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An Open-Framework Rare-Earth Acetylenedicarboxylate: MIL-95, $\mathrm{Eu^{III}_2(H_2O)_2(CO_3)_2\cdot\{O_2C{-}C_2{-}CO_2\}\cdot\{H_2O\}_x}$

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The first three-dimensional rare-earth acetylenedicarboxylate solid, MIL-95 (MIL = Material Institut Lavoisier), has been isolated and its structure solved from single-crystal X-ray diffraction data. Its two-dimensional inorganic subnetwork, built up from chains of edge-sharing nine-coordinated europium-capped square antiprisms and carbonate moieties, is pillared by the acetylenedicarboxylate groups. This leads to an open framework where small pores are filled with water molecules interacting with terminal water bound to the metal centers. TGA and X-ray thermodiffractometry show that dehydration leads to an irreversible pore contraction. The whole structure collapses above 230 °C. Crystal data for MIL-95: orthorhombic space group *Pba*2 (No. 32), with $a = 7.6762(2)$ Å, $b = 17.8448(4)$ Å, and $c = 4.8105(2)$ Å.

Introduction

The synthesis of hybrid inorganic−organic porous solids is still attractive,[1−6] because of the large number of potential applications in catalysis, shape-selective absorption, optical devices, or molecular-based magnetism. The modulation of the complexing functions (carboxylates, phosphonates, ...) and organic moieties with a wide range of metals leads to the formation of a large variety of open-framework solids with different pore shapes and dimensions including sometimes unique properties.[7,8]

Within the large number of hybrids reported so far, solids incorporating organic moieties with delocalized π electrons are now common.[5] These groups exhibit rigid spacers and/or allow an enhancement of the physical properties of the resulting solids.[7,9] However, most of these organics are built up from benzyl moieties, and it is only recently that a few metallofumarates with a single double C═C bond have been reported.[10−13] Hybrids incorporating acetylene functions are also very scarce[9,14,15] and correspond to coordination polymers. Using such groups represents several advantages compared to other carboxylates: First, its steric hindrance is much smaller than those of the usual organic moieties because of its linearity and the absence of hydrogen atoms bonded to the carbon skeleton; this could lead to the formation of porous solids with larger voids. Second, the reactivity of the triple bonds could be used to anchor chemically organic groups within the pores of the solids. However, the stability of acetylenecarboxylate under hydrothermal conditions is very poor, which limits considerably the formation of hybrids based on these acids.

In the field of lanthanide carboxylates, a lot of research has recently been performed by several groups, leading to various open-framework solids.[16−27] We also undertook a global study of the rare-earth system in water, resulting in

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Table 1. Crystallographic Data for MIL-95

empirical formula	$Eu_2O_{13.166}C_6H_{6.333}$	$F(000)$	547
fw	593	cryst size (mm^3)	0.38 × 0.04 × 0.01
temp (K)	296 (2)	θ range for data collection (deg)	2.28−29.77
wavelength (Å)	0.71073	limiting indices	$-10 < h < +9, -24 < k < +14, -5 < l < +6$
cryst syst	orthorhombic	no. of collected/unique reflns	4447/1652
space group	*Pba2* (No. 32)	no. of independent reflns	1652 ($R_{int} = 0.0437$)
unit cell dimensions (Å)	$a = 7.6762(2)$	refinement method	full-matrix least-squares on F^2
	$b = 17.8448(4)$	no. of data/restraints/params	1652/4/104
	$c = 4.8105(2)$	GOF on F^2	1.083
vol (Å^3)	658.94(4)	final R indices [$I > 2(I)$]	R1 = 0.0447, wR2 = 0.1064
multiplicity (Z)	2	R indices (all data)	R1 = 0.0591, wR2 = 0.1160
density(calcd) (mg/cm^3)	2.989	extinction coefficient	0.00104(10)
abs coeff (mm^{-1})	9.50	largest diff peak and hole ($e^-\cdot Å^3$)	1.49 and −1.769 $e^-\cdot Å^3$

pillared or open-framework solids built up from alkyl,[28−31] alcene,[32] and benzenecarboxylate[33−35] groups. This study deals with the synthesis, the crystal structure, and the thermal behavior of our first three-dimensional europium acetylenedicarboxylate: MIL-95 (MIL = Material Institut Lavoisier), $Eu^{III}_2(H_2O)_2(CO_3)_2\cdot\{O_2C-C_2-CO_2\}\cdot\{H_2O\}_x$ ($x \approx 1.1667$).

Experimental Section

Synthesis. The title solid was isolated as pure single crystals from a reaction mixture of composition 1.0 $Eu(NO_3)_3\cdot xH_2O$:1.0 ADC:1.5 NaOH:280 H_2O (ADC = acetylenedicarboxylic acid) that was held at 120 °C in a Teflon-lined autoclave for one night. The pH remains sligthly acidic (<4) throughout the synthesis. The yellow solid product was recovered by filtration, washed with deionized water, and dried at room temperature. A laboratory powder X-ray diffraction pattern showed that a novel crystalline phase had been produced.

X-ray Powder Diffraction. A laboratory X-ray diffraction pattern has been obtained on the title compound (see the Supporting Information). Despite differences in peak intensities due to the presence of a strong preferred orientation (single crystals), the experimental pattern corresponds to the calculated one. However, a small unidentified impurity is present (see the peak at $2\theta \approx 11.5°$).

Analysis. Elemental analysis indicated that the contents of Eu and C are in good agreement with the values based on the structural formula $Eu^{III}_2(H_2O)_2(CO_3)_2\cdot\{O_2C-C_2-CO_2\}\cdot\{H_2O\}_x$ ($x \approx 1.1667$). Anal. Found: Eu, 52.3; C, 10.95. Calcd: Eu, 51.3; C, 12.14. The small difference in carbon analysis might be due to the presence of an impurity observed by X-ray powder diffraction. Only traces of nitrogen have been observed (~0.1%), ruling out the presence of $-NO_3$ groups within the title solid.

Thermal Behavior. Thermal analysis (TGA TA2050 apparatus, O_2 flow, heating rate 5 $K\cdot min^{-1}$) has shown two weight losses between 298 and 873 K. The first (~11.5%) between 323 and 473 K is attributed to the departure of the free and bound water molecules. The second weight loss (~29%) between 473 and 773 K is related to the slow combustion of the acetylenecarboxylic acid and the carbonate groups of the framework. These two losses are on the whole in agreement with the theoretical values (calcd, 9.6% and 31%). The residual solid has been identified as europium oxide (Eu_2O_3).

X-ray thermodiffractometry, performed in the furnace of a Siemens D-5000 diffractometer in the $\theta-\theta$ mode, shows several steps in the decomposition for MIL-95.

Infrared Spectroscopy. Infrared spectroscopy confirms the presence of deprotonated $-C-O$ groups within the solid (bands at 1400 and 1560 cm^{-1}).

The structure of the new material was solved from single-crystal X-ray diffraction data. The formula deduced from the structure determination $Eu^{III}_2(H_2O)_2(CO_3)_2\cdot\{O_2C-C_2-CO_2\}\cdot\{H_2O\}_x$ ($x \approx 1.1667$) agrees well with the chemical results.

Structure Solution. Single-crystal X-ray diffraction data were collected for MIL-95. A needlelike single crystal was glued onto a glass fiber. The intensity data were collected respectively on a Bruker-Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using Mo Kα radiation. The reflections were corrected for Lorentz and polarization effects and absorption. The cell of MIL-95 is orthorhombic with space group *Pba2* (No. 32), $a = 7.6762(2)$ Å, $b = 17.8448$ (4) Å, $c = 4.8105$ (2) Å, and $Z = 2$. The structure was solved using the SHELXTL package.[36] Europium, oxygen atoms, and most of the carbon atoms were located first, while the disordered free water molecules and the remaining carbon atoms were found using difference Fourier maps. A partial site occupation was given to some of the free water molecules. Soft distance constraints were also applied for the carbonate moieties (C−O distances of 1.29 Å). Bond valence calculations give values of 3.3 for Europium atoms.[37] The final

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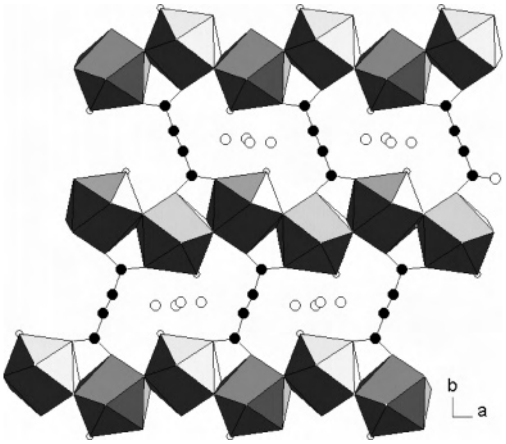

Figure 1. View of the structure of MIL-95 along the *c* axis. Europium polyhedra, carbon atoms, and water molecules are represented in gray, black, and white, respectively. For a better understanding, terminal water molecules from the europium polyhedra have been represented in a “balls and sticks” mode.

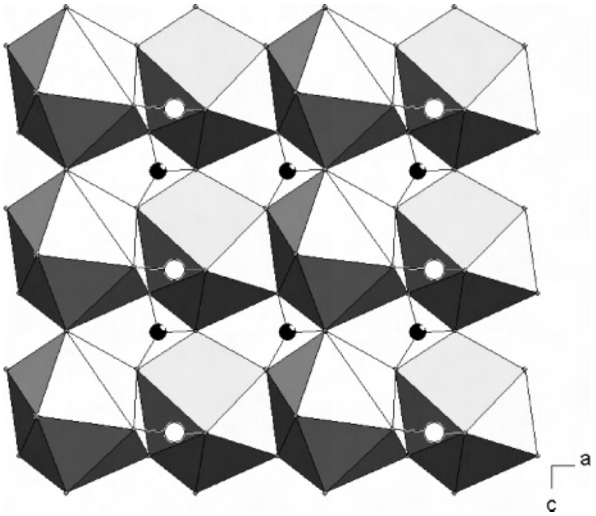

Figure 2. View of the inorganic layers of MIL-95 along the *b* axis. Europium polyhedra are represented in gray, while carbon atoms from the carbonate and the dicarboxylate are represented in black and white, respectively.

reliability factors[36] converged to R1(F) = 0.0447 and wR2(F^2) = 0.1064 (see Table 1).

Results and Discussion

MIL-95 exhibits a three-dimensional structure. It is built up from nine-coordinated europium-capped square antiprisms and carbonate and acetylenedicarboxylate ions (Figure 1). The europium subnetwork in the (101) planes can be decomposed into chains of edge-sharing polyhedra along *a* and chains of corner-sharing polyhedra along *c* (Figure 2). These corner-sharing oxygen atoms belong to carbonate groups. Thus, MIL-95 can be described as a two-dimensional europium carbonate subnetwork pillared by acetylenedicarboxylate moieties to produce a three-dimensional framework (Figure 1). This delimits a one-dimensional pore system along the *c* axis. The tunnels are filled alternately by disordered free water molecules and terminal water groups, bound to the europium atoms, which interact together through hydrogen bonds (see distances Ow1−Ow*i* of 2.67, 2.73, and 2.94 Å (i = 2, 2, 3)). The dimensions of the pore are rather small with an estimated free aperture of ~3.95 × 5.15 Å^2.

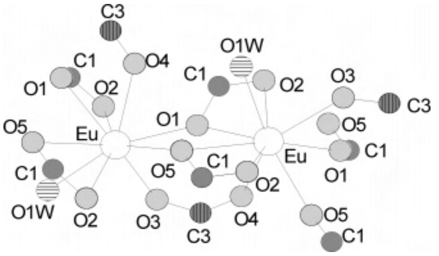

Figure 3. Asymmetric subunit of MIL-95. Europium polyhedra are represented in white, while carbon atoms from the carbonates and the dicarboxylates are represented in gray and hatched gray, respectively. Oxygen atoms are in light gray except for the terminal water molecule, which is in hatched white.

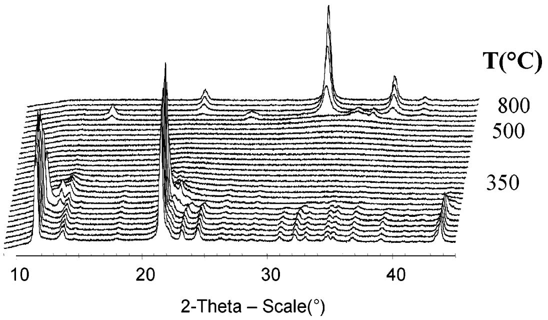

Figure 4. X-ray thermodiffractogram of MIL-95 under an air atmosphere.

Europium atoms are nine-coordinated with one terminal water molecule, two oxygen atoms from the dicarboxylate moieties, and six oxygen atoms from the carbonate groups (Figure 3). The edge-sharing mode (O1, O5) is ensured only by two separate carbonate groups, while dicarboxylate groups bridge two consecutive europium atoms from the chains (see C3, O3, and O4 in Figure 3).

Interatomic distances and angles are usual, and the values observed for the acetylene group confirm that its triple bond character is kept in MIL-95 (C3−C2−C2 angle close to 180° (174.3(8)°) and C≡C distance of 1.21(1) Å).

The presence of carbonate anions within the structure of MIL-95 was unexpected since the only anions present in the initial synthetic mixture are hydroxyl, nitrate, and acetylenedicarboxylate moieties; however, quantitative analysis ruled out the presence of nitrogen. Thus, carbonates from the inorganic subnetwork are probably issued from the partial decomposition of acetylenedicarboxylate ions under hydrothermal conditions. This shed some light on the difficulty to produce hybrid solids based on acetylene groups under hydrothermal conditions; in our case, the reactivity of rare-earth cations is probably high enough to react before all acetylenedicarboxylate groups are destroyed.

The thermal behavior of MIL-95 has also been investigated using X-ray thermodiffractometry (Figure 4). It shows that the dehydration, which occurs in one step according to TGA results, leads to an irreversible pore contraction and a strong decrease in crystallinity at 130 °C. Above 230 °C, an amorphous phase is formed which turns first into europium carbonate oxide ($Eu_2O(CO_3)_2$) at 500 °C and then into europium oxide (Eu_2O_3) at higher temperatures. Such a pore contraction upon dehydration has been previously observed in other hydrated rare-earth carboxylates.[32]

Finally, we report here the crystal structure of the first example of a three-dimensional rare-earth carboxylate incorporating an alcyne group. Due to the small pore size and the strong pore contraction occurring upon dehydration, the reactivity of the triple bond could not be tested in this case. However, this result opens the way to the hydrothermal synthesis of open-framework solids with reactive triple bonded organic moieties. Other results are in progress and will be published very soon.

Supporting Information Available: Crystallographic data in CIF format. XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data for MIL-95 have also been deposited at the Cambridge Crystallographic Data Center (Deposition No. CCDC 222758).

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