Hydrothermal versus Nonhydrothermal Synthesis for the Preparation of Organic−Inorganic Solids: The Example of Cobalt(II) Succinate

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Hydrothermal technique was used together with a room-temperature process for the synthesis of cobalt−succinate compounds. Four structures are described for two new compounds: $K_2Co(C_4H_4O_4)_2$ and $Co(H_2O)_4(C_4H_4O_4)$. Whatever the solution conditions, carboxylate ligands, which possess a strong nucleophilic character, coordinate each metal ion. However, the coordination ability of carboxylate under hydrothermal conditions is different from that under mild ones. For high-temperature phases, carboxylic groups are multidentate and the organic acts as a "template" during the condensation of the oxygen−metal networks, whereas under room temperature conditions, they are unidentate and infinite structures are obtained via the bridging role of the ligand.

Introduction

The use of an organic moiety to build infinite metal oxides is currently a very important aim of research.[1−3] A large variety of coordination polymers has been synthesized by classical solution chemistry.[4−6] Nevertheless, using hydrothermal techniques can considerably extend the range of structural types accessible for each metal−organic system. Because of the diminution of the water dielectric constant, interactions between organic and inorganic partners are different under hydrothermal conditions from those under mild ones. For positively charged organic molecules (protonated amines or alkylammonium) the condensation of the inorganic network is oriented via weak interactions (electrostatic) between the inorganic skeleton and the organic. This behavior is called "templating effect" and gives rise to a wider variety of final products.[2−3] With negatively charged species (e.g., phosphonate or carboxylate ions), the presence of electron pair donors (Lewis base) leads to the formation of coordination bonds. The organic belongs to the framework and creates most of the time, neutral open networks.[7−9]

Others and we have recently demonstrated that dicarboxylate ligands could be fruitfully used to obtain extended solids with open frameworks.[10−12] We describe herein the construction of infinite networks from cobalt(II) ions and a linear dicarboxylate, succinate, either under mild or hydrothermal conditions. Those two processes were used together to compare interaction between carboxylate ions and a metal center according to the experimental conditions.

Experimental Section

Preparation and Characterization. All the syntheses have been set up using cobalt(II) chloride hexahydrate (Aldrich), succinic acid (Prolabo), and potassium hydroxide (Prolabo) as reactants. Depending on the ratio of the base, the initial media is either a clear solution (acidic pH) or a "suspension gel" due to the precipitation of gelatinous hydrated hydroxides, $Co(OH)_2 \cdot nH_2O$. Consequently, only the final pH value is significant and will be given in the following.

Synthetic methods used to obtain $Co_5(OH)_2(C_4H_4O_4)_4$ (3) and $Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3 \cdot 2H_2O$ (4) were previously described in detail elsewhere.[9−10]

$K_2Co(C_4H_4O_4)_2$ **(1).** The initial mixture contained $CoCl_2 \cdot 6H_2O$ (1.10 g), $HCO_2(CH_2)_2CO_2H$ (0.82 g), KOH (1.29 g), and H_2O (5 mL) in the molar ratio 1:1.5:5:60. After the removal of the $Co(OH)_2 \cdot xH_2O$ precipitated, the filtrate was left undisturbed at room temperature for 3 days. The solvent slowly evaporated, resulting in the formation of violet crystals of **1**. With heating beforehand, the preparation under hydrothermal conditions does not give any "high-temperature" phase and $K_2Co(C_4H_4O_4)_2$ crystallizes from the resulting filtrate at room temperature. FT-IR spectra, recorded on a Nicolet Magna-IR 550 spectrometer, exhibit the following absorption (KBr pellet, ν/cm^{-1}): stretching bands characteristic of the carboxylic

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Table 1. Summary of Crystal Data and Structure Refinement for K₂Co(C₄H₄O₄)₂ (1), Co(C₄H₄O₄)·4H₂O (2), Co₅(OH)₂(C₄H₄O₄)₄ (3), and Co₄(OH)₂(C₄H₄O₄)₃.4H₂O (4)

	1	2	3	4
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	9.2279(3)	7.4174(5)	9.5631(2)	10.181(2)
b (Å)	21.3646(9)	14.8283(9)	9.4538(2)	10.668(2)
c (Å)	7.4461(2)	7.7865(5)	12.5554(2)	12.857(3)
α (deg)				112.97(3)
β (deg)	123.738(2)	99.799(2)	96.968(1)	91.24(3)
γ (deg)				117.96(3)
volume (Å³)	1227.53(7)	843.92(9)	1126.72(4)	1099.1(4)
D_c (g cm⁻³)	1.998	1.945	2.337	2.085
absorption coefficient (mm⁻¹)	2.107	2.049	3.697	3.053
reflections collected	4225	5849	7953	7803
independent reflections with [$I > 2\sigma(I)$]	1600	2203	3077	5511
parameters	100	155	206	377
goodness-of-fit[a] on F^2	1.075	0.978	1.044	1.003
final R1[b]	0.0487	0.0233	0.0202	0.0450
final wR2[c]	0.0933	0.0603	0.0540	0.1143
largest diff. peak and hole, e/Å³	0.429/−0.605	0.671/−0.476	0.535/−0.395	1.114/−1.337

[a] GooF = $\{\Sigma\,[w(F_o^2 - F_c^2)^2\,]/(n-p)\}^{1/2}$. [b] R1 = $\Sigma\,|\,|F_o| - |F_c|\,|/\Sigma\,|F_o|$. [c] wR2 = $\{\Sigma[w(F_o^2 - F_c^2)^2\,]/\Sigma[w(F_o^2)^2\,]\}^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + \mathrm{Max}(F_o^2,0)\,]/3$.

groups: 1610, 1563 [$\nu_{as}(CO_2^-)$] 1410, 1395 [$\nu_s(CO_2^-)$], and 1281, 1230 [$\nu_s(C-O)$]; two peaks at 1181 and 1156 attributed to $\nu_{as}(C-C)$, and the following absorption bands associated with metal−oxygen bonding and $\nu(C-H)$, 892, 809, 687, 598, 577, and 553.[13]

Co(H₂O)₄(C₄H₄O₄) (2). Le Van et al. identified this compound earlier, in 1969, but they did not solve the structure.[14] The synthesis is quite straightforward, at room temperature, starting from an aqueous solution of cobalt chloride and succinic acid. The molar ratios of the reactants are respectively 1:1.5:1:120 for cobalt(II) chloride hexahydrate (0.55 g), succinic acid (0.41 g), potassium hydroxide (0.13 g), and water (5 mL), corresponding to a solution concentration of 0.5 mol L⁻¹ based on cobalt (pH = 3). The preparation was left undisturbed at room temperature for 1 day, resulting in the formation of pink crystals. However, compound **2** can be isolated in a large range of pH, 3.5−7 (KOH/Co initial ratios from 2 to 4), by heating beforehand the solution under hydrothermal conditions (180 °C). Those preparations give crystals of Co₅(OH)₂(C₄H₄O₄) (**3**) and a pink filtrate from which phase **2** crystallizes at room temperature. Elemental analysis confirmed the composition with experimental/calculated values (mass percent): C 19.4/19.4, H 4.9/4.8, and Co 23.6/23.9. FT-IR spectra exhibits the following absorption bands (KBr pellet, ν/cm^{-1}): narrow $\nu(O-H)$ bands at 3520, 3420 cm⁻¹ associated with the existence of strong hydrogen bonds; stretching frequencies corresponding to the carboxylate ion $\nu(CO_2^-)$ and $\nu(C-O)$ at 1630, 1562 1460, 1422, 1412, 1288, and 1240 cm⁻¹; the 1175-cm⁻¹ absorption band is associated with $\nu_{as}(C-C)$ and the following absorptions with metal−oxygen bonding and with $\nu(C-H)$, 1047, 977, 805, 671, 585, and 526.[13] We have prepared the nickel analogue, Ni(H₂O)₄(C₄H₄O₄), using the same synthetic procedure.[15]

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(15) X-ray crystal data for Ni(H₂O)₄(C₄H₄O₄): light green crystals, 0.10 × 0.16 × 0.10 mm. Monoclinic, space group $P2_1/c$, $a = 7.41133(1)$, $b = 14.7467(4)$, $c = 7.7215(2)$ Å, $\beta = 99.765(1)°$, $V = 831.90(3)$ Å³, $Z = 4$, $M = 246.85$, $D_c = 1.971$ g cm⁻³, $\mu = 2.348$ cm⁻¹, index ranges $-9 \leq h \leq 10$, $-20 \leq k \leq 18$, $-10 \leq l \leq 7$; total data 5652; independent data with $I_o > 2\sigma(I_o)$ 2170. Intensity data were collected at room temperature with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector [λ Mo Kα = 0.71073 Å]. Data were corrected for Lorentz and polarization effects; absorption corrections were applied using SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares, based on F^2, using the SHELX-TL software package. All atoms were refined anisotropically except for hydrogen atoms. Number of variables, 155; final $R(F) = 0.0286$, wR(F^2) = 0.0669; GOF 1.032; minimum and maximum peak in difference electron density map −0.467 and 0.430 e⁻ Å⁻³.

Table 2. Atomic Coordinates (10⁴) and Equivalent Isotropic Displacement Parameters (10³ Å²) for Non-hydrogen Atoms: K₂[Co(C₄H₄O₄)] (1) and Co(H₂O)₄(C₄H₄O₄) (2)

	x	y	z	$U(eq)^a$
		K₂[Co(C₄H₄O₄)]		
Co(1)	0	3618(1)	2500	28(1)
O(1)	1470(4)	4212(1)	4873(4)	32(1)
O(2)	3591(4)	4476(1)	8161(4)	32(1)
O(3)	897(4)	3007(1)	1384(5)	39(1)
O(4)	2045(4)	3836(1)	844(5)	40(1)
C(1)	3002(5)	4130(2)	6575(6)	23(1)
C(2)	4069(5)	3593(2)	6575(6)	28(1)
C(3)	1786(5)	3265(2)	751(6)	31(1)
C(4)	2520(7)	2838(2)	−199(9)	40(1)
K(1)	5000	4490(1)	2500	30(1)
K(2)	0	4659(1)	7500	36(1)
H(2A)	3542(62)	3218(24)	6668(76)	50
H(2B)	3853(67)	3614(22)	5347(82)	50
H(4A)	1767(65)	2891(22)	−1740(84)	50
H(4B)	3631(67)	2968(22)	358(78)	50
		Co(H₂O)₄(C₄H₄O₄)		
Co(1)	9292(1)	1445(1)	1876(1)	17(1)
O(1)	11304(1)	1674(1)	4061(1)	24(1)
O(2)	12397(2)	295(1)	4699(2)	31(1)
O(3)	7379(1)	1284(1)	−421(1)	25(1)
O(4)	4811(1)	1326(1)	693(1)	27(1)
OW1	11162(2)	1601(1)	184(2)	23(1)
OW2	7317(2)	1295(1)	3573(2)	22(1)
OW3	8661(2)	2831(1)	1797(2)	27(1)
OW4	9796(2)	53(1)	2011(2)	31(1)
C(1)	12338(2)	1117(1)	5020(2)	19(1)
C(2)	13544(2)	1509(1)	6614(2)	24(1)
C(3)	4619(2)	802(1)	−2232(2)	24(1)
C(4)	5659(2)	1171(1)	−536(2)	18(1)
H(2A)	14431(32)	1933(15)	6158(29)	50
H(2B)	12818(31)	1881(15)	7222(31)	50
H(3A)	3788(31)	389(16)	−1927(30)	50
H(3B)	5482(31)	547(15)	−2882(31)	50
HW1	12125(35)	1480(16)	482(35)	50
HW1	11172(31)	2073(16)	−145(33)	50
HW2	6353(35)	1337(14)	2727(35)	50
HW2	7281(33)	854(17	3994(31)	50
HW3	8213(32)	3011(16)	922(32)	50
HW3	8303(32)	3059(16	2488(34)	50
HW4	9776(34)	−283(16)	1316(32)	50
HW4	10730(31)	20(17)	2843(33)	50

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

Structure Determination of K₂[Co(C₄H₄O₄)] (1) and Co(H₂O)₄(C₄H₄O₄) (2). X-ray single-crystal diffraction data were collected on a Siemens SMART diffractometer equipped

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $K_2[Co(C_4H_4O_4)]$ (1) and $Co(H_2O)_4(C_4H_4O_4)$ (2) [Symmetry Transformations Used To Generate Equivalent Atoms: See Footnotes Below]

$K_2[Co(C_4H_4O_4)]$			
Co(1)−O(1)	1.979(3)	K(1)−O(2)[e]	2.731(3)
Co(1)−O(3)	1.964(3)	K(1)−O(2)[d]	2.747(3)
O(1)−C(1)	1.287(4)	K(1)−O(4)	2.689(3)
O(2)−C(1)	1.235(4)	K(2)−O(1)[b]	2.849(3)
O(3)−C(3)	1.281(5)	K(2)−O(1)	3.092(3)
O(4)−C(3)	1.238(5)	K(2)−O(2)	3.110(3)
C(1)−C(2)	1.515(6)	K(2)−O(4)[a]	2.765(3)
C(2)−C(2)[f]	1.496(8)		
C(3)−C(4)	1.526(6)	O(3)−Co(1)−O(3)[a]	96.6(2)
C(4)−C(4)[g]	1.481(9)	O(3)−Co(1)−O(1)[a]	107.02(13)
		O(3)−Co(1)−O(1)	124.09(13)
		O(1)−Co(1)−O(1)[a]	100.2(2)

$Co(H_2O)_4(C_4H_4O_4)$			
Co(1)−O$_W$1	2.083(1)	O(2)−C(1)	1.246(2)
Co(1)−O(1)	2.090(1)	O(3)−C(4)	1.275(2)
Co(1)−O$_W$4	2.097(1)	O(4)−C(4)	1.253(2)
Co(1)−O(3)	2.099(1)	C(1)−C(2)	1.517(2)
Co(1)−O$_W$3	2.105(1)	C(2)−C(3)[h]	1.516(2)
Co(1)−O$_W$2	2.144(1)	C(3)−C(4)	1.514(2)
O(1)−C(1)	1.278(2)	C(3)−C(2)[i]	1.516(2)

Hydrogen Bonding Geometry (Å, deg)

D−H···A	D−H	H···A	D−H···A
O$_{W1}$−H$_{W1}$···O(4)	0.73(3)	1.983(2)	164.3
O$_{W1}$−H$_{W1}$···O(1)	0.75(2)	1.967(2)	177.3
O$_{W2}$−H$_{W2}$···O(2)	0.73(2)	1.977(2)	170.7
O$_{W2}$−H$_{W2}$···O(4)	0.87(3)	1.792(2)	165.5
O$_{W3}$−H$_{W3}$···O(3)	0.72(3)	2.108(2)	177.4
O$_{W3}$−H$_{W3}$···O$_{w2}$	0.75(2)	2.105(2)	169.6
O$_{W4}$−H$_{W4}$···O(2)	0.87(2)	1.782(2)	162.0

[a] $-x, y, -z + 1/2$. [b] $-x, -y + 1, -z + 1$. [c] $-x + 1, -y + 1, -z + 1$. [d] $x, y, z - 1$. [e] $-x + 1, y, -z + 3/2$. [f] $-x + 1/2, -y + 1/2, -z$. [g] $x + 1, y, z + 1$. [h] $x - 1, y, z - 1$.

with a CCD two-dimensional detector (Mo Kα radiation). About half a sphere of intensity data was collected in 1271 frames with ω scans (width of 0.30° and exposure time 30 s/frame). Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using SADABS program.[16] The structures were solved by direct methods and refined by full-matrix least-squares, based on F^2, using the SHELX-TL software package.[17] One of the violet crystals of **1** ($0.22 \times 0.10 \times 0.02$ mm³) and a pink rodlike crystal of **2** ($0.5 \times 0.4 \times 0.2$ mm³) were glued to glass fibers and mounted on the diffractometer. A summary of crystal data is presented in Table 1. For the two structures, cobalt, potassium, and oxygen atoms were first located and all the remaining atoms, including hydrogen atoms, were found by difference Fourier maps. Refinements were performed with anisotropic thermal parameters for all non-hydrogen atoms. Isotropic displacement factors were fixed at the value of 0.05 Å² for hydrogen atoms. Fractional atomic coordinates are given in Table 2 and selected bonds distances in Table 3.

Results and Discussion

Structural Description of $K_2Co(C_4H_4O_4)_2$ (1). The important feature of the crystal structure is the alternation between anionic cobalt−succinate and potassium layers. The compound is anhydrous and coordination of cobalt and potassium atoms is ensured by oxygen of the acid groups. Each metal center is 4-fold-coordinated and
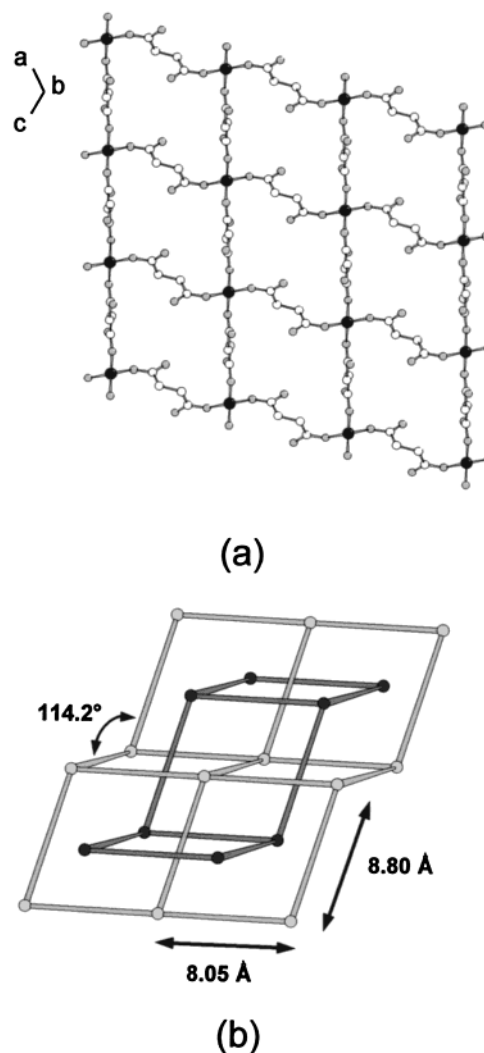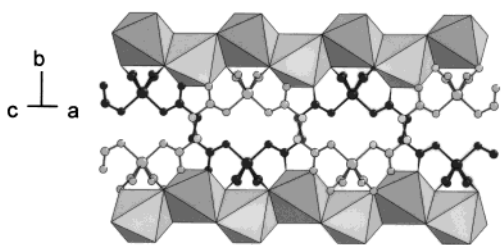
(16) Sheldrick, G. M. *SADABS. Program for Scaling and Correction of Area Detector Data*; University of Göttingen: Germany, 1997.

(17) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) *SHELX-TL version 5.03, Software Package for the Crystal Structure Determination*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1994.

Figure 1. $K_2Co(C_4H_4O_4)_2$ (**1**): (a) infinite two-dimensional network of cobalt coordinated by succinate ions (the structure is formed by two interpenetrating networks). For clarity, hydrogen atoms have been omitted. (b) Scheme illustrating the interpenetrating metal−carboxylate networks. Only Co atoms are drawn and each network is identified by a unique color. Distances between cobalt are 8.8 and 8.0 Å.
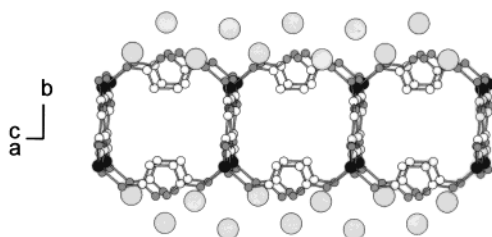
bridged to four adjacent cobalt atoms into an infinite two-dimensional net (Figure 1). This 4-coordination geometry is distorted with bond angles at Co ranging from 96.6° to 124.1° [O(1), 1.979 Å; O(3) 1.964 Å]. The anionic layer is constituted of two interpenetrating cobalt carboxylate networks (Figure 1).[4,6] Between anionic layers, oxygen−alkaline bonds form a dense network (Figure 2). One particularity of the structure is the position of the carboxylic group relative to potassium ions. K(1) presents a regular octahedral environment constituted of terminal oxygen atoms and K(2) is 8-coordinated by four terminal and four metal-bonded oxygens. The two alkaline polyhedra are linked by edges into a regular two-dimensional arrangement (Figure 3). Each of the acid groups exhibits one relatively long C−O bond (1.284 ± 0.003 Å) corresponding to unidentate bonding to the metal and one shorter for terminal oxygens (1.236 ± 0.002 Å). Calculations based on the bond-valence method, developed by N. E. Brese and M. O'Keeffe,[18] gave values of 1.8 ± 0.2 for metal-bonded oxygens and 1.5 ± 0.2 for terminal oxygen

(a)

(b)

Figure 2. $K_2Co(C_4H_4O_4)_2$ (**1**): (a) view along the [1 0 1] axis showing the alternation between potassium and cobalt−carboxylate layers. (b) Representation of one cobalt−carboxylate network parallel to the b axis; gray spheres on each side of the layer correspond to potassium ions.
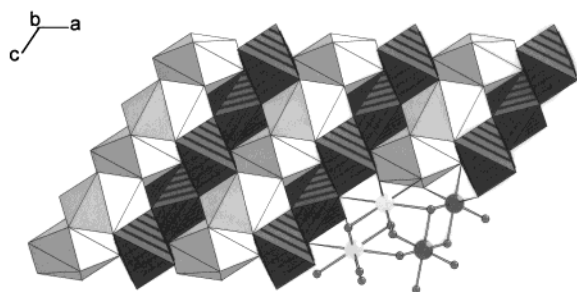

Figure 3. $K_2Co(C_4H_4O_4)_2$ (**1**): organization of the oxo-potassium network. K(1)O$_6$ is represented in gray and K(2)O$_8$ polyhedra in white. K(1)O$_6$ and K(2)O$_8$ form a dense two-dimensional network by connection through edges and corner-sharing.

atoms. The observed deficit of calculated charges is due to their strong interaction with potassium ions. Including K−O bonds in the calculation leads to a valence sum of 1.9 ± 0.2.

Structural Description of $Co(H_2O)_4(C_4H_4O_4)$ (2). The structure is one-dimensional, consisting of chains of cobalt atoms bridged by succinate ions. The carboxylic groups are monodentate and present, therefore, a free terminal oxygen. The cobalt coordination is completed to six by four equatorial water molecules leading to the polymer: *trans*-[Co(H$_2$O)$_4$(OOC−R)$_2$]n, as seen in Figure 4. The CoO$_6$ octahedron is slightly distorted with a metal−oxygen bond (Co−Ow(2); 2.144 Å) longer than the others (2.083−2.105 Å). The chains are held together by a set of strong hydrogen bonds between coordinated water molecules and carboxylic groups (Table 3). Calculations based on the bond-valence method give values of 1.7 ± 0.1 for metal-bonded oxygens and 1.5 ± 0.1 for terminal oxygen atoms. We believe that such a discrepancy between calculated and expected values is due to the presence of hydrogen bonds. This deficit is always
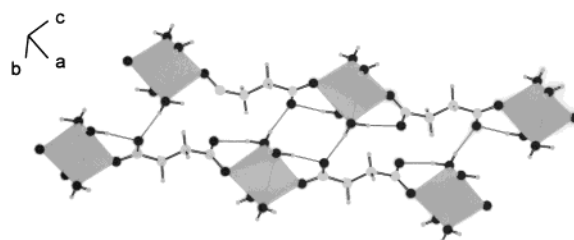
(18) Brese, N.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Figure 4. $Co(H_2O)_4(C_4H_4O_4)_2$ (**2**): representation showing two cobalt−carboxylate chains linked by hydrogen bonds.
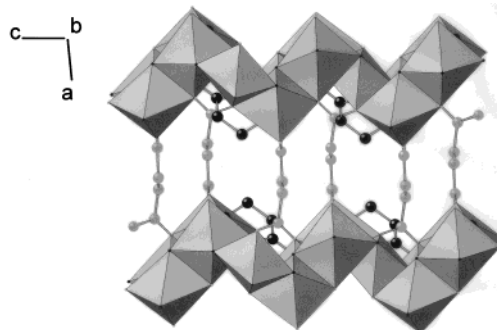

Figure 5. $Co_5(OH)_2(C_4H_4O_4)_4$ (**3**): structure with {CoO$_6$} represented by polyhedra and alkyl chains by a ball and stick.
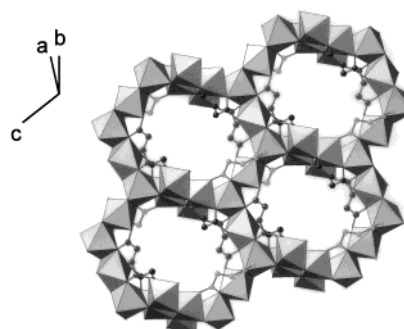

Figure 6. $Co_4(OH)_2(C_4H_4O_4)_3 \cdot 4H_2O$ (**4**): representation of one layer: {CoO$_6$} are represented by gray polyhedra and alkyl chains by a ball and stick.

observed on oxygen with hydrogen bonds but cannot be estimated by this method (including hydrogen in calculation does not significantly change the values).

Structural Description of $Co_5(OH)_2(C_4H_4O_4)_4$ (3) and $Co_4(OH)_2(H_2O)_2(C_4H_4O_4)_3 \cdot 2H_2O$ (4). Solids obtained under hydrothermal conditions, **3** and **4**, were previously described in detail elsewhere[9−10] and are represented in Figures 5 and 6, respectively.

Influence of Synthetic Conditions. Two characteristics are of importance for coordination metal polymers applications: a rigid framework and porosity, which allows accessibility of metallic sites. Under mild conditions, cobalt−oxide condensation is not favored and infinite networks are formed by the bridging role of the dicarboxylate ligand. In acidic media the complexation of the metal by two R−COO$^-$ forms a linear polymer, whereas at neutral pH all the initial water molecules have been displaced by succinate ions and a fourth coordination gives corrugated layers. In each case, the carboxylate ligand is unidentate and the free oxygen interacts strongly with water molecules (**2**) (hydrogen bonds) or alkaline ions (**1**) (ionic bonds). With this type of construction, the organic acts as a spacer between metal sites and the dimensionality of the solid depends
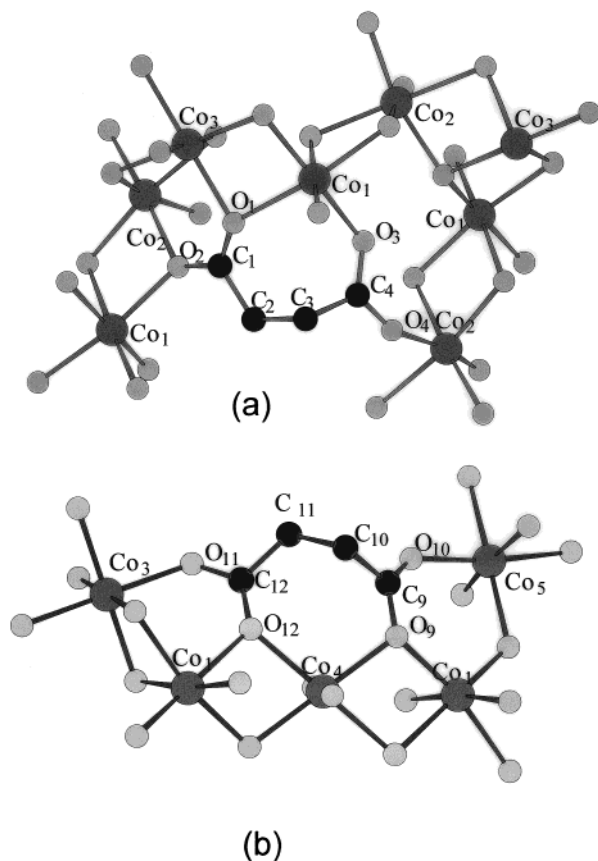
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Figure 7. Local environment of succinate ions in $Co_5(OH)_2(C_4H_4O_4)_4$ (a) and $Co_4(OH)_2(C_4H_4O_4)_3 \cdot 4H_2O$ (b).

essentially on the number and geometry of the ligands.[1-2] Consequently, the major feature that determines the final structure is the coordinating competition between water and carboxylate ligand.

At higher temperature, under hydrothermal conditions, solid-state arrangement is dominated by the formation of an infinite cobalt–oxygen network. The structure of $Co_5(OH)_2(C_4H_4O_4)_4$ (**3**) is three-dimensional and built up from layers of edge-sharing $\{CoO_6\}$ octahedra pillared by succinate ions (Figure 5). Compound **4**, $Co_4(OH)_2(C_4H_4O_4)_3 \cdot 4H_2O$, is two-dimensional and constituted by the stacking of an infinite net of cobalt octahedra in which 14-membered ring windows are stabilized by succinate anions (Figure 6).[9-10] Carbox-

ylate is in competition for the metal complexation with hydroxo and aqua ligands (due to metal charge (2+), oxo ligands are not favored). However, in those two structures, carboxylate groups are multidentate and seem to maximize coordination to metal atoms. The coordination mode of two of the succinate ions is represented in Figure 7. The organic, by being linked to the metal, plays a double role: it avoids the formation of dense simple oxides (templating effect) and stabilizes the obtained architectures. Succinate ions can interact with metal centers in different ways: unidentate, chelate, and multidentate; from our results, it seems that the coordination mode is influenced by the temperature. Under hydrothermal conditions, regarding structures **3** and **4**, carboxyl groups are di-, tri-, or tetradentate and can bridge as many as five metal centers whereas under mild conditions, structure **1** and **2** are unidentate. The inorganic condensation certainly plays an important role in the multidentate character of succinate ions with the substitution of water ligand by oxygen of the COO$^-$ groups.

Conclusion

All other parameters being equal, the system Co–succinate forms at room temperature a coordination polymer (organic–metal–organic) whereas, under hydrothermal conditions, metal–oxide condensation is favored. With a strong coordinating ligand such as water (high dielectric constant, high polarity), the synthetic strategy to build extended solids passes through the elimination of coordinated water. Under hydrothermal conditions, the temperature favors inorganic condensation (decrease of water polarity, modification of equilibrium constants). The condensation is therefore "perturbed" by the presence of the coordinated organic ligand. Under mild conditions, the stabilization of infinite networks comes from the difunctional character of the ligands, which can bridge metal centers. These conclusions are restricted to succinate ligand: the molecule is flexible and can adopt a maximum bonding conformation and the small alkyl chain moderates hydrophobic interactions.[1,19]

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