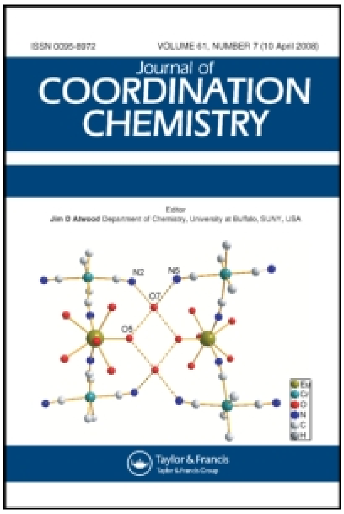

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Synthesis and structural characterization of lanthanide oxalate-oxydiacetate mixed-ligand coordination polymers {[Ln(oda)(H$_2$O)<i>_x]$_2$(ox)}<i>_n (<i>x</i> = 3 for Ln = La, Ce, Pr, Gd, Tb and <i>x</i> = 2 for Ln = Er)

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Synthesis and structural characterization of lanthanide oxalate–oxydiacetate mixed-ligand coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ ($x = 3$ for Ln = La, Ce, Pr, Gd, Tb and $x = 2$ for Ln = Er)

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Reactions of oxydiacetic acid (H_2oda) with lanthanide oxide, nitrate, chloride, and carbonate gave six lanthanide oxalate–oxydiacetate mixed-ligand coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ [$x = 3$ for Ln = La, Ce, Pr, Gd, Tb, (**1**–**5**), and $x = 2$ for Ln = Er (**6**)]. Oxydiacetic acid is decomposed into oxalic acid in this reaction. In the crystal structures of **1**–**6**, oxydiacetate and the lanthanides build a chain, and the oxalate groups bridge two chains to form 1-D double-chain ladder-shaped structures, connected by intermolecular hydrogen bonds to form a 2-D network structure. These compounds contain approximately $3.0 \times 6.4\,\text{Å}^2$ channels along the *c*-axis. The infrared spectra and thermal behaviors of **1**–**6** are also investigated.

Keywords: Oxydiacetate; Oxalate; Lanthanide coordination polymers; Crystal structures

1. Introduction

The oxydiacetate anion [oda = $O(CH_2COO)_2^{2-}$] is a versatile ligand having five potential oxygen donors from two carboxylate groups and from an ether, and may bind to metal ions in mono-, bi-, tri-, and multidentate coordination modes [1]. A number of oxydiacetate complexes have interesting physical and chemical properties as well as fascinating structures. Among these, $\{[Cu_3Ln_2(oda)_6(H_2O)_6]\cdot 12H_2O\}_n$ (Ln = Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb, Y), $[V(O)(oda)(\mu\text{-}OMe)]_2[Na(H_2O)]_2$, $[V(O)(oda)(\mu\text{-}OMe)]_2[HL]_2$ (L = 2,6-dimethylpyridine, 4-dimethylaminopyridine), $\{[Mn(oda)(H_2O)]\cdot H_2O\}_n$, and $\{[Mn(oda)(phen)]\cdot 4H_2O\}_n$ exhibited antiferromagnetic behavior [2–9]. $[Ce_2(oda)_3(H_2O)_3]\cdot 9H_2O$ has promising applications as an environmentally benign corrosion inhibitor [10–12]. Luminescent properties of $[Tb(Hoda)_3]$ and $Na_3[Eu(oda)_3]$ were applied as probes of the structure and nature of lanthanide complexes in chemistry and biology [9, 13]. $[Ln_2(oda)_3(H_2O)_x]\cdot yH_2O]$, $[Na_5Ln(oda)_3(X)_2]\cdot 6H_2O$ ($X = ClO_4$, BF_4) and $\{[Cu_3Ln_2(oda)_6(H_2O)_6]\cdot 12H_2O\}_n$

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displayed supramolecular structures [2, 14–18], $\{[Mn(oda)(H_2O)]\cdot H_2O\}_n$ a diamond-like 3-D network [8], and $\{(H_2O)_2Cu_2(\mu\text{-Ade})_4[Cu(oda)(H_2O)]_4\}\cdot 6H_2O$ (Ade = adeninato) a windmill-shaped molecular topology [19]. Oxalate (ox = $C_2O_4^{2-}$) complexes have good physical and chemical properties and/or interesting structures [20–23]. $[Er_2(ox)_2(pyzc)_2(H_2O)_2]_n$ (pyzc = 2-pyrazinecarboxylate group) displayed an intense room-temperature liquid-state emission [20]. $[Pr_2(ox)_2(pyzc)_2(H_2O)_2]_n$ and $[NBu_4][M^{II}Mn^{III}(ox)_3]$ (M^{II} = Fe, Co, Ni, Zn) exhibit antiferromagnetic interactions that give rise to ferrimagnets or weak ferromagnetic ordering [20, 22]. $K_2[MnU(ox)_4]\cdot 9H_2O$ showed a diamond-like topology [23]. Investigation of lanthanide oxalate–oxydiacetate mixed-ligand complexes could be significant, however, only neodymium oxalate–oxydiacetate $[Nd(H_2O)_3]_2(C_2O_4)][O(CH_2CO_2)_2]$ was structurally characterized [24]. We here report the synthesis, characterization, and crystal structures of six new coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ ($x = 3$ for Ln = La, Ce, Pr, Gd, Tb and $x = 2$ for Ln = Er).

2. Experimental

2.1. *Materials and measurements*

All commercially available reagents and chemicals were of analytical grade purity and used without purification. Deionized water (18 MΩ cm) was obtained by passing distilled water through a Barnstead E-pure 3-Module system. Elemental analyses (C, H) were performed on an Elementar Vario EL III analyzer. Infrared (IR) spectra were recorded as KBr disks with a Nicolet 510 P FT–IR spectrometer. Thermogravimetric analyses were record on a Mettler TG-50 thermal analyzer under an atmosphere of air at a heating rate of 10°C min^{-1}.

2.2. *Preparation of complexes*

2.2.1. $\{[La(oda)(H_2O)_3]_2(ox)\}_n$ (1). A mixture of $La_2(CO_3)_3\cdot 8H_2O$ (0.3010 g, 0.5 mmol), oxydiacetic acid (H_2oda) (0.2682 g, 2 mmol) and H_2O (20 mL) was sealed in a 25 mL stainless steel bomb with Teflon liner at 150°C for 72 h. After cooling the reaction mixture to room temperature, colorless crystals of **1** suitable for X-ray diffraction analysis were obtained. Yield: 57%. Anal. Calcd for $C_5H_{10}O_{10}La$: C, 16.27; H, 2.73. Found: C, 16.36; H, 2.61. IR (KBr, cm^{-1}): 3390 (s, br), 3251 (s, br), 2920 (w), 1680 (vs), 1635 (vs), 1587 (vs), 1464 (w), 1438 (s), 1423 (s), 1359 (w), 1312 (s), 1114 (s), 1048 (w), 931 (w), 788 (w), 739 (w), 708 (w), 601 (w), 553 (w), 504 (w).

2.2.2. $\{[Ce(oda)(H_2O)_3]_2(ox)\}_n$ (2). A mixture of $CeCl_3\cdot 7H_2O$ (0.1868 g, 0.5 mmol), oxydiacetic acid (0.1341 g, 1 mmol) and H_2O (20 mL) was sealed in a 25 mL stainless steel bomb with Teflon liner at 150°C for 72 h. After cooling to room temperature, colorless crystals of **2** suitable for X-ray diffraction analysis were obtained. Yield: 65%. Anal. Calcd for $C_5H_{10}O_{10}Ce$: C, 16.21; H, 2.72. Found: C, 16.09; H, 2.58. IR (KBr, cm^{-1}): 3426 (s, br), 3236 (s, br), 2920 (w), 1680 (vs), 1635 (vs), 1586 (vs), 1464 (w), 1438 (s), 1424 (s), 1359 (w), 1312 (s), 1116 (s), 1049 (w), 932 (w), 789 (w), 739 (w), 707 (w), 601 (w), 553 (w), 503 (w).

2.2.3. {[Pr(oda)(H_2O)$_3$]$_2$(ox)}$_n$ (3). Green crystals of **3** were obtained using a procedure similar to that reported for **1** at 150°C for 72 h but Pr_2O_3 (0.1649 g, 0.5 mmol) was used instead of $La_2(CO_3)_3 \cdot 8H_2O$. Yield: 64%. Anal. Calcd for $C_5H_{10}O_{10}Ce$: C, 16.17; H, 2.71. Found: C, 16.21; H, 2.63. IR (KBr, cm^{-1}): 3427 (s, br), 3249 (s, br), 2921 (w), 1682 (vs), 1635 (vs), 1586 (vs), 1465 (w), 1438 (s), 1424 (s), 1359 (w), 1312 (s), 1117 (s), 1050 (w), 932 (w), 789 (w), 739 (w), 706 (w), 602 (w), 553 (w), 504 (w).

2.2.4. {[Gd(oda)(H_2O)$_3$]$_2$(ox)}$_n$ (4). Colorless crystals of **4** were obtained using a procedure similar to that reported for **1** at 160°C for 72 h with Gd_2O_3 (0.1812 g, 0.5 mmol) instead of $La_2(CO_3)_3 \cdot 8H_2O$. Yield: 66%. Anal. Calcd for $C_5H_{10}O_{10}Gd$: C, 15.50; H, 2.60. Found: C, 15.43; H, 2.65. IR (KBr, cm^{-1}): 3429 (s, br), 3251 (s, br), 2924 (w), 1686 (vs), 1640 (vs), 1593 (vs), 1467 (w), 1440 (s), 1427 (s), 1359 (w), 1312 (s), 1125 (s), 1054 (w), 935 (w), 791 (w), 711 (w), 605 (w), 556 (w), 504 (w).

2.2.5. {[Tb(oda)(H_2O)$_3$]$_2$(ox)}$_n$ (5). Colorless crystals of **5** were obtained using a procedure similar to that reported for **1** at 150°C for 72 h but Tb_2O_3 (0.1832 g, 0.5 mmol) was used instead of $La_2(CO_3)_3 \cdot 8H_2O$. Yield: 65%. Anal. Calcd for $C_5H_{10}O_{10}Tb$: C, 15.44; H, 2.59. Found: C, 15.45; H, 2.52. IR (KBr, cm^{-1}): 3431 (s, br), 3258 (s, br), 2923 (w), 1687 (vs), 1639 (vs), 1591 (vs), 1467 (w), 1440 (s), 1427 (s), 1358 (w), 1312 (s), 1126 (s), 1054 (w), 935 (w), 792 (w), 713 (w), 605 (w), 556 (w), 503 (w).

2.2.6. {[Er(oda)(H_2O)$_2$]$_2$(ox)}$_n$ (6). Colorless crystals of **6** were obtained using a procedure similar to that reported for **1** at 120°C for 72 h with Er_2O_3 (0.1912 g, 0.5 mmol) instead of $La_2(CO_3)_3 \cdot 8H_2O$. Yield: 70%. Anal. Calcd for $C_5H_8O_9Er$: C, 15.82; H, 2.12. Found: C, 15.69; H, 2.08. IR (KBr, cm^{-1}): 3431 (s, br), 3256 (s, br), 2923 (w), 1692 (vs), 1645 (vs), 1590 (vs), 1466 (w), 1439 (s), 1427 (s), 1359 (w), 1311 (s), 1123 (s), 1052 (w), 934 (w), 791 (w), 708 (w), 604 (w), 555 (w), 503 (w).

2.3. *X-ray crystallography*

Single crystal X-ray diffraction data for **1**–**6** were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω scan mode at 293(2) K. Intensity data were corrected for Lp factors and empirical absorption [25]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [26]. All nonhydrogen atoms were anisotropically refined. Hydrogen atoms were located by difference Fourier syntheses and refined isotropically. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray crystallography [27]. The crystallographic data are summarized in table 1 and the La–O distances of **1**–**6** are listed in table 2.

Table 1. Summary of crystallographic data for **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_5H_{10}O_{10}La$	$C_5H_{10}O_{10}Ce$	$C_5H_{10}O_{10}Pr$	$C_5H_{10}O_{10}Gd$	$C_5H_{10}O_{10}Tb$	$C_5H_8O_9Er$
Formula weight	369.04	370.25	371.04	387.38	389.06	379.37
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cells and dimensions (Å, °)						
a	12.6506(10)	12.6041(13)	12.5661(14)	12.407(2)	12.3706(16)	11.6810(16)
b	6.8782(5)	6.8303(7)	6.7919(7)	6.6576(10)	6.6261(8)	6.5919(9)
c	11.7181(9)	11.6920(12)	11.6841(13)	11.6333(18)	11.6005(15)	11.8163(16)
β	95.5380(10)	95.5080(10)	95.435(2)	95.450(2)	95.530(2)	96.674(2)
$V(\text{Å})^3$	1014.87(13)	1001.91(18)	992.73(19)	956.6(3)	946.5(2)	903.7(2)
$D_c(\text{g cm}^{-3})$	2.415	2.455	2.483	2.690	2.73	2.788
$\mu\,(\text{mm}^{-1})$	4.252	4.587	4.951	6.978	7.518	9.319
Z	4	4	4	4	4	4
$F(000)$	708	712	716	736	740	712
Crystal size (mm^3)	0.08 × 0.13 × 0.39	0.06 × 0.10 × 0.25	0.09 × 0.12 × 0.29	0.12 × 0.16 × 0.26	0.07 × 0.10 × 0.33	0.09 × 0.13 × 0.27
θ range (°)	3.2–26.0	3.3–26.0	3.3–26.1	1.6–26.0	1.6–26.0	1.8–26.0
N_t	5396	5363	5320	5087	5061	4737
$N_t(R_{\text{int}})$	1987 (0.027)	1974 (0.015)	1952 (0.012)	1882 (0.016)	1866 (0.015)	1758 (0.014)
N_o	1876	1865	1872	1754	1774	1711
S	1.11	1.08	1.10	1.10	1.08	1.04
R^a	0.0239	0.0168	0.0152	0.0465	0.0213	0.0183
${}_wR^b$	0.0666	0.0430	0.0399	0.0465	0.0548	0.0484

Note: ${}^aR = \sum|F_o|-|F_c|/\sum|F_o|$, ${}^b{}_wR = \{\sum[w(|F_o|-|F_c|)^2]/\sum w|F_o|^2\}^{1/2}$.

Table 2. The La–O distances (Å) of **1**–**6**.

		1	**2**	**3**	**4**	**5**	**6**
Ln–O_{oda}		2.435(2)	2.422(2)	2.397(2)	2.339(2)	2.328(3)	2.299(2)
		2.488(2)	2.463(2)	2.460(2)	2.386(2)	2.373(3)	2.339(3)
		2.500(2)	2.475(2)	2.446(2)	2.396(2)	2.379(2)	2.362(3)
		2.585(2)	2.565(2)	2.544(2)	2.479(2)	2.465(3)	2.420(2)
	Mean	2.502	2.481	2.462	2.400	2.386	2.355
Ln–O_{ox}		2.570(2)	2.552(2)	2.552(2)	2.480(2)	2.466(2)	2.385(2)
		2.589(2)	2.571(2)	2.534(2)	2.483(2)	2.469(3)	2.405(2)
	Mean	2.580	2.562	2.543	2.482	2.468	2.395
Ln–O_w		2.548(2)	2.512(2)	2.489(2)	2.406(3)	2.385(4)	2.286(4)
		2.575(2)	2.551(2)	2.535(2)	2.465(3)	2.451(3)	2.316(2)
		2.610(4)	2.591(2)	2.575(2)	2.531(2)	2.516(3)	
	Mean	2.578	2.551	2.533	2.467	2.451	2.301

3. Results and discussion

The hydrothermal reaction of lanthanide oxide, nitrate, chloride, or carbonate and oxydiacetic acid (H_2oda) in the mole ratio 1 : 4 at ~150°C for 72 h led to rapid formation of single crystals of the oxalate–oxydiacetate mixed-ligand coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ (where $x = 3$ for Ln = La, Ce, Pr, Gd, Tb and $x = 2$ for Ln = Er) in high purity and yield; oxydiacetic acid decomposed into oxalic acid in this reaction. Similar situation occurred in another system [20]. All these complexes are stable crystalline solids and can be stored in air at room temperature for a long time. IR spectra and thermal behavior of these complexes are almost identical, suggesting similar structures for those complexes as confirmed by the X-ray crystal structure determination below. Conventional self-assembly reactions did not afford these kinds of coordination polymers, but gave single-ligand species $[Ln_2(oda)_3(H_2O)_3 \cdot 5H_2O]_n$ [14], and $[Er_2(oda)_3(H_2O)_4 \cdot 2H_2O]_n$ [28], or the mononuclear complex $[Gd(Hoda)_3] \cdot H_2oda \cdot H_2O$ [29].

3.1. *Syntheses*

Four factors in preparation of the complexes, e.g. the starting lanthanide, the oxydiacetic acid/lanthanide ion ratio (*R*), the temperature, and the time of reaction, were investigated.

The same complexes were obtained when Ln_2O_3, $Ln(NO_3)_3$, $LnCl_3$, and $La_2(CO_3)_3$ were used as starting materials. The products obtained by use of $PrCl_3$ and all lanthanide nitrates have been confirmed by X-ray diffraction analyses, and other products by elemental analyses.

Four different ratios ($R =$ oda/Ln $= 1$, 2, 3, and 4) were used to prepare the title compounds. The same complexes were obtained when $R = 2, 3$, and 4. The products for Nd, Gd, Tb when $R = 2$, 3 and those for Er when $R = 2, 3, 4$ were confirmed by X-ray diffraction analyses, and other products by elemental analyses.

Attempts were made to study the effect of reaction temperature and time on the products. The experiments were carried out at 120°C and 24 h; if no complexes suitable for X-ray crystal structure study were obtained, the same experiment was repeated with increase of 10°C in temperature and/or increase of 24 h in time. So the reaction condition of 150°C and 72 h means the combinations of the temperatures 120, 130, or 140°C with the time 24 or 48 h did not give the products. For the six complexes studied here, reaction temperature increase from 150°C for the lighter lanthanide elements La, Ce, and Pr, to 160°C for Gd, decrease to 150°C for Tb, and finally to 120°C for the heavier Er.

Oxalate–oxydiacetate mixed-ligand coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ can be synthesized by hydrothermal reaction of oxydiacetic acid and lanthanide oxide, nitrate, chloride, or carbonate in high purity and yield, with mole ratio of the oxydiacetic acid/lanthanide ion above 2 with sufficient reaction temperature and time. Nd complex was also obtained by reaction of neodymium oxalate and oxydiacetic acid [24].

3.2. *IR spectroscopy*

IR spectra of **1**–**6** are very similar with characteristic absorptions of coordinated water, oxydiacetate and oxalate. In particular, they feature two very strong bands at 1640 ± 5 and $1590 \pm 3\,cm^{-1}$, which correspond to the antisymmetric vibrations of the carboxylate groups (shifted from $1734\,cm^{-1}$ for oxydiacetic acid), and two strong bands at 1439 ± 1 and $1425 \pm 2\,cm^{-1}$, assigned to symmetric vibrations of the carboxylate groups [30]. The Δ values $[=\nu_{asym}(COO^-) - \nu_{syn}(COO^-)]$ for these compounds are ca. 150 and $210\,cm^{-1}$, respectively, indicating coexistence of bridging and unidentate coordination modes of the carboxylates [31]. Strong bonds at $1640 \pm 5\,cm^{-1}$ [overlapping with the $\nu_{asym}(COO^-)$] and middle strong bands at $1359\,cm^{-1}$ can be assigned to tetradentate bridging of the oxalates. Strong absorption bands observed in the $3450–3200\,cm^{-1}$ range and 1685 ± 5 and $933 \pm 3\,cm^{-1}$ are assigned to coordinated water [30]. Bands at 603 ± 3, 554 ± 4, and $503 \pm 1\,cm^{-1}$ are assigned to Ln–O modes.

It has been proposed [32], and theoretically supported [7], that the IR band corresponding to the antisymmetric COC stretch of ethereal oxygen indicates the coordination mode adopted by oxydiacetate. A planar oxydiacetate has a sharp and strong band in the region $1120–1150\,cm^{-1}$, while this band falls to around $1100\,cm^{-1}$ when the arrangement is puckered. For **1**–**6**, this absorption appears within the range $1114–1126\,cm^{-1}$, indicating planar disposition of oxydiacetate, consistent with the X-ray structural determinations of **1**–**6**.

3.3. *Thermal behaviors*

Thermogravimetric analyses of **1**–**6** are consistent with formulation of Nd compound reported by Roméro and Trombe [24].

3.4. *X-ray crystal structures*

The six compounds $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ have similar composition with different numbers of water molecules $x = 3$ for **1**–**5** and $x = 2$ for **6**. All six complexes crystallize in the monoclinic systems and space groups $P2_1/c$, consistent with the Nd compound [24]. The cell parameters and volume of the unit cell of **1**–**6** decrease (table 1), and the calculated densities increase, with decrease in the lanthanide ion radius, in agreement with the lanthanide contraction.

The asymmetric unit of **1** contains half the molecule, which is related to the other half by a center of symmetry. The molecular structure of **1** is shown in figure 1. The 1-D structure of **1** can be described as a double-chain ladder-shape, showing $3.0 \times 6.4\,\text{Å}^2$ channels along the *c* axis (figure 2). The 1-D double-chains are connected by

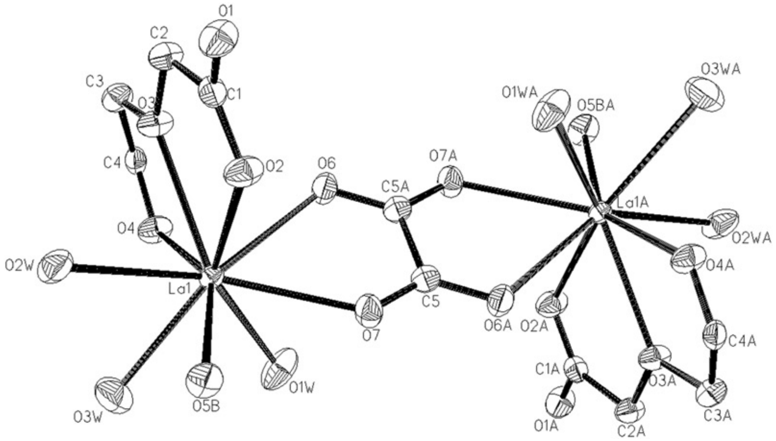

Figure 1. The molecular structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability. Compounds **2–5** have identical molecular structures and atom numbering schemes with **1**; compound **6** has the same molecular structure and atom numbering scheme as **1**, except for the absence of the third coordinated water.

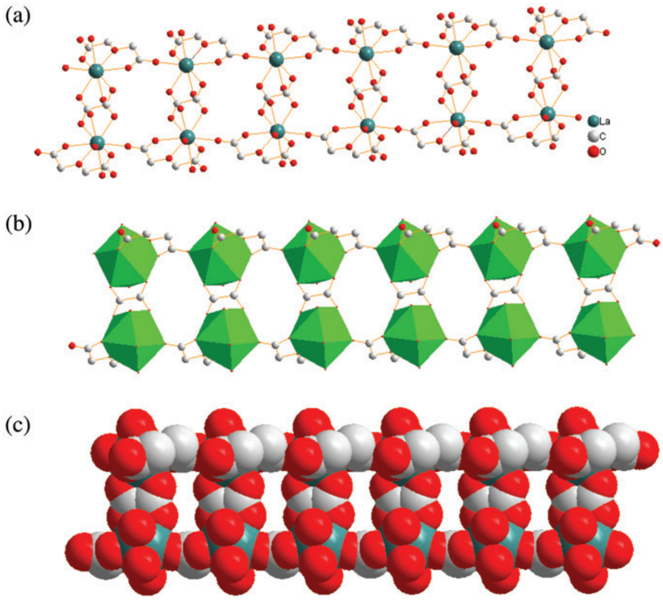

Figure 2. 1-D infinite ladder-shaped double-chain structure of **1** showing the $3.0 \times 6.4\,\text{Å}^2$ channels along the *c* axis. (a) Ball-and-stick representation, (b) Polyhedron representation, and (c) Space-filling model of the open channels.

intermolecular O(2W)···O(1) hydrogen bonds (table 3), forming a 2-D network structure (figure 3).

Each lanthanide is nine-coordinate with nine oxygen donors, three from the three water molecules, two from an oxalate group, and four from two different oxydiacetate ligands. The La–O distances vary from 2.435(2) Å to 2.610(4) Å. In three La–O bonds of the carboxylate, the La–O(5B) bond of 2.435(2) Å is the shortest with difference of distances between the other two carboxylate bonds from another oxydiacetate being 0.06 Å; this is because only the La–O(5B) bond does not involve ring tension.

Table 3. Hydrogen bond distances (Å) and angles (°) for **1**.

D–H···A	D–H	H···A	D···A	D–H···A
O_1W–H_2WA···O1	0.8196	1.9864	2.721(3)	148.75[a]
O_1W–H_1WA···O7	0.8194	2.0076	2.781(4)	157.29[b]
O_3W–H_3WA···O2	0.8200	2.1891	3.003(4)	172.07[c]
O_2W–H_2WB···O1	0.86(4)	1.92(5)	2.781(4)	176(4)[c]
O_1W–H_1WB···O4	0.76(5)	2.17(5)	2.902(3)	164(5)[d]
O_1W–H_1W···O5B	0.76(5)	2.57(5)	3.026(3)	121(3)[e]
O_3W–H_3WB···O6	0.64(8)	2.54(7)	3.070(4)	142(7)[f]

Symmetry codes: (a) $1-x$, $-y$, $2-z$; (b) $-x$, $-1/2+y$, $3/2-z$; (c) x, $1/2-y$, $-1/2+z$; (d) $-x$, $1/2+y$, $3/2-z$; (e) $-x$, $-1/2+y$, $3/2-z$; (f) x, $-1/2-y$, $-1/2+z$.

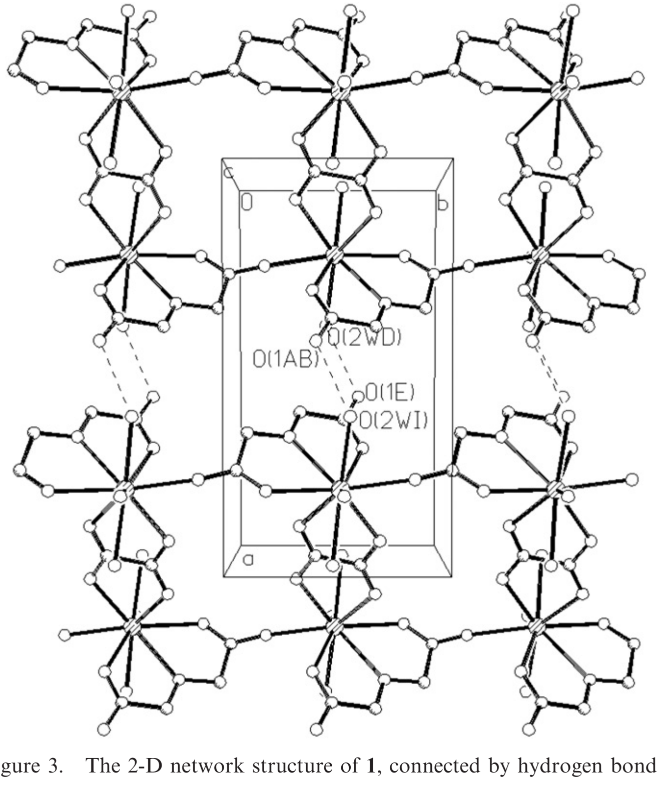

Figure 3. The 2-D network structure of **1**, connected by hydrogen bonds.

The coordination geometry around each lanthanum can be viewed as a tricapped trigonal prism [figure 4(a)]. The O(3), O(3W), and O(7) atoms with the longest distances from the lanthanum atom occupy the cap positions, and other six oxygens form a trigonal prism.

Oxalate, bischelating in the lanthanum complex, is planar and its bond lengths and angles are comparable with those of related lanthanum complexes [24, 34].

The oxydiacetate is tetradentate, with O(1) uncoordinated. The uncoordinated O(1) connects the 1-D chain polymer to form a 2-D network structure by intermolecular hydrogen bonds (figure 3 and table 3). The uncoordinated O(1) in one chain forms

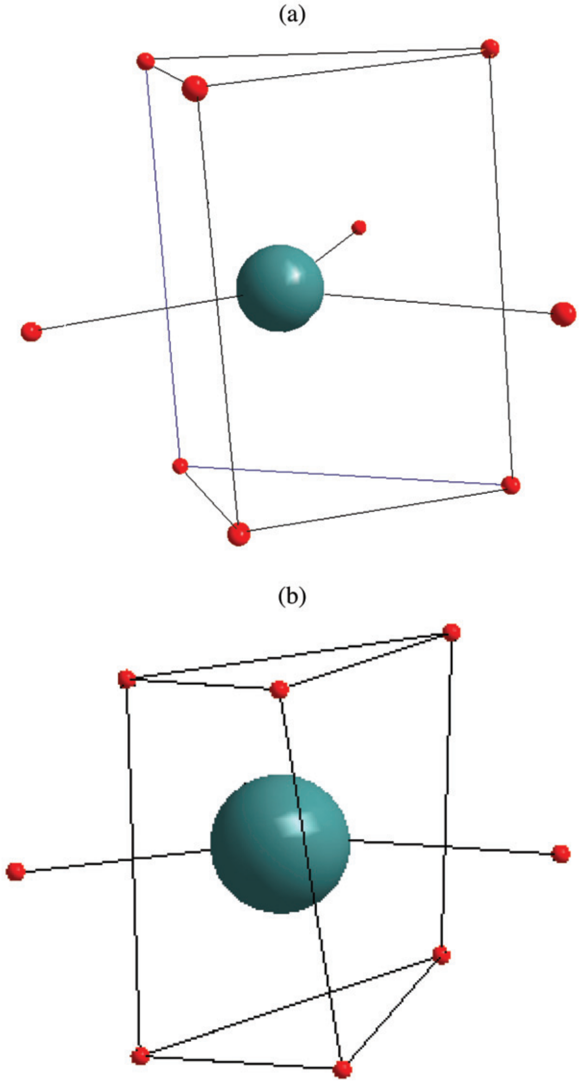

Figure 4. The coordination polyhedron of metal ions in (a) **2–5** and (b) **6**.

a hydrogen bond with water in another chain and one water in the first chain forms a hydrogen bond with uncoordinated O(1) in the second chain in the same pattern. The O(1) ··· O(W) distances are 2.721(3) and 2.781(4) Å, respectively. The interlocking mode of the double hydrogen bonding between the two polymer chains makes the structure very stable.

Structures of **2**–**5** are identical to that of **1** including the double-chain and network structures, the coordination geometry around each lanthanide, the coordination modes of oxalate, and oxydiacetate and the connecting modes of the hydrogen bonds. The structure of **6** is similar to that of **1** with the exception that the number of water molecules is 2 rather than 3, giving eight-coordinate erbium in a distorted bicapped trigonal prism [figure 4(b)].

Comparing the Ln–O bond distances of **1**–**6**, the differences of average values of $Ln–O_{oda}$, of $Ln–O_{ox}$ and of $Ln–O_w$ in **1**–**6** are in agreement with the differences of lanthanide ion radius values (table 2). In addition, the differences between the average $Ln–O_{oda}$ distances and the average $Ln–O_{ox}$ distances is 0.08 Å for **1**–**5**, but 0.04 Å for **6**, due to the eight-coordination.

4. Conclusion

Six lanthanide oxalate–oxydiacetate mixed-ligand coordination polymers $\{[Ln(oda)(H_2O)_x]_2(ox)\}_n$ have been synthesized by hydrothermal reaction of oxydiacetic acid and lanthanide oxide, nitrate, chloride, or carbonate in high purity and yield, but cannot be obtained by conventional self-assembly reactions. Oxydiacetic acid decomposed into oxalic acid in reaction. The same compounds have been obtained from different starting materials. These compounds contain approximately 3.0×6.4 Å^2 channels along the *c* axis.

Supplementary Material

Crystallographic data for the structural analysis of **1**–**6** have been deposited with the Cambridge Crystallographic Data Centre with CCDC reference numbers 627575–627577 and 627579–627581, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk, or http://www.ccdc.cam.ac.uk.

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References

[1] C.D. Nicola, A. Galindo, J.V. Hanna, F. Marchetti, C. Pettinari, R. Pettinari, E. Rivarola, B.W. Skelton, A.H. White. *Inorg. Chem.*, **44**, 3094 (2005).

[2] R. Baggio, M.T. Garland, Y. Moreno, O. Pena, M. Perec, E. Spodine. *J. Chem. Soc., Dalton Trans.*, 2061 (2000).

[3] J.-G. Mao, L. Song, X.-Y. Huang, J.-S. Huang. *Polyhedron*, **16**, 963 (1997).

[4] J.-G. Mao, J.-S. Huang, J.F. Ma, J.-Z. Ni. *Transition Met. Chem.*, **22**, 277 (1997).

[5] J.-G. Mao, L. Song, J.-S. Huang. *Chinese J. Struc. Chem.*, **16**, 228 (1997).

[6] A.C. Rizzi, R. Calvo, R. Baggio, M.T. Garland, O. Pena, M. Perec. *Inorg. Chem.*, **41**, 5609 (2002).

[7] D. del Ria, A. Galindo, R. Vicente, C. Mealli, A. Ienco, D. Masi. *Dalton Trans.*, 1813 (2003).

[8] A. Grirrane, A. Pastor, E. Alvarez, C. Mealli, A. Ienco, P. Rosa, F. Montilla, A. Galindo. *Eur. J. Inorg. Chem.*, 707 (2004).

[9] B. Barja, R. Baggio, M.T. Garland, P.F. Aramendia, O. Pena, M. Perec. *Inorg. Chim. Acta*, **346**, 187 (2003).

[10] T. Behrsing, G.B. Deacon, C.M. Forsyth, M. Forsyth, B.W. Skelton, A.H.Z. White. *Z. Anorg. Allg. Chem.*, **629**, 35 (2003).

[11] M. Bethencourt, F.I. Botana, J.J. Calvino, M. Marcos, M.A. Rodriguez-Chancon. *Corros. Sci.*, **40**, 1803 (1998).

[12] M. Forsyth, C.M. Forsyth, K. Wilson, T. Behrsing, G.B. Deacon. *Corros. Sci.*, **44**, 2651 (2002).

[13] M. Albin, R.R. Whittle, W.D. Horrocks. *Inorg. Chem.*, **24**, 4591 (1985).

[14] R. Baggio, M.T. Garland, M. Perec, D. Vega. *Inorg. Chem.*, **35**, 2396 (1996).

[15] R. Baggio, M.T. Garland, M. Perec. *Inorg. Chim. Acta*, **281**, 18 (1998).

[16] R. Baggio. *Inorg. Chim. Acta*, **303**, 306 (2000).

[17] R. Baggio, M.T. Garland, M. Perec. *Acta Crystallogr. Sect. C*, **56**, 312 (2000).

[18] F.R. Fronczek, A.K. Banerjee, S.F. Watkins, R.W. Schwartz. *Inorg. Chem.*, **20**, 2745 (1981).

[19] J.M. Gonzalez-Perez, C. Alarcon-Payer, A. Castineiras, T. Pivetta, L. Lezama, D. Choquesillo-Lazarte, G. Crisponi, J. Niclos-Gutierrez. *Inorg. Chem.*, **45**, 877 (2006).

[20] B. Li, W. Gu, L.-Z. Zhang, J. Qu, Z.-P. Ma, D.-Z. Liao. *Inorg. Chem.*, **45**, 10425 (2006).

[21] K.S. Min, J.S. Miller. *Dalton Trans.*, 2463 (2006).

[22] E. Coronado, J.R. Galán-Mascarós, C. Martí-Gastaldo. *J. Mater. Chem.*, **16**, 2685 (2006).

[23] K.P. Mörtl, J.-P. Sutter, S. Golhen, L. Ouahab, O. Kaha. *Inorg. Chem.*, **39**, 1626 (2000).

[24] S. Roméro, J.C. Trombe. *Polyhedron*, **18**, 1653 (1999).

[25] G.M. Sheldrick. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen: Göttingen, Germany (1996).

[26] G.M. Sheldrick. *SHELXTL*, v5 Reference Manual Siemens Analytical for X-ray Systems Inc, Madison, Wisconsin, USA (1996).

[27] A.J.C. Wilson. *International Tables for X-ray Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht (1992), Tables 6.1.1.4 and 4.2.6.8.

[28] I. Elding. *Acta Chem. Scand., Ser. A*, **31**, 75 (1977).

[29] R. Baggio, M.T. Garland, M. Perec. *Inorg. Chem.*, **36**, 950 (1997).

[30] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn, Wiley-Interscience, New York (1986).

[31] G.B. Deacon, R. Phillips. *J. Coord. Chem. Rev.*, **33**, 227 (1980).

[32] A. Grirrane, A. Pastor, A. Ienco, C. Mealli, A. Galindo. *J. Chem. Soc., Dalton Trans.*, 3771 (2002).

[33] S. Roméro, A. Mosset, J.C. Trombe. *J. Solid State Chem.*, **127**, 256 (1996).

[34] E. Hansson. *Acta Chem. Scand.*, **37**, 823 (1973).