NJC Letter

# Three-dimensional photoluminescent pillared metal-organic framework with $4.8^2$ topological channels obtained from the assembly of cadmium(II) acetate and trimellitic salt

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***Received (in New Haven, CT, USA) 23rd March 2003, Accepted 27th April 2003***
***First published as an Advance Article on the web 28th August 2003***



**Reaction of the piperidinium salt of trimellitic acid ($BTC^{3-}$) with cadmium(II) acetate dihydrate yields an unprecedented 3D pillared metal-organic framework, $[Cd_3(BTC)_2(H_2O)_6]\cdot 3H_2O$, showing strong blue luminescence. The framework contains $4.8^2$ topological channels, in which the 'floors' are directly connected by the pillars of the $BTC^{3-}$ benzene rings.**

The recent surge of research activity in the area of coordination polymers has been motivated by the ability of metal-ligand coordination to provide porous materials with possible technological applications such as molecular sieves, desiccants, ion exchangers, and catalysts.[1] Construction of large molecules with porous frameworks is an important step in the achievement of molecular complexity. Due to the diversity of the binding modes of the carboxylate group and the variety of dihedral angles between the plane of the carboxylate group and the benzene ring plane, novel and fantastic frameworks can be achieved by using carboxylate-containing ligands with an aromatic core. So far, extensive work has been carried out using carboxylate-containing ligands, for example trimesic acid (TMA),[2] 4,4′,4″-benzene-1,3,5-triyltribenzoic acid ($H_3BTB$),[3] 1,4-benzenedicarboxylic acid (*p*-$H_2BDC$),[4] 1,3-benzenedicarboxylic acid (*m*-$H_2BDC$)[5] and 1,2,4,5-benzenetetracarboxylic acid ($H_4BTEC$).[6]

As an analogue of TMA, however, 1,2,4-benzenetriacid, namely trimellitic acid ($H_3BTC$), has been less studied to now and only a few complexes with crystallographic data have been reported.[7,8] The specific orientations of the carboxylate groups of $H_3BTC$ may result in novel framework structures not achievable by other carboxylate-containing ligands, such as TMA or $H_3BTB$. Therefore, we chose $BTC^{3-}$ as an organic building block, and succeeded in the synthesis of a three-dimensional (3D) porous framework under moderate conditions. We report herein the first example of a 3D pillar-like structure with $4.8^2$ topological channels, $[Cd_3(BTC)_2(H_2O)_6]\cdot 3H_2O$ (**1**). For the construction of high dimensional (2D or 3D) networks with carboxylate-containing ligands, the ether–amine (or pyridine) diffusion method or hydrothermal synthesis are well documented.[2] It has been demonstrated that complete deprotonation of the triacid is essential in order to bind metal ions in a multidentate fashion.[9] Thus, we employed the piperidinium salt of trimellitic acid in this study, instead of using the triacid directly.

Compound **1** was obtained by reaction of the piperidinium salt of trimellitic acid with $Cd(OAc)_2\cdot 2H_2O$ under mild conditions. The single-crystal X-ray analysis of complex **1** revealed that there are two crystallographically independent Cd atom centers (Cd2 sits on the inversion center) in the structure, each having a different coordination environment as shown in Fig. 1. These two Cd atoms are both coordinated by six O atoms: three from three different carboxylate groups, two from one carboxylate group and one from a water molecule for Cd1; two from two different carboxylate groups and four from four water molecules for Cd2. The bond angles around the Cd1 center range from 55.23(6)° to 168.95(6)°

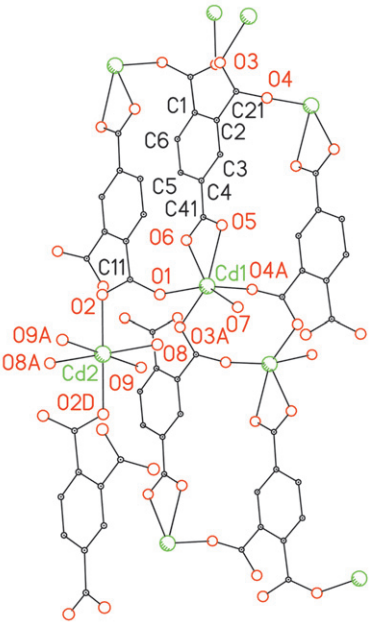


**Fig. 1** A local perspective view of $[Cd_3(BTC)_2(H_2O)_6]\cdot 3H_2O$ (**1**). Hydrogen atoms and lattice water molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Cd1–O7, 2.2388(19); Cd1–O6, 2.2957(18); Cd1–O1, 2.3242(17); Cd1–O5, 2.4217(17); Cd1–O3A, 2.2224(18); Cd1–O4A, 2.3384(18); Cd2–O8, 2.330(2); Cd2–O9, 2.2818(19); Cd2–O2, 2.2655(17); O7–Cd1–O5, 94.54(8); O7–Cd1–O6, 149.54(8); O6–Cd1–O5, 55.23(6); O7–Cd1–O1, 80.41(7); O1–Cd1–O5, 100.90(6); O6–Cd1–O1, 100.25(7); O4A–Cd–O5, 89.96(6); O3A–Cd–O5, 152.06(7); O1–Cd1–O4A, 168.95(6); O6–Cd–O4A, 87.56(7); O7–Cd1–O4A, 96.85(7); O3A–Cd–O4A, 88.25(7); O3A–Cd1–O1, 83.10(7); O3A–Cd1–O6, 96.83(7); O3A–Cd1–O7, 113.37(8); O2–Cd2–O9, 91.00(7); O9–Cd2–O8, 84.29(9); O2–Cd2–O8, 90.41(8); O2–Cd2–O9A, 89.00(7); O2–Cd2–O8A, 89.59(8); O8A–Cd2–O9, 95.71; O2–Cd2–O2A, 180.00(8).

indicating a heavy distortion of the octahedron, while those around the Cd2 center range from 84.29(9)° to 180°. In each BTC ligand, each of two carboxylate groups (O1, O2 and O3, O4) at the 1,2-positions bridges two cadmium atoms in a bis-monodentate fashion, while the third carboxylate moiety (O5, O6) at the 4-position binds to the Cd(II) atom in a bidentate mode. Thus, each $BTC^{3-}$ ligand links five Cd(II) atoms and, as a result, a 3-D pillar-like coordination polymer as illustrated in Fig. 2 is obtained. In contrast, in the reported cadmium(II) complexes with TMA ligands, for example $[Cd_3(TMA)_2]\cdot 13H_2O$[10] and $[Cd_3(TMA)_2(H_2O)_9]\cdot 2H_2O$,[11] each TMA unit binds to three Cd(II) atoms.

The formation of **1** is attributed to the three carboxylate groups having different orientations. In contrast to the small dihedral angles between the carboxylate plane and the benzene plane observed in the metal complexes of TMA,[2] the carboxylate groups at the 1,2-positions of $BTC^{3-}$ in complex **1** are twisted, giving large dihedral angles of 69.0° and 37.7° between each carboxylate plane and the benzene plane, respectively. In this way the repulsion between the oxygen atoms at the 1,2-positions is reduced greatly and the oxygen atoms can also bind to metal atoms located far away from the benzene ring plane. Thus, the ligand $BTC^{3-}$ has a tendency to form metal-organic frameworks (MOFs) with a higher dimensionality upon complexation with metal ions. The pillars (benzene rings) in complex **1** directly link the floors to generate, to the best of our knowledge, the first example of a 3D pillar-like MOF with $4.8^2$ topological channels (Fig. 3).[12,13] The distance between two adjacent floors is *ca.* 9.83 Å.

Thermogravimetric analysis (TGA) of a crystalline sample of **1** showed a weight loss of 11.7% centered at 110 °C, corresponding to the loss of six molecules of water (calcd. 11.8%), followed at 290 °C by a further weight loss (17.5% of total), corresponding to the loss of the remaining three water molecules (calcd. 17.7%). The most characteristic XRD peaks disappeared after the water molecules were removed from compound **1**. When the dehydrated sample was immersed in water, the structure of **1** could, unfortunately, not be recovered completely.

It is noteworthy that complex **1** shows a strong photoluminescence with a maximum emission band at 436 nm upon excitation at 328 nm (Fig. 4). For excitation wavelengths between 280–420 nm, there is no obvious emission observed for trimellitic acid under the same experimental conditions.

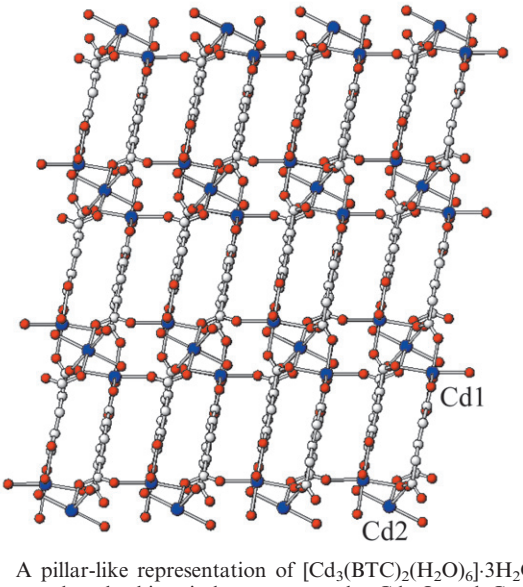


**Fig. 2** A pillar-like representation of $[Cd_3(BTC)_2(H_2O)_6]\cdot 3H_2O$ (**1**). The blue, red and white circles represent the Cd, O and C atoms, respectively.

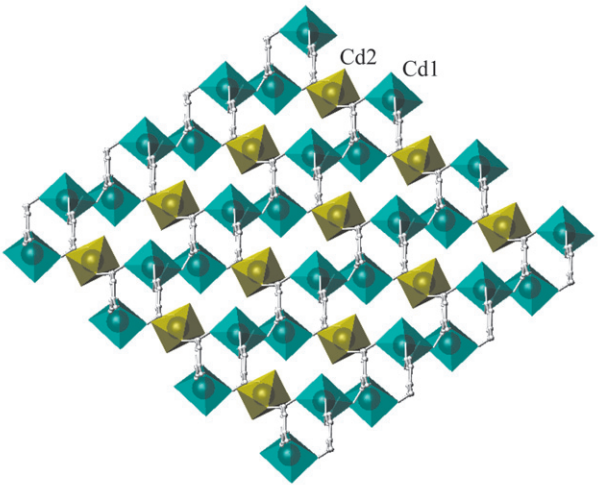


**Fig. 3** Top view of the pillar-like complex $[Cd_3(BTC)_2(H_2O)_6]\cdot 3H_2O$ (**1**) indicating the channels with $4.8^2$ topology. The polyhedral presentation indicates the octahedral coordination environments for Cd1 (blue) and Cd2 (yellow), respectively.

The result suggested that the blue emission originates from the coordination of $BTC^{3-}$ to the cadmium(II) atoms.[10]

In summary, we have synthesized and characterized a novel cadmium complex by using trimellitic salt. Complete deprotonation of the triacid in a supramolecular system provides a useful strategy for the construction of MOFs with novel structures and potentially useful physical properties.

## Experimental

The piperidinium salt of trimellitic acid was readily prepared from the reaction of piperidine with $H_3BTC$ in *N*,*N*-dimethylformamide (DMF) solution. Cadmium(II) acetate dihydrate (24 mg, 0.09 mmol) was added to a methanol solution (10 ml) of the piperidinium salt of BTC (42 mg, 0.09 mmol). The mixture was stirred at room temperature for 30 min and then was filtered. The filter cake was dissolved in 80 ml aqueous solution. Colorless crystals were obtained by slow evaporation of the aqueous solution after a few weeks (yield: 46 mg, 56%). Anal. calcd for $C_{18}H_{24}Cd_3O_{21}$: C, 23.66; H, 2.65%; found: C, 23.68; H, 2.68%.

### X-Ray crystallography

The data collections for **1** were performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å) at 200 K.

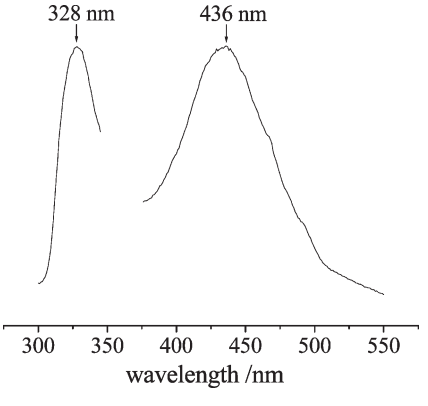


**Fig. 4** Photoluminescence spectra of complex **1** at 293 K in the solid state.

The structure was solved by direct method using SHELXS-97 and refined by full-matrix least-squares methods. Calculations were carried out on an SGI workstation with teXsan software package.

**1**: $C_{18}H_{24}Cd_3O_{21}$, $M_w = 913.57$, triclinic, space group $P\bar{1}$, $a = 7.6819(10)$, $b = 8.8715(11)$, $c = 10.3205(11)$ Å, $\alpha = 105.852(6)°$, $\beta = 93.055(7)°$, $\gamma = 105.705(3)°$, $U = 645.16(13)$ Å$^3$, $Z = 2$, $\mu = 2.549$ cm$^{-1}$. A total of 4734 reflections were collected of which 2792 were independent ($R_{int} = 0.0212$). The final $R_1$ was 0.0243 [$I > 2\sigma(I)$].†

## Acknowledgements

The authors are grateful for funding from the National Natural Science Foundation of China for financial support of this work.

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