

The first characterization of dimeric lanthanide complex anion: synthesis and crystal structure of $[\text{NH}(\text{Et})_3]_2[\text{Lu}(\text{L})_4]_2 \cdot 6\text{CH}_3\text{OH}$

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Abstract

Two lanthanide complexes with acrylic acid ligand: $[\text{Ho}(\text{L})_3(\text{CH}_3\text{OH})_2]_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{NH}(\text{Et})_3]_2[\text{Lu}(\text{L})_4]_2 \cdot 6\text{CH}_3\text{OH}$ (**2**) ($\text{L} = (E)\text{-3-(2-hydroxyl-phenyl)-acrylic acid}$) are studied. The crystal structure data for **1**: $\text{C}_{59}\text{H}_{60}\text{Ho}_2\text{O}_{24}$, orthorhombic, *Pbcn*, $a = 15.4289(12)$ Å, $b = 7.9585(6)$ Å, $c = 23.041(2)$ Å, $\beta = 99.657(2)^\circ$, $Z = 4$, $R_1 = 0.0637$, $wR_2 = 0.0919$; for **2**: $\text{C}_{27}\text{H}_{30.50}\text{LaO}_{13.75}$, triclinic, *P-1*, $a = 13.3034(4)$ Å, $b = 13.3087(4)$ Å, $c = 14.5461(6)$ Å, $\alpha = 85.932(2)^\circ$, $\beta = 64.611(2)^\circ$, $\gamma = 81.595(2)^\circ$, $Z = 2$, $R_1 = 0.0394$, $wR_2 = 0.0446$. Two structure data were collected using graphite monochromated molybdenum $K\alpha$ radiation and refined using full-matrix least square techniques on F^2 . Complex **2** is the first dimeric lanthanide complex anion. Two structures show dinuclear complexes with bis-monodentate and bidentate chelate bridge modes of carboxylato ligand. Bidentate chelate coordination mode were also included in these two complexes. The smallest bridge angle of bidentate chelate carboxylato bridge ($\eta^3\text{-O}$, $104.70(9)^\circ$) has been found for the first time. Complexes **1** and **2** act as supramolecular synthons assembled by 2D and 3D hydrogen bonding in the crystal lattices.

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1. Introduction

Lanthanide carboxylate complexes exhibit unusual structures and properties [1–6]. They have wide potential applications in biochemistry and materials science [7–11]. We have studied lanthanum complexes with a series of acrylic acid ligands [12]. The results have shown versatile coordination modes and interesting supramolecular chemistry. To extend these studies, the heavier lanthanide complexes with (*E*)-3-(2-hydroxyl-phenyl)-acrylic acid ligand, $[\text{Ho}(\text{L})_3(\text{CH}_3\text{OH})_2]_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{NH}(\text{C}_2\text{H}_5)_3]_2[\text{Lu}(\text{L})_4]_2 \cdot 6\text{CH}_3\text{OH}$ (**2**), have been synthesized. A dimeric lanthanide complex anion (complex **2**) has been found for the first time, although the mononuclear [13] and the one-dimensional lanthanide

(III) carbonato coordinated anion have been reported previously [14].

2. Experimental

Two complexes were confirmed by elemental analysis, IR spectroscopy and X-ray single crystal diffraction analysis. $[\text{Ho}(\text{L})_3(\text{CH}_3\text{OH})_2]_2 \cdot \text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**): a solution of $\text{Ho}(\text{NO}_3)_3$ (22.70 mg, 0.10 mmol) in 10 ml CH_3OH was added by solution of (*E*)-3-(2-hydroxyl-phenyl)-acrylic acid (49.44 mg, 0.30 mmol) and $\text{N}(\text{C}_2\text{H}_5)_3$ (30.36 mg, 0.30 mmol) in 10 ml CH_3OH . The reaction solution was filtrated after stirring for 3 h. Colourless plate single crystals suitable for X-ray diffraction analysis were obtained after 2 weeks by diffusion method with diethyl ether into the filtrate. The yield: 81.23 mg, 54.78%. Calcd for $\text{C}_{59}\text{H}_{60}\text{Ho}_2\text{O}_{24}$: C, 47.78; H, 4.08; N, 0.00. Found: C, 47.37; H, 4.16; N, 0.00. Selected IR (KBr, cm^{-1}): 3368.4 (m, $\nu_{\text{HO-H}}$), 3007.0 (m, $\nu_{\text{C-H}}$), 2943.6 (w, $\nu_{\text{as}(\text{CH}_2)}$), 1640.9, 1558.1 (vs, $\nu_{\text{as}(\text{COO}^-)}$), 1373.2, 1334.0 (s, $\nu_{\text{s}(\text{COO}^-)}$). $[\text{NH}(\text{C}_2\text{H}_5)_3]_2[\text{Lu}(\text{L})_4]_2 \cdot 6\text{CH}_3\text{OH}$ (**2**): a solution of

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(*E*)-3-(2-hydroxyl-phenyl)-acrylic acid (49.44 mg, 0.30 mmol) and $N(C_2H_5)_3$ (30.36 mg, 0.30 mmol) in 10 ml CH_3OH was added by solution of $Lu(NO_3)_3 \cdot 6H_2O$ (45.70 mg, 0.10 mmol) in 10 ml CH_3OH drop by drop. There are cloudy precipitates produced immediately. Colourless lath single crystals suitable for X-ray diffraction analysis were obtained after a few days. The yield: 56.5 mg, 68.58%. Calcd.: C, 45.14; H, 4.35; N, 0.00. Found: C, 45.01; H, 4.39; N, 0.00. Selected IR (KBr, cm^{-1}): 3392.4 (m, ν_{HO-H}), 3011.3 (m, ν_{C-H}), 2950.2 (w, $\nu_{as}(CH_2)$), 1640.5, 1562.1 (vs, $\nu_{as}(COO^-)$), 1370.5, 1331.8 (s, $\nu_s(COO^-)$).

Single-crystal X-ray diffraction data for **1** and **2** were collected on Bruker SMART1000 CCD area detector with graphite monochromated molybdenum $K\alpha$ ($\lambda=0.71073 \text{ \AA}$) radiation at a temperature of $150 \pm 2 \text{ K}$. Unit-cell parameters were determined from automatic centering of 25 reflections and refined by the least-squares method. The diffraction data were corrected for Lorentz and polarization effects, and absorption (empirically from ψ scan data). Two structures were solved by direct methods [15] and refined using full-matrix least square techniques on F^2 [16]. All non-hydrogen atoms were refined anisotropically.

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

	1	2
Formula	$C_{59}H_{60}HoO_{24}$	$C_{90}H_{112}Lu_2N_2O_{30}$
<i>M</i>	1482.93	2051.76
Temperature (K)	150(2)	150(2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Orthorhombic	triclinic
Space group	<i>Pbcn</i>	<i>P-1</i>
<i>a</i> (\AA)	13.6074(8)	13.3034(4)
<i>b</i> (\AA)	23.9135(15)	13.3087(4)
<i>c</i> (\AA)	21.8851(14)	14.5461(6)
α ($^\circ$)	90.00	85.932(2)
β ($^\circ$)	90.00	64.611(2)
γ ($^\circ$)	90.00	81.595(2)
Volume (\AA^3)	7121.4(8)	2301.6(2)
<i>Z</i>	4	2
ρ (calcd.) ($g \text{ cm}^{-3}$)	1.383	2.961
μ (mm^{-1})	2.275	4.425
<i>F</i> (000)	2960	2096
Crystal size (mm)	0.19 × 0.16 × 0.10	0.48 × 0.40 × 0.06
θ ($^\circ$)	2.40–28.70	2.15–28.6
Limiting indices	$-18 \leq h \leq 14$ $-31 \leq k \leq 31$ $-19 \leq l \leq 28$	$-15 \leq h \leq 17$ $-16 \leq k \leq 16$ $0 \leq l \leq 19$
Reflection collected/ unique	8420/4897	10293/9367
Data/restraints/ parameters	8420/373/170	10293/203/562
Goodness-of-fit on F^2	0.970	1.085
Final <i>R</i> indices ($I > 2\sigma(I)$)	$R_1 = 0.0487$, $wR_2 = 0.1001$	$R_1 = 0.0394$, $wR_2 = 0.0446$
<i>R</i> indices (all data)	$R_1 = 0.1210$, $wR_2 = 0.1366$	$R_1 = 0.1061$, $wR_2 = 0.1115$

Note: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_1 = \{ \sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_o^2)]^2 \}^{1/2}$.

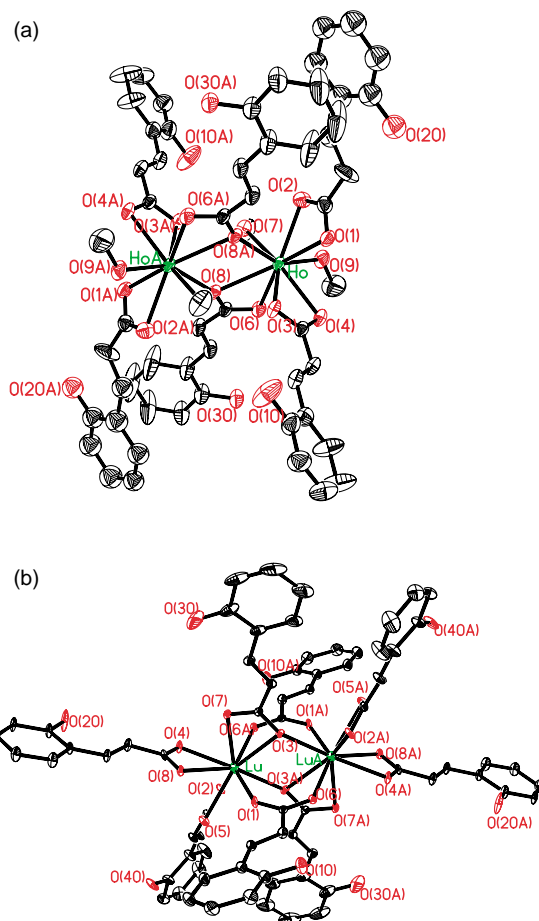


Fig. 1. ORTEP diagram (50% probability) of $[Ho(L)_3(CH_3OH)_2]_2$ (a) and $[Lu(L)_4]_2^-$ anion (b). Hydrogen atoms and solvents are omitted for clarity.

3. Results and discussion

3.1. Crystal structure of complexes **1** and **2**

The crystallographic data of complexes **1** and **2** are listed in Table 1. Two structure data were collected using graphite monochromated molybdenum $K\alpha$ radiation and refined using full-matrix least square techniques on F^2 .

Table 2
Selected bond lengths and bond angles for **1**

Ho–O1	2.395(4)	Ho–O2	2.428(4)
Ho–O3	2.391(4)	Ho–O4	2.440(4)
Ho–O6	2.389(4)	Ho–O7	2.409(4)
Ho–O8	2.543(4)	Ho–O9	2.344(4)
Ho–O(8)#1	2.327(4)	Ho–Ho	4.058
O6–Ho–O2	139.61(16)	O3–Ho–O2	129.19(15)
O9–Ho–O2	72.80(16)	O1–Ho–O2	53.72(15)
O6–Ho–O1	150.14(14)	O3–Ho–O7	143.77(14)
O1–Ho–O7	124.48(15)	O6–Ho–O8	52.73(13)
O4–Ho–O8	104.33(14)	O8–Ho–O2	133.49(14)
O9–Ho–O3	130.68(15)	O6–Ho–O3	91.00(15)
O9–Ho–O8#1	150.94(16)	Ho–O8–Ho#1	112.77(15)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+2, -z+1$.

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