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Construction of three metal-organic frameworks based on the sterically hindered V-shaped carboxylate ligand

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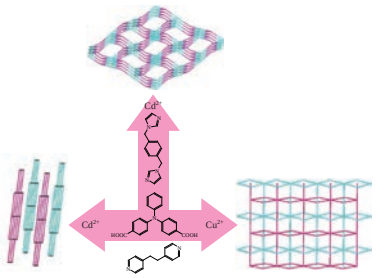
Three novel metal-organic frameworks based on an N-centered ligand H_2L [4,4′-(phenylazanediyl)dibenzoic acid], namely, $[Cd(L)(bimx)_{1/2}]$, $[Cd(L)(dpe)]\cdot H_2O$, $[Cu(L)(dpe)_{1/2}]\cdot H_2O$, [bimx = 1,4-bis(imidazol-1-ylmethyl)benzene, dpe = 1,2-di-(pyridin-4-yl)ethane], have been obtained and characterized by elemental analysis and X-ray single-crystal diffraction. Their thermal stability properties are also discussed in detail.



In the past decade, metal-organic frameworks (MOFs) have attracted considerable attention for their fascinating structures as well as potential applications.[1–10] The assembly of MOFs can be influenced by several internal factors, such as coordination geometries of the central metals,[11] configurations, and nature of the organic ligands,[12] as well as some external factors, such as temperature, solvent, pH value, template effect, *etc*.[13–18] Especially, the design and selection of organic ligands with suitable binding groups are very crucial points. In contrast to the well-known V-shaped ligands,[19,20] sterically hindered N-centered V-shaped carboxylic acid ligand, 4,4′-(phenylazanediyl)dibenzoic acid, has been rarely reported in the realm of coordination chemistry.[21–23] An application of mixed ligands incorporating N-donor ligands and multi-carboxylates has been proven to be an effective strategy to construct MOFs. Therefore, two nitrogen-containing ligands, namely, bimx,[24] and dpe,[25] were used as coligands to react with the H_2L and different bivalent metal salts. In this way three new complexes, namely, $[Cd(L)(bimx)_{1/2}]$ **1**, $[Cd(L)(dpe)]\cdot H_2O$ **2**, and $[Cu(L)(dpe)_{1/2}]\cdot H_2O$ **3**, were obtained. The details of their syntheses,[†] structures,[‡] and physical properties are reported below.

Single crystal X-ray analysis of **1** shows that one distinct unique Cd^{II} cation exists in the asymmetric unit [Figure 1(*a*)]. Cd(1) is connected with five carboxylate oxygen atoms and one nitrogen atom from bimx. This results in a distorted octahedronal coordination polyhedron of Cd(1). In L^{2-} dianion, carboxylate groups with two kinds of coordination modes (bridging and the other chelating-bridging) have been found. With this kind of connection mode, the Cd atoms and their symmetry-related Cd atoms generated by a symmetry operation are connected and form dinuclear $[Cd_2(CO_2)_4]$ cluster. Dinuclear $[Cd_2(CO_2)_4]$ cluster has dimensions about 3.835 and 3.950 Å between the metal sites

† Reagents and solvents employed are commercially available and were used as received.

General procedure for the preparation of complexes **1**–**3**. A mixture of $Cd(NO_3)_2\cdot 6H_2O$ (30.1 mg, 0.1 mmol), H_2L (33.3 mg, 0.1 mmol) and bimx ligand (16.9 mg, 0.05 mmol) was dissolved in H_2O–DMF (6 ml, 1:1 v/v). The final mixture was sealed in a 15-ml PTFE lined stainless-steel vessel under autogenous pressure and heated at 100 °C for 3 days. Large quantities of colorless-block crystals were obtained; the crystals were filtered off, washed copiously with distilled water, and dried under ambient conditions. The yield of the reaction product **1** was *ca*. 50% based on H_2L ligand. Found (%): C, 57.68; H, 3.55; N, 7.41. Calc. for $C_{27}H_{20}CdN_3O_4$ (%): C, 57.61; H, 3.58; N, 7.47.

Complex **2** was prepared in the same way using dpe (18.4 mg, 0.1 mmol) instead of bimx. Yield *ca*. 48% based on H_2L ligand. Found (%): C, 59.58; H, 4.22; N, 6.57. Calc. for $C_{32}H_{27}CdN_3O_5$ (%): C, 59.50; H, 4.21; N, 6.50.

Complex **3** was prepared analogously using $Cu(NO_3)_2\cdot 3H_2O$ (24.2 mg, 0.1 mmol) instead of $Cd(NO_3)_2\cdot 6H_2O$. Large quantities of small green-block crystals were obtained. Yield *ca*. 47% based on H_2L ligand. Found (%): C, 61.80; H, 4.17; N, 5.52. Calc. for $C_{26}H_{21}CuN_2O_5$ (%): C, 61.84; H, 4.19; N, 5.55.

‡ *Crystallographic data*.

For **1**: $C_{27}H_{20}CdN_3O_4$, M_r = 562.86, monoclinic, space group $P2_1/c$, a = 7.7408(9), b = 25.834(3) and c = 14.5772(14) Å, β = 115.804(5)°, V = 2624.4(5) Å^3, Z = 4, d_{calc} = 1.425 g cm^{-3}, μ(MoKα) = 0.868 mm^{-1}, F(000) = 1132, T = 296(2) K, 18828 reflections measured, 5471 independent reflections (R_{int} = 0.0927), final R_1 [$I > 2\sigma(I)$] = 0.0399, $wR(F^2)$ = = 0.1152, GOF = 1.065.

For **2**: $C_{32}H_{25}CdN_3O_4$, M_r = 627.95, monoclinic, space group $C2/c$, a = 27.747(4), b = 13.7883(17) and c = 17.514(2) Å, β = 97.702(2)°, V = 6640.4(14) Å^3, Z = 8, d_{calc} = 1.256 g cm^{-3}, μ(MoKα) = 0.693 mm^{-1}, F(000) = 2544, T = 296(2) K, 21046 reflections measured, 4573 independent reflections (R_{int} = 0.1028), final R_1 [$I > 2\sigma(I)$] = 0.0861, wR_2 = = 0.2343, GOF = 1.070.

For **3**: $C_{26}H_{19}CuN_2O_4$, M_r = 486.97, orthorhombic, space group $Cccm$, a = 15.758(2), b = 27.747(4) and c = 12.7832(17) Å, V = 5589.4(13) Å^3, Z = 8, d_{calc} = 1.157 g cm^{-3}, μ(MoKα) = 0.810 mm^{-1}, F(000) = 2000, T = 296(2) K, 2589 reflections measured, 1985 independent reflections (R_{int} = 0.0243), final R_1 [$I > 2\sigma(I)$] = 0.0328, wR_2 = 0.0739, GOF = 1.085.

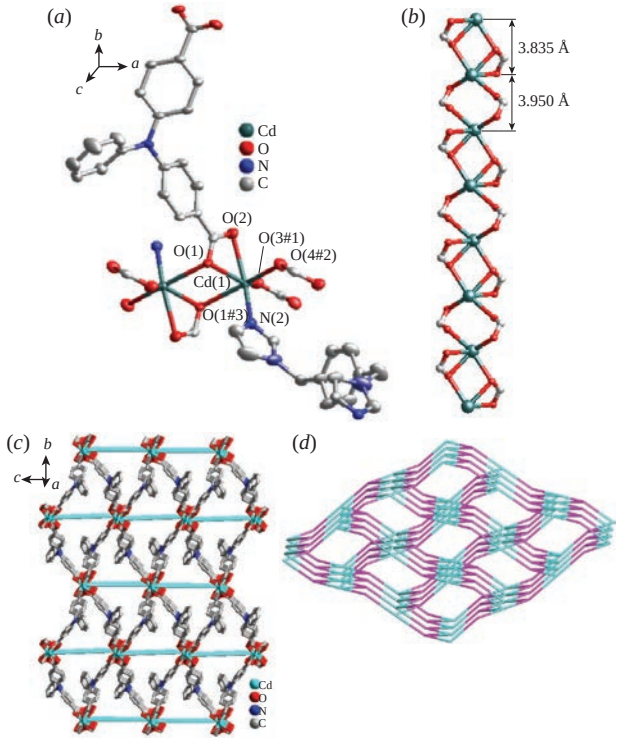


Figure 1 (*a*) Coordination environment of the Cd^{II} ions in **1**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = 1 – *x*, –0.5 + *y*, –0.5 – *z*; #2 = 1 + *x*, 0.5 – *y*, 0.5 + *z*; #3 = 1 – *x*, –*y*, –*z*. (*b*) Ball and stick representation of rod-shaped SBUs. (*c*) View of the 3D network along the crystallographic *a* axis. (*d*) Perspective view of the underlying net.

[Figure 1(*b*)]. Each dinuclear $[Cd_2(CO_2)_4]$ cluster links two neighboring clusters and constructs a rod-shaped secondary building unit (SBU). Each rod-shaped SBU is further linked to neighboring rod-shaped SBUs with bimx ligands and thus forms a three-dimensional network [Figure 1(*c*)]. As shown in Figure 1(*d*), each dinuclear $[Cd_2(CO_2)_4]$ cluster in **1** is connected to adjacent clusters through carboxylate groups of L^{2-} molecules and four bimx linkers along two other directions; each L^{2-} anion links three $[Cd_2(CO_2)_4]$ clusters. For better understanding the structure of **1**, each L^{2-} and dinuclear clusters of **1** can be defined as three and six-connected nodes, respectively; bimx acts as a linker. On the basis of this simplification,[29] the structure of **1** can be described as a 3,6-connected 3D network with the Schläfli symbol $\{4.6^2\}_2\{4^2.6^{10}.8^3\}$, which corresponds to a rutile (rtl) topology [Figure 1(*d*)].[30]

The crystal structure determination reveals that compound **2** crystallizes in the monoclinic crystal system of *C*2/*c*. The asymmetric unit contains one Cd^{II} cation, one dpe ligand, and one deprotonated L^{2-} acid [Figure 2(*a*)]. In the asymmetric unit, two carboxylate groups of L^{2-} ligand have different coordination modes, one carboxylate group takes bridge-chelate coordination mode to bridge two Cd centers, while the other carboxylate group adopts chelation in a bidentate mode. Cd^{II} is six-coordinated, bonding to four O atoms from three carboxylate groups and two N atoms from two dpe ligands. Neighboring cadmium atoms are also joined into a $[Cd_2(CO_2)_4]$ binuclear unit. L^{2-} and dpe ligands connect $[Cd_2(CO_2)_4]$ units to form a 2D sheet [Figures 2(*b*) and 2(*c*)], which manifests a sql motif with the Schläfli symbol $\{4^4.6^2\}$.

According to the crystal structure analysis, compound **3** crystallizes in the orthorhombic crystal system of *Cccm*. The asymmetric unit contains one Cu^{II} cation, one deprotonated L^{2-} ligand, one and a half dpe ligands [Figure 3(*a*)]. In the asymmetric unit, both carboxylate groups of L^{2-} ligand take bismonodentate coordination mode to bridge two Cu centers forming paddle-wheel SBUs, and the distance of Cu–Cu is 2.6476(8) Å. The Cu–O bond lengths are 1.9629(15) and 1.9631(14) Å, and the Cu–N bond length is 2.156(3) Å. All these values are similar to those found in other Cu complexes (data from the Cambridge

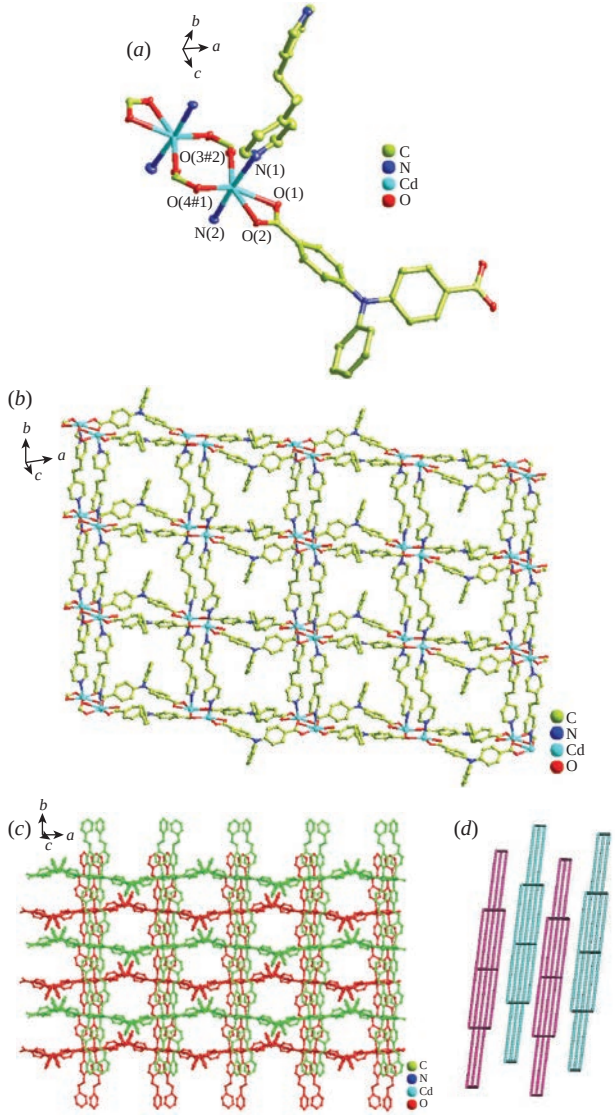


Figure 2 (*a*) Coordination environment of the Cd^{II} ions in **2**. The hydrogen atoms and solvent molecules are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = –0.5 + *x*, 1.5 – *y*, –0.5 + *z*; #2 = 1 – *x*, *y*, 0.5 – *z*. (*b*) A perspective of 2D framework. (*c*) Schematic view of structure **2**. (*d*) Schematic view of sql topology structure of **2**.

Single crystals of **1**–**3** were prepared by the methods described above. X-ray crystallographic data were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = = 0.71073 Å). Structures were solved by direct methods and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[26] A semiempirical absorption correction was applied using SADABS.[27] The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on the parent atoms. The distributions of peaks in the channels of **2** and **3** were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contributions of the electron density by the remaining solvent molecules were removed by the SQUEEZE routine in PLATON.[28]

CCDC 1054743–1054745 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

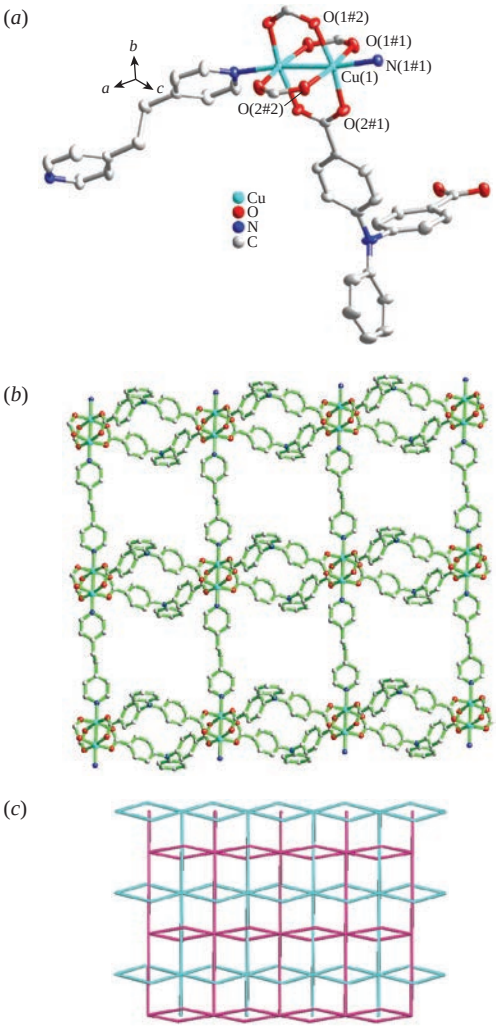


Figure 3 (*a*) Coordination environment of **3** with 30% ellipsoid probability (hydrogen atoms and water molecules are omitted for clarity). Symmetry code: #1 = 0.5 – *x*, 0.5 – *y*, *z*; #2 = 0.5 – *x*, 0.5 – *y*, 1 – *z*. (*b*) Perspective of 2D bilayer structure. (*c*) View of 2D→2D two-fold interpenetrated net (V-shaped lines represent L^{2-} ligands; straight lines represent dpe ligands).

Structural Database). The carboxylate groups of the H_2L ligand link the paddle-wheel SBUs to form a 2D layered network [Figure 3(*b*)], which manifests a sql motif with the Schläfli symbol $\{4^4.6^2\}$.

Phase purity of the bulk materials was confirmed by the comparison of their powder diffraction patterns with those calculated from single-crystal X-ray diffraction studies (Figures S1–S3, Online Supplementary Materials). Plots of thermal gravimetric analyses (TGA) of **1**–**3** are given in Figure S4. The TGA curve of **1** shows that compound **1** decomposes quickly after 450 °C, suggesting that the framework is thermally stable. For complex **2** a weight loss of 2.44% is observed from 30 to 160 °C, which is attributed to the loss of the lattice water molecules (calc. 2.80%), followed by a stable stage. Then the whole framework starts to collapse at about 380 °C. The TGA curve of compound **3** indicates that there is a weight loss of *ca*. 3.28% between 20 and 150 °C, corresponding to the loss of the guests (calc. 3.56% for one water molecule per unit formula). Then the decomposition of the ligands begins.

In summary, we have successfully synthesized three new MOFs with distinct dimensions and structures by employing sterically hindered carboxylate ligands and nitrogen-containing ligands as the organic links and metal centers. Complex **1** reveals a non-interpenetrating 3D framework with rutile topology. Complexes **2** and **3** exhibit a 2D sheet with L^{2-} and dpe ligands connecting dinuclear metal units, respectively.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.09.029.

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