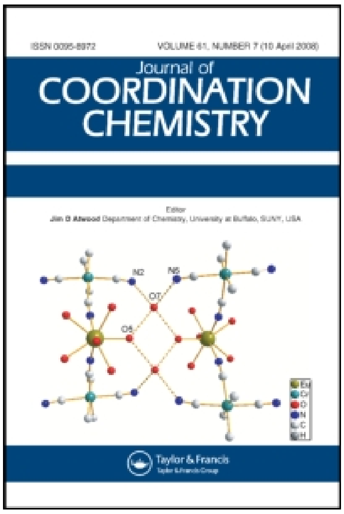

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A Novel Three-Dimensional Network Isophthalato-Bridged Lanthanide Complex: $\{Ln[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\}\cdot H_2O$

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A NOVEL THREE-DIMENSIONAL NETWORK ISOPHTHALATO-BRIDGED LANTHANIDE COMPLEX: $\{LN[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\}\cdot H_2O$

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The three-dimensional network of lanthanide (III) complexes with isophthalato (IPT) ligand, $(Eu[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\}\cdot H_2O$ **1** and $\{Sm[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)\ (H_2O)_2\}\ H_2O$ **2**, has been prepared by the hydro(solvo)thermal reaction of $Eu(C1O_4)_3\cdot 6H_2O$ or $Sm(C1O_4)_3\cdot 6H_2O$, 1,3-dicyanobenzene and acetic acid in the presence of ethanol and H_2O. In the reaction, 1,3-dicyanobenzene was hydrolyzed to give IPT ligand. Single crystal x-ray analysis revealed that crystals **1** and **2** are isomorphous with the isostructural $\{M[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\}\cdot H_2O$ unit. In **1** and **2**, IPT acts as a bridging ligand to connect three adjacent metal atoms, forming a network like an undulating sheet paralleling the *bc* plane. The carboxylate from acetate bridges two adjacent metal atoms in a tridentate mode between the different sheets to extend the structure into a three-dimensional network.

Keywords: Lanthanide complexes; Isophthalato ligand; Crystal structure; Three-dimensional network; Polymeric complexes

INTRODUCTION

Coordination polymers containing multidentate benzenecarboxylate as bridging ligands have been receiving increasing interest due to their network structure and potential application [1–3]. A multidentate benzenecarboxylate ligand is capable of forming infinite connections with metal atoms through oxygen atoms of its carboxylate groups and adopts versatile modes of bonding. Novel coordination polymers have emerged, using multidentate benzenecarboxylate ligands such as benzenehexcarboxylate [4], 1,3,5-benzenetricarboxylate [5–7], 1,4-benzenedicarboxylate [8] and 1,2-benzenedicarboxylate [9]. Although the complexes of the 1,3-benzenedicarboxylate acid (isophthalic acid) have also been extensively studied [10,11], three-dimensional network coordination polymers; containing isophthalato (IPT) as bridging ligand are rare [12].

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Here, we report a novel three-dimensional network structure consisting of lanthanide(III) complexes with IPT, $\{Eu[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\} \cdot H_2O$, and $\{Sm[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\} \cdot H_2O$, in which guest molecules are incorporated through hydrogen bonds.

EXPERIMENTAL

1,3-dicyanobenzene was purchased from Acros Chemical Co. and all other chemicals were reagent grade used as purchased.

Synthesis of 1 and 2

A heavy walled Pyrex tube containing a mixture of $Eu(ClO_4)_3 \cdot 6H_2O$ (0.1340 g, 0.24 mmol) and 1,3-dicyanobenzene (0.0256 g, 0.24 mmol) in acetic acid (0.2 mL), ethanol (0.25 mL) and H_2O (1.0 mL) was frozen and sealed under vacuum and placed inside an oven at 130°C. Colorless block crystals **1** were obtained after 48 h of heating.

An aqueous mixture (5 mL) containing $Sm(ClO_4)_3 \cdot 6H_2O$ (0.6679 g, 1.2 mmol) and 1,3-dicyanobenzene (0.1280 g, 1.0 mmol) was placed in a Parr teflon-lined stainless steel vessel (9 mL). Ethanol (1.0 mL) and acetic acid (0.2 mL) were added to this heterogeneous mixture, and the vessel was sealed and heated to 130°C for 48 h. Upon cooling to room temperature, colorless block crystals of **2** were obtained. In the reaction, 1,3-dicyanobenzene was hydrolyzed to form IPT and is considered to be the precursor of IPT.

Physical Measurements

The IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets on a Nicolet 170 SX FT-IR spectrometer. Thermogravimetric and differential thermal analyses were performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 5°C/min. Fluorescence spectra in the solid state were recorded on a SLM AMINCO Bowman Series 2 fluorescence spectrophotometer at room temperature (298 K), with the excitation band located at 394 nm for crystal **1**.

X-ray Crystallographic Analysis

Colorless block crystals **1** and **2** of dimensions $0.28 \times 0.24 \times 0.22$ and $0.41 \times 0.29 \times 0.29$ mm, respectively, were selected for x-ray analysis and mounted on a Siemens P4 four-circle diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan technique with a variable scan speed. Crystal data collection parameters are listed in Table I. For crystal **1**, unit cell parameters were obtained by a least-squares method based on the setting angles of 50 reflections in the range $5.31 < \theta < 12.53°$. A total of 2989 reflections were collected in the range $3.94 < 2\theta < 49.98°$, of which 2305 were independent ($R_{int} = 0.0336$), and 1942 were observed with $I > 2\sigma(I)$ and used in the structure solution and refinement. For crystal **2**, unit cell parameters were obtained by a least-squares method based on the setting angles of 50 reflections in the range of $5.40 < \theta < 9.90°$. A total of 2998 reflections

TABLE I Crystal data and data collection parameters for $\{[\mathrm{Eu} \cdot \mathrm{IPT} \cdot \mathrm{Ac} \cdot (\mathrm{H_2O})_2] \cdot \mathrm{H_2O}\}_n$ and $\{[\mathrm{Sm} \cdot \mathrm{IPT} \cdot \mathrm{Ac} \cdot (\mathrm{H_2O})_2] \cdot \mathrm{H_2O}\}_n$

Formula	$C_{10}H_{13}O_9Eu$	$C_{10}H_{13}O_9Sm$
Formula weight	429.16	427.55
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a(Å)	10.36699(8)	10.3871(18)
b(Å)	12.4300(13)	12.447(2)
c(Å)	10.1742(10)	10.201(2)
β(°)	94.023(8)	94.052(16)
$V(A_3)$	1307.8(2)	1315.5(4)
Z	4	4
T(K)	293(2)	293(2)
$D_{calc}(\mathrm{g\ cm^{-3}})$	2.180	2.159
F(000)	832	828
μ(Mokα) ($\mathrm{cm^{-1}}$)	4.837	4.505
Collection ranges (°)	$1.97 < \theta < 24.99$	$1.97 < \theta < 25.00$
Index ranges	$-12 < h < 12$, $-14 < k < 1$, $-1 < l < 12$	$-12 < h < 12$, $-14 < k < 1$, $-1 < l < 12$
No. of observations	2989	2998
No. of independent reflection	2305[$R_{\mathrm{int}} = 0.0336$]	2313[$R_{\mathrm{int}} = 0.0322$]
Data/restrains/parameters	2305/0/181	2313/0/190
R_{int} (1 $> 2\sigma$(I))	0.0295	0.0298
R_w (1 $> 2\sigma$(I))	0.0689	0.0750
R (all data)	0.0395	0.0358
R_w (data)	0.0736	0.0785

were collected in the range $3.94 < 2\theta < 50.00°$, of which 2313 were independent ($R_{\mathrm{int}} = 0.0322$), and 2036 were observed with $I > 2\sigma(I)$ and used in the structure solution and refinement. Intensity data were corrected for Lorentz-polarization effects and empirical absorption.

The structure was solved using the direct methods in the SHELXS-86 program [13], and refined by full-matrix least-squares on F_0^2 against all reflections, where for crystal **1**, $P = (F_o^2 + 2Fc^2)/3$ and $w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 2.3727P]$, converging to $R = 0.0395$, $R_w = 0.0736$ (all data), $R = 0.0295$, $R_w = 0.0689$ ($I > 2\sigma(I)$ observed data). For crystal **2**, $P = (F_o^2 + 2Fc^2)/3$ and $w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 2.0781P]$, converging to $R = 0.0358$, $R_w = 0.0785$ (all data), $R = 0.0298$, $R_w = 0.0750$, $I > 2\sigma(I)$ observed data). H atoms were generated geometrically and allowed to ride on their respective parent atoms. Refinement programs used are in SHELXS-93 [14]. The final atomic coordinates are listed in Tables II and III.

RESULTS AND DISCUSSION

Spectroscopic Characterization and Thermogravimetric Analysis (TGA)

IR spectra of crystals of **1** and **2** display a strong absorption at about 1605, 1544 and 1391 $\mathrm{cm^{-1}}$, which can be assigned to the characteristic ν_{as}(COO) and ν_s(COO) stretching modes of the carboxyl group. No peaks at 2230 $\mathrm{cm^{-1}}$ were found, indicating that the cyano groups no longer exist. The broad bands around 3490, 3420 and 3110 $\mathrm{cm^{-1}}$ are attributed mainly to H–O–H stretching vibrations, suggesting the existence of hydrogen bonding interactions, in **1** and **2**. The peak positions at 742

TABLE II Atomic coordination (×10^4) and equivalant isotropic displacement parameters (Å^2 × 10^3) for $\{[Eu(IPT)(Ac)(H_2O_2)_2]\cdot H_2O\}_n$

	x/a	*y/b*	*Z/c*	*U(eq)*
Eul	−1252.5(2)	1398.3(2)	50.5(2)	16.17(10)
O1	−7734(4)	−2342(4)	−3625(4)	31.9(10)
O2	−7296(4)	−1618(4)	−1671(4)	33.5(11)
O3	−3307(4)	518(4)	−749(4)	31.5(10)
O4	−1749(3)	430(3)	−2102(4)	22.3(8)
O5	551(4)	2137(3)	−1159(4)	29.5(10)
O6	935(4)	477(3)	−618(4)	26.5(9)
C1	−7011(5)	−1837(5)	−2804(5)	21.1(12)
C2	−5710(5)	−1467(5)	−3206(5)	23.2(12)
C3	−5323(6)	−1726(6)	−4452(7)	40.9(18)
C4	−4146(8)	−1351(7)	−4823(7)	54.0(2)
C5	−3358(6)	−730(7)	−3980(7)	43.2(18)
C6	−3735(5)	−470(5)	−2728(6)	22.1(12)
C7	−4930(5)	−855(5)	−2356(5)	20.9(11)
C8	−2902(5)	199(5)	−1804(6)	23.1(12)
C9	2495(9)	1347(7)	−1849(12)	80(4)
C10	1261(6)	1322(5)	−1174(6)	24.8(13)
O1W	189(5)	1314(4)	2008(5)	39.1(12)
O2W	−855(6)	3264(4)	895(5)	41(13)
O3W	899(13)	5072(12)	895(14)	132(6)
O3WA	−360(5)	3530(4)	780(6)	162(10)

TABLE III Atomic coordination (× 10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $\{[Sm(IPT)(Ac)(H_2O)_2]\cdot H_2O\}_n$

	x/a	*y/b*	*Z/c*	*U(eq)*
Sml	0.1252.7(2)	1399.79(18)	54.9(2)	15.77(12)
O1	0.7731(4)	– 2326(3)	– 3629(4)	31.5(9)
O2	– 0.7289(4)	– 1617(4)	– 1675(4)	34.3(10)
O3	– 0.3313(4)	517(3)	– 757(4)	31.9(9)
O4	– 0.1750(3)	432(3)	– 2102(4)	22.6(8)
O5	– 0.0563(4)	2150(3)	– 1153(4)	29.5(9)
O6	0.0937(4)	487(3)	– 0612(4)	26.6(8)
C1	– 0.5309(6)	– 1716(6)	– 4442(6)	38.9(15)
C2	– 0.4133(7)	– 1344(6)	– 4825(7)	47.1(18)
C4	– 0.3348(6)	– 728(6)	– 3972(6)	37.8(14)
C5	– 0.3739(5)	– 463(4)	– 2739(5)	24.0(11)
C6	– 0.4925(5)	– 844(5)	– 2357(5)	23.2(11)
C7	– 0.5713(5)	– 1460(4)	– 3213(5)	24.3(12)
C8	– 0.7004(5)	1832(4)	– 2808(5)	20.1(11)
C9	0.2911(5)	199(4)	– 1806(5)	24.2(12)
C10	0.2490(9)	1354(7)	– 1844(11)	67(3)
	0.1271(6)	1332(4)	– 1175(5)	25(12)
O1W	0.0193(5)	1302(3)	2019(5)	41.3(12)
O2W	– 0.0840(5)	3283(3)	904(4)	41.3(11)
O3W	0.0925(12)	5071(10)	884(12)	92(4)
O3WA	0.1020(5)	3590(3)	700(5)	104(10)
O3WB	– 0.1530(6)	– 1420(4)	– 4040(6)	140(2)

and 695 cm^{-1} are comparable to those of 1,3-benzenedicaroxylate acid in the standard spectra [15]. In the synthesis of **1** and **2**, 1,3-dicyanobenzene was hydrolyzed to form isophthalato ligand, which is similar to our previous report [16]. Therefore, 1,3-dicyanobenzene can be considered as the precursor of this reaction.

The DTA curve of **1** and **2** displays three endotherms between 30 and 200°C. This is mirrored in the TGA plot with three losses of 2.6, 8.8 and 13.8% for crystal **1** (2.2, 8.3 and 11.8% for crystal **2**), corresponding to one uncoordinated and two coordinated water molecules, respectively.

The fluorescence emission spectrum for crystal **1** shows peaks at 594, 619, 653 and 701 nm, which are assigned to the transitions, $^5D_0 \rightarrow {}^7F_1$, $5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ for europium(III) [17].

Description of the Structure

Complexes **1** and **2** are isomorphous with nearly isostructural $\{M[C_6H_4(COO^-)_2\text{-}1,3] \cdot (CH_3COO^-)(H_2O)_2\} \cdot H_2O$ units. The structures are so much alike that the molecular packing diagrams are indistinguishable. Only one ORTEP drawing of the partial molecule structure is shown in Fig. 1, in which M represents Eu(III) and Sm(III). Both crystal structures consist of an extended three-dimensional network of lanthanide(III) coordinated to IPT, acetate ligand and water. Selected bond lengths and angles are collected in Table IV. The M(III) is coordinated in a distorted tricapped trigonal prism coordination sphere comprised of two water molecules, four oxygen atoms of three IPT and three oxygen atoms of two acetate ligands. In complex **1**, the bond distances of Eu–O(3) (2.481(4) Å) and Eu–O(4) (2,521(4) Å) are longer than those of Eu–O(1B) (2.333(4) Å) and Eu–O(2A) (2.325(4) Å) due to different bonding modes of two carboxylate groups of IPT. The Eu–O bond distances are close to those found in $(Eu_2[C_6(COO)_6](H_2O)_8\}$ H_2O (2.355–2.529 Å) [18]. Two COO^- planes of the IPT ligand in **1**, are twisted out of the plane of the benzene

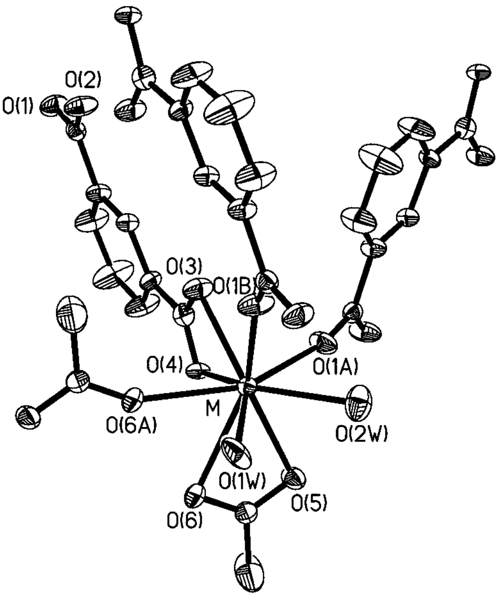

FIGURE 1 The structure around the lanthanide atom with thermal ellipsoids drawn at the 50% probability and hydrogen atoms omitted for clarity. M represents Eu(III) and Sm(III).

TABLE IV Selected bond distance (Å) and angles (°) for complexes **1** and **2**

	1*(M = Eu)*	2*(M = Sm)*
M–O3	2.481(4)	2.495(4)
M–O4	2.521(4)	2.530(4)
M–O5	2.485(4)	2.505(4)
M–O6	2.670(4)	2.673(4)
M–O6A	2.419(4)	2.432(4)
M–O1B	2.333(4)	2.351(4)
M–O2A	2.325(4)	2.335(4)
M–O1W	2.407(4)	2.421(4)
M–O2W	2.497(5)	2.525(4)
O3–M–O4	52.12(12)	51.94(12)
O3–M–O5	131.23(14)	131.21(13)
O3–M–O6	116.88(13)	116.96(12)
O3–M–O6A	75.67(14)	75.55(14)
O3–M–O1B	75.73(15)	75.78(15)
O3–M–O2A	72.59(14)	72.67(14)
O3–M–O1W	136.16(16)	136.07(16)
O3–M–O2W	129.76(17)	130.07(15)
O4–M–O5	82.01(13)	82.20(13)
O4–M–O6	72.49(12)	72.64(11)
O5–M–O6	49.49(13)	49.43(12)
O5–M–O1B	76.46(14)	76.43(13)
O6–M–O6A	62.85(15)	62.99(14)
O1B–Eul–O2A	94.38(16)	94.26(15)

ring by 7.9 and 3.7° (7.7 and 4.4 for crystal **2**), which is much less twisted than benzenehexacarboxylate in $(Eu_2[C_6(COO)_6]\ (H_2O)_8\}\ H_2O$ due to a smaller steric effect of IPT. The Eu–O(6A) and Eu–O(5) bond distances are 2.419(4) and 2.485(4) Å respectively, which are similar to those reported previously [17]. The Eu–O(6) bond distance (2.670(4) Å) is the longest in **1**. The water of crystallization, which has two hydrogen-bonding interactions with coordination water molecules, O(1 w) and O(2 w) is disordered in crystals **1** and **2**.

All Sm–O bonds are similar and are within the range for normal Sm–OCO distance [19,20]. Because of the larger size of the samarium atom, the bond lengths of Sm–O ranging from 2.335 to 2.673 Å, are consistently longer than the corresponding distances of Eu–O which vary from 2.325 to 2.670 Å. The bond angles of O–M–O for the two complexes are in excellent agreement with each other.

In crystals **1** and **2**, the carboxylate group of IPT coordinates to metal atoms as a bridging group, or as a bidentate chelate between two metal atoms. Each IPT acts as a bridging ligand connecting three neighboring metal atoms which gives rise to a network structure like an undulating sheet paralleling the *bc* plane as shown in Fig. 2. All carboxylates from acetate ligands coordinated tridentate and bridge two metal atom centers in adjacent different sheets. As a result, the lanthanide(III) complexes **1** and **2** possess *a* three-dimensional network structure as shown in Fig. 3.

Supplementary Material

Hydrogen atom coordinates, thermal parameters, observed and calculated structure factors are available from the authors upon request.

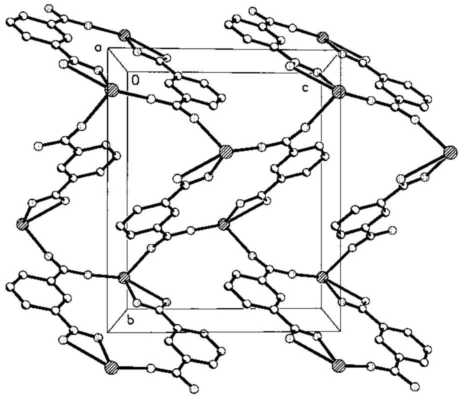

FIGURE 2 Projection down the a axis of the $\{M[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\} \cdot H_2O$ unit showing isophthalato connecting three neighboring M centers to form the network layer. For clarity, the acetate ligands and water molecules are omitted.

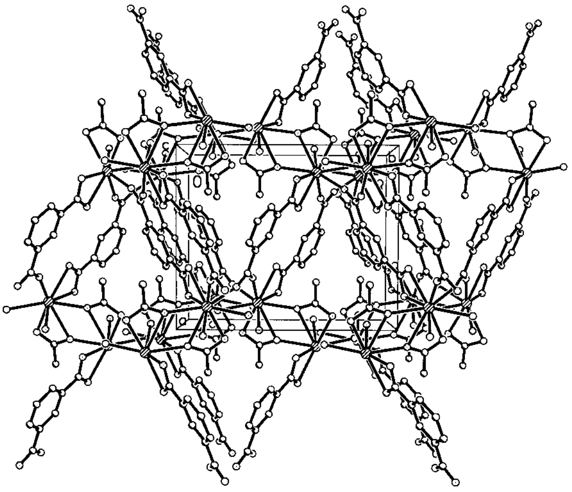

FIGURE 3 Molecular packing of the $\{M[C_6H_4(COO^-)_2\text{-}1,3](CH_3COO^-)(H_2O)_2\} \cdot H_2O$ unit, viewed down the *b* axis illustrating the connectivity by acetate ligands between different layers, like an undulating sheet.

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