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A Novel Coordination Polymer Containing Both Interdigitated 1D Chains and Interpenetrated 2D Grids

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A hydro(solvo)thermal reaction between zinc perchlorate and ethyl ester of a new pyridinecarboxylate bridging ligand of ~17.6 Å in length yields a unique coordination polymer which contains both interdigitated infinite 1D chains and interpenetrated 2D rhombohedral grids $[Zn_{2.5}(\mathbf{L})_4(\mu_3\text{-OH})]\cdot(H_2O)_5$, **1**, where **L** is 3-{[4-(4-pyridylethenyl)phenyl]ethenyl}benzoate. The 1D chains contain μ_3-bridged hydroxy groups and have a $[Zn_4(\mu_3\text{-OH})_2(L)_6]$ stoichiometry, while the 2D grids have a $Zn(\mathbf{L})_2$ formula and diagonal distances of 31.7 and 25.2 Å. Crystal data for **1**: monoclinic space group *P*2/*c*, $a = 15.686(2)$ Å, $b = 12.6103(16)$ Å, $c = 38.999(5)$ Å, $\beta = 98.397(2)°$, and $Z = 4$.

There has been intense research effort on the synthesis and characterization of coordination networks with novel topologies in recent years.[1] A detailed understanding of the structures of such hybrid inorganic–organic systems represents the first step toward the rational design of molecule-based network materials. Our group has particularly been interested in the crystal engineering of noncentrosymmetric solids for second-order nonlinear optical applications via the use of electronically asymmetric bridging ligands.[2] To this end, we have examined the solvo(hydro)thermal reaction between zinc perchlorate and ethyl ester of a new pyridinecarboxylate bridging ligand of ~17.6 Å in length and unexpectedly obtained a unique coordination polymer which contains both interdigitated infinite 1D chains and interpenetrated 2D rhombohedral grids $[Zn_{2.5}(\mathbf{L})_4(\mu_3\text{-OH})]\cdot(H_2O)_5$, **1**, where **L** is 3-{[4-(4-pyridylethenyl)phenyl]ethenyl}-benzoate.

The use of well-designed bridging ligands in combination with metal centers of diverse geometries has led to the construction of numerous coordination networks with a variety of topologies such as ladders, brick walls, honeycombs, helices, and diamondoid networks.[3] As the length of organic spacers increase, interdigitation or/and interpenetration has been commonly adopted by nature in order to avoid the formation of large open channels or cavities.[3] In almost all the cases, mutually interpenetrated networks are chemically and even crystallographically identical.[2−4] There are few examples of coordination networks that contain chemically or crystallographically distinct, polymeric building motifs.[5] Compound **1** represents a unique example of a coordination polymer in which an interdigitated infinite 1D chain and an interpenetrated 2D rhombohedral grid coexist.

The ethyl ester of 3-{[4-(4-pyridylethenyl)phenyl]ethenyl}-benzoate, **L**-Et, was synthesized in two steps in 40.4% overall yield using commercially available starting materials (Scheme 1).[6] Compound **1** was synthesized in 45.0% yield by a hydro(solvo)thermal reaction between $Zn(ClO_4)_2\cdot 6H_2O$ and **L**-Et in a 1:2 molar ratio in a mixture of pyridine, methanol, and water at 130 °C (Scheme 1). We have previously demon-

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[6] Spectroscopic data for **L**-Et: ^1H NMR ($CDCl_3$) δ 8.59 (d, 2H, $^3J_{H-H} = 4.9$ Hz), 8.21 (s, 1H), 7.95 (d, 1H, $^3J_{H-H} = 7.8$ Hz), 7.70 (d, 1H, $^3J_{H-H} = 8.2$ Hz), 7.60 (s, 4H), 7.45 (dd, 1H, $^3J_{H-H} = 8.2$ Hz, $^3J_{H-H} = 7.8$ Hz), 7.38 (d, 2H, $^3J_{H-H} = 4.9$ Hz), 7.31 (d, 1H, $^3J_{H-H} = 16.0$ Hz), 7.19 (s, 2H), 7.04 (d, 1H, $^3J_{H-H} = 16.0$ Hz), 4.42 (q, 2H, $^3J_{H-H} = 7.0$ Hz, $CO_2CH_2CH_3$), 1.43 (t, 3H, $CO_2CH_2CH_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 166.9, 150.6, 144.9, 137.8, 136.1, 133.0, 131.4, 131.1, 129.5, 129.2, 129.1, 128.6, 128.0, 127.9, 127.5, 126.3, 121.2, 61.5, 14.8.

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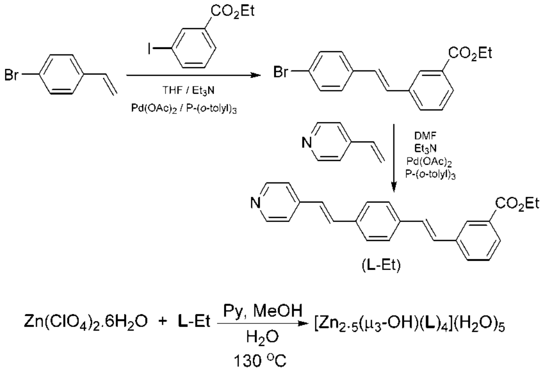
Scheme 1



strated the importance of in situ slow hydrolysis of ester or cyano ligand precursors to generate their pyridinecarboxylic acids in the growth of diffraction-quality metal pyridinecarboxylate coordination networks.[2] The use of pyridine is also essential in the present synthesis of **1**, presumably because high pH value of the solution is needed for the bridging hydroxide to be generated. The IR spectrum of **1** exhibits bands characteristic of carboxylate groups at 1595−1390 cm^{-1}.[7,8] Thermogravimetric analyses (TGA) show that **1** undergoes a gradual loss of 5.4% of total weight by 130 °C, corresponding to the loss of five water molecules per formula unit (expected 5.7%). The formulation of **1** is supported by microanalysis results.[9]

A single-crystal X-ray diffraction study performed on **1**[10] reveals a polymeric coordination network based on both 1D chain and 2D grid structural motifs. **1** crystallizes in the monoclinic space group *P*2/c. The asymmetric unit of **1** contains three Zn(II) centers with the Zn3 center lying on a crystallographic 2-fold axis, four 3-{[4-(4-pyridylethenyl)-phenyl]ethenyl}benzoate (**L**) groups, a μ_3-bridged hydroxyl group, and five water guest molecules (Figure 1a). The **L** groups in **1** adopt four different linkages: (a) an exo-tridentate linkage with a coordinating pyridyl nitrogen (N1) and μ_2,η^2-carboxylate bridge, **L**-N1; (b) an exo-tridentate linkage with a coordinating pyridyl nitrogen (N4) and a chelating carboxylate group, **L**-N4; (c) an exo-bidentate linkage with a coordinating pyridyl nitrogen (N3) and a monodendate carboxylate group, **L**-N3; (d) an endo-bidentate linkage with a noncoordinating pyridyl nitrogen (N2) and a μ_2,η^2-carboxylate bridge, **L**-N2.

The Zn1 center is coordinated to two oxygen atoms (O2 and O3) of two bridging carboxylate groups, one oxygen atom (O5B) of a monodendate carboxylate group, two oxygen atoms (O7 and O7A) of two μ_3-OH groups, and one pyridyl nitrogen atom (N3). The Zn1 center adopts a slightly distorted octahedral geometry with cis angles ranging from 82.2° to 95.6°. The Zn2 center is coordinated to two oxygen atoms (O1 and O4) of two bridging carboxylate groups, one oxygen atom of a μ_3-OH group, and a pyridyl nitrogen atom (N1). The Zn2 center adopts a slightly distorted tetrahedral geometry with the bond angles ranging from 97.2° to 123.4° (Figure 1b). The two μ_3-OH groups bridge two Zn1 centers to form two edge-sharing octahedra which also share common vertexes with two tetrahedra formed by the two

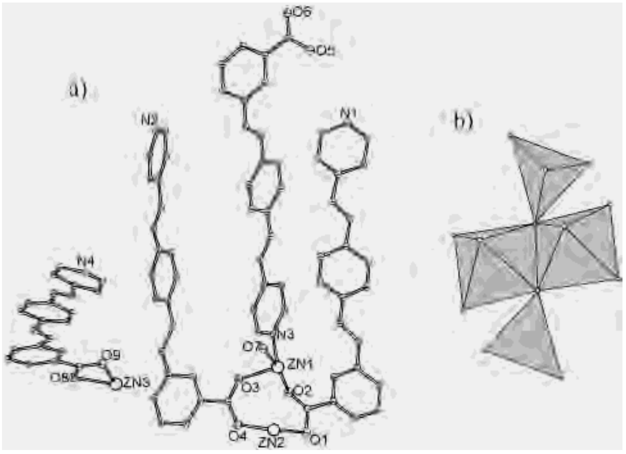


Figure 1. (a) Asymmetric unit of **1** (except water guest molecules). Key bond distances (Å): Zn1−O5B, 2.022(8); Zn1−O7, 2.083(7); Zn1−O3, 2.105(7); Zn1−N3, 2.140(9); Zn1−O7A, 2.178(6); Zn1−O2, 2.181(7); Zn2−O4, 1.936(8); Zn2−O7A, 1.952(6); Zn2−N1C, 2.04(1); Zn2−O1, 2.011(7); Zn3−N4C, 2.06(6); Zn3−O8, 2.19(2); Zn3−O9, 2.31(2). Symmetry codes: A, $-x$, $3 - y$, z; B, $-1 - x$, $4 - y$, $-z$; C, $1 + x$, $y - 1$, z. (b) Polyhedral presentation of the octahedral and tetrahedral coordination environments for Zn1 and Zn2 centers, respectively.

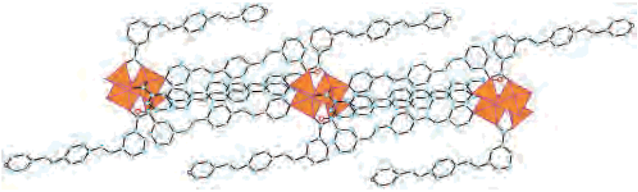


Figure 2. The formation of a 1D chain based on the Zn$_4$(**L**)$_6$(μ_3-OH)$_2$ building unit.

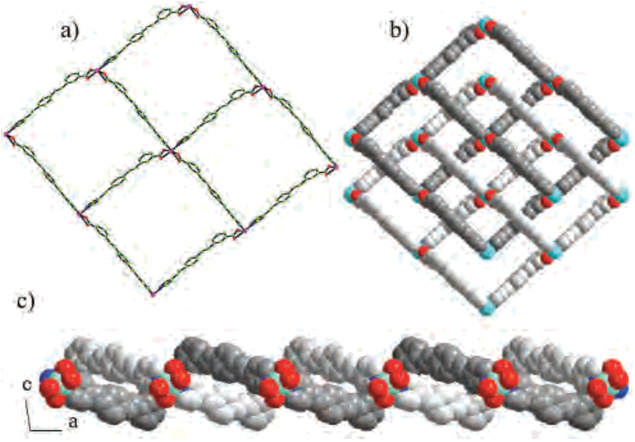


Figure 3. (a) A view of the rhombohedral grid of Zn(**L**)$_2$ in **1**. (b) A space-filling model of 2-fold interpenetrated 2D grids of Zn(**L**)$_2$ as viewed down the *c* axis. (c) A view of the double helix.

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(8) The O−H stretches for the bridging hydroxyl group (expected around 3400 cm^{-1}) have been obscured by those of included water molecules.

(9) Anal. Calcd for $C_{88}H_{75}N_4O_{14}Zn_{2.5}$: C, 67.1; H, 4.80; N, 3.55. Found: C, 66.4; H, 4.03; N, 3.50.

(10) X-ray single-crystal diffraction data for **1** was collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: monoclinic, space group *P*2/*c*, $a = 15.686(2)$ Å, $b = 12.610(2)$ Å, $c = 38.999(5)$ Å, $\beta = 98.397(2)°$, $V = 7631.6(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.37$ g cm^{-3}, μ(Mo Kα) = 0.781 mm^{-1}, Least-squares refinement based on 5265 reflections with $I > 2\sigma(I)$ and 946 parameters led to convergence, with a final R1 = 0.103, wR2 = 0.253, and GOF = 1.02. Relatively high *R* values are probably a result of weakly diffracting nature of **1**.

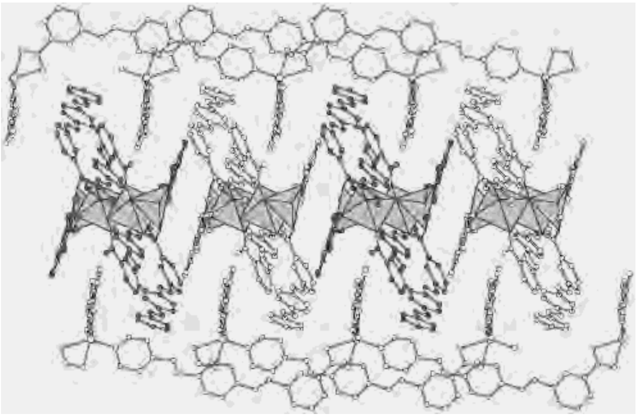

Figure 4. Stacking of 1D chains and 2D grids in **1** as viewed down the [$\bar{1}$10] axis. Interdigitation of **L** ligands is clearly visible.

Zn2 centers to result in the $Zn_4(\mathbf{L})_6(\mu_3\text{-}OH)_2$ building unit (Figure 1b). The Zn1−Zn1 separation is 3.120(2) Å, while the Zn1−Zn2 separation is 3.134(2) Å. Interestingly, each $Zn_4(\mathbf{L})_6(\mu_3\text{-}OH)_2$ building unit is linked by two **L**-N1 and two **L**-N3 ligands to two adjacent $Zn_4(\mathbf{L})_6(\mu_3\text{-}OH)_2$ building units to afford a 1D infinite chain lying along the [$\bar{1}$10] direction (Figure 2). The pyridyl nitrogen atoms of the **L**-N2 ligands are noncoordinating and dangling along the 1D chain.

The Zn3 center is coordinated to four oxygen atoms and two pyridyl atoms of two different **L**-N4 ligands to result in a highly distorted octahedral coordination geometry. Each Zn3 center is thus linked to four adjacent Zn3 centers in the *ab* plane to afford a 2D rhombohedral grid with (4,4) topology (Figure 3a). Each 2D grid has an enormous open cavity as measured by the diagonal Zn3−Zn3 distances of 31.7 and 25.2 Å, respectively. The angles for the rhombus are 102.4° and 77.6°, respectively. Even after 2-fold interpenetration of two identical 2D grids, significant void space still remains, which has diagonal distances 9.4 and 8.4 Å (Figure 3b). The bent configuration of the **L** ligands has allowed the two independent 2D grids to interwine and lead to a double-strand helix along the *a* axis (Figure 3c); adjacent helix bundles are linked to each other to form the interpenetrated 2D network.

The 1D chains and 2D grids in **1** stack alternately along the *c* axis. The bulk of bent **L**-N4 ligands fill the void space between the adjacent 1D chains (Figure 4). The dangling **L**-N2 ligands from the 1D chains in turn fill up the cavities left in the 2-fold interpenetrated 2D grids. Both interdigitation and interpenetration are utilized by **1** to pack the 1D chains and 2D grids into a bulk solid. The remaining void space is filled by five disordered water guest molecules. Compound **1** thus represents a rare example of a coordination network that is built from two chemically and structurally distinct polymeric building motifs.

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Supporting Information Available: Experimental procedures, TGA curve, two tables, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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