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Incorporating Distinct Metal Clusters To Construct Diversity of 3D Pillared-Layer Lanthanide-Transition-Metal Frameworks

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Three novel 3D pillared-layer heterometallic lanthanide-transition-metal (hetero-Ln-TM) compounds, namely, $Ln_2Cu_7I_6(ina)_7(H_2O)_6 \cdot H_2O$ [ina = isonicotinic acid; Ln = Ce (**1**), Sm (**2**)] and $Er_4(OH)_4Cu_5I_4(ina)_6(na)(2,5\text{-pdc}) \cdot 0.3H_2O$ (**3**; na = nicotinic acid, 2,5-pdc = 2,5-pyridinedicarboxylic acid), have been obtained by incorporating different metal clusters as building blocks under hydrothermal conditions. Compounds **1** and **2** are isostructural and consist of two distinct building units of dimeric $[Ln_2(ina)_6]$ cores and inorganic 2D $[Cu_8I_7]_n^{n+}$ layers based on the $[Cu_3I_3]$ and $[Cu_4I_3]^+$ clusters. Compound **3** is constructed from decanuclear $[Cu_{10}I_8]^{2+}$ clusters and inorganic 1D $[Er_4(OH)_4]_n^{8n+}$ cluster chain-based layers, which represent the first example of a 3D hetero-Ln-TM constructed by the combination of two distinct types of metal cluster units of a 1D $[Er_4(OH)_4]_n^{8n+}$ cluster polymer and a transition-metal cluster. It is interesting that decarboxylation occurred in the ortho position and 2,5-pdc^{2-} was partially transformed into na^- under hydrothermal conditions. Compounds **1**−**3** represent good examples of using different metal cluster units to construct fascinating 3D hetero-Ln-TM frameworks.

Introduction

The design and synthesis of heterometallic lanthanide-transition-metal (hetero-Ln-TM) compounds have attracted increasing interest because of their intriguing architectures[1] and potential applications in magnetism,[2] luminescence,[3] bimetallic catalysis,[4] and molecular adsorption.[5] Although a number of hetero-Ln-TM compounds with discrete structures have been well documented, the assembly of extended structures, especially three-dimensional (3D) hetero-Ln-TM metal−organic frameworks (MOFs) is still a challenge.[6–8] This is attributed to the Ln ions' tendency toward high and variable coordination numbers with low stereochemical preference,[9] which makes the Ln ions' selective introduction into a highly ordered structure more difficult.

To design hetero-Ln-TM compounds, a universal synthetic strategy is based on the connector and linker approach by assembling mixed-metal ions with multidentate ligands based on the characteristics of Ln and TM ions with different affinities for O and N donors. To date, various ligands such as pyridinecarboxylate, pyridinephosphonate, amino acids,

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imidazoledicarboxylic acid, and iminodiacetic acid have been employed as linkers to construct 3D hetero-Ln-TM coordination polymers.[6–9] Recently, polynuclear metal clusters with substituted single metal atoms have been used as connectors for high-connected 3D MOFs.[10] Compared with single metal ions, metal-cluster-based connectors generally have larger sizes and more coordination sites but smaller steric hindrance when linked by organic ligands. Therefore, it should be a rational way to introduce metal clusters to construct 3D hetero-Ln-TM structures. Furthermore, if two distinct types of Ln and TM clusters or cluster polymers incorporate into the same hetero-Ln-TM framework, much more diversity of the structures would be expected. Although many efforts have been focused on the assembly of metal clusters to construct 3D homometallic TM compounds, the synthesis of 3D hetero-Ln-TM compounds incorporating metal clusters, especially two different cluster units, are still rarely reported.[11,12]

Among the reported metal clusters, copper iodide provides a variety of oligomeric and polymeric clusters and cluster polymer motifs such as dimers, tetramers of cubane, single, and double chains, and two-dimensional (2D) layers, generally based on corner- or edge-sharing of trigonal-planar $\{CuI_3\}$ or tetrahedral $\{CuI_4\}$ subunits.[13,14] Therefore, the Cu−I clusters or cluster polymers can be used as building blocks to construct hetero-Ln-TM coordination frameworks for their rich structural variety. As a continuation of our search for new hetero-Ln-TM frameworks constructed by metal clusters, we chose mixed pyridinecarboxylate ligands based on the following considerations: (1) A pyridinecarboxylate ligand has been proven to be an effective multifunctional bridging ligand to link the TM and Ln ions with N and O donor atoms. (2) If two different types of pyridinecarboxylate ligands are involved in the same reaction system, the cooperativity of both ligands can be used to understand the effect of the ligands on the hetero-Ln-TM frameworks and may provide new opportunities for the discovery of interesting structures.

Accordingly, our aim is to synthesize 3D hetero-Ln-TM MOFs incorporating metal clusters using two different pyridinecarboxylate ligands. Here we report the systematic syntheses and structures of three hetero-Ln-TM compounds under hydrothermal reactions: $Ln_2Cu_7I_6(ina)_7(H_2O)_6 \cdot H_2O$ [Ln = Ce (**1**), Sm (**2**)] and $Er_4(OH)_4Cu_5I_4(ina)_6(na)(2,5\text{-}pdc) \cdot 0.3H_2O$ (**3**). Single-crystal X-ray diffraction revealed that two distinct pillared-layer structure types were exhibited with different ligands. Compounds **1** and **2** consist of inorganic 2D $[Cu_8I_7]_n{}^{n+}$ layers and dimeric $[Ce_2(ina)_6]$ cores. Compound **3** is constructed from the unique inorganic one-dimensional (1D) $[Er_4(OH)_4]_n{}^{8n+}$ chains and decanuclear $[Cu_{10}I_8]^{2+}$ clusters. These compounds represent good examples of using metal clusters to construct fascinating 3D hetero-Ln-TM frameworks.

Experimental Section

Materials and Methods. All chemicals were purchased commercially and used without further purification. Elemental analyses for C, H, and N were performed on a Vario EL III elemental analyzer. The Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. Thermogravimetric analyses (TGA) were performed on a Mettler TGA/SDTA 851e analyzer with a heating rate of 10 °C/min under an air atmosphere.

$Ln_2Cu_7I_6(ina)_7(H_2O)_6 \cdot H_2O$ [Ln = Ce (1), Sm (2)]. A mixture of Ln_2O_3 (CeO_2, 0.172 g; Sm_2O_3, 0.174 g), Hina (0.246 g), picolinic acid (0.237 g), CuI (0.054 g), and H_2O (10 mL) was sealed in a 30 mL Telfon-lined bomb at 170 °C for 7 days and then slowly cooled to room temperature. Yellow prismatic crystals of **1** and **2** were obtained (yield: 42% and 25% based on CuI). Anal. Calcd for $C_{42}H_{42}I_6Cu_7Ce_2 N_7O_{21}$ (**1**): C, 20.45; H, 1.72; N, 3.97. Found: C, 20.32; H, 1.76; N, 3.99. IR bands (cm^{-1}) for **1**: 3413m, 1627s, 1587vs, 1539s, 1406vs, 1225w, 1056m, 1020w, 859m, 774m, 702m. Anal. Calcd for $C_{42}H_{42}I_6Cu_7Sm_2N_7O_{21}$ (**2**): C, 20.28; H, 1.70; N, 3.94. Found: C, 20.40; H, 1.82; N, 4.13. IR bands (cm^{-1}) for **2**: 3415m, 1631vs, 1590vs, 1535s, 1405vs, 1223w, 1056m, 1020w, 858w, 770m, 702m.

$Er_4(OH)_4Cu_5I_4(ina)_6(na)(2,5\text{-}pdc) \cdot 0.3H_2O$ (3). Compound **3** was synthesized by a procedure similar to that of **1**, except that CeO_2/picolinic acid was replaced by Er_2O_3/2,5-H_2pdc (0.192/0.167 g), respectively. Black prismatic crystals of **3** were obtained (yield: 37% based on CuI). Anal. Calcd for $C_{49}H_{35.6}I_4Cu_5Er_4N_8O_{22.3}$ (**3**): C, 22.74; H, 1.39; N, 4.33. Found: C, 22.62; H, 1.69; N, 4.27. IR bands (cm^{-1}) for **3**: 3447vs, 1628vs, 1414m, 1354vs, 770w, 694w.

Single-Crystal Structure Determination. The intensity data were collected on a Mercury CCD (**1** and **2**) or a Rigaku Saturn70 CCD (**3**) with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at room temperature. All absorption corrections were

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Table 1. Crystal Data and Structure Refinement for Compounds **1**−**3**

	1	**2**	**3**
formula	$C_{42}H_{42}I_6Cu_7Ce_2N_7O_{21}$	$C_{42}H_{42}I_6Cu_7Sm_2N_7O_{21}$	$C_{49}H_{35.6}I_4Cu_5Er_4N_8O_{22.3}$
M_r	2467.25	2487.71	2587.59
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/m$	$P2_1/m$	$P\bar{1}$
a (Å)	7.1054(3)	7.0807(5)	13.583(3)
b (Å)	24.9477(10)	24.8237(18)	14.015(3)
c (Å)	18.2419(9)	18.1874(12)	19.705(4)
α (deg)	90.00	90.00	102.776(2)
β (deg)	99.522(2)	99.022(3)	109.1520(10)
γ (deg)	90.00	90.00	99.330(2)
V (Å^3)	3189.1(2)	3157.2(4)	3341.9(13)
Z	2	2	2
D_c (g cm^{-3})	2.569	2.617	2.571
μ (mm^{-1})	6.658	7.144	8.443
F(000)	2296	2312	2386
GOF	1.149	1.117	1.068
collcd reflns	24868	24637	25183
unique reflns (R_{int})	7433 (0.0254)	7389 (0.0341)	14842 (0.0259)
obsd reflns [$I > 2\sigma(I)$]	6648	6457	12636
refined param	409	409	842
R1[a]/wR2[b] [$I > 2\sigma(I)$]	0.0336/0.0858	0.0433/0.0929	0.0412/0.0999
R1[a]/wR2[b] (all data)	0.0409/0.0949	0.0521/0.0976	0.0498/0.1058
largest diff peak and hole [e Å^{-3}]	+1.502 and −1.997	+1.621 and −1.640	+1.575 and −2.703

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

performed using the multiscan program. The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the *SHELXTL-97* program.[15] The H atoms of organic ligands were geometrically placed and refined using a riding model. However, the H atoms of water molecules in **1**−**3** and hydroxy H atoms in **3** have not been included in the final refinement. All atoms except H atoms were refined anisotropically. Cu1/Cu1′ in **3** are disordered. Further details for structural **1**−**3** analyses are summarized in Table 1, and selected bond lengths of compounds **1**−**3** are listed in Tables 2 and 3. CCDC 673539 (**1**), 673540 (**2**), and 667875 (**3**) contain the crystallographic data in CIF format (see the Supporting Information).

Results and Discussion

Single crystals of **1**−**3** were obtained by hydrothermal reactions of Ln_2O_3, CuI, Hina, and picolinic acid (**1** and **2**) or 2,5-H_2pdc (**3**) in water in the presence of $HClO_4$ at pH 2 and 170 °C. X-ray crystallographic studies revealed that **1**−**3** exhibit two different types of 3D pillared-layer hetero-Ln-TM structures by incorporating different metal clusters as building blocks. Compounds **1**−**3** are air-stable and insoluble in water and common organic solvents. After compounds **1** and **2** were obtained, we tried to make other isomorphous complexes with Pr, Nd, or Pm with ionic radii between that of Ce and Sm ions under the same condition, but this was fruitless. It shows that the ionic radius of the Ln ion does not seem to be the predominant factor governing the obtained structure. In fact, the syntheses of the title compounds more broadly need the synthetic parameter space. That is, the ionic radius of the Ln ion is not the only factor governing the obtained structure; the ligands also exhibit coordination flexibility, and their variable coordination modes and connectivity are directly related to the diverse structures.

Table 2. Selected Bond Lengths (Å) for **1** and **2**[a]

	Compound **1**		
Ce−O5A	2.393(3)	Cu2−N2	2.035(6)
Ce−O6B	2.443(4)	Cu2−I2	2.685(1)
Ce−O8C	2.538(4)	Cu2−I2D	2.685(1)
Ce−OW2	2.550(4)	Cu2−I1	2.822(1)
Ce-OW3	2.557(5)	Cu3−N3	2.037(4)
Ce−O7C	2.575(4)	Cu3−I2	2.635(1)
Ce−O2	2.589(4)	Cu3−I3	2.677(1)
Ce-OW1	2.604(5)	Cu3−I4	2.686(1)
Ce−O1	2.668(4)	Cu4−N4	2.016(4)
Cu1−N1	2.017(4)	Cu4−I3	2.621(1)
Cu1−I1	2.555(1)	Cu4−I3E	2.636(1)
Cu1−I2	2.563(1)	Cu4−I4	2.682(1)
	Compound **2**		
Sm−O5A	2.329(4)	Cu2−N2	2.034(7)
Sm−O6B	2.384(5)	Cu2−I2	2.681(1)
Sm−O8C	2.464(4)	Cu2−I2D	2.681(1)
Sm−OW2	2.481(5)	Cu2−I1	2.834(2)
Sm−OW3	2.501(6)	Cu3−N3	2.032(5)
Sm−O7C	2.522(4)	Cu3−I2	2.627(1)
Sm−O2	2.530(5)	Cu3−I3	2.674(1)
Sm−OW1	2.549(6)	Cu3−I4	2.680(1)
Sm−O1	2.610(5)	Cu4−N4	2.018(5)
Cu1−N1	2.015(5)	Cu4−I3	2.619(1)
Cu1−I1	2.553(1)	Cu4−I3E	2.631(1)
Cu1−I2	2.563(1)	Cu4−I4	2.679(1)

[a] Symmetry codes: A, $-x - y + 1, -z - 1$; B, $x, y, z - 1$; C, $-x, -y + 1, -z - 2$; D, $x, -y + {}^1/_2, z$; E, $-x - 1, -y + 1, -z - 1$.

Structures of 1 and 2. Compounds **1** and **2** are constructed from two subunits, dimeric [$Ce_2(ina)_6$] and a layered inorganic $[Cu_7I_6]_n^{n+}$ cluster polymer. Compounds **1** and **2** are isomorphous; therefore, only the structure of **1** is described in detail. The asymmetric unit of **1** contains one unique Ce^{3+}, four Cu^+ ions, four I^- ions; and four ina^- ligands with three different coordination modes (Scheme 1 and Figure 1). The Ce^{3+} ion is nine-coordinated and has a tricapped trigonal-prism coordination environment: three terminal water molecules and six carboxylate atoms (O_{COO}) from four ina^- ligands (Figure S1 in the Supporting Information). The Ce−O distances range from 2.393(3) to 2.668(4) Å, and the Sm−O bonds in **2** are slightly shorter than the

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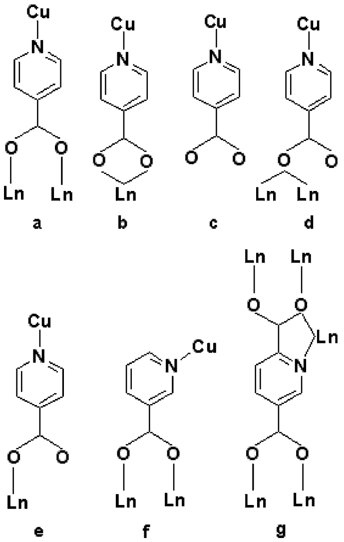
Table 3. Selected Bond Lengths (Å) for **3**[a]

Er1−O19	2.255(4)	Er4−O17	2.250(5)
Er1−O4A	2.293(5)	Er4−O10	2.282(5)
Er1−O7B	2.294(5)	Er4−O16C	2.286(6)
Er1−O21	2.298(4)	Er4−O22	2.303(4)
Er1−O5	2.414(5)	Er4−O20	2.307(4)
Er1−O1	2.451(4)	Er4−O2B	2.316(5)
Er1−N1	2.505(6)	Er4−O22C	2.343(5)
Er1−O12	2.567(5)	Cu1−N2	2.011(10)
Er1−O6	2.888(6)	Cu1−I1D	2.701(6)
Er2−O12	2.324(5)	Cu1−I3D	2.752(7)
Er2−O19	2.328(4)	Cu1−I2D	2.869(6)
Er2−O3A	2.352(5)	Cu2−N3E	1.946(8)
Er2−O20	2.353(4)	Cu2−N4	1.955(8)
Er2−O15	2.355(6)	Cu2−I4C	2.985(2)
Er2−O14	2.368(5)	Cu3−N6F	1.996(7)
Er2−O22C	2.380(5)	Cu3−N5	2.001(8)
Er2−O18C	2.400(5)	Cu3−I1	2.679(2)
Er3−O6	2.297(5)	Cu4−N7	1.998(9)
Er3−O20	2.297(4)	Cu4−I2	2.618(2)
Er3−O9	2.327(5)	Cu4−I1	2.735(2)
Er3−O21B	2.334(4)	Cu4−I3	2.766(2)
Er3−O21	2.355(4)	Cu5−N8	2.040(7)
Er3−O19	2.415(4)	Cu5−I4H	2.617(2)
Er3−O8	2.433(5)	Cu5−I4	2.684(2)
Er3−O1B	2.450(4)	Cu5−I3I	2.729(2)

[a] Symmetry codes: A, $-x + 2, -y, -z + 2$; B, $-x + 2, -y - 1, -z + 2$; C, $-x + 1, -y - 1, -z + 2$; D, $x + 1, y, z + 1$; E, $-x + 2, -y - 1, -z + 3$; F, $-x + 1, -y - 1, -z + 1$; H, $-x, -y - 2, -z + 1$; I, $x, y - 1, z$.

Scheme 1. Coordination Modes of the Ligands in **1** and **2** (a−c) and in **3** (a, d−f, and g)



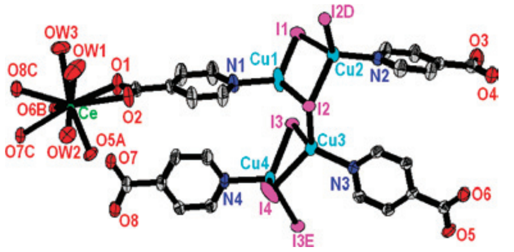


Figure 1. Coordination environment of Ce and Cu atoms in **1**. Symmetry codes for the generated atoms are the same as those in Table 2.

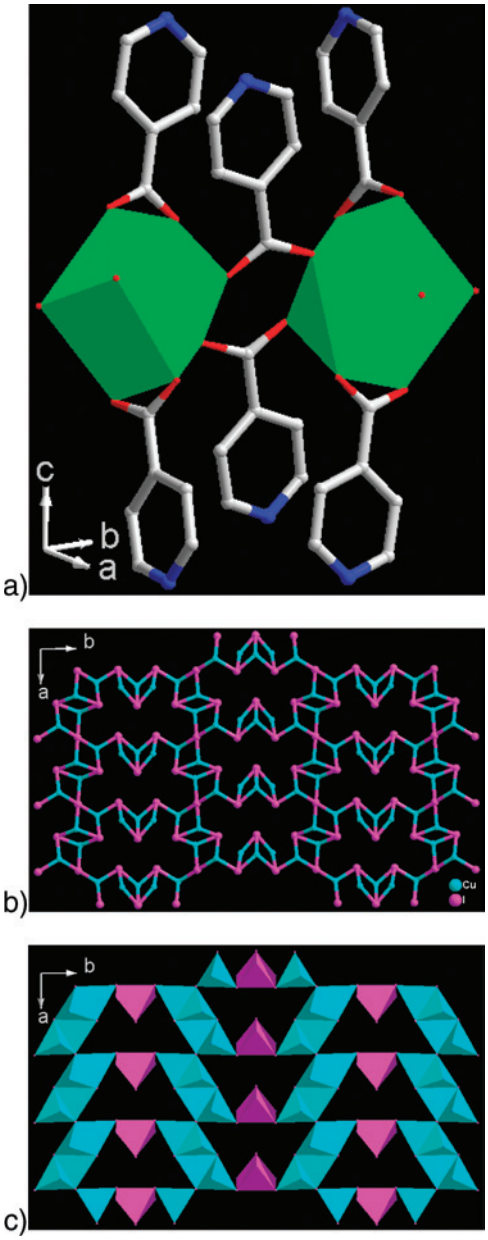


Figure 2. (a) Dimeric [$Ce_2(ina)_6$] pillar along the *c* axis. (b) Inorganic [Cu_7I_6]$_n^{n+}$ layer in the *ab* plane. (c) Polyhedral view of the 2D [Cu_7I_6]$_n^{n+}$ layer with eight rings. Color code: purple, [Cu_3I_3] cluster; cyan, [Cu_4I_3]$^+$ cluster.

corresponding Ce−O bonds in **1** (Table 2). Two crystallographically identical Ce ions are linked by six ina$^-$ ligands to give a dimeric [$Ce_2(ina)_6$] unit with a Ce···Ce distance of 5.815(1) Å (Figure 2a).

Cu1 is three-coordinated in trigonal-planar geometry with CuI_2N coordination environments, while Cu2, Cu3, and Cu4 are four-coordinated in distorted tetrahedral geometries (Figure 1) made up of CuI_3N with Cu−N and Cu−I distances varying from 2.016(4) to 2.037(4) Å and from 2.555(1) to 2.822(1) Å, respectively (Table 2). The Cu$^+$ ions are linked by μ_3-I$^-$ and μ_4-I$^-$ to give two types of small clusters: a trinuclear [Cu_3I_3] core that contains two Cu1 and one Cu2 atoms and a tetranuclear [Cu_4I_3]$^+$ core that contains two Cu3 and two Cu4 atoms. The adjacent [Cu_4I_3]$^+$ cores are corner-sharing μ_4-I$^-$ to give a 1D chain along the *a* axis and further bridged by [Cu_3I_3] cores to give a unique inorganic 2D [Cu_7I_6]$_n^{n+}$ layer along the *ab* plane with eight rings (Figure 2b,c). It is interesting to note that eight-ring CuI-layered walls are constructed from corner- and edge-sharing tetrahedral CuI_3N; the trigonal CuI_2N groups only hang in the walls.

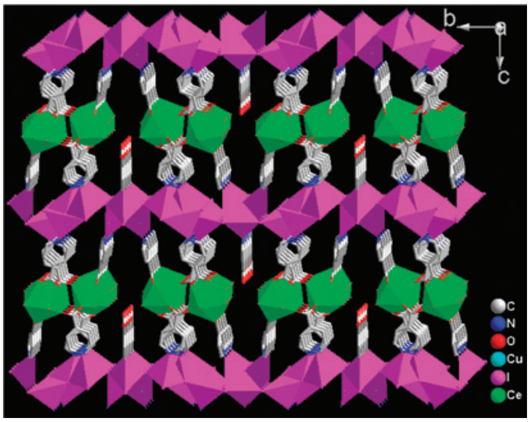


Figure 3. Framework of **1** viewed approximately down the [100] direction.

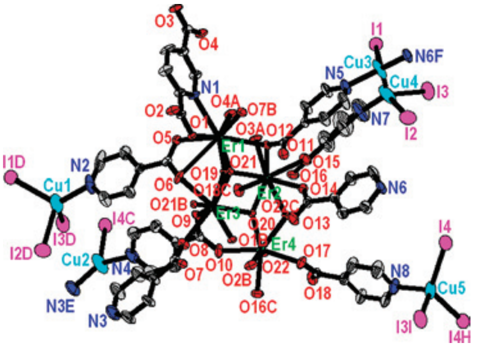


Figure 4. Coordination environment of Er and Cu atoms in **3**. Symmetry codes for the generated atoms are the same as those in Table 3.

Although a variety of CuI substructures have been well documented, 2D-layered CuI motifs are scarce.[13a,16] The linkage between dimeric [$Ce_2(ina)_6$] and layered $[Cu_7I_6]_n^{n+}$ cluster polymers gives rise to a 3D pillared-layer network (Figure 3).

Structure of 3. The framework **3** consists of two distinct building blocks of inorganic 1D $[Ln_4(OH)_4]_n^{8n+}$ cluster polymers and $[Cu_{10}I_8]^{2+}$ clusters. The asymmetric unit of **3** contains four independent Er^{3+}, five Cu^+ ions, four I^- ions, one na^- ligand, one 2,5-pdc^{2-} ligand, and six ina^- ligands with three different coordination modes (Figure 4). The Er1 is nine-coordinated with a tricapped trigonal-prism coordination environments: two μ_3-OH, four O_{COO} from three ina^- ligands, two O_{COO}, and one N_{py} from two 2,5-pdc^{2-} ligands for Er1 with a Er−N distance of 2.505(6) Å. The Er2 and Er3 ions are eight-coordinated with bicapped trigonal-prism coordination environments: three μ_3-OH, three O_{COO} from three ina ligands, one O_{COO} from a 2,5-pdc^{2-} ligand, and one O_{COO} from a na^- ligand for Er2; four μ_3-OH, three O_{COO} from three ina^- ligands, and one O_{COO} from 2,5-pdc^{2-} ligands for Er3. The Er4 is seven-coordinated and has a capped trigonal-prism coordination environment: three μ_3-OH, two O_{COO} from two ina^- ligands, one O_{COO} from a 2,5-pdc^{2-} ligand, and one O_{COO} from a na^- ligand for Er4 (Figure S2 in the Supporting Information). The Er−O bond lengths (Table 3) range from 2.254(4) to 2.568(5) Å. The Er^{3+} ions are linked by μ_3-OH to give an inorganic 1D $[Ln_4(OH)_4]_n^{8n+}$ chain (Figure 5a), which is rare in Ln-cluster chemistry.[17] These Ln-cluster chains are further linked to each other by 2,5-pdc^{2-} into 2D layers in the *ab* plane (Figure 5b). It is interesting to note that decarboxylation occurred in the ortho position and 2,5-pdc^{2-} was partially transformed into nicotinic acid under hydrothermal conditions. Although hydrothermal decarboxylation of multicarboxylic acids containing N donors has been shown to occur in the presence or absence of metal ions,[18,19] the decarboxylation of 2,5-pdc^{2-} under hydrothermal conditions has not been documented so far to the best of our knowledge.[20]

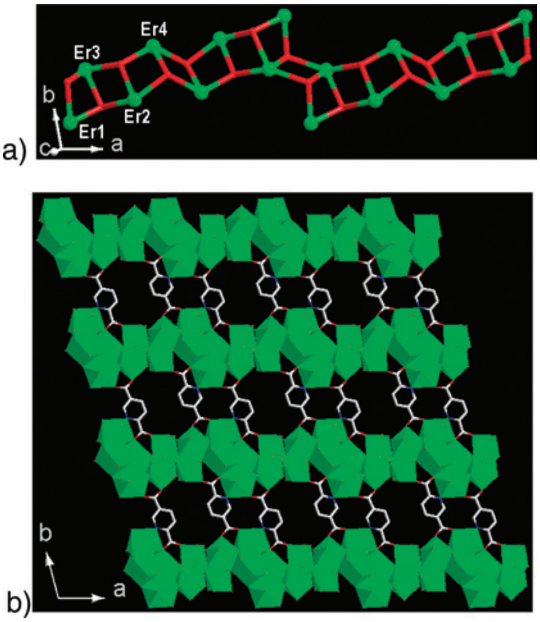


Figure 5. (a) Inorganic $[Ln_4(OH)_4]_n^{8n+}$ chain along the *a* axis. (b) Polyhedral view of the 2D Ln-organic layer in the *ab* plane.

The trigonal $Cu1I_2N$, $Cu2IN_2$, and $Cu3IN_2$ and tetrahedral $Cu4I_3N$ and $Cu5I_3N$ are bridged by μ_3-I to give a decanuclear $[Cu_{10}I_8]^{2+}$ cluster. The Cu−N and Cu−I distances vary from 1.946(8) to 2.040(7) Å and from 2.617(2) to 2.985(2) Å, respectively (Table 3 and Figure 6). The linkage between layered Ln networks and $[Cu_{10}I_8]^{2+}$ clusters by ina^- and na^- pillars along the *c* axis forms an unprecedented 3D framework (Figure 7). Remarkably, there are two distinct cluster motifs, 1D $[Ln_4(OH)_4]_n^{8n+}$ cluster chains and a decanuclear $[Cu_{10}I_8]^{2+}$ cluster, which represents the first example of such a hetero-Ln-TM framework constructed by the combination of 1D chains of Ln-cluster polymer units and TM clusters.

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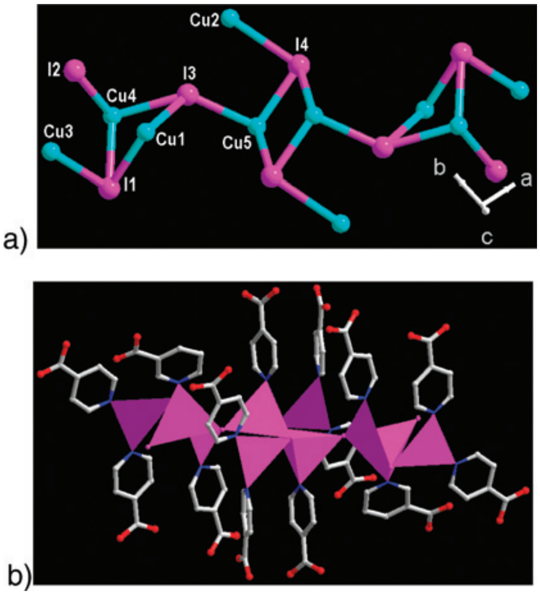

Figure 6. (a) Inorganic $[Cu_{10}I_8]^{2+}$ cluster. (b) Polyhedral view of the coordination environment of the $[Cu_{10}I_8]^{2+}$ cluster.

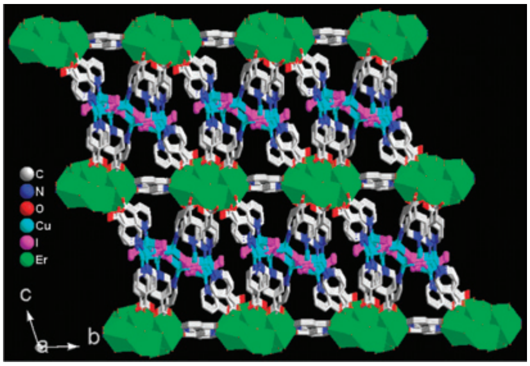

Figure 7. Framework of **3** viewed approximately down the [001] direction.

Interestingly, the syntheses of **1**−**3** rely on subtle control over various hydrothermal parameters, particularly the starting materials. It is noteworthy that picolinic acid plays a critical role in the formation of **1** and **2**, although picolinic acid is not present in compound **1**. Picolinic acid was removed from reaction, and attempts to make**1** proved fruitless under the same conditions. In **1**−**3**, I^- shows versatile coordination modes from terminal to μ_4-I^- for its larger size; a similar reaction using Cl^- and Br^- ions as halide sources could not produce the title compounds, indicating that the I^- ion is indeed critical for the formation of the title compounds. In addition, the architectures of **1**−**3** are not maintained across the whole Ln series. The ionic radii of the Ln cations decrease with increasing atomic number, which imposes evident influences on the coordination geometry and might lead to other types of structures with different Ln ions. The ligands also exhibit coordination flexibility (Scheme 1), and their variable coordination modes and connectivity are directly related to the diversity of the structures.

Owing to the structural similarity of **1** and **2**, compound **1** was selected to study their thermal stability. The thermal stabilities of **1** and **3** were examined by TGA in a dry air atmosphere from 30 to 1000 °C. The lattice−water and coordinated water molecules were gradually lost in the temperature range 30−300 °C for **1** (calcd/found: 5.1/5.5%). Above this temperature, the weight loss is due to the decomposition of the organic ligands and the collapse of the whole framework. The TGA study of **3** shows that the first weight loss from 30 to 280 °C corresponds to removal of water molecules (calcd/found: 0.21/0.75%) and the second weight loss between 280 and 1000 °C is attributable to the loss of all organic ligands (Figure S3 in the Supporting Information).

The IR spectra of **1**−**3** are similar. The strong and broad absorption bands in the range of 3000−3700 cm^{-1} in **1**−**3** are assigned as characteristic peaks of OH vibration. The strong vibrations appearing around 1600 and 1410 cm^{-1} are corresponding to the asymmetric and symmetric stretching vibrations of the carboxylate group, respectively. The absence of strong bands ranging from 1690 to 1730 cm^{-1} indicates that the ligands are deproponated (Figure S4 in the Supporting Information).

Conclusion

In summary, three 3D hetero-Ln-TM compounds are prepared under hydrothermal conditions by incorporating metal clusters. The linkage between different Ln and TM cluster-based motifs through a pyridinecarboxylate ligand results in two distinct types of pillared-layer frameworks. The successful isolation of these compounds not only provides the diversity of aesthetic hetero-Ln-TM architectures but also demonstrates that using metal clusters as building blocks is a feasible route to synthesizing 3D hetero-Ln-TM MOFs.

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Supporting Information Available: X-ray crystallographic files in CIF format for structures **1**− **3**, coordination environments of the Ce atom in **1** and the Er atoms in **3**, IR spectra, and TGA curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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