

新型稀土配位聚合物 $[\text{Ce}(\text{tda})(\text{ox})_{0.5}(\text{phen})]_n$ 的合成及拓扑结构

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摘要: 利用混合配体(H_2tda =亚硫基二乙酸, H_2ox =乙二酸, phen =1,10-菲咯啉)与 $\text{CeCl}_3 \cdot 5\text{H}_2\text{O}$ 反应, 合成了新型稀土配合物 $[\text{Ce}(\text{tda})(\text{ox})_{0.5}(\text{phen})]_n$, 单晶结构分析表明: 配合物以共边的多面体 $[\text{Ce}_2\text{O}_{12}\text{N}_4]$ 为基本单元构筑二维结构, 并通过 π - π 堆积作用拓展为三维超分子体系。该二维结构具有 (4,5) 连接的 $(4^6)(4^4 \cdot 6^6)_2$ 拓扑结构, 在拓扑结构中稀土离子呈现不寻常的 5 连接点。

关键词: 镧系配合物; 柔性配体; 合成; 拓扑结构

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Syntheses and Structures of New Ln-Coordination Polymers $[\text{Ce}(\text{tda})(\text{ox})_{0.5}(\text{phen})]_n$ with Unusual 5-Connected Node Topology

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Abstract: A novel lanthanide coordination polymer with the formulas $[\text{Ce}(\text{tda})(\text{ox})_{0.5}(\text{phen})]_n$ (H_2tda =thiodiglycolic acid, H_2ox =oxalic acid, phen =1,10-phenanthroline) have been synthesized and structurally characterized. Single crystal X-ray diffraction studies show that the coordination polymer are a 2D network and exhibit an unprecedented (4,5)-connected $(4^6)(4^4 \cdot 6^6)_2$ topology, in which the lanthanide ions act as unusual 5-connected nodes, and an edge-sharing dinuclear polyhedral $[\text{Ce}_2\text{O}_{12}\text{N}_4]$ was found. Furthermore, through strong π - π interactions, the 2D network structure are cross-linked to generate a 3D upramolecular architectures. CCDC: 764100.

Key words: lanthanide complexes; flexible ligand; syntheses; structures

There continues to be significant interest surrounding the synthesis and characterization of metal-organic frameworks (MOFs) not only because of their potential applications but also because of the aesthetic beauty associated with the fascinating coordination geometry and topology of the networks they form^[1-3]. The use of lanthanide metal ions in the synthesis of metal-organic frameworks has recently gained much interest^[4-6]. Because of the high coordination nature, controlling the overall frameworks of lanthanide-based

coordination polymers, undoubtedly, is a challenge. Up to date, the flexible carboxylic acid ligands have not been extensively exploited, except for some limited cases, this is probably because the varied conformations and geometries of these ligands make it difficult to forecast and control the final structures^[7]. Therefore, much more work is required to enrich our knowledge of lanthanide-based coordination chemistry of flexible ligands.

On the other hand, up to now, a variety of

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uninodal coordination networks have been well realized, among which three-, four-, and six-connected topologies are commonly observed^[8-10]. In particular, only several examples of frameworks with 5-connected networks have been reported to date^[11-13]. Because of the unique nature of lanthanide ions, such as their large radius, usually high and variable coordination numbers, and some of the available coordination sites often blocked by solvent molecules, lanthanide-based frameworks might also be considered as an effective route to construct novel 5-connected topology networks.

To address this issue, we focused on the synthesis of coordination polymer using thiodiglycolic acid ligand to coordinate with lanthanide metal ions. Fortunately, this effort has led to the 2D network constructed and exhibit an unprecedented (4,5)-connected (4⁶)(4⁴·6⁶)₂ topology from the H₂tda ligand coordinated to Ce³⁺ ions, namely [Ce(tda)(ox)_{0.5}(phen)]_n (H₂tda=thiodiglycolic acid, H₂ox=oxalic acid, phen=1,10-phenanthroline).

1 Experimental

1.1 Materials and methods

All available solvents and starting materials of analytical grade except CeCl₃·5H₂O, in the experiments were obtained from commercial sources and available without further purification, the CeCl₃·5H₂O were prepared according to the literature methods^[14]. Elemental analysis (C, H, N, S) was determined on a Perkin-Elmer 2400 type elemental analyzer, the rare earth ion was determined by EDTA volumetric analysis. Infrared spectra were recorded in a Bruker EQUINOX-55 spectrophotometer in the range 400~4 000 cm⁻¹ using KBr disks. Thermogravimetric analyses were recorded on a Shimadzu DTG-50 thermal analyzer.

1.2 Syntheses

A mixture of CeCl₃·5H₂O (0.3 mmol), H₂tda (0.3 mmol), oxalic acid (0.4 mmol), and NaOH (1 mmol) was dissolved in a mixed solution of distilled water (10 mL) and ethanol (5 mL). The resulting solution was stirred for about 60 min at room temperature, sealed in a 25 mL poly (tetrafluoroethylene)-lined stainless steel autoclave, and heated at 130 °C for 6 d under autogenous pressure, colorless and prismatic-shape single crystals of the lanthanide coordination polymer suitable for X-ray analyses were obtained. The crystals were collected by filtration, washed with distilled water and ethanol, and dried at room temperature in *ca.* 53.4% yield (based on lanthanide metal). Elemental analysis: calcd. for CeC₁₇H₁₂N₂O₆S(%): C 39.65, H 2.22, N 5.86, S 6.05, Ce 27.68; found(%): C 39.84, H 2.36, N 5.47, S 6.26, Ce 27.34. FTIR: Spectra (KBr pellet, cm⁻¹): $\nu_{\text{as}}(\text{CH}_2)$ 3 037, $\nu_{\text{s}}(\text{CH}_2)$ 2 972, $\nu_{\text{as}}(\text{COO})$ 1 588, $\nu_{\text{s}}(\text{COO})$ 1 415, $\nu_{\text{as}}(\text{H}_2\text{O})$ 3 453, $\nu_{\text{s}}(\text{H}_2\text{O})$ 3 297, σ 1 628, $\nu(\text{C-S})$ 727 and 715.

1.3 Crystal structure determination

Crystal data for the compound was collected 273(2) K using Bruker Smart-1000CCD diffractometer. Graphite monochromated Mo K α ($\lambda=0.071\ 073\ \text{nm}$) radiation was used. The single crystal structure of compound was solved by direct methods using the SHELXS-97^[15] and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 program package^[16]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. The crystal data and refinement details of the compound are summarized in Table 1. The selected interatomic distances and bond angles are given in Table 2.

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Table 1 Crystal data and structure refinement for the title complex

Empirical formula	CeC ₁₇ H ₁₂ N ₂ O ₆ S	$\alpha / (^\circ)$	70.866(8)
Formula weight	512.47	$\beta / (^\circ)$	85.876(7)
Crystal system	Triclinic	$\gamma / (^\circ)$	66.626(7)
Space group	$P\bar{1}$	V / nm^3	0.874 4(7)
a / nm	0.833 2(4)	$D_{\text{c}} / (\text{Mg} \cdot \text{m}^{-3})$	1.946
b / nm	0.933 3(5)	θ range for data collection / (°)	1.66~25.05
c / nm	1.2995(6)	Indices range (h, k, l)	$-9 \leq h \leq 9, -5 \leq k \leq 11, -14 \leq l \leq 15$

Continued Table 1

$\lambda(\text{Mo } K\alpha) / \text{nm}$	0.071 073	$F(000)$	500
Reflections collected	4 584	Z	2
Independent reflections	3 056	Final R	$R_1=0.021\ 6$, $wR_2=0.047\ 7$
Data / restraints / parameters	3 056 / 1 / 244	R indices (all data)	$R_1=0.025\ 1$, $wR_2=0.049\ 6$

Table 2 Selected bond lengths (nm) and angles ($^\circ$) the title complex

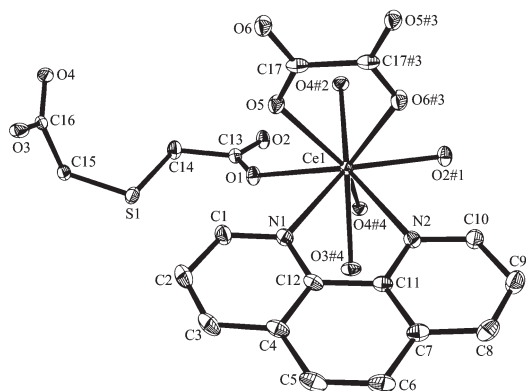
Ce1-O1	0.247 4(2)	Ce1-O4#2	0.245 7(2)	Ce1-O2#1	0.244 8(2)
Ce1-O5	0.250 7(3)	Ce1-O6#3	0.248 9(3)	Ce1-O3#4	0.255 5(3)
Ce1-O4#4	0.280 6(3)	Ce1-N1	0.267 6(3)	Ce1-N2	0.270 9(3)
O1-Ce1-O4#2	76.04(8)	O4#2-Ce1-O4#4	77.39(8)	O4#4-Ce1-O2#1	86.89(9)
O2#1-Ce1-O6#3	75.30(9)	O6#3-Ce1-N2	71.08(9)	N1-Ce1-N2	61.16(9)
O3#4-Ce1-N1	74.06(9)	N1-Ce1-O5	68.85(9)	O5-Ce1-O1	75.13(9)

Symmetry code: #1: $1-x, 2-y, 1-z$; #2: $-x, 2+y, 1-z$; #3: $1-x, 1-y, 1-z$; #4: $1+x, y, z$.

2 Result and discussion

2.1 Crystal structure of the complex

The single-crystal X-ray diffraction studies revealed that the complex $[\text{Ce}(\text{tda})(\text{ox})_{0.5}(\text{phen})]_n$ represents a 2D network. Each asymmetric unit contains one Ce^{3+} ions, one tda anionic ligands, half of ox anionic ligand, and one phen ligands, the coordination environments around Ce^{3+} ion and the numbering scheme of the compound are illustrated in Fig.1. The Ce^{3+} ion is nine-coordinated in a distorted monocapped square antiprism coordination polyhedron^[17]. The Ce^{3+} ion is coordinated with seven oxygen atoms (O1, O2#1 ($1-x, 2-y, 1-z$), O3#4 ($1+x, y, z$), O4#4, O4#2 ($-x, 2+y, 1-z$), O5, O6#3 ($1-x, 1-y, 1-z$) from four tda and one ox anionic ligands and two nitrogen atoms (N1, N2) from one phen



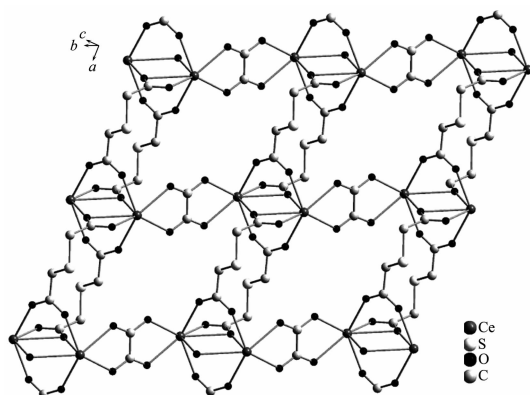
Symmetry code: #1: $1-x, 2-y, 1-z$; #2: $-x, 2+y, 1-z$; #3: $1-x, 1-y, 1-z$; #4: $1+x, y, z$; 20% the rmal ellipsoids, the hydrogen atoms are omitted for clarity

Fig.1 Environment of the Ce^{3+} cation in the compound

ligand. The bridging carboxylic O-Ce bond distances range from 0.244 8(14) to 0.280 6(15) nm, the average distance of Ce-O(bridging carboxylic) is 0.256 9 nm, the bond angles around the central Ce atom fall in the region $48.15(7)^\circ \sim 149.33(8)^\circ$, which are similar to the reported Ce-O distance and bond angles in other cerium complex^[18]. The selected bond distances and bond angles of the compound are shown in Table 2.

Two types of crystallographically independent tda ligands with identical carboxylate coordination modes are present in the framework of the compound, bis(*syn*, *syn*-bridging bidentate, chelating-bridging tridentate) mode connecting with four Ce centers, meanwhile, the ox anionic ligands adopt a bis (*syn*, *syn*-chelating bidentate, *syn*, *syn*-chelating bidentate) mode connecting with two Ce centers. The tda ligands provides μ_2 -O atom in a bridging bidentate mode and carboxyl in *syn*, *syn*-bridging bidentate mode, the ox anionic ligands offers carboxyl in *syn*, *syn*-chelating bidentate mode to bridge Ce atoms, leading to the formation of 1D infinite metallic chains (along the *b* direction) as illustrated in Fig.2. The cerium atoms are arrayed the basic unit in the order $\text{Ce1} \cdots \text{Ce1} \cdots \text{Ce1}$ with two consecutive Ce \cdots Ce distances of 0.411-31(16), 0.645 30(32) nm, respectively. Three kinds of macrocyclic rings, one is four-member ring, one is eight-member ring, and the other is five-member ring, are observed in this 1D chains. Interestingly, each tda

ligand in coordination mode is connected with four Ce^{3+} ions, while each Ce^{3+} is connected with four tda ligands and one ox anionic ligand in different directions. Hence, through tda ligand in coordination mode, the 1D metallic chains are further cross-linked to generate a 2D network structure (in ab plane) (Fig.2), in which the 2D network containing a interval group with consecutive identical $\text{Ce} \cdots \text{Ce}$ distances of 0.833 2(4) nm. A noticeable interaction in complex is the strong π - π stacking between adjacent aromatic benzene rings from the phen and another outside aromatic benzene ring from the neighboring hand-shake motif. The perpendicular distance of the two imidazole rings is 0.334 09 and 0.336 13 nm, the centroid-centroid distance between two imidazole rings is 0.367 20 and 0.375 35 nm, respectively (Fig.3). Finally, these 2D networks, via strong weak interaction, formed a complicated 3D supramolecular architectures.



Hydrogen atoms and the phen ligands are omitted for clarity

Fig.2 Two-dimensional network of the compound in ab plane

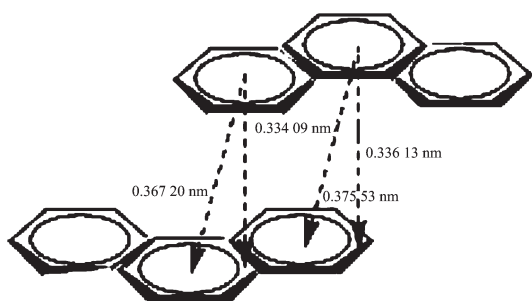


Fig.3 π - π stacking interaction in the title complex

A better insight into the nature of the complex can be achieved by the application of topological approach, that is, reducing multidimensional

structures to simple node-and-linker nets. As discussed above, each Ce center is 5-connected node through links with four tda ligand and one ox anionic ligand, likewise, the ligand of tda are 4-connected node through connected to four cerium ions, the ox anionic ligand only serves as a 2-connecting spacer. As a result, a very complicated 2D coordination framework with (4,5)-connected $(4^6)(4^4 \cdot 6^6)_2$ topology is formed (Fig.4).

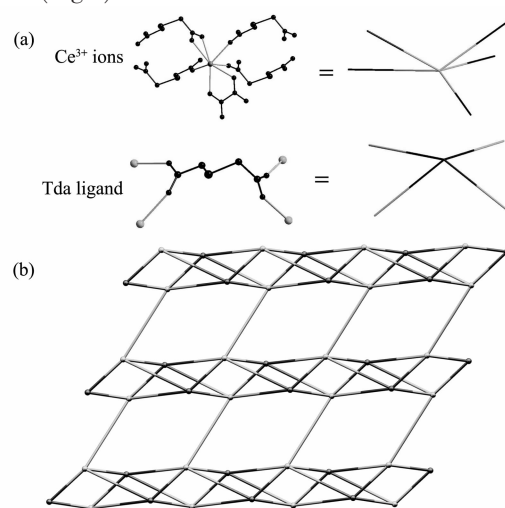


Fig.4 (a) Schematic representation of the diverse connected node, (b) 2D coordination framework with (4,5)-connectivity

2.2 Thermogravimetric analyses

Thermogravimetric analyses for the compound were performed at a heating rate of $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$ under a static air atmosphere. The thermogravimetric analysis data show that complex undergo two weight loss processes. The phen molecules are removed in a single step in the temperature range of $410 \sim 490\text{ }^{\circ}\text{C}$ for the complex, the total weight loss for phen molecules is 35.86% (calcd. 35.16%). A further sharp weight loss was observed from 530 to $770\text{ }^{\circ}\text{C}$ for complex, the tda and ox anionic ligand are removed, the final residual mass corresponds to the formation Ce_2O_3 , supported by the expected value of 32.69% (calcd. 32.02%). That is corresponds to the decomposition of the compound.

References:

- [1] Maspoeh D, Ruiz-Molina D, Veciana J. *Chem. Soc., Rev.*,

- 2007,36**:770-818
- [2] Sato O, Tao J, Zhang Y Z. *Angew. Chem., Int. Ed.*, **2007,46**: 2152-2187
- [3] HE Jin-Run(何锦润), WANG Yu-Ling(王玉玲), CAO Rong (曹荣), et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2006,22**(8):1380-1386
- [4] Kelly N R, Goetz S, Batten S R, et al. *CrystEngComm*, **2008**, **10**:1018-1026
- [5] Noro S, Kitagawa S, Kondo M, et al. *Angew. Chem., Int. Ed.*, **2000,39**:2081-2084
- [6] FENG Lin(冯林), JIANG Chong-Qiu(江崇球), SHI Jing-Min (石敬民). *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2007,23**(9):1635-1638
- [7] Kim Y J, Jung D Y. *Inorg. Chem.*, **2000,39**:1470-1475
- [8] Borel C, Håkansson M, Öhrström L. *CrystEngComm*, **2006,8**: 666-669
- [9] Ma L F, Wang L Y, Wang Y Y, et al. *CrystEngComm*, **2009**, **11**:109-117
- [10] Zou R Q, Zhong R Q, Du M, et al. *Chem. Commun.*, **2007**: 2467-2469
- [11] Wang X W, Dong Y R, Zheng Y Q, et al. *Cryst. Growth Des.*, **2007,7**:613-615
- [12] Hill R J, Long D L, Hubberstey P, et al. *J. Solid State Chem.*, **2005,178**:2414-2419
- [13] Wang J G, Huang C C, Huang X H, et al. *Cryst. Growth Des.*, **2008,8**:795-798
- [14] SU Mian-Zeng(苏勉曾), LI Gen-Pei (李根培). *Chemistry (Huaxue Tongbao)*, **1979,43**:34-35
- [15] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Determination*, University of Gottingen, Germany, **1997**.
- [16] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Gottingen, Germany, **1997**.
- [17] Fu X C, Wang C G, Li M T, et al. *Chinese J. Struct. Chem.*, **2007,26**:1419-1423
- [18] Duan L M, Xu J Q, Xie F T, et al. *Inorg. Chem. Commun.*, **2004,7**:216-219