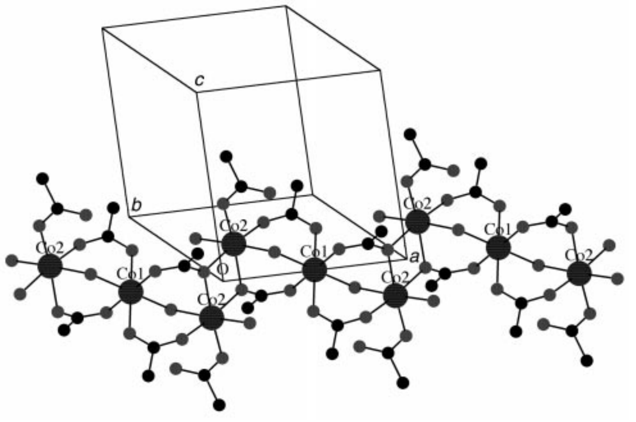

Fig. 1 Structure of a single chain of **1** showing the bridging H_2O and the modes of coordination of the carboxylate groups.

2. The asymmetric unit contains one and a half metal atoms, one CTC and four and a half molecules of water.

Since the two compounds are isostructural we will restrict our description to only the cobalt compound and we only mention pertinent points for the nickel where appropriate. The structure is formed from one-dimensional chains (Fig. 1) of octahedral cobaltous ions, CoO_6, parallel to the *x*-axis, and which are connected to one another *via* the CTC units to form a three-dimensional framework having sizable channels along all three crystallographic directions (Fig. 2). Selected bond lengths and angles are listed in Table 2. The repeating structural motif is a trimer consisting of one crystallographically independent Co(1) ion, which is located on the crystallographic special position, and two symmetry related Co(2) and Co(2′) ions. All the cobalt ions exhibit a slightly distorted octahedral geometry comprising six oxygen atoms of the CTC ligands and water molecules. The coordination geometries about Co(1) and Co(2) in the trinuclear unit are different. For Co(1) it involves two oxygen atoms of the bridging water molecules [O(7) and O(7′)] coordinated at the *trans*-positions and the four oxygen atoms of the CTC ligands [O(1), O(1′) and O(3), O(3′), respectively] and thus three different Co–O bond lengths. The longest distances of bridging water molecules [2.217(2) Å] are indicative of the axially elongated octahedral geometry of Co(1). This is in contrast to the hydroxide-bridged 1D-coordination polymer, $Co_3(OH)_2(squarate)_2{\cdot}3H_2O$,[12] in which the shortest bond length [2.064(2) Å] indicates an axially compressed octahedral geometry. For the Co(2), the bridging water molecule O(7) and terminal water molecule O(8) coordinate in the *trans*-position to each other. Four oxygen atoms of different CTCs [O(4), O(2) and O(2′) and O(5)] coordinate to Co(2) to complete its octahedral geometry. The Co(1) and Co(2) ions are bridged by two carboxylate groups and one water molecule to afford the repeating trinuclear unit. Co(2) of one trimer and Co(2′) in the neighboring trimer share one edge each of their octahedra [O(2) and O(2′)] to form the zig-zag

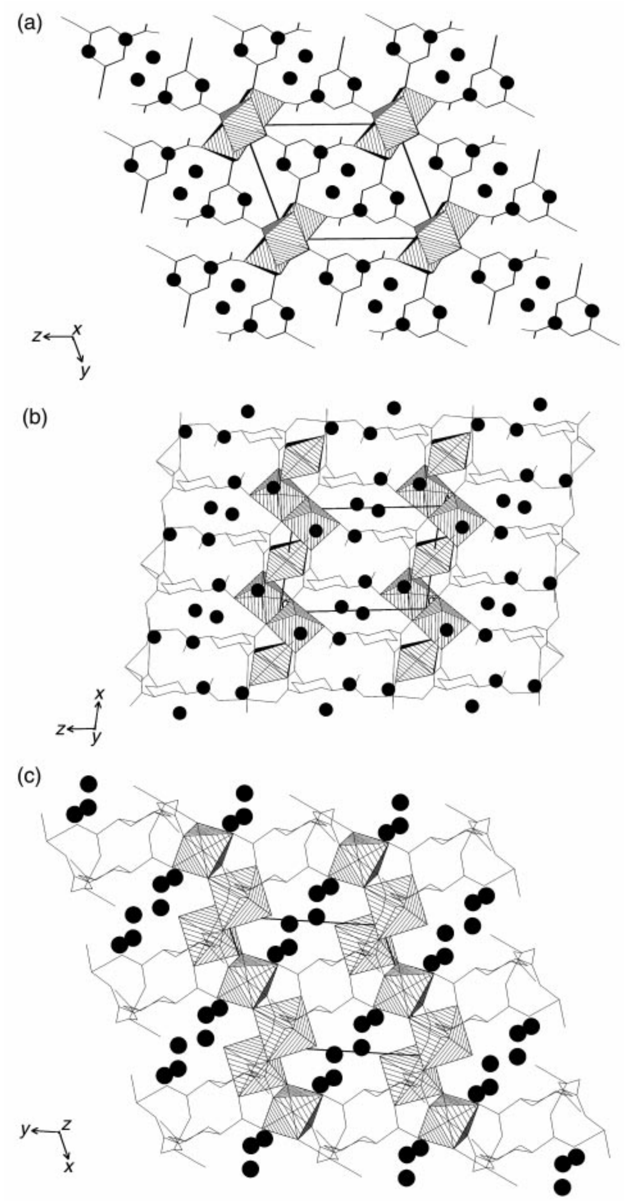

Fig. 2 Projection of the structure of **1** along the (a) *x*-, (b) *y*- and (c) *z*-axis showing the different shape of the channels. The oxygen atoms of the water molecules are shown as black circles.

Table 2 Selected bond lengths and angles of **1** and **2**

Bond length/Å	M = Co	M = Ni
M(1)–O(1)	2.102(2)	2.077(3)
M(1)–O(7)	2.217(2)	2.137(3)
M(2)–O(2′)	2.109(3)	2.050(3)
M(2)–O(5)	2.029(2)	2.008(3)
M(2)–O(8)	2.103(3)	2.085(3)
M(1)–O(3)	2.047(2)	2.027(3)
M(2)–O(2)	2.088(2)	2.054(3)
M(2)–O(4)	2.034(3)	1.998(3)
M(2)–O(7)	2.144(2)	2.081(3)
Bond angle/°		
O(1)–M(1)–O(1′)	180.0	180.0
O(1)–M(1)–O(3′)	88.5(1)	89.1(1)
O(1)–M(1)–O(7′)	100.87(9)	99.9(1)
O(3)–M(1)–O(7)	90.67(10)	89.4(1)
O(7)–M(1)–O(7′)	180.0	180.0
O(2)–M(2)–O(4)	95.2(1)	96.2(1)
O(2)–M(2)–O(7)	85.98(10)	88.2(1)
O(2′)–M(2)–O(4)	171.7(1)	172.8(1)
O(2′)–M(2)–O(7)	93.04(10)	92.2(1)
O(4)–M(2)–O(5)	95.1(1)	93.0(1)
O(4)–M(2)–O(8)	90.6(1)	88.0(1)
O(5)–M(2)–O(8)	92.9(1)	90.6(1)
M(1)–O(7)–M(2)	109.9(1)	111.5(1)
O(1)–M(1)–O(3)	91.5(1)	90.9(1)
O(1)–M(1)–O(7)	79.13(9)	80.1(1)
O(3)–M(1)–O(3′)	180.0	180.0
O(3)–M(1)–O(7′)	89.33(10)	90.6(1)
O(2)–M(2)–O(2′)	76.7(1)	77.3(1)
O(2)–M(2)–O(5)	169.2(1)	170.8(1)
O(2)–M(2)–O(8)	90.3(1)	88.5(1)
O(2′)–M(2)–O(5)	93.1(1)	93.6(1)
O(2′)–M(2)–O(8)	87.8(1)	89.0(1)
O(4)–M(2)–O(7)	87.99(10)	90.5(1)
O(5)–M(2)–O(7)	91.09(10)	92.9(1)
O(7)–M(2)–O(8)	175.9(1)	176.3(1)
M(2)–O(2)–M(2)	103.3(1)	102.7(1)

1D-chain structure which runs along the *x*-axis. The distances between the metal centers within the chain are 3.57 and 3.29 Å for Co(1)–Co(2) and Co(2)–Co(2′), respectively. These are longer than those expected in the brucite $M(OH)_2$ layer compounds (3.15 Å)[13] and in $Co_3(OH)_2(squarate)_2\cdot3H_2O$ (3.16 Å)[12] but are close to 3.286 and 3.551 Å in $Co_2(OH)_2(BDC)$,[14] where BDC = benzenedicarboxylate. The zig-zag chains are characterized by bond angles Co(1)–O(7)–Co(2) and Co(2)–O(2)–Co(2) of 109.9(1)° and 103.3(1)°, respectively. An intrachain hydrogen bonding interaction is found between the bridging oxygen O(7) and carboxylate oxygen O(6) [O(6)···O(7), 2.596(4) Å]. Atom O(7) acts as a hydrogen atom donor and O(5) acts as a hydrogen atom acceptor.

As expected the CTC adopts the same isomeric form as the starting acid. In the present case it is a trivalent anion and each carboxylate group is charge equivalent. As already known from the chemistry of BTC there is the possibility of having different coordination modes of the carboxylate groups of one acid.[15] In the present compounds, we observe three different coordination modes of the three groups (see Fig. 4b). One is monodentate, the second is bidentate and in the third the carboxylate groups coordinate to three independent metal atoms. The consequence of these differences is discussed further in the Infrared section (*vide infra*). All the cyclohexane rings of the bridging ligands exhibit the chair form.

The three-dimensional structure is reinforced by the presence of the strong Co–O bonds with the CTC units. The size and shape of the CTC prevent any possible interpenetration of the lattice. The result is the striking stability of a compound with sizable channels running in several directions. These channels are filled with water molecules (five per formula unit); their elevated temperature factors and the lack of observation of their associated hydrogen atoms suggest that these molecules are fairly mobile within the channels but limited by weak hydrogen bonds with the framework. The short interchain metal–metal distances are 8.0 Å [Co(1)–Co(2)] and 9.3 Å [Co(2)–Co(2)]. The water molecule O(9) acts as a hydrogen bonding acceptor for the bridging oxygen atom O(7) and coordinated water molecule O(8) in a different chain [O(7)···O(9), 2.982(4) Å; O(8)···O(9), 2.893(4) Å]. Thus the chains are interlinked along *b*-axis, not only by CTC, but also by hydrogen bonding interactions. The atom O(10) also interacts with water molecule O(9) and carboxylate oxygen O(6) through hydrogen bonding [O(9)···O(10), 2.742(6) Å; O(6)···O(10) 2.910(6) Å].

Infrared studies

The infrared spectra of the compounds are shown in Fig. 3 and the band wavenumbers are given in the Experimental. The spectra are characterized by a broad band at 3340 cm^{-1} due to the vibrational modes of water. A couple of weak bands at *ca.* 2950 cm^{-1} identify the C–H modes of the cyclohexane rings. At the other extreme, at low energies, are found the modes that involve the metal atoms and there is a consistent difference of a few cm^{-1} between those of cobalt and those of nickel. In the middle of the spectra is a series of strong bands due to the carboxylate vibrational modes. In theory, these bands are sensitive to the nature of the bonding and the coordination mode with the metal ions.[16] Depending on the number of bonds to the surrounding metals, several limits have been established (Fig. 4a). Here, we have for the first time an acid that displays three very different coordination modes (Fig. 4b). While the first carboxylate unit within the acid is singly coordinated, the second is doubly and the third is triply coordinated. Consequently, any definite assignment is not possible. Single coordination is found in $Co_5(OH)_8(dicarboxylate)\cdot nH_2O$[7b] and the symmetric and antisymmetric stretching modes are at 1392 and 1542 cm^{-1}. Double coordination is found in $Co(H_2O)_2(terephthalate)$[14] where the corresponding modes are slightly spread out at 1378 and 1546 cm^{-1}. Triple coordination has been identified in $Co_2(OH)_2(terephthalate)$[14] and the modes are observed at 1368 and 1592 cm^{-1}: an even larger difference in energy than for the double and single coordination modes. In the present case, if these different bands are present, they are heavily overlapped; some shoulders

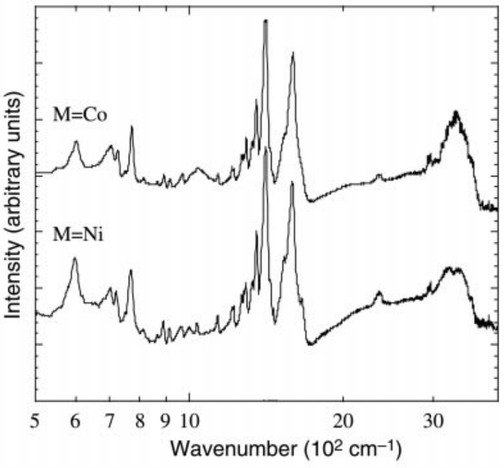

Fig. 3 Infrared spectra of **1** and **2**.

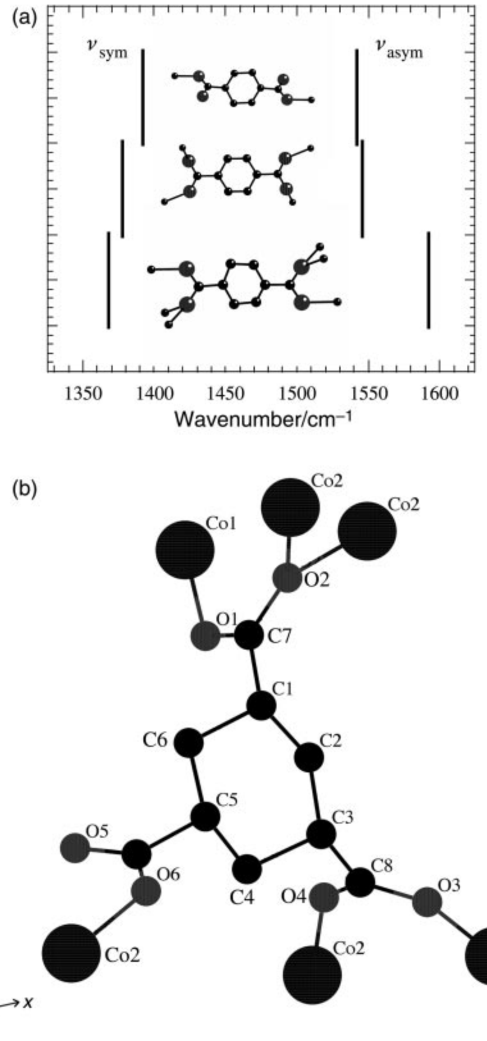

Fig. 4 (a) Observed frequencies of the symmetric and asymmetric modes of the carboxylate ion for different coordination geometries. (b) Coordination modes of cyclohexane-1,3,5-tricarboxylate in **1** and **2**.

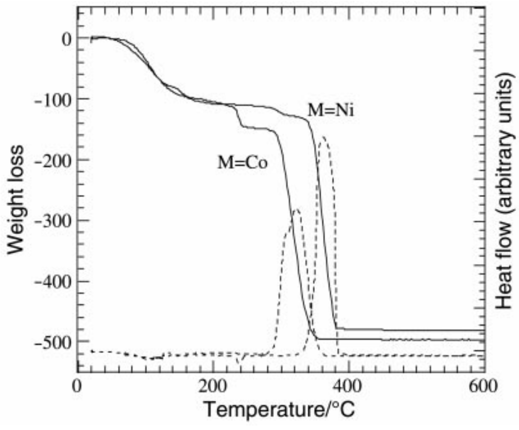

Fig. 5 Thermogravimetry (solid lines) and heat flow (dotted lines) for **1** and **2**.

on the main peak at 1596 cm^{-1} can possibly be attributed to these modes. The absolute frequencies of these bands are also modified by overlap with the bending mode of the water molecules.

Thermogravimetry

The results of the thermal analysis of the compounds and the associated heat flow are shown in Fig. 5. In both cases the crystals lose a total of five molecules of water on heating up to 200 °C. The loss of water starts as low as 50 °C in both cases. A difference between the two compounds is seen at the second stage of water loss, at which point two water molecules are lost at a lower temperature for Co, but only one molecule at a much higher temperature for Ni. The difference in decomposition temperatures between the cobalt and nickel compounds may be due to the more compact structure for the latter. All of processes involving loss of water molecules are endothermic. The final step is exothermic and corresponds to the decomposition of the organic moiety. The final products are not the expected oxides, Co_3O_4 and NiO, but products of higher masses. These are being investigated further as is the dehydration–hydration process. We are also measuring the surface area and porosity.

Magnetic properties

The magnetic properties have been studied as a function of both temperature and magnetic field. The temperature dependence of the inverse susceptibilities of the two compounds and the products of susceptibility and temperature are shown in Fig. 6. The compounds behave as paramagnets at high temperatures with Curie constants of 8.7(5) for **1** and 4.03(1) cm^3 K mol^{-1} for **2** and Weiss constants of $-27(2)$ for **1** and $-6.0(4)$ K for **2**. The Curie constants are within the range expected for high spin M^{II}.[17] The triangular arrangement of the moments appears to have some implications associated with magnetic frustration.[18] In both cases the effective moment decreases as the temperature is lowered before increasing either gradually in the case of nickel or more abruptly for cobalt. The minimum in the effective moment is observed at 4 K for **1** and at a much higher temperature of 190 K for **2**. This type of behavior may be associated with competition between antiferromagnetic and ferromagnetic interactions. It is possible that the two compounds display different dominant magnetic interactions: *viz*. antiferromagnetic for **1** and ferromagnetic for **2**. The sharp upturn at low temperature may suggest uncompensated behavior as expected for a ferrimagnetic alignment of moments within the repeating trimeric unit. The isothermal magnetization at 2 K is shown for both compounds in Fig. 7. For **1** it increases gradually to a field of *ca*. 4 kOe and then becomes linear up to the maximum field of 50 kOe. This behavior is due to a combination of AF coupling and depopulation of the lowest Kramers doublet, which favors an effective $S=\frac{1}{2}$ at low temperatures.[19] For **2** the magnetization increases as expected for a Brillouin function. It saturates at just over 2 μ_B per nickel at 50 kOe. The sharp rise in magnetization at low temperatures suggests that long-range magnetic ordering may occur below 2 K. Work is in progress to search for this phenomenon.

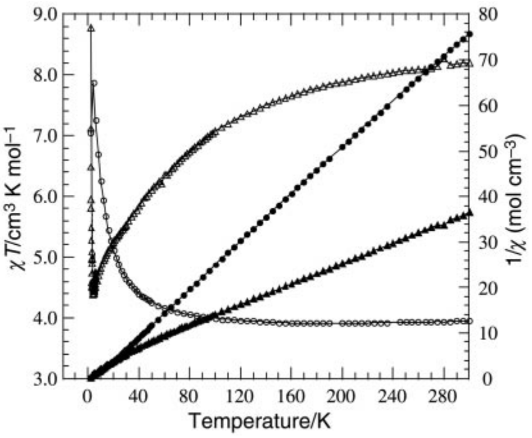

Fig. 6 Temperature dependence of the product of susceptibility and temperature (open symbols) and inverse susceptibility (closed symbols) for **1** (triangles) and **2** (circles).

Conclusion

Cyclohexane-1,3,5-tricarboxylate proved to be another good multitopic unit to generate open framework structures with sizable channels that can accommodate water molecules. The one-dimensional chain appears to be a strong structural unit in the stabilization of the framework. Due to the different coordination and spin topology the compounds behave as short-range coupled low-dimensional chains with a tendency to ferrimagnetic alignment of the moment for the cobalt compound and ferromagnetic for the nickel compound.

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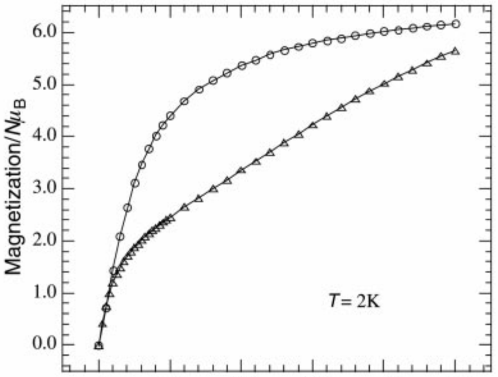

Fig. 7 Isothermal magnetization at 2 K for **1** (triangles) and **2** (circles).

References

1 P. Day, *J. Chem. Soc., Dalton Trans.*, 2000, 3483.

2 (*a*) P. Day, M. Kurmoo, T. Mallah, I. R. Marsden, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseau, J. Gaultier, G. Bravic and L. Ducasse, *J. Am. Chem. Soc.*, 1992, **114**, 10722; (*b*) M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209; (*c*) I. R. Marsden, M. L. Allan, R. H. Friend, M. Kurmoo, D. Kanazawa, P. Day, D. Chasseau, G. Bravic and L. Ducasse, *Phys. Rev.*, 1994, **B50**, 2118; (*d*) H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe and P. Cassoux, *J. Am. Chem. Soc.*, 1996, **118**, 368; (*e*) E. Coronado and C. J. Gomez-Garcia, *Chem. Rev.*, 1998, **98**, 273; (*f*) E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia and V. Laukhin, *Nature*, 2000, **408**, 447.

3 (*a*) P. G. Lacroix, *Eur. J. Inorg. Chem.*, 2001, 339; (*b*) S. Benard, P. Yu, J. P. Audiere, E. Riviere, R. Clement, J. Guilhem, L. Tchertonov and K. Nakatani, *J. Am. Chem. Soc.*, 2000, **122**, 9444.

4 (*a*) *Magnetism: A Supramolecular Function*, ed. O. Kahn, *NATO ASI Ser., Ser. C*, 1996, **C484**; (*b*) *Metal-Organic and Organic Molecular Magnets*, eds. P. Day and A. E. Underhill, *Philos. Trans. R. Soc. London*, 1999, **357**; (*c*) *Molecular Magnetism, New Magnetic Materials*, eds. K. Itoh and M. Kinoshita, Gordon Breach, 2000.

5 See for example: (*a*) Proceedings of the International conference on Synthetic Metals, *Synth. Met.*, 1999 103; (*b*) Proceedings of the International Conference on Molecule-based Magnets, *Mol. Cryst. Liq. Cryst.*, 1999, 334.

6 (*a*) G. Lagaly, *Appl. Clay Sci.*, 1999, **15**, 1; (*b*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (*c*) F. Millange, R. I. Walton, L. Lei and D. O'Hare, *Chem. Mater.*, 2000, **12**, 1990; (*d*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.

7 (*a*) M. Kurmoo, *J. Mater. Chem.*, 1999, **9**, 2595; (*b*) M. Kurmoo, *Philos. Trans. R. Soc. London, Ser. A*, 1999, **357**, 3041; (*c*) M. Kurmoo, P. Day, A. Derory, C. Estournès, R. Poinsot, M. J. Stead and C. J. Kepert, *J. Solid State Chem.*, 1999, **145**, 452; (*d*) M. Kurmoo, *Chem. Mater.*, 1999, **11**, 3370; (*e*) M. Kurmoo, *Mol. Cryst. Liq. Cryst.*, 2000, **341**, 395; (*f*) M. Kurmoo, *Mol. Cryst. Liq. Cryst.*, 2000, **342**, 167.

8 (*a*) O. M. Yaghi, R. Jernigan, H. Li, C. E. Davis and T. L. Groy, *J. Chem. Soc., Dalton Trans.*, 1997, 2383; (*b*) L. Pan, E. B. Woodlock, X. Wang and C. Zheng, *Inorg. Chem.*, 2000, **39**, 4174.

9 (*a*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2000, **122**, 5158; (*b*) C. J. Kepert, T. J. Prior and M. J. Rosseinsky, *J. Solid State Chem.*, 2000, **152**, 261; (*c*) O. M. Yaghi, C. E. Davis, G. Li and H. Li, *J. Am. Chem. Soc.*, 1997, **119**, 2861; (*d*) O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096; (*e*) M. J. Platter, A. J. Roberts, J. Marr, E. E. Lachowski and R. A. Howie, *J. Chem. Soc., Dalton Trans.*, 1998, 797; (*f*) M. J. Platter, R. A. Howie and A. J. Roberts, *Chem. Commun.*, 1997, 893; (*g*) M. J. Platter, M. R. St. J. Foreman, E. Coronado, C. J. Gomez-Garcia and A. M. Z. Slawin, *J. Chem. Soc., Dalton Trans.*, 1999, 4209; (*h*) M. R. St. J. Foreman, T. Gelbrich, M. B. Hursthouse and M. J. Platter, *Inorg. Chem. Commun.*, 2000, **3**, 234; (*i*) A. Michaelides, S. Skoulika, V. Kiritsis, C. Raotopoulou and A. Terzis, *J. Chem. Res.*, 1997, 204; (*j*) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148; (*k*) G. O. H. Gutschke, M. Molinier, A. K. Powell, R. E. P. Winpenny and P. T. Wood, *Chem. Commun.*, 1996, 823.

10 (*a*) D. J. Price, A. K. Powell and P. T. Wood, *J. Chem. Soc., Dalton Trans.*, 2000, 3566; (*b*) R. M. A. Lieth, *Preparation and crystal growth of materials with layered structure*, Plenum, New York, 1977.

11 G. M. Sheldrick, *Crystallographic Computing*, Oxford University Press, 1985.

12 G. O. H. Gutschke, D. J. Price, A. K. Powell and P. T. Wood, *Angew. Chem.*, 1999, **38**, 1088.

13 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, 1984.

14 M. Kurmoo, H. Kumagai, M. A. Green, B. W. Lovett, S. J. Blundell, A. Ardavan and J. Singleton, *J. Solid State Chem.*, 2001, in the press.

15 J. Tao, M-L. Tong and X-M. Chen, *J. Chem. Soc., Dalton Trans.*, 2000, 3669 and references therein.

16 K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, John Wiley, New York, 1986.

17 (*a*) R. L. Carlin, *Magnetochemistry*, Springer Verlag, New York, 1986; (*b*) O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993.

18 J. E. Greedan, *J. Mater. Chem.*, 2001, **11**, 37.

19 F. E. Mabbs and D. J. Machin, *Magnetism and transition metal complexes*. Chapman and Hall, London, 1973.