Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 304–306

Mendeleev
Communications

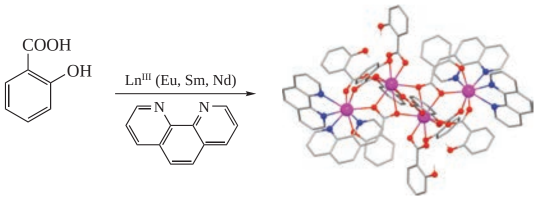
Construction of three unusual tetranuclear lanthanide complexes based on salicylate and phenanthroline ligands

Min Hu,* Ling-Yu Yue and Shao-Ming Fang

Zhengzhou University of Light Industry, Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou, Henan, 450000 P. R. China. Fax: +86 371 8660 9676; e-mail: humin@zzuli.edu.cn

DOI: 10.1016/j.mencom.2016.07.012

Three novel tetranuclear Ln^{III} complexes $[Ln_2(HSA)_4(SA)(phen)_2]_2$ (Ln = Eu, Sm and Nd) have been hydrothermally synthesized from salicylate and phen ligands.



The synthesis of lanthanide carboxylate complexes with desired structure types and functions has become an extensive research area because of their potential ability to build multifunctional materials, combining the attractive structural features with relevant physical properties (*e.g.*, luminescence and magnetism).[1–5] Variations in the coordination geometries from central lanthanide and the coordination modes from carboxylate in the lanthanide carboxylate complexes are interesting themes of structural chemistry. Among a lot of synthetic parameters affected their structural assembly, there is no doubt that organic ligands play a vital role in tuning the structural topology and functionality.[6,7] Among them, salicylic acid (H_2SA), a type of organic ligand with one carboxyl and one hydroxyl groups arranged in 1,2-fashion around the central aromatic moiety, has received much attention.[8–13] Our investigations in the Cambridge Structural Database (CSD) have shown that many lanthanide salicylate complexes are coordination polymers of low-dimensionality or zero-dimensional molecules.[8–10] However, when the second chelating ligand 1,10-phenanthroline (phen), is bonded to the lanthanide atoms, the lanthanide complexes are often dimers because the space is overcrowded.[11–13] We have constructed two trinuclear complexes $[Ln_3(HSA)_5(SA)_2(phen)_3]$ (Ln = Dy, Gd), in which the luminescent Dy_3 shows the slow magnetic relaxation processes of single ion origin.[14] As an extension of the above work, recently, three tetranuclear Ln^{III} complexes based on salicylate and phen ligands have been prepared to better understand the nature of H_2SA. Here, we report the syntheses and structures of $[Ln_2(HSA)_4(SA)(phen)_2]_2$ [Ln = Eu (**1**), Sm (**2**) and Nd (**3**)].[†]

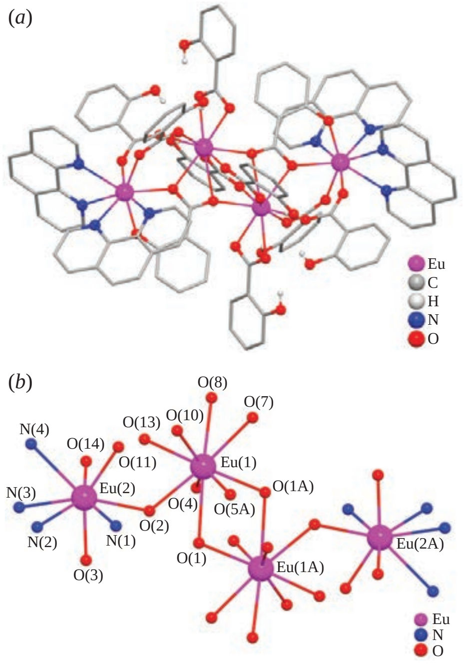


Figure 1 (*a*) Molecular structure of **1** and (*b*) the local coordination environment of Eu^{III} in **1**. Symmetry codes: A = $-x + 1, -y + 1, -z + 2$.

Single crystal X-ray diffraction analysis[‡] reveals that complexes **1**–**3** are isomorphic (Table S1, see Online Supplementary Materials). Here, we chose complex **1** to represent the detailed

---

[†] Commercial reagents and solvents were used as received.

General procedure for the preparation of complexes **1**–**3**. A mixture of Ln_2O_3 [0.2 mmol, Ln = Eu (**1**), Sm (**2**), Nd (**3**)], H_2SA (1.6 mmol), phen (0.4 mmol), and H_2O (15 ml) was placed in a Teflon-lined stainless steel vessel (23 ml), heated to 140 °C for 72 h and then cooled to room temperature at a rate of 5 K h^{-1}. Single crystals of **1**–**3** suitable for X-ray diffraction were obtained.

$[Eu_2(HSA)_4(SA)(phen)_2]_2$ **1**: yield ~45% based on H_2SA. IR (KBr pellet, ν/cm^{-1}): 3420 (br), 1627 (m), 1602 (s), 1570 (s), 1515 (m), 1485 (s), 1463 (s), 1420 (m), 1392 (s), 1369 (s), 1335 (w), 1306 (m), 1247 (w), 1146 (w), 1105 (w), 1032 (w), 893 (w), 844 (w), 758 (w), 726 (m), 703 (w), 660 (w), 603 (w), 559 (w), 468 (w). Found (%): C, 52.38; H, 2.76; N, 4.31. Calc. for $C_{59}H_{40}Eu_2N_4O_{15}$ (%): C, 52.54; H, 2.99; N, 4.15.

$[Sm_2(HSA)_4(SA)(phen)_2]_2$ **2**: yield ~42% based on H_2SA. IR (KBr pellet, ν/cm^{-1}): 3422 (br), 1629 (m), 1605 (vs), 1572 (s), 1517 (m), 1484 (s), 1465 (s), 1421 (m), 1391 (s), 1367 (s), 1334 (m), 1308 (w), 1249 (m), 1145 (m), 1103 (w), 1030 (w), 892 (w), 845 (w), 757 (m), 728 (m), 705 (w), 661 (w), 605 (w), 561 (w), 469 (w). Found (%): C, 52.49; H, 2.89; N, 4.31. Calc. for $C_{59}H_{40}N_4O_{15}Sm_2$ (%): C, 52.66; H, 3.00; N, 4.16.

$[Nd_2(HSA)_4(SA)(phen)_2]_2$ **3**: yield ~50% based on H_2SA. IR (KBr pellet, ν/cm^{-1}): 3425 (br), 1623 (m), 1605 (s), 1571 (s), 1516 (m), 1484 (s), 1462 (s), 1423 (m), 1391 (s), 1368 (s), 1337 (w), 1304 (m), 1248 (w), 1148 (m), 1106 (w), 1031 (w), 890 (w), 846 (w), 758 (m), 725 (w), 703 (w), 662 (w), 604 (w), 557 (w), 466 (w). Found (%): C, 53.36; H, 2.92; N, 4.35. Calc. for $C_{59}H_{40}N_4Nd_2O_{15}$ (%): C, 53.14; H, 3.02; N, 4.20.

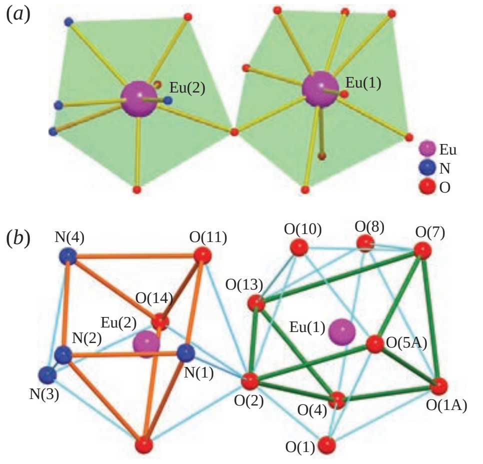


Figure 2 Coordination polyhedra for two $\mathrm{Eu^{III}}$ centers in **1**.

structure. In **1**, the asymmetric unit consists of two crystallographically unique $\mathrm{Eu^{III}}$ ions, one SA ligand, four HSA ligands and two phen ligands. The coordination environment of $\mathrm{Eu^{III}}$ ion in **1** is depicted in Figure 1. The Eu(1) center is coordinated by nine carboxylate oxygen atoms [Eu–O, 2.354(2)–2.625(2) Å] from seven HSA/SA ligands, and the $\mathrm{EuO_9}$ polyhedron can be described as a distorted tricapped trigonal prism geometry (Figure 2). As for the Eu(2) center, the coordination polyhedron is eight-coordinated in a distorted bicapped triangular prism geometric configuration with four sites occupied by four nitrogen atoms [Eu–N, 2.599(3)–2.640(3) Å] from two phen ligands, two carboxyl oxygen atoms [Eu–O, 2.321(2) and 2.334(2) Å] from two HSA ligands, one carboxyl oxygen atom [Eu–O, 2.5248(19) Å] and one hydroxy oxygen atom [Eu–O, 2.204(2) Å] from the same SA ligand. All bond lengths around the metal center are comparable to those found in other reported $\mathrm{Eu^{III}}$ complexes.[18–20] In a molecule of **1**, there are three distinct types of coordination modes for the HSA/SA ligands: a μ_2-μ^1:μ^2 bridging mode linking two lanthanide atoms, a μ_2-μ^1:μ^1 double monodentate bridging mode, and a μ_1-μ^1:μ^1 bidentate chelating mode (Figure 3). Adjacent $\mathrm{Eu^{III}}$ ions are linked *via* the μ_2-bridging carboxylate groups of the HSA/SA ligands to generate a binuclear building unit. Then, every two binuclear units are connected to form a tetranuclear pattern with the Eu(1)···Eu(2)/Eu(1)···Eu(1A) distances of 4.5205(3)/4.0895(3) Å. In addition, such $\mathrm{Eu_4}$ motifs are connected to form a 2D supramolecular network structure (Figure 4) by hydrogen bonds of C(52)–H(52A)/O(9) between the carbon atom from the phen ligand and the oxygen atom from the HSA ligand along the *ab* plane.

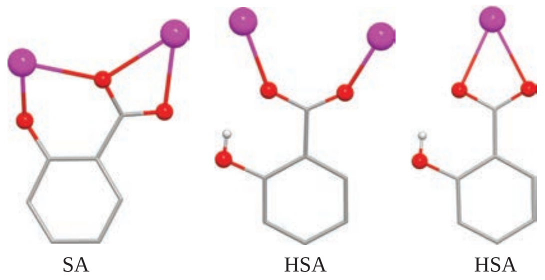


Figure 3 Coordination modes of HSA/SA ligands in **1**.

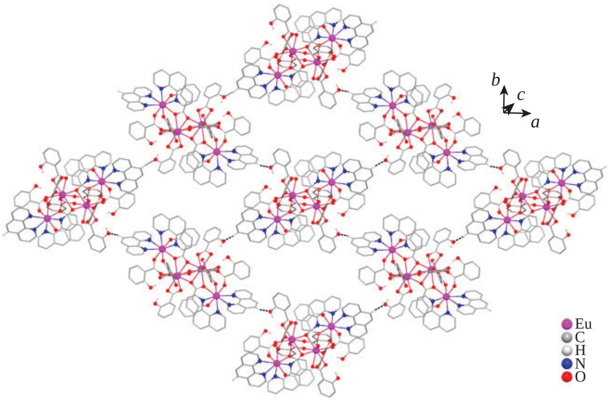


Figure 4 2D network structure with hydrogen bonds along the *ab* plane in **1**.

In summary, three unusual tetranuclear $\mathrm{Ln^{III}}$ complexes based on $\mathrm{H_2SA}$ and phen ligands were successfully constructed. The present findings reveal that the carboxyl group of $\mathrm{H_2SA}$ can exhibit diverse coordination modes; the hydroxyl group can provide an additional binding site and connect metal atoms to generate more complicated structures with incorporation of the carboxyl groups. The procedure described here can be generally used to react with other lanthanides for constructing coordination complexes with fascinating structures and potential properties.

This work was supported by the National Natural Science Foundation of China (no. 21471134), Plan for Scientific Innovation Talent of Henan Province (no. 154200510011) and Programme for Science & Technology Innovative Research Team in the University of Henan Province (no. 15IRTSTHN-002).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.012.

[‡] *Crystallographic data for* **1**–**3**. Single-crystal X-ray diffraction data were collected on an Oxford Xcalibur Gemini Eos diffractometer with MoKα radiation (λ = 0.71073 Å). Multi-scan absorption corrections were performed with the CrysAlisPro program.[15] Empirical absorption corrections were carried out using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structures were solved by direct methods and all non-hydrogen atoms were refined anisotropically by a full-matrix least-squares method with the SHELXTL crystallographic software package.[16,17] All hydrogen atoms were generated geometrically and refined isotropically as riding. For details, see Tables S1–S4 (Online Supplementary Materials).

For **1**: monoclinic, space group $P2_1/c$, a = 16.6472(4), b = 20.7052(5) and c = 16.0879(5) Å, β = 106.283°, V = 5322.8(2) Å^3, Z = 4, d_{calc} = 1.683 g cm^{-3}; μ(MoKα) = 2.410 mm^{-1}; data/restraints/parameters 9367/0/721; F(000) = = 2672; R_{int} = 0.0454. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0258, wR_2 = 0.0349; R indices (all data): R_1 = 0.0469, wR_2 = 0.0361.

For **2**: monoclinic, space group $P2_1/c$, a = 16.6472(4), b = 20.7052(5) and c = 16.0879(5) Å, β =106.283°, V = 5322.8(2) Å^3, Z = 4, d_{calc} = 1.679 g cm^{-3}; μ(MoKα) = 2.260 mm^{-1}; data/restraints/parameters 9350/0/721; F(000) = = 2664; R_{int} = 0.0314. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0246, wR_2 = 0.0391; R indices (all data): R_1 = 0.0444, wR_2 = 0.0407.

For **3**: monoclinic, space group $P2_1/c$, a = 16.6472(4), b = 20.7052(5) and c = 16.0879(5) Å, V = 5322.8(2) Å^3, β = 106.283°, Z = 4, d_{calc} = 1.664 g cm^{-3}; μ(MoKα) = 2.004 mm^{-1}; data/restraints/parameters 9367/0/712; F(000) = = 2648; R_{int} = 0.0480. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0266, wR_2 = 0.0313; R indices (all data): R_1 = 0.0541, wR_2 = 0.0325.

CCDC 1444460–1444462 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

References

1 *Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis, Topics in Current Chemistry*, ed. M. Schröder, Springer, Berlin, 2010, vol. 293.

2 M. Chen, E. C. Sañudo, E. Jiménez, S.-M. Fang, C.-S. Liu and M. Du, *Inorg. Chem.*, 2014, **53**, 6708.

3 Z.-N. Wang, X.-T. Xu, X. Lv, F.-Y. Bai, S.-Q. Liu and Y.-H. Xing, *RSC Adv.*, 2015, **5**, 104263.

4 A. J. Calahorro, I. Oyarzabal, B. Fernández, J. M. Seco, T. Tian, D. Fairen-Jimenez, E. Colacio and A. Rodríguez-Diéguez, *Dalton Trans.*, 2016, **45**, 591.

5 M. Du, C.-P. Li, C.-S. Liu and S.-M. Fang, *Coord. Chem. Rev*., 2013, **257**, 1282.

6 M.-D. Zhang, Z. Wang, Y. Qiu, J.-M. He, X. Liu and C.-Z. Zhang, *Mendeleev Commun.*, 2015, **25**, 296.

7 J. G. Małecki, A. Maroń and J. Kusz, *Mendeleev Commun*., 2015, **25**, 103.

8 J.-P. Costes, J. M. Clemente-Juan, F. Dahan, F. Nicodème and M. Verelst, *Angew. Chem. Int. Ed*., 2002, **41**, 323.

9 J. H. Burns and W. H. Baldwin, *Inorg. Chem.*, 1977, **16**, 289.

10 Z.-Q. Yan, X.-T. Meng, R.-R. Su, C.-H. Zeng, Y.-Y. Yang, S. Zhong and S. W. Ng, *Inorg. Chim. Acta*, 2015, **432**, 41.

11 N. Zhao, S.-P. Wang, R.-X. Ma, Z.-H. Gao, R.-F. Wang and J.-J. Zhang, *J. Alloys Compd.*, 2008, **463**, 338.

12 M.-C. Yin, C.-C. Ai, L.-J. Yuan, C.-W. Wang and J.-T. Sun, *J. Mol. Struct.*, 2004, **691**, 33.

13 M.-C. Yin, L.-J. Yuan, C.-C. Ai, C.-W. Wang, E-T. Yuan and J.-T. Sun, *Polyhedron*, 2004, **23**, 529.

14 C.-S. Liu, M. Du, E. C. Sãnudo, J. Echeverria, M. Hu, Q. Zhang, L.-M. Zhou and S.-M. Fang, *Dalton Trans*., 2011, **40**, 9366.

15 *CrysAlis CCD and CrysAlis RED, version 1.171.35.15*, Oxford Diffraction Ltd., Yarnton, Oxfordshire, UK, 2008.

16 G. M. Sheldrick, *SHELXTL, version 6.10*, Bruker Analytical X-ray Systems, Madison, WI, 2001.

17 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

18 H.-N. Li, H.-Y. Li, L.-K. Li, L. Xu, K. Hou, S.-Q. Zang and T. C. W. Mak, *Cryst. Growth Des.*, 2015, **15**, 4331.

19 X.-Q. Zhao, X.-H. Liu, J.-J. Lia and B. Zhao, *CrystEngComm*, 2013, **15**, 3308.

20 L.-X. You, S.-J. Wang, G. Xiong, F. Ding, K. W. Meert, D. Poelman, P. F. Smet, B.-Y. Ren, Y.-W. Tian and Y.-G. Sun, *Dalton Trans.*, 2014, **43**, 17385.

Received: 11th January 2016; Com. 16/4811