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Metal–Organic Frameworks

Metal–Organic Replica of Fluorite Built with an Eight-Connecting Tetranuclear Cadmium Cluster and a Tetrahedral Four-Connecting Ligand**

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The last decade has seen remarkable progress in the development of new materials based on transition-metal ions and organic ligands, often termed as coordination polymers (networks) or metal–organic frameworks. Although this relatively new field of chemistry aims at the discovery and synthesis of new materials for practical applications emphasizing their functional aspects, it would be difficult to achieve a true advance without understanding the structural aspects of such materials at a molecular or an atomic resolution. Recent reviews on the framework topologies and other geometrical characteristics of network solids reflect this importance.[1]

As the number of infinite network structures based on molecular building blocks increases, it becomes easier to analyze and categorize their framework topologies. It appears that for the majority of 3D metal–organic framework structures, there are well-known prototypes in metallic or binary inorganic solids. For example, diamond-related nets composed of one or two kinds of tetrahedral nodes and linear linkers are the most common,[2] and a primitive cubic net (α-Po) based on octahedral nodes with linear linkers is also frequently observed.[3] Other 3D structures have recently been reported to have the following topologies: boracite,[4] $CdSO_4$,[5] CaB_6,[6] feldspar,[7] NbO,[8] perovskite,[9] Pt_3O_4,[10] PtS,[7,11] pyrite,[12] quartz,[13] rutile,[14] sodalite,[15] $SrSi_2$,[16] and tungsten bronze.[17] Note that the connectivity of the building blocks in any of these frameworks does not exceed six and, in general, coordination networks with a local connectivity higher than six is very rare.[18] One of the most important and frequently encountered structure types in minerals that have not been reported in metal–organic frameworks is fluorite (CaF_2), in which the cation is eight coordinated in a cubic geometry and the anion is in tetrahedral environment. The

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design of a metal–organic framework with such a topology, based on deduction, would require an eight-coordinated metal center or an eight-connecting polynuclear metal cluster unit; however, none of the two can easily be envisioned since stereochemically unconstrained eight coordination almost always results in a square antiprism geometry, as exemplified by a 3D framework based on octacyanomolybdate building units,[18a] and an eight-connecting polynuclear metal cluster in a cubic geometry is hitherto unprecedented. Herein, we report a non-interpenetrating cadmium-carboxylate framework built upon a new type of tetranuclear clusters that act as eight-connecting vertices. Together with a tetrahedral four-connecting ligand, tetrakis(4-carboxyphenyl)methane (TCPM),[19] the resulting 3D framework is defined as the first metal–organic replica of fluorite.

A solvothermal reaction of $Cd(NO_3)_2{\cdot}4H_2O$ and H_4TCPM in DMF gives light brown cube-shaped crystals, which maintain single-crystallinity after washing with DMF and drying under vacuum at room temperature. A single-crystal X-ray diffraction study established the formula as $[Cd_4(TCPM)_2(DMF)_4]{\cdot}4DMF{\cdot}4H_2O$ (**1**), and the bulk purity of the product was independently confirmed by elemental analysis and X-ray powder diffraction measurements in which a number of sharp signals closely match those of a simulated diffractogram based on the single-crystal X-ray data (see Supporting Information).

In the structure, a tetranuclear cluster with a general formula $[M_4(O_2CR)_8]$ is observed in which four Cd^{II} ions lie on the same plane, and a total of eight carboxylate groups bridge the Cd ions from above and below the plane of the Cd ions (Figure 1). Along with a solvent DMF molecule bonded to each metal center, the coordination environment around the Cd ion is best described as a monocapped trigonal prism, in which the oxygen atom of the solvent molecule is capping a tetragonal face of the trigonal prism formed by six oxygen atoms from three carboxylate moieties. The Cd–O bond lengths are uniform in the range 2.263(7)–2.299(3) Å except for the bridging oxygen atoms that form asymmetrical bonds with two adjacent Cd ions (2.285(3) and 2.553(4) Å). Each Cd ion in the tetranuclear cluster is related to its neighbor by crystallographic fourfold symmetry, and the two sets of four carboxylate groups above and below the plane of Cd ions are related to each other by mirror plane symmetry. Therefore, the $[Cd_4(O_2CR)_8(DMF)_4]$ cluster mimics the geometry of a twisted square prism or tetragonally compressed cube (see below). The extension of the structure into a 3D network is accomplished by connecting eight tetrahedral shape TCPM ligands to the building block with $4/m$ symmetry. The arrangement of eight TCPM ligands around a $[Cd_4(O_2CR)_8(DMF)_4]$ cluster is shown in Figure 2.

To understand the framework topology, it is necessary to simplify the building blocks from which the 3D net of **1** is built. The $[Cd_4(O_2CR)_8(DMF)_4]$ cluster unit and TCPM ligand can be represented by cubic and tetrahedral units, respectively. The former building block is achieved by connecting the carboxylate carbon (C1) atoms to its nearest neighbors and the latter by drawing a tetrahedron around the central sp^3 carbon atom of the TCPM ligand (Figure 3a and b). This process, when repeated over the extended network, results in the simplified view of the framework of **1** as shown in Figure 3c. The (4,8)-connected net has a strong resemblance to fluorite (CaF_2), one of the most important and

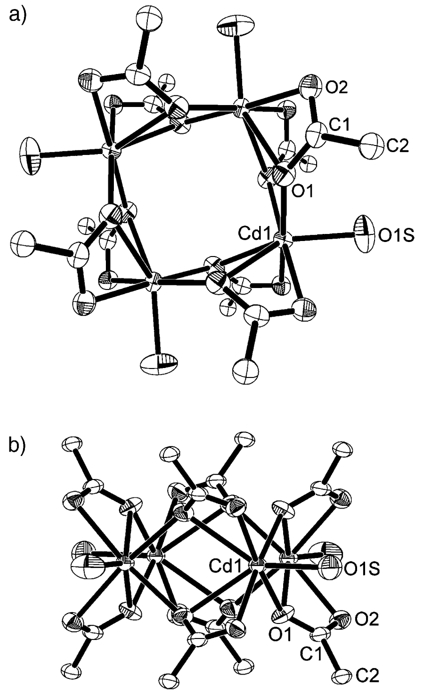

Figure 1. a) Top and b) side view of the $[Cd_4(O_2CR)_8(DMF)_4]$ building unit in the structure of **1** (ORTEP, 40% probability ellipsoids). Only oxygen atoms (O1S) of the coordinated DMF molecules are shown for clarity.

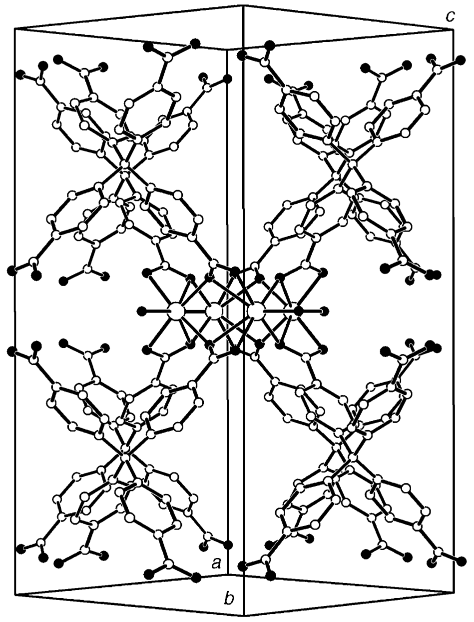

Figure 2. Perspective view showing the arrangement of eight TCPM ligands around one Cd_4 cluster in the unit cell of **1**. Solvent molecules and hydrogen atoms are omitted for clarity. Large and small open circles represent cadmium and carbon atoms, respectively, and oxygen atoms are shown as filled circles.

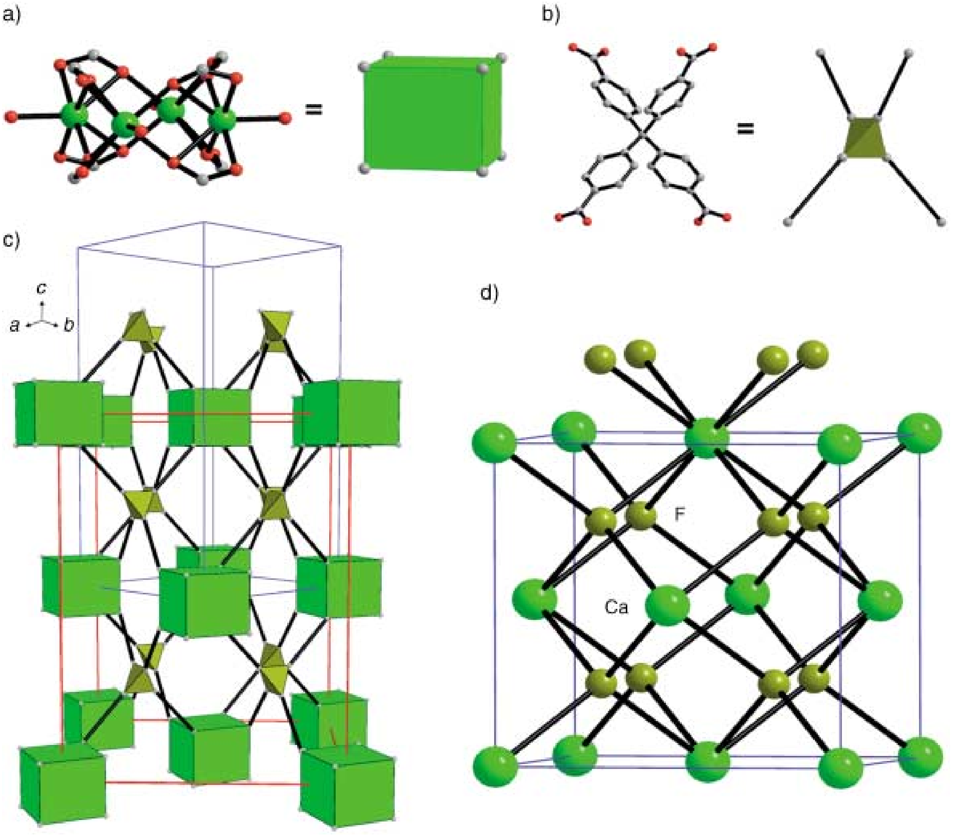

Figure 3. Simplified views of a) cubic and b) tetrahedral building blocks in **1**. c) Perspective view of the framework **1** stylized according to (a) and (b). The red lines represent an imaginary unit cell having the face-centered symmetry (not allowed in tetragonal system). d) Crystal structure of fluorite (CaF_2) in a face-centered cubic unit cell ($Fm\bar{3}m$).

preferred structure for AB_2 type compounds, and is a unique topology for connecting regular cubic and tetrahedral building blocks.[1b] In the structure of fluorite, which has a face-centered cubic symmetry, Ca^{2+} ions are coordinated by eight F^- ions in a cubic geometry, and F^- ions occupy all the tetrahedral sites in the face-centered cubic unit cell (Figure 3d). In the simplified structure of **1**, the cubic and tetrahedral building blocks replace Ca^{2+} and F^- ions in fluorite, respectively, and as one can easily see from the comparison in Figure 3, the similarity in the structures of the genuine fluorite and its metal–organic analogue is striking, except for the slight tetragonal distortion in the structure of **1**. The decorated fluorite net of **1** does not allow interpenetration owing to the size of the Cd_4 cluster, the organic linker, and the void space. The inside the cagelike substructure of **1** comprising six cubes and eight tetrahedra is divided into two compartments by coordinated DMF molecules, which lie approximately at the same height as Cd ions along the *c* axis, and the void space is occupied by solvent DMF and water molecules. A thermogravimetric analysis reveals that the free guest molecules and a coordinated DMF molecule are released from the framework upon heating to about 270 °C (see Supporting Information). Further heating results in the loss of the remaining coordinated DMF molecule before a sharp weight loss corresponding to the decomposition of the TCPM ligand is observed shortly after 370 °C.[20]

In summary, we have synthesized a metal–organic framework that contains eight-connecting tetranuclear cadmium–carboxylate clusters and tetrahedral organic building blocks. The non-interpenetrating, 3D framework is best described as a decorated fluorite net, a topology that has been expected but never been observed in metal–organic or organometallic compounds prior to this work. The new tetranuclear metal-carboxylate cluster may also prove to be a useful building motif in designing a metal–organic framework with a specific topology.

Experimental Section

1: H_4TCPM (103 mg, 0.21 mmol) and $Cd(NO_3)_2{\cdot}4H_2O$ (112 mg, 0.36 mmol) were dissolved in DMF (2.4 mL), and the solution was heated in a screw-capped vial at 95 °C for 2 days. The light brown crystals formed were collected, washed with DMF, and dried under a reduced pressure at room temperature (104 mg, 61 % based on $Cd(NO_3)_2{\cdot}4H_2O$). Elemental analysis calcd (%) for $[Cd_4(TCPM)_2(DMF)_4]{\cdot}4DMF{\cdot}4H_2O$: C 47.09, H 4.63, N 5.36; found: C 46.99, H 4.66, N 5.62. Single-crystal X-ray crystallography: The full hemisphere data were collected on a Siemens SMART CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at −60 °C. After the data integration (SAINT) and semiempirical absorption correction based on equivalent reflections (SADABS), the structure was solved by direct methods and subsequent difference Fourier techniques (SHEXLTL). Crystal data for $[Cd_4(TCPM)_2(DMF)_4]{\cdot}$

$4\,DMF{\cdot}4\,H_2O$ (**1**): crystal size $0.19\times0.17\times0.17$ mm, tetragonal, space group $I4/m$ (No. 87), $a=13.480(1)$, $c=24.582(5)$ Å, $V=4467(1)$ Å^3, $Z=2$, $\rho_{calcd}=1.555$ g cm^{-3}, $\mu=1.02$ mm^{-1}, $2\theta_{max}=52°$, $T_{max}=0.85$ $T_{min}=0.83$. Total number of reflections 2254 ($R_{int}=0.0507$). All the non-hydrogen atoms except for those of disordered solvent molecules were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. The disordered solvent molecules could not be fully modeled, and were left without hydrogen atoms. The refinements were carried out with full-matrix least-squares on F^2. $R_1=0.0522$, $wR_2=0.1298$ and GOF = 1.058 for 1824 reflections ($I>2\sigma(I)$) and 155 parameters. CCDC-221907 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[20] To study the gas-sorption property, we heated as-synthesized **1** at 120 °C under a high vacuum (10^{-5} Torr) for 24 h, upon which the sample lost its weight by 26 %; however, no significant amount of sorption was observed for N_2, or H_2, and the evacuated sample showed severe line broadening in its powder XRD pattern. This may be attributed to the instability of the framework caused by the loss of coordinated DMF molecules.