

# Aliphatic dicarboxylates with three-dimensional metal–organic frameworks possessing hydrophobic channels

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Two three-dimensional open-framework metal dicarboxylates possessing channels with a hydrophobic environment have been synthesized. One is a malonate of the formula,  $[\text{Cd}(\text{O}_2\text{C}-\text{CH}_2-\text{CO}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ , **I**, and the other a glutarate of the formula  $[\text{Mn}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{CO}_2)]$ , **II**. The three-dimensional structure of **I** is attained through infinite Cd–O–Cd corner-linkages. On the other hand, **II**, contains Mn–O–Mn layers cross-linked by  $\text{MnO}_6$  octahedra and glutarate moieties.

## Introduction

There is intense interest today in the synthesis of open-framework hybrid compounds, specially those employing rigid organic linkers such as carboxylates, bipyridyl and other multi-functional ligands.<sup>1–14</sup> Several materials with large channels and high porosity have been synthesized and characterized.<sup>15,16</sup> Important contributors to this family are Forster and Cheetham,<sup>17</sup> who have described an open-framework nickel succinate containing an infinite Ni–O–Ni framework, possessing uni-dimensional channels. The nickel succinate is quite distinct from the open-framework dicarboxylates described by Kim *et al.*<sup>18</sup> and Férey and co-workers<sup>19</sup> in that the channels have a hydrophobic environment because of the protruding methylene groups. Férey and co-workers have described cobalt succinates based on two-dimensional sheets of edge-sharing  $\text{CoO}_6$  octahedra. The  $\text{Mn}^{\text{II}}$  and  $\text{Fe}^{\text{II}}$  carboxylates, on the other hand, contain one-dimensional  $\text{MnO}_6$  ribbons and two-dimensional metal carboxylate sheets. We have synthesized two interesting three-dimensional open-framework metal dicarboxylates, a malonate  $[\text{Cd}(\text{O}_2\text{C}-\text{CH}_2-\text{CO}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ , **I**, and a glutarate  $[\text{Mn}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{CO}_2)]$ , **II**, possessing channels with hydrophobic environments. While the three-dimensional structure of **I** arises from the infinite Cd–O–Cd connectivity, that of **II** is formed by two-dimensional Mn–O–Mn layers cross-linked by the glutarate and the  $\text{MnO}_6$  octahedra.

## Experimental

Compound **I** was prepared at room temperature by reacting  $\text{CdCl}_2\cdot 2\text{H}_2\text{O}$  with malonic acid. Typically, 0.1 g of  $\text{CdCl}_2\cdot 2\text{H}_2\text{O}$  was dissolved in a n-hexanol + water (1 ml + 2 ml) mixture and 0.16 g of malonic acid and 0.1 ml of 1,2-diaminopropane added to the above mixture. The mixture was stirred to render it homogeneous. The final mixture of composition  $\text{CdCl}_2\cdot 2\text{H}_2\text{O} : 3.1\text{C}_3\text{O}_4\text{H}_4 : 2.3\text{C}_3\text{H}_7\text{N}_2 : 16.2\text{n-C}_6\text{H}_{13}\text{OH} : 223.6\text{H}_2\text{O}$ , was left in a closed polypropylene bottle for three days at room temperature. The product, colorless hexagonal plate-like crystals, was filtered off, washed with deionized water and dried under ambient conditions. The yield was about 40%. Anal. calcd.: C, 14.4; H, 2.4. Anal. obsd.: C, 14.8; H, 1.8%.

Compound **II** was synthesized by reacting manganese(II) chloride with glutaric acid under solvothermal conditions. Typically, 0.2 g of  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  was dissolved in 2 ml of n-hexanol and 0.33 g of glutaric acid and 0.22 g of piperazine added to the above. The contents were stirred to homogeneity and the final mixture of composition  $\text{MnCl}_2\cdot 4\text{H}_2\text{O} : 2.47\text{C}_5\text{H}_8\text{O}_4 : 2.53\text{C}_4\text{N}_2\text{H}_{10} : 15.58\text{n-C}_6\text{H}_{13}\text{OH}$ , was sealed in a PTFE-lined stainless steel autoclave and heated at 180 °C for 72 hours. The product, colorless hexagonal plate-like crystals, thus

obtained, was filtered off, washed with ethanol and n-butanol, and dried under ambient conditions. The yield was about 55%. Anal. calcd.: C, 32.5; H, 3.3. Anal. obsd.: C, 34.3; H, 3.2%.

Initial characterization of the products was carried out by powder X-ray diffraction (XRD), chemical analysis, thermogravimetric analysis (TGA) and IR spectroscopy. The powder XRD pattern exclusively exhibited reflections of a hitherto unknown material; the pattern was entirely consistent with the structure determined by single crystal XRD. A least squares fit (Cu-K $\alpha$ ) of the XRD patterns, using the *hkl* indices generated from the single crystal structure gave the following lattice parameters:  $a = 17.047$  (4);  $b = 17.047$  (4);  $c = 12.389$  (1) Å;  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  for **I**;  $a = 11.287$  (8);  $b = 11.287$  (8);  $c = 29.437$  (6) Å;  $\alpha = \beta = 90^\circ$  and  $\gamma = 120^\circ$  for **II**.

Infrared spectroscopic studies of KBr pellets showed the characteristic features of the dicarboxylate.<sup>20</sup> The various observed bands were:  $\nu_{\text{as}}(\text{C}=\text{O})$  at 1546(s)  $\text{cm}^{-1}$  and  $\nu_{\text{s}}(\text{C}=\text{O})$  at 1427(s)  $\text{cm}^{-1}$  (**I**) and 1561(s)  $\text{cm}^{-1}$  and 1401(s)  $\text{cm}^{-1}$  (**II**);  $\nu_{\text{s}}(\text{O}-\text{C}-\text{O})$  at 1261(s)  $\text{cm}^{-1}$  (**I**) and 1245(s)  $\text{cm}^{-1}$  (**II**);  $\delta(\text{O}-\text{C}-\text{O})$  at 829(s)  $\text{cm}^{-1}$  (**I**) and 833(s)  $\text{cm}^{-1}$  (**II**). The presence of bound water molecules in **I** gives rise to  $\rho_{\text{w}}(\text{H}_2\text{O})$  in the 550–600  $\text{cm}^{-1}$  region and  $\rho_{\text{r}}(\text{H}_2\text{O})$  at 850–900  $\text{cm}^{-1}$ . In both of the compounds multiple bands in the region 2400–3000  $\text{cm}^{-1}$  appear due to the  $\nu_{\text{s}}(\text{CH}_2)$  and  $\nu_{\text{a}}(\text{CH}_2)$  vibrations. The  $\rho_{\text{w}}(\text{CH}_2)$  and  $\rho_{\text{r}}(\text{CH}_2)$  bands occur in the 950–1200  $\text{cm}^{-1}$  region. In **I**, a broad band appears at 3604  $\text{cm}^{-1}$  due to the presence of water molecules in the structure.

## Single crystal structure determination

A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyano-acrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with  $\omega$  scans (width of 0.30° and exposure time of 20 s per frame) in the  $\theta$  range 2.07 to 23.29°. Pertinent experimental details for the structure determinations are presented in Table 1.

The structure was solved and refined using the SHELXTL-PLUS<sup>21</sup> suite of programs. An absorption correction based on symmetry equivalent reflections was applied using the SADABS program.<sup>22</sup> The hydrogen positions for both of the compounds were initially located in the difference Fourier maps, and for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, aniso-

**Table 1** Crystal data and structure refinement parameters for [Cd(O<sub>2</sub>C-CH<sub>2</sub>-CO<sub>2</sub>)(H<sub>2</sub>O)]·H<sub>2</sub>O, **I**, and, [Mn(O<sub>2</sub>C-(CH<sub>2</sub>)<sub>3</sub>-CO<sub>2</sub>)]<sub>2</sub>, **II**

Structural parameter	<b>I</b>	<b>II</b>
Chemical formula	CdC <sub>3</sub> H <sub>6</sub> O <sub>6</sub>	MnC <sub>5</sub> H <sub>6</sub> O <sub>4</sub>
Formula mass	250.48	185.04
Crystal symmetry	Rhombohedral	Rhombohedral
Space group	R3 (No. 148)	R3 (No. 148)
<i>T</i> /K	293 (2)	293 (2)
<i>a</i> /Å	17.0685 (2)	11.2944 (10)
<i>c</i> /Å	12.4302 (3)	29.4830 (4)
<i>V</i> /Å <sup>3</sup>	3136.17 (9)	3257.08 (6)
<i>Z</i>	18	18
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.387	1.698
$\mu/\text{mm}^{-1}$	3.107	1.775
No. of measured/observed reflections	4504/990	4523/957
<i>R</i> 1, <i>wR</i> 2 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0336, <sup>a</sup> 0.0898 <sup>b</sup>	0.0205, <sup>a</sup> 0.0500 <sup>b</sup>

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR_2 = \{[\sum (F_o^2 - F_c^2)^2] / [\sum (F_o^2)^2]\}^{1/2}$ .  $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ ,  $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$ , where  $a = 0.0000$  and  $b = 72.3680$  for **I** and  $a = 0.0189$  and  $b = 2.2708$  for **II**.

**Table 2** Selected bond distances (Å) and angles (°) for [Cd(O<sub>2</sub>C-CH<sub>2</sub>-CO<sub>2</sub>)(H<sub>2</sub>O)]·H<sub>2</sub>O, **I**

Cd(1)–O(10)	2.288(7)	Cd(1)–O(2)#1	2.535(6)
Cd(1)–O(1)	2.288(5)	Cd(1)–O(1)#2	2.545(5)
O(1)–Cd(1)–O(2)	82.0(2)	O(1)–Cd(1)–O(1)#2	93.7(3)
Cd(1)–O(2)	2.293(6)	O(1)–Cd(1)–O(1)#5	2.545(5)
Cd(1)–O(3)	2.312(6)	O(2)–Cd(1)–O(1)#6	2.535(6)
Cd(1)–O(4)	2.319(6)		
O(10)–Cd(1)–O(1)	165.5(2)	O(4)–Cd(1)–O(2)#1	53.6(2)
O(10)–Cd(1)–O(2)	83.6(2)	O(10)–Cd(1)–O(1)#2	85.1(2)
O(1)–Cd(1)–O(2)	82.0(2)	O(1)–Cd(1)–O(1)#2	93.7(3)
O(10)–Cd(1)–O(3)	106.7(2)	O(2)–Cd(1)–O(1)#2	89.3(2)
O(1)–Cd(1)–O(3)	83.8(2)	O(3)–Cd(1)–O(1)#2	53.2(2)
O(2)–Cd(1)–O(3)	138.6(2)	O(4)–Cd(1)–O(1)#2	174.2(2)
O(10)–Cd(1)–O(4)	89.2(2)	O(2)#1–Cd(1)–O(1)#2	124.7(2)
O(1)–Cd(1)–O(4)	92.1(2)	C(1)#5–O(1)–Cd(1)	126.7(5)
O(2)–Cd(1)–O(4)	91.3(2)	C(1)#5–O(1)–Cd(1)#5	87.1(4)
O(3)–Cd(1)–O(4)	127.9(2)	Cd(1)–O(1)–Cd(1)#5	143.1(2)
O(10)–Cd(1)–O(2)#1	86.5(2)	C(2)#6–O(2)–Cd(1)	127.7(5)
O(1)–Cd(1)–O(2)#1	105.8(2)	C(2)#6–O(2)–Cd(1)#6	87.3(5)
O(2)–Cd(1)–O(2)#1	143.6(2)	C(1)–O(3)–Cd(1)	98.3(5)
O(3)–Cd(1)–O(2)#1	77.7(2)	C(2)–O(4)–Cd(1)	97.9(5)

Symmetry transformations used to generate equivalent atoms in **I**: #1  $-x + y + 2/3, -x + 1/3, z + 1/3$ . #2  $y + 1/3, -x + y + 2/3, -z + 5/3$ . #3  $x - y, x, -z + 2$ . #4  $y, -x + y, -z + 2$ . #5  $x - y + 1/3, x - 1/3, -z + 5/3$ . #6  $-y + 1/3, x - y - 1/3, z - 1/3$ .

tropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Full-matrix-least-squares structure refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS package of programs.

CCDC reference numbers 199941 and 199942.

See <http://www.rsc.org/suppdata/dt/b2/b212314m/> for crystallographic data in CIF or other electronic format.

## Results

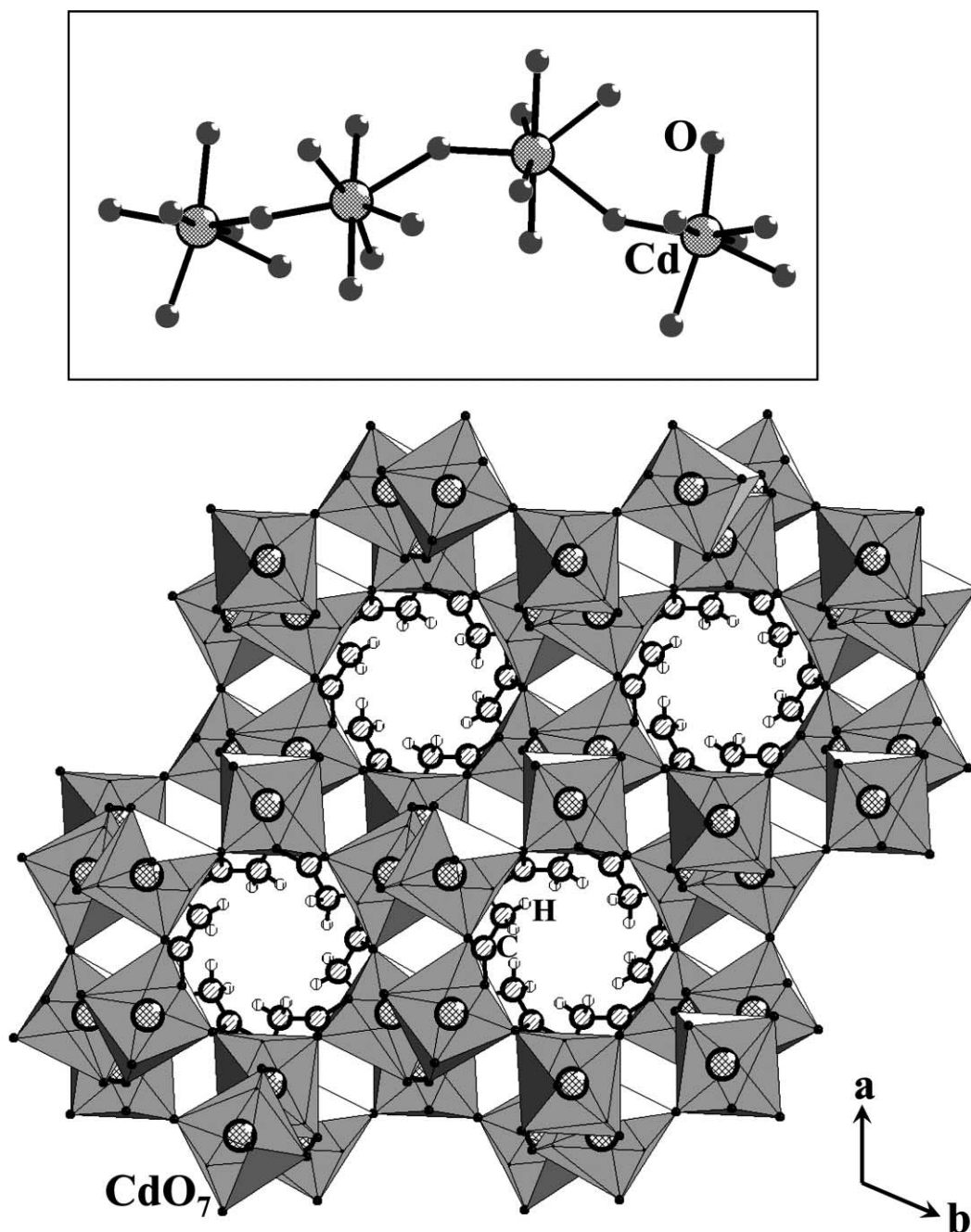
The asymmetric unit of the malonate, [Cd(O<sub>2</sub>C-CH<sub>2</sub>-CO<sub>2</sub>)(H<sub>2</sub>O)]·H<sub>2</sub>O, **I**, contains 10 non-hydrogen atoms, of which 9 belong to the cadmium malonate framework and one is the oxygen of the free water molecule. The Cd atom is seven-coordinated and has a distorted pentagonal bipyramidal arrangement. The equatorial positions are occupied by the malonate oxygen atoms and the apical positions are occupied by a water molecule and a malonate oxygen. The Cd–O distances are in the range 2.288(5)–2.545(5) Å (av. 2.369 Å) and the average O–Cd–O angle is 102.3°. The malonate unit has the expected bond distances and angles (Table 2). A similar coordination for cadmium has been observed in other cadmium dicarboxylates.<sup>24</sup> There are two types of water molecules in **I**, one bound to the Cd atom and the other present in the channels. Bond valence sum calculations<sup>23</sup> indicated the

oxidation numbers of Cd, C and O to be 2+, 4+ and 2–, as expected. Ancillary ligation by water molecules has been observed in other metal carboxylates.<sup>25,26</sup>

The structure of **I** can be described as a one-dimensional chain formed by corner-sharing CdO<sub>7</sub> pentagonal bipyramids, with the adjacent pentagonal bipyramids shifted and rotated with respect to each other, rendering the chain sinusoidal (see top of Fig. 1). Six such chains, arranged in an hexagonal array through corner-sharing, form the three-dimensional framework. Thus, the entire structure is built up of an infinite array of corner-sharing CdO<sub>7</sub> pentagonal bipyramids, with uni-directional hexagonal channels (6.95 × 6.95 Å, shortest C–C contact not including the van der Waals radii) along the *c*-axis (Fig. 1). The inner-walls of the channels are lined by the methylene groups of the malonate moiety, making them hydrophobic. The water molecule bound to Cd protrudes into the 12-membered channels along the *a*-axis, whilst the free water molecule resides in a smaller aperture formed due to corner-sharing between two adjacent chains.

The asymmetric unit of the glutarate, [Mn(O<sub>2</sub>C-(CH<sub>2</sub>)<sub>3</sub>-CO<sub>2</sub>)]<sub>2</sub>, **II**, consists of 12 non-hydrogen atoms, of which, three are crystallographically independent Mn atoms. Mn(1) has 1/3 occupancy, Mn(2) has 1/6 occupancy and Mn(3) has 1/2 occupancy. All three Mn atoms are octahedrally coordinated by the glutarate oxygens, with average Mn–O distances of 2.229 Å, 2.148 Å and 2.172 Å for Mn(1)–O, Mn(2)–O and Mn(3)–O respectively and average O–Mn–O angles of 105.1°, 108.0° and 108.07° for Mn(1), Mn(2) and Mn(3) respectively. Open-framework manganese dicarboxylates involving octahedrally coordinated Mn atoms have been reported recently.<sup>27</sup> Bond valence sum calculations<sup>23</sup> indicated that the valence states of the Mn, C and O in **II** were +2, +4 and –2 respectively. The glutarate moiety has the expected bond distances and angles (Table 3). The edge-sharing Mn(1)O<sub>6</sub> and Mn(3)O<sub>6</sub> octahedra form an infinite two-dimensional array possessing honeycomb-like apertures in the *ab*-plane (6.642 × 6.642 Å, shortest C–C contact not including the van der Waals radii) (Fig. 2). These layers are cross-linked by isolated Mn(2)O<sub>6</sub> octahedra and *out-of-plane* glutarate moieties to give rise to the three-dimensional architecture (Fig. 3). Two-dimensional structures with open architectures are known to achieve efficient packing by shifting of adjacent layers.<sup>28</sup> Accordingly, in **II** the layers formed by the edge-sharing octahedra get shifted by 1/2 the unit cell length along the *b*- and *a*-axes and thereby contribute negatively to the openness of the structure.

Thermogravimetric analysis (TGA) of **I** and **II** was carried out in a N<sub>2</sub> atmosphere (50 ml min<sup>-1</sup>) in the 25 to 700 °C range (Fig. 4). **I** showed a mass loss of 14.8% in the range 100–180 °C due to the loss of the lattice and the bonded water (calc. 14.3%), followed by a sharp mass loss of 35.4% in the range 220–350 °C due to the loss of the malonate moiety (calc. 34.6%). The



**Fig. 1** Structure of **I** showing the 12-membered, methylene-lined hydrophobic channels. Note the presence of the free water molecules in the small apertures.

powder XRD pattern of the product of decomposition of **I**, showed characteristic peaks of the mineral monteporite, CdO (JCPDS: 05-0640). **II** showed a gradual mass loss of 53.2% in the range 210–450 °C due to the loss of the glutarate moiety (calc. 53.0%). A very small weight loss is observed in the range 50–100 °C due to the loss of some adsorbed species. The product of decomposition of **II**, as revealed by the powder XRD pattern, was MnO<sub>2</sub> (JCPDS: 44-0992).

## Discussion

Both **I** and **II** have extended inorganic structures formed by corner- and edge-sharing of metal–oxygen polyhedra. **I** has a three-dimensional structure arising entirely from the infinite Cd–O–Cd connectivities while **II** exhibits infinite Mn–O–Mn connectivities in two dimensions. The three-dimensional nature of **II** is derived through the *out-of-plane* connectivities between the Mn–O–Mn sheets and the glutarate and the isolated MnO<sub>6</sub>

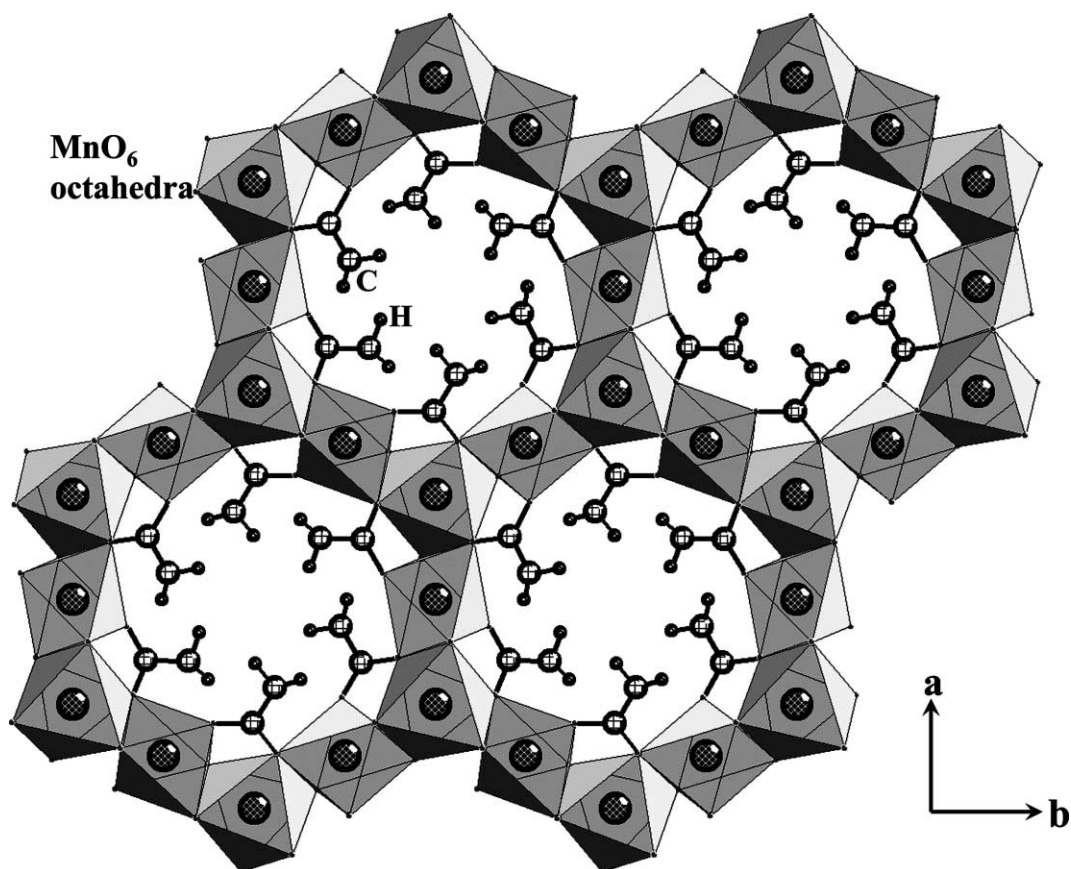
octahedral units. The M–O–M connectivity in **I** bears some resemblance to that in the Ni succinate reported by Foster and Cheetham.<sup>17a</sup> The M–O–M linkage in **I** occurs through corner-sharing of CdO<sub>7</sub> pentagonal bipyramids, whilst in the Ni succinate, it is through the edge-shared NiO<sub>6</sub> octahedra. The M–O–M linkages in **II**, are comparable to those observed in two- and three-dimensional Co succinates,<sup>19</sup> but the interlayer connectivity between the two structures is different. The Co–O–Co layers in the cobalt succinate are connected by carboxylate pillars and the Mn–O–Mn layers in **II** are linked through isolated MnO<sub>6</sub> octahedra.

Several two-dimensional metal–dicarboxylate frameworks with apertures have been reported in the literature.<sup>18,19a,27b,28,29</sup> there are also examples where organic linkers to the metal ions give rise to three-dimensional structures.<sup>15,19b</sup> Some of the possible ways of building up three-dimensional metal–dicarboxylate frameworks are illustrated in Scheme 1. Many such three-dimensional structures are known. Motif (e) in the

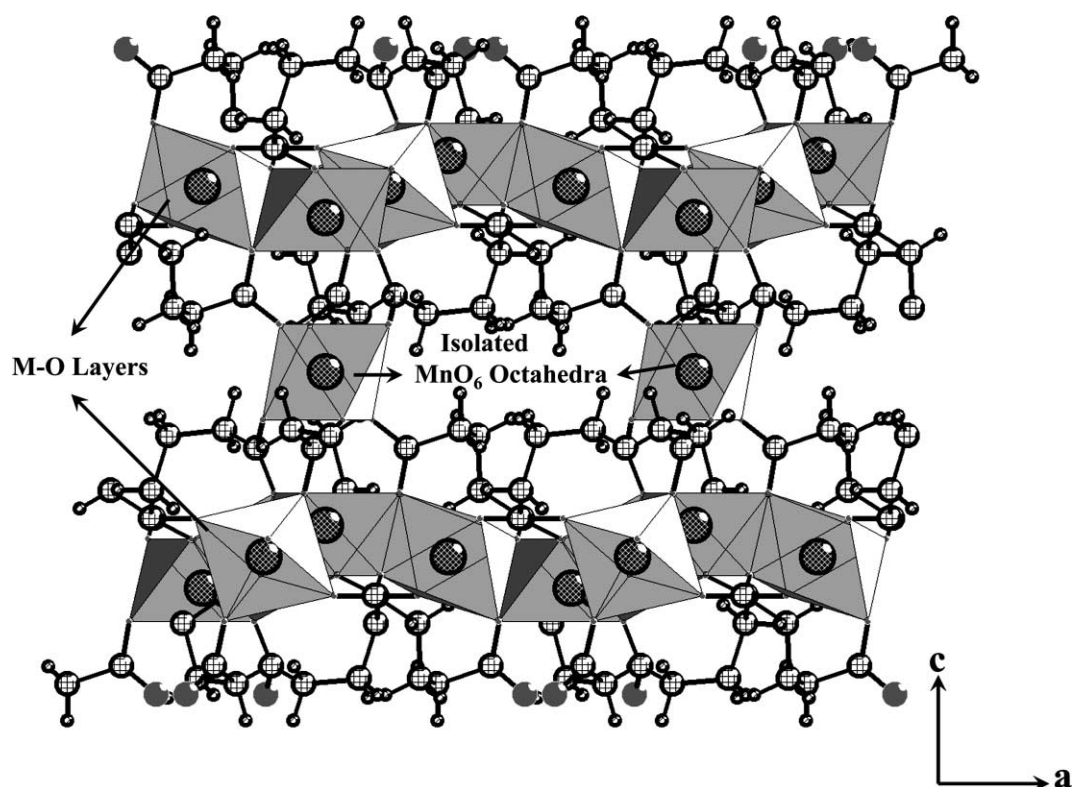
**Table 3** Selected bond distances (Å) and angles (°) for [Mn(O<sub>2</sub>C-(CH<sub>2</sub>)<sub>3</sub>-CO<sub>2</sub>)]<sub>n</sub>, **II**

Mn(1)–O(1)#1	2.1812(13)	Mn(2)–O(3)#4	2.1483(13)
Mn(1)–O(1)	2.1812(13)	Mn(2)–O(3)#2	2.1483(13)
Mn(1)–O(1)#2	2.1813(13)	Mn(2)–O(3)#5	2.1483(13)
Mn(1)–O(2)	2.2772(13)	Mn(3)–O(4)#6	2.1118(14)
Mn(1)–O(2)#1	2.2772(13)	Mn(3)–O(4)	2.1117(14)
Mn(1)–O(2)#2	2.2773(13)	Mn(3)–O(1)#6	2.1927(13)
Mn(2)–O(3)	2.1482(13)	Mn(3)–O(1)	2.1926(13)
Mn(2)–O(3)#1	2.1483(13)	Mn(3)–O(2)	2.2122(13)
Mn(2)–O(3)#3	2.1483(13)	Mn(3)–O(2)#6	2.2122(13)
O(1)#1–Mn(1)–O(1)	105.12(4)	O(3)#1–Mn(2)–O(3)#5	180
O(1)#1–Mn(1)–O(1)#2	105.12(4)	O(3)#3–Mn(2)–O(3)#5	88.60(5)
O(1)–Mn(1)–O(1)#2	105.12(4)	O(3)#4–Mn(2)–O(3)#5	88.60(5)
O(1)#1–Mn(1)–O(2)	86.89(5)	O(3)#2–Mn(2)–O(3)#5	91.39(5)
O(1)–Mn(1)–O(2)	76.64(5)	O(4)#6–Mn(3)–O(4)	180
O(1)#2–Mn(1)–O(2)	166.64(5)	O(4)#6–Mn(3)–O(1)#6	91.17(5)
O(1)#1–Mn(1)–O(2)#1	76.64(5)	O(4)–Mn(3)–O(1)#6	88.83(5)
O(1)–Mn(1)–O(2)#1	166.64(5)	O(4)#6–Mn(3)–O(1)	88.82(5)
O(1)#2–Mn(1)–O(2)#1	86.89(5)	O(4)–Mn(3)–O(1)	91.18(5)
O(2)–Mn(1)–O(2)#1	90.33(5)	O(1)#6–Mn(3)–O(1)	180
O(1)#1–Mn(1)–O(2)#2	166.64(5)	O(4)#6–Mn(3)–O(2)	89.52(6)
O(1)–Mn(1)–O(2)#2	86.89(5)	O(4)–Mn(3)–O(2)	90.48(6)
O(1)#2–Mn(1)–O(2)#2	76.64(5)	O(1)#6–Mn(3)–O(2)	102.22(5)
O(2)–Mn(1)–O(2)#2	90.33(5)	O(1)–Mn(3)–O(2)	77.78(5)
O(2)#1–Mn(1)–O(2)#2	90.32(5)	O(4)#6–Mn(3)–O(2)#6	90.48(6)
O(3)–Mn(2)–O(3)#1	88.61(5)	O(4)–Mn(3)–O(2)#6	89.52(6)
O(3)–Mn(2)–O(3)#3	91.39(5)	O(1)#6–Mn(3)–O(2)#6	77.78(5)
O(3)#1–Mn(2)–O(3)#3	91.40(5)	O(1)–Mn(3)–O(2)#6	102.22(5)
O(3)–Mn(2)–O(3)#4	180	O(2)–Mn(3)–O(2)#6	180
O(3)#1–Mn(2)–O(3)#4	91.40(5)	C(1)–O(1)–Mn(1)	125.50(12)
O(3)#3–Mn(2)–O(3)#4	88.61(5)	C(1)–O(1)–Mn(3)	133.99(12)
O(3)–Mn(2)–O(3)#2	88.61(5)	C(2)#7–O(2)–Mn(3)	132.14(13)
O(3)#1–Mn(2)–O(3)#2	88.60(5)	C(2)#7–O(2)–Mn(1)	128.82(12)
O(3)#3–Mn(2)–O(3)#2	180	C(1)–O(3)–Mn(2)	129.01(13)
O(3)#4–Mn(2)–O(3)#2	91.39(5)	C(2)–O(4)–Mn(3)	136.86(13)
O(3)–Mn(2)–O(3)#5	91.39(5)		

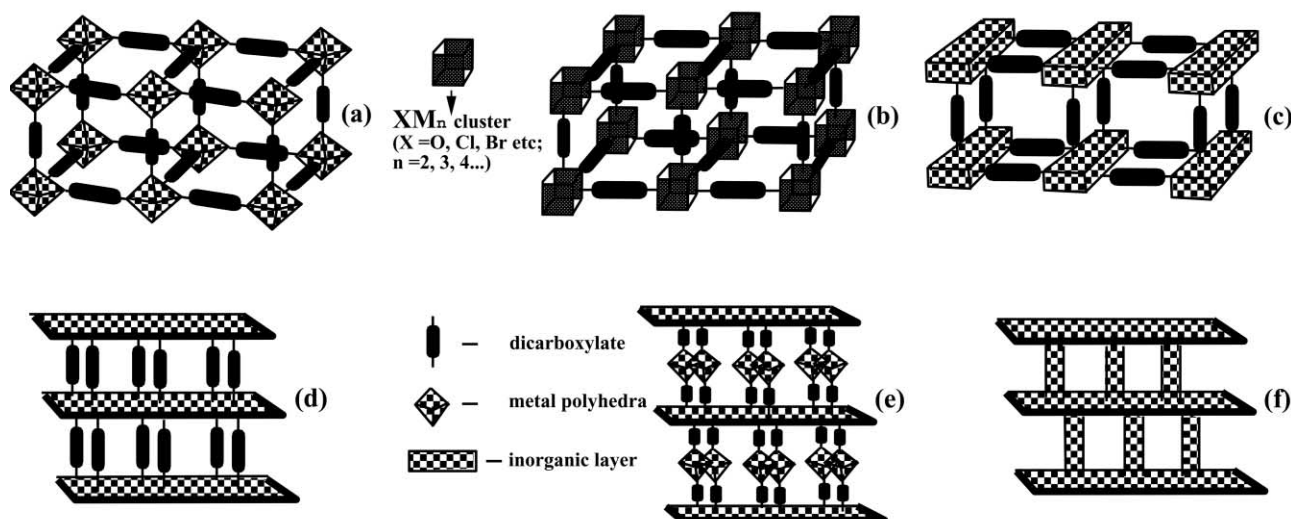
Symmetry transformations used to generate equivalent atoms in **II**: #1  $-y, x - y, z$ . #2  $-x + y, -x, z$ . #3  $x - y, x, -z$ . #4  $-x, -y, -z$ . #5  $y, -x + y, -z$ . #6  $-x - 1/3, -y - 2/3, -z + 1/3$ . #7  $y + 2/3, -x + y + 1/3, -z + 1/3$ . #8  $x - y - 1/3, x - 2/3, -z + 1/3$ . #9  $-x + y, -x - 1, z$ . #10  $-y - 1, x - y - 1, z$ .



**Fig. 2** Structure of **II** showing the 12-membered C-backbone of glutarate-lined hydrophobic channels, formed by the edge-sharing MnO<sub>6</sub> octahedra.



**Fig. 3** The connectivity between adjacent MnO layers *via* isolated Mn(3)O<sub>6</sub> octahedra. Note that the isolated octahedra are covalently linked by the glutarate units to the inorganic layers.



**Scheme 1** A schematic illustrating how different inorganic units can be linked through dicarboxylate units to generate three-dimensional open-framework architectures. Motif (a) represents isolated polyhedra, which could be a dimer or a trimer, connected in all directions by dicarboxylate linkers;<sup>17b,30</sup> (b) represents the metal clusters linked *via* dicarboxylates;<sup>15</sup> (c) shows the alignment of one-dimensional inorganic metal–oxygen chains by dicarboxylate linkers;<sup>16c,31</sup> (d) shows the classic pillaring of inorganic MO layers by the dicarboxylate units;<sup>19b,32</sup> (e) represents inorganic layers pillared by isolated polyhedra through coordinating dicarboxylate linkers (*e.g.* compound **II**); (f) shows three-dimensionality arising from the connectivities among the polyhedra (*e.g.* compound **I**).<sup>17a,33</sup> It is important to note that the dicarboxylate oxygens are directly involved in the formation of the inorganic units.

scheme is similar to compound **II** and motif (f) is similar to compound **I**.

Considering the structures of nickel<sup>17a</sup> and cobalt succinates<sup>19b</sup> along with the structure of **I**, we notice that the common feature in the compounds under discussion is the presence of channels lined by the methylene groups of the dicarboxylate moieties, giving rise to a highly hydrophobic environment within them. It is worth mentioning that a three-dimensional vanadyl carboxylate framework possessing hydrophobic channels, exhibiting interesting adsorption properties has been

reported recently.<sup>16b</sup> This is indeed a noteworthy feature and it is possible that such channels may show significant selectivity for non-polar species. The formation of compound **I** at room temperature also opens up the possibility of forming other open-framework structures with infinite M–O–M connectivities, under mild reaction conditions (*chimie douce*), instead of hydrothermal conditions.<sup>19c</sup> It is likely that many such metal–carboxylates with open-architectures can be made by a suitable choice of the metal center and the ligand, in the presence of organic amines. We are currently pursuing such experiments.

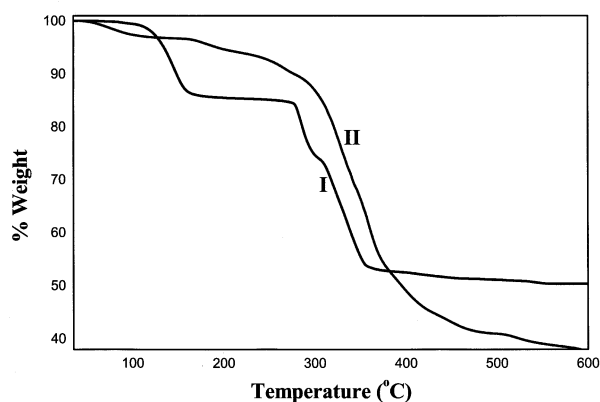


Fig. 4 TGA curves of I and II.

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