Construction of Two- and Three-Dimensional Coordination Polymers from Cobalt Trimesate

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Two new cobalt 1,3,5-benzenetricarboxylate (trimesic acid, TMA) coordination polymers were synthesized and structurally characterized: $[Co_3(H_2O)_6(TMA^{3-})(TMA^{2-})(TMA^{1-})]\cdot 2H_2O$ (**1**) and $K[Co_3(TMA^{3-})(TMA^{2-})_2]\cdot 5H_2O$ (**2**). **1** crystallizes in the hexagonal system, space group $P6_522$ (no. 179), with $a = 16.7265(2)$, $c = 20.5822(4)$ Å, $V = 4986.9(2)$ Å^3, and $D_c = 1.889$ g cm^{-3}. **2** is monoclinic, space group $P2/c$ (no. 13), with $a = 9.6096(1)$, $b = 12.5610(1)$, $c = 13.9736(2)$ Å, $\beta = 109.239(1)°$, $V = 1592.50(3)$ Å^3, and $D_c = 1.938$ g cm^{-3}. **1** is two-dimensional and formed by a "dense" stacking of $\{Co_3(H_2O)_6(TMA^{3-})(TMA^{2-})(TMA^{1-})\}$ layers. In compound **2** the connection of sinusoidal chains of cobalt octahedra by two types of trimesate ions gives a three-dimensional network with pentahydrated channels.

Introduction

Solid-state coordination chemistry is currently a successful way to control the topologies of extended networks. Yaghi et al. have demonstrated that polydentate ligands, as 1,3,5-benzenetricarboxylate ions, are suitable for constructing porous solids.[1] Carboxylate ligand has a great ability to adopt different bonding modes, unidentate, bidentate, or bridging and satisfied therefore many metal coordination preferences.[2] Rigid carboxylate ligands, with desired geometry, have been used to specifically design topologies, the organic acting as a spacer between metal sites.[3] However, predictive coordination chemistry is still a challenge and new chemistry strategies are of actuality. In solution, the coordinating competition between carboxylate ligand and water is most of the time that limits the dimensionality of the structure.[4] Two methods can favor condensation: the use of a poor coordination solvent or the heat under hydrothermal conditions to increase the lability of aqua ligand.[1−5] In this paper, we present two new compounds obtained via the hydrothermal route: a layered coordination polymer and a three-dimensional cobalt oxide.

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(1) (a) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (b) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. *Nature* **1999**, *402*, 276.

(2) (a) Dimos, A.; Michaelides, A.; Skoulika, S. *Chem. Mater.* **2000**, *12* (11), 3256. (b) Daiguebonne, C.; Guillou, O.; Gérault, Y.; Lecerf, A.; Boubekeur, K. *Inorg. Chim. Acta.* **1999**, *284*, 139. (c) Livage, C.; Egger, C.; Férey, G. *Chem. Mater.* **1999**, *11*, 1546.

(3) (a) Huang, Z.-L.; Drillon, M.; Masciocchi, N.; Sironi, A.; Zhao, J−T.; Rabu, P.; Panissod, P. *Chem. Mater.* **2000**, *12*, 2805. (b) Chui, S. S.-Y.; Los, M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *238*, 1148.

(4) Livage, C.; Egger, C.; Férey, G. *Chem. Mater.* **2001**, *13*, 410.

(5) (a) Livage, C.; Egger, C.; Nogues, M.; Férey, G. *C. R. Acad. Sci.* **2001**, *4*, 221. (b) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Solid State Chem.* **2000**, *152*, 271. (c) Chui, S. S.-Y.; Siu, A.; Williams, I. D. *Acta Crystallogr.* **1999**, *C55*, 194. (d) Livage, C.; Egger, C.; Nogues, M.; Férey, G. *J. Mater. Chem.* **1998**, *8*, 2743.

Experimental Section

FT-IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer. Thermogravimetric analyses were performed on a TA-Instruments TGA-2050 apparatus (oxygen flow 60 mL/min, 5 °C/min). X-ray powder diffraction data were collected on a Siemens D5000 diffractometer equipped with Cu Kα radiation for room-temperature measurements and Co Kα radiation for temperature-dependent ones. All the reagents were purchased from Aldrich Chemicals and used as supplied.

Synthesis and Characterization of $[Co_3(H_2O)_6(TMA^{3-})(TMA^{2-})(TMA^{1-})]\cdot 2H_2O$ (1). Reactions were carried out in a Teflon container under autogenous pressure. A mixture of cobalt(II) chloride hexahydrate (2.20 g), trimesic acid (0.97 g), potassium hydroxide (0.25 g), and H_2O (5 mL) in the molar ratio 2:1:1:60 was heated at 180 °C for 3 days. After cooling, dark violet crystals were obtained as a homogeneous solid phase. IR (KBr pellet, 4000−400 cm^{-1}): 3411(vs br), 3085 (sh), 1683 (s), 1614 (s), 1541 (s), 1457 (s), 1378 (s), 1230 (m), 1025 (m), 900 (w), 747 (s), 726 (s), 642 (w), 474 (w). A chosen single crystal was used for structure determination by X-ray diffraction. Thermal behavior of **1** was studied by thermogravimetric analysis. It decomposed through two major successive processes: the loss of water molecules and the combustion of the organic moiety. The first loss appears at 80 °C with the departure of free water molecules and is followed by the removal of coordinated ones up to 150 °C. The weight loss corresponds to eight water molecules (theoretical loss 15.3%, observed 15.2%). The second occurs in two steps, a small loss between 300 and 350 °C followed by an abrupt one characteristic for the combustion of organic moiety (theoretical weight loss 60.8%, observed 60.7%). A slow oxidation of CoO residue (theoretical 23.9%, observed 24.1%) into Co_3O_4 follows the degradation of organic residual and the X-ray powder diffraction pattern of the product after 600 °C corresponds to Co_3O_4 with a small amount of CoO. Chemical analysis calculated for $C_{27}H_{28}Co_3O_{26}$; C, 34.28; H, 2.96; Co, 18.73%. Chemical analysis found: C, 34.02; H, 2.95; Co, 18.11%.

Synthesis and Characterization of $K[Co_3(TMA^{3-})(TMA^{2-})_2]\cdot 5H_2O$ (2). **2** was hydrothermally synthesized from a mixture of cobalt(II) chloride hexahydrate (1.10 g), trimesic acid (0.97 g), potassium hydroxide (0.76 g), and H_2O (5 mL) in the molar ratio 1:1:3:60. The mixture was sealed in a Teflon-lined 23-mL autoclave and heated at 180 °C for 3 days. After

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Table 1. Summary of Crystal Data and Structure Refinements

	compound **1**	compound **2**
formula	$Co_3[(H_2O)_6(C_9H_3O_6)(C_9H_4O_6)(C_9H_5O_6)]\cdot 2H_2O$	$K[Co_3(C_9H_3O_6)(C_9H_4O_6)_2]\cdot 5H_2O$
formula wt	945.28 g·cm^{-3}	929.33 g·cm^{-3}
crystal system	hexagonal	monoclinic
space group	$P6_522$	$P2/c$
unit cell dimens	a = 16.7265(2) Å	a = 9.6096(1) Å
		b = 12.5610(1) Å
	c = 20.5822(4) Å	c = 13.9736(2) Å
		β = 109.239(1)°
vol, Z	4986.9(1) Å^3, 6	1592.50(3) Å^3, 2
calcd density	1.889 g·cm^3	1.938 g·cm^3
absorptn coefficient	1.589 mm^{-1}	1.777 mm^{-1}
F(000)	2874	934
crystal size	0.40 × 0.30 × 0.30 mm	0.35 × 0.22 × 0.12 mm
θ range for data collectn	1.41°−29.79°	1.62°−29.53°
limiting indices	$-22 \le h \le 10$; $-21 \le k \le 21$; $-26 \le l \le 27$	$-13 \le h \le 12$; $-10 \le k \le 17$; $-18 \le l \le 17$
reflectns collected	34 961	10 777
independent reflectns	4519 [R_{int} = 0.0661]	4094 [R_{int} = 0.0241]
data/restraints/ paramters	4519/11/281	4094/0/258
goodness-of-fit on F^2	1.008	1.065
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0298, wR_2 = 0.0766	R_1 = 0.0306, wR_2 = 0.0861
R indices (all data)	R_1 = 0.0351, wR_2 = 0.0788	R_1 = 0.0367, wR_2 = 0.0889
absolute structure parameter	0.00(1)	
extinctn coefficient	0.0064(5)	0.0044(6)
largest diff peak and hole	0.305 and −0.766 e·Å^{-3}	0.598 and −0.630 e·Å^{-3}

cooling at room temperature, the solid product was recovered by filtration. It corresponds to violet crystals of **2** with pink needles of a compound identified by X-ray powder diffraction as $Co_3(TMA)_2]\cdot 12H_2O$ and previously described by O. M. Yaghi et al.[6] The TG trace presents two stages. An initial weight loss (around 120 °C) corresponds to the weight loss of five water molecules (theoretical loss 9.4%, observed 9.8%) and an important weight loss, at 275 °C, characteristic for the combustion of the organic moiety (theoretical loss 59.5%, observed 58%). IR (KBr pellet, 4000−400 cm^{-1}): 3425 (vs br), 1686 (s), 1613 (s), 1558 (s), 1437 (s), 1382 (s), 1273 (m), 1105 (w), 910 (w), 751 (s), 722 (s), 685 (s), 564 (w), 525 (w), 462 (w), 418 (w).

Single-Crystal Structure Determinations of 1 and 2. Selected crystals of compounds **1** and **2** were glued to glass fibers and mounted on a Siemens SMART system using a three-circle diffractometer equipped with a CCD two-dimensional detector and a monochromatic molybdenum radiation [λ(Mo Kα) = 0.7107 Å]. Diffraction data collections were carried out at room temperature. In each case, slightly more than one hemisphere of data was collected in 1271 frames with ω scans (width of 0.30° and exposure time 30 s per frame). Data were corrected for Lorentz and polarization effects, and an semi-empirical absorption correction was applied by using the SADABS program.[7] Lattice parameters were obtained from least-squares analysis of all reflections. **1** crystallizes in the hexagonal system, while **2** crystallizes in the monoclinic one. Structures were solved in the $P6_522$ and $P2/c$ space groups respectively for **1** and **2**. All calculations were performed with the *SHELXTL* program.[8] In both cases, cobalt and few oxygen atoms were first located using the direct methods analysis. The remaining non-hydrogen atoms were then found by successive difference Fourier maps. Hydrogen atoms from the trimesate molecules were treated as riding (O−H = 0.82 and C−H = 0.93 Å) to have a perfect sp^2 geometry even if they could be deduced from difference Fourier calculations. For compound **1**, hydrogen atoms from the water molecules were found via last difference Fourier maps and refined with fixed O−H distances. One hydrogen in half-occupancy was not included in the structural model. For compound **2**, hydrogen atoms of the nonbonded water molecules were not included in the structural model. The presence of a high electronic density peak near a nonbonded water molecule (OW1) leads us to assume a disorder. A careful examination of its environment showed that it corresponds to a potassium atom. Its occupancy was fixed to half, as the water molecule, which balances the minus charge of the framework. Final refinements with anisotropic thermal parameters for all atoms except H give $R_1(F_o)$ = 0.0298 and $wR_2(F_o^2)$ = 0.0766 for 4519 reflections [$I > 2\sigma(I)$] and 281 parameters and $R_1(F_o)$ = 0.0306 and $wR_2(F_o^2)$ = 0.0861 for 4094 reflections [$I > 2\sigma(I)$] and 258 parameters respectively for compounds **1** and **2**. Crystallographic data and details on the refinements are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3 for compounds **1** and **2**, respectively.

Results and Discussion

Structural Description of $[Co_3(H_2O)_6(TMA^{3-})(TMA^{2-})(TMA^{1-})]\cdot 2H_2O$ (1). This compound is two-dimensional and better described by the stacking of $\{Co_3(H_2O)_6(TMA^{3-})(TMA^{2-})(TMA^{1-})\}$ planes along the c axis with a small mean separation of 3.4 Å. The crystallographic asymmetric unit contains two independent Co atoms, one on a 2-fold axis, Co(1), and one in general position, Co(2). Both cobalt atoms are 6-coordinated with the four equatorial positions occupied by carboxylate oxygen atoms and water molecules as axial ligands (Figure 1). The geometry in the equatorial plane is much distorted with a small O−Co−O angle, [60.44(7) and 60.69(5)° for Co(1) and Co(2), respectively] and a large one [111.51(8)° for Co(1) and 112.81(6)° for Co(2)]. This peculiar geometry allows one of the carboxylates (TMA^{3-}) to bend, in a bidentate way, the metal center (see Figure 1). The "bite" of the rigid acid group with O···O mean distance of 2.18 ± 0.01 Å is not suitable (too short) for a cobalt octahedral coordination, therefore the angle is very narrow and Co−O distances [from 2.141(2) to 2.174(2) Å] are longer than common ones. Due to this important distortion, it is obvious that only one carboxylate at a time can bind the metal in a bidentate way and that the squared plane is completed by two monodentate carboxylates. The structure presents two types of carboxylate ions: the first one is

(6) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096.

(7) Sheldrick, G. M. SADABS. Program for scaling and correction of area detector data, University of Göttingen, Germany, 1996.

(8) (a) Sheldrick, G. M. SHELXS97 and SHELXL97, University of Göttigen, Germany, 1997. (b) SHELXTL version 5.10, Software Package for the Crystal Structure Determination, Siemens Analytical X-ray Instrument Inc., Madison, WI, 1994.

Table 2. Bond Lengths [Å] and Angles [deg] for 1

Co(1)−O(9)	2.055(2)	Co(2)−O(5)	2.029(2)
Co(1)−O(9)[a]	2.055(2)	Co(2)−O(7)	2.069(2)
Co(1)−OW1[a]	2.111(2)	Co(2)−OW3	2.087(2)
Co(1)−OW1	2.111(2)	Co(2)−OW2	2.132(2)
Co(1)−O(3)[a]	2.168(2)	Co(2)−O(2)	2.141(2)
Co(1)−O(3)	2.168(2)	Co(2)−O(1)	2.174(2)
O(9)−Co(1)−O(9)[a]	111.51(8)	O(5)−Co(2)−O(7)	112.81(6)
O(9)−Co(1)−OW1[a]	89.13(7)	O(5)−Co(2)-OW3	89.97(8)
O(9)−Co(1)−OW1	90.06(7)	O(7)−Co(2)−OW3	92.67(9)
OW1[a]−Co(1)−OW1	178.57(9)	O(5)−Co(2)−OW2	89.98(8)
O(9)−Co(1)−O(3)	94.27(5)	O(7)−Co(2)−OW	89.94(8)
OW1−Co(1)−O(3)[a]	86.78(6)	OW3−Co(2)−OW2	177.20(9)
O(9)−Co(1)−O(3)	153.91(6)	O(5)−Co(2)−O(2)	95.12(6)
O(9)[a]−Co(1)−O(3)	94.27(5)	O(7)−Co(2)−O(2)	152.04(6)
OW1−Co(1)−O(3)	94.46(6)	OW3−Co(2)−O(2)	85.91(8)
O(3)[a]−Co(1)−O(3)	60.44(7)	OW2−Co(2)−O(2	91.30(7)
		O(5)−Co(2)−O(1)	155.28(6)
		O(7)−Co(2)−O(1)	91.39(6)
		OW3−Co(2)−O(1)	83.64(7)
		OW2−Co(2)−O(1)	95.27(7)
		O(2)−Co(2)−O(1)	60.69(5)
O(1)−C(5)	1.264(2)	C(1)−C(5)	1.491(2)
O(2)−C(5)	1.263(2)	C(2)−C(3)	1.392(2)
O(3)−C(6)	1.261(2)	C(2)−C(1)[c]	1.395(3)
O(4)−C(13)	1.258(2)	C(3)−C(2)[a]	1.392(2)
O(5)−C(13)	1.241(3)	C(3)−C(6)	1.502(4)
O(6)−C(14)	1.280(2)	C(4)−C(1)[d]	1.394(2)
O(7)−C(14)	1.219(2)	C(6)−O(3)[a]	1.261(2)
O(8)−C(15)	1.272(2)	C(7)−C(8)	1.389(3)
O(9)−C(15)	1.245(2)	C(7)−C(12)	1.393(2)
C(1)−C(4)	1.394(2)	C(7)−C(13)	1.505(3)
C(1)−C(2)[b]	1.395(3)	C(8)−C(9)	1.398(3)
		C(9)−C(10)	1.395(3)
		C(9)−C(14)[b]	1.493(2)
		C(10)−C(11)	1.395(3)
		C(11)−C(12)	1.399(3)
		C(11)−C(15)	1.491(2)
		C(14)−C(9)[c]	1.493(2)

Hydrogen Bonding Geometry (Å, deg)

D−H···A	D−H	H···A	D−H···A
O(6)−H(6)···O(4)	0.82	1.734(2)	143.8(3)
OW1−HW1A···O(3)[e]	0.80(3)	2.03(3)	167(3)
OW1−HW1B···OW4[f]	0.78(3)	2.00(3)	167(2)
OW2−HW2A···O(1)[g]	0.74(3)	2.01(3)	171(2)
OW2−HW2B···O(8)[e]	0.76(3)	2.48(3)	169(2)
OW3−HW3A···O(4)[h]	0.91(3)	1.82(3)	173(2)
OW3−HW3B···OW4[i]	0.84(3)	2.02(3)	160(2)
OW4−HW4A···O(2)	0.74(3)	2.01(4)	162(3)
OW4−HW4B	0.76(3)		

Symmetry transformations used to generate equivalent atoms: [a] $x - y, -y, -z$. [b] $x - y + 1, -y + 1, -z$. [c] $x - y, -y + 1, -z$. [d] $x - y + 1, -y + 2, -z$. [e] $x - y, x, z - 1/6$. [f] $x - y, x - 1, z - 1/6$. [g] $x, x - y + 1, -z - 1/6$. [h] $-y + 1, -x + 1, -z + 1/6$. [i] $y, -x + y + 1, z + 1/6$.

located on a 2-fold axis and has C−O bonds in the narrow range of 1.261(2)−1.264(2) Å, corresponding to deprotonated oxygens; the second presents three unidentate carboxylic groups with terminal C−O bonds, one of them being protonated with a relatively long C−O bond [1.280(2) Å]. To ensure the neutrality of the compound, half of this TMA has to have two protonated terminal oxygens. Calculations based on the bond-valence method[9] give values ranging from 1.69 to 1.71 for oxygens of chelate acid group, 1.90 to 1.95 for unidentate ones, and 1.35 and 1.43 for terminal oxygens. Therefore, the organic molecule presents three states of protonation, TMA^{3-}, TMA^{2-}, and TMA^{-}, each of them acting as a triangular connector for cobalt atoms. This

(9) Brese, N.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Table 3. Bond Lengths [Å] and Angles [deg] for 2

Co(1)−O(1)	2.026(2)	Co(2)−O(3)	1.994(2)
Co(1)−O(2)	2.071(2)	Co(2)−O(3)[b]	1.994(2)
Co(1)−O(8)	2.108(2)	Co(2)−O(9)	2.049(2)
Co(1)−O(6)	2.118(2)	Co(2)−O(9)[b]	2.049(2)
Co(1)−O(7)	2.253(2)	Co(2)−O(6)[b]	2.176(2)
Co(1)−O(8)[a]	2.255(2)	Co(2)−O(6)	2.176(2)
O(1)−Co(1)−O(2)	84.40(6)	O(3)−Co(2)−O(3)[b]	180.0
O(1)−Co(1)−O(8)	93.87(6)	O(3)−Co(2)−O(9)	87.57(7)
O(2)−Co(1)−O(8)	104.48(6)	O(3)−Co(2)−O(9)[b]	92.43(7)
O(1)−Co(1)−O(6)	155.07(5)	O(9)−Co(2)−O(9)[b]	180.0
O(2)−Co(1)−O(6)	95.82(5)	O(3)−Co(2)−O(6)[b]	89.90(6)
O(8)−Co(1)−O(6)	110.07(6)	O(9)−Co(2)−O(6)[b]	97.27(6)
O(1)−Co(1)−O(7)	95.27(6)	O(3)−Co(2)−O(6)	90.10(6)
O(2)−Co(1)−O(7)	87.45(6)	O(9)−Co(2)−O(6)	82.73(6)
O(8)−Co(1)−O(7)	165.63(6)	O(6)[b]−Co(2)−O(6)	180.0
O(6)−Co(1)−O(7)	59.90(5)		
O(1)−Co(1)−O(8)[a]	88.38(6)		
O(2)−Co(1)−O(8)[a]	172.58(6)		
O(8)−Co(1)−O(8)[a]	77.66(6)		
O(6)−Co(1)−O(8)[a]	90.01(5)		
O(7)−Co(1)−O(8)[a]	91.53(5)		
O(1)−C(5)	1.264(2)	C(4)−C(3)[e]	1.391(2)
O(2)−C(6)	1.262(2)	C(5)−O(1)[a]	1.264(2)
O(3)−C(6)[b]	1.253(2)	C(6)−O(3)[b]	1.253(2)
O(4)−C(13)[c]	1.311(3)	C(7)−C(12)[f]	1.387(3)
O(5)−C(13)	1.212(3)	C(7)−C(8)	1.399(3)
O(6)−C(14)	1.281(2)	C(7)−C(13)	1.490(3)
O(7)−C(14)	1.254(2)	C(8)−C(9)	1.392(3)
O(8)−C(15)	1.276(2)	C(9)−C(10)	1.402(2)
O(9)−C(15)	1.240(2)	C(9)−C(14)	1.490(2)
C(1)−C(2)	1.398(2)	C(10)−C(11)[f]	1.392(2)
C(1)−C(2)[a]	1.398(2)	C(11)−C(10)[c]	1.392(2)
C(1)−C(5)	1.500(3)	C(11)−C(12)	1.400(3)
C(2)−C(3)[d]	1.391(2)	C(11)−C(15)	1.499(2)
C(3)−C(2)[d]	1.391(2)	C(12)−C(7)[c]	1.387(3)
C(3)−C(4)	1.391(2)	C(13)−O(4)[f]	1.311(3)
C(3)−C(6)	1.504(2)		

Hydrogen Bonding Geometry

D−H···A	D−H, Å	H···A, Å	D−H···A, deg
O(4)−H(4)···OW3[g]	0.82	1.909(2)	169.7(3)

Symmetry transformations used to generate equivalent atoms: [a] $-x, y, -z + 1/2$. [b] $-x, -y + 2, -z$. [c] $x - 1, y, z$. [d] $-x, -y + 1, -z$. [e] $-x, y, -z - 1/2$. [f] $x + 1, y, z$. [g] $-x, y + 1, -z + 1/2$.

connection leads to the formation of a nearly planar infinite net with a pseudo-3-fold symmetry (Figure 2). This topology creates triangular cavities made from three cobalt atoms and three carboxylate ions, half of them being occupied by water molecules. The solid is constituted by the stacking of six types of layers, chemically identical, but shifted in the *ab* plane. This arrangement results in an A B C D E F pattern along the *c* axis, all the layers being related by the 6-fold screw axis (Figure 3). These layers are held together by $\pi-\pi$ interactions and hydrogen-bonding between water ligand of one layer and carboxylate oxygens of an adjacent layer (Table 2).[10] The coexistence of three different states of protonation for the TMA is indicative of the fact that protonation does not only depend on pH of the medium but mostly upon condensation with transition metal.

Structural Description of $K[Co_3(TMA^{3-})(TMA^{2-})_2]\cdot 5H_2O$ (2). The three-dimensional open structure can be described from sinusoidal chains of cobalt octahedra running along *c* axis and connected via TMA^{3-} along the *b* axis and TMA^{2-} along the *a* axis (see Figure 4).

(10) Carlin, R. L. Magnetochemistry; Springer-Verlag: Berlin, New York, 1986.

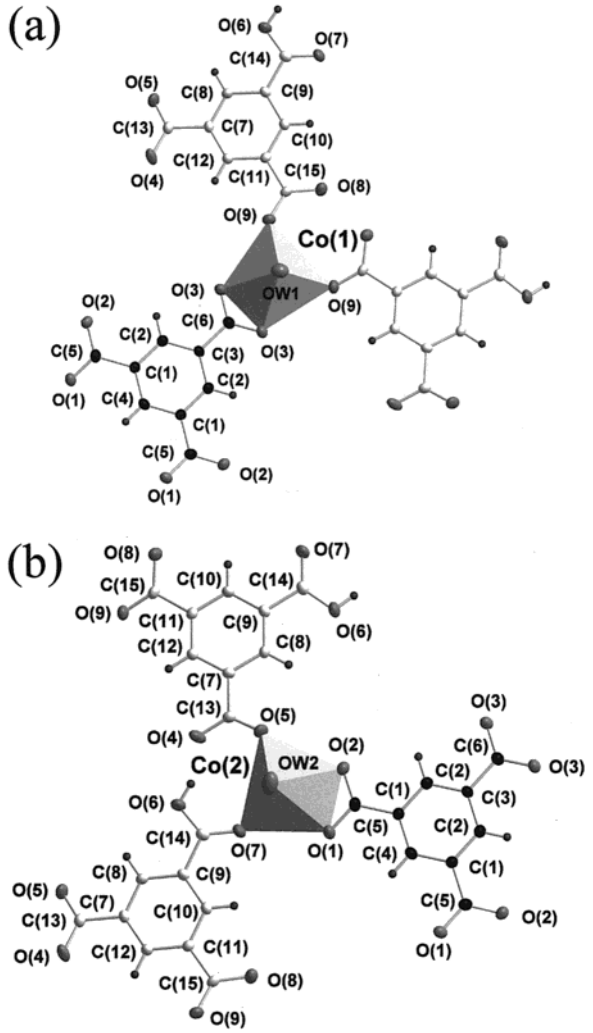

Figure 1. Views of Co(1) (a) and Co(2) (b) environments in compound **1** with organic moieties represented by a ball-and-stick mode: TMA^{-3} in dark gray and TMA^{-2} and (or) TMA^{-1} in light gray (50% probability thermal ellipsoids).

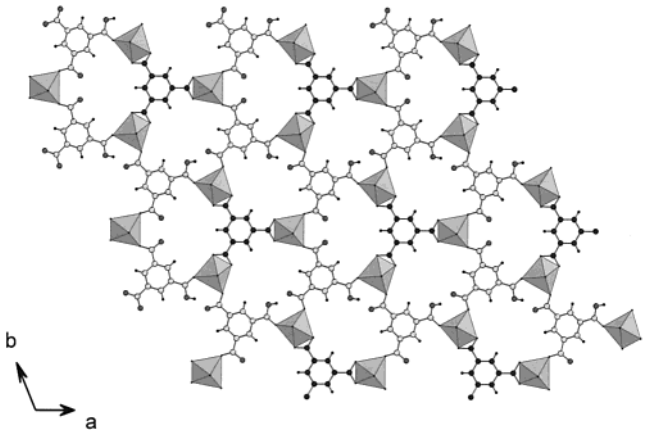

Figure 2. Projection along the *c* axis of one layer showing the triangular cavities in compound **1**.

The crystallographic unit contains two independent Co atoms, 6-coordinated by oxygen atoms of the carboxylate ions. Co(2) on the 2-fold axis is connected by six organic molecules (Figure 5b), two TMA^{3-} as axial ligands and four TMA^{2-} defining a squared plane, and Co(1) in general position is connected by five molecules (Figure 5a), two TMA^{3-} and three TMA^{2-}. As previously de-

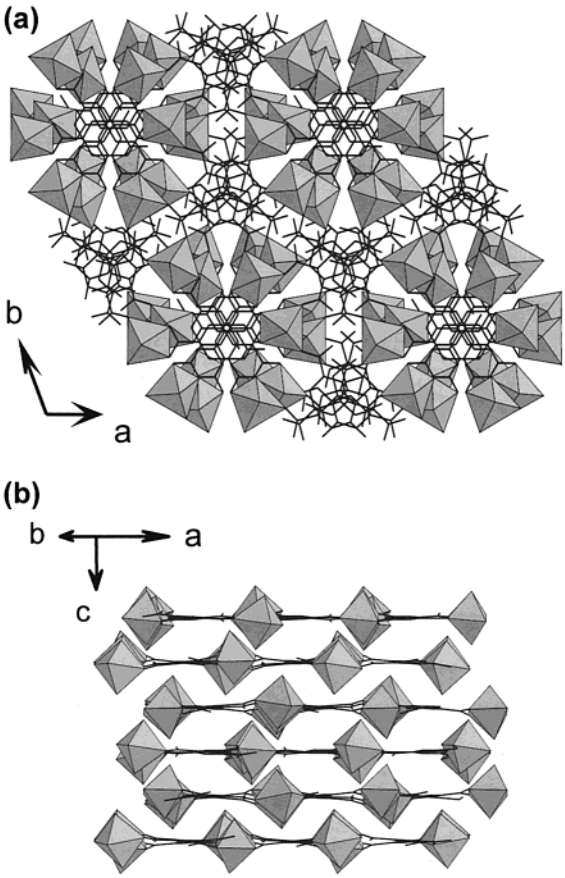

Figure 3. Views of the structure of **1**: (a) showing the six chemically identical layers related by the 6_5 screw axis; (b) showing the stacking of the six layers. Organic moieties are represented by a stick mode.

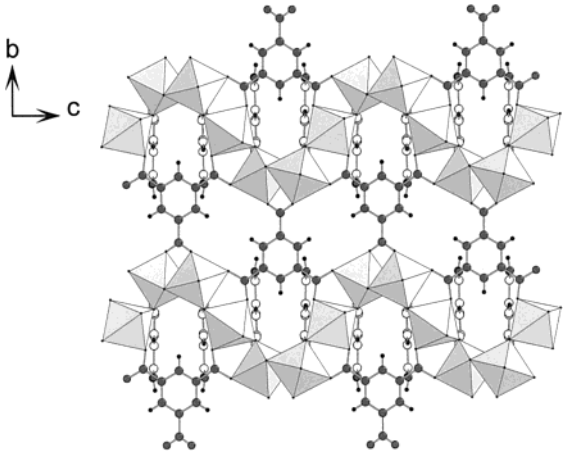

Figure 4. Projection of the structure of **2** along the *a* axis showing the sinusoidal chains of cobalt octahedra. Organic moieties are represented by a ball-and-stick mode: TMA^{3-} in dark gray and TMA^{2-} in light gray.

scribed for compound **1**, one TMA^{2-} coordinates Co(1) in a bidentate way, leading to a very distorted cobalt environment. A small O−Co−O angle of 59.90(5)° trans to a large one of 110.07(6)° is observed. In the chains, two Co(1) octahedra form dimer units by sharing an edge. Adjacent dimers are connected via a $\{Co(2)O_6\}$ octahedron by sharing vertexes. As shown in Figure 4, it can be noticed that the period of the sinusoid is strongly correlated to the geometry of the TMA^{3-} organic molecule. The structure presents two types of

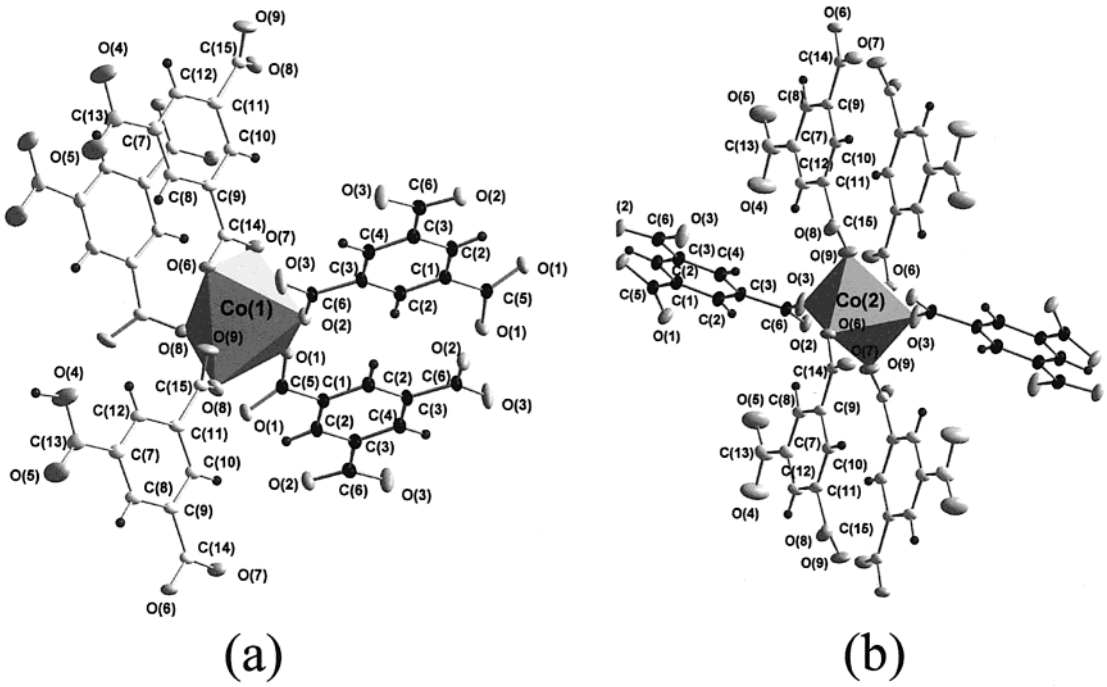

Figure 5. Views of Co(1) (a) and Co(2) (b) environments in compound **2**. TMA^{3-} is represented in dark gray and TMA^{2-} in light gray (50% probability thermal ellipsoids).

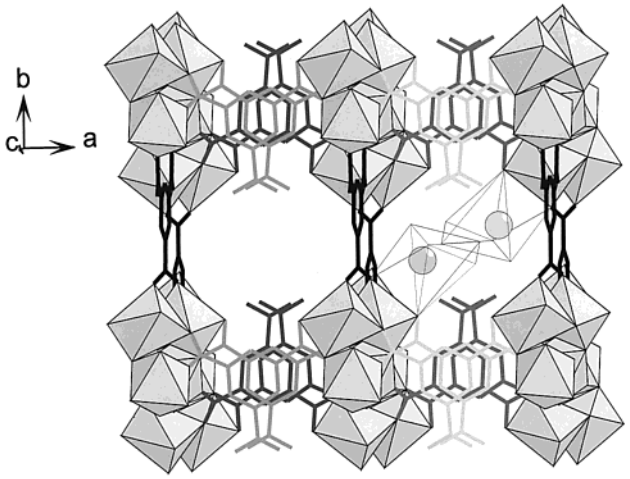

Figure 6. View of two rectangular channels delineated by four cobalt oxide chains and carboxylate ions in **2**. Potassium polyhedra, $KO_2(H_2O)_4$, have been represented by thin lines in one of the two represented channels.

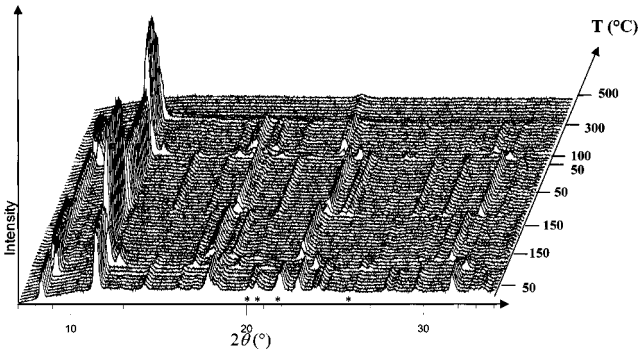

Figure 7. Thermal evolution of the diffractograms during the dehydration−rehydration (50−150−50 °C) and the decomposition (up to 500 °C) processes of compound **2**. Spurious diffraction lines corresponding to a small amount of $Co_3(TMA)_2 \cdot 12H_2O$ are indicated by asterisks.[6]

carboxylate ions: the first one, located on the 2-fold axis, has bridging carboxylate groups with C−O bonds in the range 1.253(2) − 1.264(2) Å corresponding to deprotonated oxygens; the second presents one bidentate, one bridging, and one noncoordinated acid groups with a long C−OH bond of 1.311(3) Å. Calculations based on the bond-valence method give values of 1.90 and 1.93 for bidentate oxygens, 1.81 to 1.89 for oxygens of bridging acid groups, and 1.62 and 1.24 for terminal C═O and C−OH, respectively. The sinusoidal chains are connected by the bridging TMA^{3-} in the *bc* plane and by the two deprotonated groups of the TMA^{2-} along the *a* axis. The protonated group points toward the center of rectangular channels running along the *c* axis and delineated by four sinusoidal chains of cobalt oxide (Figure 6) connected by TMA ions. Water molecules and potassium (in half-occupancy) are located inside these rectangular tunnels. Six oxygen atoms in a much-distorted geometry surround the potassium ion with bond lengths between 2.708(3) and 3.148(3) Å. The Co(1) polyhedron shares an edge with the alkaline ion, the remaining coordinating atoms corresponding to four water molecules (Figure 6). The free acid group is strongly linked via a hydrogen bond to OW3 [O(4)−H(4)···OW3, 1.909(2) Å]. Short OW−O distances seem to indicate that hydrogen bonds hold all water molecules to the network. Thermal behavior under air of **2** and especially its dehydration−rehydration process (50−150 and 150−50 °C) was investigated by X-ray powder diffraction (Figure 7). The loss of the five water molecules occurs in two steps: one at 120 °C and a second one at 150 °C. Dehydration is reversible and the XRD pattern of the rehydrated powder corresponds to that of the initial compound. However, contrary to that observed for dehydration, rehydration happens in a single step at 100 °C. This experiment indicates the existence of an intermediate hydrated phase upon heating but further studies are necessary to characterize

it. X-ray diffraction shows that combustion of the organic parts begins under air around 320 °C.

Magnetic Results. The temperature dependence of the magnetic susceptibility was measured with a Quantum Design Squid magnetometer under an applied field of 5000 Oe. The data were not corrected for the core diamagnetism, which represents less than 1% of the signal. The two cobalt compounds are essentially Curie–Weiss paramagnetic throughout the whole temperature range, even if a small increase of susceptibility can be seen for compound **1** below 30 K. The curves fits give $C = 10.0$ emu·mol^{-1} and $\theta_p = -17$ K for **1** and $C = 9.4$ emu·mol^{-1} and a θ_p value close to zero for **2**. These values lead to an effective magnetic moment of 5.2 and 5.0 μ_B per atom for **1** and **2**, respectively, which is commonly observed for octahedral Co^{2+}.[2c] Some studies on magnetic interactions of mixed Fe/Co isostructural with compound **2** are currently in progress.[12]

Conclusion

We have previously shown that under hydrothermal conditions the diversity of architectures made from cobalt and succinate ion ($^-OOC-(CH_2)_2-COO^-$) was essentially due to the flexibility of the organic molecules.[4] The solid-state arrangement is dominated by the formation of an infinite metal oxide network with the succinate adopting a conformation that maximizes metal bonding. With a carboxylate such as 1,3,5-benzenetricarboxylate, the rigidity of the molecule limits the inorganic condensation and the system should have fewer arrangements and more predictive ones. However, $Co_3(TMA)_2 \cdot 4H_2O$,[11] $Co_3(TMA)_2 \cdot 12H_2O$, previously described by Yaghi et al.,[6] and isolation of the two herein described structures are a demonstration of the variability of obtained architectures. The 1,3,5-benzenetricarboxylate molecule can adopt several modes of bonding in the same compound: **1** presents bidentate and unidentate coordination modes and **2** bidentate, bridging, and unidentate. Small changes in experimental conditions (concentration, molecular ratio, etc.) can lead to very different architectures: molecular,[11] one-dimensional,[6] layered **(1)**, and three-dimensional **(2)**. Moreover, protonation of the carboxylic depends mostly upon its reaction with metal ions and three states of protonation can be encountered in the same phase. This versatility makes this chemistry difficult to predict.

Acknowledgment. We are very grateful to Marc Nogues, from the Laboratoire de Magnétisme et d'Optique, Université de Versailles St-Quentin, for magnetic measurements.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and displacement parameters, bond lengths and angles, and hydrogen coordinates for **1** and a figure of the temperature dependence of $1/\chi_m$ (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Guillou, N.; Livage, C.; Marrot, J.; Férey, G. *Acta Crystallogr.* **2000**, *C56*, 1427.
(12) Riou-Cavellec, M., et al., to be published.