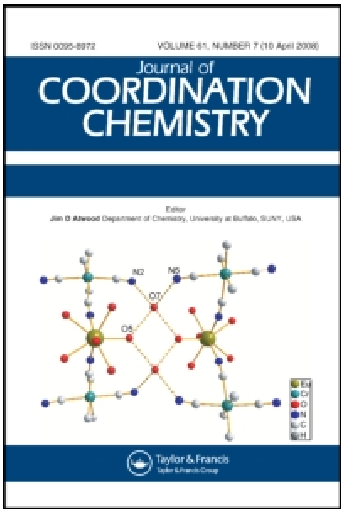


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Isomorphous La, Nd, and Gd-PCPA-based polymers

Zhen Wang[a]; Dong-Sheng Liu[b]; Han-Hui Zhang[a]; Chang-Cang Huang[a]; Yan-Ning Cao[a]; Xiao-Hong Yu[a]
[a] Department of Chemistry, Fuzhou University, Fuzhou, Fujian, P.R. China [b] Chemistry Department of Jinggangshan Normal College, Ji'an, Jiangxi, P.R. China

First published on: 27 August 2007

To cite this Article Wang, Zhen , Liu, Dong-Sheng , Zhang, Han-Hui , Huang, Chang-Cang , Cao, Yan-Ning and Yu, Xiao-Hong(2008) 'Isomorphous La, Nd, and Gd-PCPA-based polymers', Journal of Coordination Chemistry, 61: 3, 419 — 425, First published on: 27 August 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701343580

URL: http://dx.doi.org/10.1080/00958970701343580

Journal of Coordination Chemistry
Vol. 61, No. 3, 10 February 2008, 419–425

Isomorphous La, Nd, and Gd-PCPA-based polymers

ZHEN WANG†, DONG-SHENG LIU‡, HAN-HUI ZHANG*†,
CHANG-CANG HUANG†, YAN-NING CAO† and XIAO-HONG YU†

†Department of Chemistry, Fuzhou University, Fuzhou,
Fujian, 350002, P.R. China
‡Chemistry Department of Jinggangshan Normal College, Ji'an,
Jiangxi, 343009, P.R. China

(*Received 3 April 2006; revised 29 June 2006; in final form 30 June 2006*)

An isomorphous series of three novel lanthanide coordination polymers $[Ln(PCPA)_3(glycol)]_n$, [where, Ln = La(**1**); Nd(**2**); Gd(**3**); PCPA = *p*-chlorophenoxyacetate] have been synthesized under hydrothermal conditions and characterized by elemental analyses, IR spectra, TG analysis, fluorescence spectra and single crystal X-ray diffraction analysis. The results reveal that all of them form a chain-like one-dimensional structure. Photoluminescent properties for the complexes are also reported.

Keywords: Lanthanide; Coordination polymer; Crystal structure; Luminescence; hydrothermal synthesis

1. Introduction

There has been intense interest in low-dimensional coordination polymers due to their intriguing structural features and potential as functional materials different from those of 3-D coordination polymers [1–4]. Ln-carboxylates for potential use as biological luminescent probes [5] and MRI contrast agents [6, 7] have also been reported. In contrast to transition-metal organic coordination polymer, lanthanide complexes exhibit fascinating structural features as a result of large radii, high coordination numbers and promising physical properties such as magnetism and special fluorescence. We attempt to construct metal organic coordination polymers from lanthanide and the flexible ligand PCPA–a widely used herbicide, the coordination chemistry of which has been extensively studied and well understood for mono- and dinuclear complexes but few polymers. Herein, we report the synthesis, crystal structure and photoluminescence of three novel lanthanide coordination polymers $[Ln(PCPA)_3(glycol)]_n$.

---

*Corresponding author. Fax: (+86)-591-87893239. Email: zhanghh1840@hotmail.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701343580

2. Experimental

2.1. *General*

All reagents were used as purchased without further purification. Elemental analyses of C and H were performed with an Elementar Vario EL III elemental analyzer. The IR spectra were recorded with a Perkin–Elmer Spectrum 2000 FT-IR spectrometer in the range of 400–4000 $\mathrm{cm^{-1}}$ using KBr pellets. Thermogravimetric analyses were conducted on a NETZSCH STA 449C Thermal Analyzer in an argon atmosphere with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ from room temperature to 1000°C. Fluorescence spectra were measured with an Edinburgh F920 analytical instrument.

2.2. *Synthesis of [Ln(PCPA)$_3$(glycol)]$_n$, [Ln = La(1); Nd(2); Gd(3)]*

Synthesis of the compounds was achieved by the hydrothermal technique, in a Teflon-lined autoclave and under synthetic reaction conditions determined empirically.

The compounds were prepared by reacting 0.1 mmol of Ln_2O_3 or $Ln(NO_3)_3$ [where, Ln = La(**1**); Nd(**2**); Gd(**3**)], 0.5 mmol of *p*-chlorophenoxyacetic acid, and 0.5 mmol of IN (IN = isonicotinic acid) in 4 mL H_2O and 2 mL glycol under autogenous pressure to 160°C for 4 days and then kept at 70°C for a further 12 h. Upon cooling to room temperature, the unexpected product appeared as long colorless (for complexes **1** and **3**) or pink (for complex **2**) parallelepipeds in about 70% yield based on Ln_2O_3. Anal. Calcd for **1**: C, 41.21; H, 3.19; for **2**: C, 40.92; H, 3.17; for **3**: C, 40.24; H, 3.12; found for **1**: C, 40.22; H, 3.39; for **2**: C, 39.87; H, 3.36; for **3**: C, 40.66; H, 3.28.

2.3. *X-ray crystallography*

The reflection intensities of **1**, **2** and **3** were collected on a Bruker APEXII CCD area-detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298 ± 2 K. An empirical absorption correction was applied to the data using the multi-scan technique. Lp correction and a ψ empirical absorption correction were made for the intensity data. The structures of **1**, **2** and **3** were solved by the Patterson method and successive Fourier difference syntheses, and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXTL-97). All hydrogen atoms were generated geometrically and not refined. Crystallography data are given in table 1. Selected bond lengths are listed in table 2. The bond length tables are combined into one to show the similarity and differences between complexes. All calculations were performed on a computer with the SHELXTL-PC program package [8, 9].

3. Results and discussion

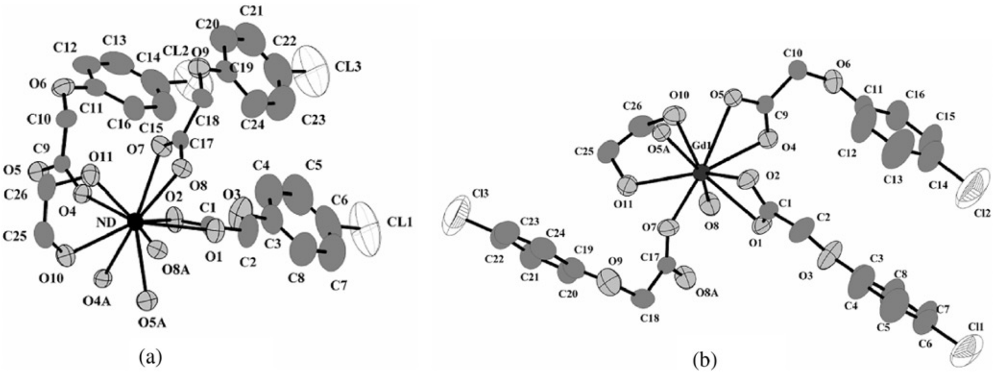
3.1. *Structural description of [Ln(PCPA)$_3$(glycol)]$_n$*

The immediate coordination environment around the Ln centers in [Ln(PCPA)$_3$(glycol)]$_n$ is shown in figure 1(a) (for complex **1** and **2**) and figure 1(b) (for complex **3**). The La(III) and Nd(III) ions lie in decacoordinate environments,

Table 1. Crystallographic data and structure refinement for **1**, **2** and **3**.

Complex	**1**	**2**	**3**
Empirical Formula	$C_{26}H_{24}O_{11}C_{13}La$	$C_{26}H_{24}O_{11}C_{13}Nd$	$C_{26}H_{24}O_{11}C_{13}Gd$
Formula mass	757.71	763.04	776.05
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.8687(4)	8.7460(3)	9.0002(6)
b (Å)	10.1811(5)	10.2184(4)	10.0739(6)
c (Å)	17.9103(9)	17.8131(7)	17.7613(11)
α (°)	76.957(7)	77.4560(5)	76.821(8)
β (°)	76.550(6)	77.0510(5)	76.372(8)
γ (°)	70.634(6)	71.1440(5)	69.738(8)
V (Å^3)	1464.26(12)	1450.01(9)	1449.13(16)
D_c (g cm^{-3})	1.719	1.748	1.779
Z	2	2	2
F(000)	752	758	766
λ(Mo-Kα) (Å)	0.71073	0.71073	0.71073
Measured reflections	17802	14621	17504
Independent reflections	7082	6836	7000
Observed reflections	6058	5824	6290
R_{int}	0.0274	0.0264	0.0213
Final R indices	R_1[a], 0.0279; wR_2[b], 0.0618	R_1[a], 0.0293; wR_2[b], 0.0623	R_1[a], 0.0216; wR_2[b], 0.0533,

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



(a) (b)

Figure 1. Perspective view of the coordination environment of the Ln(III)(Ln = La or Nd) in **1** and **2** (a) and Gd(III) in **3** (b). Hydrogen atoms were removed for clarity.

consisting of two oxygen atoms from one glycol molecular and eight oxygen atoms from PCPA ligands leading to a highly distorted bicapped square antiprism geometry. Compared to **1** and **2**, a slight different coordination environment is found for the Gd(III) centers due to the smaller ionic radius of Gd(III) as compared to the La(III) and Nd(III) ions. As shown in figure 1(b), Gd(III) is located in a nine-coordinate environment consisting of two oxygen atoms from one glycol molecular and other seven oxygen atoms from PCPA ligands leading to a highly distorted monocapped square antiprism.

The carboxylate groups have two different coordination modes: in **1** and **2**, a common bidentate chelating mode and a tridentate bridging mode, result in a dimeric unit with centrosymmetry and further lead to a polymeric chain along a (figure 2a).

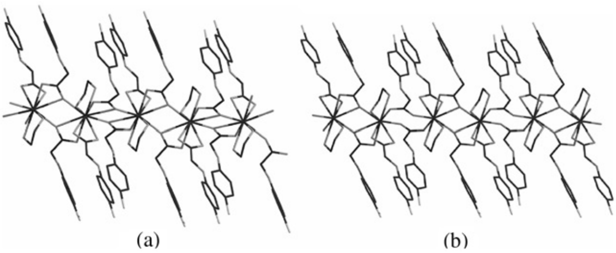


Figure 2. 1D chain structure of complexes **1**, and **2** (a) and **3** (b), showing identical structure motifs but different coordination modes of the ligand PCPA.

Table 2. Selected bond lengths (Å) for **1**, **2** and **3**.

1^{c}, **2**^{d} and **3**^{e}			
La–O(5)#1^{c}	2.4772(15)	La–O(2)	2.4794(15)
Nd–O(4)	2.4115(18)	Nd–O(8)#1^{d}	2.4148(17)
Gd(1)–O(8)#1^{e}	2.2784(15)	Gd(1)–O(5)#2^{e}	2.3535(14)
La–O(1)#2^{c}	2.5631(17)	La–O(7)	2.5818(16)
Nd–O(5)#2^{d}	2.5032(18)	Nd–O(2)	2.5230(18)
Gd(1)–O(7)	2.3922(16)	Gd(1)–O(10)	2.4698(16)
La–O(4)	2.5846(16)	La–O(10)	2.6084(18)
Nd–O(7)	2.5234(18)	Nd–O(11)	2.5554(18)
Gd(1)–O(2)	2.4780(16)	Gd(1)–O(4)	2.4799(16)
La–O(8)	2.6240(17)	La–O(11)	2.6312(17)
Nd–O(10)	2.5725(18)	Nd–O(1)	2.5737(19)
Gd(1)–O(1)	2.5306(14)	Gd(1)–O(11)	2.5435(16)
La–O(5)	2.7331(16)	La–O(2)#2^{c}	2.7801(16)
Nd–O(8)	2.7010(18)	Nd–O(4)#2^{d}	2.7788(18)
Gd(1)–O(5)	2.6280(14)		
O11 $\cdots$ O(7) #2^{c} (H-bonds)	2.680	O10 $\cdots$ O(8)#1^{c}(H-bonds)	2.881
O10 $\cdots$ O(2) #1^{d} (H-bonds)	2.678	O11 $\cdots$ O(1) #2^{d}(H-bonds)	2.819
O10 $\cdots$ O(2) #2^{e} (H-bonds)	2.755	O11 $\cdots$ O(1) #1^{e}(H-bonds)	2.758

Symmetry codes: [c] 1 $-x+1, -y+1, -z+1$; #2 $-x+2, -y+1, -z+1$; [d] #1 $-x+1, -y+1, -z+1$; #2 $-x, -y+1, -z+1$; [e] #1 $-x, -y+1, -z+1$; #2 $-x+1, -y+1, -z+1$.

In complex **3** they exhibit three coordination modes: a common bidentate chelating mode, a bidentate bridging mode and a tridentate briging mode to form a 1D chain along *a* (figure 2b). The bond lengths of Ln–O range from 2.4772(15)–2.7801(16) Å for **1**, 2.4115(18)–2.7788(18) Å for **2** and 2.2784(15)–2.6280(14) Å for **3** (table 2), consistent with those of reported polymers [10–12]. The distances between the two Ln ions in the dimeric units are: 4.420(2) and 4.466(2) Å between La(III) ions, 4.348(0) and 4.418(0) Å between Nd(III) ions, 4.215(3) and 4.803(2) Å between Gd(III) ions.

The three ligands of **1** contain significantly different torsion angles, with C1–C2–O3–C3 = 65.923(5)°, C9–C10–O6–C11 = 79.767(5)° and C17–C18–O9–C19 = 175.372(3)°; for **2** C1–C2–O3–C3 = 174.710(3)°, C9–C10–O6–C11 = 66.447(3)° and C17–C18–O9–C19 = 81.539(3)°, for **3** C1–C2–O3–C3 = 178.113(5)°, C9–C10–O6–C11 = 78.650(7)° and C17–C18–O9–C19 = 71.090(7)°. This may be a consequence of the packing and stacking arrangement of the *p*-chlorophenoxy groups as the molecule aligns itself to form the crystal. Interestingly, the three complexes exhibit aromatic stacking interactions. Partly overlapped parallel benzene rings of the three complexes are

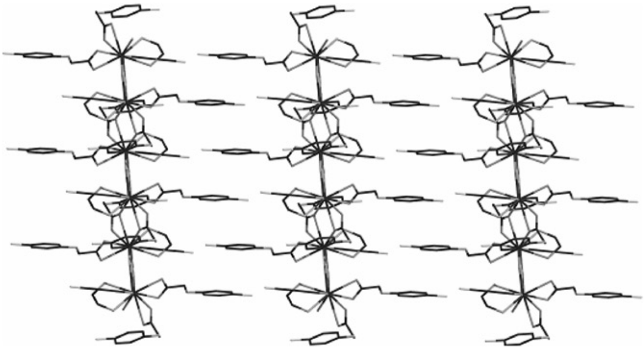


Figure 3. View of aromatic stacking and weak interactions between two chains in the three complexes.

observed in the crystal as shown in figure 3, which indicates weak π–π interactions between adjacent chains. The interplanar distances between two aromatic rings in a roughly "face-to-face" orientation are in the range of 3.54–3.58 Å for all three complexes, suggesting the presence of weak intermolecular stacking interactions. Stacking requires two aromatic π systems to overlap and maximal displacement is usually determined by the size of the stacked rings; a substituent with lone pair(s), which may conjugate with a π system, will increase possible overlap in the direction of the substituent [13]. Therefore in the case of the three complexes, the substituent chlorine in the ligands PCPA may enhance the π–π interactions.

3.2. *Infrared spectra*

The IR spectra of **1**, **2** and **3** clearly show the presence of PCPA and coordinated glycol. The absence of the expected absorption at 1690–1730 cm^{-1} for the protonated carboxylate groups illustrates complete deprotonation of the ligands in the reaction with lanthanide. The strong absorptions at 1575 and 1430 for **1**, 1575 and 1436 for **2**, and 1580 and 1438 cm^{-1} for **3**, correspond to asymmetric and symmetrical stretching vibrations, – ν_{as}(COO) and ν_s(COO), respectively – of the coordinated carboxylate groups. The differences ($\Delta = \nu_{as} - \nu_s$) between ν_{as}(COO) and ν_s(COO) (145 cm^{-1} for **1**, 139 cm^{-1} for **2**, and 142 cm^{-1} for **3**) are significantly smaller than the corresponding value of 187 cm^{-1} for the free PCPA anions, indicating a bidentate bridging coordination mode of carboxylate groups. The strong C–O stretching vibrations at about 1240 cm^{-1} in the spectra of **1**, **2**, and **3**, and the ligand PCPA suggest that the oxygen atom from phenoxy may not coordinate to metal centres. This is in accordance with the result of X-ray diffraction analysis.

3.3. *TG analysis*

The three complexes were investigated by the thermogravimetric (TG) techniques to characterize the thermal stability. The TG analysis curve recorded at 20–1000°C reveals that the structures of **1**, **2** and **3** show approximately identical thermal decomposition behavior since they are isostructural. Complex **3** for example, figure 4, shows two main

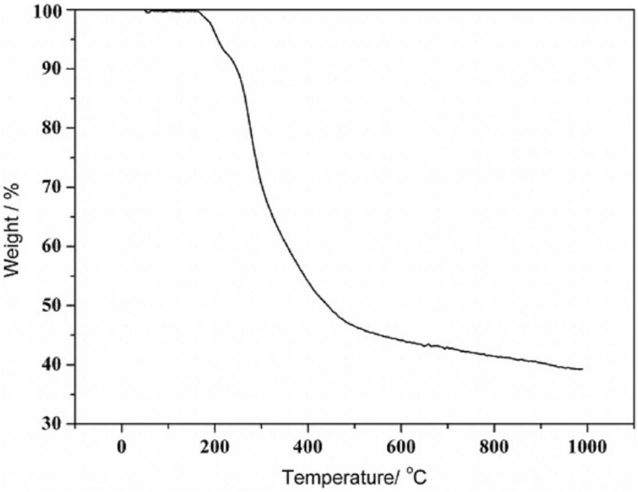


Figure 4. TGA diagram for **3**.

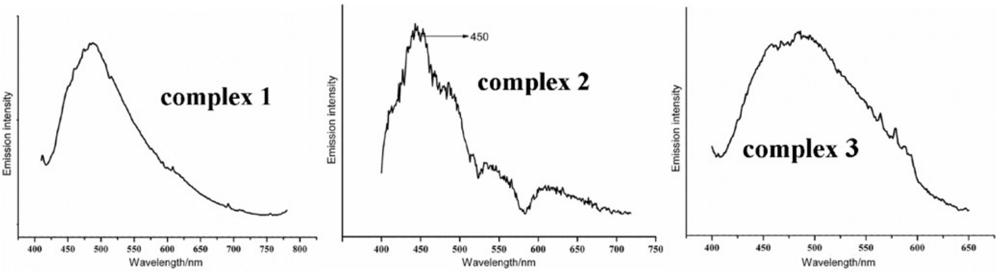


Figure 5. Solid-state emission spectra of **1**, **2** and **3** at room temperature.

steps of weight loss. The initial weight loss of 7.69% (Calculated 7.47%) started at about 170°C and ended at about 230°C corresponding to the removal of the coordinate glycol ligands. The second step that started at about 230°C is attributed to elimination and/or decomposition of PCPA ligands.

3.4. *Fluorescent properties*

Figure 5 shows the emission spectra of the complex **1**, **2** and **3** in the solid state at room temperature. We cannot see the characteristic emission of Ln(III) from the emission spectrum of the three complexes. As shown in figure 5, the complexes exhibit similar fluorescence emission bands mainly ranging from 450 to 550 nm with the maximum emission wavelengths at 487 nm for **1**, 453 nm for **2**, and 488 nm for **3** upon photoexcitation at 380 nm, which are attributed to the coordinated ligands since PCPA ligand exhibits photoemission at 311 nm upon photoexcitation at 270 nm. Therefore, energy is transferred from ligands to Ln(III) ions but not enough to sensitize the luminescence of Ln ions [14].

4. Conclusion

In summary, hydrothermal reaction of the carboxylate-based ligands with Ln_2O_3 afforded an isomorphous series of three lanthanide coordination polymers $[Ln(PCPA)_3(glycol)]_n$, all of which form a chain-like one-dimensional structure. The coordination geometries of the metal centres are different in **1**, **2** and **3**, yet the overall crystal structure topologies appear to be quite similar as a result of the smaller ionic radius of the Gd(III) ion as compared to La(III) and Nd(III). The complexes show similar weak fluorescence in the solid state at room temperature.

Supplementary materials

Crystallographic data for **1**, **2** and **3** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC- 291358–291360). These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44–1223–336–033; Email: deposit@ccdc.cam.ac.uk].

References

[1] X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem., Int. Ed.*, **41**, 1029 (2002).
[2] S.L. Zheng, J.P. Zhang, W.T. Wong, X.M. Chen. *J. Am Chem. Soc.*, **125**, 6882 (2003).
[3] M.L. Tong, S. Kitagawa, H.C. Chang, M. Ohba. *Chem. Commun.*, **418** (2004).
[4] X.M. Zhang, M.L. Tong, M.L. Gong, H.K. Lee, L. Luo, J.H. Li, Y.X. Tong, X.M. Chen. *Chem-Eur. J.*, **8**, 3187 (2002).
[5] G.R. Choppin, J.C.G. Bunzli (Eds). *Lanthanide Probes in Life, Chemical and Earth*, Elsevier, Amsterdam (1989).
[6] P. Caravan, J.J. Ellison, T.J. McMurry, R.B. Lauffer. *Chem. Rev.*, **99**, 2293 (1999).
[7] F.A. Hart. In *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds), p. 1059, Pergamon, Oxford (1987).
[8] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Gottingen, Gottingen, Germany (1997).
[9] G.M. Sheldrick. *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Gottingen, Gottingen, Germany (1997).
[10] J.G. Mao, H.J. Zhang, J.Z. Ni, S. Wang, T.C.W. Mak. *Polyhedron*, **18**, 1519 (1999).
[11] B.L. An, M.L. Gong, K.W. Cheah, W.K. Wong, J.M. Zhang. *J. Alloy. Compd.*, **368**, 326 (2004).
[12] Q.X. Zhou, Y.J. Wang, H.B. Song, X.Q. Zhao, L. Yue. *Spectrosc. Spect. Anal.*, **25**, 730 (2005).
[13] M.L. Główka, D. Martynowski, K. Kozàowska. *J. Mol. Struct.*, **474**, 81 (1999).
[14] Y.S. Song, B. Yan, Z.X. Chen. *J. Mol. Struct.*, **750**, 101 (2005).