Synthesis of Cadmium(II) Organic Framework Based on Feist's Acid

Young Seop Kim, YongBok Go, Jaheon Kim,[†] Nakcheol Jeong,[‡] and Hee K. Chae[*]

Department of Chemistry, Hankuk University of Foreign Studies, Youngin 449-791, Korea
*[†]Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, USA*
[‡]Department of Chemistry, Korea University, Seoul 136-701, Korea
Received March 20, 2002

Since M. Gramaccioli published the paper on crystal structures of zinc glutamate dihydrate,[1] a large number of coordination polymers with carboxylate ligands have been structurally characterized and the design of coordination polymers with specific physicochemical properties have been to elicit intense interest.[2] Nowadays, metal-organic framework (MOF) structures expect to be predictable on the basis of organic ligand design and known metal coordination patterns, even though most of these materials have not been discovered in serendipitous mode with respect to potential applications.[3] The recent interest in new porous MOF materials with advanced functionality has concentrated on the design of porous network materials with the aid of crystal engineering techniques from pre-designed molecular building blocks.

Limited studies, however, have been only available regarding the applications of MOF materials to catalysts so far, while Aoyama has reported the use of organic zeolitic materials to enhance endo-selectivity in Diels-Alder reactions.[4,5] For example, [Zn₃O(L-H)₆]·2H₃O·12H₂O (L = $C_{12}H_{14}O_5$, POST-1) shows enantioselective catalytic activity for the transesterification of 1-phenyl-2-propanol with few % enantiomeric excess.[4] It is the first chiral catalyst of porous MOF complexes using a chiral organic building block, although Cd(4,4'-bipyridine)₂(NO₃)₂ and Zr₂(PO₄)(PV)X₃ are catalysts for the cyanosilylation of aldehydes and the production of H_2O_2 from H_2 and O_2, respectively. POST-1 used the well-defined chiral tartaric derivative as a building block. Feist's acid has a similar structural character with tartaric acid. It has been used for the conformationally restricted analogues of amino acid or asymmetric synthesis of chiral compounds as starting material.[6] Here we describe the synthesis and structure of MOF using a chiral organic building block, Feist's acid, 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid (H₂MCPD).

H₂MCPD
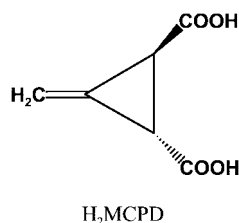
Experimental Section

Feist's acid, cadmium(II) nitrate tetrahydrate and N,N-dimethylformamide (DMF) were used as received from Aldrich. A DMF /toluene (3.5 mL) mixture of Cd(II) nitrate tetrahydrate (14.9 mg, 0.05 mmol) and Feist's acid (7.1 mg, 0.05 mmol) was added into a small vial, which was placed in a larger vial containing 1 wt% of triethylamine in toluene (3 mL). The larger vial was sealed and left undisturbed at room temperature for 6 days. The block crystals were isolated and then washed with 3 × 10 mL of toluene to give 20 mg (56%) of product. Anal. Calcd. For $Cd_2C_{18}H_{27}O_{12}N_4$ = $Cd_2(MCPD)_{1.5}(NO_3)(DMF)_3$: C, 30.18; H, 3.80; N, 7.82. Found: C, 30.53; H, 3.80; N, 7.73. FT-IR (KBr, 3500-400 cm⁻¹): 3450 (br), 2941 (w), 1659 (vs), 1559 (vs), 1495 (s),

Table 1. Crystal Data and Structure Refinement for $Cd_2(MCPD)_{1.5}$-$(NO_3)(DMF)_3$

Empirical formula	$C_{18} H_{27} Cd_2 N_4 O_{12}$
Formula weight	716.24
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Trigonal, $R(-3)c$ (No. 167)
Unit cell dimensions	a = 13.1232(8) Å α = 90°
	b = 13.1232(8) Å β = 90°
	c = 52.655(3) Å γ = 120°
Volume	7853.3(7) Å³
Z	12
Density (calculated)	1.817 Mg/m³
Absorption coefficient	1.689 mm⁻¹
F(000)	4260
Crystal size	0.26 × 0.24 × 0.10 mm³
θ range for data collection	1.95 to 28.38°
Limiting indices	-17 <= h <= 16, -10 <= k <= 17, -69 <= l <= 68
Absorption correction	SADABS (T_{max} = 1.000, T_{min} = 0.871)
Reflections collected/unique	14374/2097 [R(int) = 0.0268]
Data/restraints/parameters	2097/4/125
Goodness-of-fit on F^2	1.185
Final R indices [I>2σ (I)]	R1 = 0.0696, wR2 = 0.1179
R indices (all data)	R1 = 0.0964, wR2 = 0.1271
Largest diff. peak and hole	1.179 and -1.040 e.Å⁻³

908   *Bull. Korean Chem. Soc.* **2002**, Vol. 23, No. 6

Notes

1387 (vs), 1291 (s), 1118 (m), 1072 (w), 1037 (w), 986 (w), 935 (w), 802 (w), 690 (m), 665 (m), 568 (w).

Single crystal X-ray diffraction data were collected on a standard Bruker SMART APEX CCD-based X-ray diffractometor equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å). Data frames for the Ewald hemisphere were collected with a scan width of 0.3° in ω with an exposure time of 20 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 14374 reflections to a maximum 2θ value of 56.76° of which 2097 were independent and 1581 were greater than 2 $\sigma(I)$. The final cell constants (Table 1) were based on xyz centroids of 3964 reflections above 10 $\sigma(I)$. The collected X-ray data with Ewald hemisphere containing Friedel pairs' reflections are composed of many sets of redundant reflections. These data were merged to produce unique reflections. This gave rise to the conspicuous reduction of the number of reflections from 14374 to 2097. Analysis of the data showed negligible decay during data collection. The structure was solved by direct methods and the subsequent difference Fourier methods. Refinement processes were carried out with the Bruker SHELXTL (version 5.10) software package, using the centrosymmetric space group $R(-3)c$ with $Z = 12$ for the formula.[7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were also included with ideal geometry. The reliability factors converged to $R_1(F_0) = 0.0696$ and $wR_2(F_0^2) = 0.1179$. Additional details are presented in Table 1 and selected bond distances and angles in Table 2. Fractional atomic coordinates, anisotropic displacement parameters, and hydrogen coordinates are given as supplementary.

Results and Discussion

Block crystals of this compound were produced at room temperature upon diffusing triethylamine into a clear DMF/toluene solution containing $Cd(NO_3)_2\cdot4H_2O$ and H_2MCPD in an 1 : 1 mole ratio. Its FT-IR spectrum showed the expected absorptions for the vibrations of MCPD (1659 and 1495 cm^{-1}), DMF (1559 cm^{-1}), and nitrate (1387 cm^{-1}). It showed no absorptions for any protonated MCPD (1699 cm^{-1}), indicating the complete deprotonation of H_2MCPD by addition of triethylamine to the reaction mixture.[8]

A single-crystal X-ray diffraction study revealed an extended 2-D framework formulated as $Cd_2(MCPD)_{1.5}(NO_3)(DMF)_3$, which is consistent with that derived from elemental microanalysis. Selected bond lengths and angles are given in Table 2. The fundamental building unit of the crystal structure is shown in Figure 1. It is composed of two different cadmium (II) centers (Cd1, Cd2) that bridged by carboxylates (O1, O2; O1C, O2C; O1D, O2D) of separate MCPD units. All the symmetry equivalent O1 atoms are linked to Cd1, and all the symmetry equivalent O2 atoms are linked to Cd2. Progre-
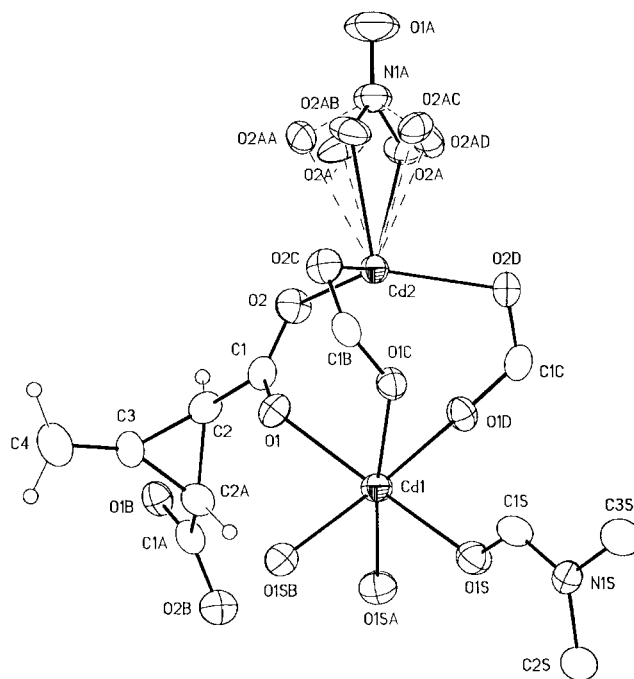
Table 2. Selected Bond Lengths [Å] and Angles [°] for $Cd_2(MCPD)_{1.5}$-$(NO_3)(DMF)_3$

Cd(1)-O(1)	2.275(5)	Cd(1)-O(1S)	2.253(6)
Cd(2)-O(2)	2.197(5)	Cd(2)-O(2A)	2.51(2)
Cd(2)-O(2A')	2.25(2)	O(1)-C(1)	1.247(9)
O(2)-C(1)	1.238(9)	C(1)-C(2)	1.523(10)
C(2)-C(2A)	1.499(14)	C(2)-C(3)	1.456(11)
C(3)-C(4)	1.303(18)	O(1S)-C(1S)	1.181(10)
O(1S)-Cd(1)-O(1)	173.1 (2)	O(2)-Cd(2)-O(2C)	118.22(7)
O(1S)-Cd(1)-O(1C)	88.3(2)	O(2)-Cd(2)-O(2D)	118.22(7)
O(1SB)-Cd(1)-O(1)	88.3(2)	O(2D)-Cd(2)-O(2C)	118.22(7)
O(1SA)-Cd(1)-O(1C)	173.1(2)	O(2D)-Cd(2)-O(2A)	88.2(15)
O(1S)-Cd(1)-O(1D)	97.46(19)	O(2)-Cd(2)-O(2A)	81.3(12)
O(1SA)-Cd(1)-O(1)	97.47(19)	O(2C)-Cd(2)-O(2A)	123.1(5)
O(1C)-Cd(1)-O(1)	86.02(19)	O(2)-Cd(2)-O(2A')	74.2(10)
O(1D)-Cd(1)-O(1)	86.02(19)	O(2C)-Cd(2)-O(2A')	101(3)
C(1)-O(1)-Cd(1)	136.3(5)	C(1S)-O(1S)-Cd(1)	125.2(6)
C(1)-O(2)-Cd(2)	108.3(5)	O(2)-C(1)-O(1)	124.1(7)
O(2)-C(1)-C(2)	114.3(7)	O(1)-C(1)-C(2)	121.6(8)
C(3)-C(2)-C(2A)	59.0(4)	C(3)-C(2)-C(1)	118.4(6)
C(2A)-C(2)-C(1)	116.5(8)	C(4)-C(3)-C(2)	149.0(4)
C(4)-C(3)-C(2A)	149.0(4)	C(2)-C(3)-C(2A)	61.9(7)

Figure 1. A perspective drawing of the building block unit for the structure of $Cd_2(MCPD)_{1.5}(NO_3)(DMF)_3$, represented by 30% thermal ellipsoids. The coordinated nitrate anion is statistically disordered about the crystallographic 3-fold axis of the unit cell which passes through Cd1, Cd2, N1A and O1A.
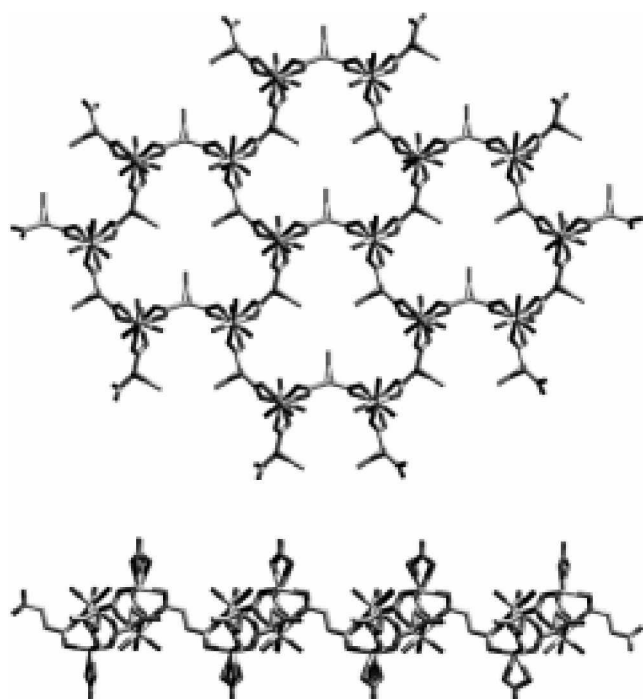
of 2.25(2) Å, which does not allow for their ion exchange. It should be noted that the low precision of the final bond lengths and angles is not unexpected given by the inherent disorder of the nitrate ion. This building unit is connected to another building unit through carboxylates of the ligand to form a dimer, [Cd$_4$(MCPD)$_3$(NO$_3$)$_2$(DMF)$_6$], each of which MCPD ligands is linked together. This arrangement leads to a 12-membered ring composed of 6 dimers linked by three MCPD units, and the overall crystal structure of this material results from fusing such rings together as shown in Figure 2. Extension of the structure gives a 2-D layered Cd-MCPD network as shown in Figure 3, which is the projection view of the packing framework along the c direction. Two neighboring layers are separated by c/6 (1/6 distance of the c-axis length) and related by an inversion symmetry. One enantiomeric MCPDs are participated in one layer and the other MCPDs in the other layer, which means that each layer is chiral but the adjacent layer has its mirror configuration. Therefore these layers are alternatively stacked along the c-axis to give a centrosymmetric and achiral structure.

A thermogravimetric study of Cd$_2$(MCPD)$_{1.5}$(NO$_3$)(DMF)$_3$ was performed in a nitrogen atmosphere. Two distinct losses of mass were observed around 150 and 320 °C. It shows that the complex is stable up to 150 °C because there is no expected space available for guest molecules in the 12-membered ring, which can affect the framework's stability. At 150 °C, the observed mass loss of 24% corresponds to 3 DMFs bound per formula unit. Between 150 and 320 °C slow mass loss of 30% corresponds to 1.5 MCPDs. The next mass loss of 9% around 320 °C corresponds to coordinated nitrate.

In conclusion, a new cadmium(II) 3-methylenecyclopropane-t-1,2-dicarboxylate compound was synthesized as a single crystal by slow diffusion method. It is the first MOF using MCPD, which framework supports a 2-D layered structure
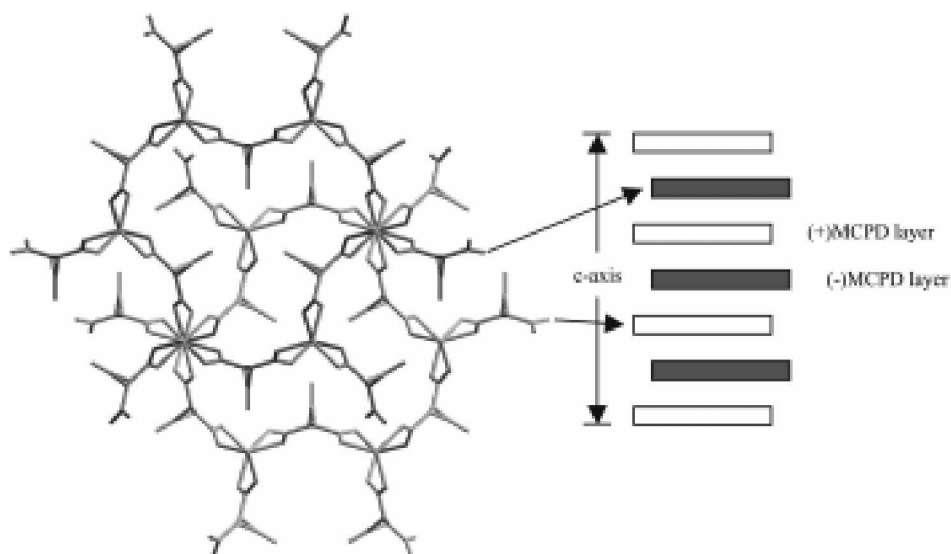

Figure 2. Topological views of the Cd-MCPD framework layer of Cd$_2$(MCPD)$_{1.5}$(NO$_3$)(DMF)$_3$ in the *ab* plane (top) and *bc* plane (bottom).

ssion of the framework in the structure employs this unit and its linkage motif using the remaining carboxylate oxygens (O1B, O2B). In this way, each MCPD unit acts as a tetra-dentate unit, linking two pairs of cadmium atoms to yield a tightly held framework. The remaining positions on Cd1 and Cd2 are respectively, occupied by three DMF ligands (O1S, O1SA, O1SB: Cd1-O1S 2.253(6) Å) and one disordered bidentate nitrate (O2A, O2AA) ligand. The nitrate ions are bound tightly to the cadmium to give a Cd2-O2A' distance

Figure 3. Projection view of the framework of Cd$_2$(MCPD)$_{1.5}$(NO$_3$)(DMF)$_3$ along the c direction. Each chiral layer is separated by c/6 and stacked alternatively by an inversion symmetry along the c direction. Shaded bars mean (−) MCPD layers and unshaded bars mean (+) MCPD layers.

that may be useful for the chiral recognition when the similar structure forms using one of enantiomers of Feist's acid. A variety of chiral carboxylate ligands as building blocks for inorganic framework are now under investigation.

References

1. Gramaccioli, M. *Acta Crystallogr.* **1966**, *21*, 600.
2. For recent reviews: (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (c) Batten, S. R.; Robson, R. *Angew. Chem., Int.*

Ed. **1998**, *37*, 1460.
3. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.
4. Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.
5. (a) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117. (b) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 775. (c) Reis, K. P.; Joshi, V. K.; Thompson, M. E. *J. Catal.* **1996**, *161*, 62.
6. (a) Doering, W. von E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825. (b) Wichmann, J.; Adam, G. *Eur. J. Org. Chem.* **1999**, 3131. (c) Ramasubbu, N.; Venkatesan, K. *Acta Cryst.* **1982**, *B38*, 976.
7. Sheldrick, G. M. *SHELXTL*, v. 6.10; Bruker Analytical X-ray: Madison, WI, 2000. Sheldrick, G. M. SADABS, v. 2.03. *Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 2000.
8. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958.