

含吡啶-2,5-二羧酸稀土-锌配位聚合物的合成结构和性能

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Gd_2O_3 , $Zn(CH_3COO)_2 \cdot 2H_2O$ 和吡啶-2,5-二羧酸(H_2pydc)的水热反应导致一个新颖的钆-锌配位聚合物 $[La_2Zn_2(pydc)_3(H_2O)_2]_n(1)$ 。化合物1的晶体属单斜晶系,空间群 $P2_1/c$, $a=9.5869(1)$, $b=20.4862(3)$, $c=10.1105(2)$ Å, $\beta=97.4890(10)^\circ$, $V=1968.76(5)$ Å³, $Z=4$ 。在同样的条件下, Er_2O_3 或 Tb_4O_7 , $Zn(CH_3COO)_2 \cdot 2H_2O$ 和 H_2pydc 的水热反应产生了与化合物1结构不同的配位聚合物 $[Ln_2Zn(pydc)_3(H_2O)_8 \cdot H_2O]_n$ ($Ln=Er(2)$; $Ln=Tb(3)$)。化合物2和3异质同晶,空间群 $P\bar{1}$, 对2: $a=7.8708(7)$, $b=9.2665(8)$, $c=13.0232(11)$ Å, $\alpha=75.295(1)^\circ$, $\beta=75.000(2)^\circ$, $\gamma=79.109(2)^\circ$, $V=879.67(13)$ Å³, $Z=1$; 对3: $a=7.9105(5)$, $b=9.3453(6)$, $c=13.0005(9)$ Å, $\alpha=75.3380(10)^\circ$, $\beta=75.0460(10)^\circ$, $\gamma=79.0050(10)^\circ$, $V=890.17(10)$ Å³, $Z=1$ 。X-射线单晶结构研究表明化合物1是一个三维网状结构,而化合物2和3为管状结构。热重分析研究表明所有化合物在380℃以下稳定。

关键词: 稀土 配位聚合物 水热反应

分类号: O614.33 O614.24+1

Preparation, Structure and Property of Novel Lanthanide(III)-Zinc(II) Coordination Polymers Containing Pyridine-2,5-dicarboxylic Ligand

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Hydrothermal reaction of La_2O_3 , $Zn(CH_3COO)_2 \cdot 2H_2O$ and pyridine-2,5-dicarboxylic acid (H_2pydc) in water gave rise to a La(III)-Zn(II) coordination polymer, $[La_2Zn_2(pydc)_3(H_2O)_2]_n(1)$, which crystallizes in monoclinic space group $P2_1/c$ with $a=9.5869(1)$, $b=20.4862(3)$, $c=10.1105(2)$ Å, $\beta=97.4890(10)^\circ$, $V=1968.76(5)$ Å³, $Z=4$. However, under the same condition, hydrothermal reaction of Er_2O_3 or Tb_4O_7 , $Zn(CH_3COO)_2 \cdot 2H_2O$ and H_2pydc resulted in the formation of a polymer $[Ln_2Zn(pydc)_3(H_2O)_8 \cdot H_2O]_n$ ($Ln=Er(2)$; $Ln=Tb(3)$). Compound 2 and 3 are isomorphous and crystallize in triclinic space group $P\bar{1}$ with $a=7.8708(7)$, $b=9.2665(8)$, $c=13.0232(11)$ Å, $\alpha=75.295(1)^\circ$, $\beta=75.000(2)^\circ$, $\gamma=79.109(2)^\circ$, $V=879.67(13)$ Å³, $Z=1$ for 2, and $a=7.9105(5)$, $b=9.3453(6)$, $c=13.0005(9)$ Å, $\alpha=75.3380(10)^\circ$, $\beta=75.0460(10)^\circ$, $\gamma=79.0050(10)^\circ$, $V=890.17(10)$ Å³, $Z=1$ for 3. All polymers have been characterized by single crystal X-ray diffraction analyses. 1 displays a three-dimensional network structure, while the crystal structure of 2 and 3 possess a tubule shape structure. Thermal gravimetric analysis studies of 1 and 2 display that the frameworks of the all compounds exist stably below 380℃ although the discrete and coordination water molecules lost in the range of 50~260℃.

Keywords: lanthanide coordination polymer hydrothermal synthesis

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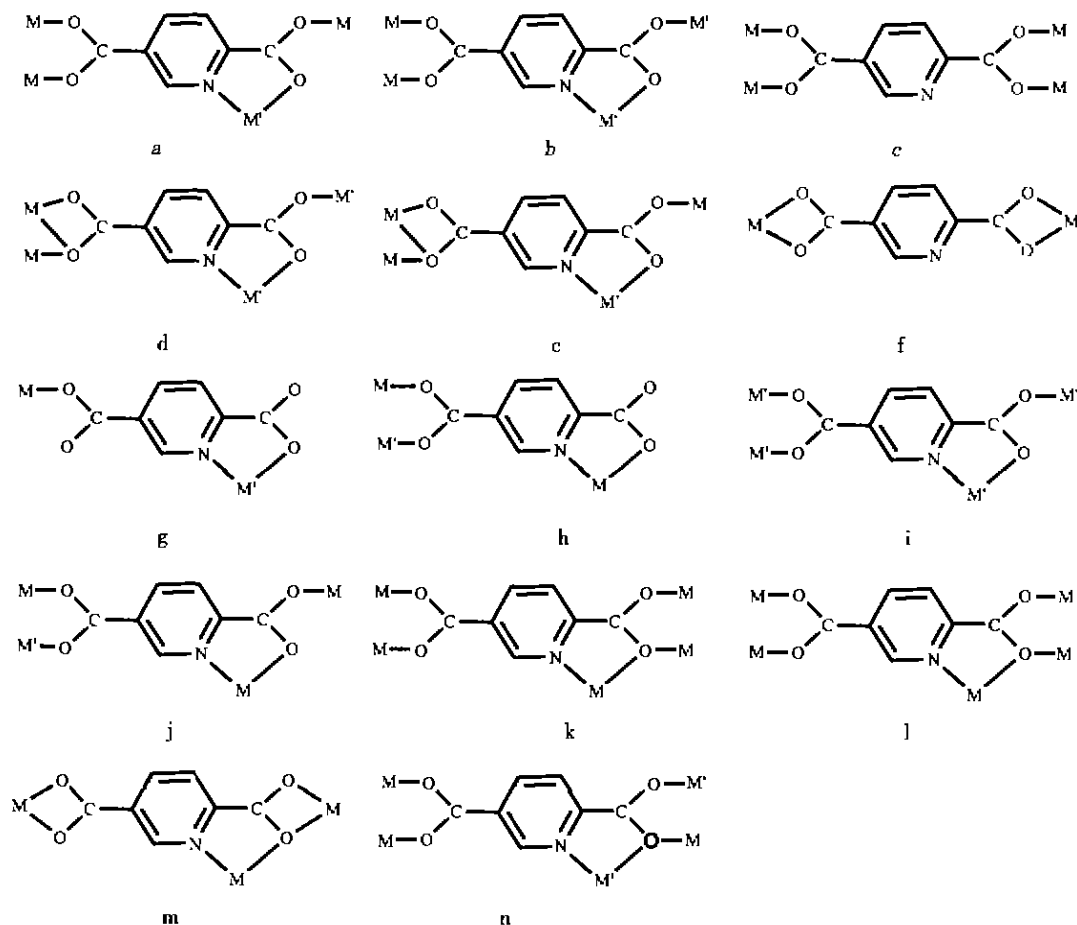
0 Introduction

Recently, heterometallic coordination complexes containing Lanthanide-transition metal have extremely attracted the attention of both physicists and chemists because they possess potential application on magnetic, luminescent and fiber optical materials as well as La-doped semiconducting technology. However, the studies are essentially focused on $\text{Ln}-\text{M}$ ($\text{M} = \text{Cu}, \text{Co}, \text{Cr}$) compounds of 3d and 4f systems^[1-11], although several $\text{Ln}-\text{M}'$ ($\text{M}' = \text{Zn}, \text{Cd}, \text{Hg}$) chalcogenide compounds were reported, of which many were discrete molecule^[12-15].

From coordination chemistry point of view, since $\text{Ln}(\text{III})$ displays a large and variable coordination number^[16], the control of the coordination spheres around $\text{Ln}(\text{III})$ thus mainly depends on the pre-organization of the coordinating units which limits the structural flexi-

bility and increases the thermodynamic stability^[17]. Therefore, the selection of the suitable ligand are very important during the preparation of the compounds. Some macrocyclic and compartmental Schiff bases have been selected as ligands and several $\text{Ln}(\text{III})$ or $\text{Ln}(\text{III})-\text{M}(\text{II})$ ($\text{M} = \text{Zn}, \text{Fe}$) compounds with discrete structures have been systematically studied^[15,18]. Surprisingly, up to now, $\text{Ln}(\text{III})-\text{Zn}(\text{II})$ coordination polymers containing carboxylic acid ligand have been explored less attention, although a $\text{Sm}(\text{III})-\text{Zn}(\text{II})-\text{Se}(\text{Te})$ polymer and several $\text{Ln}(\text{III})-\text{Zn}(\text{II})$ compounds with discrete structures have recently appeared in literature^[19,20].

To prepare lanthanide-transition metal polymers, the rigid ligand of multifunctional carboxylic acid containing hybrid atom is one of the several best choices. Pyridine-2, 5-dicarboxylic acid possesses many possible coordination modes, as shown in Scheme 1, and may be a good choice for bridge ligand to construct $\text{Ln}-\text{Zn}$



Scheme 1 Coordination modes of pydc ligand

coordination polymers. By the conventional synthetic method, unfortunately, the reaction of lanthanide nitrate or perchlorate and transition-metal salt with ligand in solution form uncharacterized precipitate that does not dissolve in water and common organic solvents. It was very apparent that the reaction speed must be lowered to avoid the quick polymerization. Hydrothermal technique was employed to obtain single crystals suitable for X-ray analysis. Thus, the directed reaction of lanthanide metal oxide with zinc salt and H_2pydc under hydrothermal condition generated a series of $Ln(III)-Zn(II)$ coordination polymers, $[La_2Zn_2(pydc)_5(H_2O)_2]_n$ (**1**), $[Er_2Zn(pydc)_4(H_2O)_3 \cdot H_2O]_n$ (**2**), $[Tb_2Zn(pydc)_4(H_2O)_3 \cdot H_2O]_n$ (**3**), having network or tubule shape structure. Herein, the reported are preparation, crystal structures, and thermal stability of these polymers.

1 Results and Discussion

1.1 Syntheses and Structures

In the study of the $Ln(III)-Zn(II)$ -dicarboxylate reaction system, it was very difficult to grow single crystal suitable for X-ray analysis by conventional solution synthetic method and quickly entrains uncharacterized precipitate which does not dissolve in most of common solvents. In order to solve the problem, selection of reaction materials and synthesis technique were tried. Finally, we were succeeded in starting materials of lanthanide metal oxide, transition-metal salts and H_2pydc and hydrothermal technique. By the hydrothermal reaction of La_2O_3 (lanthanide metal oxide in group 1), $Zn(CH_3COO)_2 \cdot 2H_2O$, H_2pydc and H_2O at $170^\circ C$, crystalline product of **1** was obtained with high yield. X-ray single crystal diffraction analysis revealed that the structure of **1** constitutes from the neutral basic unit structure of $[La_2Zn_2(pydc)_5(H_2O)_2]$, as shown in Fig. 1. Each $Zn(II)$ atom is chelated by two oxygen and two nitrogen atoms of different $pydc$ ligand and further coordinated by oxygen atom of carboxylate group of another $pydc$ ligand to form a highly-distorted trigonal bipyramidal coordination geometry. The bond length of $Zn-O$ and $Zn-N$ range from $1.996(4) \sim 2.048$

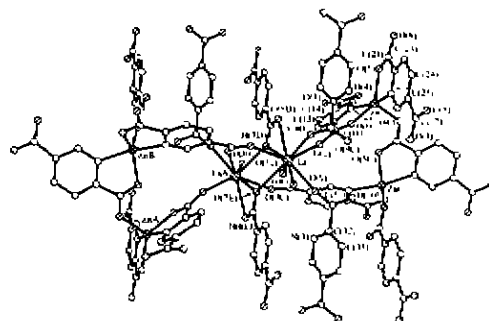


Fig. 1 Building block structure of **1**

(4) Å and $2.082(5) \sim 2.094(5)$ Å, respectively. The bond angles of $N(1)-Zn-O(1)$, $N(2)-Zn-O(5)$, $O(1)-Zn-O(5)$ and $O(1)-Zn-O(6C)$ are $79.53(18)$, $78.26(18)$, $135.40(19)$ and $112.12(18)^\circ$, respectively. Each La atom is coordinated by nine oxygen atoms, of which eight from carboxylate groups of $pydc$ ligands, one from water molecule. The La-O bond lengths fall in range $2.401(4) \sim 2.732(4)$ Å. All O-La-O bond angles range from $48.23(12)$ to $153.27(16)^\circ$. Adjacent La atom is linked together through bridging oxygen atom of carboxylate groups of $pydc$ ligand. The La and Zn atoms are linked together by carboxylate groups of $pydc$ ligands to generate an extended three-dimensional network structure (Fig. 2). Scheme 1(a), (c) and (d) demonstrate the coordination modes of $pydc$ ligand in **1**. The N donor of the $pydc$ ligand ligates to Zn sites and the O donor of the $pydc$ ligand is bonded to different metal atoms (La or Zn).

In general, the lanthanide series can be divided

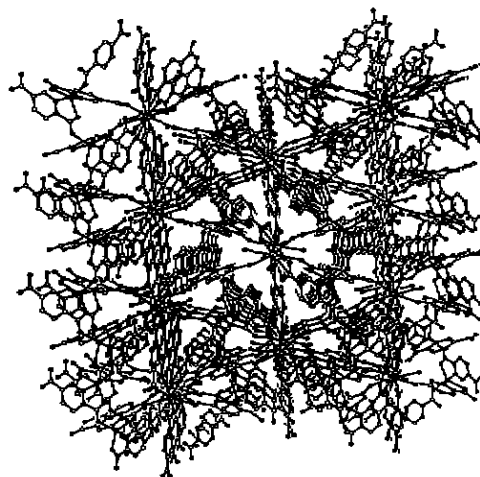


Fig. 2 Packing structure of **1** along a axis

into three groups according to their masses: the lighter one (La-Pm, group 1), the middle one (Sm-Dy, group 2), and the heavier one (Ho-Lu, group 3). Under the same condition, hydrothermal reaction of Er_2O_3 from group 3, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and H_2pydc resulted in a crystalline product of **2** with high yield. X-ray diffraction analysis showed that the crystal structure of **2** is completely different that of **1**. Its structure consists of $\text{Er}_2\text{Zn}(\text{pydc})_4$, coordination water and discrete water molecule, as shown in Fig. 3. The O donor and N atom of pydc ligand not only coordinate with Zn atom, but also coordinate with Er atom. The coordination mode of the pydc ligand is shown in Scheme 1 (g) and (h). Each Zn atom is chelated by two nitrogen and oxygen atoms of two pydc ligands to form like planar coordination and further coordinated by two oxygen atom of carboxylate group of two pydc ligands from up and down apices direction to form octahedral geometry. The Zn atom coordination can be viewed as sharing square

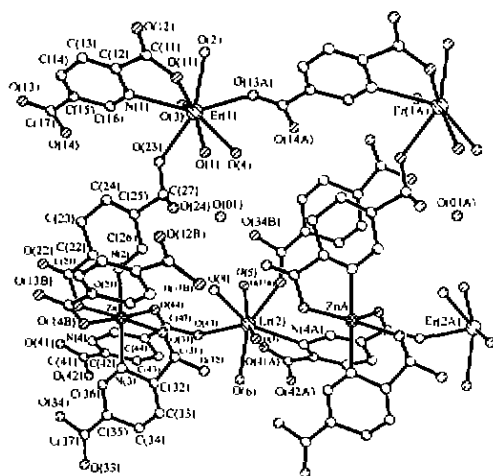


Fig. 3 Unit structure of **2**

double-pyramid geometry. The distance of Zn-O range from 2.01(3) ~ 2.43(3) Å. The Zn-N is 2.05(4) and 2.09(3) Å. Each Er(III) is coordinated by one N and three oxygen atoms from three pydc ligands and four O atoms from coordinated water molecules. The bond length of the Er-O range from 2.23(3) ~ 2.49(2) Å. The distance of Er(1)-N(1) and Er(2)-N(2) is 2.58(2) and 2.44(3) Å, respectively. Three Er and two Zn atoms form a pentacyclic ring $[\text{Er}_3\text{Zn}_2]$ construct blocking through pydc ligand. The subunit $[\text{Er}_3\text{Zn}_2]$ is further linked into infinite structure through pydc ligand. One water molecule lies in Er_3Zn_2 center. At the same time, the ligand of the coordinated to Zn atoms from peak of the pyramid further coordinated to Er atom to generate spring tube. Thus, whole framework displays a 2D helical tubule structural type (Fig. 4). Since existence of coordination water molecule and non-bonded oxygen atom of carboxylate group, the 2D structure was further linked 3D packing structure through hydrogen bond interaction of neighbor tube units.

If Th_4O_7 replaced Er_2O_3 , the heating reaction of Th_4O_7 , $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and H_2pydc led to the formation of a crystalline product of **3**. The crystal structure of **3** is isomorphous to that of **2**, only very small metric differences have been observed for the three compounds. Because the radius of a Th(III) ion is slightly smaller than that of a Er(III) ions. Thus all of the metal-ligand bonds in **3** are slightly longer than the corresponding bonds in **2**, as compared in Table 2. At the same time, all of bond angles in compound **3** have a slightly difference corresponding to that of complex **2**.

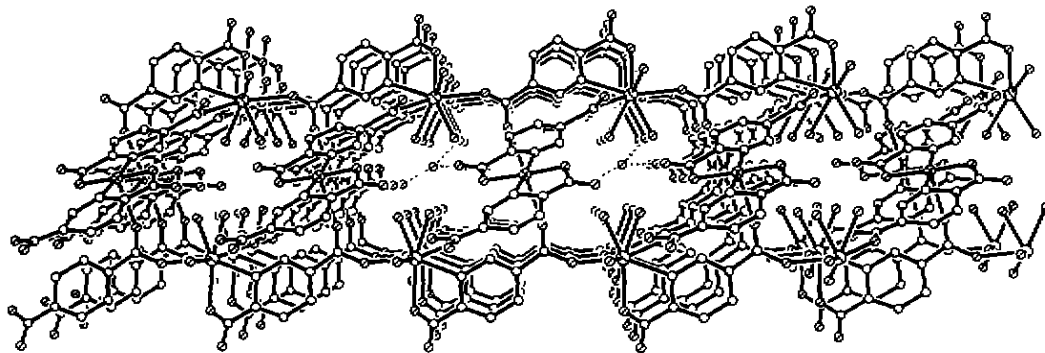


Fig. 4 Packing structure of **2** along *a* axis

In above studies, representative rare-earth metals from each group were selected and investigated. We find that there is a slight difference among three groups. At first, in rare-earth metal coordination number, group 1 nine-coordinated and group 3 is eight-coordinated; with the change of coordinated number of rare-earth ions from different group, the coordinated number of zinc ion also generates change from five to six. Second, the coordination modes or structures are greatly different.

1.2 Thermal Gravimetric Analyses

In order to examine the thermal stability of these coordination polymers, thermal gravimetric analyses (TGA) were carried out for compound 1 and 2. Polycrystalline samples of complex 1 and 2 were each heated from 50°C to 596°C in nitrogen gas. The TGA curve for 1 displays that the first weight loss of 3.092% between 110 to 255°C corresponds to the loss of two coordination water (calculated: 2.84%), leaving a framework of $[\text{La}_2\text{Zn}(\text{pydc})_3]$. This framework structure can exist stably in range of 255 ~ 380°C and decomposes slowly above 380°C. The TGA curve for 2 displays that the first weight loss of 4.071% between 50 to 150°C corresponding to the loss of three water molecules (calculated: 4.42%), the second step starts at 150°C and stops at 220°C corresponding loss of six coordinated water molecules to turn into $[\text{Er}_2\text{Zn}(\text{pydc})_4]$. The decomposition of $[\text{Er}_2\text{Zn}(\text{pydc})_4]$ starts above 360°C.

2 Experimental

2.1 Materials and Physical Techniques

All reagents were commercially available and used without further purification. The IR spectra were recorded on a Magna750 FT-IR spectrophotometer in range of 4000 ~ 400 cm^{-1} using the KBr pellet technique. Elemental analysis of C, H, N was carried out by the chemistry analysis group of this institute with a Perkin-Elmer model 240C automatic instrument. The magnetic susceptibility data were collected as polycrystalline samples at an external field of 1KG on a Quantum Design PPMS Model 6000 magnetometer in the temperature range from 5 to 300K. The output data

were corrected for experimentally determined diamagnetism of the sample holder and the diamagnetism of the samples calculated from the Pascal's constants^[21].

2.2 Syntheses of Complexes

2.2.1 Synthesis of $[\text{La}_2\text{Zn}(\text{pydc})_3(\text{H}_2\text{O})_2]_n$ (1)

The mixture of $\text{Zn}(\text{CH}_3\text{COO}) \cdot 2\text{H}_2\text{O}$ (0.110g, 0.5mmol), La_2O_3 (0.081g, 0.25mmol), pyridine-2,5-dicarboxylic acid (0.210g, 1.25mmol) and 16mL H_2O were sealed in a 25mL stainless-steel reactor with Teflon liner and heated at 170°C for 80hour, then slowly cooled to 20°C at 1.5625°C per hour. The light orange crystals of 1 were obtained in yield 65%. IR (KBr pellet, cm^{-1}): 3408(br, m), 1684(br, s), 1670(br, s), 1622(br, s), 1589(vs), 1404(vs), 1365(vs), 1286(m), 1043(m), 839(s), 764(s), 523(m). $\text{C}_{35}\text{H}_{19}\text{La}_2\text{N}_5\text{O}_{22}\text{Zn}_2$ (1270.12), Calcd. C: 33.10, H: 1.51, N: 5.52%. Found C: 33.21, H: 1.59, N: 5.57%.

2.2.2 Synthesis of $[\text{Er}_2\text{Zn}(\text{pydc})_4(\text{H}_2\text{O})_8 \cdot \text{H}_2\text{O}]_n$ (2)

The reaction process is similar to compound 2, only replacement of Sm_2O_3 with Er_2O_3 . Yield: 73%. IR (KBr pellet, cm^{-1}): 3232(br, m), 1647(vs), 1610(vs), 1587(vs), 1558(vs), 1481(m), 1398(vs), 1362(vs), 1348(vs), 1286(m), 1043(m), 823(m), 764(s), 696(m), 534(m), 513(m). $\text{C}_{28}\text{H}_{30}\text{Er}_2\text{N}_4\text{O}_{25}\text{Zn}$ (1222.45), Calcd. C: 27.51, H: 2.47, N: 4.58%. Found C: 27.64, H: 2.57, N: 4.51%.

2.2.3 Synthesis of $[\text{Tb}_2\text{Zn}(\text{pydc})_4(\text{H}_2\text{O})_8 \cdot \text{H}_2\text{O}]_n$ (3)

The reaction process is similar to compound 2, only replacement of Sm_2O_3 with Tb_4O_7 . Yield: 73%. IR (KBr pellet, cm^{-1}): 3219(br, m), 1647(s), 1608(vs), 1585(vs), 1554(s), 1481(m), 1398(s), 1360(vs), 1346(vs), 1286(m), 1041(m), 823(m), 764(s), 696(m), 532(m), 509(m). $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_{25}\text{Tb}_2\text{Zn}$ (1205.77), Calcd. C: 27.89, H: 2.51, N: 4.65%. Found C: 27.76, H: 2.49, N: 4.62%.

3 Crystallography

Single crystals of suitable size for the seven compounds were selected and coated with epoxy glue and

mounted on glass fiber in a random orientation. The crystal data and data collection parameters to **1**, **2**, and **3** are summarized in Table 1. Only special feature of the analysis is noted here. The intensity data of **1**~**3** were collected on a SIEMENS SMART CCD diffrac-

tometer with graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation in the ω - 2θ Scanning mode at room temperature. The data were corrected for Lorentz and Polarization effects as well as absorption. The structure was solved using direct methods. The weight

Table 1 Crystal Data for **1**, **2**, and **3**

compound	1	2	3
formula	$\text{C}_{35}\text{H}_{19}\text{La}_2\text{N}_3\text{O}_{12}\text{Zn}_2$	$\text{C}_{28}\text{H}_{30}\text{Er}_2\text{N}_4\text{O}_{23}\text{Zn}$	$\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_{23}\text{Th}_2\text{Zn}$
Fw	1270.12	1221.45	1205.77
crystal size/mm	$0.22 \times 0.14 \times 0.10$	$0.12 \times 0.27 \times 0.06$	$0.68 \times 0.20 \times 0.08$
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	9.58690(10)	7.8708(7)	7.9105(5)
$b/\text{\AA}$	20.4862(13)	9.2665(8)	9.3453(6)
$c/\text{\AA}$	10.1105(2)	13.0232(11)	13.0005(9)
$\alpha/^\circ$	90	75.2950(10)	75.3380(10)
$\beta/^\circ$	97.4890(10)	75.000(2)	75.04600(10)
$\gamma/^\circ$	90	79.109(2)	79.0050(10)
$V/\text{\AA}^3$	1968.76(5)	879.67(13)	890.17(10)
Z	4	1	1
$\rho_{\text{calc}}/(\text{g} \cdot \text{cm}^{-3})$	2.143	2.308	2.249
μ/mm^{-1}	3.428	5.512	4.706
T/K	293(2)	293(2)	293(2)
$\lambda(\text{Mo K}\alpha)/\text{\AA}$	0.71073	0.71073	0.71073
reflections collected	7294	4554	4669
unique reflections	3456	3729	3795
observed reflections ($P = 2.0\sigma(F)$)	3454	3727	3795
parameters	299	542	542
S on F^2	1.062	1.021	0.998
R_1^a	0.0380	0.0512	0.0266
R_w^b	0.0814	0.1114	0.0693
$\Delta\rho_{\text{max}}$ and $\rho_{\text{min}}/(\text{e} \cdot \text{\AA}^{-3})$	0.811 and -0.740	1.338 and -1.848	1.425 and -1.429

a: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; b: $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^2]^{1/2}$.

Table 2 Selected Bond Lengths($\text{\AA}$) and Angles($^\circ$) for **1**~**3**

1							
La-O(10D)	2.401(4)	La-O(9)	2.413(4)	La-O(4C)	2.490(5)	La-O(2)	2.516(4)
La-O(3B)	2.563(4)	La-O(7E)	2.567(4)	La-O(8D)	2.667(4)	La-O(12)	2.667(5)
La-O(7D)	2.732(4)	Zn-O(6C)	1.996(4)	Zn-O(1)	2.048(4)	Zn-O(5)	2.081(4)
Zn-N(2)	2.082(5)	Zn-N(1)	2.094(5)				
O(10D)-La-O(9)	87.46(15)	O(10D)-La-O(4C)	140.28(17)	O(9)-La-O(4C)	72.12(16)	O(10D)-La-O(2)	75.04(16)
O(9)-La-O(2)	86.05(16)	O(4C)-La-O(2)	70.00(15)	O(10D)-La-O(3B)	85.90(15)	O(9)-La-O(3B)	129.90(16)
O(4C)-La-O(3B)	133.33(15)	O(2)-La-O(3B)	138.78(15)	O(10D)-La-O(7E)	147.93(15)	O(9)-La-O(7E)	88.31(14)
O(4C)-La-O(7E)	67.03(15)	O(2)-La-O(7E)	136.29(14)	O(3B)-La-O(7E)	72.74(14)	O(10D)-La-O(8D)	76.49(14)
O(9)-La-O(8D)	153.27(16)	O(4C)-La-O(8D)	107.20(15)	O(2)-La-O(8D)	69.35(16)	O(3B)-La-O(8D)	70.81(15)
O(7E)-La-O(8D)	116.54(13)	O(10D)-La-O(12)	67.94(15)	O(9)-La-O(12)	68.73(16)	O(4C)-La-O(12)	129.42(15)
O(2)-La-O(12)	135.41(15)	O(3B)-La-O(12)	62.80(15)	O(7E)-La-O(12)	80.93(14)	O(8D)-La-O(12)	122.17(15)
O(10D)-La-O(7D)	123.83(13)	O(9)-La-O(7D)	137.23(14)	O(4C)-La-O(7D)	65.25(14)	O(2)-La-O(7D)	76.63(14)
O(3B)-La-O(7D)	84.81(14)	O(7E)-La-O(7D)	78.64(13)	O(8D)-La-O(7D)	48.23(12)	O(12)-La-O(7D)	145.66(14)
O(6C)-Zn-O(1)	112.12(18)	O(6C)-Zn-O(5)	112.32(19)	O(1)-Zn-O(5)	135.40(19)	O(6C)-Zn-N(2)	98.5(2)
O(1)-Zn-N(2)	91.77(18)	O(5)-Zn-N(2)	78.26(18)	O(6C)-Zn-N(1)	98.38(19)	O(1)-Zn-N(1)	79.53(18)
O(5)-Zn-N(1)	97.57(18)	N(2)-Zn-N(1)	162.9(2)				

2							
Er(1)-O(11)	2.27(3)	Er(1)-O(13A)	2.36(3)	Er(1)-O(23)	2.38(3)	Er(1)-O(2)	2.41(3)
Er(1)-O(3)	2.41(2)	Er(1)-O(1)	2.41(3)	Er(1)-O(4)	2.49(2)	Er(1)-N(1)	2.58(2)
Er(2)-O(5)	2.23(3)	Er(2)-O(43)	2.24(3)	Er(2)-O(33B)	2.29(2)	Er(2)-O(8)	2.32(3)
Er(2)-O(41A)	2.334(18)	Er(2)-O(7)	2.34(3)	Er(2)-O(6)	2.35(2)	Er(2)-N(4A)	2.44(3)
Zn-O(31)	2.01(3)	Zn-O(21)	2.05(3)	Zn-N(2)	2.05(4)	Zn-N(3)	2.09(3)
Zn-O(14B)	2.39(3)	Zn-O(44)	2.43(3)				
O(11)-Er(1)-O(13A)							
84.0(11)	O(11)-Er(1)-O(23)	114.2(10)	O(13A)-Er(1)-O(23)	142.7(10)	O(11)-Er(1)-O(2)	76.2(10)	
O(13A)-Er(1)-O(2)	72.5(12)	O(23)-Er(1)-O(2)	141.4(8)	O(11)-Er(1)-O(3)	129.8(10)	O(13A)-Er(1)-O(3)	116.4(11)
O(23)-Er(1)-O(3)	77.9(9)	O(2)-Er(1)-O(3)	68.7(9)	O(11)-Er(1)-O(1)	77.1(10)	O(13A)-Er(1)-O(1)	78.7(12)
O(23)-Er(1)-O(1)	74.6(9)	O(2)-Er(1)-O(1)	142.3(8)	O(13)-Er(1)-O(1)	148.1(9)	O(11)-Er(1)-O(4)	150.8(8)
O(13A)-Er(1)-O(4)	73.7(10)	O(23)-Er(1)-O(4)	76.4(8)	O(2)-Er(1)-O(4)	113.2(9)	O(3)-Er(1)-O(4)	78.0(8)
O(1)-Er(1)-O(4)	80.2(8)	O(11)-Er(1)-N(1)	67.5(10)	O(13A)-Er(1)-N(1)	145.8(10)	O(23)-Er(1)-N(1)	69.7(8)
O(2)-Er(1)-N(1)	82.4(9)	O(3)-Er(1)-N(1)	73.1(9)	O(1)-Er(1)-N(1)	111.0(10)	O(4)-Er(1)-N(1)	139.1(9)
O(5)-Er(2)-O(43)	83.4(13)	O(5)-Er(2)-O(33B)	70.7(9)	O(43)-Er(2)-O(33B)	141.3(11)	O(5)-Er(2)-O(8)	82.0(12)
O(43)-Er(2)-O(8)	74.3(11)	O(33B)-Er(2)-O(8)	74.0(9)	O(5)-Er(2)-O(41A)	76.7(11)	O(43)-Er(2)-O(41A)	86.1(11)
O(33B)-Er(2)-O(41A)	114.1(8)	O(8)-Er(2)-O(41A)	152.5(10)	O(5)-Er(2)-O(7)	145.7(11)	O(43)-Er(2)-O(7)	110.7(13)
O(33B)-Er(2)-O(7)	80.1(10)	O(8)-Er(2)-O(7)	72.8(11)	O(41A)-Er(2)-O(7)	133.3(10)	O(5)-Er(2)-O(6)	143.9(10)
O(43)-Er(2)-O(6)	72.5(12)	O(33B)-Er(2)-O(6)	142.6(10)	O(8)-Er(2)-O(6)	115.5(11)	O(41A)-Er(2)-O(6)	75.1(10)
O(7)-Er(2)-O(6)	69.8(10)	O(5)-Er(2)-N(4A)	108.6(11)	O(43)-Er(2)-N(4A)	144.1(11)	O(33B)-Er(2)-N(4A)	73.3(9)
O(8)-Er(2)-N(4A)	139.5(9)	O(41A)-Er(2)-N(4A)	65.3(8)	O(7)-Er(2)-N(4A)	78.6(10)	O(6)-Er(2)-N(4A)	79.3(11)
O(31)-Zn-O(21)	175.7(18)	O(31)-Zn-N(2)	99.8(16)	O(21)-Zn-N(2)	81.9(16)	O(31)-Zn-N(3)	80.0(11)
O(21)-Zn-N(3)	97.9(11)	N(2)-Zn-N(3)	175.0(19)	O(31)-Zn-O(14B)	92.6(11)	O(21)-Zn-O(14B)	83.9(11)
N(2)-Zn-O(14B)	79.6(13)	N(3)-Zn-O(14B)	95.4(10)	O(31)-Zn-O(44)	90.7(11)	O(21)-Zn-O(44)	92.9(11)
N(2)-Zn-O(44)	98.8(15)	N(3)-Zn-O(44)	86.2(10)	O(14B)-Zn-O(44)	176.5(12)		
3							
Tb(1)-O(11)	2.241(15)	Tb(1)-O(13A)	2.375(11)	Tb(1)-O(23)	2.387(12)	Tb(1)-O(1)	2.389(11)
Tb(1)-O(3)	2.397(13)	Tb(1)-O(2)	2.446(15)	Tb(1)-O(4)	2.486(14)	Tb(1)-N(1)	2.552(14)
Tb(2)-O(43)	2.301(13)	Tb(2)-O(5)	2.312(15)	Tb(2)-O(33B)	2.338(15)	Tb(2)-O(6)	2.389(15)
Tb(2)-O(8)	2.401(12)	Tb(2)-O(7)	2.409(13)	Tb(2)-O(41A)	2.443(14)	Tb(2)-N(4A)	2.523(16)
Zn-O(21)	2.000(14)	Zn-N(3)	2.057(19)	Zn-O(31)	2.072(13)	Zn-N(2)	2.076(17)
Zn-O(14B)	2.364(15)	Zn-O(44)	2.430(13)				
O(11)-Tb(1)-O(13A)							
86.3(5)	O(11)-Tb(1)-O(23)	115.8(6)	O(13A)-Tb(1)-O(23)	140.2(5)	O(11)-Tb(1)-O(1)	76.8(5)	
O(13A)-Tb(1)-O(1)	80.1(5)	O(23)-Tb(1)-O(1)	74.1(5)	O(11)-Tb(1)-O(3)	130.1(5)	O(13A)-Tb(1)-O(3)	114.3(5)
O(23)-Tb(1)-O(3)	77.7(5)	O(11)-Tb(1)-O(2)	148.0(4)	O(11)-Tb(1)-O(2)	74.9(6)	O(13A)-Tb(1)-O(2)	73.9(5)
O(23)-Tb(1)-O(2)	141.4(5)	O(11)-Tb(1)-O(2)	142.4(4)	O(3)-Tb(1)-O(2)	69.1(5)	O(11)-Tb(1)-O(4)	151.5(5)
O(13A)-Tb(1)-O(4)	70.9(5)	O(23)-Tb(1)-O(4)	76.1(5)	O(11)-Tb(1)-O(4)	82.5(5)	O(3)-Tb(1)-O(4)	76.4(5)
O(2)-Tb(1)-O(4)	113.0(5)	O(11)-Tb(1)-N(1)	65.1(5)	O(13A)-Tb(1)-N(1)	146.6(5)	O(23)-Tb(1)-N(1)	71.5(5)
O(1)-Tb(1)-N(1)	107.8(5)	O(3)-Tb(1)-N(1)	76.6(5)	O(2)-Tb(1)-N(1)	81.9(5)	O(4)-Tb(1)-N(1)	141.3(5)
O(43)-Tb(2)-O(5)	82.1(6)	O(43)-Tb(2)-O(33B)	142.3(6)	O(5)-Tb(2)-O(33B)	70.6(5)	O(43)-Tb(2)-O(6)	72.7(6)
O(5)-Tb(2)-O(6)	144.6(5)	O(33B)-Tb(2)-O(6)	142.2(5)	O(43)-Tb(2)-O(8)	76.2(5)	O(5)-Tb(2)-O(8)	77.8(6)
O(33B)-Tb(2)-O(8)	73.0(5)	O(6)-Tb(2)-O(8)	118.2(6)	O(43)-Tb(2)-O(7)	112.6(5)	O(5)-Tb(2)-O(7)	145.2(5)
O(33B)-Tb(2)-O(7)	80.4(5)	O(6)-Tb(2)-O(7)	69.3(5)	O(8)-Tb(2)-O(7)	75.8(5)	O(43)-Tb(2)-O(41A)	86.7(5)
O(5)-Tb(2)-O(41A)	78.2(6)	O(33B)-Tb(2)-O(41A)	111.6(5)	O(6)-Tb(2)-O(41A)	75.9(6)	O(8)-Tb(2)-O(41A)	152.1(5)
O(7)-Tb(2)-O(41A)	131.7(5)	O(43)-Tb(2)-N(4A)	145.0(5)	O(5)-Tb(2)-N(4A)	109.1(6)	O(33B)-Tb(2)-N(4A)	70.8(5)
O(6)-Tb(2)-N(4A)	80.9(6)	O(8)-Tb(2)-N(4A)	137.9(4)	O(7)-Tb(2)-N(4A)	77.5(5)	O(41A)-Tb(2)-N(4A)	64.6(4)
O(21)-Zn-N(3)	95.9(6)	O(21)-Zn-O(31)	175.0(9)	N(3)-Zn-O(31)	80.7(7)	O(21)-Zn-N(2)	81.3(6)
N(3)-Zn-N(2)	176.2(10)	O(31)-Zn-N(2)	101.9(7)	O(21)-Zn-O(14B)	89.7(5)	N(3)-Zn-O(14B)	96.7(7)
O(31)-Zn-O(14B)	94.4(6)	N(2)-Zn-O(14B)	86.0(6)	O(21)-Zn-O(44)	92.3(5)	N(3)-Zn-O(44)	81.9(7)
O(31)-Zn-O(44)	83.5(6)	N(2)-Zn-O(44)	95.6(7)	O(14B)-Zn-O(44)	177.6(7)		

atom was located from the E-map. Other non-hydrogen atoms were derived from the successive difference Fourier syntheses. The structure was refined on F^2 by full-matrix least-squares methods using the

SHELXTL-97 program package on a legend 586 computer. All non-hydrogen atoms were refined anisotropically. Atomic coordinates of the non-hydrogen atoms of compounds 1 ~ 3 are given out in supplementary materials. Selected bond lengths and angles of complexes

1~3 are given in Table 2. Crystallographic data excluding structural factors for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Nos. CCDC-151987 and to 151991 for 1 and 2, respectively. CCDC-167858 for 7. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB1Ez, UK fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk.

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