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Lanthanide Coordination Polymers Constructed from Infinite Rod-Shaped Secondary Building Units and Flexible Ligands

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Abstract: Three lanthanide coordination polymers constructed from infinite rod-shaped secondary building units (SBUs), $[Nd_2(H_2O)_2(cis\text{-chdc})_2(trans\text{-chdc})]\cdot 2H_2O$ (**1**), $Nd_2(H_2O)_4(trans\text{-chdc})_3$ (**2**), and $[Sm_2(H_2O)_2(cis\text{-chdc})(trans\text{-chdc})_2]\cdot 4H_2O$ (**3**) (chdcH$_2$ = 1,4-cyclohexanedicarboxylic acid), were hydrothermally synthesized and structurally characterized. The structures of **1**–**3** are modulated by different ratios of the *cis* and *trans* configurations of chdc^{2-} ligands, which was achieved by temperature control in the hydrothermal reactions. Crystal-structure analysis revealed that **1** is a four-connected pcu-type rod packing network built from cross-linking of rod-shaped neodymium–oxygen SBUs by *cis*- and *trans*-chdc^{2-} ligands in a 2:1 ratio, **2** displays a complicated six-connected hex-type rod packing structure built by connection of rod-shaped neodymium–oxygen SBUs and *trans*-chdc^{2-} ligands, and **3** features an unprecedented five-connected rod packing pattern constructed from rod-shaped samarium–oxygen SBUs and *cis*- and *trans*-chdc^{2-} ligands in a 1:2 ratio.

Keywords: coordination modes · lanthanides · neodymium · polymers · samarium

Introduction

The crystal engineering of coordination polymers (CPs) is now possible through the right choice of metals and organic ligands, and it has become a flourishing research field focusing on the design and isolation of topological structures and the investigation of the fundamental correlation between structure and function.[1–4] More recently, the construction of CPs has been greatly advanced through the concept of secondary building units (SBUs), which was promoted by Yaghi,[2] Williams,[3] and Kitagawa[4] and their co-workers and is now widely used for understanding and predicting the topologies of structures. The development of methods to construct CPs with given SBUs is of primary importance. Triangular, square, tetrahedral, and octahedral building-block geometries have been categorized in detail,[2e] and design strategies for nets based on these SBUs are well-advanced. However, a recent review by O'Keeffe, Yaghi, and co-workers documented a subclass of CPs based on infinite rod-shaped SBUs,[5] and 14 CPs produced from the reactions of transition-metal (TM) salts and aromatic carboxylate ligands were investigated and classified systematically.[5]

It is well-known that aromatic carboxylate ligands are excellent candidates for building CPs with well-defined SBUs and versatile architectures; consequently, numerous CPs have been isolated by using TMs and rigid aromatic carboxylate ligands.[6–8] However, research on CPs constructed from flexible aliphatic carboxylate ligands is now undergoing a period of rapid development in comparison to aromatic carboxylate CPs. Besides, lanthanide ions, which generally adopt coordination numbers higher than those of 3d metals, can become important choices in the design of novel CPs.[7a,9] CPs built by lanthanide ions are expected to have intriguing structural features and interesting luminescent and magnetic properties.[10] Inspired by the aforementioned considerations, our current synthetic strategy is to synthesize CPs based on infinite rod-shaped SBUs by linking lanthanide ions with flexible aliphatic carboxylate ligands.

We have been focusing on finding reactions whereby the *cis* and *trans* conformations of 1,4-cyclohexanedicarboxylic acid (chdcH$_2$) can be modulated or separated under certain conditions. We successfully controlled the *cis* and *trans* con-

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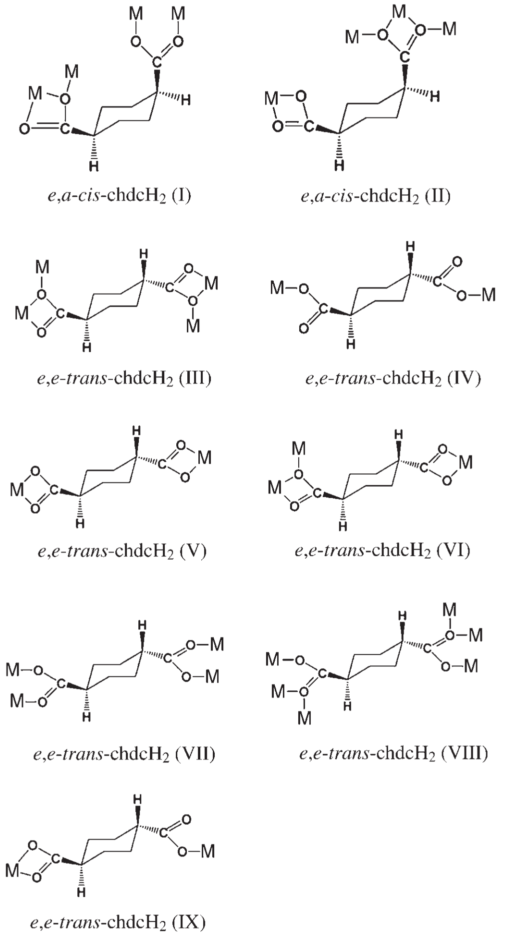
formations of chdc^{2-} in the synthesis of Cd^{II} polymeric complexes in hydrothermal reactions by changing the reaction temperature and pH.[10c] In general, low temperatures and pH values help the formation of *cis*-chdc^{2-} complexes, whereas high temperatures and pH values result in *trans*-chdc^{2-} compounds. Furthermore, the coordination modes (Scheme 1) and linking modes (bridging and/or chelating) of the chdc^{2-} ligands are well-defined. It is therefore believed that rational design, at least partly, of CPs is achievable by considering the basic rules. As part of our ongoing study of the metal–chdcH$_2$ system,[11] lanthanides (neodymium and samarium herein) were exploited to prepare new CPs. Three lanthanide CPs constructed from infinite rod-shaped SBUs, namely, [Nd$_2$(H$_2$O)$_2$(*cis*-chdc)$_2$(*trans*-chdc)]·2H$_2$O (**1**), Nd$_2$(H$_2$O)$_4$(*trans*-chdc)$_3$ (**2**), and [Sm$_2$(H$_2$O)$_2$(*cis*-chdc)(*trans*-chdc)$_2$]·4H$_2$O (**3**) were successfully synthesized. Structural analysis revealed that **1** has a four-connected pcu-type rod packing network built from cross-linking of rod-shaped neodymium–oxygen SBUs, **2** displays a complicated six-connected hex-type rod packing structure built by connection of rod-shaped neodymium–oxygen SBUs, and **3** features an unprecedented five-connected rod packing pattern constructed from rod-shaped samarium–oxygen SBUs.


e,a-cis-chdcH$_2$ (I)
e,a-cis-chdcH$_2$ (II)
e,e-trans-chdcH$_2$ (III)
e,e-trans-chdcH$_2$ (IV)
e,e-trans-chdcH$_2$ (V)
e,e-trans-chdcH$_2$ (VI)
e,e-trans-chdcH$_2$ (VII)
e,e-trans-chdcH$_2$ (VIII)
e,e-trans-chdcH$_2$ (IX)

Scheme 1. The coordination modes of chdc^{2-} ligands.

Abstract in Chinese:

本文报道了三个基于棒状基本构筑单元的镧系元素配合物的水热合成和结构表征：[Nd$_2$(H$_2$O)$_2$(*cis*-chdc)$_2$(*trans*-chdc)]·2H$_2$O (**1**), [Nd$_2$(H$_2$O)$_4$(*trans*-chdc)$_3$] (**2**), 和 [Sm$_2$(H$_2$O)$_2$(*cis*-chdc)(*trans*-chdc)$_2$]·4H$_2$O (**3**) (chdcH$_2$ = 1,4-cyclohexanedicarboxylic acid)。化合物 **1–3** 可以通过温度控制配体顺-反-式构型的比例得到。**1** 的结构是通过顺-反-2:1 的 chdc^{2-} 配体连接 Nd/O 棒状基本单元形成，表现为四连接的 pcu 结构类型。**2** 是通过反式 chdc^{2-} 配体连接 Nd/O 棒状基本单元形成，表现为六连接的 hex 结构类型。**3** 是通过顺-反-1:2 的 chdc^{2-} 配体连接 Sm/O 棒状基本单元形成，表现为一个有趣的五连接网络结构。同时，**3** 也是第一个基于棒状构筑单元的五连接网络结构。

Results

Crystal Structure of 1

Compound **1** is isostructural to the two lanthanum complexes [Ln$_2$(H$_2$O)$_2$(*cis*-chdc)$_2$(*trans*-chdc)]·2H$_2$O (Ln = La and Pr).[12] X-ray crystal-structure analysis reveals that the central neodymium atom, which displays tricapped triprismatic geometry (Figure 1 and Table 1), links to eight oxygen donors from six chdc^{2-} ligands and a terminal aqua ligand (Nd–O = 2.385–2.688 Å). The six chdc^{2-} ligands coordinating each Nd atom are composed of two chelating–bridging *cis*-chdc^{2-}, two bridging *cis*-chdc^{2-}, and two chelating–bridging *trans*-chdc^{2-} ligands. The overall ratio of *cis*- to *trans*-chdc^{2-} ligands is 2:1. The *cis*-chdc^{2-} ligands display the type I coordination mode, and the *trans*-chdc^{2-} ligands adopt the type III coordination mode. Each Nd ion is connected to two adjacent metals by pairs of μ_3-O atoms to generate an infinate 1D rod (Figure 2a). Within the 1D rod, {NdO$_8$(H$_2$O)} tricapped triprisms arrange in an edge-sharing mode (Figure 2b).

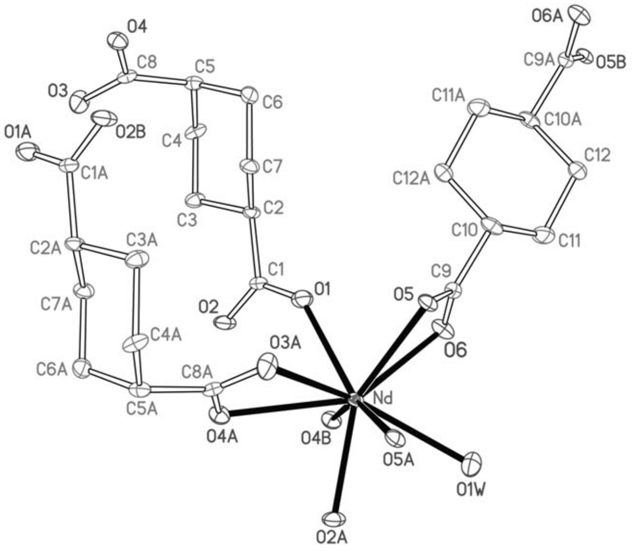


Figure 1. ORTEP drawing of the basic building unit in **1**, showing the coordination environment around the neodymium atom with thermal ellipsoids at 30% probability. Hydrogen atoms and uncoordinated water molecules are omitted.

Table 1. Crystal data and structure refinement for **1**–**3**.

Compound	**1**	**2**	**3**
Formula	$C_{12}H_{19}NdO_8$	$C_{24}H_{38}Nd_2O_{16}$	$C_{24}H_{42}O_{18}Sm_2$
M_r	435.48	870.94	919.38
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pccn*
a [Å]	7.9374(6)	11.4531(7)	36.7878(2)
b [Å]	9.0362(7)	12.0064(7)	10.43930(1)
c [Å]	10.5305(8)	12.3765(7)	16.1676(2)
α [°]	72.428(2)	94.79(1)	90
β [°]	84.039(2)	115.9150(1)	90
γ [°]	84.146(2)	101.0780(1)	90
V [Å^3]	714.16(9)	1474.95(2)	6208.99(1)
Z	2	2	8
$R1$[a] ($I>2\sigma(I)$)	0.0470	0.0337	0.0492
$wR2$[b]	0.1069	0.0718	0.1206

[a] $R1=\Sigma||F_0|-|F_c||/\Sigma|F_0|$. [b] $wR2=\{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

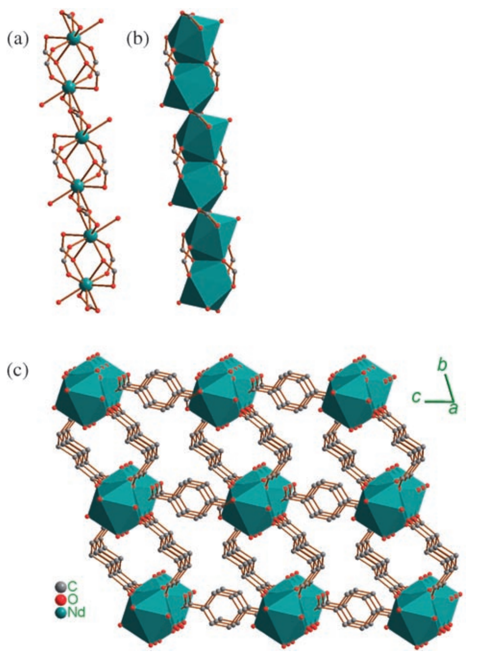


Figure 2. Compound **1**: a) Ball-and-stick representation of the SBU, b) the SBU with neodymium atoms shown as polyhedra, and c) view of the crystalline framework with inorganic SBUs linked together by chdc^{2-} ligands (uncoordinated H_2O molecules are omitted for clarity).

The rods run parallel to the *a* axis; they act as infinite rod-shaped SBUs and are connected into a 3D architecture by the aliphatic backbones of the chdc^{2-} ligands. Each rod-shaped unit is directly connected to four neighboring rods through the chdc^{2-} ligands (Figure 2c), two in the *b* direction by single *trans*-chdc^{2-} bridges, and two in the *c* direction by pairs of *cis*-chdc^{2-} bridges. The free water molecules reside in the void of the framework structure through hydrogen bonding. According to the identification in the literature of possible infinite rod-packing constructions of metal carboxylate structures, the structure of **1** displays pcu-type rod packing.[3]

Crystal Structure of 2

X-ray crystal-structure analysis reveals that there are two crystallographically independent neodymium atoms in the structure of **2** (Figure 3 and Table 1). The distorted tricapped triprismatic coordination environment around the Nd1 atom is defined by seven oxygen donors from four chelating–bridging (type III mode) and one monodentate *trans*-chdc^{2-} ligand (type IV mode), as well as two aqua ligands (Nd1−O = 2.484–2.716 Å). The 10-coordinated Nd2 atom bonds to eight oxygen donors from four chelating–bridging (type III mode) and one chelating *trans*-chdc^{2-} ligands (type V mode), as well as two aqua ligands (Nd2−O = 2.469–2.827 Å), to give a distorted bicapped square-antiprismatic coordination environment. The chdc^{2-} ligands in **2** are in the *trans* conformation and display three types of coordination modes. Alternate linkage of $\{NdO_7(H_2O)_2\}$ tricapped triprisms and $\{NdO_8(H_2O)_2\}$ bicapped square antiprisms through edge sharing results in an undulating rod with adjacent Nd ions bridged by pairs of μ_3-O atoms (Figure 4a and b). The rods run along the [011] direction; they act as infinite rod-shaped SBUs and are connected into a 3D network by the aliphatic backbones of the chdc^{2-} ligands. As shown in Figure 4c, each rod is directly connected to six neighboring rods through the chdc^{2-} ligands. There are three types of bridges present, with each type bridging a pair of rods in opposite positions. The versatile coordination modes of the *trans*-chdc^{2-} ligands result in a rather complicated overall topology. Although infinite packings of parallel rods have

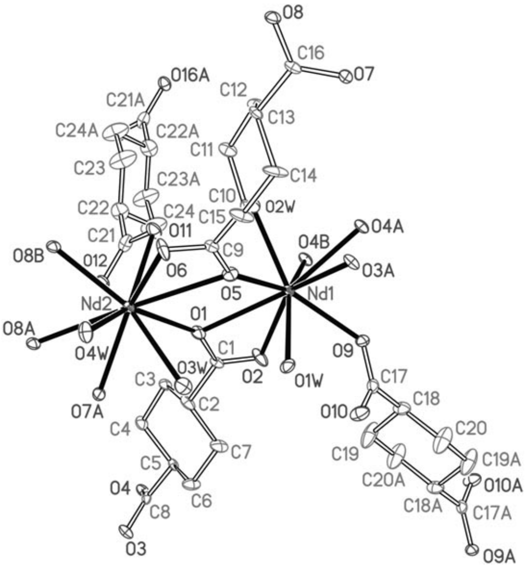


Figure 3. ORTEP drawing of the basic building unit in **2**, showing the coordination environment around the neodymium atom with thermal ellipsoids at 30 % probability. Hydrogen atoms are omitted.

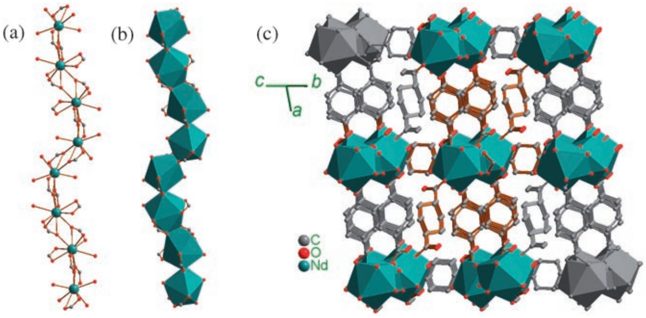


Figure 4. Compound **2**: a) Ball-and-stick representation of the SBU, b) the SBU with neodymium atoms shown as polyhedra, and c) view of the crystalline framework with inorganic SBUs linked together by chdc^{2-} ligands (uncoordinated H_2O molecules are omitted for clarity).

been identified, in which each rod is connected to six others (hex-type rod packing),[3] the geometry of **2** is significantly different and less regular.

Crystal Structure of 3

X-ray crystal-structure analysis reveals that there are two crystallographically independent samarium sites in the asymmetric unit of **3** (Figure 5 and Table 1). The Sm1 atom is coordinated by nine carboxy oxygen atoms that belong to one chelating–bridging *cis*-chdc^{2-} (type I mode), one bridging *cis*-chdc^{2-} (type I mode), one chelating *trans*-chdc^{2-} (type VI mode), and three chelating–bridging *trans*-chdc^{2-} ligands (two from type III and one from type VI mode) (Sm1−O = 2.346–2.689 Å), thus forming a distorted tricapped triprism. The nine-coordinated Sm2 atom coordinates to seven carboxylate oxygen atoms from one bridging *cis*-chdc^{2-} (type I mode), one chelating–bridging *cis*-chdc^{2-} (type I mode), and three chelating–bridging *trans*-chdc^{2-} (type III mode) ligands, as well as to two aqua ligands (Sm2−O = 2.406–2.617 Å) to give a monocapped square-antiprismatic coordination environment. The overall ratio of *cis*- to *trans*-chdc^{2-} ligands in **3** is 1:2. {SmO_9} tricapped triprisms and {$SmO_7(H_2O)_2$} monocapped square antiprisms are connected together through edge sharing to form an infinate 1D rod. Adjacent Sm centers are bridged by pairs of μ_3-O atoms (Figure 6a and b). The rods run parallel to the *c* axis; they act as infinite rod-shaped SBUs and are connected into a 3D framework by the chdc^{2-} ligands. Each rod is directly connected to five neighboring rods through the chdc^{2-} ligands: four by single *trans*-chdc^{2-} bridges and one by pairs of double *cis*-chdc^{2-} bridges (Figure 6c). Fivefold connectivity is rare in network structures, owing in part, no doubt, to crystallographic symmetry requirements. This is highlighted by the fact that a packing arrangement in which each rod is connected to five others has not been identified previously.

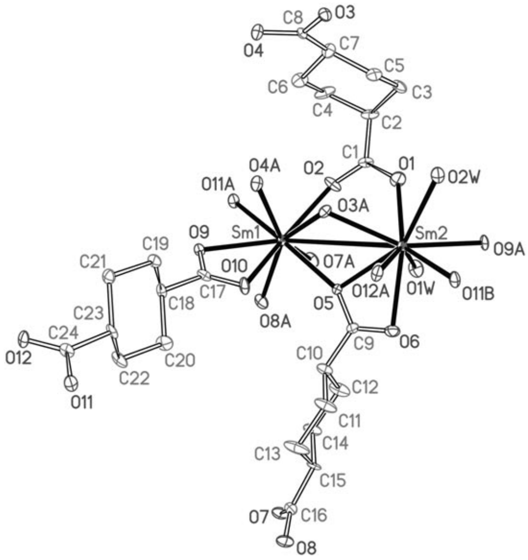


Figure 5. ORTEP drawing of the basic building unit in **3**, showing the coordination environment around the samarium center with thermal ellipsoids at 30% probability. Hydrogen atoms and uncoordinated water molecules are omitted.

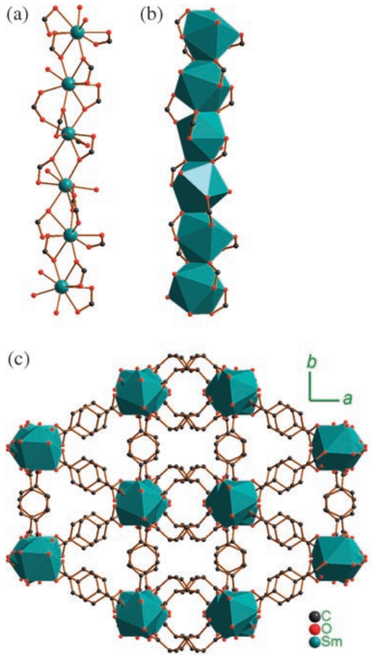


Figure 6. Compound **3**: a) Ball-and-stick representation of the SBU, b) the SBU with samarium atoms shown as polyhedra, and c) view of the crystalline framework with inorganic SBUs linked together by chdc^{2-} ligands (uncoordinated H_2O molecules are omitted for clarity).

Discussion

Notably, *cis*-chdc^{2-} ligands exhibit one type of coordination mode (type I), whereas *trans*-chdc^{2-} ligands display four types of modes (type III–VI) in the structures of **1**–**3**. The *cis*-chdc^{2-} ligands also behave as doubly bridging pairs, but the *trans*-chdc^{2-} ligands act as single bridges between the rods. Thus, despite the fact that, within each SBU of **1**–**3**, every pair of adjacent metal ions is associated with six chdc^{2-} ligands, the overall structures exhibit four-, six-, and five-connected rod packing, respectively. In fact, the connectivity follows the simple relation $N=2n-m$, in which N denotes the network connectivity, n is the number of chdc^{2-} ligands per metal ion, and m is the number of those ligands that have the *cis* configuration.

This is particularly significant because, as described earlier, the conformations of the chdc^{2-} ligand can, to some extent, be controlled by the reaction conditions. As ligand conformations also determine the rod packing (i.e., more *cis* ligands leads to lower connectivity), it follows that the structures obtained can be directed by careful control of the reaction conditions. Furthermore, as lanthanide ions generally display higher coordination numbers than transition metals, the possibility exists of obtaining new structures with rod packings of higher connectivity than can be achieved for transition metals (by using a high content of *trans*-ligand conformation). Alternatively, low-connectivity rod packings can be obtained by using a high content of *cis*-ligand conformation.

Although coordination polymers based on rodlike SBUs have been extensively reviewed and the most likely network structures identified and predicted, these structures display rod packings mostly built by transition or main-group metals and rigid aromatic carboxylate ligands. The achievement of complicated rod packing nets requires the formation of architectures with more complex rod SBUs and link metrics. In this regard, the choice of flexible ligands is logical because such ligands often adopt a variety of conformations and coordination modes that offer the possibility of realizing complex SBUs and linking matrices, as shown in this current work.

Thermogravimetric (TG) Analysis

The TG curves of **1**–**3** exhibit similar two-step mass losses in the temperature range 30–800 °C (Figure 7). The first weight losses of 8.87 % (for **1**), 8.26 % (for **2**), and 12.24 % (for **3**) before 220 °C correspond to the removal of the noncoordinated and coordinated water molecules (calcd: 8.27 % for **1** and **2**, 11.75 % for **3**). The other mass losses of 51.99 % (for **1**), 51.52 % (for **2**), and 50.49 % (for **3**) in the temperature range 340–680 °C arise from the decomposition of the organic ligands (calcd: 53.11 % for **1** and **2**, 50.31 % for **3**). The total weight losses of 60.84 % (for **1**), 59.71 % (for **2**), and 62.71 % (for **3**) are in good accordance with the calculated values (61.38 % for **1** and **2**, 62.06 % for **3**; residue: lanthanide oxides).

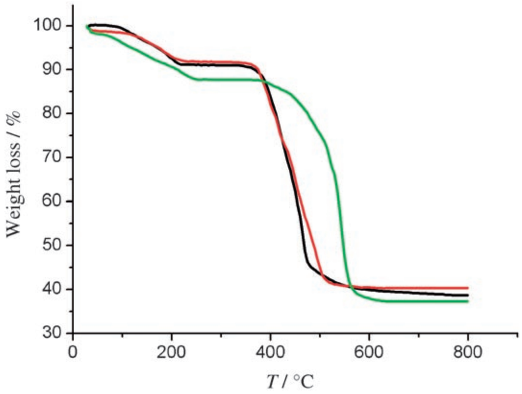


Figure 7. TG plots for **1** (black), **2** (red), and **3** (green).

Conclusions

We have reported three lanthanide coordination polymers constructed from infinite rod-shaped secondary building units, $[Nd_2(H_2O)_2(\textit{cis}\text{-chdc})_2(\textit{trans}\text{-chdc})]\cdot 2H_2O$ (**1**), $Nd_2(H_2O)_4(\textit{trans}\text{-chdc})_3$ (**2**), and $[Sm_2(H_2O)_2(\textit{cis}\text{-chdc})(\textit{trans}\text{-chdc})_2]\cdot 4H_2O$ (**3**). Compound **1** has a four-connected (pcu-type), **2** has a six-connected (hex-type), and **3** has an unprecedented five-connected rod packing architecture. The connectivities of the rod packing structures of **1**–**3** can be roughly predicted by the different ratios of the *cis* and *trans* configurations of the chdc^{2-} ligands according to their different coordination features presented in these network structures. Moreover, the configurations of the chdc^{2-} ligands are likely to be realized by adjusting the reaction temperatures and pH values. In this way, rational design of CPs built by lanthanide ions and chdc^{2-} ligands is achievable. Successful isolation of the compounds also indicates that the exploition of lanthanides and flexible organic ligands is an effective and desirable way to prepare novel functional CPs.

Experimental Section

General Procedures

All chemicals were commercially available and used without purification. Elemental analysis (C and H) was carried out with an Elementar Vario EL III analyzer. Nd and Sm were determined by a Jobin Yvon Ultima2 ICP atomic emission spectrometer. Infrared (IR) spectra were recorded with a PerkinElmer Spectrum One spectrometer as KBr pellets in the range 400–4000 cm^{-1}. TG analysis was performed with a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under nitrogen. X-ray powder diffraction (XRPD) was performed with a Rigaku DMAX 2500 diffractometer. Single-crystal X-ray diffraction was carried out on a Bruker SMART 1K diffractometer.

Syntheses

1: $Nd(NO_3)_3\cdot 6H_2O$ (0.22 g, 0.5 mmol) and chdcH$_2$ (*cis*/*trans* = 3:2, 0.17 g, 1.0 mmol) were dissolved in distilled water (20 mL), and the pH was adjusted to about 3.0 with dilute aqueous KOH. The solution was heated in a 25-mL teflon-lined reaction vessel at 130 °C for 50 h and then cooled to room temperature over 12 h. Colorless prism crystals of **1** were collected with a yield of about 72 %. Elemental analysis: calcd (%) for $C_{12}H_{19}NdO_8$: C 33.09, H 4.4, Nd 33.11; found: C 33.49, H 4.32, Nd 30.71.

2: $Nd(NO_3)_3\cdot 6H_2O$ (0.22 g, 0.5 mmol) and chdcH$_2$ (*cis*/*trans* = 3:2, 0.26 g, 1.5 mmol) were dissolved in distilled water (20 mL), and the pH was adjusted to about 8.0 with dilute aqueous KOH. The solution was heated at 180 °C for 80 h and then cooled to room temperature over 12 h. Colorless crystals of **2** were collected with a yield of about 48 %. Elemental analysis: calcd (%) for $C_{12}H_{19}NdO_8$: C 33.09, H 4.4, Nd 33.11; found: C 32.72, H 4.44, Nd 33.71.

3: $Sm(NO_3)_3{\cdot}6H_2O$ (0.22 g, 0.5 mmol) and $chdcH_2$ (*cis*/*trans* = 3:2, 0.17 g, 1.0 mmol) were dissolved in distilled water (20 mL), and the pH was adjusted to about 5.0 with dilute aqueous KOH. The solution was heated in a 25-mL teflon-lined reaction vessel at 130 °C for 50 h and then cooled to room temperature over 12 h. Colorless block crystals of **3** were collected with a yield of 64%. Elemental analysis: calcd (%) for $C_{24}H_{42}O_{18}Sm_2$: C 31.35, H 4.6, Sm 32.72; found: C 31.77, H 4.67, Sm 32.16.

X-ray Data Collection and Structure Solutions and Refinements

Diffraction intensities for **1**–**3** were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated $Mo_{K\alpha}$ radiation with a radiation wavelength of 0.71073 Å by using the ω-scan technique. All absorption corrections were performed with the SADABS program.[13] Structures were solved by direct methods and refined on F^2 by full-matrix least squares with the SHELXTL-97 program package.[14] All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were positioned geometrically. A summary of the crystallographic data and structure determination for **1**–**3** is provided in Table 1. CCDC-646833 (**1**), -646834 (**2**), and -646835 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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