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Hybrid open frameworks (MIL-*n*). Part 5† Synthesis and crystal structure of MIL-9: a new three-dimensional ferrimagnetic cobalt(II) carboxylate with a two-dimensional array of edge-sharing Co octahedra with 12-membered rings

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$Co_5(OH)_2(C_4H_4O_4)_4$, a new cobalt(II) succinate with an open framework, was prepared hydrothermally (180 °C, 72 h, autogenous pressure) from a 2 : 3 : 8 : 120 mixture of Co(II) chloride, succinic acid, potassium hydroxide and water. Its monoclinic structure was solved by single crystal X-ray diffraction [space group $P2_1/c$ (no. 14) with $a=9.5631(2)$ Å, $b=9.4538(2)$ Å, $c=12.5554(2)$ Å, $\beta=96.968(1)°$, $V=1126.72(4)$ Å^3, $Z=4$] from 3077 unique reflections [$I\geqslant 2\sigma(I)$], $R1=0.020$ and $wR2=0.054$. The three-dimensional structure is built up from layers of edge sharing octahedra pillared by succinate ions. Within the layers, cobalt octahedra form 12-membered ring windows. Below 10 K, $Co_5(OH)_2(C_4H_4O_4)_4$, exhibits ferrimagnetic behavior.

Introduction

The preparation of three-dimensional open frameworks based on transition metals is one of the most important aims of research due to their practical application as catalysts, hosts in intercalation compounds and their potential electronic properties.[1–3] Among the 3d metal zeolite analogues, some of the most promising and studied materials are those based on cobalt.[4–7] With the utilization of the hydrothermal technique, considerable progress has been reported on the development of open framework compounds based on cobalt, and the literature already contains numerous examples of cobalt phosphates and phosphonates with a large structural variety.[8–14] We recently introduced a new way for obtaining microporous materials in which both organic (dicarboxylates) and inorganic species build the open framework.[3,15,16] We present here the synthesis and characterization of $Co_5(OH)_2(C_4H_4O_4)_4$, a new cobalt carboxylate with a two dimensional array of edge-sharing Co^{2+} octahedra pillared by succinate ions. $Co_5(OH)_2(C_4H_4O_4)_4$ is denoted MIL-9 for Materials of Institut Lavoisier.

Experimental

Materials and methods

Hydrothermal reactions were carried out in 23 ml Teflon-walled Parr acid digestion bombs. X-Ray powder diffraction data were collected on a Siemens D5000 diffractometer (Cu-Kα radiation). FTIR spectra were obtained on a Nicolet Magna-IR 550 spectrometer. TG measurements were done using a TA-instrument 2050 thermo-analyser (oxygen gas flow, 5 °C min^{-1}). Susceptibility measurements were carried out using a SQUID magnetometer; data were not corrected for diamagnetism.

Hydrothermal synthesis and characterization of $Co_5(OH)_2(C_4H_4O_4)_4$

A hydrothermal synthesis has been set up using $CoCl_2\cdot 6H_2O$ as the cobalt source. The starting mixture, corresponding to the molar composition of 2 $CoCl_2\cdot 6H_20$: 3 CO_2H-$(CH_2)_2CO_2H$: 8 KOH : 120 H_2O, was homogenized for 10 min in an ultrasonic bath and the resulting solution was heated for three days at 180 °C under autogenous pressure (pH around 6). The resulting solid phase was collected by filtration, washed with distilled water and dried at room temperature. The solid product was a single phase with large hexagonal dark red crystals of the title compound and was obtained in a yield based on cobalt of around 70%. The X-ray powder diffraction pattern is in agreement with that calculated after resolution of the structure. A single crystal of suitable size was used for structure determination by X-ray diffraction. IR spectra exhibited the following relevant features (KBr pellet): a narrow band due to the hydroxyl group, ν(CoO–H) 3330 cm^{-1}; ν(C–H) stretching bands characteristic of CH_2 groups between 2910 and 3000 cm^{-1}; a very broad band, composed of four peaks between 1510 and 1610 cm^{-1}, associated with the deprotonated carboxylic groups, and the following relevant bands; 1460, 1440, 1420, 1410, 1325, 1305, 1275, 1240, 1225, 1180, 1165, 1035, 865, 810, 680, 660, 565, 510 and 380 cm^{-1}. TG measurements under oxygen gas flow showed a unique and abrupt weight loss around 320 °C characteristic of the combustion of the organic moiety (theoretical weight loss 53%, observed 56%). The resulting product at 350 °C is CoO. Satisfactory elemental analysis was obtained.

Single crystal structure determination

One of the dark red hexagonal crystals of $Co_5(OH)_2(C_4H_4O_4)_4$ (0.5 × 0.3 × 0.15 mm) was glued to a glass fiber and mounted on a Siemens SMART CCD diffractometer using monochromatic molybdenum radiation [λ(Mo$K\alpha$)$=0.7107$ Å]. Intensity data were collected on a one half sphere in 1271 frames with ω scans (width of 0.30° and exposure time 30 s per frame). A summary of crystal data is presented in Table 1. The data collected (7953 total reflections, 3077 unique) were corrected for Lorentz and polarization effects. Absorption corrections were applied using the SADABS program.[17] The structure was solved by direct methods and standard difference Fourier techniques (SHELXL-93).[18] Cobalt and oxygen atoms were first located and all the remaining atoms, including hydrogen

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†Part 4: preceding paper.

Table 1 Summary of crystal data and structure refinement

Formula weight	396.5
Space group	$P2_1/c$
Unit cell dimensions	
a/Å	9.5631(2)
b/Å	9.4538(2)
c/Å	12.5554(2)
β/degrees	96.9680(10)
Volume/Å^3, Z	1126.72(4), 2
D_c/Mg m^3	2.337
Absorption coefficient/mm^{-1}	3.697
F(000)	786
Crystal size/mm	$0.5 \times 0.3 \times 0.15$
θ range for data collection/degrees	2.70–30.24
Limiting indices	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 11$
Goodness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0202$, $wR2 = 0.0540$
R indices (all data)	$R1 = 0.0236$, $wR2 = 0.0551$
Largest diff. peak and hole/e Å^{-3}	0.535 and -0.395

atoms, were found by difference Fourier maps. Refinements (206 parameters) were performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms. The reliability factors converged to $R1(F_O) = 0.020$ and $wR2(F_O{}^2) = 0.054$. Fractional atomic coordinates are given in Table 2 and selected bonds distances and angles in Table 3.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/121.

Results

Structure of $Co_5(OH)_2(C_4H_4O_4)_4$

The three-dimensional framework consists of an infinite two-dimensional array of edge-sharing cobalt octahedra (b, c plane) covalently linked by two different succinate anions (Fig. 1). The layers are stacked along the a axis, the length of which is the interlayer spacing (9.56 Å). Cobalt atoms occupy three different crystallographic sites with an octahedral coordination of oxygen atoms arising from the two succinate ions and one hydroxyl group. A representation of the local connectivity of the three Co^{2+} ions is given in Fig. 2. $Co(1)O_6$ and $Co(2)O_6$ octahedra are strongly distorted, with three short Co–O bond distances (2.02–2.09 Å), two medium (2.17–2.22 Å) and one long [2.368(1) and 2.314(1) Å]. By contrast, Co(3), which lies on an inversion center, has a regular octahedral geometry with Co–O bonds of *ca.* 2.11 ± 0.05 Å. The hydroxide oxygen atom, O(9), is shared between the three distinct cobalt atoms with Co–μ_3-O(H) bonds between 2.02 and 2.11 Å. Only one noticeable hydrogen bond linkage exists in the solid, a bond between the hydrogen atom of the hydroxide group and an oxygen atom of a neighboring octahedron [(O(9)–H(9)···O(3) 2.073 Å]. The metallic oxide framework can be described as an infinite square net of edge-sharing cobalt octahedra. Co(3) octahedra occupy the vertices of this square net. The topology creates lozenge-shaped cavities made from 12 edge-sharing octahedra in which one of the two alkyl chain [carbons C(1)–C(4)] is located (Fig. 3). Each dicarboxylate anions has covalent bonds with the three different cobalt atoms: with one carboxylic group bridging two pairs of cobalt octahedra (Co–μ_2-O, bond lengths between 2.06 and 2.31 Å) and the other linking two cobalt octahedra (Co–μ_1-O, bond lengths between 2.02 and 2.09 Å). The first succinate is in the layers [carbons C(1)–C(4)] while the second one [carbons C(5)–C(8)], in which the same type of linkage occurs, acts as a pillar leading to a three-dimensional structure (Fig. 4). This structure can be estimated as a class IV solid for cobalt compounds in the classification of Stucky.[10]

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (10^{-3} Å^2) for non-hydrogen atoms

Atom	x	y	z	$U_{eq}{}^a$
Co(1)	8853(1)	2072(1)	1645(1)	14(1)
Co(2)	11659(1)	3195(1)	3457(1)	14(1)
Co(3)	10000	0	0	12(1)
O(1)	8741(1)	1902(1)	−127(1)	17(1)
O(2)	9520(1)	2268(1)	3356(1)	18(1)
O(3)	8519(1)	4230(1)	1632(1)	22(1)
O(4)	12546(1)	1280(1)	3921(1)	29(1)
O(5)	11299(1)	2546(1)	1767(1)	17(1)
O(6)	11696(1)	3642(1)	5272(1)	18(1)
O(7)	13551(1)	4184(1)	3464(1)	23(1)
O(8)	6708(1)	1577(1)	1592(1)	22(1)
O(9)	9497(1)	41(1)	1591(1)	13(1)
C(1)	8734(2)	2819(2)	−877(1)	16(1)
C(2)	7740(3)	4072(3)	−913(2)	45(1)
C(3)	6832(2)	4237(2)	12(1)	21(1)
C(4)	12342(2)	−33(2)	4015(1)	17(1)
C(5)	12138(2)	2996(2)	6153(1)	15(1)
C(6)	13747(2)	2938(2)	6425(2)	22(1)
C(7)	15642(2)	5552(2)	3533(2)	26(1)
C(8)	14024(2)	5442(2)	3467(1)	17(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Magnetic properties

The presence of the infinite array of edge sharing Co^{2+} octahedra has, of course, an important effect on the magnetic properties of the compound, with the predicable existence of strong magnetic couplings between the d^7 centers. The temperature dependence of χ^{-1}, measured with a SQUID susceptometer (100 G), is shown in Fig. 5 with the magnetization *vs.* the applied magnetic field at 2 K. The linear fit of $\chi^{-1}(T)$ data above 50 K indicates a Curie–Weiss law ($C = 18.73$ emu mol^{-1} and $\theta_P = -72.5$ K) as well as the room temperature effective moment of 5.5 μ_B per atom which is slightly larger than the commonly observed magnetic moments for independent Co^{2+} octahedra.[19] Around 25 K a marked change in the $\chi^{-1}(T)$ curve, characterized by an important increase of susceptibility, indicates a ferrimagnetic behavior confirmed by the $M(H)$ curve below the critical temperature ($T_C \approx 10$ K). The ferrimagnetism of the title compound can be easily understood from structural considerations and superexchange analysis.[20] Indeed, another way of describing the layers starts from the fact that the different cobalt sites of the structure have different

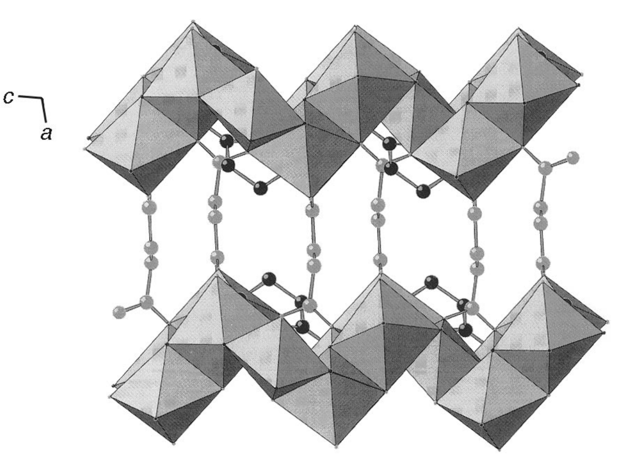


Fig. 1 Representation of the structure parallel to the crystallographic a axis. Black spheres are carbon atoms C(1)–C(4) which connect the octahedra in the cobalt layer. Gray spheres [C(5)–C(8)] correspond to the second succinate ion linking two successive layers.

Table 3 Selected bond lengths (Å) and angles (degrees) for $Co_5(OH)_2(C_4H_4O_4)_4$[a]

Co(1)–O(9)	2.0199(10)	Co(3)–O(1)	2.1587(10
Co(1)–O(3)	2.0649(12)	Co(3)–O(1)^d	2.1587(10)
Co(1)–O(8)	2.0973(12)	O(1)–C(1)	1.279(2)
Co(1)–O(2)	2.1730(11)	O(2)–C(1)^e	1.294(2)
Co(1)–O(1)	2.2211(11)	O(3)–C(4)^a	1.289(2)
Co(1)–O(5)	2.3682(11)	O(4)–C(4)	1.264(2)
Co(2)–O(7)	2.0357(11)	O(5)–C(5)^b	1.284(2)
Co(2)–O(4)	2.0536(12)	O(6)–C(5)	1.289(2)
Co(2)–O(9)^a	2.0634(10)	O(7)–C(8)	1.272(2)
Co(2)–O(5)	2.1960(11)	O(8)–C(8)^c	1.278(2)
Co(2)–O(2)	2.2149(11)	C(1)–C(2)	1.516(2)
Co(2)–O(6)	2.3138(11)	C(2)–C(3)	1.540(3)
Co(3)–O(6)^b	2.0644(11)	C(3)–C(4)^a	1.535(2)
Co(3)–O(6)^e	2.0644(11)	C(5)–C(6)	1.536(2)
Co(3)–O(9)	2.1111(11)	C(6)–C(7)^f	1.541(2)
Co(3)–O(9)^d	2.1112(11)	C(7)–C(8)	1.543(2)
O(9)–Co(1)–O(3)	170.53(5)	O(9)^a–Co(2)–O(2)	81.08(4)
O(9)–Co(1)–O(8)	95.07(4)	O(5)–Co(2)–O(2)	78.37(4)
O(3)–Co(1)–O(8)	94.02(5)	O(7)–Co(2)–O(6)	90.25(5)
O(9)–Co(1)–O(2)	93.45(4)	O(4)–Co(2)–O(6)	85.70(5)
O(3)–Co(1)–O(2)	87.16(4)	O(9)^a–Co(2)–O(6)	79.55(4)
O(8)–Co(1)–O(2)	102.67(5)	O(5)–Co(2)–O(6)	169.99(4)
O(9)–Co(1)–O(1)	82.84(4)	O(2)–Co(2)–O(6)	91.85(4)
O(3)–Co(1)–O(1)	94.28(4)	O(6)^b–Co(3)–O(6)^c	180.0
O(8)–Co(1)–O(1)	91.37(5)	O(6)^b–Co(3)–O(9)	95.53(4)
O(2)–Co(1)–O(1)	165.77(4)	O(6)^c–Co(3)–O(9)	84.47(4)
O(9)–Co(1)–O(5)	83.05(4)	O(6)^b–Co(3)–O(9)^d	84.47(4)
O(3)–Co(1)–O(5)	87.96(4)	O(6)^c–Co(3)–O(9)^d	95.53(4)
O(8)–Co(1)–O(5)	177.31(4)	O(9)–Co(3)–O(9)^d	180.0
O(2)–Co(1)–O(5)	75.58(4)	O(6)^b–Co(3)–O(1)	85.07(4)
O(1)–Co(1)–O(5)	90.31(4)	O(6)^c–Co(3)–O(1)	94.93(4)
O(7)–Co(2)–O(4)	93.89(5)	O(9)–Co(3)–O(1)	82.29(4)
O(7)–Co(2)–O(9)^a	94.83(4)	O(9)^d–Co(3)–O(1)	97.71(4)
O(4)–Co(2)–O(9)^a	162.87(5)	O(6)^b–Co(3)–O(1)^d	94.93(4)
O(7)–Co(2)–O(5)	99.67(5)	O(6)^c–Co(3)–O(1)^d	85.07(4)
O(4)–Co(2)–O(5)	92.23(5)	O(9)–Co(3)–O(1)^d	97.71(4)
O(9)^a–Co(2)–O(5)	100.79(4)	O(9)^d–Co(3)–O(1)^d	82.29(4)
O(7)–Co(2)–O(2)	174.98(5)	O(1)–Co(3)–O(1)^d	180.0
O(4)–Co(2)–O(2)	90.81(5)		
Magnetic couplings			
Within the pentamer		Between pentamers	
Co(1)–O(1)–Co(3)	91.5	Co(1)–O(5)–Co(2)	98.8
Co(1)–O(9)–Co(3)	98.9	Co(1)–O(2)–Co(2)	104.4
Co(1)–O(9)–Co(2)	129.8		
Co(2)–O(9)–Co(3)	97.9		
Co(2)–O(6)–Co(3)	91.9		

Symmetry transformations used to generate equivalent atoms: $^a -x+2,\ y+1/2,\ -z+1/2$; $^b -x+2,\ y-1/2,\ -z+1/2$; $^c x,\ -y+1/2,\ z-1/2$; $^d -x+2,\ -y,\ -z$; $^e x,\ -y+1/2,\ z+1/2$; $^f -x+3,\ -y+1,\ -z+1$.

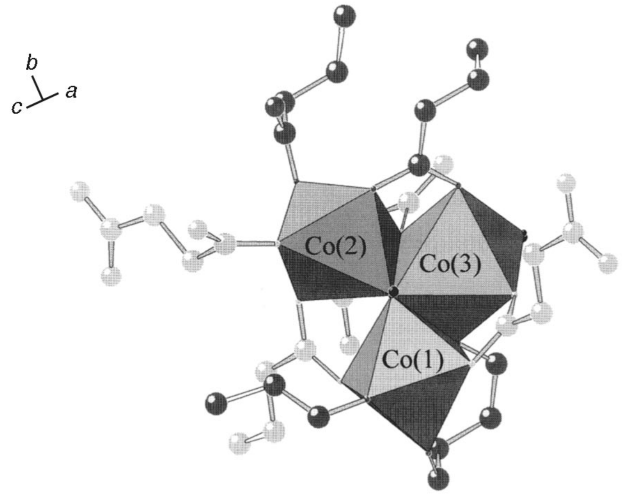


Fig. 2 Local connectivity for the three Co^{2+}. $\{CoO_6\}$ octahedra are represented by a polyhedral representation and organic alkyl chains by a ball and stick representation [black spheres C(1)–C(4) and gray spheres C(5)–C(8)]. The small black sphere corresponds to the hydroxyl group O(9)–H.

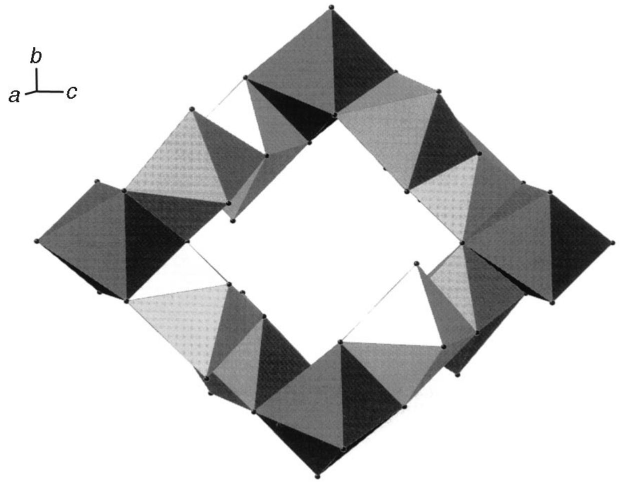


Fig. 3 Polyhedral representation of the twelve-membered rings cavity defined by the 2-D array of Co–O–Co. The organic moieties, covalently bond to cobalt atoms, have been omitted for clarity.

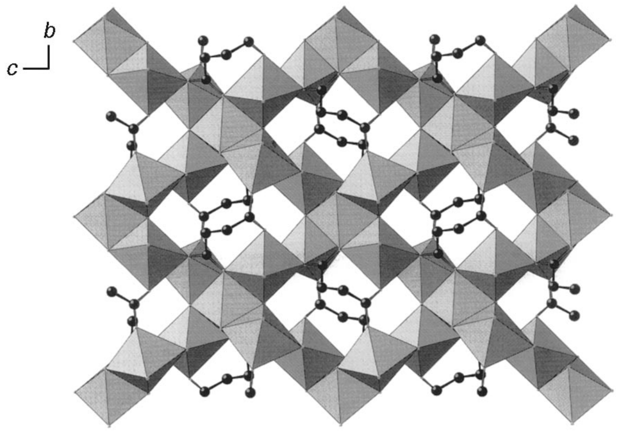


Fig. 4 Representation of one layer of the structure of $Co_5(OH)_2(C_4H_4O_4)_4$. $\{CoO_6\}$ octahedra are represented by a polyhedral representation and organic alkyl chains by a ball-and-stick representation.

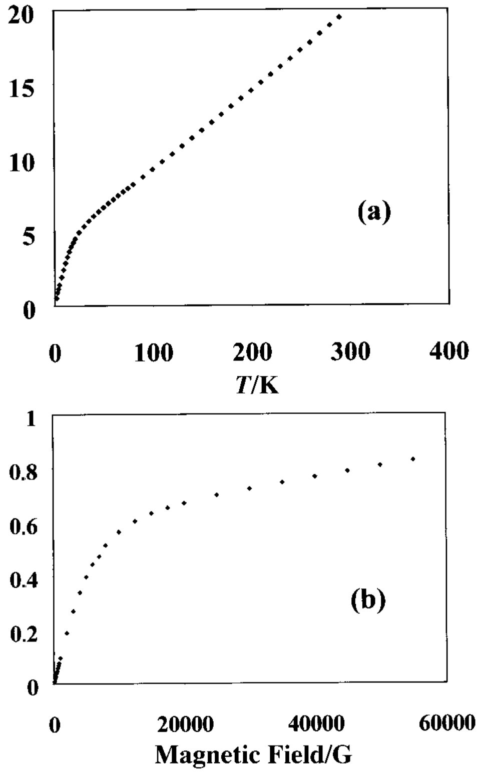


Fig. 5 Temperature dependence of χ^{-1} (a) and $M(H)$ at 2 K (b).

multiplicities, the Wyckoff positions being 4e, 4e and 2a for Co(1), Co(2) and Co(3) respectively. Therefore, Co(3) is surrounded by two Co(1) and two Co(2), and generates a pentameric unit in which Co(1) and Co(2) octahedra are linked by corners [O(9) atoms] and share edges with Co(3) (Fig. 6). The layer is generated by the connection of these pentamers by edges. In terms of superexchange magnetic couplings, this structure exhibits, according to Goodenough,[20] 180° [Co(1)–Co(2)] and 90° interactions [Co(1)–Co(3), Co(2)–Co(3), Co(1)–Co(2) (between pentamers)]. Table 3 gives the values of the different superexchange angles. If the d^7–d^7 superexchange 180° interactions are always antiferromagnetic, the 90° ones can be either antiferromagnetic (e_g–p–t_{2g}) or ferromagnetic (e_g–p_σ–p_σ–e_g), the latter case being illustrated for instance by Co_2PO_4F.[21] In our case, the value of θ_P (−72 K) indicates moderate antiferromagnetic interactions. If all the interactions, whatever the superexchange angle, were AF, a larger value of θ_P would be expected.

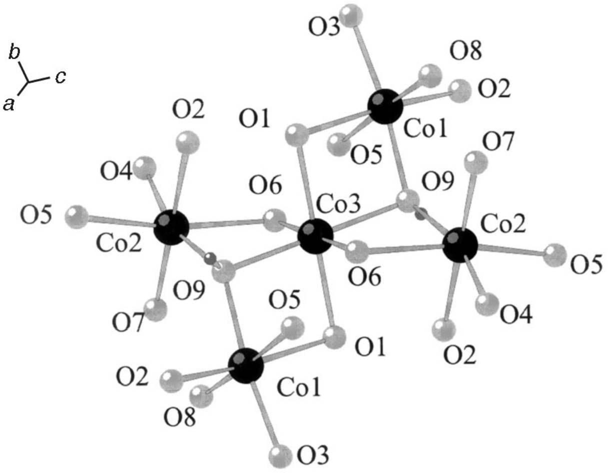
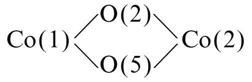


Fig. 6 Representation showing the connectivity between cobalt octahedra within the pentamers. The organic chains have been omitted for clarity.

Therefore, the observed ferrimagnetic behavior can be justified assuming (i) antiferromagnetic couplings within the pentamer, which leads, owing to the different multiplicities of the Co sites, to a resulting moment of $^{3\mu}Co^{2+}$; (ii) a ferromagnetic coupling between the pentamers to avoid the compensation of the moments, which implies a



$$Co(1)\begin{matrix} \diagup O(2) \diagdown \\ \diagdown O(5) \diagup \end{matrix}Co(2)$$

ferromagnetic interaction in agreement with the largest superexchange angles of the structure, and (iii) a ferromagnetic coupling between the layers. Such a proposal is currently being studied by neutron diffraction.

Conclusion

Owing to the difficulties in synthesizing pure metal oxides with an open framework, synthetic strategies using organic agents are of interest for the self-assembly of infinite solids.[3,6] Dicarboxylic acids have long been known to act as chelating ligands, generating isolated metal complexes. With the synthesis of $Co_5(OH)_2(C_4H_4O_4)_4$ we have demonstrated that, using a hydrothermal technique, dicarboxylic acids can participate in the skeleton with inorganic species and lead to non templated open framework solids, in which they act both as part of the oxide sheet and as pillars between the latter. This type of building leads also to magnetic solids. Study of the magnetic structure of the title compound is currently in progress. Complementary studies are on the way for tailoring the structure by changing the length of the dicarboxylate chains.

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