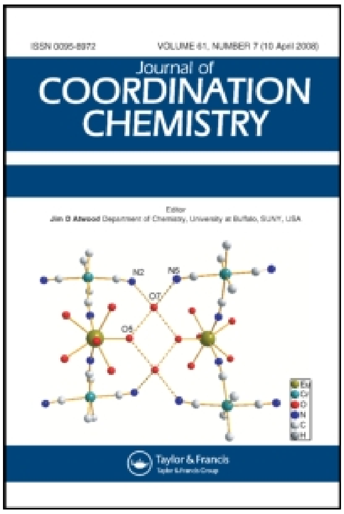

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structures of lanthanide complexes with foliage growth regulator: phenoxyalkanoic acid

Shao-Ming Shi[a]; Zhen-Feng Chen[a]; Yan-Cheng Liu[a]; Li Mao[a]; Hong Liang[a]; Zhong-Yuan Zhou[b]
[a] The Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education), School of Chemistry and Chemical Engineering, Guilin 541004, People's Republic of China [b] Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hong Kong, People's Republic of China

To cite this Article Shi, Shao-Ming , Chen, Zhen-Feng , Liu, Yan-Cheng , Mao, Li , Liang, Hong and Zhou, Zhong-Yuan(2008) 'Synthesis and crystal structures of lanthanide complexes with foliage growth regulator: phenoxyalkanoic acid', Journal of Coordination Chemistry, 61: 17, 2725 — 2734

To link to this Article: DOI: 10.1080/00958970801961455

URL: http://dx.doi.org/10.1080/00958970801961455

Journal of Coordination Chemistry
Vol. 61, No. 17, 10 September 2008, 2725–2734

Synthesis and crystal structures of lanthanide complexes with foliage growth regulator: phenoxyalkanoic acid

SHAO-MING SHI†, ZHEN-FENG CHEN*†, YAN-CHENG LIU†, LI MAO†,
HONG LIANG*† and ZHONG-YUAN ZHOU‡

†The Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education), School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, People's Republic of China
‡Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hong Kong, People's Republic of China

(*Received 11 July 2007; in final form 21 September 2007*)

Reactions of $Ln(ClO_4)_3 \cdot 6H_2O$ (Ln=La(III), Eu(III), Nd(III)), 1,10-phenanthroline (phen) and phenoxyacetic acid (PA) or 2,4-dichlorophenoxyacetic acid (2,4-D) yield $[La(PA)_2(phen)_2]_2(ClO_4)_2$ (**1**), $[Eu(2,4\text{-}D)_2(phen)_2]_2(ClO_4)_2$ (**2**) and $[Nd(2,4\text{-}D)_3(C_2H_5OH)]_n$ (**3**). Compounds **1**–**3** are characterized by elemental analyses, IR, UV–Vis, ESI-MS spectra and TGA. **1** is also characterized by ^1H and ^{13}C NMR. Single crystal X-ray diffraction analyses reveal that **1** and **2** are binuclear, and **3** has a one-dimensional polymeric structure. The La(III), Eu(III) and Nd(III) are nine-coordinate with a distorted tricapped trigonal-prism geometry.

Keywords: Lanthanide complexes; Phenoxyacetic acid; 2,4-Dichlorophenoxyacetic acid; Crystal structures; Lanthanum; Neodymium; Europium

1. Introduction

Lanthanide complex chemistry has been studied intensively over the past two decades, stimulated by well-defined, kinetically robust systems tailored to applications as bioactive probes for magnetic resonance and luminescence [1, 2]. The lanthanides easily coordinate to various carboxylates [3–7] and a diversity of ligands containing O or N donors such as 1,10-phenanthroline, 8-hydroxyquinoline and crown ethers [8–10] to form complexes with diverse stereochemistries. As phenoxyalkanoic acid herbicides show considerable biological activity, their interactions with metal ions have been a subject of extensive studies. The properties of a number of complexes have been described in the literature: 2,4-dichlorophenoxyacetic acid (2,4-D) with Ca(II) [11], Cu [12–14], Zn [14–16], Co [14, 17], Mn [14, 16], Ag [18], Ni, Cd, Fe [14], and Gd(III) [11], and phenoxyacetic acid (PA) with Cu [19–21], Co [22], Ni [23], Pt [24], Sn [25]

---

*Corresponding authors. Email: chenzfgxnu@yahoo.com; hliang@mailbox.gxnu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970801961455

and Mg [22]. There have also been studies on mixed ligands which, apart from the phenoxy acid herbicide, contain other organic donors [26–28]. However, crystal structures of lanthanides with 2,4-dichlorophenoxyacetic acid and phenoxyacetic acid are very rare [29, 30]. We have initiated studies on the coordination of carboxylate-containing herbicide agents with lanthanide ions in an attempt to examine their mode of binding and possible synergetic effects. Herein, we report the synthesis and crystal structures of three lanthanide complexes with foliage growth regulator 2,4-dichlorophenoxyacetic acid or phenoxyacetic acid.

2. Experimental

2.1. *Materials*

All chemicals were purchased from commercial sources and used without further purification. $RE(ClO_4)_3 \cdot 6H_2O$ (RE = La(III), Nd(III), Eu(III)) were prepared according to literature methods [31].

2.2. *Physical measurements*

C, H and N data were obtained using Perkin-Elmer 2400II CHNS/O elemental analyzer. UV-Vis spectra were recorded on a Shimadzu UV-265 spectrophotometer. Infrared spectra were measured on a Nicolet FT-IR with KBr pellets in the range 400–4000 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE AV 500M Hz spectrometer using DMSO-d_6 as a solvent with TMS as an internal standard. ESI-MS spectra were performed on Thermo-Finnigan LCQ/AD Quadrupole Ion Trap ESI-MS spectrometer.

2.3. *Synthesis of compounds*

2.3.1. $[La(PA)_2(phen)_2]_2(ClO_4)_2$ (1). Phenoxyacetic acid (PA) (0.228 g, 1.5 mmol) was dissolved in aqueous ethanol ($H_2O : CH_3CH_2OH$ 1 : 2, 15 mL), and the pH was adjusted to 7–8 with dilute NaOH solution; phen (0.099 g, 0.5 mmol) in ethanol (10 mL) was then added. To the resulting solution, $La(ClO_4)_3 \cdot 6H_2O$ (0.558 g, 1 mmol) in ethanol (10 mL) was added dropwise. The reaction mixture was stirred at 70–80°C for 10 h. The precipitate was filtered off, and the filtrate was left for slow evaporation. After three weeks, red block crystals of **1** suitable for structural analysis were isolated in 38% yield. Calcd for $C_{80}H_{60}Cl_2La_2N_8O_{20}$: C, 53.32; H, 3.36; N, 6.22%. Found: C, 53.46; H, 3.39; N, 6.31%. Main IR (KBr, cm^{-1}): 3426(w), 1630(m), 1588(w), 1518(m), 1479(w), 1455(w), 1425(m), 1342(w), 1289(w), 1094(s), 847(m), 769(w), 726(m), 623(m), 422(w). ^1H NMR (500 M Hz, DMSO-d_6, ppm): 9.18 (s, 8H), 8.56 (d, $J = 7.83$ Hz, 8H), 8.03 (s, 8H), 7.81 (dd, $J = 12.245$ and 3.485 Hz, 8H), 7.20 (t, $J = 15.4$ and 7.675 Hz, 8H), 6.85 (m, 12H), 4.31 (s, 8H). ^{13}C NMR (125 M Hz, DMSO-d_6, ppm): 178.07, 159.01, 150.58, 145.77, 137.22, 129.61, 129.07, 127.20, 123.92, 120.74, 115.06, 57.41. ESI-MS: $[La(PA)_2(phen)_2]^+ = 801$.

2.3.2. $[Eu(2,4\text{-}D)_2(phen)_2]_2(ClO_4)_2$ (2). This compound was prepared in a similar process as for **1**. 2,4-D and $Eu(ClO_4)_3 \cdot 6H_2O$ were used instead of PA and $La(ClO_4)_3 \cdot 6H_2O$, respectively. Pink cubic crystals of **2** suitable for structural analysis were isolated. Yield: 25–30%. Calcd for $C_{80}H_{52}Cl_{10}Eu_2N_8O_{20}$: C, 45.67; H, 2.49; N, 5.33%. Found: C, 46.85; H, 2.57; N, 5.39%. Main IR (KBr, cm^{-1}): 3430(w), 1658(s), 1630(s), 1589(m), 1516(m), 1480(m), 1451(m), 1425(m), 1343(w), 1291(m), 1264(m), 1236(m), 1102(s), 861(w), 845(w), 727(m), 642(w), 622(w), 421(w). ESI-MS: $[Eu(2,4\text{-}D)_2(phen)_2]^+ = 952$.

2.3.3. $[Nd_2(2,4\text{-}D)_6(C_2H_5OH)_2]_n$ (3). This compound was prepared in a process similar to **1**. 2,4-D and $Nd(ClO_4)_3 \cdot 6H_2O$ were used instead of PA and $La(ClO_4)_3 \cdot 6H_2O$, respectively, and phen was not used. Purple prismatic crystals of **3** suitable for structural analysis were isolated from the mother solution after one week. Yield: 30–40%. Calcd for $C_{52}H_{42}Cl_{12}Nd_2O_{20}$: C, 36.72; H, 2.49%. Found: C, 36.83; H, 2.56. Main IR (KBr, cm^{-1}): 1623(s), 1494(m), 1429(s), 1219(s), 1068(s), 846(m), 727(m), 418(w). ESI-MS: $[M + Na]^+ = 1723$.

2.4. *X-ray structure determination*

Details of unit cells and data collection and refinement for **1**, **2**, and **3** are listed in table 1. All intensities for **1–3** were collected with a Bruker CCD area detector diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å, 50 kV, 150 mA) using the ω–θ scan mode at 294(2)K. Raw fame data were integrated with the SAINT program [32]. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares using SHELXL-97 [33]. An empirical absorption correction was applied with SADABS [34]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were set

Table 1. Crystallographic data and refinement details for **1–3**.

Complexes	**1**	**2**	**3**
Formula	$C_{80}H_{60}Cl_2La_2N_8O_{20}$	$C_{40}H_{26}Cl_5EuN_4O_{10}$	$C_{52}H_{42}Cl_{12}Nd_2O_{20}$
Formula weight	1802.08	1051.86	1700.79
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P2(1)/n$	$P\bar{1}$
a (Å)	13.726(8)	13.0863(18)	7.9472(12)
b (Å)	21.783(12)	17.352(3)	12.933(2)
c (Å)	13.726(8)	18.811(3)	15.403(2)
α (°)	90.00	90.00	80.454(3)
β (°)	112.875(8)	104.521(3)	77.663(3)
γ (°)	90.00	90.00	87.259(3)
V (Å^3)	3781(4)	4135.1(10)	1525.1(4)
Z	2	4	1
D_{Calcd} (Mg m^{-3})	1.583	1.690	1.850
μ (mm^{-1})	1.265	1.903	2.282
Crystal size (mm^3)	0.34 × 0.30 × 0.26	0.36 × 0.32 × 0.30	0.32 × 0.30 × 0.26
$F(000)$	1808	2088	836
$R_1{}^a[I > 2\sigma(I)]$	0.0531	0.0405	0.0304
$wR_2{}^b$	0.1329	0.0774	0.0712

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

in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations were performed on a PC computer with SHELXTL [33].

3. Results and discussion

3.1. *Synthesis*

Complexes **1**, **2** and **3** were synthesized by a similar process, lanthanide perchlorates reacting with phenoxyalkanoic acid under basic conditions, but the results are different depending on whether phen was used. When phen was used, **1** and **2** formed dimeric structures; **3** generated a one-dimensional chain polymer.

3.2. *Structural description of [La(PA)$_2$(phen)$_2$]$_2$(ClO$_4$)$_2$ (1)*

[La(PA)$_2$(phen)$_2$]$_2$(ClO$_4$)$_2$ (**1**), *bis*(μ_2-phenoxyacetato-κ^3O,O,O′)-*bis*(μ_2-phenoxy acetato-κ^2O,O′)-tetra(1,10-phenanthroline-κ^2*N*,*N*′)-di-lanthanum(III)-*bis*-perchlorate, shown in figure 1, consists of dinuclear [La(PA)$_2$(phen)$_2$]$_2^{2+}$ cations and two ClO_4^- anions. In the cation, the two La(III) ions are nine-coordinate by two phen ligands and bridged by two carboxylate groups from PA in *syn*-*syn* mode and two tridentate PA ligands, thus giving rise to an eight-membered ring [La(1)O(1)C(25)O(2)La(1A)O(1A)C(25A)O(2A)] and four-membered ring [La(1)O(4)La(1A)O(4A)]. The structure is similar to [Eu$_2$(*o*-ClC$_6$H$_4$OCH$_2$COO)$_6$(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$]$\cdot$(CH$_3$)$_2$SO [28], but the former complex is in a more distorted coordination mode due to a higher *trans* influence and asymmetry erected by a greater steric effect than the latter complex.

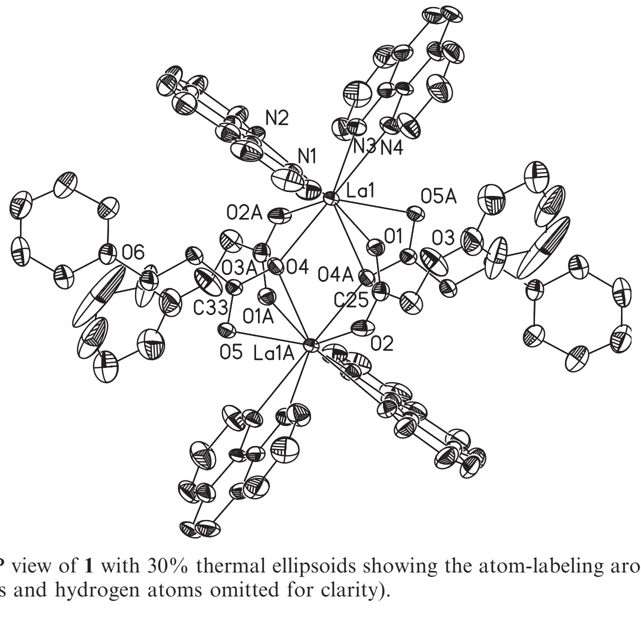

Figure 1. ORTEP view of **1** with 30% thermal ellipsoids showing the atom-labeling around the lanthanum (perchlorate groups and hydrogen atoms omitted for clarity).

The coordination geometry of La(1) is a distorted tricapped trigonal prism defined by O(1), O(2A), O(4), O(4A), O(5A), N(1), N(2), N(3) and N(4). Selected bond distances and angles are given in table 2. The La(1)–O distances are in the range 2.456(3) to 2.665(3) Å and those of La(1)–N are in the range 2.687(4) to 2.763(4) Å; the La ⋯ La separation is 4.0958(17) Å, indicating no metal–metal interaction.

3.3. *Structural description of [Eu(2,4-D)$_2$(phen)$_2$]$_2$(ClO$_4$)$_2$ (2)*

[Eu(2,4-D)$_2$(phen)$_2$]$_2$(ClO$_4$)$_2$, *bis*(μ_2-2,4-dichlorophenoxyacetato-κ^3O,O′,O′)-*bis*(μ_2-2,4-dichlorophenoxyacetato-κ^2O,O′)-tetra(1,10-phanothrine-κ^2*N*,*N*′)di-europium(III)-*bis*-perchlorate, similar to **1** (figure 2), consists of a dinuclear [Eu(2,4-D)$_2$(phen)$_2$]$_2^{2+}$

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

La(1)–O(1)	2.456(3)	La(1)–N(1)	2.763(4)
La(1)–O(2A)	2.459(3)	La(1)–N(2)	2.706(4)
La(1)–O(4)	2.485(3)	La(1)–N(3)	2.733(4)
La(1)–O(4A)	2.665(3)	La(1)–N(4)	2.687(4)
La(1)–O(5A)	2.574(3)	La(1) ⋯ La(1A)	4.0958(17)
O(1)–La(1)–O(2A)	135.76(10)	O(1)–La(1)–O(5A)	75.33(10)
O(1)–La(1)–O(4)	73.50(9)	O(1)–La(1)–O(4A)	71.36(9)
O(2A)–La(1)–O(4)	73.48(9)	O(4)–La(1)–O(5A)	122.50(10)
O(4)–La(1)–O(4A)	74.68(9)	O(1)–La(1)–N(4)	84.53(11)
O(4)–La(1)–N(4)	147.08(10)	O(1)–La(1)–N(2)	134.67(10)
O(4)–La(1)–N(2)	90.02(10)	N(1)–La(1)–N(2)	59.98(12)
N(1)–La(1)–N(3)	119.25(12)	N(2)–La(1)–N(4)	88.34(12)
N(2)–La(1)–N(3)	76.25(11)	N(4)–La(1)–N(3)	60.89(13)

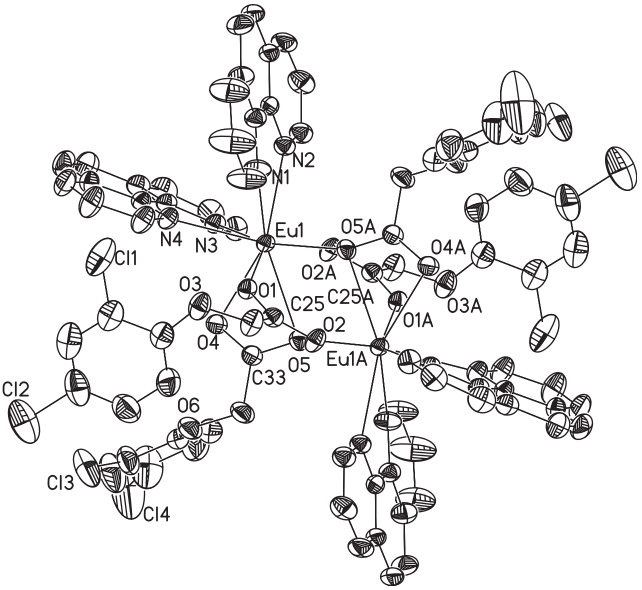

Figure 2. ORTEP view of **2** with 30% thermal ellipsoids showing the atom-labeling around europium (perchlorate groups and hydrogen atoms attached to C atoms omitted for clarity).

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Eu(1)–O(1)	2.3975(18)	Eu(1)–N(1)	2.637(3)
Eu(1)–O(2A)	2.342(2)	Eu(1)–N(2)	2.624(2)
Eu(1)–O(4)	2.500(2)	Eu(1)–N(3)	2.626(2)
Eu(1)–O(5A)	2.3557(19)	Eu(1)–N(4)	2.576(3)
Eu(1)–O(5)	2.623(2)	Eu(1) ··· Eu(1)#1	4.0357(6)
O(1)–Eu(1)–O(2A)	135.18(7)	O(1)–Eu(1)–N(1)	74.96(7)
O(1)–Eu(1)–O(4)	74.49(7)	O(1)–Eu(1)–N(2)	136.58(8)
O(1)–Eu(1)–O(5)	70.29(7)	O(1)–Eu(1)–N(4)	82.03(7)
O(1)–Eu(1)–O(5A)	73.99(7)	O(4)–Eu(1)–N(4)	75.15(8)
O(2A)–Eu(1)–O(4)	95.69(8)	N(1)–Eu(1)–N(2)	61.82(8)
O(2A)–Eu(1)–O(5)	70.18(7)	N(1)–Eu(1)–N(3)	114.57(8)
O(4)–Eu(1)–O(5)	50.46(6)	N(2)–Eu(1)–N(3)	71.28(7)
O(4)–Eu(1)–O(5A)	120.58(7)	N(3)–Eu(1)–N(4)	63.33(8)

cation and two ClO_4^- anions. The $[Eu(2,4\text{-}D)_2(phen)_2]_2^{2+}$ cation is a centrosymmetric dimer, in which the two Eu(III) ions are chelated by two phen ligands and bridged by four carboxylate groups from 2,4-D ligands. The coordination geometry of Eu(III) can be best described as distorted tricapped trigonal-prism (TTP), surrounded by four nitrogens from two phen ligands and five oxygens from four carboxylate groups of 2,4-dichlorophenoxy acetate. The structure is similar to $[Eu_2(o\text{-}ClC_6H_4OCH_2COO)_6(C_{12}H_8N_2)_2(H_2O)_2]\cdot(CH_3)_2SO$ [28], in which the carboxylate groups exhibit two different coordination modes: bridging bidentate in the *syn-syn* configuration (Eu1–O1–C25 136.2(2)° and Eu1A–O2–C25 139.93(19)°) and chelating-bridging tridentate. Selected bond distances and angles are given in table 3. The Eu(1)–O distances are in the range 2.341(3) to 2.622(2) Å and Eu(1)–N 2.576(3) to 2.635(3) Å, all in normal range. The $Eu–O_{carboxylate}$ distances are in the order: Eu–O(bidentate bridging) < Eu–O(tridentate bridging). The Eu ··· Eu separation of 4.0357 Å is longer than that of $[Eu(o\text{-}ClC_6H_6H_6OCH_2COO)_6(H_2O)_2]$ (Eu–Eu 4.019 Å) [28], indicative of no metal-metal interaction.

3.4. *Structural description of $[Nd_2(2,4\text{-}D)_6(C_2H_5OH)_2]_n$ (3)*

$[Nd_2(2,4\text{-}D)_6(C_2H_5OH)_2]_n$ (**3**), catena-(tri(μ_2-2,4-dichlorophenoxyacetato-κ^3O,O′,O′)-tri(μ_2-2,4-dichlorophenoxy acetato-κ^2O,O′)-*bis*(ethanol)-di-neodymium(III)), is shown in figure 3. Selected bond lengths and angles for **3** are listed in table 4. Similar to $[Gd(2,4\text{-}D)_3(H_2O)_2\cdot 2dmf]_n$ [11], **3** is a one-dimensional polymer with $\{Nd_2(2,4\text{-}D)_6(C_2H_5OH)_2\}$ dimeric repeat units. Unlike **1** and **2**, Nd is coordinated by nine oxygens, eight from three 2,4-D ligands and one from an ethanol. Each Nd(III) is a distorted tricapped trigonal prism. The distances of $Nd–O_{carb}$ vary from 2.394 to 2.563 Å and O–Nd–O bond angles are in the range 50.85(7) to 143.29(7)°, in the normal range. Ethanol coordinated to Nd(III) (Nd–O distance of 2.499(2) Å) is rare. The Nd ··· Nd separation of 4.0574 Å is longer than that of $[Nd_2(bdc)(Hbdc)_2(H_2O)]_n\cdot nH_2O$ (Nd···Nd separation of 3.841 Å) [35]. Similar to PA of **1**, 2,4-D coordinates to Nd(III) in two modes: chelating-bridging tridentate and *syn–syn* bridging bidenate. However, differing from $[Gd(2,4\text{-}D)_3(H_2O)_2\cdot 2dmf]_n$ [11], whose 2,4-D exhibited three coordination modes including bidentate chelate. Comparing to **1** and **2**, the absence of 1,10-phenanthroline in **3**, Nd(III) ions are

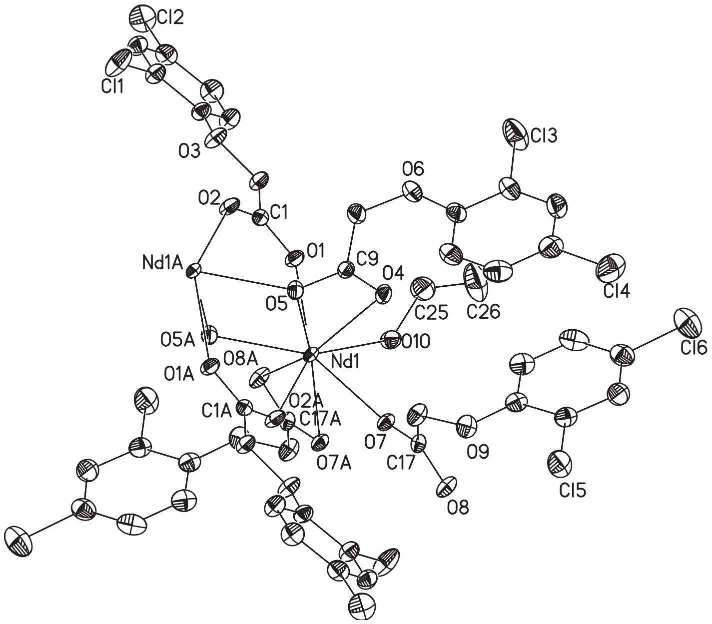

Figure 3. ORTEP view of **3** with 30% thermal ellipsoids showing the atom-labeling around lanthanum (all hydrogen atoms omitted for clarity).

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Nd(1)–O(1)	2.394(2)	Nd(1A)–O(7)	2.552(2)
Nd(1)–O(2A)	2.547(2)	Nd(1)–O(8A)	2.563(2)
Nd(1)–O(4)	2.553(2)	Nd(1)–O(10)	2.499(2)
Nd(1)–O(5A)	2.431(2)	Nd(1)–O(5)	2.553(2)
Nd(1)–O(7)	2.444(1)	Nd(1)···Nd(1A)	4.0574(7)
O(1)–Nd(1)–O(2A)	136.74	O(4)–Nd(1)–O(7)	75.52(7)
O(1)–Nd(1)–O(5A)	72.33(7)	O(5A)–Nd(1)–O(7)	142.91(7)
O(1)–Nd(1)–O(4)	75.20(8)	O(5A)–Nd(1)–O(10)	139.83(7)
O(1)–Nd(1)–O(5)	70.84(7)	O(2A)–Nd(1)–O(7)	70.27(7)
O(1)–Nd(1)–O(7)	143.29(7)	O(5)–Nd(1)–O(4)	50.85(7)
O(1)–Nd(1)–O(10)	77.71(7)	O(5)–Nd(1)–O(10)	122.91(7)
O(5)–Nd(1)–O(7)	106.01(6)	O(2A)–Nd(1)–O(5)	73.32(7)

alternatively connected into a one-dimensional chain (figure 4) by (i) two chelating-bridging tridentate 2,4-D ligands; (ii) two chelating-bridging tridentate and bridging bidentate 2,4-D, with two different Nd ··· Nd separations of 4.218 and 4.057 Å. Viewing down the *a*-axis, the 2,4-D and ethanol sheaths are around the coordination polymer (figure 5).

3.5. *UV-Vis spectra*

The UV-Vis spectra (ca $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) $[La(PA)_2(phen)_2]_2(ClO_4)_2$ (**1**), $[Eu(2,4\text{-}D)_2(phen)_2]_2(ClO_4)_2$ (**2**) and $[Nd(2,4\text{-}D)_3(C_2H_5OH)]_n$ (**3**) in DMSO solution were determined at the same conditions. The maximum absorption wavelengths and

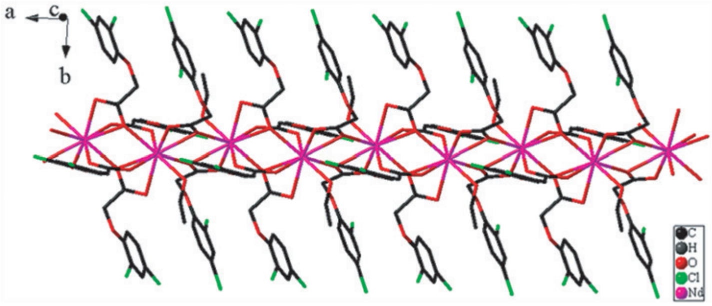

Figure 4. A one-dimensional linear chain of **3**.

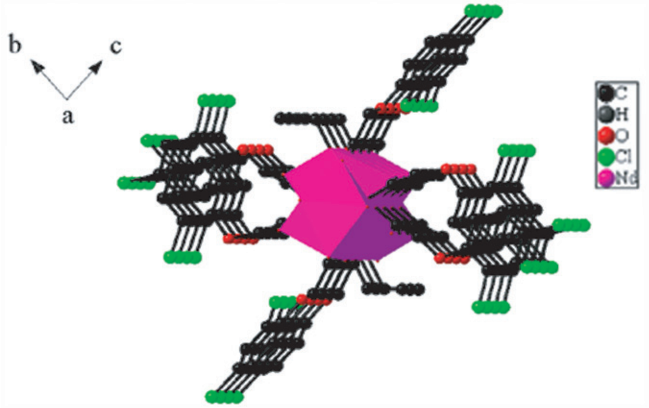

Figure 5. A one-dimensional chain representation, viewing down the *a*-axis, highlighting the Nd tricapped trigonal prism and the 2,4-D and ethanol sheaths around the coordination polymer.

Table 5. The UV–Vis spectra data for the free ligands and **1**–**3**.

Sample	λ_{max} (nm)	ε ($mol^{-1} dm^3 cm^{-1}$)
PA	280	5.272×10^3
2,4-D	285	5.109×10^3
Phen	265	2.3462×10^4
$[La(PA)_2(phen)_2]_2(ClO_4)_2$	272	2.6695×10^4
$[Eu(2,4\text{-}D)_2(phen)_2]_2(ClO_4)_2$	268	2.6865×10^4
$[Nd(2,4\text{-}D)_3(C_2H_5OH)]_n$	275	2.6935×10^4

molar absorption coefficients are given in table 5. The maximum absorption positions of the broad absorptions for **1**, **2** and **3** in dilute solutions undergo blue-shifts compared with those of PA and 1,4-D and red-shift in contrast to those of phen, attributed to reduction of $\pi \rightarrow \pi^*$ energy gap caused by metal coordination [36, 37].

3.6. *Infrared spectra*

Comparing the IR spectra of **1**–**3** with those of 2,4-D, PA and phen, the characteristic stretching vibrations of free carboxylic acid (PA and 2,4-D) at 1730 cm^{-1} disappeared and split into two peaks: 1630 ($\nu_{as}(COO^-)$) and 1425 cm^{-1} ($\nu_s(COO^-)$) for **1** with $\Delta\nu = 205\,cm^{-1}$; 1623 and 1429 cm^{-1} for **2** with $\Delta\nu = 194 cm^{-1}$; and 1622 (ν_{as} (COO^-)) and 1426 cm^{-1} ($\nu_s(COO^-)$) for **3** with $\Delta\nu = 196\,cm^{-1}$. The splitting of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ indicate that carboxylate groups PA$^-$ or 2,4-D$^-$ function in two different coordinated modes [38] (chelating-bridging tridentate and bridging bidentate), consistent with the crystal structures of **1**, **2** and **3**. For **1** and **2**, two well-defined bands are observed at 1094 and 1102 cm^{-1}, respectively, characteristic of Cl–O bond, indicating perchlorate groups, as confirmed by X-ray structural analyses.

3.7. *Thermogravimetric analysis*

When **1** was heated to 220°C, a sharp weight loss was found (40.6%), attributed to the loss of four phen molecules (40.0%); from 350°C, the compound starts to decompose. TGA of **2** shows an apparent weight loss step of 75% from 190 to 360°C corresponding to loss of four 2,4-D and phen molecules, respectively. When **3** was heated from room temperature to 175°C, a weight loss of 5.3% occurs corresponding to the loss of coordinated ethanol; the second weight loss of 78.2% occurs in the range 175 to 370°C and corresponds to the loss of the 2,4-D ligands (77.6%).

4. Conclusion

In summary, three lanthanide phenoxyalkanoates have been synthesized and characterized. While **1** and **2** are binuclear complexes, **3** exhibits one-dimensional polymeric structure. The phenoxyalkanoates (PA$^-$ and 2,4-D$^-$) adopt two different coordination modes (chelating-bridging tridentate and bridging bidentate). In addition, the steric hindrance of ligands and the atomic radius play important roles in the structures; the separations of $M \cdots M$ are in agreement with the lanthanide contraction rule, $La \cdots La > Nd \cdots Nd > Eu \cdots Eu$.

Supplementary materials

Crystallographic data for the crystal structures of **1**, **2** and **3** reported in this article have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 296819, 296817, 296818), respectively. These materials can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

The NSF of Guangxi (No. 0575046, 0575049) and the Program for New Century Ten-Hundred-Thousand Excellent Talents of Guangxi (No. 2003223), as well as the

National Natural Science Foundation of China (No. 20361002, 30460153), are thanked for support. This work is also supported by TRAPOYT and NCET-04-0836 of Ministry of Education China.

References

[1] D. Parker. *Chem. Soc. Rev.*, **33**, 156 (2004).
[2] H.C. Aspinall. *Chem. Rev.*, **102**, 1807 (2002).
[3] S.Y. Niu, J. Jin, W.M. Bu, G.D. Yang, J.Q. Cao, B. Yang. *Chinese J. Struct. Chem.*, **18**, 245 (1999).
[4] S.Y. Niu, Z.Z. Yang, Q.C. Yang, B. Yang, J.Q. Cao, G.D. Yang, E.Z. Shen. *Polyhedron*, **16**, 1629 (1997).
[5] S. Aime, F. Benetollo, G. Bombieri, S. Colla, M. Fasano, S. Paoletti. *Inorg. Chim. Acta*, **254**, 63 (1997).
[6] P.R. Wei, D.D. Wu, Z.Y. Zou, T.C.W. Mak. *Polyhedron*, **17**, 497 (1998).
[7] J.G. Mao, L. Song, X.Y. Huang, J.S. Huang. *Polyhedron*, **16**, 963 (1997).
[8] W.J. Evans, R.D. Clark, M.A. Ansari, J.W. Ziller. *J. Am. Chem. Soc.*, **120**, 9555 (1998).
[9] J.P. Costes, F. Dahan, A. Dupuis, S. Lagrave, J.P. Laurent. *Inorg. Chem.*, **37**, 153 (1998).
[10] C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.C.G. Bünzli, G. Hopfgartner. *J. Chem. Soc., Dalton Trans.*, 421 (1997).
[11] C. Dendrinou-Samara, D. Drosou, L. Iordanidis, A. Terzis, D.P. Kessissoglou. *J. Inorg. Biochem.*, **92** (2002).
[12] A. Genske, K. Götzschel. *Z. Chem.*, **22**, 147 (1982).
[13] G. Smith, E.J. O'Reilly, C.H.L. Kennard. *Inorg. Chim. Acta*, **49**, 53 (1981).
[14] J. Ristici. *Bull. Stiint. The Inst. Politen. Tiisoara.*, **19**, 229 (1974).
[15] C.H.L. Kennard, G. Smith, E.J. O′Reilly, K.M. Stadnicka, B.J. Oleksyn. *Inorg. Chim. Acta*, **59**, 241 (1982).
[16] W.F. Shul'gin, O.W. Konnik. *Ukr. Khim. Zh.*, **55**, 1011 (1989).
[17] W.F. Shul'gin, O.W. Konnik, I.G. Timofeev. *Zh. Neorg. Khim.*, **35**, 365 (1990).
[18] T.C.W. Mak, W.-H. Yip, C.H.L. Kennard, G. Smith, E.J. O'Reilly. *J. Chem. Soc., Dalton Trans.*, 2353 (1988).
[19] C.K. Prout, R.A. Armstrong, J.R. Carruthers, J.G. Forrest, P. Murray-Rust, F.J.C. Rossotti. *J. Chem. Soc. A*, 2791 (1968).
[20] C.K. Prout, M.J. Barrow, F.J.C. Rossotti. *J. Chem. Soc. A*, 3326 (1971).
[21] C.V. Goebel, R.J. Doedens. *Inorg. Chem.*, **10**, 2607 (1971).
[22] G. Smith, E.J. O'Reilly, C.H.L. Kennard. *J. Chem. Soc., Dalton Trans.*, 2462 (1980).
[23] C.K. Prout, C. Walker, F.J.C. Rossotti. *J. Chem. Soc. A*, 556 (1971).
[24] W. Henderson, A.G. Oliver. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, **55**, 1408 (1999).
[25] M. Bao, Q. He, B. Liu, Y. Xing, Y. Liu. *Chin. J. Inorg. Chem.*, **14**, 114 (1998).
[26] R. Sahai, S.S.S. Kushwaha. *J. Indian Chem. Soc.*, **61**, 205 (1984).
[27] R. Sahai, A.K. Chaudhary. *Monatsh. Chem.*, **113**, 681 (1982).
[28] W. Jähnig, R. Stösser, U. Ewert, K. Götzschel. *J. Prakt. Chem.*, **322**, 321 (1980).
[29] X. Li, L.-P. Jin, S.-T. Wang, Y. Li. *Chin. J. Inorg. Chem.*, **15**, 305 (1999).
[30] H. Deng, Q.-Q. Chen, L.-F. Liang, L.-L. Li. *Chinese J. Inorg. Chem.*, **16**, 969 (2000).
[31] (a) L. Ma, O.R. Evans, B.M. Foxman, W. Lin. *Inorg. Chem.*, **38**, 5837 (1999); (b) J.-G. Mao, H.-J. Zhang, J.-Z. Ni, S.-B. Wang, T.C.W. Mak. *Polyhedron*, **17**, 3999 (1998); (c) R.-G. Xiong, J. Zhang, Z.-F. Chen, X.-Z. You, C.-M. Che, H.-K. Fun. *J. Chem. Soc., Dalton Trans.*, 780 (2001).
[32] Siemens. *SAINT*: *Area Detector Control and Integration Software*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA (1996).
[33] G.M. Sheldrick. *SHELXTL Software Reference Manual* (*Version 5.1*), Bruker AXS Inc., Madison, WI, USA (1997).
[34] G.M. Sheldrick. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).
[35] L.-P. Zhang, Y.H. Wan, L.P. Jin. *Polyhedron*, **22**, 981 (2003).
[36] W.M. Lu, B. Wu, L.N. Wang. *Chem. J. Chinese Universities*, **22**, 535 (2001).
[37] B.L. An, M.L. Gong, M.X. Li, J.M. Zhang. *J. Mol. Struct.*, **687**, 1 (2004).
[38] G.B. Deacon, R.J. Philips. *Coord. Chem. Rev.*, **33**, 227 (1980).