

Two Novel Lanthanide Coordination Polymers: Synthesis, Structures, Fluorescence, and Thermal Properties

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Two novel 1-D chain lanthanide coordination polymers, $\{[Pr(\mu_2-L)_2(\eta^2-NO_3)(CH_3OH)(H_2O)_2]\cdot H_2O\}_n$ (1) and $\{[Ho(\mu_2-L)_2(\eta^2-NO_3)(CH_3OH)(H_2O)]\cdot H_2O\}_n$ (2) (HL = *N*-benzoyl-*N*'-(4-benzoxy)thiourea) have been prepared and characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction. The fluorescence properties and themostabilities of the two polymers were determined as well.

Keywords coordination polymers, crystal structures, fluorescence properties, thermal properties

INTRODUCTION

The field of coordination polymers and metal–organic frameworks has seen a tremendous expansion in research efforts over the past several years.^[1–9] As part of a study on the crystal engineering of network solids, a series of coordination polymers have been prepared using lanthanide salts and bridging ligands derived from carboxylate^[10–13] or pyridyl^[14–17] or sulfonate^[18] molecules, and so on. Among various multidentate species, compounds bearing carboxylate functions are often the most preferred and widely studied ligands for generating stable lanthanide coordination polymers, mainly because of the versatile ligating abilities of the –COO[–] moieties and the enhanced affinity of these metal ions towards such O donors.^[10–13] Thus, people have used many kinds of carboxylate ligands to prepare novel lanthanide coordination polymers.

It is to be pointed out that there are no examples of lanthanide coordination polymers constructed from the organic carboxylate compound *N*-benzoyl-*N*'-(4-benzoxy)thiourea (HL) in the references. In this contribution, we explore this type of novel polymers containing both HL and lanthanide ions. We utilized NaL to react with lanthanide ions to afford two novel complexes {[$Pr(\mu_2-L)_2(\eta^2-NO_3)(CH_3OH)(H_2O)_2$]·H₂O}_n (1) and {[$Ho(\mu_2-L)_2(\eta^2-NO_3)(CH_3OH)(H_2O)$]·H₂O}_n (2), characterized their single-crystal structures, and further studied their fluorescent and thermal properties. The emission spectra of the two complexes reflected that the ligands predominate the fluorescence properties.



EXPERIMENTAL

General Materials and Instruments

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. HL was prepared according to the literature method.^[19] Its sodium salt was prepared by the reaction of it with sodium methoxide.

IR spectra were recorded on a Nicolet NEXUS 470-FTIR spectrophotometer as KBr pellets in the 400–4000 cm⁻¹ region. Elemental analyses (C, H and N) were carried out on a FLASH EA1112 elemental analyzer. Fluorescence spectrum of the three complexes was characterized at room temperature by a F-4500 fluorescence spectrophotometer (240 nm/min). TG-DSC measurements were performed by heating the crystalline sample from 20 to 800°C at a rate of 10°C·min⁻¹ in air on a Netzsch STA 409PC differential thermal analyzer.

Synthesis of $[{\Pr(\mu_2-L)_4(\eta^2-NO_3) (CH_3OH) (H_2O)_2} \cdot H_2O]_n (1)$

NaL (16.1 mg, 0.05 mmol) in 3 mL of methanol solution was added dropwise to a methanol solution (4 mL) of

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 TABLE 1

 The crystallographic data for complexes 1 and 2

Compound	1	2
Formula	$C_{63.5}H_{54}N_{10}O_{25.5}Pr_2S_4$	C ₃₁ H ₂₇ N ₅ O ₁₃ HoS ₂
Formula weight	1775.27	906.63
T(K)	293(2) K	291(2) K
Crystal system	Triclinc	Triclinc
Space group	<i>P</i> -1	<i>P</i> -1
Crystal size(mm ³)	$0.20 \times 0.20 \times 0.20$	$0.20\times0.16\times0.16$
$a(\text{\AA})$	9.6062(19)	9.835(2)
b (Å)	9.817(2)	10.351(2)
<i>c</i> (Å)	21.220(4)	18.781(2)
α (°)	77.71(3)	84.61(3)
β (°)	80.65(3)	84.43(3)
γ (°)	76.73(3)	84.42(3)
$V(\text{\AA}^3)$	1889.4(6)	1887.1(7)
$Dc (Mg m^{-3})$	1.560	1.596
Z	1	2
$\mu (\mathrm{mm}^{-1})$	1.467	2.274
<i>F</i> (000)	891	902
Reflens collected/unique	18860 / 6631	19115/6641
	R(int) = 0.0198	R(int) = 0.1625
Data/restraints/parameters	6631/0/481	6641/0/459
Fina R indices [I>2sigma(I)]	$R_1 = 0.0344$	$R_1 = 0.1520$
	$wR_2 = 0.1155$	$wR_2 = 0.3718$
R indices (all data)	$R_1 = 0.0355$	$R_1 = 0.1708$
	$wR_2 = 0.1165$	$wR_2 = 0.3897$
Goodness-of-fit on F^2	1.205	1.223

Symmetry transformations used to generate equivalent atoms. For complex 1: #1 = -x+1, -y+1, -z; For complex 2: #1 = -x+1, -y+1, -z+1; #2 = -x+2, -y+1, -z+1.

Pr(NO₃)₃·6H₂O (43.5 mg, 0.1 mmol). The resulting colorless mixture was allowed to stand at room temperature. Good quality colorless crystals of **1** were obtained after one month. Yield: 58.2%. Anal. calcd.(%) for C_{63.5}H₅₄O_{25.5}N₁₀S₄Pr₂: C, 42.96; H, 3.09; N, 7.89; S, 7.23. Found: C, 42.86; H, 3.01; N, 8.06; S, 7.63. IR (cm⁻¹, KBr): 3381 (m), 3284 (m), 3179 (s), 2364 (m), 1938 (w), 1603 (s), 1560 (m), 1404 (s), 1336 (s), 1257 (s), 1177 (s), 1103 (m), 1021 (w), 891 (s), 837 (m), 784 (s), 721 (s), 706 (s), 664 (w), 626 (m), 511 (s), 470 (w).

Synthesis of ${[Ho(\mu_2-L)_2(\eta^2-NO_3)(CH_3OH)(H_2O)]}$ H₂O $_n$ (2)

The complex **2** was prepared in a manner analogous to that used to prepare **1**. Reaction of Ho(NO₃)₃·6H₂O with NaL gave **2** as colorless single crystals. Yield: 61%. Anal. calcd. (%) for $C_{62}H_{54}O_{26}N_{10}S_4Ho_2$: C, 41.07; H, 3.00; N, 7.72; S, 7.07. Found: C, 41.39; H, 3.26; N, 8.02; S, 7.62. IR (cm⁻¹, KBr): 3361 (m), 3278 (m), 1604 (s), 1536 (s), 1409 (s), 1336 (s), 1257(w), 1177 (m), 1103 (m), 1070 (w), 891 (m), 838 (m), 783 (s), 722 (s), 663 (w), 622 (w), 561 (w), 511 (w).

X-Ray Crystallography

Crystal data and experimental details for compounds **1** and **2** are contained in Table 1. All measurements were made on a Rigaku SATURN-724 imaging plate area detector with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.710$ 73 Å). Colorless prismatic single crystals of **1** ($0.20 \times 0.20 \times 0.20$ mm) and of **2** ($0.20 \times 0.16 \times 0.16$ mm) were selected and mounted on a glass fiber. All data were collected at a temperature of 291(2) K using the ω -2 θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The two structures were solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included, but not refined. The final cycle of full-matrix least squares refinement was based on 6631 observed reflections and 481 variable parameters for **1** and 6641 observed reflections and 459 variable parameters for **2**. All calculations were performed using the SHELX-97 crystallographic software package.^[20] Selected bond lengths and bond angles are listed in Table 2.

Beleeted					
1					
Pr(1)-O(24)#1	2.406 (3)	Pr(1)–O(3)	2.421(3)		
Pr(1)-O(4)	2.449 (3)	Pr(1)-O(27)	2.571(3)		
Pr(1)-O(20)	2.583 (4)	Pr(1)-O(21)	2.652(4)		
O(24)#1-Pr(1)-O(2)	87.40 (11)	O(24)#1-Pr(1)-O(4)	91.82(10)		
O(24)#1-Pr(1)-O(26)	76.94 (14)	O(4)—Pr(1)—O(25)	142.25(12)		
O(27) - Pr(1) - O(21)	132.38 (13	O(4)—Pr(1)—O(20)	120.61(12)		
O(2) - Pr(1) - O(3)	78.58 (11)	O(25)-Pr(1)-O(21)	100.17(14)		
O(26)–Pr(1)–O(21)	65.90 (14)	O(2) - Pr(1) - O(21)	125.18(11)		
O(27)–Pr(1)–O(25)	126.88 (12)	O(3)–Pr(1)–O(25)	134.04(11)		
O(27) - Pr(1) - O(20)	138.76 (12)	O(3)–Pr(1)–O(20)	73.84(12)		
O(26)–Pr(1)–O(27)	133.66 (14)	O(2)-Pr(1)-O(27)	72.45(11)		
O(3)–Pr(1)–O(26)	134.76 (13)	O(3) - Pr(1) - O(4)	79.95(10)		
O(24)#1-Pr(1)-O(3)	141.64 (12)	O(20) - Pr(1) - O(21)	48.32(13)		
O(4) - Pr(1) - O(21)	73.00 (12)	O(24)#1-Pr(1)-O(21)	142.21(13)		
O(26)-Pr(1)-O(25)	68.20 (13)	O(26)—Pr(1)—O(20)	86.90(15)		
O(2) - Pr(1) - O(25)	70.57 (12)	O(2)-Pr(1)-O(20)	80.23(12)		
O(4) - Pr(1) - O(27)	73.29 (11)	O(24)#1-Pr(1)-O(27)	70.81(12)		
O(2)—Pr(1)—O(26)	138.68 (13)	O(2)-Pr(1)-O(4)	143.93(11)		
	2	2			
Ho(1)-O(3)	2.267 (8)	Ho(1)-O(6)	80.23(12)		
Ho(1)-O(7)	2.532 (10)	Ho(1)-O(5)#1	2.302(8)		
Ho(1)-O(10)	86.90 (15)	Ho(1)-O(11)	2.394(9)		
Ho(1)-O(2)#2	2.303 (8)	Ho(1)–O(9)	2.400(10)		
O(3)-Ho(1)-O(6)	153.4 (3)	O(3)-Ho(1)-O(5)#1	85.1(3)		
O(9)-Ho(1)-O(7)	51.3 (3)	O(10)-Ho(1)-O(7)	140.6(3)		
O(2)#2-Ho(1)-O(7)	71.2 (3)	O(6)-Ho(1)-O(7)	75.5(3)		
O(3)-Ho(1)-O(7)	125.6 (3)	O(10)-Ho(1)-O(9)	134.3(3)		
O(2)#2-Ho(1)-O(9)	73.5 (3)	O(6)-Ho(1)-O(9)	126.8(3)		
O(3)-Ho(1)-O(9)	76.1 (3)	O(2)#2-Ho(1)-O(11)	144.2(3)		
O(5)#1-Ho(1)-O(11)	74.9 (3)	O(3)-Ho(1)-O(11)	76.4(3)		
O(2)#2-Ho(1)-O(10)	75.0 (3)	O(6)-Ho(1)-O(10)	86.3(3)		
O(3)-Ho(1)-O(10)	84.3 (3)	O(6)-Ho(1)-O(2)#2	92.1(3)		
O(3)-Ho(1)-O(2)#2	109.4 (3)	O(5)#1-Ho(1)-O(2)#2	139.7(3)		
O(6)-Ho(1)-O(5)#1	88.6 (3)	O(11)-Ho(1)-O(7)	135.4(3)		
O(5)#1-Ho(1)-O(7)	70.0 (3)	O(5)#1-Ho(1)-O(9)	74.1(3)		
O(11)-Ho(1)-O(9)	139.8 (3)	O(10)-Ho(1)-O(11)	70.4(3)		
O(6)-Ho(1)-O(11)	77.0 (3)	O(5)#1-Ho(1)-O(10)	145.2(3)		

TABLE 2Selected bond distances (Å) and angles (deg) for 1 and 2^a

RESULTS AND DISCUSSION

Crystal Structure of $[{Pr(\mu_2-L)_4(\eta^2-NO_3) (CH_3OH)(H_2O)_2} + H_2O]_n$ (1)

X-ray diffraction analysis of compound **1** shows that it crystallizes in the space group P_1 . Compound **1** contains an infinite chain $\{Pr(\mu_2-L)_4(\eta^2-NO_3)(CH_3OH)(H_2O)_2\}_n$, one crystallization water molecules. It is a double-cross one-dimensional coordination polymer, in which NO_3^- anion as a bidentate chelating ligand and the carboxylate group of L^- as a bidentate bridg-

ing ligand link the central ion Pr(III) ions to form a 1D chain (Figure 1).

There is only one crystallographically independent Pr(III) ion in the crystal lattice. As shown in Figure 1, each ninecoordinate Pr(III) ion is joined to the two oxygen atoms from chelated η^2 -NO₃, four oxygen atoms from four bridging μ_2 -L, one oxygen atom from methanol molecule and two oxygen atoms from two water molecules forming a distorted tricapped trigonal prism coordination polyhedron (Figure 2). The bond length of Pr-O is between 2.406(3) Å and 2.652(4)



FIG. 1. One-dimensional chain structure of polymer 1 (Hydrogen atoms and solvent molecules omitted for clarity).

Å (the average bond length of Pr-O being 2.518(6) Å). The Pr-O distances are within the range of those observed for other Pr(III) complexes with oxygen donor ligands,^[21–25] for example in { $[Pr(mptc)(H_2O)_4] \cdot _3H_2O$ }_n (H₃mptc = 6-methyl-2,3,5-pyridinetricarboxylic acid) (Pr-O: 2.389(2)–2.516(3) Å),^[21] [Ln(HPPDA)(PPDA)(H_2O)_2] \cdot 2H_2O (H₂PPDA = (2,3-f)-pyrazino(1,10)phenanthroline-2,3-dicarboxylic acid) (Pr-O: 2.440(3)–2.618(3) Å),^[22] {[$Pr(C_2O_4)(ClO_4)(H_2O)$]·Cl}_n (Pr-



FIG. 2. The coordination environment around the central Pr atom.

O: 2.44(2)–2.67(3) Å)^[23], {NH₄[Pr(OVA)₄]}_n (OVA = 2hydroxy-3-methoxybenzoate) (Pr-O: 2.4088(15)-2.5717(14) Å)^[24] and { $[Pr(pzdc)_{1.5}(H_2O)_3] \cdot 0.5H_2O$ }, (pzdc = 2,5pyrazinedicarboxylate) (Pr-O: 2.434(3)-2.529(3) Å).^[25] The bond angles around Pr(III) change within the scope of 51.2(2)°- $152.7(3)^{\circ}$. The intrachain distances between metallic cations are 5.471 Å for Pr1... Pr1A, which is largely shorter than that in the reported polymer ${[Pr(mptc)(H_2O)_4] \cdot _3H_2O_n}$ (10.116) Å),^[21] however, slightly longer than that in the polymer ${\rm NH}_{4}[{\rm Pr}({\rm OVA})_{4}]_{n}$ (4.516 Å).^[24] Obviously, this is due to the different coordination modes of the different carboxylate ligands. The dihedral angles between the phenyl rings C2-C6 (the mean deviation from the plane is 0.0097 Å) and C9–C14 (the mean deviation from the plane is 0.0071 Å) or C16–C20 (the mean deviation from the plane is 0.0036 Å) and C24-C29 (the mean deviation from the plane is 0.0097 Å) in the same ligand L^{-} are 7.1° or 29.0°, respectively.

In the solid-state structure, the 1-D chains pack each other through the Van der Waals interactions. Figure 3 gives the crystal packing structure of polymer **1**.

Crystal Structure of $\{[Ho(\mu_2-L)_2(\eta^2-NO_3) (CH_3OH)(H_2O)]\cdot H_2O\}_n$ (2)

X-ray diffraction analysis of compound **2** shows that it crystallizes in the space group Pî as polymer **1**. The structure of **2** is made up of a one-dimensional array of $[Ho(\eta^2-NO_3)(H_2O)_2]$ units bridged by μ_2 -L ligands. The ORTEP plot showing the structural unit of **2** is illustrated in Figure 4.



FIG. 3. Crystal packing of 1 in the solid state.

The Ho (III) atoms are eight-coordinated by two oxygen atoms from chelated η^2 -NO₃, four oxygen atoms from four bridging μ_2 -OOCC₆H₄N₂C₅O₂ and two oxygen atoms from one water and one methanol molecules. The coordination polyhedron is a slightly distorted bicapped trigonal prism (Figure 5). The bond length of Ho–O is between 2.259(7) Å and 2.561(9) Å. The average bond length of Ho–O is 2.375(6) Å. The Ho–O distances can be compared to those found in the reported Ho(III) coordination polymer {NH₄[Ho(OVA)₄]}_n Å (Ho–O: 2.259(3)–2.43(3) Å).^[24] The bond angle around Ho(III) changes within the scope of 51.2(2)°–152.7(3)°. The intrachain distances between metallic cations are 4.727 Å for Ho1... Ho1A and 5.117

Å for Ho1... Ho1B, respectively, which are consistent with that of the polymer $\{NH_4[Ho(OVA)_4]\}_n$ (4.825 Å).^[24] The dihedral angles between the phenyl rings C2–C6 (the mean deviation from the plane is 0.0145 Å) and C9–C14 (the mean deviation from the plane is 0.0301 Å) or C16–C20 (the mean deviation from the plane is 0.0036 Å) and C24–C29 (the mean deviation from the plane is 0.0063 Å) in the same ligand L⁻ are 26.0° or 165.8°, respectively. These values can be compared to the cases in polymer **1**.

In this complex, all the NO_3^- as a bidentate chelating ligand, the carboxylate group of L as a bidentate ligand bridging central Ho(III) ions form a novel 1D chain coordination polymer



FIG. 4. Perspective view of polymer 2 with atom labeling scheme (H atoms omitted for clarity).





FIG. 5. The coordination environment around the central Ho atom.

(Figure 6). Furthermore, these chains are connected by the Van der Waals interactions to construct three-dimensional networks (Figure 7).

To the best of our knowledge, the reported Ho(III) carboxylate-based coordination polymers are limited. Only several examples can be found in the references. For example, Czakis-Sulikowska and co-workers have reported the synthesis and properties of a Ho(III) complex ${[Ho(4,4-bipy)(CCl_2HCOO)_3] \cdot H_2O}_n$ with 4,4'-bipyridine and dichloroacetates.^[26] Cunha-Silva and co-workers have studied photoluminescence and catalysis studies of multi-functional rare-earth hybrid layered network, [Ho(H₂cmp)(H₂O)] (H₅cmp *N*-(carboxymethyl)iminodi(methylphosphonic acid).^[27] = Also, there are other several Ho(III) polymers built by succinic acid,^[28,29] 4-aminobenzoate, ^[30] and 5-nitroisophthalic acid.^[31] The successful preparation of polymer 2 gives us more chance to study the properties of this kind of coordination polymer.



FIG. 6. 1-D chain structure of 2 (the C₆H₅-C(O)-NH-C(S)-NH-C₆H₅- unit of L omitted for clarity).



FIG. 7. Crystal packing of **2** in the solid state along *a*-bxis.



FIG. 8. Fluorescence emission spectrum of the complexes **1** (a), **2** (b) and the corresponding ligand NaL (c) in the solid state.

IR Spectroscopy

The infrared spectral data (400–4000 cm⁻¹) of the two complexes are in perfect agreement with their single-crystal Xray analyses. The strong absorption bands at 1660 cm⁻¹ and 1400 cm⁻¹ are assigned to $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$ vibrations, respectively (1: 1603 cm⁻¹ and 1405 cm⁻¹; **2**: 1604 cm⁻¹and 1410 cm⁻¹), which are close to the reported values in the literatures.^[32] The difference between $v_{as}(COO^{-})$ and $v_s(COO^{-})$ is lower than 200 cm⁻¹, which indicates the μ_2 -bridging mode of the carboxylate group to the metal ion. Stretching vibration peak of v (N–H) in the free ligand appears at 3376 cm⁻¹, which can be found in the two complexes (1:3381 cm⁻¹; 2:3362 cm⁻¹). The peak of δ (CO–CH₃) can be found in 1405 cm⁻¹ for **1** or 1410 cm⁻¹ for **2**, respectively.

Fluorescence Spectrum

Recently, several coordination polymers containing Eu(III), Tb(III) or other lanthanide have been explored due to their attractive emissive properties.^[33,34] Usually metal–organic coordination polymers with lanthanide ion exhibit interesting photoluminescent properties. The fluorescence properties of complexes **1** and **2** and the corresponding ligand NaL were examined in the solid state at room temperature.

As shown in Figure 8, the emission of NaL and complexes 1 and 2 were observed in a range of 300–460 nm by selective excitation at 330 nm. The free NaL ligand shows two main emission peaks with at 399 nm and 427 nm, respectively, which is due to π - π * transitions. Complex 1 also shows two emission bands at 392 nm and 422 nm, respectively, which are similar to NaL. The fluorescence intensity of complex 1 is visible weakened. The complex 2 shows one broad emission band around 439 nm. Compared with the emission spectrum of NaL, red shift of 17 nm in 2 has been observed. Obviously, the fluorescence emission of the complexes 1 and 2 might be attributed to ligand-to-ligand charge transfer (L* \rightarrow L).^[35,36]

Thermogravimetric Analysis

The TG-DSC measurements of polymers 1 and 2 were determined in the range of $20-800^{\circ}$ in air.

As shown in Figure 9, polymer 1 underwent a three-step decomposition process, with its first weight loss occurring at $64-175^{\circ}$ C. The weight loss corresponded to one coordinated methanol molecule and two coordinated water molecules per formula unit (found 8.5%, calcd 8.4%). Increasing temperature



FIG. 9. Thermogravimetric curve of complex 1.



FIG. 10. Thermogravimetric curve of complex 2.

led to the second decomposition of the compound in the range of 187 to 516°C. The final decomposition of the compound occurred in the range of 516 to 600°C. The latter two steps of weight loss corresponded to the decomposition of the organic ligand and the nitrate (found 65.8%, calculated 65.9%). Finally, a plateau region is observed from 600 to 800°C, giving a green powder of mixture Pr_2O_3 and PrO_2 (found 25.68%). For polymer **1**, there are one weak endothermic peak (128°C), two weak exothermic peaks (205°C and 483°C), and one strong exothermic peak (598°C) in the DSC curve.

It can be seen from Figure 10, the polymer **2** indicated the fast weight loss process in the temperature of $50-275^{\circ}$ C, and then slowly lost weight from 275 to 600° C (found 63.8%). The total weight loss is corresponding to losses of solvent molecules, the organic ligand HL and the nitrate anion. Finally, a plateau region is observed from 600 to 800° C. A white amorphous residue is assigning to be Ho₂O₃(found 36.20%, calculated 35.7%). There are one weak endothermic peak (161° C) and one very strong exothermic peak at 258°C on the DSC curve of polymer **2**.

CONCLUSIONS

Two novel lanthanide coordination polymers with Nbenzoyl-N'-(4-benzoxy)thiourea have been prepared in solution. Their molecular structures were characterized by elemental analyses, IR data and single crystal X-ray analysis. They show novel double-cross one-dimensional chain structures. Their thermal data are consistent with the crystal data.

SUPPLEMENTARY MATERIALS

Crystallographic data for these structures reported in this paper in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 761427 and 761428 for the complexes **1** and **2** respectively. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

REFERENCES

- Biradha, K., Ramanan, A., and Vittal, J.J. Coordination polymers versus metal-organic frameworks. *Cryst. Growth Des.*, 2009, 9, 2969–2970.
- Constable, E.C. Silver coordination polymer-from simple complexes to functional networks. *Aust. I. Chem.*, 2006, 59, 1–2.
- Mueller, U., Schubert, M., Teich, F., Puetter, H., Schierle-Arndt, K., and Pastré, J. Metal-organic frameworks-prospective industrial applications. *J. Mater. Chem.*, 2006, 16, 626–636.
- Kesanli, B., and Lin, W. Chiral porous coordination networks: rational design and applications in enantioselective processes. *Coord. Chem. Rev.*, 2003, 246, 305–326.
- Krishnan, S.M., Supkowski, R.M., and LaDuca, R.L. Generation of threedimensional networks through aliphatic chain disorder in a divalent metal dicarboxylate/organodiimine coordination polymer system. *Cryst. Growth Des.*, 2009, 9, 358–363.
- Zhang, X.-M., Fang, R.-Q., and Wu, H.-S. A twelve-connected Cu₆S₄ cluster-based coordination polymer. J. Am. Chem. Soc., 2005, 127, 7670– 7671.
- Fox, S., Büsching, I., Barklage, W., and Strasdeit, H. Coordination of biologically important α-amino acids to calcium(II) at high PH: insights from crystal structures of calcium α-aminocarboxylates. *Inorg. Chem.*, 2007, 46, 818–824.
- Sun, J., Zhou, Y., Fang, Q., Chen, Z., Weng, L., Zhu, G., Qiu, S., and Zhao, D. Construction of 3D layer-pillared homoligand coordination polymers from a 2D layered precursor. *Inorg. Chem.*, 2006, 45, 8677–8684.
- Kumar, D.K., Jose, D.A., Das, A., and Dastidar, P. From diamondoid network to (4,4) net: effect of ligand topology on the supramolecular structural diversity. *Inorg. Chem.*, 2005, 44, 6933–6935.
- Zhu, Q.L., Sheng, T.L., Fu, R.B., Hu, S.M., Chen, J.S., Xiang, S.H., Shen, C.J., and Wu, X.T. Novel structures and luminescence properties of lanthanide coordination polymers with a novel flexible polycarboxylate ligand. *Cryst. Growth Des.*, 2009, 9, 5128–5134.
- Prasad, T.K., and Rajasekharan, M.V. Cerium(IV)-lanthanide(III)pyridine-2,6-dicarboxylic acid system: coordination salts, chains, and rings. *Inorg. Chem.*, 2009, 48, 11543–11550.
- Zhao, X.-Q., Zhao, B., Wei, S., and Cheng, P. Synthesis, structures, and luminescent and magnetic properties of Ln-Ag heterometal-organic frameworks. *Inorg. Chem.*, 2009, 48, 11048–11057.
- Michaelides, A., and Skoulika, S. Crystallographic evidence for ionic molecular building blocks in the assembly of a two-dimensional metal–organic framework. *Cryst. Growth Des.*, 2009, 9, 4998–5002.
- Song, X.Q., Zhou, X.Y., Liu, W.S., Dou, W., Ma, J. X., Tang, X.L., and Zheng, J.R. Synthesis, structures, and luminescence properties of lanthanide complexes with structurally related new tetrapodal ligands featuring salicylamide pendant arms. *Inorg. Chem.*, 2008, 47, 11501–11513.
- Bučar, D.-K., Papaefstathiou, G.S., Hamilton, T.D., and MacGillivray, L.R. A lanthanide-based helicate coordination polymer derived from a rigid monodentate organic bridge synthesized in the solid state. *New J. Chem.*, 2008, 797–799.
- Kelly, N.R., Goetz, S., Batten, S.R., and Kruger, P.E. Synthesis and structural characterisation of lanthanide coordination polymers featuring 4,4',6,6'-tetra-carboxy-2,2'-bipyridine and rare network topology. *Cryst. Eng. Comm.*, **2008**, 1018–1026.
- de Lill, D.T., de Bettencourt-Dias, A., and Cahill, C.L. Exploring lanthanide luminescence in metal-organic frameworks: synthesis, structure, and guestsensitized luminescence of a mixed europium/terbium-adipate framework and a terbium-adipate framework. *Inorg. Chem.*, 2007, 46, 3960– 3965.
- Yang, X.P., Rivers, J.H., McCarty, W.J., Wiester, M., and Jones, R.A. Synthesis and structures of luminescent ladder-like lanthanide coordination polymers of 4-hydroxybenzenesulfonate. *New J. Chem.*, 2008, 790–793.
- Zhang, Y.-M., Wei, T.-B., and Gao, L.-M. Synthesis and biological activity of *N*-aroyl-N'-substituted thiourea derivatives. *Syn. Commun.*, 2001, 31, 3099-3105.

- Sheldrick, G.M. SHELX-97, Program for the Solution and Refinement of Crystal Structures; University of Göttingen: Germany. 1997.
- Yang, A.-H., Zhao, L.-H., Quan, Y.-P., Gao, H.-L., Cui, J.-Z., Shi, W., and Cheng, P. Formation of the water layer in lanthanide coordination polymers with 6-methyl-2,3,5-pyridinetricarboxylate as a novel bridging ligand. *Cryst. Growth Des.*, **2010**, 10, 218–223.
- 22. Weng, Z.H., Liu, D.C., Chen, Z.L., Zou, H.H., Qin, S.N., and Liang, F.P. Two types of lanthanide coordination polymers of (2,3-f)pyrazino(1,10)phenanthroline-2,3-dicarboxylic acid: Syntheses, structures, and properties. *Cryst. Growth Des.*, **2009**, 9, 4163–4170.
- Ma, J.-X., Huang, X.-f., Wei, R.-P., Zhou, L.-Q., and Liu, W.-S. Hydrothermal synthesis and crystal structures of two lanthanide coordination polymers with novel tetradentate- coordinated perchlorates. *Inorg. Chim. Act.*, 2009, 362, 3440–3446.
- Zhang, M.-L., Xin, F.-G., and Wang, Z.-L. Syntheses, characterization, and crystal structures of coordination polymers: {NH₄[Ln(OVA)₄]}_n (Ln = Pr, Nd, Gd, and Ho; OVA = 2-hydroxy-3-methoxybenzoate). *J. Coord. Chem.*, 2009, 62, 2347–2357.
- Yang, P., Wu, J.-Z., and Yu, Y. Ultramicroporous channel lanthanide coordination polymers of 2,5-pyrazinedicarboxylate. *Inorg. Chim. Acta.*, 2009, 362, 1907–1912.
- Czakis-Sulikowska, D., Czylkowska, A., Markiewicz, M., and Frajtak, M. Synthesis and Properties of Complexes of Gd(III), Tb(III), Ho(III) and Tm(III) with 4,4'-Bipyridine and Dichloroacetates. *Pol. J. Chem.*, 2009, 83, 1893–1901.
- Pillinger, M., Rocha, J., Silva, P., Cunha-Silva, L., Ananias, D., Lima, S., Mafra, L., Carlos, L.D., Valente, A.A., and Paz, F. A. A. Multi-functional rare-earth hybrid layered networks: photoluminescence and catalysis studies. *J. Mater. Chem.*, **2009**, 19, 2618–2632.
- Bernini, M.C., Garro, J.C., Brusau, E.V., Narda, G.E., and Varetti, E.L. Experimental and theoretical vibrational study of tetraaqua-

tris(succinate)diholmium(III) hexahydrate, a bidimensional hybrid coordination polymer. J. Mol. Struct., **2008**, 888, 113–123.

- Yu, B., Wang, X.Q., Wang, R.J., Shen, G.Q., and Shen, D.Z. Poly[[diaqua-mu(6)-succinato-di-mu(5)-succinato-diholmium(III)] monohydrate]. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2006, 623, M1620–M1622.
- Feng, Y.L., Xu, J.S., Kuang, D.Z., and Peng, Y.L. A twodimensional holmium(III) coordination polymer: poly[amino-tris(μ-4aminobenzoato)holmium(III)]. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2007, 63, M2338–U843.
- Ren, Y.X., Chen, S.P., and Gao, S.L. Preparation, crystal structure and enthalpy change of formation of the reaction in liquid phase of a new three-dimensional mixed-ligand holmium(III) coordination polymer based on strong pi-pi stacking interactions. *Chin. J. Chem.*, 2007, 25, 63–67.
- Marten, J., Seichter, W., and Weber, E. 3-(Arylhydrazono)pentane-2, 4diones and their complexes with copper(II) and nickel(II): synthesis and crystal structures. Z. Anorg. Allg. Chem., 2005, 631, 869–877.
- de Bettencourt-Dias, A. Isophthalato-Based 2D coordination polymers of Eu(III), Gd(III), and Tb(III): enhancement of the terbium-centered luminescence through thiophene derivatization. *Inorg. Chem.*, 2005, 44, 2734– 2741.
- Chandler, B.D., Cramb, D.T., and Shimizu, G.K.H. Microporous metal-organic frameworks formed in a stepwise manner from luminescent building blocks. J. Am. Chem. Soc., 2006, 128, 10403–10412.
- Xu, H., Cao, Z.Y., Sang, Y.L., and Hou, H.W. Two Pb(II) coordination polymers constructed from dicarboxamido-(2-pyridyl)-pyridine by varying ratios of mixed solvents. *Inorg. Chem. Commun.*, 2006, 12, 1436– 1440.
- 36. Xiong, R.G., Zuo, J.L., You, X.Z., Abrahams, B.F., Bai, Z.P., Che, C.M., and Fun. K.K. Opto-electronic multifunctional chiral diamondoid-network coordination polymer: bis{4-[2-(4-pyridyl)ethenyl]benzoato}zinc with high thermal stability. *Chem. Commun.*, 2000, 20, 2061–2062.

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