Syntheses and Characterizations of Multidimensional Metal-Organic Frameworks Based on Rings and 1D Chains

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Four novel multidimensional coordination polymers, {[Cd(3-PYD)$_2$(H$_2$O)]·2H$_2$O}$_n$ (**1**), [Pb(3-PYD)$_2$]$_n$ (**2**), {[Cu$_{1.5}$(3-PYD)$_3$(H$_2$O)]·1.5H$_2$O}$_n$ (**3**) and [Zn(3-PYD)$_2$(H$_2$O)$_2$]$_n$ (**4**), have been hydrothermally synthesized from 3-(3-pyridyl)acrylic acid (3-HPYD). In **1**, 3-PYD in a head-to-head arranged fashion bridges Cd^{II}, generating a two-dimensional layer, which is further extended into a three-dimensional supramolecular network by hydrogen-bonding interactions. Compound **2** shows a two-dimensional wave-like layer that consists of {Pb(3-PYD)}$_4$ rings from head-to-tail arranged 3-PYD. Compound **3** is a twofold interpenetrating three-dimensional network consisting of {Cu(3-PYD)}$_6$ rings formed through the mixed head-to-head and head-to-tail arrangements of 3-PYD. However, **4** is a three-dimensional supramolecular framework constructed by one-dimensional zinc-3-PYD chains through hydrogen-bonding interactions.

Introduction

The rational design and syntheses of multidimensional coordination polymers have been of increasing interest recently in material science and chemical research.[1,2] This is justified not only by their unique application as functional materials but also by the particular structural diversity of their architectures,[3−5] which can be much greater than those of metal oxides and other simple inorganic solid materials, owing to incorporation of many organic ligands.[6] As a result, the selection of organic ligands with appropriate coordination sites linked by specific connectors is the key to forming metal-organic complexes with desirable physical and chemical properties.

Multidentate N- or O-donor ligands have been employed extensively as organic spacers in the construction of extended structures. For example, the use of 4,4′-bipyridine[7] and its analogues,[8] as neutral N-donor ligands, is a most promising approach towards the syntheses of extended metal-organic frameworks owing to their simple bridging mode and strong coordination ability to transition metal ions. However, assembly of these ligands with metal ions is heavily dependent on the presence of different counterions. Conversely, di-[9] or polycarboxylate[10] ligands, as O-donor ligands via anionic groups, are another candidate for the preparation of multidimensional coordination networks, owing to the rich coordination modes of the carboxylate groups, and can afford neutral metal-organic frameworks. Our research aim is to incorporate both neutral and anionic donor groups into a single organic ligand that can be used to construct desired coordination polymers. Different donor groups can hold great promise for incorporating accessibility, structural diversity and geometrical control of properties into the resulting coordination networks. Moreover, both neutral and anionic donor groups can coordinate to metal centers, and afford opportunities for generating neutral polymeric networks without counterions, thereby simplifying the control of final products.[11,12] In this context, extended coordination structures have been constructed using rigid pyridinecarboxylate ligands.[12−14] We employed 3-(3-pyridyl)acrylic acid (3-HPYD), which possesses an appropriate angle (120°) and a long arm between coordination sites. Assembly of 3-HPYD with metal ions not only can produce aesthetically beautiful complexes with useful properties, which can not be obtained by common pyridinecarboxylate ligands, but can also generate some predicted, controlled structural frameworks through changing the coordination nature of metal ions. However, few compounds with 3-HPYD have been reported.[14] Herein, we report the syntheses and characterizations of four coordination polymers: {[Cd(3-PYD)$_2$(H$_2$O)]·2H$_2$O}$_n$ (**1**), [Pb(3-PYD)$_2$]$_n$ (**2**), {[Cu$_{1.5}$(3-PYD)$_3$(H$_2$O)]·1.5H$_2$O}$_n$ (**3**) and [Zn(3-PYD)$_2$(H$_2$O)$_2$]$_n$ (**4**), constructed from 3-HPYD with different metal ions.

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Results and Discussions

Syntheses

Two distinct characteristics of 3-HPYD, an angle of 120° and a long arm between pyridyl and carboxylate donor

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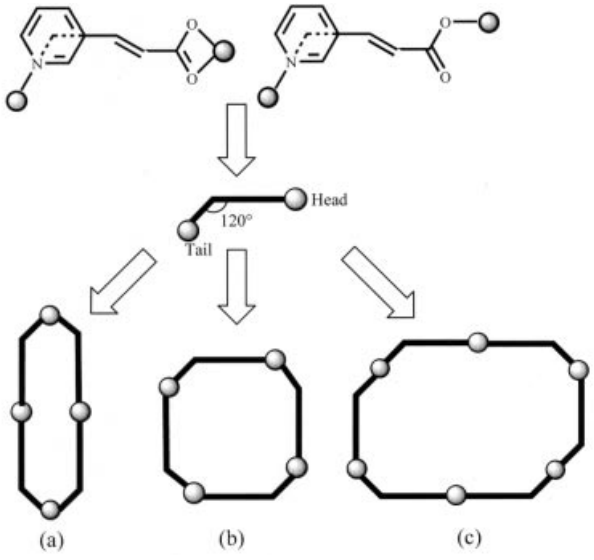
groups, render it ideal for the assembly of molecular polygons. Two types of polygons can be obtained from head-to-head or head-to-tail arrangement of the deprotonated 3-HPYD (3-PYD) when using four ML units with 120° corners (Scheme 1, a and b). In addition, their mixed arrangement can also generate other building units, such as a $\{ML\}_6$ basal ring (Scheme 1, c). Based on these points, we carried out a series of hydrothermal reactions of 3-HPYD and transition metal ions to formulate novel coordination polymers. As expected, when Cd^{II} and Cu^{II} was used as nodes, compound **1** based on $\{ML\}_4$ rings from the head-to-head arrangement of 3-PYD, and compound **3** based on $\{ML\}_6$ rings from the head-to-head and head-to-tail mixed arrangements of 3-PYD, were successfully obtained, respectively. However, the compound containing $\{ML\}_4$ rings from head-to-tail arrangement of 3-PYD was not obtained, although other transition metal ions, such as Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+}, were employed. Notably, the hydrothermal reaction of Zn^{2+} and 3-HPYD produced compound **4**, which was not from the ring units but from 1D zinc-carboxylate chains extended by hydrogen-bonding interactions. Pb^{2+}, which has an ample coordination preference,[15] was used to investigate further the conformation and arranged fashion of 3-PYD. Consequently, compound **2**, a 2D network consisting of $\{Pb(3\text{-PYD})\}_4$ basal rings from head-to-tail arrangement of 3-PYD, was produced. Accordingly, the diverse geometries of different metal ions may play critical roles in the assembly of metal-organic frameworks with various structures. This has also been testified to in some other research systems.[16]



Scheme 1. (a) $\{ML\}_4$ ring from head-to-head (or tail-to-tail) arrangement of 3-PYD; (b) $\{ML\}_4$ ring from head-to-tail arrangement of 3-PYD; (c) $\{ML\}_6$ ring from head-to-head and head-to-tail mixed arrangements of 3-PYD

Structural Descriptions

$\{[Cd(3\text{-PYD})_2(H_2O)]\cdot 2H_2O\}_n$ (1): Single-crystal X-ray diffraction analysis reveals that **1** is a 3D supramolecular network consisting of $\{Cd(3\text{-PYD})\}_4$ rings derived from head-to-head arranged 3-PYD. The asymmetric unit of **1** consists of one Cd^{II}, two 3-PYD, one coordinated water molecule and two free water molecules (Figure 1). Each Cd^{II} is in a distorted pentagonal bipyramidal geometry. The equatorial basal plane is determined by two chelating carboxylate groups from different 3-PYD and one coordinated water molecule. Cd−O bond lengths are in the range 2.303(8)−2.462(10) Å. Apical positions are occupied by two pyridyl nitrogen atoms from different 3-PYD, with an average Cd−N distance and N(1)−Cd−N(2) bond angle of 2.382(8) Å and 164.0(3)°, respectively. The Cd^{II} is approximately coplanar with the mean plane of the five equatorial atoms, with a deviation of 0.1000 Å. 3-PYD acts as a bridging ligand, through its pyridyl nitrogen atom and chelating carboxylate group, linking different Cd^{II} centers. Four 3-PYD with a head-to-head aggregation link Cd^{II} into a $\{Cd(3\text{-PYD})\}_4$ ring (Scheme 1, a), in which four metal ions and four 3-PYD are all in one plane (Figure 2, a). Based on $Cd^{II}\cdots Cd^{II}$ distances, the ring is 7.449 × 15.139 $Å^2$. Interestingly, each $\{Cd(3\text{-PYD})\}_4$ ring is surrounded by four other perpendicular $\{Cd(3\text{-PYD})\}_4$ rings through shar-

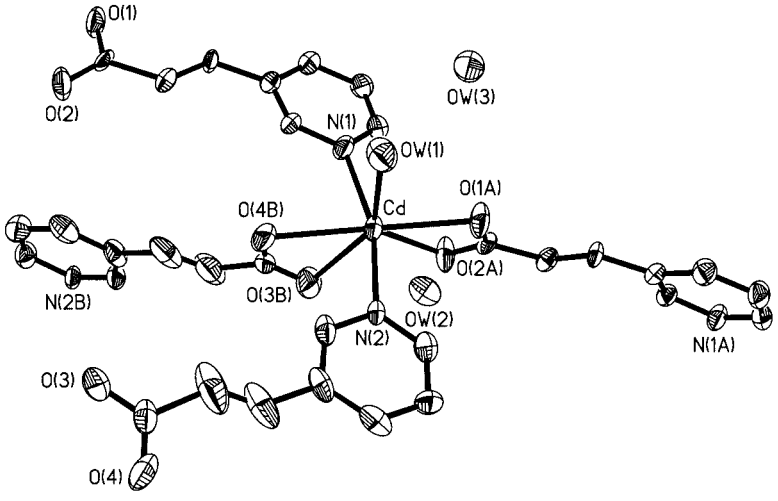


Figure 1. Coordination environment around Cd^{II} in **1** with the thermal ellipsoids at 30% probability level

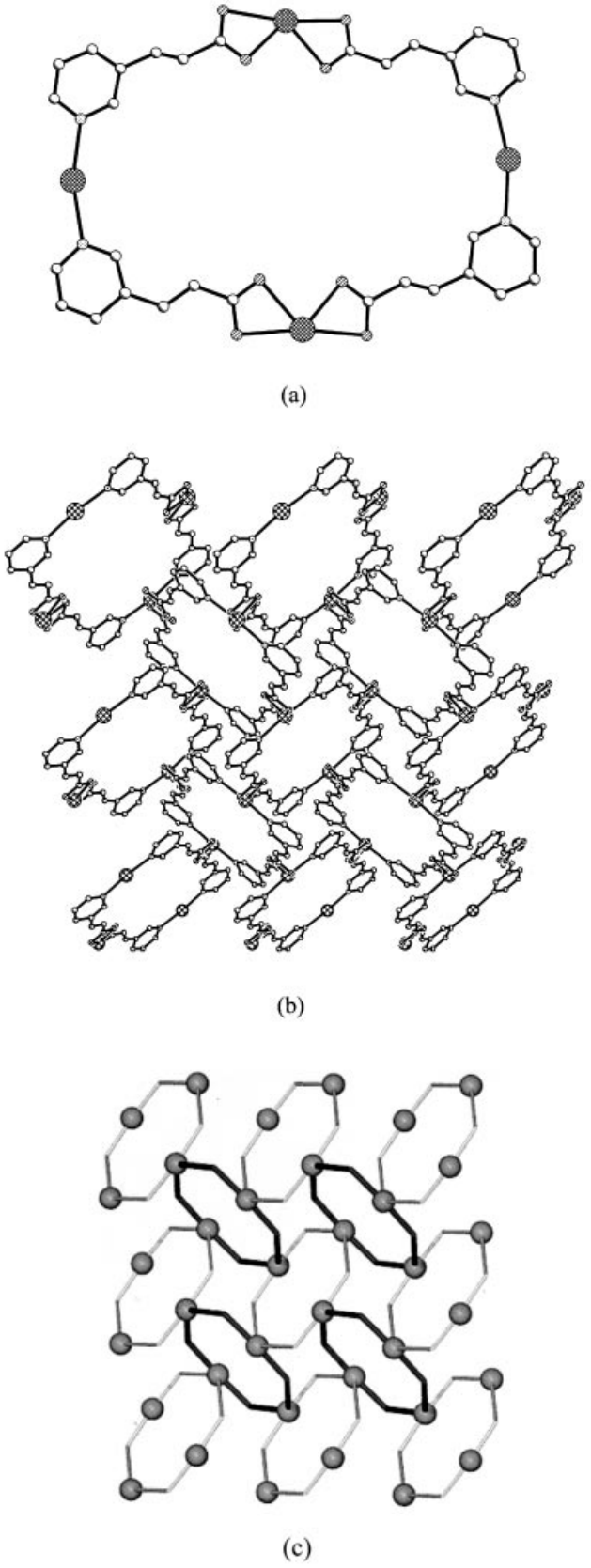


Figure 2. (a) $\{Cd(3\text{-PYD})\}_4$ ring from head-to-head arrangement of 3-PYD; (b) a 2D layer in **1** along the *c* axis; free water molecules omitted for clarity; (c) schematic showing the 2D layer derived from reciprocally vertical $\{Cd(3\text{-PYD})\}_4$ rings; only the Cd^{II} centers are shown for clarity, with the bonds representing bridging ligands

ing Cd^{II} joints, which may be due to the proper geometry of the metal ion. Thereby, a 2D layer framework is generated from the reciprocally vertical $\{Cd(3\text{-PYD})\}_4$ rings (Figure 2, b and c); the free water molecules are accommodated in the rings. Finally, neighboring layers are further extended into a 3D supramolecular architecture through hydrogen-bonding interactions between coordinated water molecules and carboxylate oxygen atoms [$OW(1)-H\cdots O(4)^i$ 2.701 Å; symmetry codes: (i) $x - 1/2, -y + 5/2, z - 1/2$] (Figure 3). Thus, hydrogen-bonding interactions play an important role in the construction and stabilization of the extended structure.

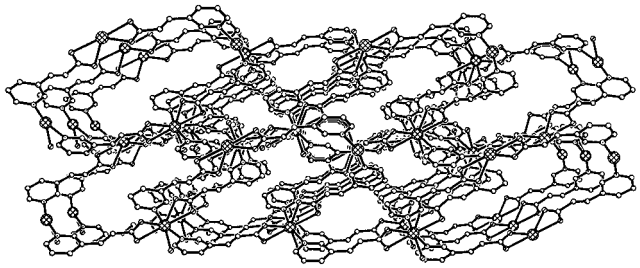


Figure 3. Packing structure of **1** along the *b* axis; free water molecules omitted for clarity

$[Pb(3\text{-PYD})_2]_n$ (2): 2 is a 2D wave-like layer based on $\{Pb(3\text{-PYD})\}_4$ rings from head-to-tail arranged 3-PYD. The four-coordinate Pb^{II} is in a highly distorted tetragonal pyramid geometry (Figure 4). The basal plane is defined by two pyridyl nitrogen atoms and two carboxylate oxygen atoms from different 3-PYD, while Pb^{II} occupies the apex. Pb^{II} deviates from the N_2O_2 basal plane by 0.9217 Å. Average Pb−N and Pb−O distances are 2.652(8) and 2.374(7) Å, respectively, and the N(1A)−Pb−N(2) and O(1)−Pb−O(3B) bond angles are 158.8(3) and 79.3(2)°, respectively. Unlike **1**, 3-PYD bridges Pb^{II} through its pyridyl nitrogen atom and monodentate carboxylate group, generating a head-to-tail aggregated $\{Pb(3\text{-PYD})\}_4$ ring (Scheme 1, b). In the $\{Pb(3\text{-PYD})\}_4$ ring, four Pb^{II} ions and four 3-PYD are *not* coplanar, which may be due to the different arrangement of 3-PYD and the coordination geometry of the metal ion. The $\{Pb(3\text{-PYD})\}_4$ rings are further extended into a 2D wave-like layer by sharing Pb^{II} joints and 3-PYD edges (Figure 5). Although there is large void space in the wave-like layer, no guest or water molecules are included. Adjoining layers are 4.348 Å apart, and there are no hydrogen bonding or other weak interactions between them (Figure 6).

$\{[Cu_{1.5}(3\text{-PYD})_3(H_2O)]\cdot 1.5H_2O\}_n$ (3): 3 is a twofold interpenetrating 3D framework based on $\{Cu(3\text{-PYD})\}_6$ rings formed through head-to-head and head-to-tail mixed arrangements of 3-PYD (Scheme 1, c). There are two crystallographically independent Cu^{II} centers (Figure 7). Cu(1) adopts a distorted square-pyramidal coordination geometry. Two *trans*-carboxylate oxygen atoms and two *trans*-pyridyl nitrogen atoms of different 3-PYD comprise the equatorial plane. Average Cu(1)−O and Cu(1)−N bond lengths are 1.960(2) and 2.024(4) Å, respectively. Cu(1) deviates from the mean plane determined by the four equatorial atoms by

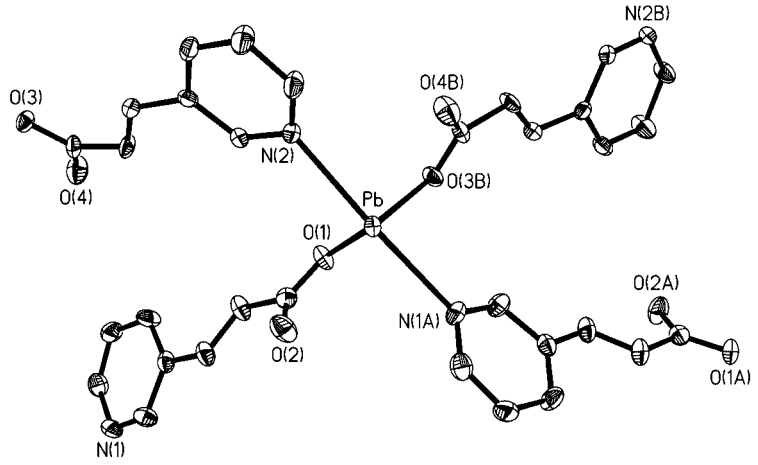


Figure 4. Coordination environment around Pb^{II} in **2** with thermal ellipsoids at 30% probability level

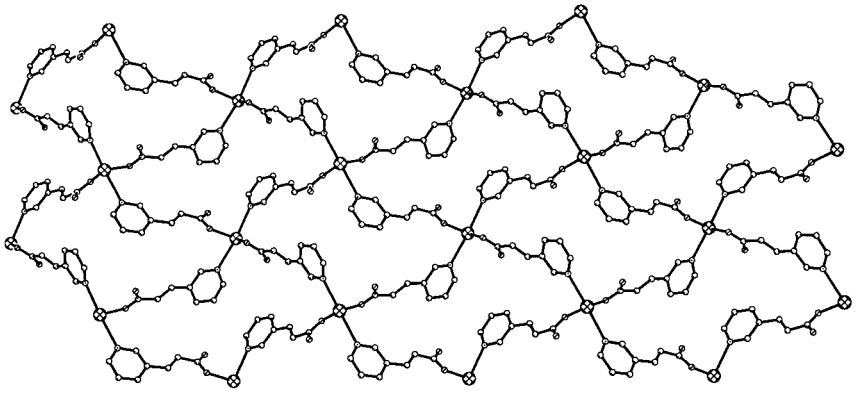


Figure 5. Two-dimensional wave-like layer in **2**

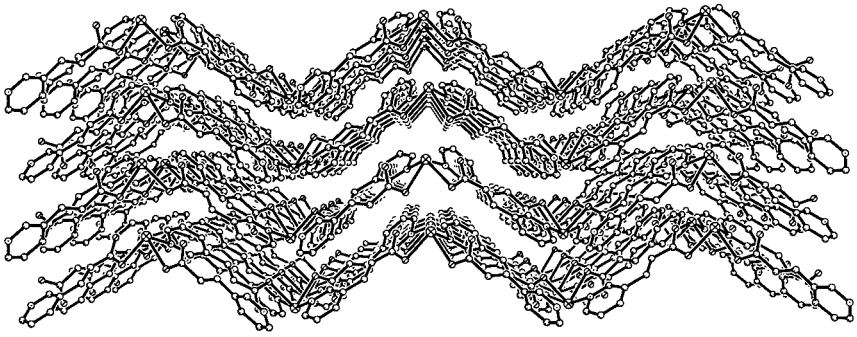


Figure 6. Packing diagram of **2** along the *a* axis

0.0827 Å. One water molecule occupies its axial position with the Cu(1)−OW(1) bond length is 2.403(3) Å. However, Cu(2) is in a square-planar geometry defined by two *trans*-carboxylate oxygen atoms [O(3) and O(3C)] and two *trans*-pyridyl nitrogen atoms [N3 and N(3C)] of different 3-PYD. The bond lengths of Cu(2)−O(3) and Cu(2)−N(3) are 1.959(3) and 2.008(3) Å, respectively. Similar to that in **2**, 3-PYD also uses its nitrogen atom and monodentate carboxylate group to bridge metal centers.

The most interesting feature of the structure is the chair-like $\{Cu(3\text{-PYD})\}_6$ ring arising from four Cu(1) atoms and two Cu(2) atoms connected by six 3-PYD through both head-to-head and head-to-tail aggregations (Figure 8, a). Each chair-like $\{Cu(3\text{-PYD})\}_6$ ring is further surrounded by six identical units through sharing the metal ions; thereby, a 3D framework is generated (Figure 8, b). However, owing to the absence of guest molecules to fill the large voids in the $\{Cu(3\text{-PYD})\}_6$ rings, the voids are filled via mutual interpenetration of independent equivalent frameworks to generate a twofold interpenetrating 3D architecture (Figure 9). Hydrogen-bonding interactions between coordinated water molecules and carboxylate oxygen atoms of 3-PYD as well as between uncoordinated water molecules and carboxylate oxygen atoms of 3-PYD, with lengths from 2.565 to 2.893 Å, further stabilize the whole framework.

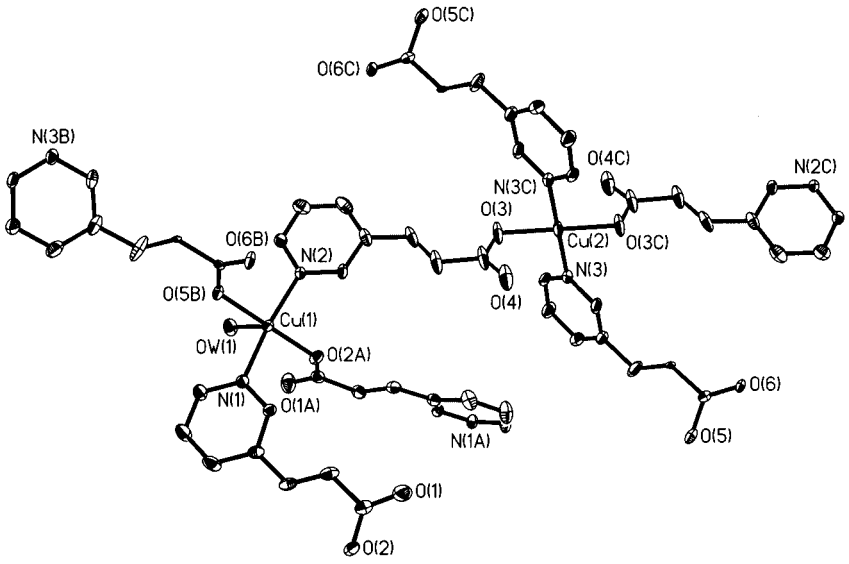


Figure 7. Coordination environment around Cu^{II} in **3** with thermal ellipsoids at 30% probability level

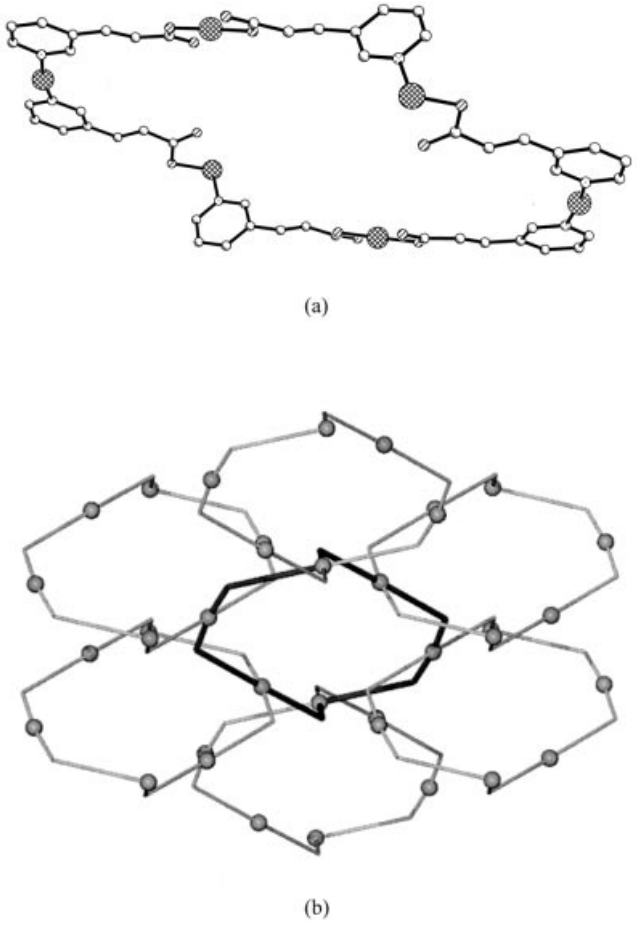


Figure 8. (a) $\{Cu(3\text{-}PYD)\}_6$ ring formed by four Cu(1), two Cu(2) atoms and six 3-PYD; (b) perspective of a chair-like $\{Cu(3\text{-}PYD)\}_6$ ring surrounded by six identical units; 3-PYD ligands omitted for clarity

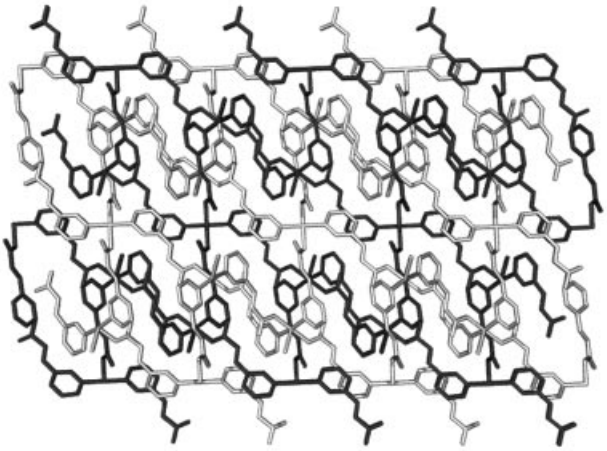


Figure 9. View of a twofold interpenetrating 3D network in **3** along the *b* axis

$[Zn(3\text{-}PYD)_2(H_2O)_2]_n$ (4): Unlike compounds **1**−**3** based on $\{ML\}_4$ or $\{ML\}_6$ rings, **4** is a 3D supramolecular framework constructed by 1D metal-3-PYD chains through hydrogen-bonding interactions. Figure 10 shows that each Zn^{II} is coordinated by four oxygen atoms from one chelating carboxylate group of 3-PYD, two water molecules, and two nitrogen atoms from different 3-PYD, in a distorted octahedral geometry. The equatorial plane is determined by N(2), O(3A), O(4A) and OW(2), while axial positions are occupied by N(1) and OW(1) with the N(1)−Zn−OW(1) bond angle being 176.31(4)°. There are two kinds of 3-PYD: one acts as a bridging ligand through its pyridyl nitrogen atom and chelating carboxylate group; the other serves as a terminal ligand through its pyridyl nitrogen atom participating in coordination, the carboxylate group is not involved in the coordination and acts as an acceptor of the hydrogen bonding. Hence, the Zn^{II} center is linked by bridging 3-PYD to generate a neutral 1D metal-3-PYD chain with the help of terminal 3-PYD (Figure 11). The 1D chains are further extended into a 3D supramolecular network through the abundant hydrogen-bonding interactions

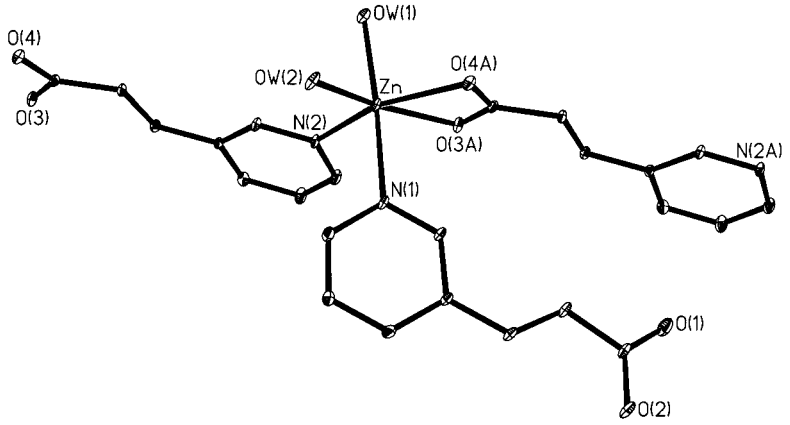


Figure 10. Coordination environment around Zn^{II} in **4** with thermal ellipsoids at 30% probability level

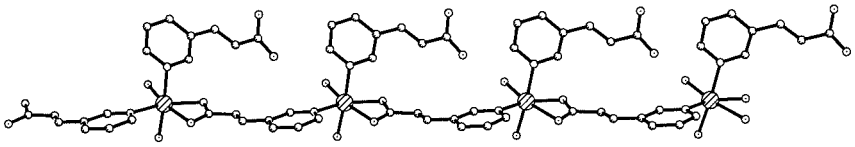


Figure 11. One-dimensional metal-3-PYD chain in **4**

between coordinated water molecules and carboxylate groups [OW(1)−H···O3^{i} 2.797 Å; OW(2)−H···O2^{ii} 2.602 Å; OW(2)−H···O2^{iii} 2.661 Å; symmetry codes: (i) $-x$, $-y$ + 4, $-z$ + 1; (ii) x −1, y + 1, z; (iii) $-x$ + 1, $-y$ + 4, $-z$] (Figure 12).

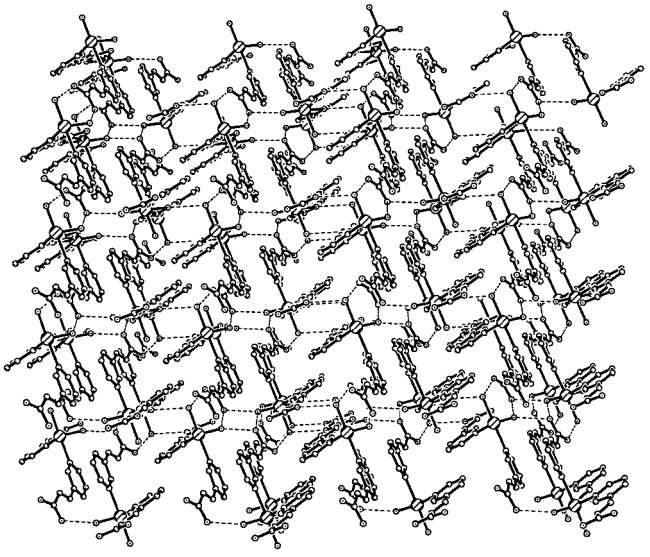


Figure 12. Three-dimensional supramolecular network formed by 1D metal-3-PYD chains through hydrogen-bonding interactions along the *b* axis in **4**

IR Spectroscopy

The IR spectrum of **1** shows a strong, broad peak at 3413 cm^{-1}, which can be ascribed to the presence of water molecules. Characteristic carboxylate group bands appear at 1552 and 1400 cm^{-1} for asymmetric and symmetric vibrations, respectively. Δ, which represents the separation between ν_{asym}(COO) and ν_{sym}(COO) and reflects the coordination modes of the carboxylate groups,[17] is 152 cm^{-1}. For **2**, bands characteristic of the carboxylate group are exhibited at 1564 cm^{-1} for asymmetric vibrations and at 1354 cm^{-1} for symmetric vibrations; Δ is 210 cm^{-1}. For **3**, similar to **1**, the strong, broad band at 3433 cm^{-1} indicates the presence of water molecules. Absorption peaks at 1562 and 1378 cm^{-1} display the asymmetric and symmetric vibrations, respectively; Δ is 184 cm^{-1}. The single Δ in the three compounds is consistent with a single coordination mode of carboxylate group in their structures.[18] For **4**, the strong, broad peak at 3109 cm^{-1} also displays the presence of water molecules. Interestingly, besides the asymmetric (1546 cm^{-1}) and symmetric (1363 cm^{-1}) vibrations (Δ of ca. 183 cm^{-1}), the strong characteristic band at 1407 cm^{-1} indicates the presence of uncoordinated carboxylate group, which is in agreement with the results of its crystal structure.

Thermogravimetric Analyses

The thermal stability of **1**−**4** has been determined on polycrystalline samples in a nitrogen atmosphere by thermogravimetric analysis (TGA). For **1**, the weight loss of 11.55% from 61 to 118 °C is equivalent to the loss of one coordinated water molecule and two free water molecules [$3H_2O$/$Cd(3\text{-}PYD)_2(H_2O)]\cdot 2H_2O$, calculated: 11.68%). The second weight loss of 60.68%, from 331 to 900 °C, corresponds to the decomposition of **1**. The residual weight of 27.77% is ascribed to CdO (calculated: 27.75%). For **2**, TGA shows that chemical decomposition starts at 338 °C and ends at 398 °C with the weight loss of 55.59%; the remaining weight (44.41%) corresponds to PbO (calculated: 44.33%). For **3**, TGA exhibits two weight losses: One (7.52%) from 49 to 120 °C is attributed to the loss of coordinated water molecule and free water molecules ($2\cdot 5H_2O$/$[Cu_{1.5}(3\text{-}PYD)_3(H_2O)]\cdot 1.5H_2O$, calculated: 7.70%), suggesting the

weak interaction of Cu(1)−OW(1) [2.403(3) Å]. The other (64.92%), from 245 to 478 °C, corresponds to the decomposition of **3**. In **4**, a weight loss of 9.12% from 119 to 160 °C displays the loss of two coordinated water molecules [$2H_2O$/$Zn(3\text{-PYD})_2(H_2O)_2$, calculated: 9.06%]. Above 268 °C, the framework starts to decompose.

Conclusions

Hydrothermal reactions of 3-(3-pyridyl)acrylic acid (3-HPYD) with different metal ions have afforded four coordination polymers based on $\{ML\}_4$ and $\{ML\}_6$ rings or metal-carboxylate chains, respectively. It may be conceivable to design and synthesize desired metal-organic frameworks when using the selected organic ligands with special conformations.

Experimental Section

Materials and General Methods: 3-(3-Pyridyl)acrylic acid was purchased from Aldrich and used without further purification; all other reagents were commercially available and used as purchased. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate of 15 °C min^{-1}, nitrogen stream). IR spectra were recorded as KBr pellets with a Magna 750 FT-IR spectrophotometer. Elemental analyses of C, H and N were determined using a Perkin-Elmer 240C elemental analyzer.

Synthesis of $\{[Cd(3\text{-PYD})_2(H_2O)]\cdot 2H_2O\}_n$ (1): A mixture of 3-HPYD (0.037 g, 0.25 mmol), $Cd(NO_3)_2\cdot 4H_2O$ (0.077 g, 0.25 mmol), KOH (0.014 g, 0.25 mmol) and H_2O (18 mL) was placed in a Teflon-lined stainless steel vessel and heated to 170 °C for 72 hours. The reaction system was then cooled to room temperature during 24 hours, and the resulting solution was filtered and left undisturbed in the air. After a day, light yellow block crystals of **1** (0.065 g) were obtained. Yield: 56% (based on Cd). $C_{16}H_{18}CdN_2O_7$ (462.72): calcd. C 41.53, H 3.92, N, 6.05; found C 41.55, H 3.82, N 6.13. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3413 (s), 1640 (s), 1552 (vs), 1478 (s), 1437 (w), 1400 (vs), 984 (s), 749 (m), 692 (s).

Synthesis of $[Pb(3\text{-PYD})_2]_n$ (2): $Pb(NO_3)_2$ (0.066 g, 0.20 mmol) and 3-HPYD (0.019 g, 0.125 mmol) in H_2O (18 mL) were stirred for 20 min, and then the pH was adjusted to 5 with Et_3N. After stirring for another 20 min, the mixture was transferred to a 25 mL stainless steel reactor with a Teflon liner and heated to 150 °C for 96 hours. The reaction system was then cooled to room temperature during 24 hours. A large amount of yellow cube-shaped crystals of **2** (0.078 g) was obtained. Yield: 78% (based on Pb). $C_{16}H_{12}PbN_2O_4$ (503.47): calcd. C 38.17, H 2.40, N 5.56; found C 38.12, H 2.48, N 5.55. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3445 (w), 1642 (s), 1564 (vs), 1420 (s), 1354 (vs), 1294 (m), 1242 (m), 806 (s), 693 (vs), 639 (vs).

Synthesis of $\{[Cu_{1.5}(3\text{-PYD})_3(H_2O)]\cdot 1.5H_2O\}_n$ (3): $Cu(NO_3)_2\cdot 3H_2O$ (0.036 g, 0.15 mmol) and 3-HPYD (0.030 g, 0.20 mmol) in H_2O (18 mL) were stirred for 20 min; the pH was then adjusted to 4 with Et_3N. After stirring for a further 20 min, the mixture was transferred to a 25 mL stainless steel reactor with a Teflon liner and heated to 165 °C for 96 hours. The reaction system was then cooled to room temperature during 24 hours. Blue block crystals of **3** (0.022 g) were obtained (based on Cu). Yield: 38%. $C_{24}H_{23}Cu_{1.5}N_3O_{8.5}$ (584.76): calcd. C 49.30, H 3.96, N 7.19; found C 49.27, H 4.10, N 7.11. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3433 (s), 3107 (w), 1644 (s), 1602 (w), 1562 (vs), 1474 (w), 1431 (s), 1378 (vs), 1053 (m), 988 (s), 805 (s), 693 (s), 606 (m).

Table 1. Crystal data and structure determination summary for **1**−**4**

	1	**2**	**3**	**4**
Formula	$C_{16}H_{18}CdN_2O_7$	$C_{16}H_{12}N_2O_4Pb$	$C_{24}H_{23}Cu_{1.5}N_3O_{8.5}$	$C_{16}H_{16}N_2O_6Zn$
Fw	462.72	503.47	584.76	397.68
Crystal size (mm)	0.40 × 0.16 × 0.14	0.60 × 0.24 × 0.14	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	12.0510(9)	10.3546(7)	13.342(13)	7.552(2)
b (Å)	12.1079(9)	17.0014(11)	11.016(4)	9.627(3)
c (Å)	12.4511(10)	8.6821(6)	16.404(14)	11.897(4)
β (°)	102.948(2)	93.864(1)	91.862(12)	81.748(9)
V ($Å^3$)	1770.6(2)	1524.95(18)	2410(3)	786.2(4)
Z	4	4	4	2
$D_{calcd.}$ ($g\cdot cm^{-3}$)	1.736	2.193	1.612	1.680
μ (mm^{-1})	1.275	11.085	1.394	1.600
T (K)	293(2)	293(2)	173(2)	173(2)
λ (Mo-K_α) (°)	0.71073	0.71073	0.71073	0.71073
Reflections collected	3139	4846	18440	6308
Unique reflections	1651	2684	5532	3766
R_{int}	0.0511	0.0306	0.0245	0.0107
Parameters	235	208	392	242
S on F^2	1.299	1.118	1.041	0.913
R_1 [$I > 2\sigma(I)$][a]	0.0591	0.0417	0.0521	0.0249
wR_2 [$I > 2\sigma(I)$][b]	0.1554	0.1136	0.1394	0.0975
R_1 (all data)	0.0751	0.0506	0.0600	0.0260
wR_2 (all data)[b]	0.1706	0.1237	0.1464	0.0994
$\Delta\rho_{min.}$ and $_{max.}$ ($e/Å^3$)	0.948 and −1.312	1.253 and −2.438	0.820 and −0.678	1.492 and −0.492

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Synthesis of $[Zn(3\text{-}PYD)_2(H_2O)_2]_n$ (4): $Zn(NO_3)_2{\cdot}6H_2O$ (0.037 g, 0.125 mmol) and 3-HPYD (0.030 g, 0.20 mmol) in H_2O (18 mL) were stirred for 20 min, and the pH was then adjusted to 5 with Et_3N. After stirred for a further 20 min, the mixture was transferred to a 25 mL stainless steel reactor with a Teflon liner and heated to 165 °C for 96 hours. After cooling the reaction system to room temperature during 24 hours, yellow block crystals of **4** (0.026 g) were obtained. Yield: 52% (based on Zn). $C_{16}H_{16}ZnN_2O_6$ (397.68): calcd. C 48.32, H 6.59, N 7.04; found C 48.29, H 6.65, N 6.98. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3109 (s), 1645 (s), 1546 (vs), 1481 (s), 1407 (vs), 1363 (vs), 1268 (w), 996 (m), 975 (m), 885 (w), 808 (s), 750 (m), 689 (s), 645 (w), 602 (w).

Table 2. Selected bond lengths (Å) and angles (°) for **1**−**4**

Compound **1**			
Cd−OW(1)	2.303(8)	Cd−N(2)	2.363(8)
Cd−O(1A)	2.391(8)	Cd−O(3B)	2.439(8)
Cd−O(2A)	2.394(8)	Cd−O(4B)	2.462(10)
Cd−N(1)	2.401(9)		
OW(1)−Cd−N(2)	94.3(3)	N(2)−Cd−O(3B)	89.4(3)
OW(1)−Cd−O(1A)	77.7(3)	O(1A)−Cd−O(3B)	135.0(3)
N(2)−Cd−O(1A)	88.3(3)	O(2A)−Cd−O(3B)	83.6(3)
OW(1)−Cd−O(2A)	127.0(3)	N(1)−Cd−O(3B)	83.7(3)
N(2)−Cd−O(2A)	102.0(3)	OW(1)−Cd−O(4B)	95.0(4)
O(1A)−Cd−O(2A)	53.2(3)	N(2)−Cd−O(4B)	84.9(3)
OW(1)−Cd−N(1)	83.9(3)	O(1A)−Cd−O(4B)	169.6(4)
N(2)−Cd−N(1)	164.0(3)	O(2A)−Cd−O(4B)	136.1(4)
O(1A)−Cd−N(1)	106.7(3)	N(1)−Cd−O(4)	79.5(3)
O(2A)−Cd−N(1)	91.6(3)	O(3B)−Cd−O(4B)	52.9(3)
OW(1)−Cd−O(3B)	147.2(3)		
Compound **2**			
Pb−O(3B)	2.354(7)	Pb−O(1)	2.395(7)
Pb−N(2)	2.637(9)	Pb−N(1A)	2.668(9)
O(3B)−Pb−O(1)	79.3(2)	O(3B)−Pb−N(1A)	76.4(3)
O(3B)−Pb−N(2)	87.4(3)	O(1)−Pb−N(1A)	83.6(3)
O(1)−Pb−N(2)	80.0(3)	N(2)−Pb−N(1A)	158.8(3)
Compound **3**			
Cu(1)−OW(1)	2.403(3)	Cu(2)−O(3)	1.959(3)
Cu(1)−O(5B)	1.956(2)	Cu(2)−O(3C)	1.959(3)
Cu(1)−O(2A)	1.964(2)	Cu(2)−N(3)	2.008(3)
Cu(1)−N(1)	2.024(3)	Cu(2)−N(3C)	2.008(3)
Cu(1)−N(2)	2.025(3)		
O(5B)−Cu(1)−O(2A)	178.60(10)	N(1)−Cu(1)−N(2)	170.34(10)
O(5B)−Cu(1)−N(1)	91.66(11)	O(5B)−Cu(1)−OW(1)	83.80(12)
O(2A)−Cu(1)−N(1)	89.39(11)	O(2A)−Cu(1)−OW(1)	95.17(12)
O(5B)−Cu(1)−N(2)	92.17(11)	N(1)−Cu(1)−OW(1)	95.76(10)
O(2A)−Cu(1)−N(2)	86.95(11)	N(2)−Cu(1)−OW(1)	93.47(10)
O(3)−Cu(2)−N(3)	91.27(11)	O(3)−Cu(2)−N(3C)	88.73(11)
O(3C)−Cu(2)−N(3)	88.73(11)	O(3C)−Cu(2)−N(3C)	91.27(11)
Compound **4**			
Zn−OW(2)	1.9977(13)	Zn−OW(1)	2.1368(13)
Zn−N(2)	2.1002(13)	Zn−N(1)	2.2307(14)
Zn−O(4A)	2.1191(12)	Zn−O(3A)	2.2326(13)
OW(2)−Zn−N(2)	98.95(6)	O(4A)−Zn−N(1)	88.84(5)
OW(2)−Zn−O(4A)	105.98(5)	OW(1)−Zn−N(1)	176.31(4)
N(2)−Zn−O(4A)	154.90(5)	OW(2)−Zn−O(3A)	166.68(5)
OW(2)−Zn−OW(1)	89.56(5)	N(2)−Zn−O(3A)	94.22(5)
N(2)−Zn−OW(1)	88.95(5)	O(4A)−Zn−O(3A)	60.77(5)
O(4A)−Zn−OW(1)	93.99(5)	OW(1)−Zn−O(3A)	92.65(5)
OW(2)−Zn−N(1)	87.37(5)	N(1)−Zn−O(3A)	90.80(5)
N(2)−Zn−N(1)	89.49(5)		

Symmetry code: for 1 (A) $x + 1/2, -y + 3/2, z - 1/2$, (B) $-x + 1/2, y - 1/2, -z + 5/2$. 2 (A) $-x + 1, y + 1/2, -z - 1/2$, (B) $-x, y + 1/2, -z - 1/2$. 3 (A) $-x + 2, y - 1/2, -z + 1/2$, (B) $x - 1, -y + 1/2, z - 1/2$, (C) $-x + 3, -y, -z$. 4 (A) $x, y - 1, z$.

X-ray Crystallographic Study: Intensity data for **1** and **2** were measured with a Siemens Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature;[19] empirical absorption corrections were applied by using the SADABS program. Measurements of **3** and **4** were conducted on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at −100 °C.[20] Structures for **1**−**4** were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXL-97 program package.[21] For **3**, C17, C18 and O6 were handled as disordered at two positions with occupancies of 50%. The positions of H atoms were generated geometrically (C−H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. Crystal data and structure determination summaries (Table 1) and selected bond lengths and angles (Table 2) for **1**−**4** are given here.

CCDC-245500 to -245503 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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