3256 *Chem. Mater.* **2000,** *12,* 3256−3258

A Molecular Bilayer Motif Constructed from a Three-Connected Organic Ligand and Cd^{2+} Cations: Crystal Structure of $[Cd_3(trimesate)_2{\cdot}(H_2O)_9]{\cdot}2H_2O$

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Received July 27, 2000
Revised Manuscript Received September 22, 2000

The designed self-assembly of metal-organic framework solids is a topic of intense current research and many two- and three-dimensional structures with specific network topologies (e.g., ladder, honeycomb, etc.) have been constructed in recent years.[1−3] Apart from the aesthetically attractive structural aspect of these novel compounds, their inherently open architecture offers the opportunity for applications as microporous solids.[4]

Here, we report a bilayer-type framework that is constructed from trimesic anions acting as three-metal connectors and Cd^{2+} cations acting as spacers (Scheme 1a). Three compounds, isomorphous between them, exhibiting this type of framework have been published recently but, in these cases, trigonally coordinated metal cations act as nodes while the organic ligand (bipyridine) acts simply as a linear spacer (Scheme 1b).[5−7] Previous studies, based on the Cambridge Structural Database, showed that the Cd^{2+} cation binds preferably to carboxylic acids in the chelate bidentate mode.[8] This is probably of some importance because the chelate effect is expected to reinforce the framework stability.[9] Moreover, recent crystallographic studies on polymeric cadmium complexes with dicarboxylic acids[10,11] showed that both carboxylate groups are used to bind the metal in the above-mentioned coordination mode. We therefore reasoned that if all carboxylate groups are used for metal binding in the case of trimesic acid, too, then the motif formed would give rise, depending on the experimental conditions, to various crystal architectures. The interaction of Cd^{2+} with trimesic acid was studied potentiometrically in aqueous solution some years ago.[12] Moreover, crystalline metal-organic microporous materials based on trimesic acid and different cations (including Cd^{2+}) were described in a recent patent.[13]

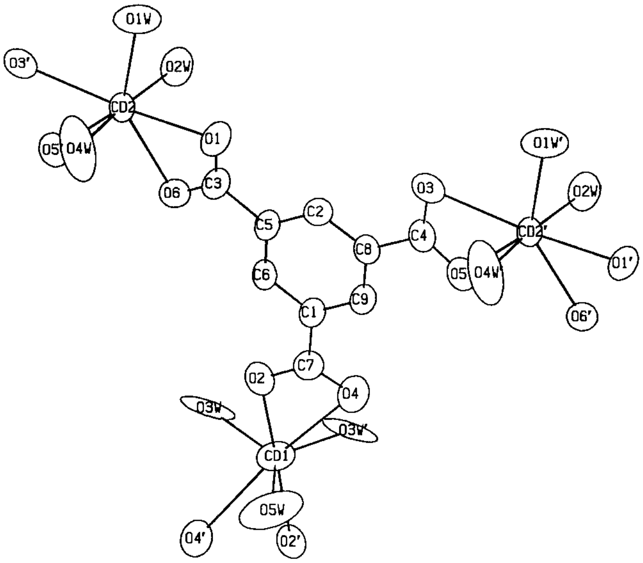
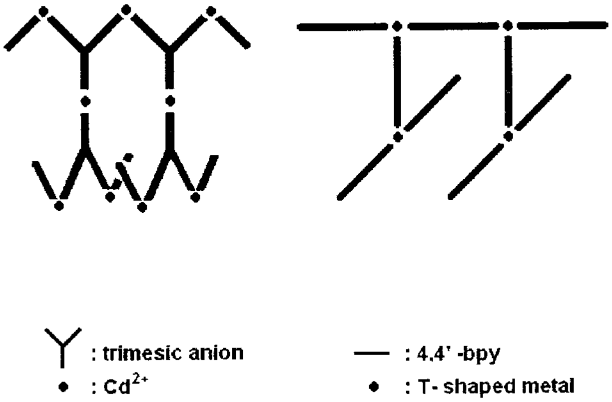


Figure 1. Ortep view of the coordination environment of the two cadmium cations.

Scheme 1



Crystals of $[Cd_3(trim)_2{\cdot}(H_2O)_9]{\cdot}2H_2O$, **1** (trim = trimesate anion), were prepared by the silica gel method. An appropriate gel column was prepared by mixing 16 mL of 0.001 M trimesic acid with 4 mL of 1 M HNO_3 and brought to pH 5.9 by a solution of silica (density = 1.06 g cm^{-3}) obtained by dilution of a commercially available silica solution (Merck, density = 1.37 g cm^{-3}). The final concentration of trimesic acid was estimated to be 5×10^{-4} M. The gelling solution was allowed to stand for about 2 days and then an aqueous solution of 1.5×10^{-2} M $Cd(NO_3)_2$ was added at the top of the gel. The volume of the metal compound solution was equal

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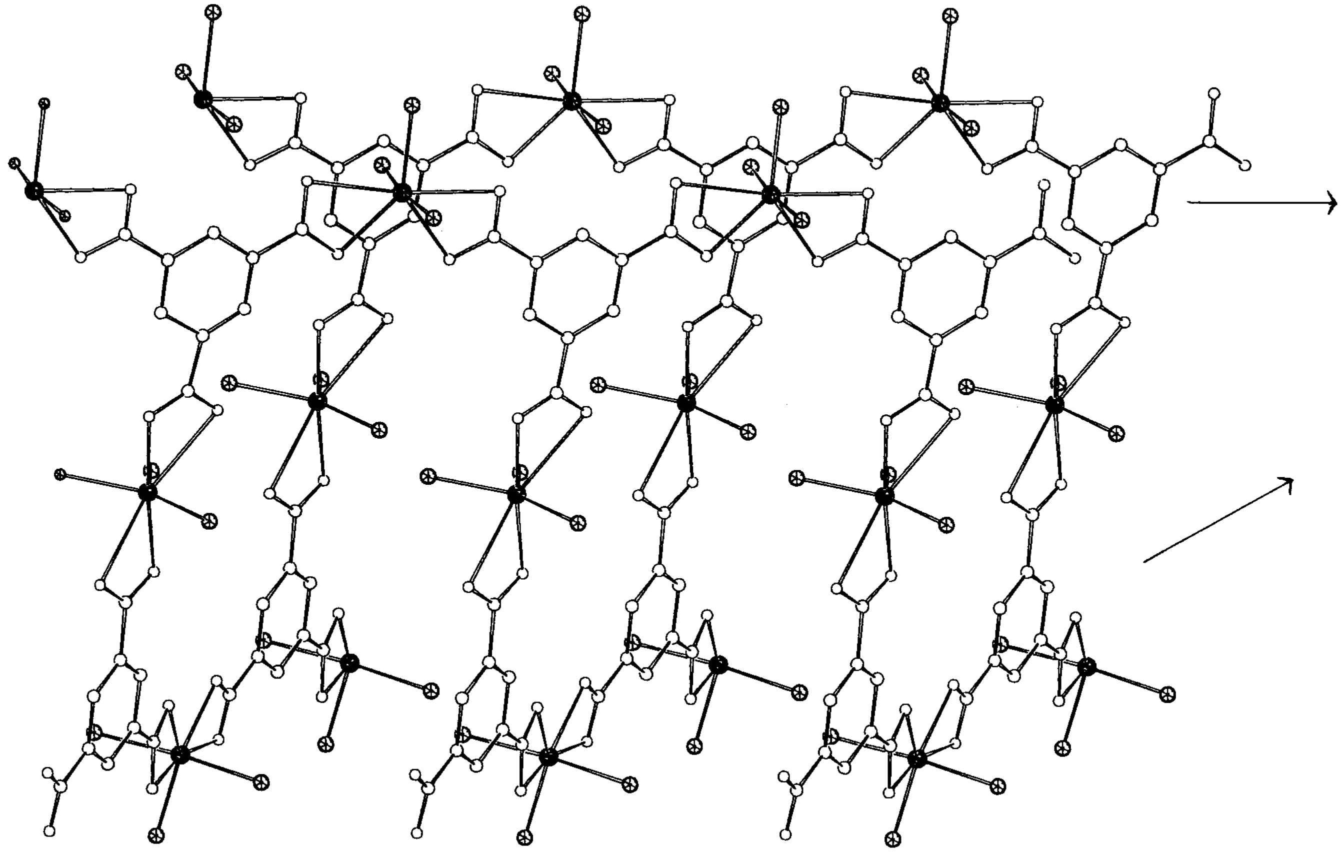

Figure 2. Schakal view of a molecular bilayer. The direction of the chains is indicated by the arrows. Filled circles represent cadmium cations while the shaded ones represent coordinated water oxygens.

to that of the gel and we estimate that the metal-to-ligand ratio was 1:1. Precipitation of dendritic crystals occurred almost immediately. Few (4−5) well-shaped transparent, colorless crystals were formed after about 4 days. The crystals are indefinitely stable in air. The crystal structure was solved from room-temperature data collected on a Bruker P4 diffractometer.[14]

As expected, all three carboxylate groups participate in the metal complexation (Figure 1). There are two crystallographically independent cadmium cations, one of them (Cd1) being located on a 2-fold axis. Both cations are (5 + 2)-O coordinated through 4 carboxylate oxygen atoms and through 3 water oxygen atoms. However, the coordination geometry around the Cd1 center can be described as a distorted pentagonal bipyramid while that of Cd2 as a distorted capped trigonal prism. The 5 short metal−oxygen contacts are in the range 2.243−2.477 Å for Cd1 and 2.260−2306 Å for Cd2. The two longer metal−oxygen distances are 2.549(3) and 2.620(3) Å for Cd2 and 2.736(3) Å for Cd1. Such long contacts have also been observed in other cadmium carboxylates,[15,16] and may be considered as semicoordinative bonds.[17] Indeed, valence bond calculations[18] for Cd1 gave a bond valence sum of 1.95 when including the 5 shorter contacts, while a value of 2.14 was obtained for 7-fold coordination. The corresponding values for Cd2 are 1.80 and 2.08.

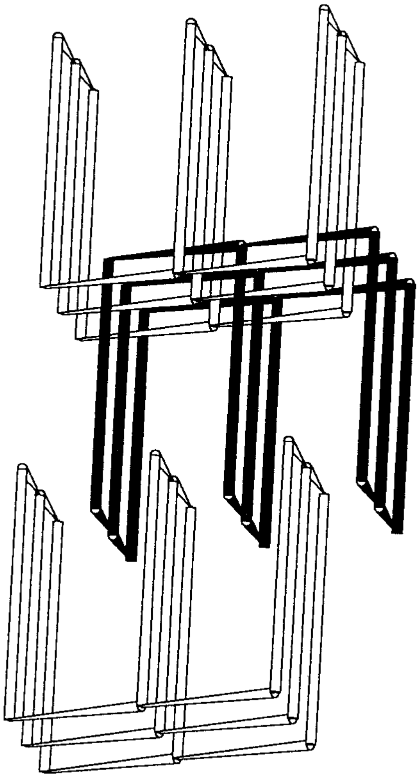

Figure 3. View of three intedigitated bilayers. The nodes represent the centers of the trimesate anions.

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[14] Crystal data: $Cd_3(C_9H_3O_6)_2 \cdot 11H_2O$, monoclinic, space group *C*2/*c* (No. 15), $Z = 4$, Mo Kα radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, $a = 19.010(1)$ Å, $b = 7.396(1)$ Å, $c = 20.446(1)$ Å, $\beta = 97.17(1)°$, $V = 2852.2(4)$ Å^3, $0.35 \times 0.25 \times 0.15$ mm^3, refinement on F^2, R1 = 0.0277, wR2 = 0.0740, GOF = 1.084 for 245 parameters and 2312 reflections with $I > 2\sigma(I)$.

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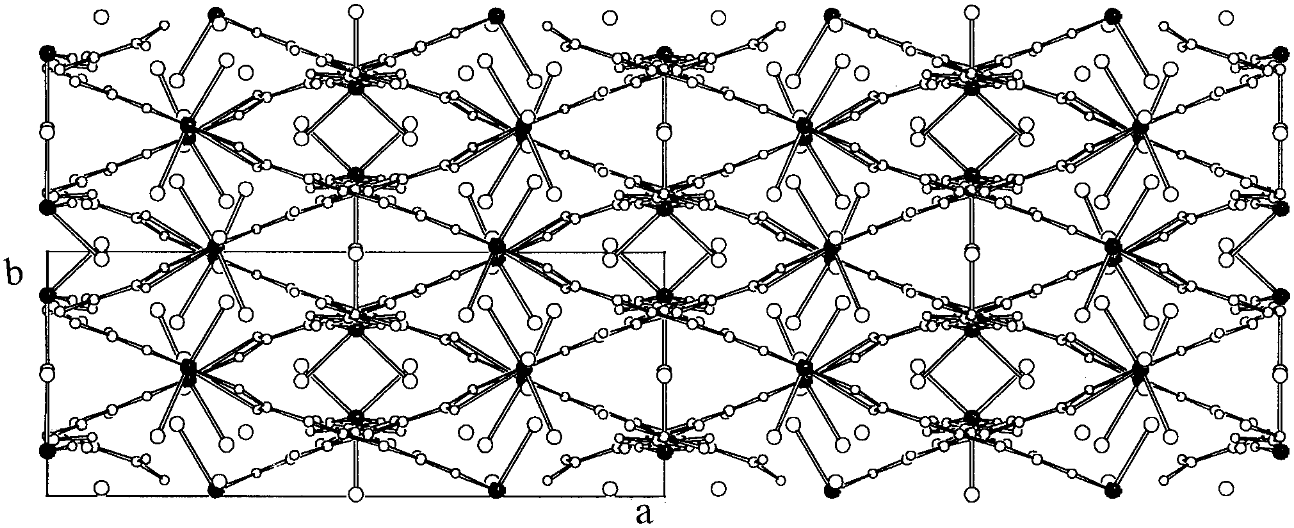

Figure 4. View of the structure along the *c* axis. The open big circles represent coordinated water oxygens.

Each trimesate anion bridges three metal centers (Figure 2). The network formed may be described as composed of two sets of infinite one-dimensional chains of −Cd2−trimesate anion−Cd2− parallel to the $(a + b)$ and $(a - b)$ directions. These chains are cross-linked by the Cd1 cations. This network is topologically equivalent to the so-called molecular bilayer network found recently in the isomorphous compounds $[M_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot xH_2O$ (M = Co, Ni, Zn),[5] $[Co_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot 2CS_2$,[6] and $[Ni_2(4,4'\text{-bpy})_3(NO_3)_4]\cdot 2EtOH$,[7] (4,4′-bpy = 4,4′-bipyridine). In our case, the interesting feature is that, contrary to the previous examples, the ligand acts as a node while the metal acts as a spacer. It is worth noting that there are only a few examples in the literature presenting this mode of network construction.[1a]

The assembly of these bilayers results in the so-called tongue-and-groove structure,[5] schematically shown in Figure 3. The structure is stabilized by extensive $\pi-\pi$ interactions between the interdigitated bilayers and by numerous hydrogen bonds involving both coordinated and lattice water molecules and carboxylate oxygen atoms.

As shown in Figure 3 the open space is partially filled by the interdigitated networks. The coordinated water molecules point inside the cavities formed (Figure 4). The disordered lattice water molecules are also located in these cavities. Physical measurements (thermal analysis, estimation of the pores) were not undertaken due to the very limited amount of material at our disposition.

The question that arises from this work is whether other architectures (for example, ladder) can be obtained by modifying the experimental conditions, in close analogy with the 4,4′-bipyridine/T-shaped metal systems. Work in this direction is in progress.

Acknowledgment. The authors thank the Authorities of the Region of Epirus for the purchase of the X-ray equipment.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and structure factor tables for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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