

# Two-dimensional rare earth coordination polymers involving different coordination modes of thiodiglycolic acid

Yuan-Zhu Zhang, Jun-Ran Li <sup>\*</sup>, Song Gao <sup>\*</sup>, Hui-Zhong Kou, Hao-Ling Sun, Zhe-Ming Wang

State Key Laboratory of Rare Earth Materials Chemistry and Applications, PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China

Received 29 May 2001; accepted 22 October 2001

## Abstract

Two coordination polymers  $[\text{La}_2(\text{tdga})_3(\text{H}_2\text{O})_2]_n$  (**1**) and  $\{[\text{Pr}_2(\text{tdga})_3(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$  (**2**) were obtained by the reaction between  $\text{Ln}(\text{OH})_3$  ( $\text{Ln} = \text{La}, \text{Pr}$ ) and thiodiglycolic acid ( $\text{H}_2\text{tdga} = \text{H}_2\text{S}(\text{CH}_2\text{CO}_2)_2$ ), which have a novel double-layered and a single-layered structure, respectively. In the complexes, new coordination modes of the ligand were observed. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Coordination polymer; Coordination modes; Double-layered structure; Lanthanide

## 1. Introduction

Coordination polymers of rare earth elements have received significant attention in recent years because of their potential optical, magnetic, and porous properties, especially for the carboxylates [1–13]. We are interested in a series of structurally similar carboxylic acids: iminodiacetic acid ( $\text{H}_2\text{IMA}$ ), oxydiacetic acid ( $\text{H}_2\text{ODA}$ ) and thiodiacetic acid ( $\text{H}_2\text{tdga}$ ), and their rare earth polynuclear complexes. Some novel polymeric or polynuclear structures were obtained by means of the former two ligands in our lab, such as homo-metallic two-dimensional RE–IMA ( $\text{RE} = \text{Y}, \text{Pr}$ ), hetero-metallic three-dimensional RE–Cu–ODA ( $\text{RE} = \text{La}, \text{Ce}$ ), and heptanuclear RE–Cu<sub>6</sub>–IMA ( $\text{RE} = \text{La}, \text{Tb}$ ) [14–17]. For the last ligand, only one sample of lanthanide,  $[\text{NaNd}(\text{tdga})_2]$ , has been reported [18]. In these complexes of the three ligands, the bridging coordination modes of the ligands (**a–i**) are summarized as in Scheme 1, and generally only one type of mode was involved in every complex except for  $[\text{NaNd}(\text{tdga})_2]$ , in which two

types of modes (**e,f**) were found. Herein two novel layered lanthanide complexes of tdga were structurally characterized, in which new bridging coordination modes (**g,h**) or (**g,i**) occur in each compound.

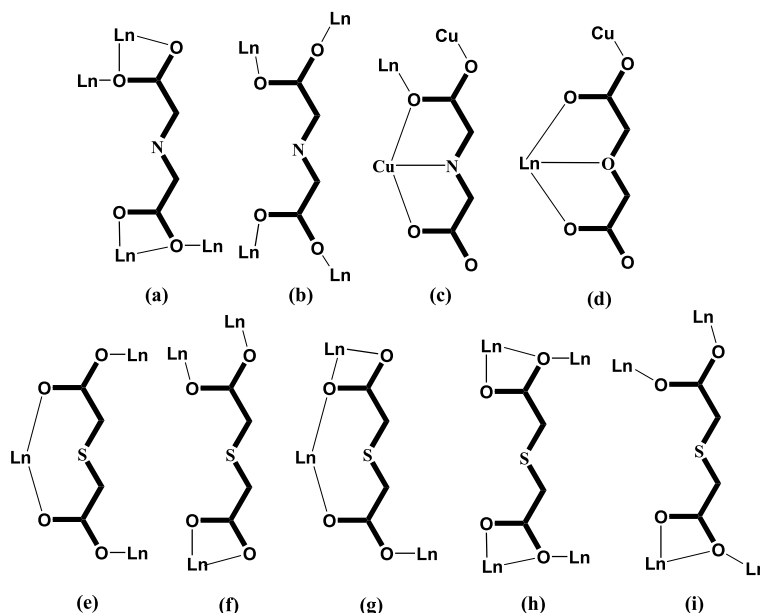
## 2. Experimental

### 2.1. Synthesis

Compound **1** was prepared by mixing  $\text{La}(\text{OH})_3$  (0.2 g, 1.0 mmol) and  $\text{S}(\text{CH}_2\text{COOH})_2$  (0.23 g, 1.5 mmol) in 20 ml water. The mixture was heated under stirring for 2 h. Perchloric acid was then added drop-wise. The solution became clear gradually. The pH value of the solution was adjusted to 4 using aqueous ammonia. The resulting solution was condensed to 15 ml and left to stand at room temperature. Single crystals were obtained after two weeks. Compound **2** was obtained following the same procedure as **1** but  $\text{Pr}(\text{OH})_3$  was used in place of  $\text{La}(\text{OH})_3$ . Elemental analysis: Calc. for compound **1** ( $\text{La}_2\text{C}_{12}\text{H}_{16}\text{O}_{14}\text{S}_3$ ): C 19.00%; H, 2.11%; S, 12.66%. Found: C, 19.31%; H, 2.41%; S, 12.54%. Calc. for compound **2** ( $\text{Pr}_2\text{C}_{12}\text{H}_{18}\text{O}_{15}\text{S}_3$ ): C, 18.46%, H, 2.31%. Found: C, 18.46%; H, 2.40%.

<sup>\*</sup> Corresponding author. Fax: +86-10-6275-1708.

E-mail addresses: jrli@chem.pku.edu.cn (J.-R. Li), gao-song@pku.edu.cn (S. Gao).



Scheme 1. The bridging coordination modes of iminodiacetic acid (H<sub>2</sub>IMA), oxydiacetic acid (H<sub>2</sub>ODA) and thiodiacetic acid (H<sub>2</sub>tdga).

## 2.2. X-ray crystallography

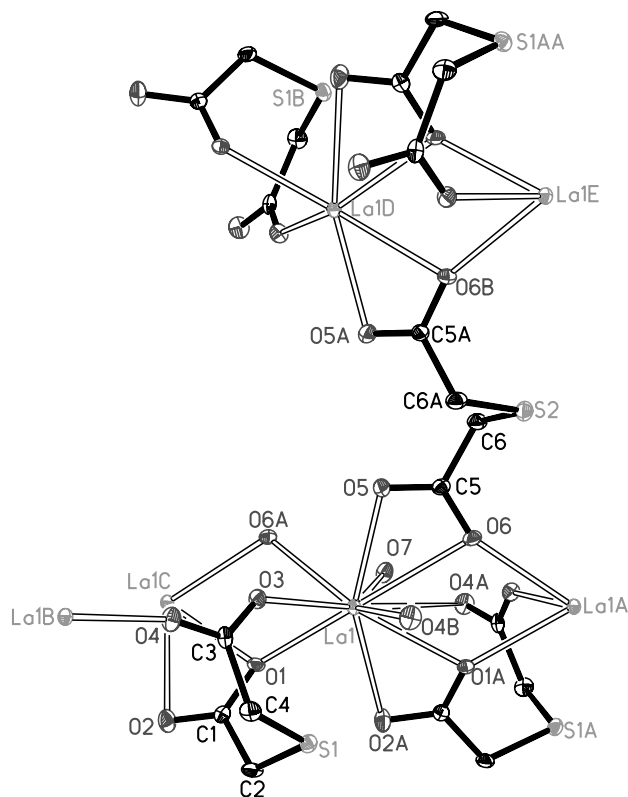
Data were collected on Nonius KappaCCD diffractometer, using Mo-K $\alpha$  graphite-monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ).

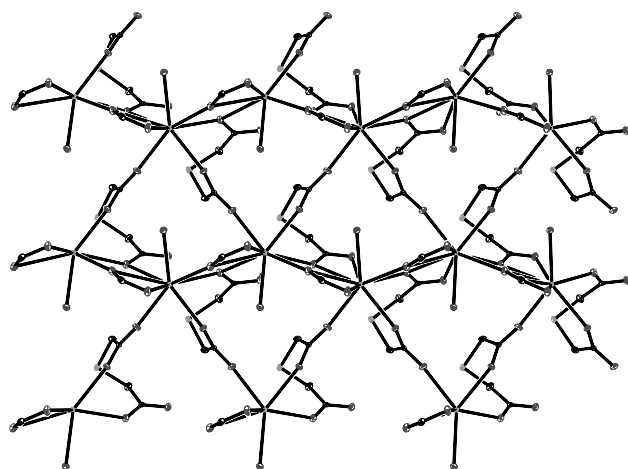
Crystal data for complex **1**: formula La<sub>2</sub>C<sub>12</sub>H<sub>16</sub>O<sub>14</sub>S<sub>3</sub>,  $M = 758.25$ , orthorhombic, space group Pbcn,  $a = 7.1254(4)$ ,  $b = 8.6973(4)$ ,  $c = 33.1270(15) \text{ \AA}$ ,  $U = 2052.94(18) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 2.453 \text{ Mg m}^{-3}$ ,  $\mu = 4.481 \text{ mm}^{-1}$ ,  $F(000) = 1448$ ,  $GoF = 0.975$ , the final  $R1$  and  $wR2$  are 0.0365 and 0.0726 (all data), respectively, for 149 parameters.

Crystal data for complex **2**: formula Pr<sub>2</sub>C<sub>12</sub>H<sub>18</sub>O<sub>15</sub>S<sub>3</sub>,  $M = 780.26$ , triclinic, space group P-1,  $a = 8.5262(17)$ ,  $b = 8.7466(17)$ ,  $c = 15.073(3) \text{ \AA}$ ,  $\alpha = 96.56(3)^\circ$ ,  $\beta = 100.98(3)^\circ$ ,  $\gamma = 97.43(3)^\circ$ ,  $U = 1083.0(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 2.393 \text{ Mg m}^{-3}$ ,  $\mu = 4.807 \text{ mm}^{-1}$ ,  $F(000) = 752$ ,  $GoF = 0.997$ , the final  $R1$  and  $wR2$  are 0.0400 and 0.0799 (all data), respectively, for 293 parameters.

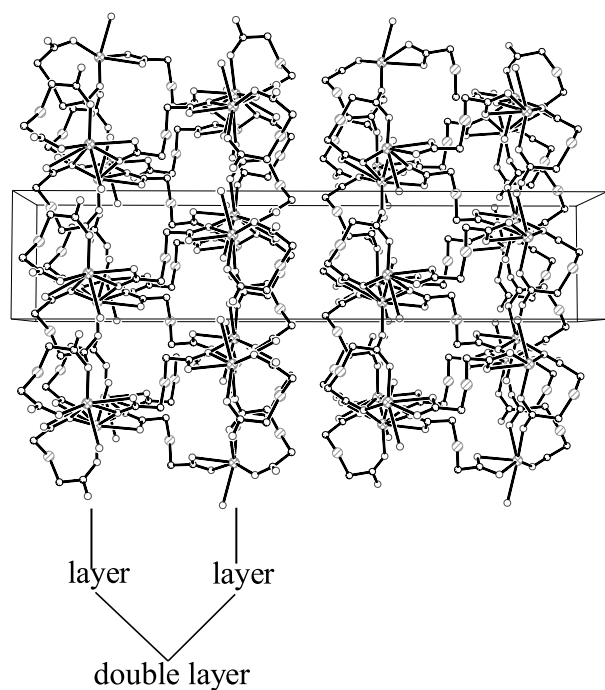
## 3. Results and discussion

In [La<sub>2</sub>(tdga)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (**1**), the tdga ligand is coordinated to the La(III) ions in two different coordination modes (**g** and **h**) (Fig. 1). In the **g**-mode, four carboxyl oxygen atoms are coordinated to three La ions. The carboxyl group with the bridging oxygen ( $\mu_2$ -O) connects two neighboring La ions in a tridentate-bridging mode, forming a one-dimensional chain through  $\mu_2$ -O bridges. The other carboxyl group acting as a bidentate bridge connects two La ions from adjacent chains, forming a two-dimensional plane (Fig. 2(a)). In the





(a)



(b)

Fig. 2. (a) Single-layer in complex 1 with fans structure. (b) Double-layer structure in complex 1 viewed along the *a*-axis.

through two  $\mu_2$ -O atoms is 4.585 Å. The La–La distance through the carboxyl bridges is 7.155 Å within each layer. The La–La distance through the *h*-type bridges is 8.187 Å between the double-layer. The La ion is nine-coordinate, and surrounded by eight carboxyl oxygen atoms (O1, O3, O1A, O2A, O4D from three *g*-type ligands; and O5, O6, O6D from two *h*-type ligands) and a water molecule.

A particularly significant structural characteristic of complex 1, which makes it different from the other two-dimensional complexes, is that each layer can be described as V-shaped fans sharing the edges (Fig. 2(a)). It is also unusual for rare earth complexes to have ligands

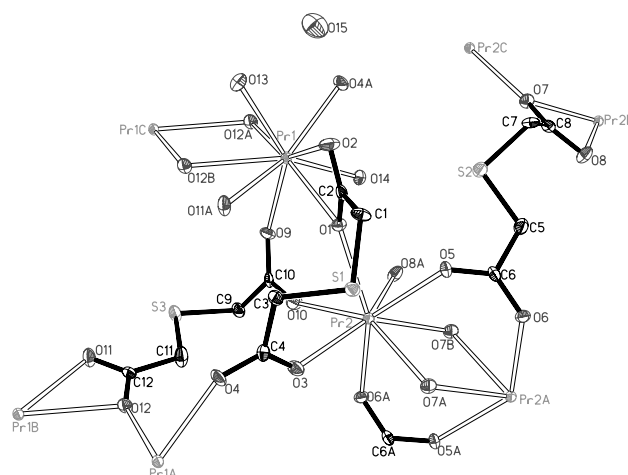


Fig. 3. ORTEP drawing of complex 2.

coordinated in two kinds of coordination modes and form a double-layered structure.

Compound 2 consists of a two-dimensional single-layer structure. Fig. 3 shows that there are two crystallographically independent praseodymium(III) ions (Pr1, Pr2) in compound 2. The coordination polyhedron of the nine-coordinated Pr1 is a distorted tricapped trigonal prism comprised of seven oxygen atoms (O1, O2, O4A, O9, O11A, O12A, O12B from five *tdga* ligands), and O13, O14 of two water molecules. Pr2 is eight-coordinated with eight oxygen atoms (O1, O3, O5, O6A, O7A, O7B, O8C and O10) from six *tdga* ligands, forming a distorted square antiprism coordination polyhedron. The coordination types of the carboxyl groups in each *tdga* are different, one contains a  $\mu_2$ -O, and the other acts as a bidentate bridge. However, there are two coordination modes (*g* and *i*) in complex 2. In the *g*-mode, the ligand is coordinated to two Pr1 and one Pr2 ions, the carboxyl group with  $\mu_2$ -O is chelated to Pr1, and bridges the Pr1 and Pr2 ions, the bidentate bridge links Pr2 and another Pr1. In the *i*-mode, the ligand is coordinated to four different Pr ions, among which two Pr ions are bridged by  $\mu_2$ -O. Two adjacent Pr1 ions constitute a four-membered ring (Pr<sub>2</sub>O<sub>2</sub>) with two  $\mu_2$ -O atoms, while there are a four-membered ring (Pr<sub>2</sub>O<sub>2</sub>) with two  $\mu_2$ -O and an eight-membered ring (Pr<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) with two COO<sup>−</sup> groups between adjacent Pr2 ions. The six-membered ring is comprised of Pr1, Pr2,  $\mu_2$ -O and a COO<sup>−</sup> group (Fig. 4). In these rings, the distances between Pr1–Pr1, Pr2–Pr2 and Pr1–Pr2 are 4.244, 4.205 and 4.767 Å, respectively. As a result of the linkage between Pr ions, complex 2 adopts a two-dimensional honeycomb-like layer with Pr ions located at the apexes of each hexagon (Fig. 4).

The topology of complex 2 is more complicated than that of complex 1. It is very uncommon that two kinds of bridging coordination modes exist in one complex for ligand *tdga*.

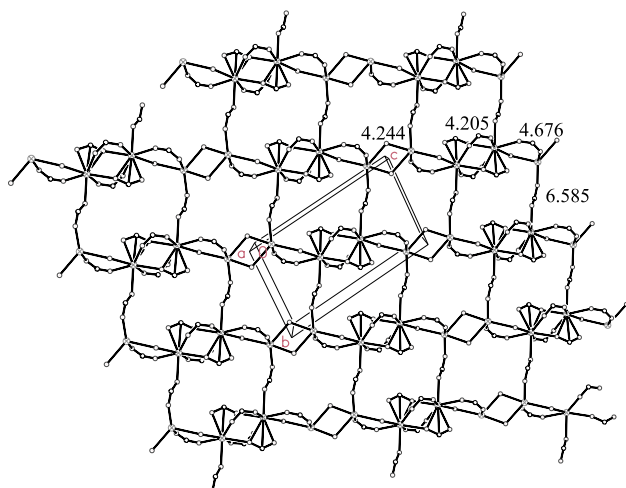


Fig. 4. Two-dimensional honeycomb-like layer for complex **2**. Some atoms of the tdga ligands are omitted for clarity.

In complexes **1** and **2**, the La–S (3.188 Å) and Pr2–S (3.058 Å) separations are shorter than Nd–S (3.451 Å) [18] suggesting possible interaction between the La or Pr ion and the sulfur atom in tdga. But all these metal–sulfur distances are slightly longer than the sum of the radii of the participating ions (La–S is 3.06 Å and Pr–S is 2.97 Å). Therefore, the interactions between the metal ions and the sulfur atoms in tdga in complexes **1** and **2** are weak; they did not form covalent bonds. However, the shape of the coordination polyhedron around the metal ion is surely affected by the sulfur atom in the vicinity of the metal ion. As a result, the coordination polyhedron of La in compound **1** is a significantly distorted tricapped trigonal prism. This is different from M–ODA (M = Nd, Gd, Yb) [19] Ce–ODA [20] and Eu–ODA [21] complexes, where the ether oxygen atom is coordinated to the metal ion, because the sulfur atom is softer base than oxygen atom.

### Acknowledgements

This work is supported by the National Natural Science Foundation of China (No. 20023005), National

Key Project for Fundamental Research (G1998061305), and the Excellent Young Teachers Fund of MOE, People's Republic of China.

### References

- [1] B.D. Alleyne, A.R. Williams, L.A. Hall, A.J.P. White, D.J. Williams, *Inorg. Chem.* 40 (2001) 1045.
- [2] C. Seward, N.X. Hu, S.N. Wang, *Chem. Soc. Dalton Trans.* (2001) 134.
- [3] Y.C. Liang, R. Cao, W.P. Su, M.C. Hong, W.J. Zhang, *Angew. Chem.-Int. Ed.* 39 (2000) 3304.
- [4] B.Q. Ma, D.S. Zhang, S. Gao, T.Z. Jin, C.H. Yan, G.X. Xu, *Angew. Chem.-Int. Ed.* 39 (2000) 3644.
- [5] Q.D. Liu, J.R. Li, S. Gao, B.Q. Ma, Q.Z. Zhou, K.B. Yu, H. Liu, *Chem. Commun.* (2000) 1685.
- [6] L. Pan, E.B. Woodlock, X.T. Wang, C. Zheng, *Inorg. Chem.* 39 (2000) 4174.
- [7] R. Baggio, M.T. Garland, Y. Moreno, O. Pena, M. Pereg, E. Spodine, *Chem. Soc. Dalton Trans.* (2000) 2061.
- [8] L. Pan, X.Y. Huang, J. Li, Y.G. Wu, N.W. Zheng, *Angew. Chem.-Int. Ed.* 39 (2000) 527.
- [9] V.D. Bermudez, L.D. Carlos, M.M. Silva, M.J. Smith, *J. Chem. Phys.* 112 (2000) 3293.
- [10] L. Ma, O.R. Evans, B.M. Fowman, W.B. Lin, *Inorg. Chem.* 38 (1999) 5837.
- [11] J.G. Mao, H.J. Zhang, J.Z. Ni, S.B. Wang, T.C.W. Mak, *Polyhedron* 18 (1999) 1519.
- [12] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi, *J. Am. Chem. Soc.* 121 (1999) 1651.
- [13] R. Baggio, M.T. Garland, M. Pereg, D. Vega, *Inorg. Chem.* 35 (1996) 2396.
- [14] J.R. Li, L.P. Zhou, T.Z. Jin, K.B. Yu, *Chem. J. Chin. Univ.* 18 (1997) 1255.
- [15] J.R. Li, Z.M. Wang, C.H. Yan, L.P. Zhou, T.Z. Jin, *Acta Cryst. C55* (1999) 2073.
- [16] Q.D. Liu, S. Gao, J.R. Li, Q.Z. Zhou, K.B. Yu, B.Q. Ma, S.W. Zhang, X.X. Zhang, T.Z. Jin, *Inorg. Chem.* 39 (2000) 2488.
- [17] Q.D. Liu, J.R. Li, S. Gao, B.Q. Ma, F.H. Liao, Q.Z. Zhou, K.B. Yu, *Inorg. Chem. Commun.* 4 (2001) 301.
- [18] C.J. Kepert, B.W. Skelton, A.H. White, *Aust. J. Chem.* 52 (1999) 617.
- [19] J. Albertsson, *Acta Chem. Scand.* 22 (1968) 1563.
- [20] J. Albertsson, I. Elding, *Acta Chem. Scand. A* 31 (1977) 21.
- [21] M. Albin, R.R. Whittle, W.Dew. Horrocks Jr., *Inorg. Chem.* 24 (1985) 4591.