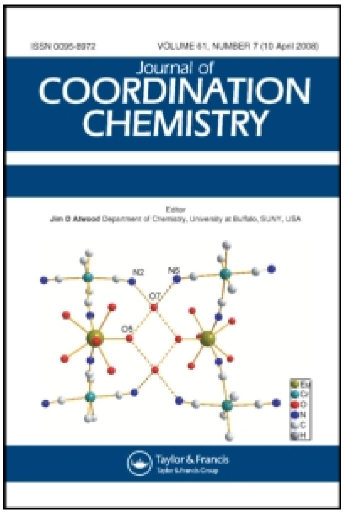

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SYNTHESIS, SPECTRA AND CRYSTAL STRUCTURE OF *BIS*(1,10-PHENANTHROLINE)Di(μ-α-METHYLACRYLATO) LANTHANIDE(III)DIMERS

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SYNTHESIS, SPECTRA AND CRYSTAL STRUCTURE OF *BIS*(1,10-PHENANTHROLINE)DI(μ-α-METHYLACRYLATO) LANTHANIDE(III)DIMERS

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The homodinuclear complexes, $[RE(CH_2C(CH_3)COO)_3(phen)]_2$ (RE=La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Y, phen=1,10-phenanthroline), have been synthesized and characterized by elemental analysis, molar conductance, IR and NMR. The complex $[La(CH_2C(CH_3)COO)_3(phen)(HL)]_2$ $(HL)=CH_2C(CH_3)COOH)$ crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$. Cell dimensions are $a = 9.878(2)$, $b = 11.071(1)$, $c = 26.528(3)$ Å, $\beta = 94.02(1)°$ and the structure was refined to $R = 0.036$ for 4136 observed reflections. The structure consists of a centrosymmetric dinuclear molecule. Lanthanum(III) atoms are bridged by two bidentate and two terdentate carboxylato groups with an La...La separation of 4.0456(4) Å. Each lanthanum(III) atom is nine-coordinated and exhibits a slightly distorted, tricapped, trigonal prism. The La-O and La-N bond distances are in the range 2.473–2.738 and 2.696–2.722 Å, respectively.

Keywords: Lanthanide; α-methylacrylato; 1,10-phenanthroline; X-ray structure

INTRODUCTION

There is increasing interest in the stereochemistry of lanthanide complexes of unsaturated carboxylic acids primarily because of their potential use as extraction agents, fluorescent probes and the effect of the α C=C double bond on coordination of carboxylato ligands with lanthanide. Several papers have been published on the preparation, properties and crystal structures of such mononuclear or homopolynuclear lanthanide complexes.[1-4] Some heterocyclic amine lanthanide complexes, on the other hand, also possess fluorescent properties

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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. However, a bidentate carboxylate group is much less common because of the four-membered chelate ring produced; of all possible modes of attachment to a metal, this would be the least favoured. For this reason, cases where the carboxylates act not only as bridging ligands, but also as chelating ligands are very rare indeed. The present investigation was undertaken in order to further study fluorescent properties of complexes and as part of our molecular structural studies on the rare earths with unsaturated carboxylic acids.

EXPERIMENTAL

Preparation of Complexes

Lanthanide α-methylacrylates were prepared following a method reported in a previous publication.[4] Crystals of lanthanide α-methylacrylate (1.5 mmol) were dissolved (ethanol : water = 4:1, v/v), and the solution mixed with one of phen (La : phen = 1:1 mol ratio; same solvent). The resulting solution was set aside at the room temperature and crystals of the complexes were obtained after a few days. Analytical results show that the complexes have the formula $C_{24}H_{23}REN_2O_6$ (Table I). Single crystals of $[La(CH_2C(CH_3)COO)_3 (phen) (CH_2C(CH_3)COOH)]_2$ suitable for X-ray work were obtained when two drops of α-methylacrylic acid were added to the above solution, containing La.

IR spectra were recorded on a Perkin Elmer 683 spectrometer (KBr dises). The ^1H NMR spectrum was recorded on a Bruker AC 80 spectrometer, and chemical shifts are given in ppm with respect to TMS. Elemental analyses were carried out on a Carlo–Erba 1106 instrument and all values given are the average of at least two independent determinations. Electrolytic conductances were measured at 25°C (~ 10^{-3} M) in dimethylformamide.

Crystal Structure Determination

A crystal of the lanthanum complex was mounted on an Enraf–Nonius CAD4 diffractometer. A unique data set for the crystal was measured in conventional ω /2θ scan mode at room temperature with Mokα radiation ($\lambda = 0.7107$ Å). Final lattice parameters and crystal orientations were calculated from least–squares refinement within the 2θ range 11–14°. During the data collection, three

TABLE I Analytical data for the complexes

Complex	*C %*		*H %*		*N %*		*RE %*	
	calc.	*found*	*calc.*	*found*	*calc.*	*found*	*calc.*	*found*
$C_{24}H_{23}LaN_2O_6$	50.18	49.75	4.04	4.16	4.88	4.83	24.18	24.18
$C_{24}H_{23}CeN_2O_6$	50.08	50.01	4.03	4.00	4.87	4.67	24.34	24.25
$C_{24}H_{23}PrN_2O_6$	50.01	49.83	4.02	4.02	4.86	4.63	24.45	25.44
$C_{24}H_{23}NdN_2O_6$	49.72	49.22	4.00	4.02	4.83	4.64	24.88	24.94
$C_{24}H_{23}SmN_2O_6$	49.20	48.94	3.96	4.20	4.78	4.57	25.67	25.69
$C_{24}H_{23}EuN_2O_6$	49.07	48.95	3.95	4.12	4.77	4.59	25.87	25.63
$C_{24}H_{23}GdN_2O_6$	48.63	48.82	3.91	4.08	4.73	4.52	26.53	26.59
$C_{24}H_{23}TbN_2O_6$	48.50	48.34	3.90	4.00	4.71	4.49	26.74	26.81
$C_{24}H_{23}DyN_2O_6$	48.20	48.18	3.88	4.02	4.68	4.50	27.17	27.25
$C_{24}H_{23}HoN_2O_6$	48.01	48.36	3.86	4.07	4.67	4.54	27.47	27.57
$C_{24}H_{23}ErN_2O_6$	47.82	48.19	3.84	4.06	4.65	4.56	27.75	27.91
$C_{24}H_{23}TmN_2O_6$	47.69	47.83	3.84	3.96	4.63	4.67	27.95	27.99
$C_{24}H_{23}YbN_2O_6$	47.37	47.47	3.81	3.92	4.60	4.55	28.44	28.40
$C_{24}H_{23}YN_2O_6$	54.97	54.93	4.42	4.38	5.34	5.16	16.96	16.78

reflections chosen in different regions of reciprocal space were monitored every 60 minutes. The intensities were corrected for Lorenz polarization and absorption (empirically).

The structure was solved by the heavy atom method. All non-hydrogen atoms were located by difference Fourier syntheses and refined by full-matrix least-squares methods including anisotropic temperature factors. Most of the H atoms were located by the same method and a few H atoms connected with the phen ring were calculated based on the known atomic configuration of the attached atoms and assuming C-H bond lengths of 1.0 Å. The positions of the all H atoms were refined with a common isotropic thermal parameter in the last cycle. The scattering factors for neutral atoms were taken from the *International Tables for X-ray Crystallography* (Vol. IV, 1974) and were included in the program package. The final deviation factors are $R = 0.036$ and $R_w = 0.042$. All calculations were performed on a VAX II computer using the Structure Determination Package program system.[5] Details are given in Table II and complete data are available from the authors upon request, (H atom positions, full lists of bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors).

RESULTS AND DISCUSSION

Solubility, Molar Conductivity, NMR and IR Spectra

The complexes are soluble in dimethylformamide, dimethylsulfoxide and tetrahydrofuran. They are insoluble in water, methanol, ethanol, carbon tetrachloride, chloroform and ethyl acetate. Molar conductivity values are 3.4~6.7 S cm^2 mol^{-1} (Table III), which suggest that the complexes are non-electrolytes.[6] The complexes have no obvious melting point and decompose at 495~525 K.

Infrared data for the complexes are listed in Table III. Published data on ligands and unsaturated carboxylates[2,7] were used to assign the frequencies. A comparison of the spectrum of $CH_2C(CH_3)COOH$ with those of its complexes reveals that considerable changes in frequencies have occur upon coordination. A peak assigned as O-H at 1710 cm^{-1} in $CH_2C(CH_3)COOH$ disappears. The antisymmetric stretching frequencies of the OCO groups increase with decreasing ionic(III) radii of the action and the symmetric stretching frequencies of the OCO group decrease. According to Deason,[8] the separation of the two C-O stretching frequencies ($\Delta\nu$) can be used to distinguish between the different coordination modes of the OCO group (*i.e.*, ionic, unidentate or bidentate). In the present case, the values separate the complexes into two groups. One from La to Tb complexes, has $\Delta\nu$ values (137~142 cm^{-1}) less than that of $NaCH_2C(CH_3)COO$ (146 cm^{-1}). The observed data are considered indicative of carboxylato groups chelating and bridging with central atoms, there being no criterion for distinguishing between them. The other group is from Dy to Yb

TABLE II Crystal and data collection parameters for the complex $[La(CH_2C(CH_3)COO)_3(phen)(HL)]_2$

Chemical formula	$C_{56}H_{58}La_2N_4O_6$
Molecular weight	1320.91
Crystal system	monoclinic
Space group	$P2_1/c$
Crystal size (mm)	0.28 × 0.21 × 0 .11
a(Å)	9.878(2)
b(Å)	11 .071(1)
c(Å)	26.528(3)
β(°)	94.02(1)
V(Å^3)	2894.0(9)
Z	2 (dimer)
F(000)	1328
D*calc*(g/cm^3)	1.513
μ (cm^{-1})	15.275
No. of reflection measured	5703
No. of independent reflections	5033
No. of observed reflections [$I>3\sigma(I)$]	4136
Absorption correction (min,max)	0.827, 0.998
Intensity variation	0.013
$h\ k\ l$	$0 \to 11; 0 \to 13; -31 \to 31$
R_{in}	0.017
R	0.036
R_w	0.042
Weighting scheme	unit weights
(Δ/σ) max	0.02
$(\Delta[\rho])$ min, max (e/Å^3)	−0.457, 0.632
Goodness of fit	2.214

TABLE III Selected IR data (cm^{-1}, and molar conductivity values (S cm^2 mol^{-1}) for the complexes

v			IR	data				Molar
	$v_{c=c}$	$v_{s(oco)}$	$v_{as(oco)}$	$\Delta V_{(oco)}$	$v_{(phen)}$	$v_{C\text{-}H(phen)}$	$v_{RE\text{-}O}$	conductivity
phen					1561	739, 851		
HL	1650		1440					
NaL	1656	1570	1424	146				
$C_{24}H_{23}LaN_2O_6$	1657	1573	1436	137	1527	730, 849	412	6.7
$C_{24}H_{23}CeN_2O_6$	1658	1574	1436	138	1525	730, 849	413	5.5
$C_{24}H_{23}PrN_2O_3$	1658	1568	1438	130	1528	730, 849	412	5.9
$C_{24}H_{23}NdN_2O_6$	1656.5	1575	1433	139	1525	729, 848	410	5.0
$C_{24}H_{23}SmN_2O_6$	1656.5	1575	1434	140	1525	739, 846	411	3.7
$C_{24}H_{23}EuN_2O_6$	1656.5	1575	1435	140	1522	729, 845	410	4.6
$C_{24}H_{23}GdN_2O_6$	1657.5	1576	1435	141	1525	729, 846	411	3.5
$C_{24}H_{23}DyN_2O_6$	1658	1576	1435	142	1525	729, 847	411	5.0
$C_{24}H_{23}DyN_2O_6$	1662	1623	1434	189	1530	730, 849	412	5.0
$C_{24}H_{23}HoN_2O_6$	1664	1626	1434	192	1528	730, 850	412	3.4
$C_{24}H_{23}ErN_2O_6$	1664	1625	1431	194	1529	730, 850	409	3.7
$C_{24}H_{23}TmN_2O_6$	1659	1600	1434	166	1527	728, 845	405	4.0
$C_{24}H_{23}YbN_2O_6$	1665	1628	1436	192	1530	731, 850	410	3.6
$C_{24}H_{23}YN_2O_6$	1663	1624	1433	191	1526	729, 849	411	3.9

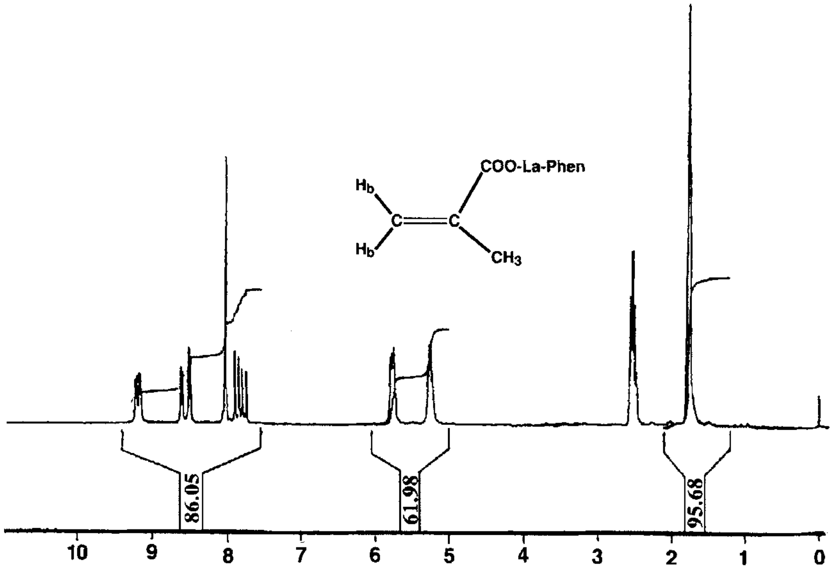

FIGURE 1 H NMR spectrum of $[La(CH_2C(CH_3)COO)_3(phen)]_2$.

including Y with Δν values (~190 cm^{-1}) significantly larger than that of $NaCH_2C(CH_3)COO$; this suggests that unidentate carboxylate groups are present. The IR spectrum also shows peaks due to the C=C and C-H stretches ~1660 and ~2970 cm^{-1}, respectively. The characteristic ring stretch[9] of phen at 1561 cm^{-1} is decreased to 1525 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 ~730 and ~847 cm^{-1} and split into several peaks due to loss of phen symmetry (C_{2v}); this is evidence of phen ligands coordinating with lanthanide atoms. Weak ν (RE-O) and ν (RE-N) modes appear at ~410 and ~285 cm^{-1}, respectively.

The ^1H NMR spectrum observed for the lanthanum complex, shown in Figure 1, displays peaks due to phen (multiplets at δ 9.22 – 7.74 ppm), $-CH_2$ (two quartets δ H_a at 5.75 and δ H_b at 5.26 ppm) and $-CH_3$ (singlet at δ 1.77 ppm) with an intensity ratios of 8 : 6 : 9. The assignment of the peaks is in accordance with those of phen and α-methylacrylic acid in which multiplets were observed at 9.17 – 7.72 ppm for phen, a quartet at 6.05 ppm for H_b, a quartet at 5.66 ppm for H_a, a singlet at 1.86 ppm for $-CH_3$ and another at 11.4 ppm for O-H protons. All peaks of the α-methylacrylato group shift upfield in the complex and the O-H peak disappears. Antimagnetic heterogeneity of β protons (H_a and H_b) increases, which would result from an increase of the effect of α protons ($-CH_3$) on H_a and

H_b due to a decrease in π-electron density. The phenomenon also occurs in the complex of $[La(CH_2C(CH_3)COO)_3(H_2O)_2]_2$ and contrasts with the complex $La(CH_2CHCOO)_3 \cdot H_2O$. The spectrum of the yttrium complex closely resembles that of lanthanum.

The complexes from La to Tb may be isomorphous as their IR spectra and molar conductivities are all similar and compositions agree through analysis. The structures from Dy to Yb complexes may be also isomorphous for the same reason.

Crystal Structure Analysis of the La Complex

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 2 shows an ORTEP diagram of the molecular structure with the numbering scheme. Figure 3 is a perspective view of the coordination around the pair of lanthanum(III) ions. Each Lanthanum(III) is nine-coordinated by two N atoms of phen and seven O atoms from three different kinds of carboxylate groups, with a slightly distorted tricapped trigonal prism. N(2), O(21), O(31), O(32), O(41) and O(42) atoms form the prism with N(1), O(22) and $O(41^i)$ capping the rectangular faces. The structure consists of a centrosymmetric, dimeric unit of lanthanum(III) ions bridged by bidentate and terdentate carboxylato groups. One α-methylacrylato group acts as a conventional bidentate bridging ligand, bonding into La through O(31) and to La^i through $O(32^i)$. The other is chelated to La through $O(41^i)$ and O(42), with $O(41^i)$ also linked to La^i. The third carboxylato group [O(21), C(21), O(22)] forms a chelating ring with an La ion. The four-atom mean plane [La, $O(41^i)$, La^i, O(41)] and eight-atom mean plane [La, O(31), C(31), $C(32^i)$, La^i, $O(31^i)$, $C(31^i)$, O(32)] make a dihedral angle of 83.53(5)° and the deviation of all these atoms from their mean planes is negligible except for O(31) atom (0.102 Å).

TABLE IV Fractional coordinates and equivalent isotropic temperature factors (Å^2) of the non-H atoms

Atom	*x/a*	*y/b*	*z/c*	*Beq*^{a}
La	0.11507(3)	0.08541(3)	0.55521(1)	3.268(5)
O(21)	0.1714(4)	0.0300(4)	0.6495(1)	4.47(9)
O(22)	−0.0190(4)	0.1289(4)	0.6328(2)	4.52(9)
O(31)	−0.0841(4)	0.2056(4)	0.5242(2)	4.39(9)
O(32)	0.2229(4)	−0.1051(4)	0.5301(2)	4.52(9)
O(41)	−0.0646(4)	−0.0722(4)	0.5474(1)	4.11(8)
O(42)	0.2124(4)	0.2037(4)	0.4839(2)	5.1(1)
N(1)	0.3827(5)	0.1315(5)	0.5789(2)	3.9(1)
N(2)	0.1895(5)	0.3010(4)	0.5956(2)	4.1(1)

TABLE IV *(Continued)*

Atom	*x/a*	*y/b*	*z/c*	*Beq*^{a}
C(1)	0.4789(6)	0.0529(6)	0.5703(3)	4.9(1)
C(2)	0.6150(7)	0.0729(7)	0.5828(3)	5.9(2)
C(3)	0.6547(6)	0.1770(7)	0.6054(3)	5.9(2)
C(4)	0.5589(6)	0.2638(7)	0.6148(2)	5.0(1)
C(5)	0.5922(7)	0.3798(7)	0.6375(3)	6.6(2)
C(6)	0.4975(8)	0.4611(7)	0.6460(3)	6.9(2)
C(7)	0.3566(7)	0.4386(6)	0.6320(2)	5.2(1)
C(8)	0.2537(8)	0.5211(6)	0.6393(3)	6.1(2)
C(9)	0.1240(8)	0.4934(6)	0.6247(3)	5.9(2)
C(10)	0.0940(7)	0.3817(6)	0.6035(3)	5.1(1)
C(11)	0.3198(6)	0.3267(5)	0.6095(2)	4.1(1)
C(12)	0.4232(6)	0.2386(6)	0.6006(2)	3.9(1)
C(21)	0.0630(5)	0.0785(6)	0.6636(2)	3.9(1)
C(22)	0.0318(6)	0.0719(6)	0.7184(2)	4.8(1)
C(23)	0.1050(9)	−0.0048(8)	0.7507(3)	7.4(2)
C(24)	−0.0751(8)	0.1454(8)	0.7327(3)	7.3(2)
C(31)	−0.1870(6)	0.1985(5)	0.4941(2)	3.9(1)
C(32)	−0.2732(7)	0.3095(6)	0.4858(2)	4.9(1)
C(33)	−0.2246(9)	0.4177(7)	0.5024(3)	7.8(2)
C(34)	−0.4064(7)	0.2971(7)	0.4613(3)	7.6(2)
C(41)	−0.1388(5)	−0.1635(5)	0.5525(2)	3.8(1)
C(42)	−0.1400(7)	−0.2255(6)	0.6026(2)	4.7(1)
C(43)	−0.0428(9)	−0.2064(7)	0.6381(3)	7.0(2)
C(44)	−0.2501(9)	−0.3075(8)	0.6099(3)	8.3(2)
O(51)	0.4139(5)	−0.0430(4)	0.6875(2)	6.3(1)
O(52)	0.3400(6)	−0.2251(5)	0.7043(3)	8.9(2)
C(51)	0.4306(8)	−0.1529(6)	0.7058(3)	5.7(2)
C(52)	0.5681(8)	−0.1747(7)	0.7289(3)	6.3(2)
C(53)	0.590(1)	−0.2734(8)	0.7563(3)	8.8(3)
C(54)	0.6715(8)	−0.0856(9)	0.7231(4)	8.9(3)

[a] The isotropic equivalent displacement parameter is defined as: $Beq=(4/3)[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

TABLE V Relevent bond distances (Å) and angles (°)

La-La^{i}	4.0456(4)	La-O(41)	2.483(2)
La-O(21)	2.598(2)	La-O(41^{i})	2.738(3)
La-O(22)	2.571(3)	La-O(42)	2.541(3)
La-O(31)	2.473(3)	La-N(1)	2.722(3)
La-O(32)	2.478(3)	La-N(2)	2.696(3)
O(21)-La-O(22)	50.35(9)	O(32)-La-N(1)	77.85(9)
O(21)-La-O(31)	124.13(9)	O(32)-La-N(2)	138.62(9)
O(21)-La-O(32)	89.37(9)	O(41)-La-O(41^{i})	78.52(9)
O(21)-La-O(41)	91.04(9)	O(41)-La-O(42)	127.13(9)
O(21)-La-O(41^{i})	163.13(9)	O(41)La-N(1)	145.63(9)
O(21)-La-O(42)	140.44(9)	O(41)La-N(2)	145.69(9)
O(21)-La-N(1)	71.43(9)	O(41^{i})La-O(42)	48.65(8)
O(21)-La-N(2)	78.02(9)	O(41^{i})La-N(1)	110.25(9)
O(22)-La-O(31)	73.85(9)	O(41^{i})-La-N(2)	117.90(9)
O(22)-La-O(32)	129.15(9)	O(42)-La-N(1)	70.44(9)
O(22)-La-O(41)	78.08(9)	O(42)-La-N(2)	74.60(9)
O(22)-La-O(41^{i})	137.57(9)	N(1)La-N-(2)	60.77(9)

TABLE V *(Continued)*

O(22)-La-O(42)	137.86(9)	La-O(21)-C(21)	93.0(2)
O(22)-La-N(1)	109.09(9)	La-O(22)-C(21)	95.2(2)
O(22)-La-N(2)	69.87(9)	La-O(31)-C(31)	140.6(2)
O(31)-La-0(32)	135.98(9)	La-O(32)-C(31^i)	136.7(2)
O(31)-La-O(41)	78.66(9)	La-O(41)-La^i	101.5(1)
O(31)-La-O(41^i)	67.15(8)	La-O(41)-C(41)	165.9(2)
O(31)-La-O(42)	78.93(9)	La-O(41^i)-C(41)	89.7(2)
O(31)-La-N(1)	135.68(9)	La-O(42)-C(41^i)	99.3(2)
O(31)-La-N(2)	80.95(9)	La-N(1)-C(1)	122.5(2)
O(32)-La-O(41)	72.49(9)	La-N(1)-C(12)	120.5(2)
O(32)-La-O(41^i)	74.94(9)	La-N(2)-C(10)	118.8(3)
O(32)-La-O(42)	92.65(9)	La-N(2)-C(11)	121.5(2)
Hydrogen bonding			
O(51)-O(21)	2.663(4)	O(21)-H(511)-O(51)	157.8(2)

Symmetry codes, (i): $-x$ $-y$, $1-z$.

The La...La separation (4.046 Å) in the dimer just exceeds the sum of the two ionic radii and is shorter than that in $[\{La(CH_2C(CH_3)COO)_3(H_2O)_2\}_2]$ (4.274 Å).[4] It is, to our knowledge, the shortest in lanthanum(III) carboxylate complexes. We note that the angle O(41)-La-(41^i), 78.5° is larger than the corresponding angle(70.2°) in $[\{La(CH_2C(CH_3)COO)_3(H_2O)_2\}_2]$. The short separation, therefore,

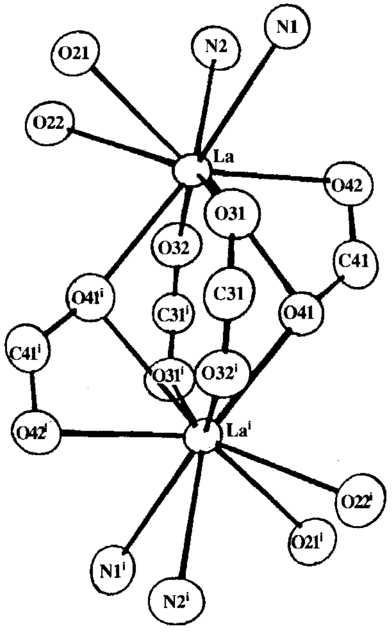

FIGURE 2 A drawing of the La complex showing the atom numbering scheme.

thermal ellipsoids are at 50% probability level may be attributed to the simultaneous existence of four-membered and eight-membered rings between the two lanthanum atoms. The structure has two distinct La-O distances; the average La-$O_{bridging}$ bond length is 2.494 Å and that of La-$O_{chelating}$ is 2.612 Å. The latter is significantly larger than the sum of covalent radii of the two atoms and is to be expected because the angles O(21)-La-O(22) or O(42^i)-La-O(42) of about 50° indicate ring strain. The phen ligands possess local C_{2v} symmetry and the structure of the phen group is almost identical to that in the structures of [{$RE(CCl_2COO)_3$(phen)(EtOH)}$_2$] complexes.[10] The atoms of the phen group, including the La atom do not deviate significantly from the containing least-squares plane. The average La-N bond distance is 2.709 Å.

The structure of [{$La(CH_2C(CH_3)COO)_3(H_2O)_2$}$_2$] suggests that *N*-bidentate heterocyclic amines may have stronger coordination ability to lanthanide ions than water molecules. The phenomenon also is noticed in[$RE(CHCl_2COO)_3(phen)_2$] complexes.[11,12] Another important observation is that the linear structure of [{$La(CH_2C(CH_3)COO)_3(H_2O)_2$}$_2$] changes to dimeric units when the water ligands

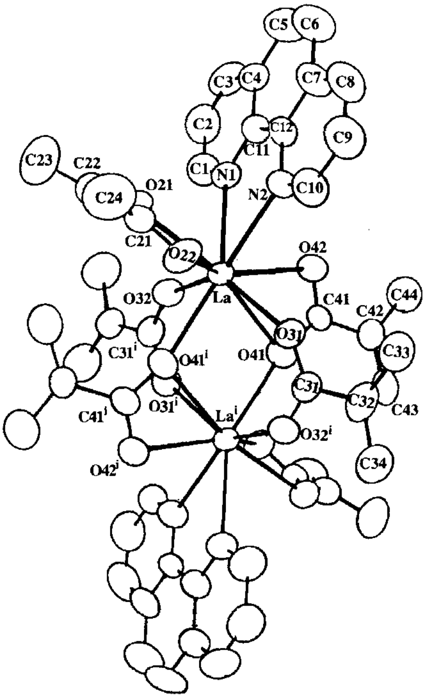

FIGURE 3 Perspective view of coordination around the pair of lanthanum ions.

are replaced by phen group, though the coordination number around each lanthanum(III) atom does not change. One free α-methylacrylic acid molecule is connected with O(21) atom by hydrogen bond.

Acknowledgments

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