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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF THE BIS(1,10-PHENANTHROLINE) TRI(*TRANS*-2,3-DIMETHYLACRYLATO) LANTHANIDE(III) DIMER

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF THE BIS(1,10-PHENANTHROLINE) TRI(*TRANS*-2,3-DIMETHYLACRYLATO) LANTHANIDE(III) DIMER

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Novel dinuclear lanthanide complexes, $[REL_3(\text{phen})]_2$ (where $RE = \text{La, Ce, Pr, Nd, Sm, Eu, Gd}$; $HL = \textit{trans}$ -2,3-dimethylacrylic acid, $\text{phen} = 1,10\text{-phenanthroline}$), have been synthesized. The single crystal structures of $[\text{LaL}_3\text{phen}]_2$ and $[\text{GdL}_3\text{phen}]_2$ have been determined by X-ray crystallography, which shows that they are isomorphous. Lanthanum(III) or Gadolinium(III) atoms are bridged by two bidentate and two terdentate carboxylato groups to give centrosymmetric dimers with an $\text{La} \cdots \text{La}$ separation of 4.09 Å and a $\text{Gd} \cdots \text{Gd}$ separation of 3.98 Å. Each metal atom is nine coordinate and exhibit a distorted, tricapped trigonal prismatic geometry.

Keywords: Lanthanide; *Trans*-2,3-dimethylacrylic acid; 1,10-phenanthroline; Crystal structure

INTRODUCTION

The stereochemistry of complexes of rare earth ions with unsaturated carboxylic acids is of interest because of their potential use as extraction agents, fluorescent probes and the effect of the $\alpha - \text{C}=\text{C} -$ double bond on coordination of the carboxylato ligand with the lanthanide [1–4]. *Trans*-2,3-dimethylacrylic acid is a prochiral compound often used as model

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substrate in asymmetric hydrogenation catalysis [5]. The stereochemistry of its complexes is helpful in clarifying the mechanism of asymmetric homogeneous hydrogenation. Some heterocyclic amine lanthanide complexes, on the other hand, also possess fluorescent properties believed to be caused by coupling of *f*-electrons of the central ion and π -electrons of the heterocyclic ligand. Lanthanide carboxylate compounds are often polymeric in the solid state, with the COO^- group functioning as a bridging ligand involving two or three metal atoms. In the present paper, bridged dimer complexes of rare earth metals with molecular formula $[\text{REL}_3\text{phen}]_2$ are reported. The crystals and molecular structures of the La and Gd complexes are discussed.

EXPERIMENTAL

Compound Preparation

Trans-2,3-dimethylacrylic acid (1.5 mmol) and $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$ and Gd) (0.3 mmol) were dissolved in 12 ml of mixed solvent (ethanol:water = 1:1, v/v) and adjusted to pH 4.3 with NaOH (10%) solution. An ethanolic solution of 1,10-phenanthroline (0.3 mmol) was added to the solution with stirring. After filtration, the filtrate was evaporated at room temperature and single crystals suitable for X-ray work were obtained after a few days. Compositions were determined as $\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{RE}_2$ by analyses (Tab. I).

Instrumentation

Elemental analyses were carried out using a Carlo–Erba 1106 instrument and electrolytic conductance was measured at 20°C ($\sim 10^{-4}\text{M}$) in dimethylsulfoxide (DMSO). IR and electronic spectra (dissolved in DMSO) were recorded using MAGNA-IR 560 E.S.P. (KBr discs, 4000–400 cm^{-1})

TABLE I Analytical data (%) for the complexes

Complex	C		H		N		RE	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{La}_2$	52.60	52.70	4.74	4.60	4.54	4.67	22.53	22.20
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Ce}_2$	52.50	52.55	4.74	4.84	4.53	4.49	22.69	22.30
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Pr}_2$	52.44	52.36	4.73	4.61	4.52	4.49	22.78	22.90
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Nd}_2$	52.16	52.25	4.70	4.59	4.51	4.40	23.20	23.10
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Sm}_2$	51.65	51.23	4.66	4.69	4.46	4.42	23.94	24.10
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Eu}_2$	51.51	51.29	4.64	4.51	4.45	4.34	24.14	24.38
$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Gd}_2$	51.09	51.07	4.60	4.59	4.41	4.22	24.77	24.89

and Shimadzu UV-265 spectrophotometers, respectively. The ^1H NMR spectrum of the La complex was recorded on a Bruker AC 80 spectrometer and chemical shifts are given in ppm with respect to TMS.

Crystal Structure Determination

A single crystal with suitable dimensions was mounted on a glass fibre and data collection was performed on a Rigaku AFCTR7 diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) at 293 K using the $\omega - 2\theta$ scan technique.

An empirical absorption correction using the program DIFABS [6] was applied, with transmission factors ranging from 0.81 to 1.14 for the La complex and from 0.86 to 1.15 for the Gd complex. The data were also corrected for Lorentz and polarization effects. The structures were solved by Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed on an IRIS INDIGO 4000 computer with the Crystal Structure Analysis Package [7]. Crystal data collection and refinement parameters are summarized in Table II.

TABLE II Crystal data, data collection and refinement parameters for the La and Gd complexes

Formula	$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{La}_2$	$\text{C}_{54}\text{H}_{58}\text{O}_{12}\text{N}_4\text{Gd}_2$
Formula weight	1232.88	1269.57
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.962(4)	12.936(4)
b (Å)	13.283(4)	13.045(4)
c (Å)	15.485(5)	15.435(5)
β (°)	95.45(2)	94.70(3)
V (Å ³)	2654(1)	2595(1)
D_{calc} (g cm ⁻³)	1.543	1.624
Z	2	2
Crystal size (mm)	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.15
$F(000)$	1240	1268
2θ max(°)	51.0	51.0
μ (cm ⁻¹)	16.45	26.05
Reflections measured	4627	5460
Unique reflections	4392	5063
Observed reflections ($I > 2.5\sigma(I)$)	3112	2795
No. of Variables	325	325
Range of hkl	$h: 0-13, k: 0-16,$ $l: -18-18$	$h: 0-15, k: 0-15,$ $l: -18-18$
Goodness of fit	1.32	1.48
R	0.033	0.053
R_w	0.040	0.061

RESULTS AND DISCUSSION

Solubility and Molar Conductivity, NMR, Electronic and IR Spectra

The complexes are soluble in dimethylformamide and dimethylsulfoxide, but insoluble in water, methanol, ethanol, carbon tetrachloride, chloroform and ethyl acetate. Values of molar conductivity vary from 16.7 to 32.8 $\text{S cm}^2 \text{mol}^{-1}$ (Tab. III), which suggests that the complexes are non-electrolytes [8]. Like other heterocyclic amine lanthanide carboxylate complexes, they have no obvious melting point. Decomposition temperatures decrease gradually from 540 K for La to 526 K for Gd (Tab. III).

Spectroscopic data for the complexes are listed in Table III. Electronic spectra of all complexes are striking similar and but slightly changed compared with $\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)\text{COOH}$. Published data for IR of ligands and unsaturated carboxylates were used to assign IR frequencies [2, 9]. A comparison of the spectrum of $\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)\text{COOH}$ with those of its complexes reveals considerable changes upon coordination. A peak at $\sim 1672 \text{ cm}^{-1}$ in $\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)\text{COOH}$ assigned as $-\text{C}=\text{O}$ disappears after coordination. The antisymmetric and symmetric stretching frequencies of OCO groups in the complexes increase with decreasing ionic(III) radii of action, which results in $RE-\text{O}$ bond strength increasing and bondlength decreasing.

According to Deason [10], $\Delta\nu$ can be used to distinguish between different coordination modes of the OCO group in transition metal complexes (*i.e.*, ionic, unidentate or bidentate). In the present case, the separations for all complexes are significantly less than the ionic value and are considered indicative of chelating or bridging carboxylato groups with central atoms. However, in heterocyclic amine lanthanide carboxylate complexes IR

TABLE III Characteristic IR (cm^{-1}), UV data (nm), molar conductivity values ($\text{S cm}^2 \text{mol}^{-1}$) and Decomposition temperature ($^\circ\text{C}$) for the complexes

Compound	IR				UV max	Molar conductivity	Decomposition temperature
	$\nu \text{ C}=\text{C}$	$N_{as(\text{OCO})}$	$\nu_{as(\text{OCO})}$	$\Delta V_{(\text{OCO})}$			
HL	1640				264.8		
NaL	1662	1404	1574,	170			
Phen					269		
[LaL ₃ phen] ₂	1659	1418	1563, 1518	145, 100	266.3	26.9	267
[CeL ₃ phen] ₂	1659	1422	1565, 1518	143, 95	266.2	26.9	266
[PrL ₃ phen] ₂	1660	1422	1565, 1517	143, 95	266.2	26.2	262
[NdL ₃ phen] ₂	1659	1424	1567, 1518	143, 94	266.2	23.6	260
[SmL ₃ phen] ₂	1659	1426	1569, 1519	143, 93	266.2	32.8	258
[EuL ₃ phen] ₂	1659	1429	1570, 1517	141, 88	266.2	25.5	255
[GdL ₃ phen] ₂	1660	1429	1572, 1518	143, 89	266.4	16.7	253

spectra are more complex if more than one coordination modes of the OCO group occurs simultaneously in the molecule. We have analyzed the IR spectra of the complexes and found that the antisymmetric stretching frequencies of the OCO groups split into two peaks upon coordination. They lie in the range 1563 to 1572 cm^{-1} and about 1518 cm^{-1} , respectively. Separations ($\Delta\nu = \sim 143\text{ cm}^{-1}$) of the two C—O stretches of the former are less than (170 cm^{-1}) in $\text{Na}[\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)\text{COO}]$ and we assign these frequencies of bridging carboxylato groups. Those ($\Delta\nu = \sim 95\text{ cm}^{-1}$) of the latter are much less than that of the corresponding sodium salt and we assign as frequencies of chelating carboxylato groups. The characteristic ring stretch of phen at 1561 cm^{-1} is decreased to $\sim 1525\text{ cm}^{-1}$ for the complexes and the strong C—H out-of-plane bend is lowered from 739 and 851 cm^{-1} in free phen to ~ 733 and $\sim 848\text{ cm}^{-1}$ and split into several peaks due to loss of phen symmetry (C_{2v}); this is firm evidence of phen ligands coordinating with the lanthanide atoms.

The ^1H NMR spectrum observed for the lanthanum complex displays peaks due to phenanthroline (multiplets at $\delta 9.10$ – 7.71 ppm), CH (doublets at $\delta 6.46$ and 6.52 ppm) and CH_3 (singlet at $\delta 1.67$ ppm) with an intensity ratio of 8 : 3 : 18. The assignments of the peaks are in accordance with those of phenanthroline and *trans*-2,3-dimethylacrylic acid in which a multiplet was observed at 9.17 – 7.72 ppm for the phenanthroline, a quartet at 6.71 and 6.74 ppm for the CH, a singlet at 1.74 ppm for the — CH_3 , and a singlet at 11.8 ppm for the O—H protons. All peaks of dimethylacrylato groups shift upfield after coordination. The O—H peak disappears at the same time and is important evidence that dimethylacrylato groups have been coordinated.

Crystal Structure Analysis of the Complexes

Final atomic coordinates and equivalent temperature factors for non-hydrogen atoms are given in Table IV. Selected bond distances and angles are listed in Table V. Figure 1 shows an ORTEP diagram of the molecular structure with the numbering scheme for the La complex. The structure consists of a centrosymmetric dimers lanthanum (III) ions bridged by two bidentate and two terdentate carboxylato groups. Three dimethylacrylato groups use different coordination modes. One acts as a conventional bidentate bridging ligand, bonding to La through O(1) and La* through O(2). The other is chelated to La through O(3) and O(4), with O(4) also linked to La*. The third carboxylato group [O(5), C(23), O(6)] forms a chelating ring with a La(III) ion. The coordination geometry about the La

TABLE IV Fractional coordinates and equivalent isotropic temperature factors (\AA^2) of non-H atoms for the lanthanum complex

<i>Atom</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B(eq)</i>
La	-0.01046(2)	0.12903(2)	-0.07252(2)	2.328(7)
O(1)	0.1561(3)	0.1170(3)	0.0173(3)	3.7(1)
O(2)	0.1762(3)	-0.0340(3)	0.0786(3)	3.6(1)
O(3)	-0.0655(3)	0.2103(3)	0.0663(2)	3.6(1)
O(4)	-0.0490(3)	0.0470(3)	0.0847(2)	3.2(1)
O(5)	-0.0546(3)	0.0958(3)	-0.2357(2)	3.8(1)
O(6)	0.0896(3)	0.1782(3)	-0.1982(2)	4.0(1)
N(1)	-0.1518(4)	0.2686(3)	-0.1348(3)	3.0(1)
N(2)	0.0427(4)	0.3302(3)	-0.0737(3)	3.0(1)
C(1)	-0.2452(5)	0.2397(5)	-0.1668(4)	3.8(2)
C(2)	-0.3204(5)	0.3056(5)	-0.2033(4)	4.4(2)
C(3)	-0.2996(5)	0.4048(5)	-0.2080(4)	4.3(2)
C(4)	-0.2023(5)	0.4398(4)	-0.1741(4)	3.5(1)
C(5)	-0.1721(6)	0.5439(5)	-0.1750(4)	4.4(2)
C(6)	-0.0780(6)	0.5744(4)	-0.1459(4)	4.2(2)
C(7)	0.0003(5)	0.5033(4)	-0.1130(4)	3.6(1)
C(8)	0.1016(5)	0.5322(5)	-0.0839(4)	4.2(2)
C(9)	0.1709(5)	0.4609(5)	-0.0529(4)	4.3(2)
C(10)	0.1367(5)	0.3595(4)	-0.0474(4)	3.7(1)
C(11)	-0.0264(5)	0.4002(4)	-0.1070(3)	2.9(1)
C(12)	-0.1289(5)	0.3687(4)	-0.1393(3)	3.0(1)
C(13)	0.2090(4)	0.0512(4)	0.0582(4)	3.0(1)
C(14)	0.3206(5)	0.0753(5)	0.0859(4)	4.0(2)
C(15)	0.3471(6)	0.1849(7)	0.0895(7)	7.8(3)
C(16)	0.3879(5)	0.0043(6)	0.1028(5)	5.0(2)
C(17)	0.5018(6)	0.0172(8)	0.1301(6)	7.6(3)
C(18)	-0.0786(4)	0.1326(4)	0.1097(4)	2.9(1)
C(19)	-0.1312(5)	0.1402(4)	0.1909(4)	3.3(1)
C(20)	-0.1992(6)	0.0541(5)	0.2121(5)	5.9(2)
C(21)	-0.1153(5)	0.2208(6)	0.2405(4)	4.4(2)
C(22)	-0.1536(7)	0.2402(8)	0.3272(5)	7.7(3)
C(23)	0.0264(5)	0.1390(4)	-0.2550(3)	3.2(1)
C(24)	0.0469(5)	0.1439(4)	-0.3494(3)	3.6(1)
C(25)	-0.0241(7)	0.0814(6)	-0.4104(4)	6.4(2)
C(26)	0.1225(6)	0.2009(6)	-0.3713(4)	4.7(2)
C(27)	0.1521(6)	0.2172(7)	-0.4625(5)	6.5(2)
Gd	-0.01144(5)	0.12709(5)	-0.07150(4)	1.97(1)
O(1)	0.1481(6)	0.1200(7)	0.0134(5)	3.1(2)
O(2)	0.1698(6)	-0.0347(6)	0.0741(5)	2.7(2)
O(3)	-0.0688(7)	0.2078(7)	0.0590(5)	2.9(2)
O(4)	-0.0455(6)	0.0424(7)	0.0844(5)	2.6(2)
O(5)	-0.0560(7)	0.0905(6)	-0.2281(5)	3.0(2)
O(6)	0.0892(6)	0.1708(7)	-0.1933(5)	2.9(2)
N(1)	-0.1483(7)	0.2609(8)	-0.1321(6)	2.5(2)
N(2)	0.0432(7)	0.3232(8)	-0.0172(6)	2.0(2)
C(1)	-0.240(1)	0.2293(10)	-0.1641(8)	3.2(3)
C(2)	-0.319(1)	0.297(1)	-0.2016(9)	4.0(4)
C(3)	-0.295(1)	0.398(1)	-0.2072(10)	3.9(4)
C(4)	-0.200(1)	0.435(1)	-0.1712(8)	3.0(3)
C(5)	-0.171(1)	0.540(1)	-0.1752(10)	4.0(4)
C(6)	-0.076(1)	0.570(1)	-0.1449(10)	4.4(4)
C(7)	0.003(1)	0.497(1)	-0.1120(9)	3.3(3)
C(8)	0.103(1)	0.529(1)	-0.085(1)	4.5(4)

TABLE IV (Continued)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B(eq)</i>
C(9)	0.172(1)	0.456(1)	-0.0531(10)	3.8(4)
C(10)	0.1378(10)	0.355(1)	-0.0477(9)	3.4(3)
C(11)	-0.025(1)	0.3963(7)	-0.1069(8)	2.4(3)
C(12)	-0.1269(9)	0.3614(9)	-0.1378(7)	2.1(2)
C(13)	0.2024(9)	0.0526(10)	0.0547(8)	2.2(3)
C(14)	0.312(1)	0.081(1)	0.0840(9)	3.5(3)
C(15)	0.335(1)	0.193(1)	0.095(1)	5.8(5)
C(16)	0.381(1)	0.009(1)	0.0984(10)	4.1(4)
C(17)	0.497(1)	0.020(2)	0.128(1)	7.4(6)
C(18)	-0.0783(8)	0.131(1)	0.1062(7)	2.6(3)
C(19)	-0.1330(10)	0.137(1)	0.1867(8)	3.0(3)
C(20)	-0.208(1)	0.055(1)	0.206(1)	5.0(4)
C(21)	-0.115(1)	0.218(1)	0.2379(9)	3.9(4)
C(22)	-0.154(2)	0.237(2)	0.325(1)	7.0(6)
C(23)	0.0254(10)	0.132(1)	-0.2489(8)	2.9(3)
C(24)	0.045(1)	0.137(1)	-0.3435(7)	3.2(3)
C(25)	-0.025(1)	0.072(1)	-0.4034(9)	5.3(4)
C(26)	0.123(1)	0.197(1)	-0.3668(9)	3.9(4)
C(27)	0.151(1)	0.214(1)	-0.458(1)	5.5(5)

TABLE V Relevant bond distances (Å) and bond angles (°) for the complexes

Atom	<i>La complex</i>	<i>Gd complex</i>	Atom	<i>La complex</i>	<i>Gd complex</i>
Ln—O(1)	2.460(4)	2.355(8)	Ln—N(2)	2.760(5)	2.65(1)
Ln—O(2)*	2.486(4)	2.374(8)	O(1)—C(13)	1.246(6)	1.26(1)
Ln—O(3)	2.567(4)	2.441(8)	O(2)—C(13)	1.260(6)	1.26(1)
Ln—O(4)	2.756(4)	2.716(9)	O(3)—C(18)	1.253(6)	1.25(1)
Ln—O(4)*	2.474(4)	2.344(9)	O(4)—C(18)	1.272(6)	1.28(1)
Ln—O(5)	2.575(4)	2.484(8)	O(5)—C(23)	1.257(7)	1.25(1)
Ln—O(6)	2.525(4)	2.440(8)	O(6)—C(23)	1.257(7)	1.25(1)
Ln—N(1)	2.718(4)	2.605(10)			
O(1)—Ln—O(2)*	134.2(1)	134.8(3)	O(3)—Ln—N(1)	77.2(1)	76.3(3)
O(1)—Ln—O(3)	81.5(1)	82.5(3)	O(3)—Ln—N(2)	71.8(1)	71.4(3)
O(1)—Ln—O(4)	72.4(1)	71.9(3)	O(4)—Ln—O(4)*	77.1(1)	76.5(3)
O(1)—Ln—O(4)*	73.7(1)	75.1(3)	O(4)—Ln—O(5)	139.2(1)	137.9(3)
O(1)—Ln—O(5)	130.2(1)	131.1(3)	O(4)—Ln—O(6)	158.8(1)	155.9(3)
O(1)—Ln—O(6)	88.0(1)	86.5(3)	O(4)—Ln—N(1)	114.2(1)	115.8(3)
O(1)—Ln—N(1)	140.4(1)	139.9(3)	O(4)—Ln—N(2)	117.1(1)	116.9(3)
O(1)—Ln—N(2)	82.0(1)	79.4(3)	O(4)*—Ln—O(5)	78.8(1)	77.6(3)
O(2)*—Ln—O(3)	86.4(1)	85.0(3)	O(4)*—Ln—O(6)	89.9(1)	87.9(3)
O(2)*—Ln—O(4)	66.7(1)	66.8(3)	O(4)*—Ln—N(1)	145.3(1)	144.2(3)
O(2)*—Ln—O(4)*	78.0(1)	78.3(3)	O(4)*—Ln—N(2)	146.6(1)	145.5(3)
O(2)*—Ln—O(5)	76.4(1)	75.8(3)	O(5)—Ln—O(6)	51.0(1)	52.5(3)
O(2)*—Ln—O(6)	127.4(1)	128.3(3)	O(5)—Ln—N(1)	71.9(1)	71.5(3)
O(2)*—Ln—N(1)	77.4(1)	76.9(3)	O(5)—Ln—N(2)	101.1(1)	103.1(3)
O(2)*—Ln—N(2)	135.0(1)	135.9(3)	O(6)—Ln—N(1)	85.9(1)	87.5(3)
O(3)—Ln—O(4)	48.6(1)	50.4(3)	O(6)—Ln—N(2)	66.3(1)	67.5(3)
O(3)—Ln—O(4)*	125.1(1)	126.6(3)	N(1)—Ln—N(2)	59.8(1)	61.8(3)
O(3)—Ln—O(5)	147.2(1)	145.4(3)	Ln—O(4)—Ln*	102.9(1)	103.5(3)
O(3)—Ln—O(6)	137.8(1)	138.8(3)			

* Symmetry code: $-x, -y, -z$.

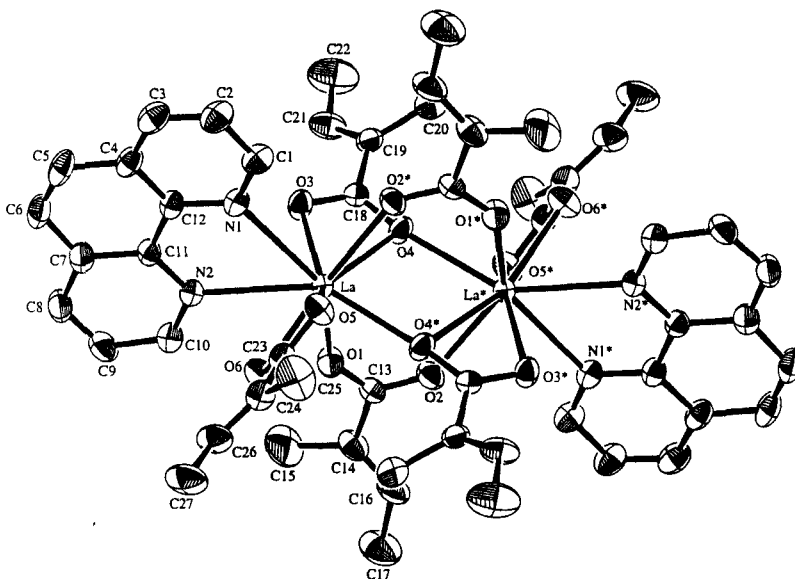


FIGURE 1 Ortep diagram of the La structure showing the atom numbering scheme. The Gd structure is isomorphous.

atom may be described as a distorted tricapped trigonal prism. O(1), O(2)*, O(3), O(4)*, O(6), N(1) atoms form the prism and O(4), O(5) and N(2) atoms cap the rectangular faces. Dihedral angles between the rectangular faces are 59.1, 62.2 and 56.9°, respectively.

The structure also has three distinct Ln—O distances involving methylacrylate groups depending on three coordination modes with La or Gd atoms; average bondlengths of Ln—O_{bridging}, Ln—O_{chelating} and Ln—O_{terdentate} are 2.473, 2.556, 2.615 Å for the La complex, and 2.365, 2.455 and 2.530 Å for the Gd complex, respectively. This indicates that the order of ring strain is terdentate > chelating > bridging. Compared with [La(CH₂C(CH₃)COO)₃(phen)(HL)]₂ [11], average bondlengths are nearly the same (2.476, 2.570 and 2.611 Å), which shows that different carboxylate groups with the same mode of coordination with Ln(III) ion have essentially the same bond requirements. The separation of La...La* (4.094 Å) in the dimer just exceeds the sum of the two ionic radii and is significantly shorter than in [La(CH₂C(CH₃)COO)₃(H₂O)₂]₂ (4.274 Å) [12]. We note that the O(4)—La—O(4)* angle of about 77.1(1)° is larger than the corresponding angle (70.24°) in [La(CH₂C(CH₃)COO)₃(H₂O)₂]₂. The short separation, therefore, may be attributed to the simultaneous appearance of four-membered and eight-membered rings between the two lanthanum atoms. The

average La—N and Gd—N bond distances are 2.739 and 2.628 Å, respectively. Structures, including the complexes $[\text{Ln}(\text{CH}_2\text{C}(\text{CH}_3)\text{COO})_3(\text{phen})(\text{HL})_2]$ [11, 12] and $[\text{Ln}(\text{CHCl}_2\text{COO})_2(2,2'\text{-bipy})(\text{H}_2\text{O})_2]^+ [(\text{CHCl}_2\text{COO})^-]$ [13] suggest strongly that *N*-bidentate heterocyclic amines as ligands have stronger coordination ability for lanthanide ions than *N*-unidentates which are hard, and much less common.

The complexes from La to Gd appear to be isomorphous as their IR or UV and molar conductivities are all similar, the structure of La and Gd complexes are nearly the same and compositions agree through analysis.

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