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3D Coordination Framework $[Ln_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3]$ (IN = Isonicotinate): Employing 2D Layers of Lanthanide Wheel Clusters and 1D Chains of Copper Halide Clusters

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Two novel 3D heterometallic coordination polymers, $Ln_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3$ (Ln = Nd (**1**), Pr (**2**); HIN = isonicotinic acid, HOAc = acetic acid), have been synthesized under hydrothermal conditions and characterized by elemental, infrared, and thermogravimetric analyses and single-crystal X-ray diffraction. Both compounds are isostructural and crystallize in the monoclinic system, space group $P2_1/c$. Both polymers are constructed from 2D lanthanide-cluster polymers based on the $\{Ln_{16}\}$ wheel-cluster and 1D copper-cluster polymers based on the $\{Cu_6I_5\}$ cluster, which represent the first examples of 3D coordination frameworks created by using a combination of two different types of metal-cluster polymer units, namely, a high-nuclearity lanthanide-cluster polymer and a transition-metal-cluster polymer.

Introduction

The design and synthesis of high-nuclearity clusters have received intense interest due to their intriguing variety of architectures and potential applications in various aspects such as magnetism, catalysis, optics, and electronics.[1] In contrast to the well-established cluster chemistry of the transition metals,[2−6] the analogous chemistry of the lanthanides is virtually underdeveloped because of some intrinsic characteristics of lanthanide ions such as the high and variable coordination numbers as well as the small energy difference among various coordination geometries.[7] Up to now, although there have been many attempts to synthesize high-nuclearity lanthanide clusters, most of the resulting clusters still possess discrete structures in the crystallographic viewpoint.[7,8] The synthesis of high-nuclearity lanthanide-cluster polymers remains a big challenge to chemists. Additionally, transition-metal-cluster polymers have received much attention owing to their remarkable structures and properties compared with those of discrete transition-metal clusters.[9] If these two different types of

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cluster polymers could be combined into one coordination framework, the as-obtained coordination polymers might exhibit interesting structures and properties. It can be stated that the available heterometallic coordination frameworks were constructed from the discrete units of heterometallic clusters or metal centers,[10] and no efforts have been devoted to the combination of these two different types of cluster polymer units. To realize this kind of assembly, one problem must be solved, that is, how to harmonize the subtle relationship between these two different types of metal-cluster polymer units in one coordination framework.

As we know, lanthanide and transition-metal ions possess different affinities for oxygen and nitrogen donors on the basis of the hard−soft acid base classification.[11] Such a characteristic provides us the impetus to construct interesting lanthanide−transition-metal (Ln−M) heterometallic coordination frameworks.[12] We have recently designed and synthesized a series of 3D Ln−M heterometallic coordination frameworks,[13] which demonstrate that isonicotinic acid (HIN) is an excellent candidate to construct high-dimensional heterometallic coordination frameworks. Considering the mixed coordination sites of the HIN ligand, we wondered if this ligand could be used as the linker to bind these two different types of metal-cluster polymer units into one framework. Here, we report two novel 3D coordination polymers $Ln_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3$ (Ln = Nd (**1**), Pr (**2**); HOAc = acetic acid). These compounds represent the first examples of the creation of 3D heterometallic coordination frameworks by using a combination of high-nuclearity lanthanide-cluster polymer and transition-metal-cluster polymer units.

Experimental Section

Materials and General Methods. All chemicals were of reagent grade and used without further purification. Distilled water was used in all reactions. The elemental analyses (C, H, and N) were carried out a Perkin-Elmer 240C elemental analyzer. The infrared spectra were recorded (400−4000 cm^{-1} region) on an Alpha Centaurt FT/IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) was performed on an SDT Q600 instrument in a flowing nitrogen atmosphere with a heating rate of 10 °C/min.

Synthesis of $[Nd_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3]$ (1). A mixture of Nd_2O_3 (0.168 g, 0.5 mmol), CuI (0.190 g, 1.0 mmol), HIN (0.246 g, 2.0 mmol), HOAc (0.060 g, 1.0 mmol), and H_2O (15 mL) was placed in a 23 mL Teflon reactor and kept under autogenous pressure at 160 °C for 9 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and yellow crystals were obtained (yield: 38% based on Nd). Elem Anal. Calcd for $C_{54}H_{43}Cu_6I_5N_8Nd_4O_{24}$: C, 23.30; H, 1.55; N, 4.03. Found: C, 23.41; H, 1.64; N, 4.14. IR (KBr pellet cm^{-1}): 3428(m), 1592(s), 1540(s), 1396(s), 1209(w), 1048(w), 865(w), 772(m), 691(m), 540(w), 433(w).

Table 1. Crystal Data and Structure Refinement for Compounds **1** and **2**

	compound	
	1	**2**
empirical formula	$C_{54}H_{43}Cu_6I_5\text{-}N_8Nd_4O_{24}$	$C_{54}H_{43}Cu_6I_5\text{-}N_8Pr_4O_{24}$
fw	2780.66	2767.34
temp (K)	293	293
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	18.0567(9)	18.0965(11)
b (Å)	18.3122(9)	18.3267(12)
c (Å)	21.6870(11)	21.7131(12)
β (deg)	96.233(3)	96.159(4)
V (Å^3)	7128.6(6)	7159.6(8)
Z	4	4
ρ_{calcd} (g cm^{-3})	2.591	2.567
μ (mm^{-1})	6.852	6.644
F(000)	5176	5160
reflns collected/ unique	53655/20705	45672/15808
GOF	1.018	1.014
$R_1{}^a/R_2{}^b$ [$I > 2\sigma(I)$]	0.0384/0.0804	0.0509/0.0683

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Synthesis of $[Pr_4(\mu_3\text{-}OH)_2Cu_6I_5(IN)_8(OAc)_3]$ (1). A procedure identical with that of **1** was followed to prepare **2** except that Nd_2O_3 was replaced by Pr_6O_{11} (0.204 g, 0.2 mmol). Red crystals were obtained (yield: 21% based on Pr). Elem Anal. Calcd for $C_{54}H_{43}Cu_6I_5N_8Pr_4O_{24}$: C, 23.42; H, 1.55; N, 4.05. Found: C, 23.49; H, 1.69; N, 4.19. IR (KBr pellet cm^{-1}): 3422(m), 1597(s), 1543(s), 1403(s), 1213(w), 1051(w), 857(w), 770(m), 696(m), 543(w), 431(w).

X-ray Crystallographic Study. The collection of crystallographic data was carried out on a Bruker SMART Apex CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Empirical absorption correction was applied. Both structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the *SHELXTL* crystallographic software package.[14] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms for C−H were placed in idealized positions. The Cu5 and Cu6 atoms in **1** are disordered. The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1. Selected bond lengths and angles for compound **1** are listed in Tables 2 and Supporting Information S1.

Results and Discussion

Single-crystal X-ray analysis reveals that **1** and **2** crystallize in the monoclinic space group $P2_1/c$ and possess a 3D coordination framework based on the linkage of 2D lanthanide wheel-cluster polymers and 1D copper−iodine

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

Nd(1)−O(1)	2.480(3)	Nd(1)−O(2)	2.473(3)
Nd(1)−O(22)	2.537(3)	Nd(1)−O(8)	2.388(3)
Nd(1)−O(13)	2.475(3)	Nd(1)−O(4)	2.395(3)
Nd(1)−O(6)	2.401(3)	Nd(1)−O(9)	2.439(4)
Nd(2)−O(1)	2.454(3)	Nd(2)−O(2)	2.421(3)
Nd(2)−O(19)	2.487(4)	Nd(2)−O(20)	2.624(3)
Nd(2)−O(14)	2.456(4)	Nd(2)−O(2)$^{\#4}$	2.443(3)
Nd(2)−O(3)$^{\#4}$	2.379(3)	Nd(2)−O(11)	2.379(4)
Nd(3)−O(1)	2.456(3)	Nd(3)−O(20)	2.503(3)
Nd(3)−O(24)	2.486(3)	Nd(3)−O(10)	2.362(3)
Nd(3)−O(7)	2.439(3)	Nd(3)−O(18)	2.430(3)
Nd(3)−O(12)	2.623(4)	Nd(3)−O(21)$^{\#2}$	2.482(3)
Nd(4)−O(23)	2.624(3)	Nd(4)−O(24)	2.557(3)
Nd(4)−O(15)	2.424(3)	Nd(4)−O(17)	2.427(4)
Nd(4)−O(5)$^{\#2}$	2.338(3)	Nd(4)−O(23)$^{\#5}$	2.459(3)
Nd(4)−O(16)$^{\#5}$	2.474(4)	Nd(4)−O(21)$^{\#2}$	2.527(3)
Nd(4)−O(22)$^{\#2}$	2.749(3)	Cu(1)−I(1)$^{\#1}$	2.6087(9)
Cu(1)−I(3)	2.6361(9)	Cu(1)−I(5)	2.6907(9)
Cu(2)−I(4)	2.6358(9)	Cu(2)−I(3)	2.6588(8)
Cu(2)−I(5)	2.6920(8)	Cu(3)−I(5)	2.6461(9)
Cu(3)−I(2)	6.6729(9)	Cu(4)−I(4)	2.7126(10)
Cu(5)−I(3)$^{\#2}$	2.955(5)	Cu(6)−I(1)$^{\#3}$	2.869(5)
Cu(1)−N(1)	2.037(5)	Cu(2)−N(2)	2.040(4)
Cu(3)−N(3)	2.042(4)	Cu(4)−N(4)	2.038(5)
Cu(5)−N(6)	1.953(7)	Cu(6)−N(7)	1.971(6)

[a] Symmetry codes for **1**: (#1) x, $^3/_2 - y$, $^1/_2 + z$; (#2) $-x$, $-^1/_2 + y$, $^1/_2 - z$; (#3) $-1 - x$, $-^1/_2 + y$, $^1/_2 - z$; (#4) $-x$, $1 - y$, $-z$; (#5) $-x$, $1 - y$, $1 - z$.

cluster polymers by IN linkers. Because **1** and **2** are isostructural, only the structure of **1** is described in detail. An ORTEP view of **1** is shown in Figure 1. The asymmetric unit consists of four crystallographically unique neodymium ions, six copper ions, five iodine ions, eight IN ligands, three OAc ligands, and two μ_3-OH groups. The Nd1, Nd2, and Nd3 centers are all eight-coordinated: five oxygen atoms from five IN ligands, one oxygen atom from one OAc ligand, and two μ_3-OH groups for Nd1; three oxygen atoms from three IN ligands, two oxygen atoms from one OAc ligand, and three μ_3-OH groups for Nd2; and four oxygen atoms from four IN ligands, three oxygen atoms from three OAc ligands, and one μ_3-OH group for Nd3. The Nd4 center is nine-coordinated, surrounded by four oxygen atoms from four IN ligands and five oxygen atoms from three OAc ligands. The Nd−O bond lengths vary from 2.338(3) to 2.749(3) Å, and the O−Nd−O bond angles are in the range of 48.3(1)−161.77(14)°. The Cu1, Cu2, Cu3, and Cu4 centers are all four-coordinated by three iodine ions and a nitrogen atom from one IN ligand, while both Cu5 and Cu6 centers are three-coordinated via one iodine ion and two nitrogen atoms from two IN ligands. The Cu−I and Cu−N bond lengths range from 2.6087(9) to 2.955(5) Å and from 1.939(5) to 2.042(4) Å, respectively, which are similar to those lengths found in the related Cu(I) complexes.[15]

Eight unique IN ligands exhibit only one kind of bridging coordination mode: the nitrogen atom coordinates to one copper center, while the carboxylate coordinates to two neodymium centers with the bis-monodenate mode (Chart 1a). Three unique OAc ligands display two kinds of chelating and bridging coordination modes (Charts 1b and 1c). In these organic species, all carboxyl groups are deprotonated, in agreement with the IR data in which no strong absorption peaks around 1700 cm^{-1} for −COOH are observed.

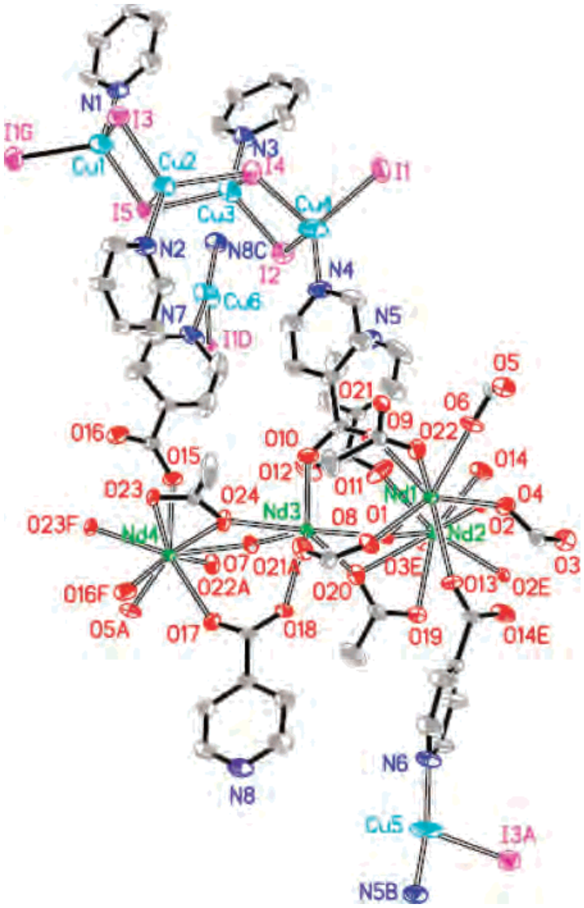
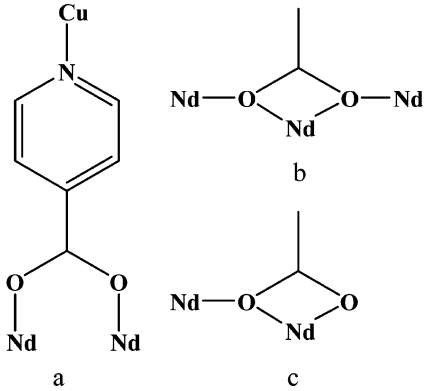


Figure 1. ORTEP plot of the asymmetric unit of **1** (50% probability ellipsoids). All H atoms are omitted for clarity.

Chart 1. Coordination Modes of IN and OAc in **1**



In the structure of **1**, three unique neodymium centers, Nd1, Nd2, and Nd3, are linked by one μ_3-OH group to give a $[Nd_3(\mu_3\text{-}OH)_2]^{7+}$ cluster core, and then the $[Nd_3(\mu_3\text{-}OH)_2]^{7+}$ core links another $[Nd_3(\mu_3\text{-}OH)_2]^{7+}$ core from the adjacent asymmetric unit through two μ_3-OH groups to form a $[Nd_6(\mu_3\text{-}OH)_4]^{14+}$ cluster core, $\{Nd_6\}$. The Nd−O(μ_3-OH) distances are in the range of 2.421(3)−2.580(3) Å. Different

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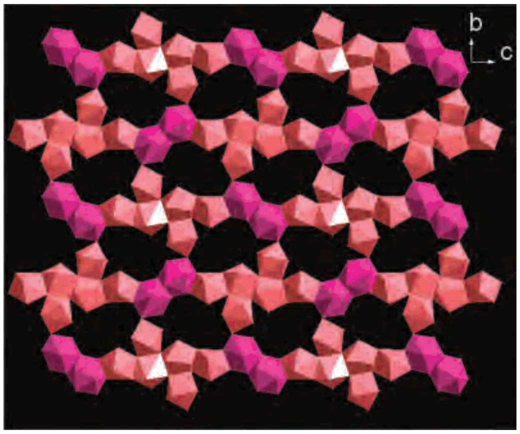

Figure 2. View of the 2D cluster network constructed by neodymium wheel clusters with an eight-membered ring in **1**. The C atoms in the IN and OAc ligands are omitted for clarity. {Nd_6} clusters, brick red; {Nd_2} clusters, purple.

from the closed hexanuclear lanthanide cores,[8f,g] the chairlike {Nd_6} core in **1** is unusual among the known {Ln_6} cores. Moreover, two Nd4 centers are linked to each other by two oxygen atoms from two OAc ligands to form a dimeric core, {Nd2}. The {Nd_6} and {Nd_2} cores are connected alternately to form a nanosize {Nd_{16}} wheel with an eight-membered ring with the size of 12.59 and 9.13 Å (defined by the distances between two Nd4 centers and two Nd2 centers, respectively) (Figure S2 in the Supporting Information). Two OAc ligands with mode b, which coordinate to three neodymium centers, are trapped in the inner of the eight-membered ring and play an important role in stabilizing the lanthanide wheel.[7b] The third OAc ligand with mode c, which coordinates to two neodymium centers, extends out of the wheel-cluster plane. Different from other discrete lanthanide wheel clusters,[7d] each {Nd_{16}} wheel cluster in **1** is linked to surrounding wheel clusters by sharing the oxygen atoms in the organic ligands to form a layered cluster network (Figures 2 and Supporting Information S3). The presented wheel-cluster polymer is unusual in cluster chemistry.[16]

The presented structure of the transition-metal-cluster moiety in **1** is the first example of a sawtooth chain formed by {Cu_6I_5} clusters (Figure 3). The {Cu_6I_5} cluster is built from six unique Cu centers and five I atoms by coordination bonds. In the chain, each {Cu_6I_5} cluster is linked to adjacent clusters by sharing its I1 atoms. Different from the other four copper centers, both Cu5 and Cu6 centers hang in the chain through Cu−I bonds. Another unusual feature of this chain is its relatively short Cu−Cu distances (Cu1−Cu2 2.5976(11) Å, Cu2−Cu3 2.7235 (10) Å), which are much shorter than the double van der Waals radius of the Cu(I) ion (1.4 Å), implying a strong Cu−Cu interaction. The phenomenon of Cu−Cu interaction has been observed for other multinuclear copper(I) complexes.[15] It should be noted that the Cu5 and Cu6 centers are disordered and occupy 80 and 63.72% of the corresponding sites, respectively.

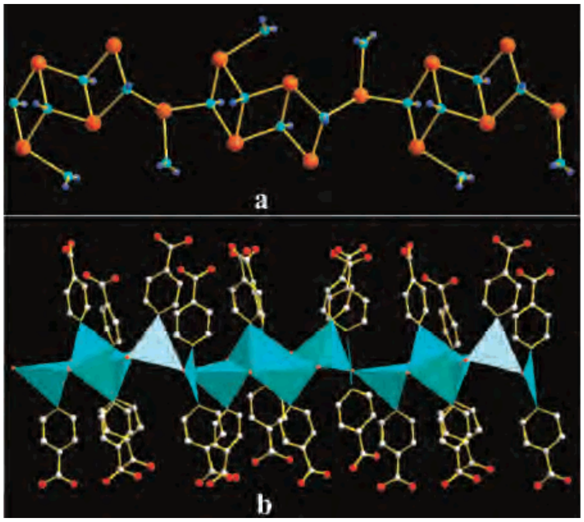

Figure 3. (a) View of the 1D chain built from {Cu_6I_5} clusters in **1**. The pyridine rings and carboxyl groups in IN ligands are omitted for clarity. Cu, azure; I, orange; N, navy blue. (b) Polyhedral view of the whole structure of the 1D copper−iodine cluster polymer.

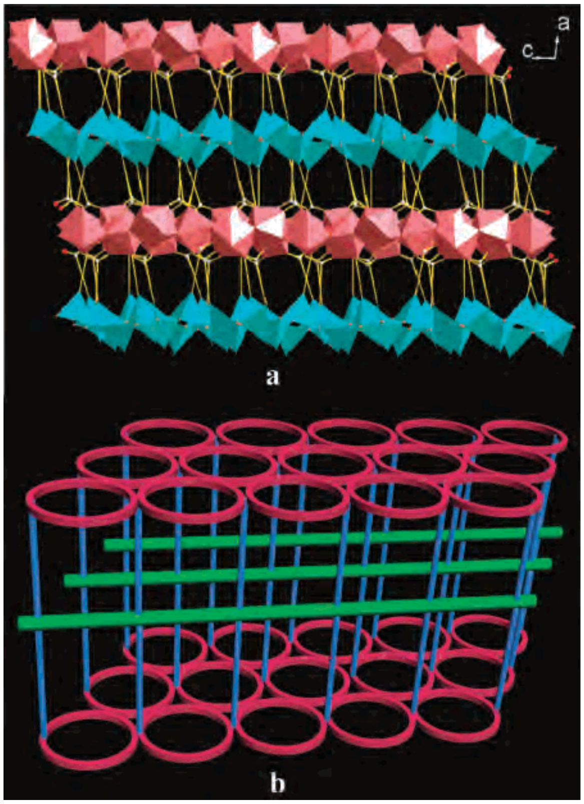

Figure 4. (a) View of the 3D coordination framework based on the linkage of 2D neodymium cluster layers and 1D copper−iodine cluster chains by IN linkers in **1**. Nd polyhedra, brick red; Cu polyhedra, azure. The yellow lines represent the pyridine rings of IN linkers. (b) A schematic illustration of the 3D coordination framework of **1**. The red moiety represents the 2D neodymium wheel-cluster polymer, the green moiety represents the 1D copper−iodine cluster polymer, and the blue moiety represents the IN ligand.

It is interesting that the linkage between the 2D neodymium wheel-cluster layers and the 1D copper halide cluster chains by IN ligands gives rise to an unprecedented 3D coordination framework (Figure 4). The structure is of strictly

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alternating lanthanide-cluster layers and copper−iodine cluster chains. The distance of the adjacent lanthanide-cluster layers is 17.95 Å, which is due to the incorporation of the linear IN ligands and copper−iodine chains. In the structure of **1**, all IN ligands adopt one kind of bridging coordination mode, which provides the possibility of linking two types of metal-cluster polymer units. In the 3D framework, each $\{Cu_6I_5\}$ core links two $\{Nd_{16}\}$ clusters by eight IN ligands; thus, these copper−iodine clusters are connected by I1 atoms to form a new cluster chain $Cu_6I_5(IN)_8$ pillared between adjacent lanthanide-cluster layers (Figure S4 in the Supporting Information). Therefore, the structure of **1** can also be regarded as the 3D sandwich framework constructed from the 2D lanthanide-cluster layers pillared by the cluster chain of $Cu_6I_5(IN)_8$. Compared to other Ln−M coordination polymers built from discrete heterometallic clusters or metal centers,[10,12] compound **1** is based on the assembly of 2D layers of lanthanide clusters and 1D chains of copper−iodine clusters by IN linkers with mixed coordination sites. This type of assembly mode is unusual, which also testifies to the validity of our present strategy.

TGA. Owing to the similarity of the structures for **1** and **2**, compound **1** was selected for the TGA to examine the thermal stability of both compounds. The TG curve was obtained in a N_2 atmosphere for a crystalline sample of **1** in the temperature range of 40−950 °C. It can be seen from the TG curve (Figure S8 in the Supporting Information) that there is no weight loss between 40 and 310 °C. Such a thermal stability of **1** may be attributed to the formation of the 2D layer of lanthanide clusters and the 1D chain of copper−iodine clusters. Above 310 °C, the weight loss is due to the loss of all the organic components and the collapse of the whole framework.

Conclusion

In summary, we have synthesized two novel 3D coordination polymers, which are constructed from 2D lanthanide wheel-cluster polymers and 1D copper halide cluster chains by introducing a linear IN ligand with preferable coordination sites. These two compounds represent the first examples of 3D heterometallic coordination frameworks created by using a combination of high-nuclearity lanthanide-cluster polymer and transition-metal-cluster polymer units. The self-assembly of different types of high-nuclearity metal-cluster polymers into one framework structure provides us a potential route to crystallographically design heterometallic coordination polymers at the nanosize level, which may possess interesting structure topologies and properties.

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Supporting Information Available: X-ray crystallographic file (CIF) for compounds **1** and **2**, IR spectra, TG curves, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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