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Synthesis, Structure, and Magnetic Properties of Two New Vanadocarboxylates with Three-Dimensional Hybrid Frameworks

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$(V^{III}(OH))_2\{C_6H_2(CO_2)_4\}\cdot 4H_2O$ (labeled MIL-60) and $V^{III}(OH)\{_2(O_2C)C_6H_2(COOH)_2\}\cdot H_2O$ (labeled MIL-61) were hydrothermally synthesized from mixtures of VCl_3, 1,2,4,5-benzenetetracarboxylic acid, and water heated for 3 days at 473 K. The structure of MIL-60 was solved from single-crystal X-ray diffraction data in the triclinic centrosymmetric *P*1 (No. 2) space group with lattice parameters $a = 6.3758(5)$ Å, $b = 6.8840(5)$ Å, $c = 9.0254(5)$ Å, $\alpha = 69.010(2)°$, $\beta = 85.197(2)°$, $\gamma = 79.452(2)°$, $V = 363.53(5)$ Å^3, and $Z = 1$. The structure of MIL-61 was *ab initio* determined from an X-ray powder diffraction pattern. MIL-61 crystallizes in the *Pnma* (No. 62) orthorhombic space group with lattice parameters $a = 14.8860(1)$ Å, $b = 6.9164(1)$ Å, $c = 10.6669(2)$ Å, $V = 1098.23(3)$ Å^3, and $Z = 4$. Both structures contain the same inorganic building block that consists of trans chains of $V^{III}O_4(OH)_2$ octahedra. The three-dimensional frameworks of MIL-60 and MIL-61 are constituted by the linkage of these chains via the organic molecules so delimiting the channels or cages where the water molecules are encapsulated. The magnetic behavior of these two phases is presented: MIL-60 is paramagnetic, and MIL-61 antiferromagnetically orders below $T_N = 55(5)$ K.

Introduction

The synthesis of hybrid organic—inorganic compounds is a very fruitful tool for obtaining frameworks with porous properties.[1−4] Two different series are investigated: the coordination polymers[5−7] whose connections between the organic and inorganic moieties are ensured by heteroatoms (such as nitrogen) directly involved in the surrounding of the metallic cations and the infinite solids whose structures are built up from inorganic building blocks linked by organic molecules functionalized by complexing groups such as phosphonates[8,9] or carboxylates.[10−13] The control of the steric hindrance of the organic linker allows for the modulation of the porosity of the final solid. Yaghi et al. recently exemplified this capacity of the hybrid compounds with the series of copper carboxylate IRMOF-n;[14] the same inorganic cluster linked by terephthalate or triphenyldicarboxylate anions deals with a similar structural type whose free volume increases from 55.8 to 91.1%.

Another challenge consists of the development of the physical properties of the hybrid compounds by the cooperative association of the organic and inorganic moieties available to induce such properties. We reported with the first vanado(III)carboxylate, labeled MIL-47,[15] that its three-dimensional hybrid framework is built up from the connection of octahedral chains by terephthalate linkers. This compound exhibits both porous properties and antiferromagnetic behavior below $T_N = 95(5)$ K. To more completely

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investigate the family of vanadocarboxylate hybrid compounds, we systematically studied the association of carboxylic acid to vanadium moieties. By using isophthalic acid, one obtains $(V^{III}(H_2O))_3O\{O_2C-C_6H_4-CO_2\}_3\cdot(Cl, 9H_2O)$, or MIL-59,[16] whose framework is built up from the connection of octahedral trimers joined via the organic linkers to generate cuboidal cages with occluded moieties (chlorine and water).

This paper deals with the hydrothermal synthesis and structure characterization of two new examples obtained with 1,2,4,5-benzenetetracarboxylic acid. $(V^{III}(OH))_2\{C_6H_2(CO_2)_4\}\cdot 4H_2O$ (labeled MIL-60) and $V^{III}(OH)\{_2(O_2C)C_6H_2(COOH)_2\}\cdot H_2O$ (labeled MIL-61) present evident structural relationships with previously described MIL-47 but are magnetically very different.

Experimental Section

Hydrothermal Syntheses. MIL-60 and MIL-61 were hydrothermally synthesized from mixtures of VCl_3, 1,2,4,5-tetracarboxylic acid, and deionized water in the molar ratios 1:0.2:250 and 1:1:250, respectively. Both mixtures were sealed into Teflon-lined steel autoclaves from Parr and then heated for 72 h at 473 K. After heating, the solids were isolated by filtration, washed with water, and then dried in air at room temperature. For the two preparations, the pH is driven by the strong acidic character of the VCl_3 solutions; measured *ex situ* before and after heating, it remains equal to 1. MIL-60 was obtained as pure parallelepipedic crystals with a yield close to 30%, estimated by reference to VCl_3. MIL-61 was prepared as a pure light-pink powder with a yield close to 40%.

Chemical Analyses. Elemental analyses were performed for both compounds to confirm their chemical formula deduced from the structural determinations. MIL-60: V, 22.27% expected versus 21.98% measured; C, 26.20% expected versus 26.93% measured. MIL-61: V, 15.17% measured versus 15.09 theoretical; C, 35.71% measured versus 35.50% theoretical.

The thermograms were registered with a TGA 2050 TA Instruments apparatus under an oxidizing atmosphere (O_2 flow, heating rate of 1°/min). MIL-60 dehydrates below 100 °C with an observed weight loss of 5.7% versus a theoretical value of 6%. The combustion of the organic moieties occurs in the temperature range 380−550 °C and induces the complete destruction of the structures. The X-ray diffraction (XRD) pattern of the calcined residue corresponds to mixtures of vanadium oxides (principally V_3O_7). Consequently, the theoretical weight losses should be approximately 54.2%; the observed one is 48.4%. The thermogram curve of MIL-61 presents two successive weight losses of 6.3 and 66.9% occurring between 200 and 275 °C and between 275 and 380 °C, respectively. They are in good agreement with both the dehydration and the combustion of the organic moieties (73.9% calculated). The residue was identified by XRD as a mixture of vanadium oxides (principally VO_2 and V_2O_5).

Density experiments were performed using a Micromeritics multipycnometer operating under He flow.

Infrared spectroscopy (Figure 1) was performed for the two compounds in KBr pellets with a Nicolet-Magna IR550 apparatus. The two spectra show the characteristic bands of the water molecules, the hydroxyl group, and even the protonated acid function in the 3000−3600 cm^{-1} range; the numerous bands located around 1500 cm^{-1} are attributed to the $C{=}C$ bonds of the phenyl rings. More interesting are the two bands at 1740 and 1710 cm^{-1} observed on the spectrum of MIL-61; they are characteristic of $C{=}O$ bonds. They are not shown for the MIL-60 compound, which is in good agreement with the structural results; indeed, all the oxygen atoms of the carboxylate functions are linked to metal centers, whereas in the MIL-61 structure, half of the carboxylate functions involving $C{=}O$ bonds are protonated and terminal.

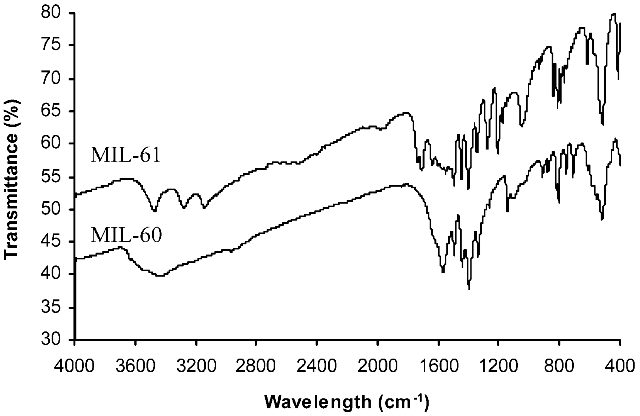

Figure 1. IR spectra of MIL-60 and MIL-61.

MIL-60: ν_{O-H} 3460 cm^{-1}; $\nu_{C=C}$ 1570, 1500, 1440 cm^{-1}. MIL-61: ν_{O-H} 3480, 3280, 3150 cm^{-1}; $\nu_{C=O}$ 1740, 1710 cm^{-1}; $\nu_{C=C}$ 1610, 1550, 1500, 1450 cm^{-1}. Detailed spectra are given in the Supporting Information.

XRD. One crystal of MIL-60 (dimensions 0.16 × 0.06 × 0.04 mm) was optically selected and then glued on a glass fiber mounted on a goniometer head. The intensities were collected with a Siemens SMART three-circle diffractometer equipped with a CCD detector and using the monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å). The reciprocal space was scanned with an ω step of 0.03° and a time per step of 30 s; the crystal−detector distance of 4.5 cm allowed a collection up to $2\theta \sim 60°$. Data were reduced with the SAINT program, and then a semi-empirical absorption correction based on the Blesing method[17] was applied using the SADABS program.[18] The structure was solved in the centrosymmetric $P1$ (No. 2) triclinic space group. The locations of the vanadium, oxygen, and carbon atoms were found from the direct methods of SHELX-TL,[19] and then those of the hydrogen atoms of the phenyl rings were found by applying geometrical constraints. Only the hydrogen atoms of the hydroxyl functions were deduced from Fourier difference syntheses.

The structure of MIL-61 was *ab initio* determined from its XRD powder pattern. A pure powder of MIL-61 was first ground in a McCrone apparatus for a good homogenization of the grain size and then introduced into a McMurdie sample holder to prevent strong preferential orientation effects. The pattern was monitored with a Siemens D5000 diffractometer equipped with a secondary monochromator in the θ range 8−120° with a step size of 0.02°. The time per step was initially 23 s up to 48°, and then it was increased to 46 s for the upper angles to improve the signal/background ratio. The indexation was made using the DICVOL91[20] program, and an orthorhombic solution was found with satisfactory

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Table 1. Principal Crystallochemical Data and Structure Refinements for MIL-60 and MIL-61

	MIL-60	MIL-61
empirical formula	$C_{10}H_{12}O_{14}V_2$	$C_{10}H_7O_{10}V$
formula weight	458 g mol^{-1}	338 g mol^{-1}
crystal system	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	*Pnma* (No. 62)
lattice parameters	$a = 6.3758(5)$ Å	$a = 14.8860(2)$ Å
	$b = 6.8840(5)$ Å	$b = 6.9164(1)$ Å
	$c = 9.0254(7)$ Å	$c = 10.6669(2)$ Å
	$\alpha = 69.010(2)°$	
	$\beta = 85.197(2)°$	
	$\gamma = 79.452(2)°$	
volume	363.53(5) Å^3	1098.3(2) Å^3
Z	1	4
density (calcd/meas)	2.093/2.03(1) g cm^{-3}	2.045/2.036(2) g cm^{-3}
independent reflections	1821 [*R*(int) = 0.0243]	949 (5601 profile points)
reliability factors	R1^a = 0.0499, wR2^a = 0.1329	11.6:15.1% R_P/R_{wP}^{b}
		8.45:7.19% R_{Bragg}/R_F^{b}

[a] Crystal data: $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] Powder data: $R_P = \sum_n|y_i(\text{obs}) - (1/c)y_i(\text{calc})|/\sum_n y_i(\text{obs})$; $R_{wP} = \{\sum_n\omega_i[y_i(\text{obs}) - (1/c)y_i(\text{calc})]^2/\sum\omega_i[y_i(\text{obs})^2]\}^{1/2}$; $R_{Bragg} = \sum_n|I(\text{obs}) - I(\text{calc})|/\sum_n I(\text{obs})$; $R_F = \sum_n|I(\text{obs})^{1/2} - I(\text{calc})^{1/2}|/\sum_n I(\text{obs})^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for MIL-60 and MIL-61

atoms	*x*	*y*	*z*	U_{eq}^{a}
		MIL-60^b		
V(1)	0	5000	5000	12(1)
V(2)	0	0	5000	12(1)
O(1)	−107(5)	2011(4)	6076(3)	16(1)
O(2)	1933(4)	1573(4)	3209(3)	18(1)
O(3)	1746(4)	4887(4)	6848(3)	17(1)
O(4)	2520(4)	−1870(4)	6310(3)	17(1)
O(5)	2683(4)	4221(4)	3856(3)	18(1)
C(1)	3961(6)	−4561(6)	8586(4)	14(1)
C(2)	2677(6)	−3812(6)	7113(4)	12(1)
C(3)	4060(6)	3936(6)	1443(4)	14(1)
C(4)	2826(6)	3141(6)	2969(4)	14(1)
C(5)	3055(6)	4359(6)	34(4)	14(1)
Ow(1)	−1882(12)	1032(10)	9079(6)	102(2)
Ow(2)	4052(13)	734(11)	8065(9)	114(3)
H(5)	1756(6)	3914(6)	57(4)	17
H(1)	−657(93)	1626(95)	6834(69)	35(17)
		MIL-61		
V	0	−0.5	0	1.27(7)
O(1)	−0.1293(4)	−0.5872(9)	−0.0359(6)	1.64(9)
O(2)	−0.0407(6)	−0.25	−0.0736(9)	1.64(9)
O(3)	0.0372(4)	−0.5870(9)	−0.1698(5)	1.64(9)
O(4)	0.3103(6)	−0.25	−0.3128(8)	1.64(9)
O(5)	0.6838(6)	−0.25	0.7108(8)	1.64(9)
O(6)	−0.1059(6)	−0.75	−0.3730(7)	1.64(9)
O(7)	0.0942(6)	−0.25	0.5793(8)	1.64(9)
C(1)	0.1652(7)	−0.25	0.032(1)	1.2(1)
C(2)	0.9453(7)	−0.75	0.523(1)	1.2(1)
C(3)	0.0467(6)	−0.75	−0.4655(9)	1.2(1)
C(4)	0.3069(7)	−0.25	0.1540(9)	1.2(1)
C(5)	0.0999(7)	−0.75	0.6543(8)	1.2(1)
C(6)	0.2686(6)	−0.25	0.0296(9)	1.2(1)
C(7)	0.9121(7)	−0.25	0.5817(9)	1.2(1)
C(8)	0.7696(7)	−0.25	0.715(1)	1.2(1)
C(9)	0.0512(9)	−0.75	0.773(1)	1.2(1)
C(10)	0.3156(7)	−0.25	−0.0866(9)	1.2(1)
Ow	0.2271(6)	0.273(4)	−0.0661(7)	2^c

[a] U_{eq} is defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Atomic coordinates × 10^4. [c] Fixed value.

figures of merit $M/F(20) = 41.5/76.6$ (0.0064, 41). The systematic absences $0kl$ ($k + l = 2n + 1$) and $hk0$ ($h = 2n + 1$) were consistent with the centrosymmetric *Pnma* (No. 62) space group. The pattern matching was adjusted with the Fullprof2k program integrated in the WinPLOTR software,[21] and a structure solution was found by applying the direct methods of SIR97.[22] Distance constraints (C−C, C−O, and V−O) were applied during the refinement. Thermal factors were refined for each group of atoms (V, O, and C), and a fixed value of 2 was applied for the water molecule. The final stage of calculations led to satisfactory agreement factors (Table 1); the final Rietveld plot is given in the Supporting Information.

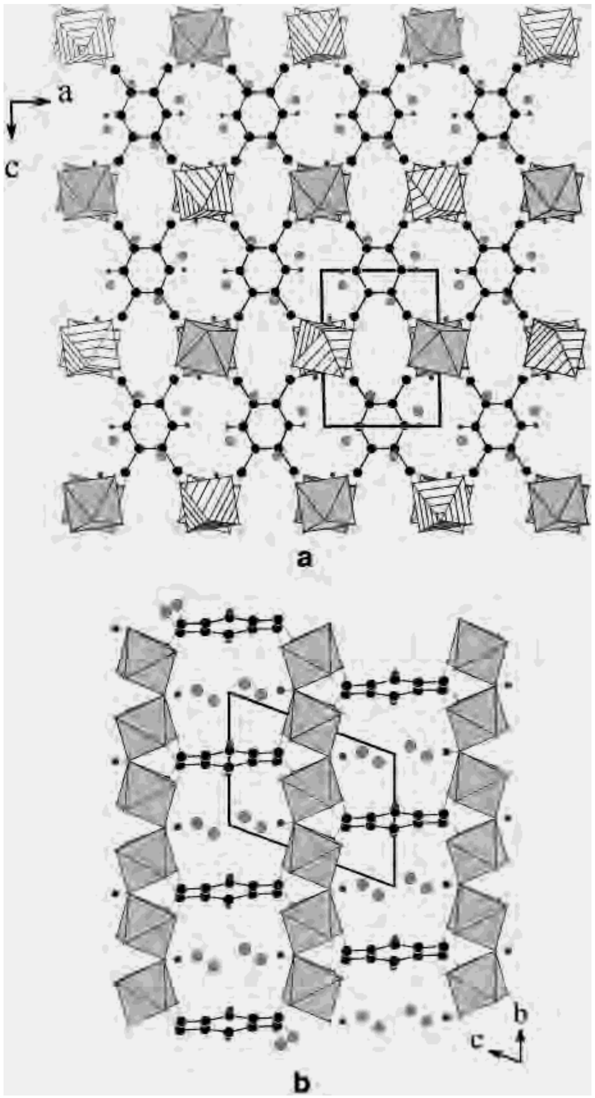

Figure 2. (a) Projection of the structure of MIL-60 along [010] *(hatched polyhedra for the supplementary octahedral chains compared to the MIL-47 framework)*. (b) Projection of the structure of MIL-60 along [100] showing the octahedral chains connected by the organic linkers to delimit channels with encapsulated water molecules.

The principal conditions for data collection are summarized in Table 1, and the atomic coordinates are given in Table 2 for MIL-60 and MIL-61.

Magnetic Measurements. The magnetization (*M*) was measured as a function of the temperature for the two compounds in the range 2−300 K using a Squid quantum design device. The resulting magnetic susceptibilities $\chi = M/H$ were then deduced.

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Table 3. Principal Interatomic Distances (Å) in MIL-60 and MIL-61

a. MIL-60

1,2,4,5-tetracarboxylate		$VO_4(OH)_2$ octahedra	
O(2)−C(4)	1.254(5) (2×)	V(1)−O(1)	1.947(3) (2×)
O(3)−C(2)	1.258(5) (2×)	V(1)−O(5)	2.011(3) (2×)
O(4)−C(2)	1.261(5) (2×)	V(1)−O(3)	2.053(3) (2×)
O(5)−C(4)	1.261(5) (2×)		
C(1)−C(5)	1.389(5) (2×)	V(2)−O(1)	1.945(3) (2×)
C(1)−C(3)	1.402(5) (2×)	V(2)−O(4)	2.027(3) (2×)
C(1)−C(2)	1.497(5) (2×)	V(2)−O(2)	2.051(3) (2×)
C(3)−C(5)	1.383(5) (2×)		
C(3)−C(4)	1.501(5) (2×)		

b. MIL-61

$V^{III}O_4(OH)_2$ octahedra		1,2,4,5-benzenetetracarboxylic acid	
V−O(1)	2.054(5) (2×)	O(1)−C(1)	1.247(8)
V−O(2)	1.994(5) (2×)	O(3)−C(9)	1.301(9)
V−O(3)	1.986(5) (2×)	O(4)−C(8)	1.20(1)
		O(5)−C(8)	1.28(1)
		O(6)−C(2)	1.35(1)
		C(1)−C(6)	1.54(1)
		C(2)−C(3)	1.52(1)
		C(3)−C(5)	1.50(1)
		C(3)−C(7)	1.38(1)
		C(4)−C(5)	1.39(1)
		C(4)−C(6)	1.44(1)
		C(5)−C(9)	1.45(2)
		C(6)−C(10)	1.42(1)
		C(7)−C(10)	1.44(1)
		C(8)−C(10)	1.54(2)

Descriptions of Structures and Magnetism

MIL-60. MIL-60 presents a three-dimensional hybrid framework built up from chains of $V^{III}O_4(OH)_2$ octahedra linked via the organic 1,2,4,5-benzenetetracarboxylate anions (Figure 2a,b). Inside the chains, the vanadium atoms are located at the center of almost regular octahedra (Table 3a) with four V−O distances slightly larger than 2 Å in the same plane and, perpendicular to those, two V−O(1) distances slightly smaller than 2 Å. Bond-valence calculations[23] show that this geometry deals with vanadium in the +3 oxidation state and that O(1) corresponds to a hydroxyl group. The carboxylate functions of the organic molecules ensure a bridging role between two consecutive octahedra. As a consequence, the octahedra are strongly tilted and the V(1)−O(1)−V(2) angle is equal to 124.4(1)°, very far from the 180° expected if the chains of trans-shared octahedra were perfectly linear. Furthermore, each organic linker shares its four carboxylate functions with four different octahedral chains in such a way that all the phenyl rings are perpendicular to the mean direction of the chains. These types of connections between the organic and inorganic moieties generate intersecting tunnels, encapsulating water molecules. Along [100], these channels exhibit an almost square section with a free aperture close to 4 Å (Figure 2b). However, the hydrogen atoms of the hydroxyl functions point toward these channels, explaining that even after dehydration the title compound does not present any specific surface area.

MIL-60 is paramagnetic, whatever the temperature is, with a Curie constant of 0.99, very close to the theoretical spin-only value of 1.00 expected for a V^{3+} ($3d^2$) cation. The $\chi^{-1} = f(T)$ curve is fitted with a Curie−Weiss law, and the observed θ_P value of −10.0(5) K indicates weak antiferromagnetic couplings between the magnetic cations.

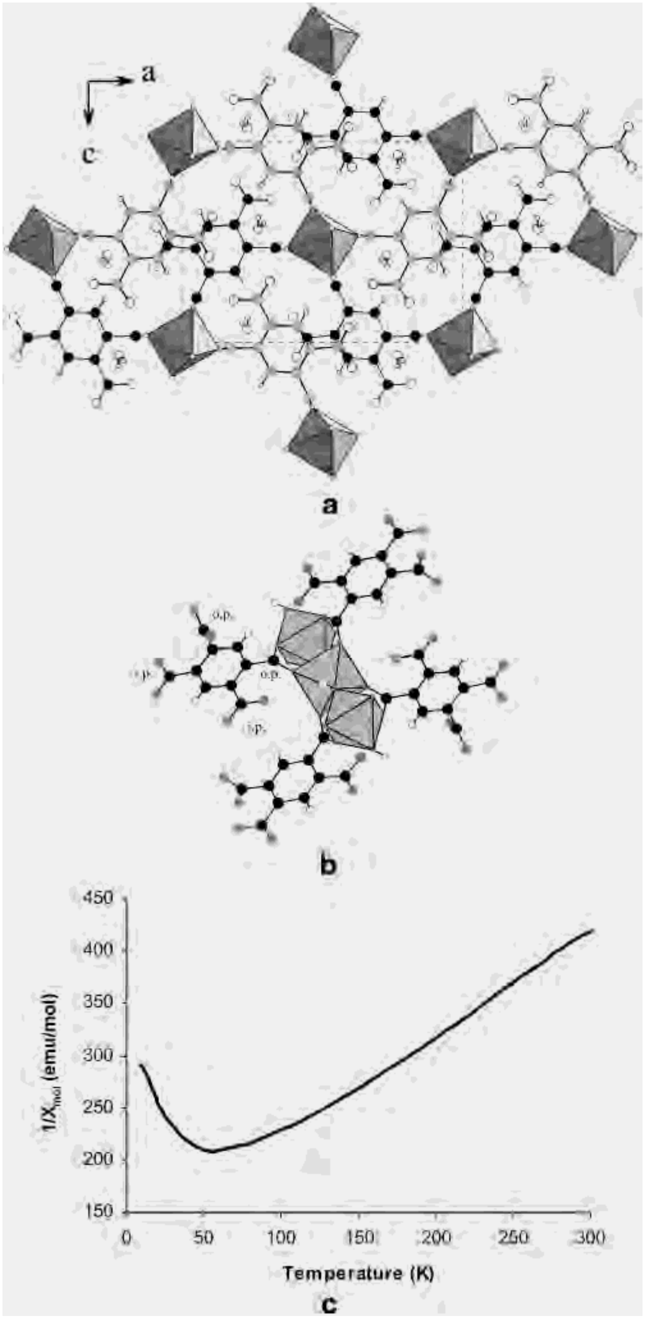

Figure 3. (a) Projection of the structure of MIL-61 along [010]. A balls-and-sticks model is used for the water and organic molecules (black and gray spheres for the carbon atoms located at $y = 1/4$ and $3/4$, respectively), and a polyhedral representation of the inorganic moieties is chosen. (b) Connections between the 1,2,4,5-benzenetetracarboxylate anions and one chain of the corner-linked $V^{III}O_4(OH)_2$ octahedra in MIL-61. For one 1,2,4,5-benzenetetracarboxylate anion, the two different positions of the carboxylate functions in reference to the phenyl ring are indicated by i.p. for "in plane" and o.p. for "out of plane". (c) $\chi^{-1} = f(T)$ curve for MIL-61, showing a minimum at $T = 55(5)$ K.

MIL-61. MIL-61 presents a complex three-dimensional hybrid framework built up from chains of corner-linked octahedra connected by carboxylate linkers (Figure 3a). Inside the inorganic chains, each vanadium atom is octahedrally coordinated with six V−O distances close to 2 Å. Oxygens [O(2)] trans-located in each octahedron correspond

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[23] Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

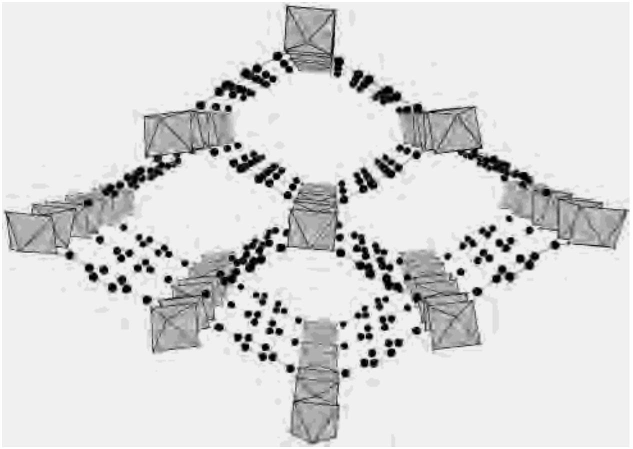

Figure 4. Perspective view of the structure of MIL-47.

to hydroxyl functions, as is demonstrated by valence-bond calculations.[21] The same calculations also give evidence of vanadium in the trivalent oxidation state. The connections between the octahedra occur via the OH functions, giving rise to infinite chains running along [010]. Furthermore, two consecutive octahedra in one chain are bridged by two carboxylate functions of two different organic linkers, inducing a strong tilting of the octahedra (Figure 3b). Consequently, the V−OH−V angle of 120.276(2)° is much lower than 180°, as could be observed in a quite linear chain. In the latter, the y coordinates of the vanadium atoms are alternatively 0 and $^1/_2$ in such a way that the phenyl rings located between the octahedra are located alternatively at $y = {}^1/_4$ on one side of the chain and $y = {}^3/_4$ on the other side of the same chain (Figure 3a). A particular feature of the organic molecules could be noted: over the four carboxylates grafted on one phenyl ring, two of them participate in the three-dimensional structure by bridging octahedra of two different octahedral chains, whereas the two remaining are terminal. Geometrically, the two latter carboxylates are in the plane of the ring, whereas the two other ones are perpendicularly disposed (Figure 3b). The terminal ones give rise to hydrogen bonds with water molecules occluded in the cavities of the framework.

The $\chi^{-1} = f(T)$ curve of MIL-61 shows a minimum at temperature $T = 55(5)$ K (Figure 3c). The fitting of the linear part of the χ^{-1} curve provides (i) a Curie constant of 0.98 in perfect agreement with the theoretical spin-only value of +1 expected for V^{3+} ($3d^2$) and, by extrapolation, (ii) a Curie−Weiss temperature of $\theta_P = -111(5)$ K, indicating strong antiferromagnetic couplings between magnetic cations.

Discussion

Recently, we reported MIL-47_{as},[13] whose three-dimensional hybrid structure is built up from chains of $V^{III}O_4(OH)_2$ octahedra connected by terephthalate linkers. The connections of the inorganic and organic moieties generate one-directional tunnels filled by disordered unprotonated terephthalic acid. This compound exhibits an antiferromagnetic transition below $T = 95(5)$ K. Furthermore, the calcination of MIL-47_{as} leads to MIL-47 (Figure 4), whose the structure is built up from topologically similar chains of $V^{IV}O_6$ octahedra, the elimination of the unlinked organic molecules allowing a specific surface area of 930 m^2 g^{-1}.

The comparison between the structures of MIL-47 and MIL-60 could lead to a description of the MIL-60 framework as the interpenetrating association of two MIL-47 frameworks. Effectively, in a first approach, if we consider only the linkage of the vanadium chains of MIL-60 by one single-pair type of trans-located carboxylate functions (pairs 1,4 or 2,5) of the 1,2,4,5-benzenetetracarboxylate anions (Figure 2a), we so describe an MIL-47 framework whose channels are filled by an extra octahedral chain. These extra chains are connected together by the unconsidered pairs of carboxylate functions to form a second MIL-47 framework. As a consequence, MIL-60 cannot possess any specific surface area. This description shows that the structural relationships between the two compounds are very strong. However, MIL-60 does not correspond to the interpenetration of the two independent frameworks because the organic linkers are common to the two subnetworks.

More curiously, the magnetic behaviors of the two compounds are quite different even though the two structures are built up from the same polyhedral chains. The explanation for this should be found in the efficiency of the different organic linkers to ensure the transmission of the magnetic couplings. It could be dependent on the number, position, and geometry (in or out of the aromatic plane) of the complexing carboxylate functions. In MIL-47, the two carboxylate groups located on the 1 and 4 positions are in the same plane of the phenyl ring. In MIL-61, the bridging functions are on the 1 and 5 positions, perpendicularly disposed to the phenyl ring, and the carboxylates in the 2 and 4 positions are terminal and in-plane. In both cases, the compounds are antiferromagnetic and their Curie−Weiss temperatures are of the same order of magnitude. On the other hand, the four carboxylate functions of MIL-60 bridge the vanadium atoms of the octahedral chains and make a dihedral angle with the phenyl ring close to 45° versus equivalent angles close to 0 and 90° for MIL-47 and MIL-61, respectively. In such a case, one observes that the resulting compound does not present any magnetic ordering. In the present, we are only able to notice these experimental facts, and the curious magnetic behavior of MIL-61 will possibly be more easily understood when the number of compounds in the vanadocarboxylate series is increased, authorizing some more general comparisons.

However, these octahedral chains correspond to chains of $S = 1$ magnetic centers. Consequently, the magnetic behavior of these vanado(III)carboxylates needs to be revisited using the Haldane gap model.[24] This comparative study is currently in progress and will be published elsewhere.

Supporting Information Available: Complete crystallochemical data, structural refinements, and IR spectra for MIL-60 and MIL-61, structure factors for MIL-61, the Rietveld plot for MIL 61, and a crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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