Contents lists available at ScienceDirect





Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

# Hydrothermal synthesis and structure of three novel open-framework lanthanide sulfate-oxalates

## Li Li <sup>a,b</sup>, Ranbo Yu <sup>c</sup>, Dan Wang <sup>a,\*</sup>, Xiaoyong Lai <sup>a</sup>, Dan Mao <sup>a</sup>, Mei Yang <sup>a</sup>

<sup>a</sup> State Key Laboratory of Multi-Phase & Complex Systems, Institute of Processing Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

<sup>b</sup> Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

<sup>c</sup> Department of physical chemistry, University of Science and Technology Beijing, Beijing 100086, PR China

#### ARTICLE INFO

Article history: Received 28 January 2010 Accepted 2 April 2010 Available online 12 April 2010

Keywords: Hydrothermal synthesis Inorganic–organic hybrid material Open-framework Crystal structure

### ABSTRACT

Three novel hybrid open-framework lanthanide sulfate–oxalates,  $\{[NH_4][Ln(H_2O)(SO_4)(C_2O_4)]\}_n$  [Ln = Y (I), La (II), Sm (III)] have been synthesized via hydrothermal reaction, and characterized by single crystal X-ray diffraction, powder X-ray diffraction, infrared spectrophotometry, thermal gravimetric analysis and fluorescence analysis. These three compounds were isostructural, and all crystallized into the monoclinic system with space group of P2<sub>1</sub>/n. In their structures, LnO<sub>8</sub> dodecahedra, SO<sub>4</sub> tetrahedral and C<sub>2</sub>O<sub>4</sub> groups are linked to give rise to a three-dimensional open-framework, which contains two kinds of 12-membered ring channel systems running along the *a* and *b* axis, respectively.

© 2010 Elsevier B.V. All rights reserved.

Crystal engineering of inorganic open-framework materials has attracted considerable interests due to their fascinating structural diversity and potential applications [1]. A variety of inorganic frameworks mostly involving with silicate [2] and phosphate [3] tetrahedral anionic moieties have been well reported. Nowadays, great researches are devoted to the design and synthesis of new inorganic framework materials with different compositions and structures. While SO<sub>4</sub> ions and PO<sub>4</sub> ions have different charges, they are of similar size and shape. It can also be effectively used to construct materials with new topological structures and interesting properties [4]. The lanthanide centers have high and variable coordination numbers and a wide variety of coordination environments compared with other transition metals. Therefore, it is possible to lead to unusual topological frameworks [5]. Work reported on lanthanide sulfate mainly focused on inorganic hydrates and species of whose structures containing alkali metal, or ammonium ions, or organic amines template [6,7]. Selection of multidentate ligands as spacers to link multiple lanthanide ions as nodes under suitable reaction conditions has been proved to be a powerful methodology, and important progress has been achieved [8]. However, it is still a challenge for preparing lanthanide sulfate using the organic component as ligand directly coordinated to the lanthanide sulfate scaffolding to form the organic-inorganic hybrid materials. Oxalic acid has been well reported to build up a 3D metal-organic framework [9,10]. Herein, the three-dimensional open-framework lanthanide sulfate-oxalates  $\{[NH_4][Ln(H_2O)(SO_4)(C_2O_4)]\}_n$  were reported and the synthesis, structure, and fluorescent properties of these lanthanide sulfate-oxalates were discussed.

Colorless columnar crystals of compound I were obtained by heating a mixture of  $Y_2O_3$ ,  $H_2SO_4$ ,  $(NH_4)_2SO_4$ , oxalic acid,  $H_2O$  and ethanol in the molar ratio of 1:8:4:2:833:74 at 160 °C for 3 days. Syntheses of compounds II and III were similar to that of compound I, except that  $La_2O_3$  and  $Sm_2O_3$  were used to replace  $Y_2O_3$  respectively.

Crystallographic analysis reveals that all the three compounds are isostructural [11–13]. Therefore, only the crystal structure of compound I is described in detail. The single crystal X-ray diffraction study of the compound showed that the framework structure is made up of YO<sub>8</sub> dodecahedra, SO<sub>4</sub> tetrahedra and oxalate groups (Fig. 1).

Each oxalate group links two Y ions in a bidentate mode, showing a zigzag chain along *b* axis (Fig. 2a). The sulfate groups adopting  $\eta^3$ ,  $\mu_3$ -tridentate coordinated mode connect with YO<sub>8</sub> dodecahedra at three vertices, with the fourth one being a free terminal oxygen, to form a one-dimensional chain along the *a* axis as shown in Fig. 2b. The inorganic  $[Y_2(O-S-O)_2]$  chain is further linked via oxalate groups to produce an open-framework structure with one-dimensional channels running along the *a* and *b* axes, respectively. Those along the *a* axis have a 12-membered window (six  $YO_8$ , two  $SO_4$  and four  $C_2O_4$ ) with a diagonal of 12.6 Å as shown in Fig. 3a. The channel systems along the b axis also have a 12-membered window (six YO<sub>8</sub>, four SO<sub>4</sub> and two  $C_2O_4$ ) (Fig. 3b). It has a pore opening of 7.2 Å×4.0 Å. The pore is generated by the removal of free ammonium molecules, and the void volumes are 49.9% (I), 53.1% (II) and 56.1% (III) respectively as estimated by PLATON [14]. The ammonium cations are located in the 12-membered windows to balance the framework's negative charge.

The  $Y^{3+}$  ions are eight-coordinate and described as a dodecahedron: three oxygen atoms from three  $SO_4^{2-}$  with distances in the range

<sup>\*</sup> Corresponding author. Tel./fax: +86 10 62631141. *E-mail address:* danwang@home.ipe.ac.cn (D. Wang).

<sup>1387-7003/\$ –</sup> see front matter 0 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2010.04.004



Fig. 1. The asymmetric unit of compound I. Color code: Y, azure; S, yellow; N, dark blue; C, green; O, red; and H, gray.



Fig. 2. Structures of 1D zigzag chain formed by Y and oxalate group (a),  $\left[Y(SO_4)(H_2O)\right]$  inorganic chain (b).

of 2.300–2.319 Å, four oxygen atoms from two  $C_2O_4^{2-}$  anions with distances in the range of 2.380–2.416 Å [11] and one terminal water molecule with distance Y–O(w) = 2.372 Å[15]. Each SO<sub>4</sub><sup>2-</sup> anion adopts a tridentate coordination mode bridging three Y<sup>3+</sup> ions with a free S(1)–O(2) of the shortest bond distance 1.460 Å. The average S–O bond distance and O–S–O angle are 1.472 Å and 109.47°, respectively [6,7,16]. The O–Y–O bond angle becomes relatively

small, as for [O(5)-Y(1)-O(7)], [O(6A)-Y(1)-O(8A)], when the oxygen atoms are coordinated with carbon atoms of the oxalate group [17]. All the other bond distances and angles are in the range expected for this type of bonding and match well with those reported previously in the literature.

The thermal stability was examined by TGA in a dry air atmosphere from 20 to 1000 °C. Four distinct mass losses were observed, as shown in Fig. 1S. The first mass loss (4.50%) occurs between 80 and 200 °C corresponding to the loss of ammonia molecule (calcd. 5.50%). The second mass loss of about 37.05% in the range of 280–700 °C corresponds to the loss of bound water and oxalate molecules (calcd. 37.22%). The white production after calcining at 700 °C is  $Y_2(SO_4)_3$  according to the XRD spectra. Between 700 and 900 °C, the TGA curve shows a continuous loss, which is associated with the loss of SO<sub>3</sub> groups. The powder X-ray diffraction pattern of the sample heated at 1000 °C corresponds to  $Y_2O_3$  (Fig. 2S), which indicates the destruction of the framework structure upon heating as described by the following reaction:

$$2\{[\mathrm{NH}_4][\mathrm{Y}(\mathrm{SO}_4)(\mathrm{C}_2\mathrm{O}_4)(\mathrm{H}_2\mathrm{O})]\}_n \rightarrow 2n\mathrm{NH}_3 + 3n\mathrm{H}_2\mathrm{O} + 4n\mathrm{CO}_2 + 2n\mathrm{SO}_2 + n\mathrm{Y}_2\mathrm{O}_3$$

The emission spectra of compounds and oxalic acid are shown in Fig. 3S. It exhibits strong fluorescence emission bands at 530 and 792 nm ( $\lambda_{ex} = 266$  nm), which can be assigned to the intraligand fluorescent emission of oxalate ligands attributed to the  $\pi$ - $\pi$ \*



Fig. 3. The polyhedral diagram of compound I viewed along the *a* axis (a) and *b* axis (b), respectively.

transition. The fluorescent intensity of the compounds is enhanced significantly compared with oxalic acid. This is probably due to the coordination of oxalate to Ln, which increases the ligand conformational rigidity, and reduces the nonradiative decay of the intraligand excited state.

In summary, three novel lanthanide coordination compounds  $\{[NH_4][Ln(C_2O_4)(SO_4)(H_2O)]\}_n$  [Ln = Y (I), La (II), Sm (III)] were prepared by hydrothermal reactions. Due to the coordination of oxalate to Ln, the fluorescent intensity is significantly enhanced compared with that free of oxalate ligands. It would be worth exploring the possibility of introducing other appropriate structure-directing agents and flexible spacer pillars to prepare new hybrid inorganic–organic sulfates and phosphates of lanthanum metals with novel magnetic and fluorescent properties.

#### Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 20401015, 20731001, 20971125) and the Beijing Municipal Natural Science Foundation (2082022, 2092019).

#### Appendix A. Supplementary material

CCDC 665771, 688417 and 688418 contain the supplementary crystallographic data for polymers I, II and III. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. inoche.2010.04.004.

#### Reference

- [1] (a) B. Wang, A.P. Cote, H. Furukawa, M. O'Keeffe, O.M. Yaghi, Nature 453 (2008) 207–211;
  - (b) Y. Liu, X. Xu, F.K. Zheng, Y. Cui, Angew. Chem. Int. Ed. 47 (2008) 4538–4541;
    (c) A.J. Lan, K.H. Li, H.H. Wu, D.H. Olson, T.J. Emge, W. Ki, M.C. Hong, J. Li, Angew.
  - Chem. Int. Ed. 48 (2009) 2334–2338; (d) J.P. Zhang, X.M. Chen, J. Am. Chem. Soc 131 (2009) 5516–5521;
  - (e) Y.F. Zeng, X. Hu, F.C. Liu, X.H. Bu, Chem. Soc. Rev. 38 (2009) 469–480.
- [2] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, London, 1982.
- [3] H. Robson, K.P. Lillerud (Eds.), Verified Syntheses of Zeolitic Materials, second ed, Elsevier, Amsterdam, 2001.
- [4] (a) G. Paul, A. Choudhury, C.N.R. Rao, Chem. Mater. 15 (2003) 1174–1180;
- (b) A. Choudhury, J. Krishnamoorthy, C.N.R. Rao, Chem. Commun. (2001) 2610–2611;
- (c) Y. Yuan, R. Wang, D. Kong, J. Mao, A. Clearfild, J. Solid State Chem. 178 (2005) 2030–2035:
- (d) C.N.R. Rao, J.N. Behera, M. Dan, Chem. Soc. Rev. 35 (2006) 375-387.
- [5] (a) D. Wang, R.B. Yu, H. Wang, X.T. Li, X.R. Xing, Microporous Mesoporous Mater. 101 (2007) 66–72;
  - (b) R.B. Yu, D. Wang, Y.F. Chen, X.R. Xing, S. Ishiwata, T. Saito, M. Takano, Chem. Lett. 33 (2004) 1186–1187;
  - (c) R.B. Yu, D. Wang, S. Ishiwata, T. Saito, M. Azuma, M. Takano, Y.F. Chen, J.H. Li, Chem. Lett. 33 (2004) 458–459;
  - (d) R.B. Yu, D. Wang, T. Takei, H. Koizumi, N. Kumada, N. Kinomura, J. Solid State Chem. 157 (2001) 180–185;
  - (e) R.B. Yu, D. Wang, N. Kumada, N. Kinomura, Chem. Mater. 12 (2000) 3527–3529.

- [6] (a) Y. Xu, S. Ding, X. Zheng, J. Solid State Chem. 180 (2007) 2020–2023;
  (b) Q. Zhang, C. Lu, W. Yang, S. Chen, Y. Yu, Inorg. Chem. Commun. 7 (2004)
  - 889–894; (c) S. Ding, Y. Xu, L. Nie, W. Feng, J. Clust. Sci. 17 (2006) 627–636.
- [7] (a) Y. Xing, Y. Liu, Z. Shi, H. Meng, W. Pang, J. Solid State Chem. 174 (2003) 381–385;
  - (b) T. Bataille, D. Louer, J. Mater. Chem. 12 (2002) 3487–3493;
  - (c) M. Dan, J.N. Beheraa, C.N.R. Rao, J. Mater. Chem. 14 (2004) 1257-1265;
  - (d) M. Doran, A.J. Norquist, D. O'Hare, Chem. Commun. (2002) 2946;
  - (e) Y.L. Zhu, G.P. Zhou, Y. Xu, D.R. Zhu, X.F. Zheng, Z. Anorg. Allg. Chem. 634 (2008) 545–548;
- (f) W. Zhou, Q. Chen, D. Zhu, Z.Y. Xu, Z. Anorg. Allg. Chem. 635 (2009) 572–576.
  [8] (a) N. Xu, W. Shi, D.Z. Liao, S.P. Yan, P. Cheng, Inorg. Chem. 47 (2008) 8748–8756.
  - (b) F. Gándara, A. García-Cortés, C. Cascales, B. Gómez-Lor, E. Gutiérrez-Puebla, M. Iglesias, A. Monge, N. Snejko, Inorg. Chem. 46 (2007) 3475–3484;
  - (c) L. Pan, K.M. Adams, H.E. Hernandez, X.T. Wang, C. Zheng, Y. Hattori, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 3062–3067;
  - (d) Y.Q. Sun, J. Zhang, Y.M. Chen, G.Y. Yang, Angew. Chem. Int. Ed. 44 (2005) 5814–5817.
- [9] (a) Z.A.D. Lethbridge, G.J. Clarkson, S.S. Turner, R.I. Walton, Dalton Trans. (2009) 9176–9182;
  - (b) C.M. Wang, Y.Y. Wu, Y.W. Chang, K.H. Lii, Chem. Mater. 20 (2008) 2857-2859;
  - (c) M.F. Tang, Y.H. Liu, P.C. Chang, Y.C. Liao, H.M. Kao, K.H. Lii, Dalton Trans. (2007) 4523–4528;
  - (d) C.M. Wang, Y.Y. Wu, Y.W. Chang, K.H. Lii, Chem. Mater 20 (2008) 2857-2859;
  - (e) P. Ramaswamy, N.N. Hegde, R. Prabhu, V.M. Vidya, A. Datta, S. Natarajan, Inorg. Chem. 48 (2009) 11697–11711;
  - (f) Y.P. Yuan, J.L. Song, J.G. Mao, Inorg. Chem. Commun. 7 (2004) 24-26;
  - (g) H.C. Liu, I.H. Chen, A. Huang, S.C. Huang, K.F. Hsu, Dalton Trans. (2009) 3447-3456
  - (h) N. Xu, Y. Xing, X. Liu, D. Song, L. Ma, X. Sun, Z. Anorg. Allg. Chem. 635 (2009) 558–662.
- [10] R.B. Yu, X.R. Xing, T. Saito, M. Azuma, M. Takano, D. Wang, Y.F. Chen, N. Kumada, N. Kinomurad, Solid State Sci. 7 (2005) 221–226.
  [11] IR (KBr, cm<sup>-1</sup>): ν= 3459 m, 3245 w, 1639 s, 1427 m, 1327 m, 1121 s, 928 w, 799m,
- [11] IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3459 m, 3245 w, 1639 s, 1427 m, 1327 m, 1121 s, 928 w, 799m, 613 m, 507 m. Anal. Calcd: C, 7.76; H, 1.94; N, 4.53. Found: C, 7.81; H, 1.98; N, 4.62; yield: 80% based on metal oxide. Crystal data for 1: FW, 309.05; Monoclinic; space group, P2(1)/n; cell dimensions: *a* = 6.5341(13) Å, *b* = 8.5266(17) Å, *c* = 13.745(3) Å,  $\beta$  = 92.87(3)°, V = 764.8(3) Å<sup>3</sup>, Z = 4,  $\mu$  = 7.934 mm<sup>-1</sup>, T = 293(2)K. Reflections collected: 7330; independent reflections: 1738; Final *R* indices [I>2 $\sigma$ (I)]: R<sub>a</sub> = 0.0253, R<sub>w</sub> = 0.0680.
- [12] IR (KBr, cm<sup>-1</sup>):  $\nu$  = 3440 m, 3041 w, 1635 s, 1420 m, 1321 m, 1110 s, 920 w, 797 m, 598 m, 501 m. Anal. Calcd: C, 6.68; H, 1.67; N, 3.90. Found: C, 6.70; H, 1.72; N, 3.97; yield: 74% based on ligand. Crystal data for 2: FW, 359.05; Monoclinic; space group, P2(1)/n; cell dimensions: a = 6.6294(13)Å, b = 8.6727(17)Å, c = 13.867(3)Å,  $\beta = 93.35(3)^\circ$ , V = 795.9(3)Å<sup>3</sup>, Z = 4,  $\mu = 5.664$  mm<sup>-1</sup>, T = 293(2)K. Reflections collected: 7474; independent reflections: 1823; Final *R* indices [I>2 $\sigma$ (I)]:  $R_a = 0.0550$ ,  $R_w = 0.1516$ .
- [13] IR (KBr, cm<sup>-1</sup>):  $\nu = 3445$  m, 3040 w, 1672 s, 1608 s, 1465 w, 1320 m, 1146 s, 981 w, 789 m, 653 m, 611 m, 494 m. Anal. Calcd: C, 6.48; H, 1.62; N, 3.78. Found: C, 6.56; H, 1.65; N, 3.82; yield: 84% based on ligand. data for 3: FW, 370.49; Monoclinic; space group, P2(1)/*n*; cell dimensions: a = 6.6189(13)Å, b = 8.6598(17)Å, c = 13.853(3)Å,  $\beta = 93.30(3)^\circ$ ,  $\nu = 792.7(3)$ Å<sup>3</sup>, Z = 4,  $\mu = 7.706$  mm<sup>-1</sup>, T = 293(2)K. Reflections collected: 7208; independent reflections: 1819; Final *R* indices [I>2 $\sigma$ (1)]:  $R_a = 0.0319$ ,  $R_w = 0.0835$ .
- [14] A.L. Spek, PLATON99, A Multipurpose Crystallogr. Tool, , Utrecht University, Utrecht, The Netherlands, 1999.
- [15] (a) X.J. Zhang, Y.H. Xing, C.G. Wang, J. Han, J. Li, M.F. Ge, X.Q. Zeng, S.Y. Niu, Inorg. Chim. Acta 36 (2009) 1058–1064;
  - (b) S. Mishra, E. Jeanneau, H. Chermette, S. Daniele, L.G.H. Pfalzgraf, Dalton Trans. (2008) 620–630.
- [16] (a) J. Yang, N. Lu, G. Zhang, L. Cheng, S.H. Gou, Polyhedron 27 (2008) 2119–2126;
  (b) Y.Q. Sun, G.Y. Yang, Dalton Trans. (2007) 3771;
  - (c) H. Akkari, P. Bénard-Rocherullé, H. Mérazig, T. Roisnel, J. Rocherullé, Solid State Sci. 8 (2006) 704–715.
- [17] (a) T. Bataille, D. Louër, Acta Crystallogr., Sect. B: Struct. Sci. 56 (2000) 998-1002;
  - (b) F.A.A. Paz, J. Klinowski, Chem. Commun. (2003) 1484-1485.