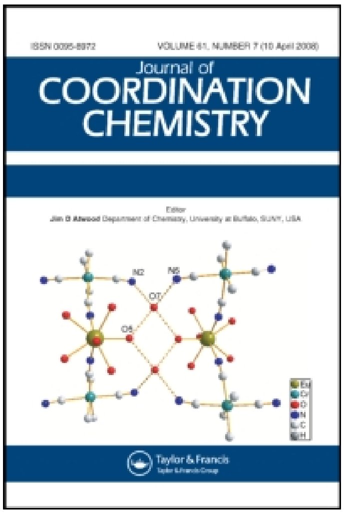

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$\{Na_2[Nd_4(OX)(BDC)_6(H_2O)_6]\}_n$: A 3-D coordination polymer with hybrid dicarboxylates

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The hydrothermal reactions of lanthanide ions, oxalates and benzenedicarboxylate with ratio of 4 : 1 : 8 at 190°C afford the three-dimensional coordination polymer $Na_2[Nd_4(OX)(BDC)_6(H_2O)_6]$ (OX = oxalate and BDC = 1,3-benzenedicarboxylate dianion). Crystal data: $C_{25}H_{18}NaNd_2O_{17}$ $M = 901.86$, Triclinic, $P\bar{1}$, $a = 10.335(6)$, $b = 11.497(6)$, $c = 12.238(7)$ Å, $\alpha = 93.015(9)$, $\beta = 114.892(8)°$, $\gamma = 95.970(10)°$, $V = 1304.3(12)$ Å^3, $Z = 2$, $F(000) = 870$, $R_1 = 0.0322$, $wR_2 = 0.0683$. The central oxalate of the unit cell coordinates with four lanthanides to form a four metal cluster $[Ln_4(OX)]$. The luminescence spectrum shows weak photoluminescence in infrared and near-infrared.

Keywords: Crystal structure; Nd; Oxalates; Coordination polymer

1. Introduction

Lanthanide complexes have high coordination numbers and geometry determined by the nature of the coordinating ligands, lanthanide center, competitive solvents and other environments. Most trivalent lanthanide cations form eight- or nine-coordinate complexes in which distortions accommodate steric interactions [1, 2]. Lanthanide complexes have been used in luminescence, with line-like metal-centered visible or near-infrared emissions of Nd(III), Eu(III), Tb(III), Yb(III) used as a luminescent flag for labeling biological materials or probing metallic environments; the specific splitting pattern of the emission bands can be explained by microsymmetry of the crystal field [3, 4]. Bridging oxalate and benzenedicarboxylate have been extensively used as building blocks with various lanthanides to produce a variety of topologies. Few examples were tried to assemble three-dimensional networks by these bridging ligands simultaneously [5–8]. An unsymmetrical coordination field, necessary for f–f transition of lanthanide complexes, could be constructed by such ligands. Here a ternary complex, $Na_2[Nd_4(OX)(BDC)_6(H_2O)_6]$ (OX = oxalate, BDC = 1,3-benzenedicarboxylate), was prepared and characterized. The central oxalate of the unit cell coordinates with four neodymium ions to form a four-metal cluster $[Nd_4(OX)]$, and these units are linked by BDC bridges to form a three-dimensional coordination polymer.

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2. Experimental

2.1. *Physical measurements*

Carbon and hydrogen elemental analyses were carried out with a Perkin-Elmer analyzer model 240. Infrared spectroscopy on KBr pellets was performed on a Magma IR 560 infrared spectrophotometer in the 4000–600 cm^{-1} region. UV–Vis spectra were obtained on a GBC Cintra 10e UV–Visible spectrometer. Emission spectra were obtained on a Shimadzu RF-5301PC spectrofluorimeter at room temperature. UV–Vis and emission spectroscopic analysis were carried out in 1.0×10^{-3} mol L^{-1} ethanol solutions.

Caution: Perchlorate salts are potentially explosive and should only be handled in small quantities.

2.2. *Preparation*

To a solution of NaHBDC (0.52 g, 4.0 mmol) was added an aqueous solution of $Nd(ClO_4)_3 \cdot 6H_2O$ (1.10 g, 2.0 mmol), and then $K_2(OX)$ (0.08 g, 0.5 mmol). The resulting mixture was placed in a Parr Teflon-lined autoclave. The autoclave was then sealed and heated at 190°C for three days. Pink crystals of the title complex suitable for X-ray crystallography were obtained with 68% yield. The compound is stable in air and insoluble in common solvents. Elemental analysis calcd (%) for $C_{25}H_{18}NaNd_2O_{17}$: C, 33.29; H, 2.01. Found: C, 33.40; H, 2.06. IR (KBr, cm^{-1}): 3358(m), 2963(w), 1638(vs), 1582(m), 1540(vs), 1405(s), 1395(s), 1348(w), 936(w), 776(w), 730(w), 522(w).

2.3. *Crystallographic studies*

Determination of the unit cell and data collection were performed at room temperature on a BRUKER SMART 1000 using a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS-97 and refined by least-squares procedures on F_o^2 with SHELXL-97 by minimizing the function $W(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors [9]. The hydrogens of solvent were not added, and other hydrogens were located geometrically and refined isotropically. Information concerning crystallographic data collection and refinement of the structure is compiled in table 1.

3. Results and discussion

3.1. *Crystal structures*

The ORTEP drawing of the complex is shown in figure 1 and selected bond lengths and angles are listed in table 2. The X-ray structural analysis shows a complex three-dimensional network. There is a tetranuclear $Nd_4(OX)$ in the center of each crystal cell. The centric $O_2C–CO_2$ ligand is planar with D_{2h} symmetry, though

Table 1. Summary of crystallographic data for the complex.

Formula	$C_{25}H_{18}NaNd_2O_{17}$
Formula weight	901.86
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.335(6)
b	11.497(6)
c	12.238(7)
α	93.015(9)
β	114.892(8)
γ	95.970(10)
V (Å^3)	1304.3(12)
Z	2
$F(000)$	870
D_{Calcd} (g cm^{-3})	2.296
R_1 [$I > 2\sigma(I)$]	0.0322
wR_2 [$I > 2\sigma(I)$]	0.0683

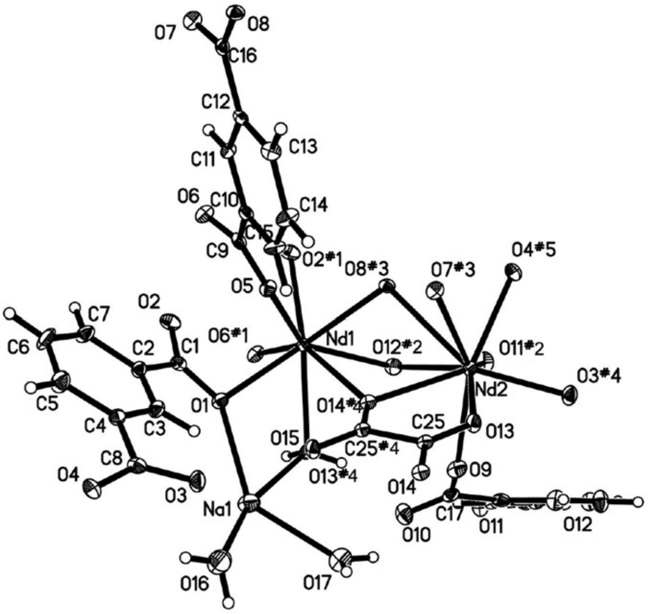


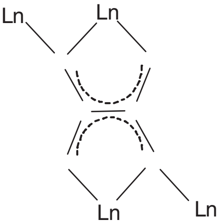
Figure 1. ORTEP view of the complex with the labeling scheme.

calculations for isolated oxalate have revealed that the more stable rotamer is the one with D_{2d} symmetry [10]. Four Nd ions are are located in the plane of oxalate; O13, O14A of the oxalate chelates to Nd2 and O14A is monodentate to Nd1; O13A and O14 adopt similar coordination modes (scheme 1). O14 has a μ_3 connection, which exists in a few oxalate lanthanide complexes but hasn't been found in transition metals [11].

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

Nd1–O1	2.447(4)	Nd2–O9	2.449(4)
Nd1–O5	2.404(4)	Nd2–O13	2.487(4)
Nd1–O15	2.558(4)	Nd2–O11#2	2.501(4)
Nd1–O2#1	2.380(4)	Nd2–O12#2	2.771(4)
Nd1–O6#1	2.378(4)	Nd2–O7#3	2.561(4)
Nd1–O12#2	2.444(4)	Nd2–O8#3	2.644(4)
Nd1–O8#3	2.470(4)	Nd2–O3#4	2.313(4)
Nd1–O14#4	2.673(4)	Nd2–O14#4	2.540(4)
C25–C25#4	1.566(11)	Nd2–O4#5	2.414(4)
O5–Nd1–O1	73.27(14)	O9–Nd2–O13	80.56(14)
O6#1–Nd1–O1	85.55(14)	O3#4–Nd2–O9	81.56(15)
O1–Nd1–O15	67.29(13)	O4#5–Nd2–O9	147.95(13)
O1–Nd1–O14#4	83.94(12)	O9–Nd2–O11#2	76.31(14)
O2#1–Nd1–O1	121.47(14)	O9–Nd2—O14#4	73.85(13)
O12#2–Nd1–O1	136.74(14)	O9–Nd2–O7#3	142.78(14)
O1–Nd1–O8#3	136.54(13)	O9–Nd2–O8#3	124.16(14)
O1–Nd1–Nd2	122.88(10)	O9–Nd2–O12#2	72.25(14)
Nd1#3–O8–Nd2#3	101.54(13)	Nd2#4–O14–Nd1#4	98.93(12)
Nd1#2–O12–Nd2#2	98.72(13)	C25–O13–Nd2	121.8(4)

Symmetry code: #1: $-x, -y+2, -z$; #2: $-x+1, -y+3, -z+1$; #3: $-x-1, -y+2, -z$; #4: $-x, -y+2, -z+1$; #5: $x, y+1, z$; #6: $-x+1, -y+2, -z+1$.



Scheme 1. The coordination mode of oxalate.

There are two crystallographically independent Nd ions. Nd1 has seven monodentate carboxylates, and an aqua molecule bridging Nd1 and Na1, in an eight-coordinate environment. The $Nd^{III}O_8$ forms an eight-coordinate square antiprism in which the set O1, O5, O2#1, O6#1 and the set of O15, O12#2, O8#3, O14#4 form two approximate squares [figure 2(a)]. The Nd1–O bond distances are from 2.380(4) to 2.673(4) Å and the mean distance is 2.469 Å. Nd2 has seven carboxylate groups with two carboxylates (O7#3, C16#3, O8#3 and O11#2, C24#2, O12#2) chelating Nd2 for a nine-coordinate environment. The $Nd^{III}O_9$ forms a square face capped square antiprism in which the set of O9, O11#2, O8#3, O14#4 and O13, O7#3, O3#4, O4#5 form two approximate squares, respectively [figure 2(b)]. The O12#2 is above the plane formed by O9, O11#2, O8#3, O14#4. The bond distances of Nd2–O are from 2.313(4) to 2.771(4) Å with mean about 2.520 Å.

The oxalates bridge four Nd atoms in a $Nd_4(OX)$ unit which link to each other by bridging BDC ligands into a 3-D network (figure 3). A pyramidal cage was formed by one oxalate and four BDC ligands. One counter sodium and three water molecules per Nd_2 were accommodated.

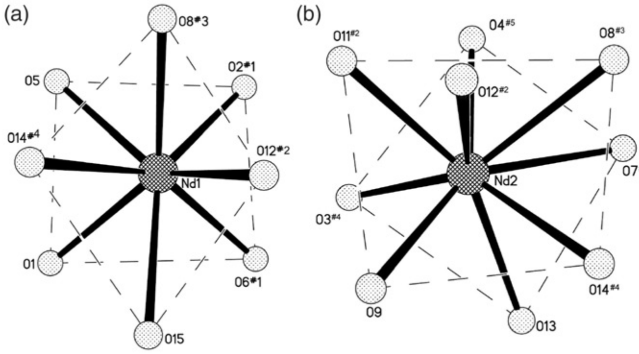


Figure 2. View of the coordination environment around neodymium: (a) around Nd1, (b) around Nd2.

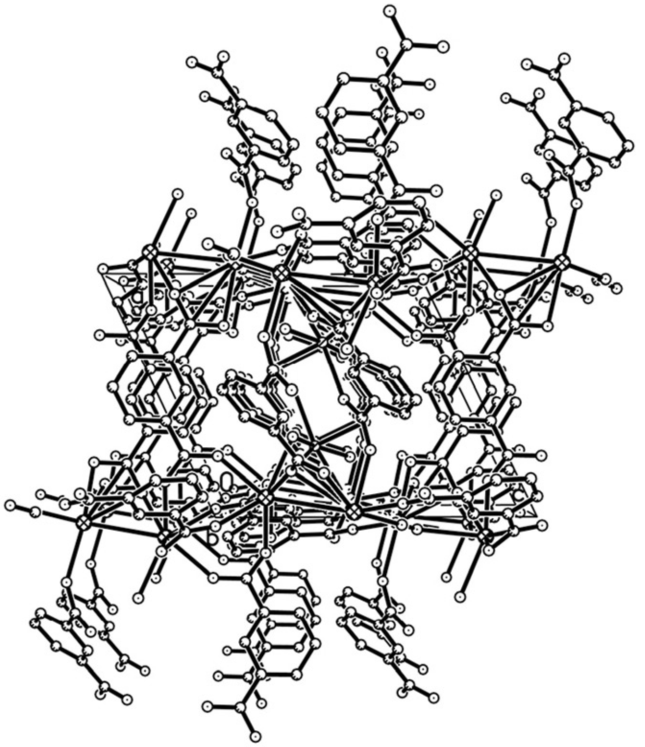


Figure 3. The projection of the complex onto the ac plane.

3.2. *Spectral properties*

There is a broad ν(OH) of H_2O near 3360 cm^{-1} showing H_2O in the complex. The absence of 1750 cm^{-1} and 1710 cm^{-1} for ν_{as}(COOH) of aryl carboxylic acid and oxalic acid, respectively, in the IR spectra indicates complete deprotonation of all carboxylates. The ν_{as}(COO) at 1642 cm^{-1} (non-bridging carboxylates) and 1582 cm^{-1} (bridging carboxylates) appear and ν_s(COO) at 1360 cm^{-1} blue-shifts to 1395 cm^{-1} (bridging carboxylates) and 1405 cm^{-1} (non-bridging carboxylates), confirming that

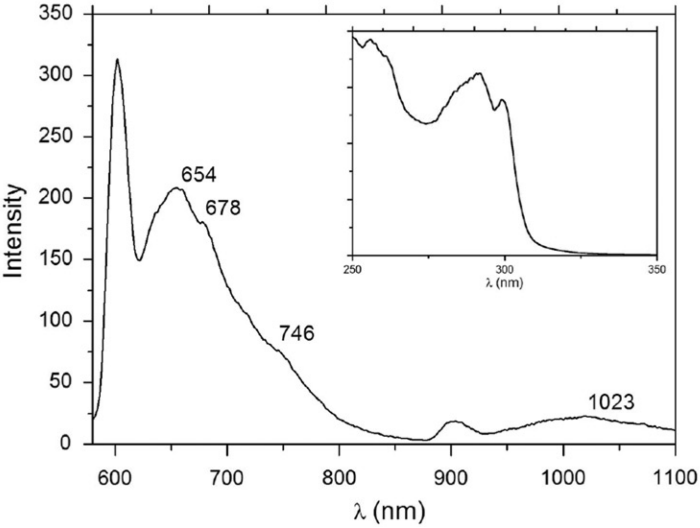


Figure 4. The emission spectra of the complex ($\lambda_{ex} = 300$ nm).

some O atoms of –COO$^-$ coordinate to the central Nd^{III} ion but also to the other Nd^{III} ion.

Luminescence measurements have been carried out at room temperature. The excitation and emission spectra are displayed in figure 4. Upon excitation at the ligand absorption band ($k_{ex} = 300$ nm), characteristic Nd^{3+} emissions are observed. The emission spectrum displays two main bands in the 600–1100 nm range. The broad band at 1023 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) is weak, different from previously reported spectra of organic neodymium complexes [12, 13], where an intense band at about 1060 nm is observed. The other band is observed in the range 630~770 nm as a broad band attributed to several transitions from high energy levels to low energy levels such as $^4G_{5/2}$ to $^4I_{9/2}$.

The 4f–4f transitions in free lanthanide are generally parity forbidden. The existence of the 4f–4f transitions is attributed to an asymmetric coordination field. The existence of photoluminescence indicates that the ligands are unsymmetric with Nd^{3+}, in accord with the crystal structure.

In conclusion, a ternary lanthanide coordination polymer was synthesized, with a new three-dimensional network formed from mixed bridging ligands of oxalate and isophthalate; the oxalate has a coordination mode of [Ln_4(OX)].

Acknowledgement

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