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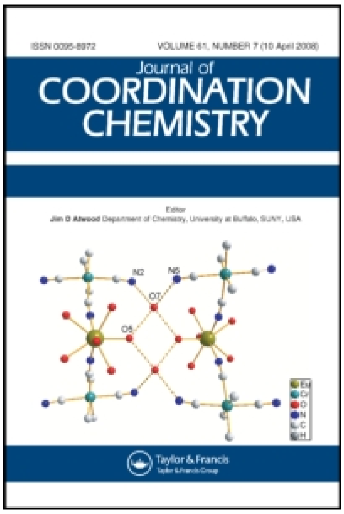

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Syntheses, structure and properties of two ternary lanthanum oxalates from hydrothermal reactions

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Two ternary lanthanide compounds, $[La_2(OX)(BC)_2(H_2O)_4]\cdot H_2O$ **1** ($H_2OX =$ oxalic acid, $H_2BC = 1$, 2-benzenedicarboxylic acid) and $[La_2(OX)(MBC)_2(H_2O)_4]\cdot 2H_2O$ **2** ($H_2MBC =$ 5-hydroxyl-1,3-benzenedicarboxylic acid), have been hydrothermally synthesized and structurally characterized. Complex **1** crystallizes in the monoclinic space group *C2/c* with $a = 20.165(7)$, $b = 6.084(2)$, $c = 20.653(7)$ Å, $\beta = 111.378(5)^\circ$, $U = 2359.3(13)$ Å^3; complex **2** in the triclinic space group *P-1* with $a = 7.744(4)$, $b = 8.799(5)$, $c = 10.482(5)$ Å, $\alpha = 67.673(8)$, $\beta = 71.239(8)$, $\gamma = 74.188(7)^\circ$ $U = 616.3(6)$ Å^3. Thermogravimetric analyses on compounds **1** and **2** show high structural stability to 400°C.

Keywords: Crystal structure; Lanthanides; Oxalates; TGA

1. Introduction

Design and synthesis of d-block transition metal-carboxylic coordination polymers were investigated for their interesting structural topologies and crystal-packing motifs with potential applications in absorption, separation, and catalysis [1–4]. However, research on f-block lanthanide coordination polymers is less common for the high and variable coordination numbers of lanthanide ions would be a barrier for open framework formation [5–9]. These characteristics may lead, however, to unusual molecular architectures [10–14]. A ternary complex $[Tb_4(H_2O)_2](C_2O_4)_2(C_5H_6O_4)_4$ was synthesized by Trombe [15]. In this complex, sheets constructed by terbium, oxalate and glutarate were connected by glutarate groups to form a 3D structure. There was no void big enough to accommodate small molecules in the open framework for the distortion of the aliphatic chains. To introduce rigid ligands to construct the multidimensional framework of lanthanides, different benzenedicarboxylic acids and oxalic acid were used. In this paper, by adjusting the pH value and controlling the temperature we have isolated two new ternary carboxylic ligand-lanthanides,

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$[La_2(OX)(BC)_2(H_2O)_4] \cdot H_2O$ **1** $[La_2(OX)(HBC)_2(H_2O)_4] \cdot 2H_2O$ **2**. There are one and two water molecules per Ln_2 unit in their voids for complex **1** and **2**, respectively.

2. Experimental

2.1. *Physical measurements*

Elemental analyses of carbon and hydrogen were carried out with a Perkin–Elmer analyzer model 240. Infrared spectroscopy as KBr pellets was performed on a Magma IR 560 infrared spectrophotometer in the 4000–600 cm^{-1} region. Thermal gravimetric analyses (TGA) were carried out under N_2 at 10°C min^{-1} between 25 and 700°C.

2.2. *Crystallographic studies*

Determination of the unit cell and data collection was performed at room temperature on BRUKER SMART 1000, using a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined by least-squares procedures on Fo^2 with SHELXL-97 by minimizing the function $w(Fo^2\text{-}Fc^2)^2$, where Fo and Fc are, respectively, the observed and calculated structure factors [16]. The hydrogen atoms of solvent molecules were not added, and the other hydrogen atoms were located geometrically and refined isotropically. Information concerning crystallographic data collection and refinement of the structures for compound **1** and **2** are compiled in table 1.

2.3. *Preparation*

Aqueous NaOH was added to an aqueous solution of H_2BC (1, 2-benzenedicarboxylic acid 0.50 g, 3.0 mmol) to adjust the pH value of the mixture to approximately 6.

Table 1. Summary of crystallographic data for complexes **1** and **2**.

	1	**2**
Formula	$C_{18}H_{18}La_2O_{17}$	$C_{18}H_{20}La_2O_{20}$
Formula weight	784.14	834.16
Crystal system	monoclinic	Triclinic
Space group	C2/c	P1
a, Å	20.165(7)	7.744(4)
b, Å	6.084(2)	8.799(5)
c, Å	20.653(7)	10.482(5)
α, deg	90	67.673(8)
β, deg	111.378(5)	71.239(8)
γ, deg	90	74.188(7)
V, Å^3	2359.3(13)	616.3(6)
Z	4	2
Reflections collected/unique	6337/2412 ($R_{\text{int}} = 0.0335$)	3185/2162 ($R_{\text{int}} = 0.0341$)
$F(000)$	1504	402
ρ_{calc}, g/cm^3	2.208	2.248
μ (Mo-Kα), mm^{-1}	3.457	3.516
T, K	293.3(2)	293.3(2)
R_1 [$I > 2\sigma$(I)]	0.0266	0.0447
wR$_2$ [$I > 2\sigma$(I)]	0.0586	0.1112

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Aqueous solutions of $La(ClO_4)_3 \cdot 6H_2O$ (1.10 g, 2.0 mmol) and $K_2C_2O_4 \cdot 6H_2O$ (0.20 g, 1.0 mmol) were added. The resulting mixture was placed in a Parr Teflon-lined autoclave. The autoclave was then sealed and heated at 140°C for three days. Colorless crystals of **1** suitable for X-ray crystallography were obtained, yield 48%. Compound **2** was prepared in a similar way to **1**, except that H_2MBC (H_2MBC = 5-hydroxyl-1, 3-benzenedicarboxylic acid) was used instead of H_2BC; colorless crystals were obtained in 52% yield. Elemental analysis calcd (%) for **1**, $C_{18}H_{18}La_2O_{17}$: C 27.62, H 2.36; found: C 27.57, H 2.31; for **2**, $C_{18}H_{20}La_2O_{20}$: C 26.04, H 2.51; found: C 25.89, H 2.42.

3. Results and discussion

These reactions are carried out in an autoclave and all crystals are stable in air and insoluble in water and most common organic solvents. FT-IR spectra showed the expected strong characteristic absorptions for the asymmetric vibrations of BC and MBC (1646 (**1**) and 1649 cm^{-1} (**2**) for ν(C=O)), and the water ligands (about 3400 cm^{-1} for ν(O–H)). It showed no absorptions for protonated-COOH (1765–1680 cm^{-1}), thus confirming complete deprotonation of H_2BC and H_2MBC.

3.1. *The structures of compound 1*

The structure of **1** is a neutral dinuclear unit with formula $[La_2(OX)(BC)_2(H_2O)_4]$ and one water molecule. The nine-coordinate La^{III} ion is surrounded by two oxalic oxygen atoms, five BC ligand-oxygen atoms and two water molecules. Bond distances and angles are given in table 2 and the lanthanum coordination is shown in figure 1.

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

La1-O1	2.555(3)	La1–O3C	2.495(3)
La1–O2	2.586(3)	La1–O6A	2.544(3)
La1–O5	2.523(3)	La1–O4B	2.578(3)
La1–O7	2.528(3)	La1–O3B	2.664(3)
La1–O8	2.498(3)		
O1–La1–O2	50.59(8)	O3C–La1–O1	81.36(10)
O5–La1–O1	122.69(10)	O6A–La1–O1	75.66(10)
O7–La1–O1	74.58(9)	O1–La1–O3B	122.44(9)
O8–La1–O1	143.23(10)	O1–La1–O4B	129.07(10)
O5–La1–O6A	64.04(9)	O4B–La1–O3B	49.37(8)
O2–La1–O3B	76.47(8)	O3C–La1–O2	77.24(9)
O3C–La1–O3B	64.58(10)	O8–La1–O6A	131.00(9)
O8–La1–O(5)	67.99(9)	O8–La1–O7	75.87(10)
O(5)–La1–O7	74.09(10)	O(5)–La1–O6A	64.04(9)
O7–La1–O6A	99.68(10)	O8–La1–O4B	86.50(9)
O7–La1–O4B	150.41(9)	O(5)–La1–O4B	77.34(10)
O8–La1–O3B	70.66(9)	O6A–La1–O4B	74.13(9)
O8–La1–O2	143.37(9)	O(5)–La1–O2	142.57(9)
O7–La1–O2	123.85(9)	O6A–La1–O2	79.77(9)
O4B–La1–O2	84.17(9)	O(5)–La1–O3B	112.73(9)
O7–La1–O3B	139.04(9)	O6A–La1–O3B	119.97(9)
O3C–La1–O4B	113.85(9)		

Symmetry code: A $-x, -y+2, -z+1$; B $-x+1/2, -y+3/2, -z+1$; C $x, y+1, z$.

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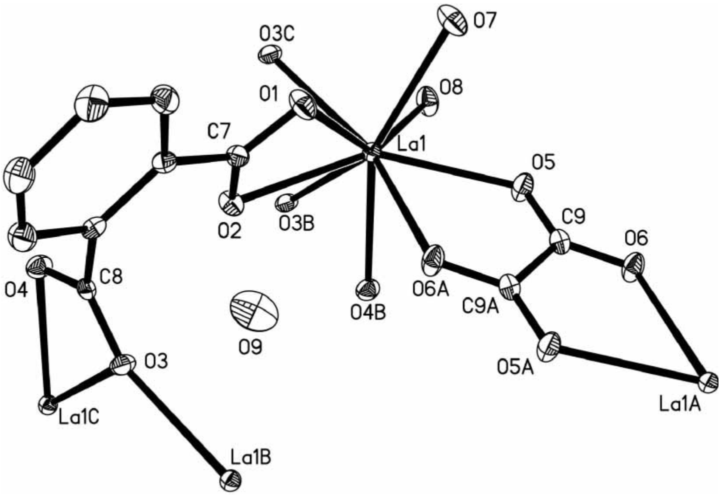

Figure 1. A view of the environment of La^{III} ions.

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The La–O bond distances range from 2.498 Å to 2.664 Å. The oxalate atoms constitute a basic plane, the largest diviation from planarity being 0.0028 Å. Two La^{III} ions are bridged by an oxalato ligand with the distance of 6.518 Å. The La atoms lie in the plane with deviation of ±0.1767 Å. In the *ab* plane, four carboxylate groups from two bidentate BC ligands bridge two adjacent La$_2$ units forming a zigzag chain. Two oxygen atoms from the two BC ligands coordinate to two La^{III} ions of adjacent chains in monodentate mode to construct a 2D network (figure 2a). Viewed along the *b* axis, the resulting 2D network of the complex forms open rectangular channels, as can be seen from figure 2b. The channels have the largest cavity size at about 4 and 4.5 Å, as measured by the shortest O···O distance between two diametrically opposing La$_2$ units. One water molecule per La$_2$ unit inserts between the layers and hydrogen bonds to the coordinating oxygen molecules with O(w)–H···O distance of 2.819 Å.

3.2. *The structures of compound 2*

The structure of **2** is a neutral dinuclear unit with formula [La$_2$(OX)(MBC)$_2$(H$_2$O)$_4$] and two water molecules. The eight-coordinate La^{III} is surrounded by two-oxalic oxygen atoms, four MBC ligand-oxygen atoms and two water molecules. Bond distances and angles are given in table 3 and the lanthanum coordination is shown in figure 3. The La–O bond distances range from 2.400 to 2.600 Å. The oxalate atoms constitute a basic plane, the largest deviation from planarity being 0.0020 Å. Two La^{III} ions are bridged by an oxalato ligand with the distance of 6.490 Å. However, the La atoms deviate from the plane ±0.4688 Å. Complex **2** has a complicated 3-D structure. When all oxalates and water molecules are omitted for clarity, its structure shows distinct layers parallel with the *ac* plane (figure 4). Four carboxylate oxygen atoms of MBC coordinate as monodentate ligands to four La^{III} ions. In the *ac* plane, MBC and lanthanides construct a network shown in figure 4a. One aslant oxalate points to the top layer, the next points below, and oxalates bridge these layers to

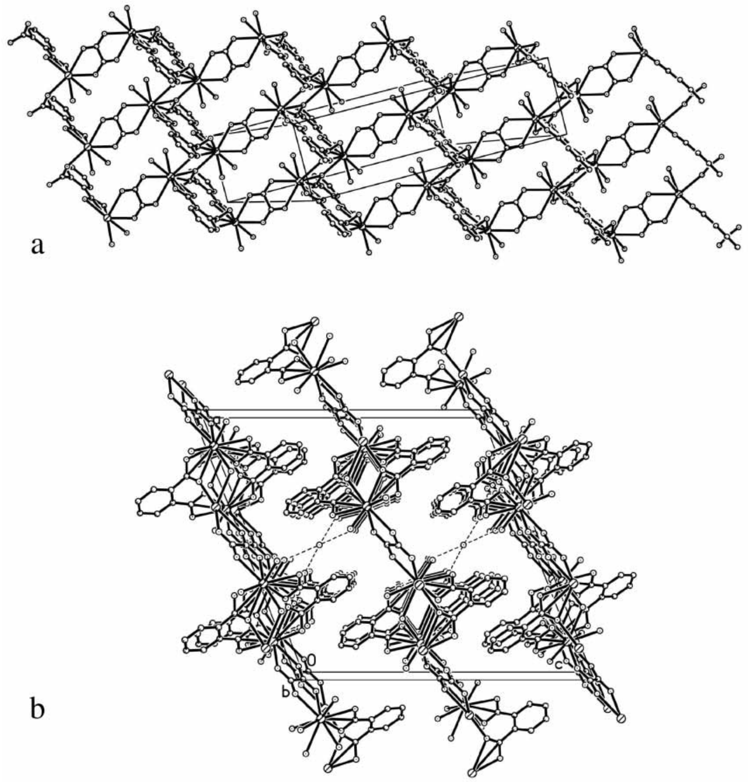

Figure 2. The projection of complex **1** onto the *ab* plane (a), and *ac* plane (b).

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

La1–O1	2.415(5)	La1–O4C	2.400(5)
La1–O6	2.528(5)	La1–O2D	2.461(5)
La1–O8	2.535(5)	La1–O3B	2.513(5)
La1–O9	2.600(5)	La1–O7A	2.540(5)
O1–La1–O6	70.34(19)	O1–La1–O2D	97.75(18)
O1–La1–O8	143.45(19)	O1–La1–O3B	140.62
O1–La1–O9	73.17(19)	O1–La1–O7A	80.78(18)
O4C–La1–O1	95.36(19)	O6–La1–O7A	63.85(15)
O4C–La1–O2D	150.11(19)	O4C–La1–O3B	107.42(18)
O2D–La1–O3B	78.22(17)	O4C–La1–O6	136.59(17)
O2D–La1–O6	73.28(17)	O3B–La1–O6	71.07(19)
O4C–La1–O8	74.66(18)	O2D–La1–O8	78.85(18)
O3B–La1–O8	74.9(2)	O6–La1–O8	139.46(18)
O4C–La1–O7A	73.64(17)	O2D–La1–O7A	135.00(17)
O3B–La1–O7A	75.69(18)	O7A–La1–O9	143.40(17)
O8–La1–O7A	127.09(16)	O4C–La1–O9	83.53(18)
O2D–La1–O9	74.82(18)	O3B–La1–O9	139.6(2)
O6–La1–O9	126.80(17)	O8–La1–O9	70.82(18)

Symmetry code: A $-x$, $-y$, $-z+2$; B x, $y-1$, $z+1$; C $-x+1$, $-y+1$, $-z+1$; D $-x$, $-y+1$, $-z+2$.

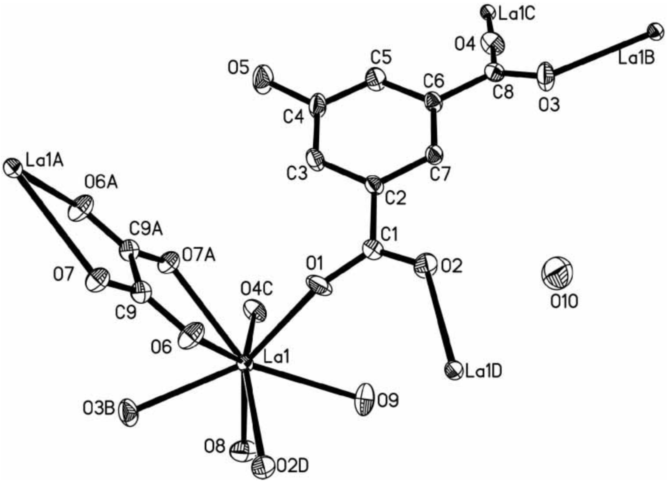

Figure 3. An ORTEP view of complex **2**.

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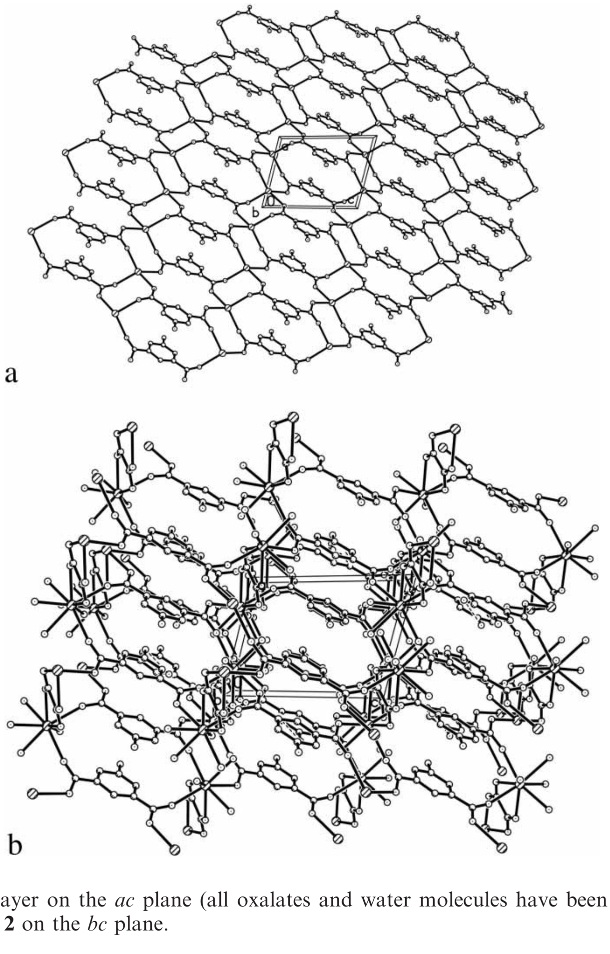

Figure 4. (a) One layer on the *ac* plane (all oxalates and water molecules have been omitted for clarity); (b) the projection of **2** on the *bc* plane.

form a 3-D structure (figure 4b). The oxygen atoms of hydroxybenzene do not coordinate to metal ions. The resulting 3D network forms closed cavities with four aryls and two oxalates, as seen in figure 4b. The cavity has the largest size at about 5.2, 6.1 and 8.6 Å. Two uncoordinated water molecules per La_2 unit insert into the void between layers and hydrogen bonds to the uncoordinated hydroxyl with a distance of 2.634 Å.

3.3. *Thermogravimetric analyses*

Thermal gravimetric analyses (TGA) were carried out in N_2 to examine dehydration and stability (figure 5). For complex **1**, the first loss of 10.0% from 25 to 180°C corresponds to the loss of non-coordinated water and four coordinated water molecules per Ln_2 unit (calculated 11.5%). For complex **2**, the first loss of 11.3% corresponds to the loss of two non-coordinated waters and four coordinated waters per Ln_2 unit (calculated 12.9%). The discrepancies between experimental and calculated values could be due to dehydration of the uncoordinated waters from these powders. At 400°C, the weight began to decrease slowly. The weight losses of 3.4% for **1** (calculated 3.5%) and 3.3% for **2** (calculated 3.3%) from 400 to 490°C correspond to loss of carbon monoxide from decomposition of oxalate. After 570°C, the rapid losses of weight correspond to the decomposition of aryl ligands. These phenomena are consistent with the crystal structures of these complexes. In general, the decomposition of oxalate and the formation of lanthanide carbonates are in the range of 300 and 590°C [13, 17–19]. The thermal decomposition temperature (T_d) always relates to the interaction between La^{3+} and oxalate ions. The T_d of oxalate ions for **1** and **2** (400°C) is higher than that of $La_2(OX)_3$ (375°C) [19]. A possible reason might be the high coordination number which leads to longer distances and weaker interaction between La^{3+} and oxalate ions.

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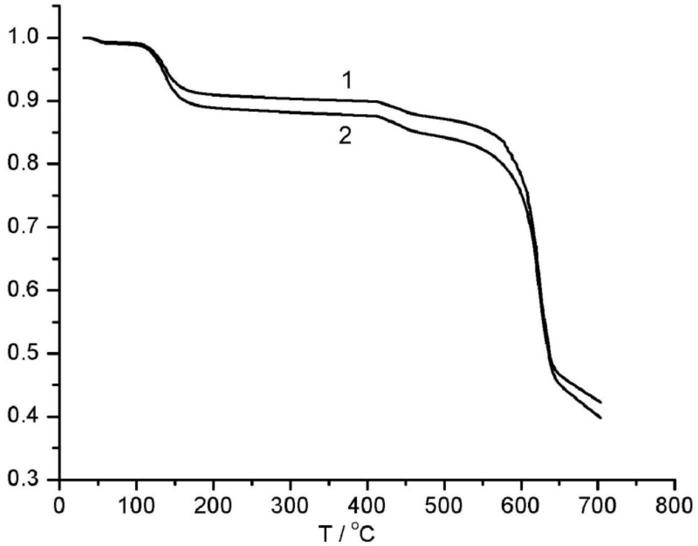

Figure 5. TGA curves for compound **1** and **2**.

These compounds, in general, keep their framework until the decomposition of oxalates. For both complexes, thermal analyses are difficult up to 400°C due to formation of carbonates. The temperature platforms of these complexes from 180 to 400°C show good stability.

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