Structurally different cadmium(II) and lead(II) supramolecular polymers with the same benzene-1,2,3,4-tetracarboxylate dianion as bridging ligands from hydrothermal reactions

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Structurally different cadmium(II) and lead(II) supramolecular polymers with the same benzene-1,2,3,4-tetracarboxylate dianion as bridging ligands from hydrothermal reactions

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Two crystalline metal-organic frameworks, $[Cd_2(o\text{-BTC})(H_2O)_2]_n$ (**1**) and $[Pb_2(o\text{-BTC})]_n$ (**2**) (o-BTC = benzene-1,2,3,4-tetracarboxylic), were synthesized under hydrothermal conditions and characterized by analytical, spectroscopic and single crystal X-ray diffraction studies, which reveal three-dimensional reticular structures *via* M^{2+} and carboxylate ligands. All carboxyl groups of o-BTC are deprotonated, in agreement with the IR data. The Cd^{2+} centers of **1** have one coordination environment, while Pb^{2+} centers of **2** have two coordination environments. Both **1** and **2** form 3D interpenetrated grid structures along the b and c axes, respectively.

1. Introduction

Transition metal coordination polymers containing polycarboxylate groups have intriguing structural diversity and potential applications as new materials [1–3]. Metal-organic coordination compounds with bridging aromatic polycarboxylate ligands are good building blocks for construction of coordination polymers and multi-dimensional supramolecular networks [4–11]. Benzenetetracarboxylic acid (H_4BTC) is especially of interest [7–9] with carboxyl groups inducing versatile coordination modes with transition metal ions [12]. Thus, BTC is a good candidate for construction of multi-dimensional coordination polymers and structurally interesting supramolecules. Some transition metal complexes bridged by BTC^{4-}(1,2,4,5-benzenetetracarboxylic) have been studied [6, 13–16], but examples of transition metal complexes formed with 1,2,3,4-benzenetetracarboxylic (o-BTC)

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ligand are rarely observed. Here, we report 3D cadmium(II) and lead(II) supra-molecular polymers **1** and **2** which were synthesized by reaction *o*-BTC and $M(NO_3)_2$ (M = Cd,Pb) under hydrothermal conditions.

2. Experimental

All analytical grade chemicals and solvents were purchased commercially and used without further purification. Benzene-1,2,3,4-tetracarboxylic acid was synthesized by our laboratory. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer in KBr pellets in the range $400 \sim 4000 \, cm^{-1}$. A Perkin-Elmer Pyris-1 differential scanning calorimeter (DSC) (sample mass 1.0 mg in flowing nitrogen, reference α-Al_2O_3, heating rate 10 C min^{-1}) was used for DSC measurements. A Perkin-Elmer Pyris-1 thermogravimeter (TG) analyzer (sample mass 1.0 mg in dry oxygen-free nitrogen, heating rate of $10°C \, min^{-1}$) was used for thermogravimetric analysis.

2.1. *Syntheses of $[Cd_2(o\text{-}BTC)(H_2O)_2]_n$ (1) and $[Pb_2(o\text{-}BTC)]_n$ (2)*

Compounds **1** and **2** were prepared using identical procedures. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.308 g, 1 mmol) or $Pb(NO_2)_2$ (0.331 g, 1 mmol), benzene-1,2,3, 4-tetracarboxylic acid (0.254 g, 1 mmol), NaOH (0.08 g, 2 mmol) and H_2O (20 mL) was sealed in a 25 mL stainless-steel reactor with a Teflon liner and heated to 160°C for 72 h. After the mixture cooled to room temperature, pale yellow column crystals and needle crystals were collected with yields of 19.7 and 24.2% for **1** and **2**, respectively (based on benzene-1,2,3,4-tetracarboxylic acid). Anal. Calcd for **1**: C, 23.5; H, 1.2. Found: C, 22.8; H, 1.6. Anal. Calcd for **2**: C, 18.7; H, 0.3. Found: C, 17.9; H, 0.4. IR data (KBr pellet, ν cm^{-1}) for **1**: 3432(br), 1620(br), 1388(m), 775(w), 523(m). IR data (KBr pellet, $\nu \, cm^{-1}$) for **2**: 3437(s), 1631(m), 1393(w), 1118(br). mp: DSC and TG-DTG, no change occurred until above 400°C where a vigorous exothermic mass loss decomposition occurs.

2.2. *X-ray crystallographic studies*

Data collection was performed on a Bruker SMART 1000 CCD diffractometer at 50 kV and 20 mA by using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 294(2) K with phi and omega scan techniques. Semi-empirical absorption corrections were applied using the SADABS program [17], and the structure was solved by direct methods and refined by full-matrix least squares techniques based on F^2 with the SHELXTL 97 program package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were generated geometrically and treated by a constrained refinement. Detailed information about the crystal data and determination is summarized in table 1. The selected bond lengths and angles are listed in table 2.

Table 1. Summary of crystallographic data for **1** and **2**.

Compound	**1**	**2**
Formula	$C_5H_3CdO_5$	$C_{10}H_2O_8Pb_2$
M	255.47	664.50
T(K)	294(2)	294(2)
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2(1)/n$
Z	8	4
Unit cell dimensions		
a (nm)	1.57213(3)	0.6851(2)
b (nm)	1.0610(2)	1.7996(3)
c (°)	0.7461(1)	0.9174(2)
β (°)	110.626(2)	108.596(3)
V (nm^3)	1.1646(4)	1.0719(3)
Density Calcd (Mg m^{-3})	2.914	4.118
μ (mm^{-1})	3.711	31.411
Crystal size (mm^{-3})	$0.22 \times 0.20 \times 0.18$	$0.16 \times 0.10 \times 0.08$
Reflections collected	3217	5937
Independent reflections/Rint	1193/0.0481	2177/0.0706
Data/restraints/parameters	1193/3/101	2177/0/181
GoF on F^2	1.110	1.052
R_1/wR_2 ($F^2 > 2\sigma(F^2)$] (all data)	0.0272/0.0681, 0.0300/0.0698	0.0318/0.0723, 0.0375/0.0753
Largest difference peak and hole (e.A^{-3})	0.865/−1.366	2.042/−2.827

Table 2. Selected bond distances (nm) and angles (°) for **1** and **2**.

Cd(1)–O(5)	0.2263(2)	O(5)–Cd(1)–O(1)	101.52(10)	O(2)#1–Cd(1)–O(4)#3	87.81(9)
Cd(1)–O(1)	0.2273(3)	O(5)–Cd(1)–O(2)#1	85.19(10)	O(3)#2–Cd(1)–O(4)#3	96.83(9)
Cd(1)–O(2)#1	0.2289(3)	O(1)–Cd(1)–O(2)#1	84.89(9)	O(5)–Cd(1)–O(4)#2	89.55(9)
Cd(1)–O(3)#2	0.23109(2)	O(5)–Cd(1)–O(3)#2	85.99(9)	O(1)–Cd(1)–O(4)#2	76.06(9)
Cd(1)–O(4)#3	0.2318(3)	O(1)–Cd(1)–O(3)#2	128.82(10)	O(2)#1–Cd(1)–O(4)#2	158.81(8)
Cd(1)–O(4)#2	0.2584(3)	O(2)#1–Cd(1)–O(3)#2	146.25(9)	O(3)#2–Cd(1)–O(4)#2	53.23(8)
		O(5)–Cd(1)–O(4)#3	171.05(9)	O(4)#3–Cd(1)–O(4)#2	98.95(8)
		O(1)–Cd(1)–O(4)#3	83.36(9)		
Pb(1)–O(8)#1	0.2382(6)	O(8)#1–Pb(1)–O(3)#2	75.8(2)	O(2)–Pb(2)–O(1)	51.18(19)
Pb(1)–O(3)#2	0.2436(6)	O(8)#1–Pb(1)–O(1)	81.4(2)	O(4)#2–Pb(2)–O(1)	73.9(2)
Pb(1)–O(1)	0.2513(6)	O(3)#2–Pb(1)–O(1)	87.5(2)	O(6)#4–Pb(2)–O(1)	70.3(2)
Pb(1)–O(6)#3	0.2604(6)	O(8)#1–Pb(1)–O(6)#3	69.5(2)	O(2)–Pb(2)–O(5)#4	118.40(19)
Pb(1)–O(7)#1	0.2609(6)	O(3)#2–Pb(1)–O(6)#3	72.4(2)	O(4)#2–Pb(2)–O(5)#4	94.49(19)
Pb(2)–O(2)	0.2379(6)	O(1)–Pb(1)–O(6)#3	147.7(2)	O(6)#4–Pb(2)–O(5)#4	49.20(17)
Pb(2)–O(4)#2	0.2539(7)	O(8)#1–Pb(1)–O(7)#1	52.09(19)	O(1)–Pb(2)–O(5)#4	67.86(18)
Pb(2)–O(6)#4	0.2551(6)	O(3)#2–Pb(1)–O(7)#1	126.8(2)	O(2)–Pb(2)–O(5)#5	65.95(19)
Pb(2)–O(1)	0.2669(6)	O(1)–Pb(1)–O(7)#1	93.7(2)	O(4)#2–Pb(2)–O(5)#5	84.21(19)
Pb(2)–O(5)#4	0.2742(6)	O(6)#3–Pb(1)–O(7)#1	79.5(2)	O(6)#4–Pb(2)–O(5)#5	133.98(18)
Pb(2)–O(5)#5	0.2760(6)	O(2)–Pb(2)–O(4)#2	78.2(2)	O(1)–Pb(2)–O(5)#5	116.07(17)
		O(2)–Pb(2)–O(6)#4	97.4(2)	O(5)#4–Pb(2)–O(5)#5	175.15(11)
		O(4)#2–Pb(2)–O(6)#4	136.4(2)		

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

3. Results and discussion

The crystal structure of $[Cd_2(o\text{-BTC})(H_2O)_2]_n$ is constructed from a unit composed of one octahedral Cd(II) center, four o-BTC links and one terminal water. All carboxylates
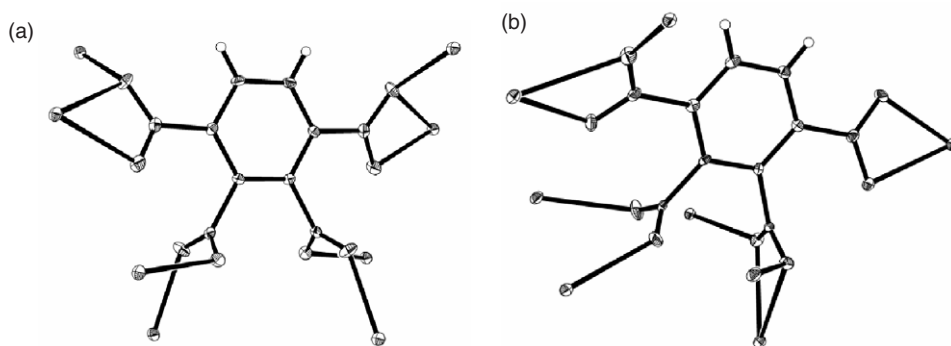
Figure 1. (a) Coordination mode of **1**. (b) Coordination mode of **2**.
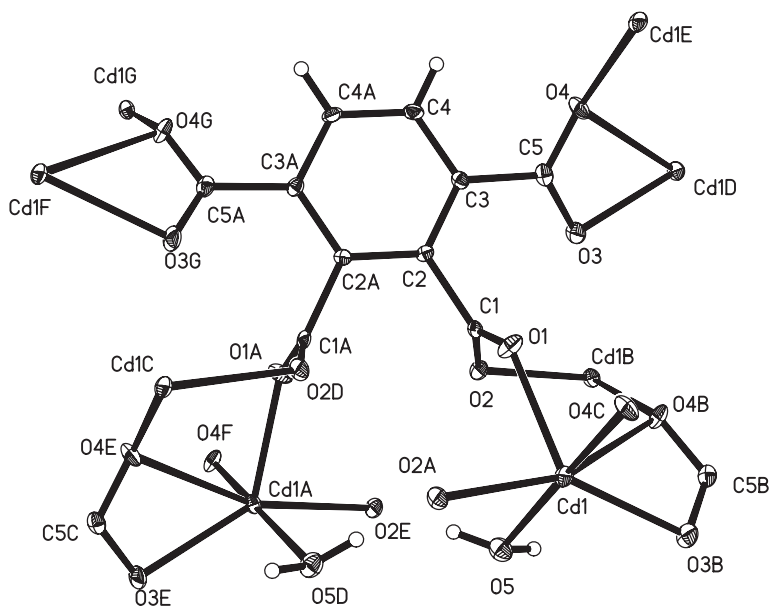

Figure 2.   Coordination environment of Cd(II) in **1** with the atom numbering scheme.

of *o*-BTC are deprotonated, in agreement with the IR data in which no strong absorption peaks around $1700 \, cm^{-1}$ for –COOH are observed. The vibrations of the carboxylate groups at $1620 \, cm^{-1}$ (br), 1468, and $1338 \, cm^{-1}$ are attributed to $\nu_{as}(COO–)$ and $\nu_{s}(COO–)$ stretching vibrations of the coordinated carboxylate groups, suggesting different coordination modes of the carboxylates.

In each unit, the carboxylates of four *o*-BTC ligands bridge the Cd(II) center in two modes figure 1(a): two neighboring carboxylates are bidentate and two opposite carboxylates are chelating-bridging. As shown in figure 2, the central cadmium ion is coordinated by six oxygen atoms from four carboxylate groups and a water in a distorted octahedron. The Cd–O bond lengths range from 0.2263 to 0.2584 nm, similar to related Cd–O distances [19].
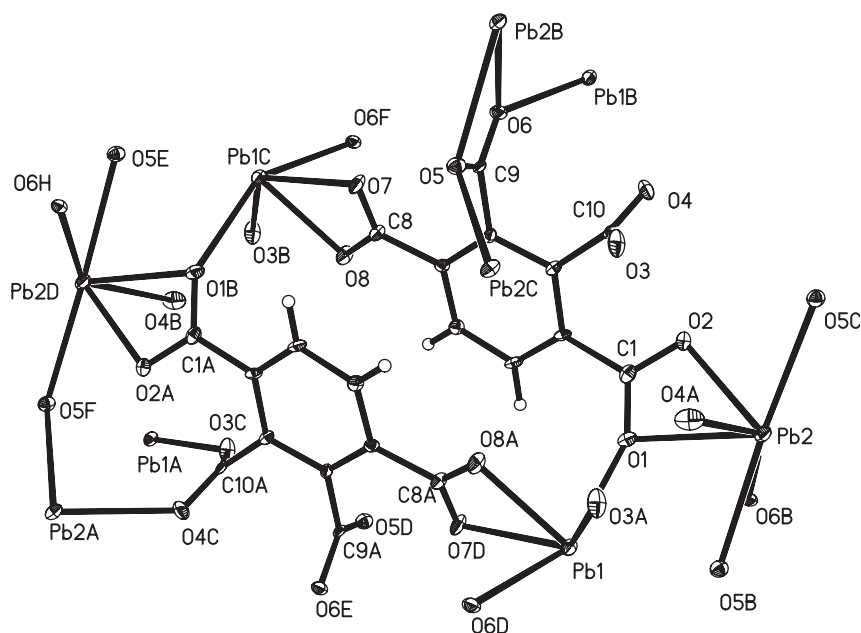
Figure 3. Coordination environment of Pb(II) in **2** with the atom numbering scheme.
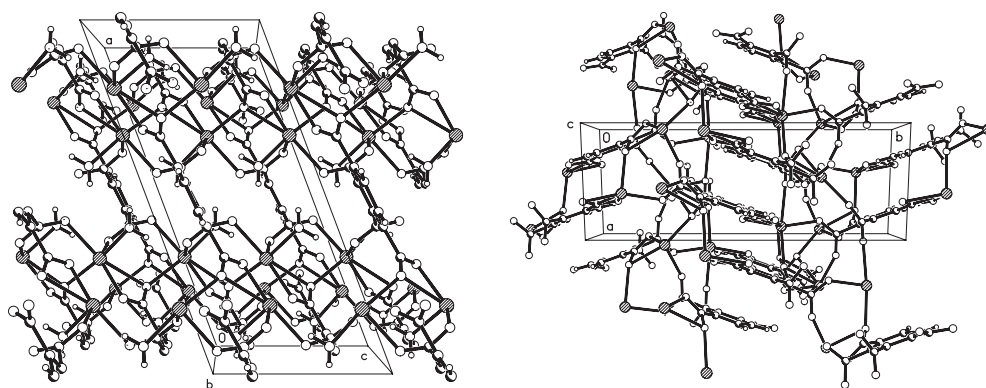

Figure 4. Grid structure of **1** and **2** along *b* and *c* direction, respectively.

Complex **2** contains lead in two different coordination environments, pentacoordinate (Pb1) and hexacoordinate (Pb2) figure 3. The Pb1 and Pb2 distance is 0.4221 nm. As for **1**, all carboxylates of *o*-BTC are deprotonated, in agreement with the IR data. Four carboxylate groups coordinate to lead with four different modes figure 1(b): bidentate, chelating, chelating-monobridging and chelating-dibridging. Therefore, in **2**, hexacoordinate lead is linked by four carboxylate groups from four carboxylate ligands (two of four carboxylate ligands are chelating), and pentacoordinate lead is also bridged by four carboxylates from four carboxylate ligands (one is chelating).

As shown in figure 3, the geometry of Pb1 and Pb2 are a distorted trigonal bipyramid and octahedron, respectively. The distorted geometries of both are like a claw.

The Pb1–O bonds range from 0.2382(6) to 0.2609(6) nm and the Pb2–O bonds range from 0.2379(6) to 0.2760(6) nm, both normal.

In **1** and **2**, each ligand has two almost co-planar carboxylate groups para, which link the metals into a layer. The ortho carboxylate groups, however, are nearly vertical to the plane of benzene, cross-linking the layers to form a three-dimensional interpenetrated framework with large packing grids along the *b* and *c* axes, respectively figure 4.

Supplementary data

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Center, CCDC reference number 633333 and 633334 for **1** and **2**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

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