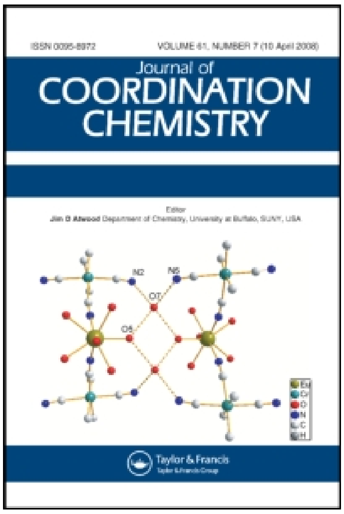

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structures of two rare-earth metal polymers of olsalazine

Yun-Zhi Tang[a]; Yu-Hui Tan[b]; Zong-Tang Ge[a]; Zhen-Xin Liu[a]; Chun-FA Liao[a]; Xiao-Bin Xie[a]
[a] School of Material Science & Chemistry Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, P.R. China [b] Department of Pharmacy, Gannan Medical University, Ganzhou 341000, P.R. China

First published on: 24 May 2010

To cite this Article Tang, Yun-Zhi , Tan, Yu-Hui , Ge, Zong-Tang , Liu, Zhen-Xin , Liao, Chun-FA and Xie, Xiao-Bin(2009) 'Synthesis and crystal structures of two rare-earth metal polymers of olsalazine', Journal of Coordination Chemistry, 62: 16, 2682 — 2688, First published on: 24 May 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970902906268

URL: http://dx.doi.org/10.1080/00958970902906268

Journal of Coordination Chemistry
Vol. 62, No. 16, 20 August 2009, 2682–2688

Taylor & Francis
Taylor & Francis Group

Synthesis and crystal structures of two rare-earth metal polymers of olsalazine

YUN-ZHI TANG*†, YU-HUI TAN‡, ZONG-TANG GE†, ZHEN-XIN LIU†,
CHUN-FA LIAO† and XIAO-BIN XIE†

†School of Material Science & Chemistry Engineering, Jiangxi University of
Science and Technology, Ganzhou, 341000, P.R. China
‡Department of Pharmacy, Gannan Medical University, Ganzhou, 341000, P.R. China

(*Received 16 August 2008; in final form 30 December 2008*)

Two 1-D linear coordination polymers, $\{[Gd_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot 2(EtOH)\}_n$ (**1**) (H_2L = olsalazine) and $\{[Eu_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot EtOH\}_n$ (**2**), were obtained from self-assembly of $Gd(NO_3)_3 \cdot 8H_2O$ or $Eu(NO_3)_3 \cdot 8H_2O$ with olsalazine. Both complexes are 1-D polymers, for **1** with crystal data: $P\bar{1}$, $a = 11.651(4)$, $b = 11.865(4)$, and $c = 12.296(4)$ Å, $\alpha = 77.984(4)^\circ$, $\beta = 65.559(4)^\circ$, and $\gamma = 74.558(5)^\circ$, $V = 1482.1(8)$ Å^3, $Z = 1$, $R_1 = 0.0389$, $wR_2 = 0.0793$, and **2** with crystal data: $P\bar{1}$, $a = 11.626(3)$, $b = 11.834(3)$, $c = 12.287(4)$ Å, $\alpha = 77.743(3)$, $\beta = 65.576(3)$, $\gamma = 74.371(3)^\circ$, $V = 1472.5(5)$ Å^3, $Z = 1$, $R_1 = 0.0609$, $wR_2 = 0.1185$. Central atoms (Gd or Eu) in both complexes adopt nine-coordinate tricapped trigonal prism geometry. CCDC No.: 694918 (**1**), 694919 (**2**).

Keywords: Olsalazine; Crystal structure; Gadolinium complex; Europium complex

1. Introduction

Because of their properties and applications in functional materials, the synthesis of organic–inorganic open framework complexes has received considerable interest [1–4]. Carboxylates are especially attractive as metal binding units in coordination networks as they bind strongly to metals, which contribute to the robust nature of the resulting coordination networks. Polycarboxylate aromatic ligands, such as 1,4-benzenedicarboxylate, 1,3-benzenedicarboxylate, 1,3,5-benzenecarboxylate, and 1,2,4,5-benzenetetracarboxylate, have been employed in the construction of high-dimensional structures [5–11]. While the variety of coordination modes available to carboxylate-based ligands (monodentate, chelating, and/or bridging) allows access to a wide variety of structures, it also makes it difficult to predict coordination geometries and node connectivity.

To better understand coordination of azodibenzoate ligands and the type of coordination polymers that form, we have undertaken a study of coordination polymers based upon olsalazine 3,3-azo-*bis*(6-hydroxybenzoic acid). In our previous work, we have reported the structures of Cd [9], Zn [10], Cd and Co [11], Mn [12], Ca and Mg [13]

---

*Corresponding author. Email: tangyunzhi75@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902906268

complexes of 3,3-azo-*bis*(6-hydroxybenzoic acid); the complexes display a wide variety of structures and interesting properties, however, structures of rare-earth complexes with 3,3-azo-*bis*(6-hydroxybenzoic acid) have not been reported. As part of our systematic work, in this article we report the hydrothermal reactions of this ligand with $Gd(NO_3)_3 \cdot 8H_2O$ or $Eu(NO_3)_3 \cdot 8H_2O$, which yield two 1-D coordination polymers $\{[Gd_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot 2EtOH\}_n$ (**1**) ($H_2L =$ olsalazine), and $\{[Eu_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot EtOH\}_n$ (**2**).

2. Experimental

Olsalazine sodium was obtained commercially; other chemicals and solvents were purchased from Aldrich and used as received. FT-IR spectra were recorded as KBr pellets from 4000–400 cm^{-1} on a Nicolet Inpact 170S FT-IR spectrometer. Elemental analysis was performed on a Perkin–Elmer 240C elemental analyzer.

2.1. *Synthesis of* $\{[Gd_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot 2EtOH\}_n$ *(1) and* $\{[Eu_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot EtOH\}_n$ *(2)*

A mixture of $Gd(NO_3)_3 \cdot 8H_2O$ or $Eu(NO_3)_3 \cdot 8H_2O$ and olsalazine sodium with molar ratio 1 : 1 in ethanol and water (V : V = 2 : 1) was stirred and refluxed at 100°C for 4 h, then filtered. Beautiful golden block-like crystals were obtained from the filtrate about 1 week later. For **1**, yield: 0.613 g (79%) on the basis of olsalazine sodium; Calcd for $C_{56}H_{48}Gd_2N_{10}O_{22}$ (%): C, 43.99; H, 3.14; N, 9.17. Found (%): C, 43.59; H, 3.01; N, 9.21. IR (KBr, cm^{-1}): 3438(m), 2922(w), 2361(m), 1927(w), 1588(s), 1484(s), 1445(vs), 1370(w), 1314(s), 1284(vs), 1005(m), 836(m), 796(w), 685(w), 497(s), 466(w). For **2**, yield: 0.423 g (76%) on the basis of olsalazine sodium; Calcd for $C_{54}H_{42}Eu_2N_{10}O_{21}$ (%): C, 44.12; H, 2.86; N, 9.53. Found (%): C, 44.32; H, 2.95; N, 9.51. IR (KBr, cm^{-1}): 3438(m), 1589(s), 1480(s), 1441(vs), 1370(m), 1314(s), 1284(vs), 1136(m), 1005(m), 836(m), 796(w), 685(w), 497(s), 466(w).

2.2. *Single crystal structure determination*

A golden block-like crystal of **1** with dimensions $0.086 \times 0.147 \times 0.301$ mm^3 was selected and placed in a Bruker P4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 292 K using the θ–2θ scan technique. The data were corrected for Lp and absorption effects. The crystal structure was solved using direct methods with SHELXS-97 [14]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. All hydrogen atoms were located from successive difference Fourier syntheses. The non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques [15]. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The same manipulation for **2** was conducted. Detailed information about the crystal data and structure determination for both compounds are summarized in table 1. Selected bond distances and angles are given in table 2.

Table 1. Crystal data and structure refinement for **1** and **2**.

Empirical formula	$C_{56}H_{48}Gd_2N_{10}O_{22}$	$C_{54}H_{42}Eu_2N_{10}O_{21}$
Formula weight	1527.54	1468.88
T (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)		
a	11.651(4)	11.626(3)
b	11.865(4)	11.834(3)
c	12.296(4)	12.287(2)
α	77.984(4)	77.743(3)
β	65.559(4)	65.576(3)
γ	74.558(5)	74.371(3)
V (Å^3)	1482.1(8)	1472.5(5)
Z	1	1
ρ (Calcd) (Mg m^{-3})	1.711	1.656
μ (Mo-Kα) (mm^{-1})	2.306	2.195
F(000)	758	728
Crystal size (mm^3)	$0.086 \times 0.147 \times 0.301$	$0.110 \times 0.122 \times 0.221$
θrange for data collection (°)	1.79–25.99	1.80–27.92
Index ranges	$-14 \leq h \leq 8$, $-14 \leq k \leq 14$, $-15 \leq l \leq 13$	$-12 \leq h \leq 14$, $-15 \leq k \leq 13$, $-11 \leq l \leq 16$
Reflections collected	7901	8539
Independent reflections	36652 [R(int) = 0.0156]	7128 [R(int) = 0.0553]
Data/restraints/parameters	6652/6/827	7128/6/800
Final R indices [$I > 2\sigma(I)$] (6699)	$R_1 = 0.0291$, $wR_2 = 0.0735$	$R_1 = 0.0609$, $wR_2 = 0.1606$
R indices (all data)	$R_1 = 0.0389$, $wR_2 = 0.0793$	$R_1 = 0.1185$, $wR_2 = 0.1762$
Minimum, Maximum ρ (e Å^{-3})	1.307, −1.007	1.421, −1.093

3. Results and discussion

The IR spectrum of both compounds display three strong absorptions at 1626, 1555, and 1449 cm^{-1} for **1** and 1627, 1562, and 1448 cm^{-1} for **2**, due to the characteristic υ_{as}(COO) and υ_s(COO) stretching modes of carboxylates [16]. A broad band around 3410 cm^{-1} suggests water exists in both compounds.

The 1-D structures of both complexes were revealed by the X-ray single-crystal structure analysis. Crystallographic data (as shown in table 1) indicate that $\{[Gd_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)] \cdot 2(EtOH)\}_n$ (**1**) and $\{[Eu_2(L)_2 \cdot (Phen)_2 \cdot 2(H_2O) \cdot 2(NO_3)]\,EtOH\}_n$ (**2**) belong to the triclinic system, with space group $P\bar{1}$ and $Z = 1$. Some high values of the largest diffraction peak and hole in both complexes, all are located around the heavy atom (Gd or Eu) from the effect of serial end interruption.

There are two crystallographically independent Gd atoms in **1**, although the coordination geometries around both are distorted tricapped trigonal prisms (figure 1). Gd1 is nine-coordinate from two bidentate carboxylates from different olsalazine ligands, two bidentate 1,10-phenanthrolines, one bidentate nitrate, and one water molecule. Around each Gd1, there are two crystallization ethanol molecules. Gd2 adopts the same coordination as Gd1, but there are no crystallization ethanol molecules. Each olsalazine in **1** is a tetradentate ligand bridging two Gds resulting in a 1-D zigzag structure. The gadoliniums stand in the vertex of the catenarian structure (as shown in figure 2).

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

*Bond lengths for **1***			
Gd(1)–O(21)	2.373(16)	Gd(1)–O(16)	2.405(16)
Gd(1)–O(2W)	2.405(15)	Gd(1)–O(22)	2.437(14)
Gd(1)–O(18)	2.414(14)	Gd(1)–O(17)	2.474(13)
Gd(1)–N(6)	2.508(16)	Gd(1)–O(11)	2.548(16)
Gd(1)–N(9)	2.608(17)	Gd(2)–O(10)#1	2.375(17)
Gd(2)–O(1W)	2.391(14)	Gd(2)–O(20)	2.427(16)
Gd(2)–O(9)#1	2.484(16)	Gd(2)–O(19)	2.478(11)
Gd(2)–N(7)	2.462(18)	Gd(2)–O(3)	2.537(19)
Gd(2)–N(8)	2.539(11)	Gd(2)–O(2)	2.603(15)
Symmetry transformations used to generate the equivalent atoms. #1: x + 1, y, z − 2			
*Bond lengths for **2***			
Eu(1)–O(1W)	2.40(2)	Eu(1)–O(17)	2.35(3)
Eu(1)–O(2)#1	2.40(2)	Eu(1)–O(3)#1	2.46(2)
Eu(1)–O(11)	2.49(2)	Eu(1)–O(13)	2.49(2)
Eu(1)–N(5)	2.55(2)	Eu(1)–N(10)	2.613(16)
Eu(1)–O(10)	2.606(18)	Eu(2)–N(9)	2.41(3)
Eu(2)–O(18)	2.43(2)	Eu(2)–O(16)	2.42(2)
Eu(2)–O(2W)	2.408(19)	Eu(2)–O(9)	2.47(2)
Eu(2)–O(12)	2.48(2)	Eu(2)–O(15)	2.486(16)
Eu(2)–O(14)	2.55(3)	Eu(2)–N(6)	2.54(3)
Symmetry transformations used to generate the equivalent atoms. #1: x + 1, y, z + 2			
*Bond angles for **1***			
O(21)–Gd(1)–O(16)	151.8(6)	O(21)–Gd(1)–O(2W)	124.4(6)
O(16)–Gd(1)–O(2W)	76.3(6)	O(21)–Gd(1)–O(22)	51.5(5)
O(16)–Gd(1)–O(22)	149.5(5)	O(2W)–Gd(1)–O(22)	74.3(6)
O(21)–Gd(1)–O(18)	80.5(5)	O(16)–Gd(1)–O(18)	71.7(6)
O(2W)–Gd(1)–O(18)	122.4(5)	O(22)–Gd(1)–O(18)	118.3(5)
O(21)–Gd(1)–O(17)	83.2(6)	O(16)–Gd(1)–O(17)	83.7(6)
O(2W)–Gd(1)–O(17)	77.1(5)	O(22)–Gd(1)–O(17)	81.7(5)
O(10)#1–Gd(2)–O(1W)	120.5(6)	O(10)#1–Gd(2)–O(20)	123.3(6)
O(1W)–Gd(2)–O(20)	69.9(5)	O(10)#1–Gd(2)–O(9)#1	53.6(5)
O(1W)–Gd(2)–O(9)#1	75.4(6)	O(20)–Gd(2)–O(9)#1	82.6(5)
O(10)#1–Gd(2)–O(19)	82.8(5)	O(1W)–Gd(2)–O(19)	124.2(4)
O(20)–Gd(2)–O(19)	56.1(4)	O(9)#1–Gd(2)–O(19)	84.5(5)
O(10)#1–Gd(2)–N(7)	139.3(5)	O(1W)–Gd(2)–N(7)	99.1(6)
O(20)–Gd(2)–N(7)	76.5(6)	O(9)#1–Gd(2)–N(7)	159.0(5)
Symmetry transformations used to generate the equivalent atoms. #1: x + 1, y, z − 2			
*Bond angles for **2***			
O(1W)–Eu(1)–O(17)	120.3(8)	O(1W)–Eu(1)–O(2)#1	121.2(7)
O(17)–Eu(1)–O(2)#1	82.8(9)	O(1W)–Eu(1)–O(3)#1	69.6(7)
O(17)–Eu(1)–O(3)#1	122.1(9)	O(2)#1–Eu(1)–O(3)#1	53.7(6)
O(1W)–Eu(1)–O(11)	77.9(8)	O(17)–Eu(1)–O(11)	68.7(9)
O(2)#1–Eu(1)–O(11)	151.3(8)	O(3)#1–Eu(1)–O(11)	146.6(7)
O(1W)–Eu(1)–O(13)	74.6(8)	O(17)–Eu(1)–O(13)	54.1(8)
O(2)#1–Eu(1)–O(13)	82.1(8)	O(3)#1–Eu(1)–O(13)	81.1(9)
O(11)–Eu(1)–O(13)	83.3(8)	O(1W)–Eu(1)–N(5)	100.4(8)
O(17)–Eu(1)–N(5)	138.5(8)	O(2)#1–Eu(1)–N(5)	83.0(8)
O(3)#1–Eu(1)–N(5)	77.7(8)	O(11)–Eu(1)–N(5)	116.5(8)
O(13)–Eu(1)–N(5)	158.5(8)	O(1W)–Eu(1)–N(10)	146.6(7)
O(17)–Eu(1)–N(10)	77.7(8)	N(4)–Eu(1)–H(1WA)	89(2)
N(9)–Eu(2)–O(18)	75.4(8)	N(9)–Eu(2)–O(16)	127.8(8)
O(18)–Eu(2)–O(16)	119.2(7)	N(9)–Eu(2)–O(2W)	144.4(7)
O(18)–Eu(2)–O(2W)	121.0(7)	O(16)–Eu(2)–O(2W)	74.7(8)
N(9)–Eu(2)–O(9)	77.4(7)	O(18)–Eu(2)–O(9)	120.0(8)
O(16)–Eu(2)–O(9)	119.8(7)	O(2W)–Eu(2)–O(9)	67.0(7)
N(9)–Eu(2)–O(12)	127.3(9)	O(18)–Eu(2)–O(12)	51.9(7)
O(16)–Eu(2)–O(12)	83.7(8)	O(2W)–Eu(2)–O(12)	76.7(8)
O(9)–Eu(2)–O(12)	126.9(7)	N(9)–Eu(2)–O(15)	85.1(7)
O(18)–Eu(2)–O(15)	80.0(8)	O(16)–Eu(2)–O(15)	53.6(7)
Symmetry transformations used to generate the equivalent atoms. #1: x + 1, y, z + 2			

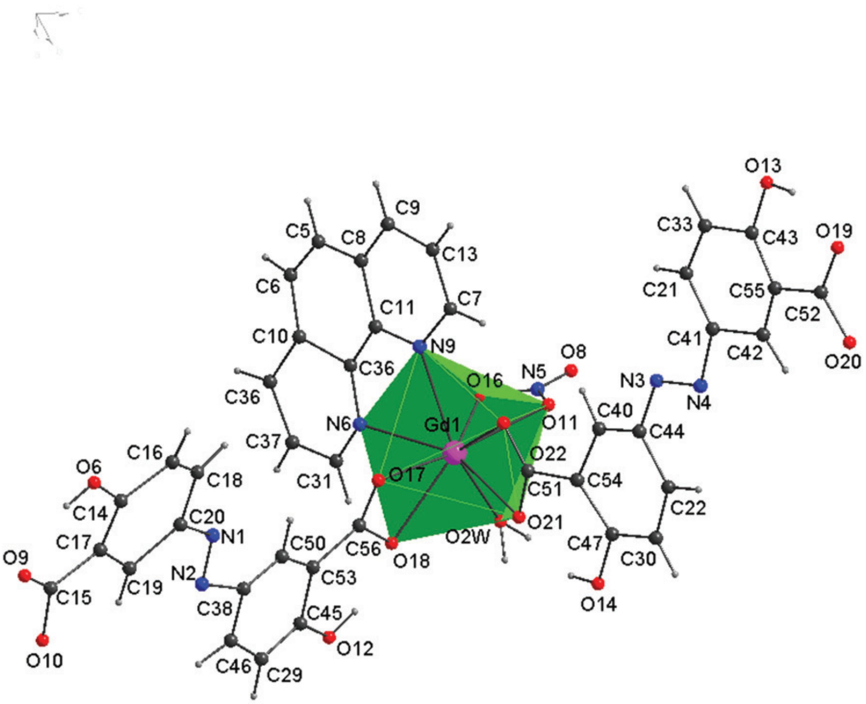

Figure 1. Polyhedral representation of **1** showing the coordination geometry around Gd as a distorted tricapped trigonal prism.

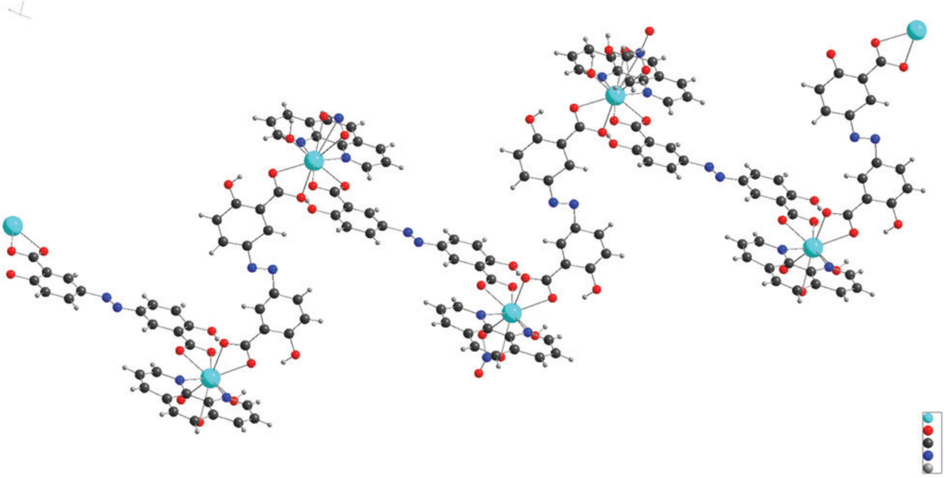

Figure 2. One-dimensional zigzag infinite linear structure of **1**.

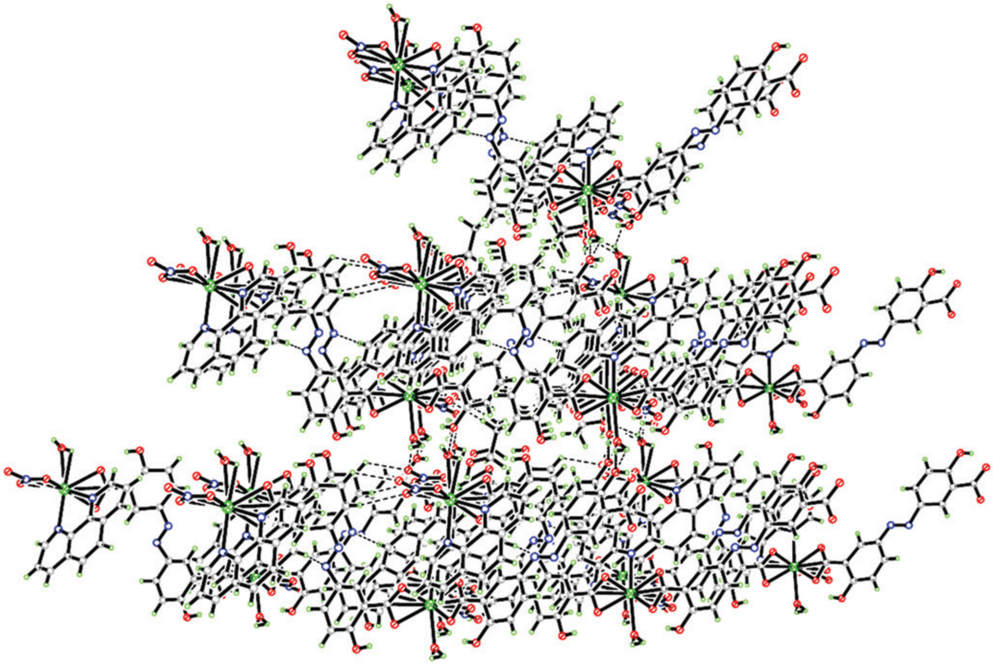

Figure 3. A simple hydrogen-bonding network representation of **1**.

The europiums in **2** also adopt distorted tricapped trigonal prism coordination, completed by two bidentate carboxylates of different olsalazines, two bidentate 1,10-phenanthrolines, one bidentate chelating nitrate, and one water molecule. There is only one ethanol molecule around europium in **2**. Its 1-D zigzag linear structure is shown in "Supplementary material".

Table 2 shows selected bond lengths and angles of **1** and **2**. In **1**, the Gd(2)–O2 2.603 Å distance is obviously longer than other Gd–O distances; also for **2**, the Eu(1)–O(10) 2.606 Å distance is longer than other Eu–O distances, suggesting both metals are highly unsymmetrical. All other bond distances, Gd–O (2.373–2.548 Å) and Gd–N (2.462–2.608 Å) in **2**, are similar to other Gd(III) [17] complexes and within the range for normal Gd–N and Gd–O distances. Similarly, Eu–O (2.35–2.55 Å) and Eu–N (2.41–2.61 Å) bond distances agree with their normal distances [18].

Strong hydrogen bonds (O–H···O) exist between uncoordinated oxygens from carboxylates and hydrogens of water, O2W–H2WA···O6 (1.878 Å), O4–H4A···O11 (1.878 Å), O6–H6A···O9 (1.74 Å) for **1** (figure 3) and O8–H8A···O12 (1.978 Å), O7–H7A···O13 (1.695 Å), O4–H4A···O3 (1.78 Å) for **2**. The shortest face-to-face distance between phenyl rings (olsalazine) is 3.807 Å, indicating weak π–π stacking interactions, important in supramolecular assembly and stabilization of the lattice [19].

4. Conclusion

We have synthesized two new Gd(III) and Eu(III) coordination polymers based on the drug olsalazine and 1,10-phenanthroline ligand as building blocks. Central atoms

(Gd or Eu) in both complexes adopt the same coordination modes with nine-coordinated tricapped trigonal prism geometry.

Supplementary material

The CCDC No. for compound **1** is 633035 and for compound **2** 633034. Detailed information about both crystal data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax +44(0)1223336033 or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.ck.

Acknowledgments

This work was supported by the Natural Science Foundation of Jiangxi Province (Code No. 2008GZH0064) and Jiangxi Provincial Sustentation Fund of Education Department (Code No. GJJ08275).

References

[1] K. Biradha, M. Fujita. *J. Chem. Soc., Dalton Trans.*, 3805 (2000).
[2] C. Janiak. *Angew. Chem. Int. Ed. Engl.*, **36**, 1431 (1997) and references therein.
[3] C.J. Kepert, M.J. Rosseinsky. *Chem. Commun.*, 375 (1999).
[4] M.J. Zaworotko. *Chem. Commun.*, 1 (2001).
[5] J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **123**, 8239 (2001).
[6] C. Livage, N. Guillou, J. Marrot, G. Ferey. *Chem. Mater.*, **13**, 4387 (2001).
[7] T. Loiseau, H. Muguerra, M. Haouas, F. Taulelle, G. Ferey. *Solid State Sci.*, **7**, 603 (2005).
[8] Z.-F. Chen, Z.-L. Zhang, Y.-H. Tan, Y.-Z. Tang, H.-K. Fun, Z.-Y. Zhou, B.F. Abrahams, H. Liang. *Cryst. Eng. Comm.*, **10**, 217 (2008).
[9] Y.-Z. Tang, Y.-H. Tan, J.-W. Zhu, F.-M. Ji, C.-F. Liao. *Cryst. Growth Des.*, **8**, 1801 (2008).
[10] Y.-Z. Tang, Y.-H. Tan, Y.-L. Tan. *Z. Anorg. Allg. Chem.*, **633**, 332 (2007).
[11] Y.-Z. Tang, S.-P. Yang, Y.-H. Tan, S.-H. Chen, Y.-W. Cao. *Chinese J. Inorg. Chem.*, **23**, 70 (2007).
[12] Y.-Z. Tang, Y.-H. Tan, Y.-W. Cao. *Acta Crystallgr., Sect. E*, **63**, m1175 (2007).
[13] Y.-Z. Tang, Y.-H. Tan, S.-H. Chen, Y.-W. Cao, *et al. J. Coord. Chem.*, **61**, 1244 (2008).
[14] G.M. Sheldrick. *SHELXS-97, Programm zur Lösung von Kristallstrukturen*, University of Göttingen, Germany (1997).
[15] G.M. Sheldrick. *SHELXS-97, Programm zur Verfeinerung von Kristallstrukturen*, University of Göttingen, Germany (1997).
[16] J. Sheals, P. Persson, B. Hedman. *Inorg. Chem.*, **40**, 4302 (2001).
[17] L.C. Delgado, J. Pasan, O. Fabelo, M.H. Molina, F. Lloret, M. Julve, C.R. Perez. *Inorg. Chem.*, **45**, 10585 (2006).
[18] R.S. Dickins, S. Aime, A.S. Batsanov, A. Beeby, M. Botta, I.J. Bruce, J.A.K. Howard, C.S. Love, D. Parker, R.D. Peacock, H. Puschmann. *J. Am. Chem. Soc.*, **124**, 12697 (2002).
[19] W. Clegg, J.T. Cressy, A. Mocamky. *Acta Crystallogr., Sect. C*, **51**, 234 (1995).