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Notes

Assembly of a Porous Three-Dimensional Coordination Polymer: Crystal Structure of $\{[La_2(adipate)_3(H_2O)_4]6H_2O\}_n$

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Introduction

The construction of infinite frameworks by linking small organic multifunctional ligands with metal cations is a topic with a relatively long history.[1] These molecular-based solids are of intense current interest both for their potential applications in solid-state technology and for their fascinating network topologies.[2]

A particularly attractive goal has been the assembly of porous networks of potential utility in catalysis, adsorption and host−guest chemistry.[2a,3] The main problems encountered when trying to construct molecular-based microporous materials (either coordination polymers or hydrogen bonded organic solids) is obstruction of the pores by interpenetration of networks[4] or collapse of the structure upon removal of the guest molecules enclathrated in the cavities.[5] There are, however, some rare examples where the host structure is not destroyed when the guests are either exchanged[3,6] or removed (partially or completely).[7] A somewhat intermediate case was recently reported by Endo et al.[8] in which removal of the guest reversibly transforms a porous structure (2D purely organic) into a nonporous one.

When attempts are made to construct coordination polymers, rigid ligands are frequently employed, which, in some favorable cases, permit reasonable prediction to be made about the structure. In this work, we use a flexible ligand, namely adipic acid, and La^{3+} to construct a coordination polymer. It was expected that the combination of a cation with a high coordination number with a long chain dicarboxylic acid would result in a 3D structure without interpenetration. Furthermore, the flexibility of the ligand might prevent collapse of the structure upon departure of the enclathrated solvent. The structure we describe here, $\{[La_2(ad)_3(H_2O)_4]6H_2O\}_n$ (ad = adipato; $C_6H_8O_4^{2-}$) (**1**), is indeed a porous polymer which, upon dehydration, transforms reversibly into the crystalline nonporous $[La_2(ad)_3(H_2O)_2]_n$ (**2**).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer using the KBr pellet technique. Thermal analysis was performed on a TRDA3-H (Chyo Balance Corp.) thermal analyzer, under air flow (40 L/min), at a heating rate of 5 °C/min. X-ray powder diffraction (XRPD) spectra were recorded on a Philips PW 1050/70 diffractometer ($\lambda = 1.54051$ Å). Simulation of the XRPD spectra was carried out with the X-ray Powder Diffract program.[9]

Preparation of $\{[La_2(ad)_3(H_2O)_4]6H_2O\}_n$. A sodium silicate solution (Merck, $d = 1.1$) was slowly added to a 0.01 M aqueous solution of adipic acid until the pH reached the value of 5.9. The resulting gelling solution was poured in a test tube and allowed to stand for about 24 h. An aqueous solution of 0.01 M $La(NO_3)_3$ (Fluka) or 0.05 M $LaCl_3$ (Fluka) was then carefully added at the top of the gel. Colorless prismatic crystals are formed within 3−4 days. Anal. Calcd: C, 24.27; H, 4.94. Found: C, 25.05; H, 4.90. Main IR frequencies: 3340, 1520, 1450, 1440, 1420, 1400, 1350, 1135, and 1115 cm^{-1}.

Preparation of $[La_2(ad)_3(H_2O)_2]_n$. This compound is prepared by heating overnight in air, at 115 °C, a certain amount of **1**. The conversion is quantitative. Anal. Calcd: C, 28.96; H, 3.75. Found: C, 27.86; H, 3.70. Main IR frequencies: 3330, 3260, 1570, 1545, 1510, 1450, 1430, 1405, 1390, 1330, 1300, and 1125 cm^{-1}.

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Table 1. Crystallographic Data for **1**

empirical formula	$La_2O_{22}C_{18}H_{44}$
fw	890.35
space group	$P\bar{1}$ (No. 2)
T	20 °C
λ	0.710 73 Å
a	9.239(2) Å
b	9.790(2) Å
c	0.709(1) Å
α	68.04(1)°
β	84.49(1)°
γ	62.01(1)°
V	789.5(7) Å^3
Z	1
d_{cald}	1.873 g cm^{-3}
μ(Mo Kα)	2.755 cm^{-1}
final R indices [$I > 2\sigma(I)$]	R1^a = 0.0136, wR2^b = 0.0356
R indices (all data)	R1^a = 0.0157, wR2^b = 0.0361

[a] Based on F's. [b] Based on F^2 with $w = 1/(\sigma^2(F_o)^2 + (0.0203P)^2 + 0.2547P)$ and $P = (\text{Max}(F_o{}^2,o)+2F_c{}^2)/3$.

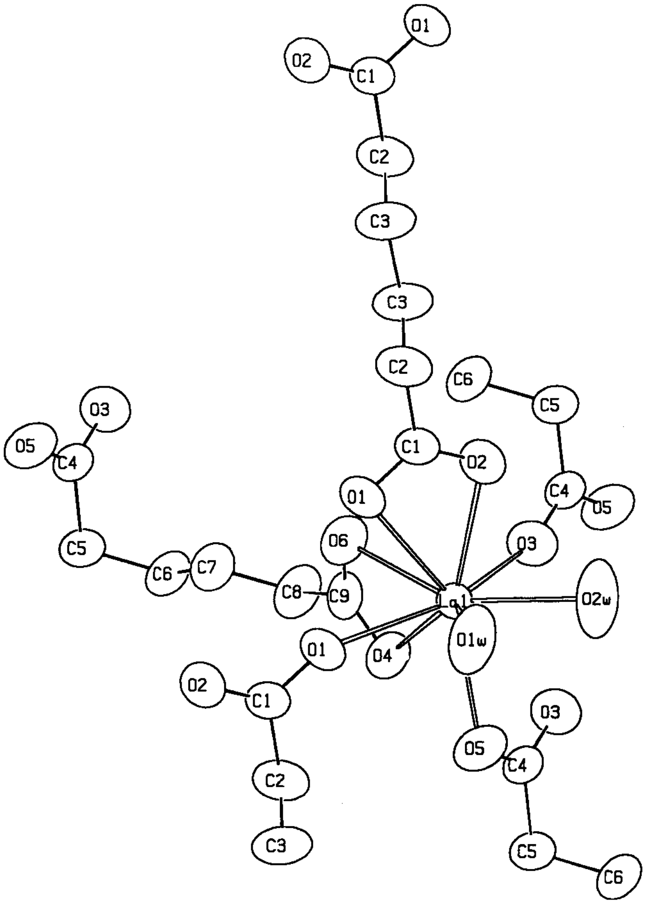

Figure 1. ORTEP view of the coordination environment (90% probability ellipsoids).

X-ray Crystallography. A prismatic crystal of **1,** of approximate dimensions 0.2 × 0.2 × 0.1 mm, was used. Data were collected at room temperature, on an Enraf-Nonius CAD4 diffractometer, with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710$ 73 Å), $\theta - 2\theta$ scan mode ($2° < 2\theta < 60°$). The structure was solved with SHELXS-86 and refined with SHELXL-97. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference maps and refined isotropically. For reasons that will be explained below, two hydrogen atoms, one bound to OW4 and one to OW5 should be disordered and therefore each one was refined over two positions with occupancy factor 0.5. This resulted in a more satisfactory refinement model with significantly improved thermal parameters for these atoms. A summary of the crystallographic data and structure refinement is given in Table 1.

Table 2. Positional (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1** (Esd's in Parentheses)

atom	x	y	z	U(eq)^a
La(1)	2247(1)	5438(1)	−159(1)	15(1)
O(1)	−220(1)	5318(1)	−1346(1)	24(1)
O(2)	1275(2)	6342(2)	−2663(1)	29(1)
O(3)	5010(1)	−4490(1)	1102(1)	26(1)
O(4)	4220(1)	2656(1)	1730(1)	24(1)
O(5)	2524(1)	−3780(2)	1768(1)	27(1)
O(6)	3085(1)	2329(1)	227(1)	24(1)
C(1)	133(2)	5947(2)	−2520(1)	20(1)
C(2)	−746(2)	6163(2)	−3748(2)	28(1)
C(3)	424(2)	4948(2)	−4398(2)	29(1)
C(4)	4002(2)	−4120(2)	1948(1)	18(1)
C(5)	4564(2)	−4114(2)	3219(1)	22(1)
C(6)	5370(2)	−2994(2)	2950(2)	22(1)
C(7)	4228(2)	−1161(2)	2152(2)	23(1)
C(8)	5146(2)	−148(2)	1905(2)	26(1)
C(9)	4074(2)	1712(2)	1250(1)	20(1)
O(1W)	−371(2)	8118(2)	−380(2)	34(1)
O(2W)	2548(2)	8011(2)	−1498(2)	38(1)
O(3W)	−273(2)	983(2)	−2434(2)	42(1)
O(4W)	1505(2)	−1384(2)	−5030(2)	44(1)
O(5W)	5547(4)	1230(3)	4528(2)	66(1)

[a] $U(\text{eq}) = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

La(1)−O(3)(a)	2.511(2)	La(1)−O(2W)	2.522(2)
La(1)−O(5)(b)	2.525(2)	La(1)−O(1W)	2.545 (2)
La(1)−O(1)(c)	2.546(2)	La(1)−O(2)	2.593(2)
La(1)−O(4)	2.600(2)	La(1)−O(6)	2.634(2)
La(1)−O(1)	2.783(2)		

O(3)(a)−La(1)−O(2W)	72.91(5)	O(3)(a)−La(1)−O(5)(b)	107.19(5)
O(2W)−La(1)−O(5)(b)	81.00(6)	O(3)(a)−La1−O(1W)	139.82(4)
O(2W)−La(1)−O(1W)	67.52(5)	O(5)(b)−La1−O(1W)	73.59(4)
O(3)(a)−La(1)−O(1)(c)	148.60(4)	O(2W)−La(1)−O(1)(c)	138.29(4)
O(5)(b)−La(1)−O(1)(c)	80.38(5)	O(1W)−La(1)−O(1)(c)	71.52(5)
O(3)(a)−La(1)−O(2)	80.38(5)	O(2W)−La(1)−O(2)	72.82(5)
O(5)(b)−La(1)−O92)	149.33(4)	O(1W)−La(1)−O(2)	81.70(5)
O(1)(c)−La(1)−O(2)	108.94(5)	O(3)(a)−La(1)−O(4)	74.78(5)
O(2W)−La(1)−O(4)	130.83(5)	O(5)(b)−La(1)−O(4)	74.36(5)
O(1W)−La(1)−O(4)	138.87(5)	O(1)(c)−La(1)−O(4)	78.32(5)
O(2)−La(1)−O(4)	135.49(4)	O(3)(a)−La(1)−O(6)	77.38(4)
O(2W)−La(1)−O(6)	147.43(5)	O(5)(b)−La(1)−O(6)	121.06(4)
O(1W)−La(1)−O(6)	138.03(4)	O(2)−La(1)−O(6)	89.49(4)
O(4)−La(1)−O(6)	49.54(4)	O(3)(a)−La(1)−O(1)	116.62(5)
O(2W)−La(1)−O(1)	112.36(5)	O(5)(b)−La(1)−O(1)	136.17(4)
O(1W)−La(1)−O(1)	74.07(5)	O(1)(c)−La(1)−O(1)	61.72(5)
O(2)−La(1)−O(1)	47.77(4)	O(4)−La(1)−O(1)	114.96(4)
O(6)−La(1)−O(1)	69.88(4)		

[a] Symmetry codes: (a) $1 - x, -y, -z$; (b) $x, 1 + y, z$; (c) $-x, 1 - y, -z$.

Results and Discussion

The crystals of **1** are stable in air indefinitely. X-ray analysis shows that each lanthanum cation binds to nine oxygen donor atoms, two of which belong to water molecules and the remaining seven to five adipate dianions (Figure 1). Final fractional coordinates and equivalent isotropic thermal parameters are given in Table 2. The metal−oxygen bonds (Table 3) are between 2.512 and 2.780 Å and are within the range of those usually encountered for 9-fold lanthanum−oxygen coordination.[10] In Chart 1 we depict the mode of binding of the two crystallographically independent organic ligands. Both organic ligands adopt a "linear" conformation and form the "walls" of infinite interconnected channels running in the three directions of space. Figure 2 presents a section of such a channel. The ligands shown parallel to the figure belong to

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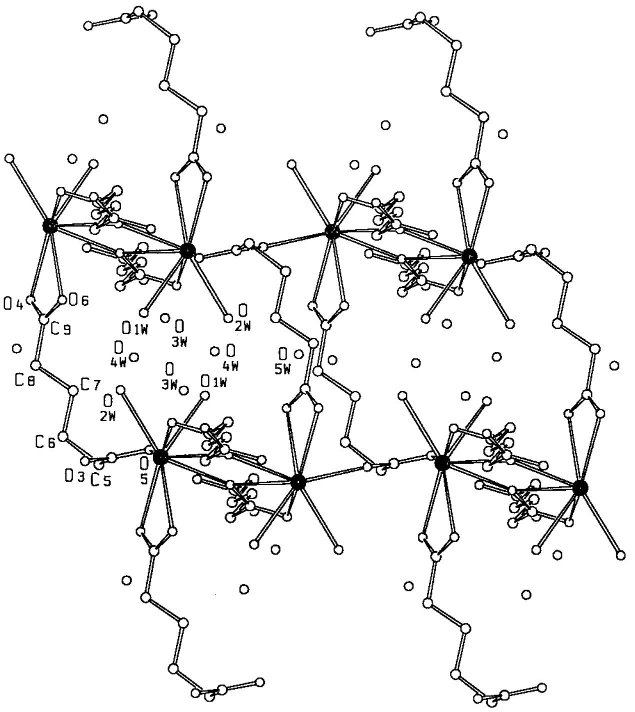
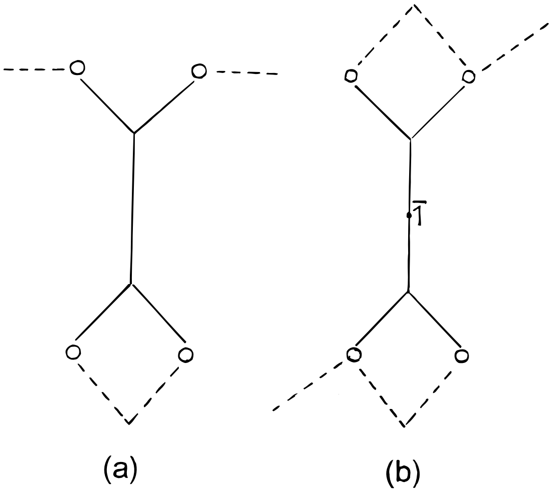


Figure 2. SCHAKAL view of the structure along the *c* axis. Solid spheres represent lanthanum cations.

Chart 1. (a) Type 1 Ligand; (b) Type 2 Ligand



type 1 while those perpendicular to the figure plane belong to type 2. Figure 3 presents a section of the channel along *a*. The channels along *a* have the largest opening with a maximum La−La distance of about 17 Å. To the best of our knowledge, this type of structure is unprecedented in rare-earth carboxylates.

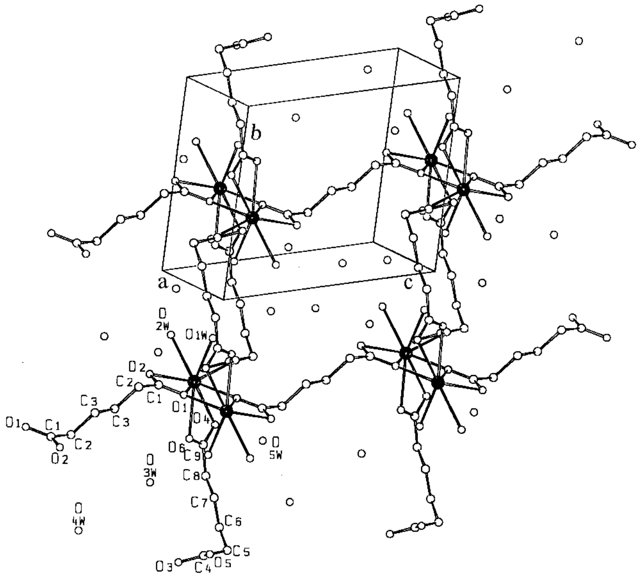


Figure 3. SCHAKAL view of the structure along the *a* axis.

Table 4. Hydrogen Bonding Geometry[a]

D−H···A	*d*(D···A)	*d*(H···A)	∠(DHA)
O(1W)−H(1A)···O(6) (a)	2.721(2)	1.96(3)	166(3)
O(1W)−H(1B)···O(3W) (b)	2.882(2)	2.08(3)	162(2)
O(2W)−H(2A)···O(3W) (b)	2.732(2)	1.95(3)	159(3)
O(2W)−H(2B)···O(4) (c)	2.748(2)	2.00(3)	168(3)
O(3W)−H(3A)···O(4W) (d)	2.865(3)	2.01(4)	173(3)
O(3W)−H(3B)···O(5) (e)	2.857(2)	2.05(3)	164(3)
O(4W)−H(4A)···O(2) (f)	2.748(2)	1.88(3)	175(3)
O(W4)−H(4B1)[b]···O(4W) (d)	2.846(4)	1.99(6)	171(7)
O(W4)−H(4B2)[b]···O(5W) (g)	2.907(3)	2.15(7)	168(6)
O(5W)−H(5A)···O(4)	2.899(3)	2.16(4)	167(4)
O(5W)−H(5B1)[b]···O(5W) (h)	2.848(5)	1.99(6)	164(6)
O(5W)−H(5B2)[b]···O(4W) (g)	2.907(3)	2.20(8)	151(8)

[a] Symmetry codes: (a) −*x*, 1 − *y*, −*z*; (b) *x*, 1 + *y*, *z*; (c) 1 − *x*, 1 − *y*, −*z*; (d) −*x*, −*y*, −1 − *z*; (e) −*x*, −*y*, −*z*; (f) *x*, 1 − *y*, *z*; (g) 1 − *x*, −*y*, −*z*; (h) 1 − *x*, −*y*, 1 − *z*. [b] Occupancy factor 0.5.

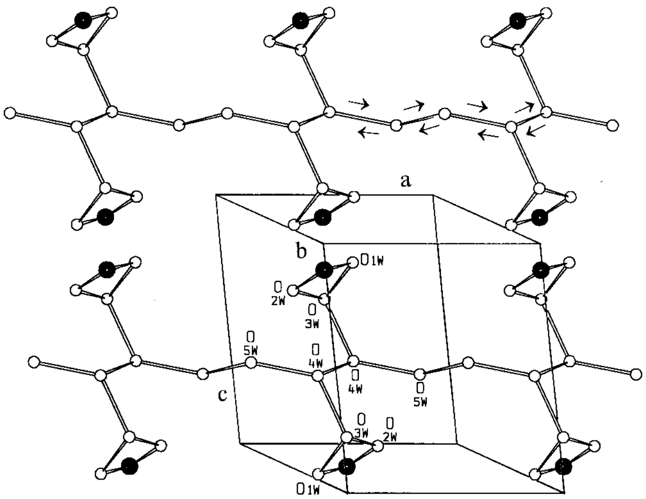


Figure 4. View of the hydrogen-bonded network of the water molecules. The direction of the arrows indicates the direction of donation of protons. The two configurations of the chain are represented by the two sets of arrows pointing to the same direction.

The water molecules (both guest and coordinated ones) and the carboxylate oxygen atoms form a complex hydrogen-bonded network. The geometry of the hydrogen bonding is shown in Table 4. It is worth noting that O3W and O4W are fully coordinated (four-coordinated) and O1W, O2W, and O5W are three-coordinated. The guest molecules form infinite chains along the *a* axis (Figure 4) and are connected to the coordinated water molecules via O3W. Additional hydrogen bonds link all water molecules to carboxylate oxygen atoms (Table 4). It is interesting to note that all hydrogen atoms contributing to the chain −O5W−O4W−O4W−O5W−O5W−O4W− should be disordered. This arises from the fact that crystallographic inversion centers are located in the middle of the bonds O4W−O4W and O5W−O5W. If, for instance, O4W donates a proton to its symmetry-related atom, then the latter should also donate

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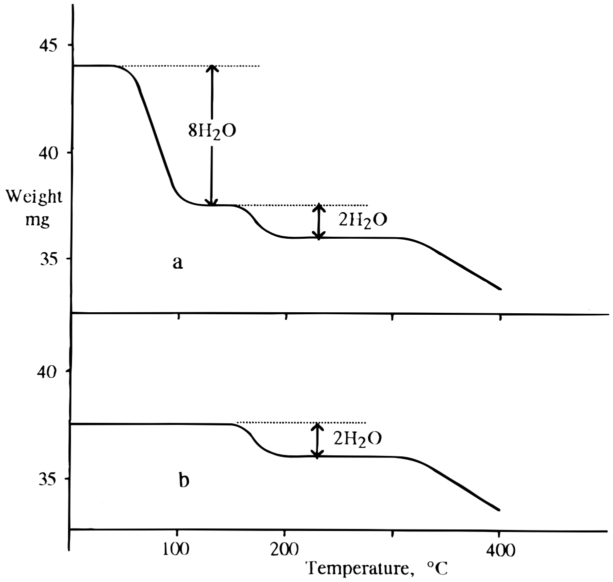

Figure 5. TGA curves of (a) **1** and (b) **2**.

back a proton. In this case the bond O4W−O4W would possess two protons while the bond O4W−O5W would be proton deficient. The same reasoning holds also for the O5W−O5W bonds. Such a configuration is unlikely to occur unless the hydrogen positions are disordered so that both are not simultaneously occupied. It is generally believed that such cooperativity in water networks is energetically favored.[11]

The thermal decomposition of **1** was investigated by thermogravimetric analysis (Figure 5). The first step (45−107 °C) corresponds to the loss of eight water molecules per formula unit, two of which are coordinated ones. The XRPD spectra showed that compound **2** is formed at the end of this step. Compound **2** loses its two coordinated water molecules during the second step (160−205 °C). Decomposition occurs beyond 320 °C, but no attempt was made to identify the final residue. Adsorption studies showed that **2** has a specific area of only 8 m^2/g and therefore the porous host structure is not retained. Interestingly, the transformation from **1** to **2** is reversible. When **2** is left overnight in an open glass vessel, under stirring, in the presence of water, it transforms to **1** as shown by the equilibrium

$$\mathbf{1}\text{ (powder)} \underset{+8\,H_2O}{\overset{-8\,H_2O}{\rightleftarrows}} \mathbf{2}\text{ (powder)}$$

The identification of **1**, obtained by the above transformation, was established by IR spectroscopy, elemental analysis (calcd, C, 24.27; H, 4.94; found, C, 24.60; H, 4.95), and thermogravimetry. Furthermore, its XRPD pattern was in good agreement with the simulated pattern reproduced from the F_c values of the calculated crystal structure of **1** (see Supporting Information).

In conclusion, we have shown that it is possible to construct 3D molecular-based microporous materials using flexible multidentate ligands and metal centers with high coordination numbers. This is a rare example of a porous 3D coordination polymer which is not irreversibly destroyed upon removal of its solvent. Future work on similar metal−ligand systems is in progress.

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Supporting Information Available: Tables of crystallographic data, hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters of non-hydrogen atoms, bond lengths and angles, simulated and experimental XRPD spectra, and perspective view of the structure of **1** along *a* (12 pages). Ordering information is given on any current masthead page.

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