The Crystal and Molecular Structure of the Hydrated Light Lanthanoid(III) Chloroacetates, $[\{M(ClCH_2CO_2)_3\}_3(H_2O)_5]_n$, (M=La, Pr, Nd, and Eu)

Takashi Imai, Mamoru Shimoi, and Akira Ouchi*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo,
Komaba, Meguro-ku, Tokyo 153

(Received May 19, 1986)

The crystal and molecular structures of the hydrated lanthanum(III), neodymium(III), and europium(III) chloroacetates indicated in the title were determined by the single-crystal X-ray diffraction method; these three salts as well as the praseodymium(III) salt are apparently isomorphous. By the same synthetic technique, gadolinium(III) or heavier lanthanoid(III) did not give the isomorphous salts. Their crystals are monoclinic with the space group of $P2_1/c$, and the cell constants of the neodymium(III) salt, for example, are, a=14.805(4), b=18.765(4), c=14.403(5) Å, β=95.13(3)°. There are crystallographically independent three kinds of nine-coordinated metal atoms: Nd(1), Nd(2), and Nd(3). Among them, Nd(1) and Nd(2) are best approximated as being in a tricapped trigonal prism geometry. The Nd(3) is best regarded as being in a monocapped square-antiprism geometry, although one more additional oxygen atom, O(35), approaches one side face. In the lanthanum(III) complex, O(35) is thought to be ligated to La(3), while in the europium(III) complex O(35) is perfectly removed from Eu(III), being accompanied by a change in the coordination geometry of the ligand. In the crystal, the metal atoms are bridged by carboxylato ligands, forming polymeric chains approximately along [−110] or [110] axis. There are no carboxylato bridges between respective chains, although there are some hydrogen-bondings linking them with each other.

The variety of the coordinating structures of metal carboxylates, where the metal atoms are linked by the ligands, is one of the interesting thèmes of structural chemistry.[1] Especially, the lanthanoid(III) carboxylates are found to form many kinds of the chain structures where the carboxylate ions act as the bridges between the metal atoms.[2–9] Although the lanthanoid formate can make a two-dimensional polymeric structure,[10] the carboxylates generally form a dimer or a linear polymeric chain.[4]

In the case of cerium(III) acetate, it is in a polymeric form, where the respective pairs of the metal atoms, being nine-coordinated in a tricapped trigonal prism geometry, are bridged by three acetato ligands.[7] On the other hand, the holmium(III) acetate is in a dimer form, in which the metal atom is nine-coordinated, being bridged by two carboxylate ions.[6]

The neodymium(III) (methylthio)acetate has the nine-coordinated neodymium(III) atoms in the tricapped trigonal prism geometry, being bridged by two to four carboxylato ligands into a linear polymeric chain.[2] On the other hand, in the case of ytterbium(III) (methylthio)acetate, which is also in a linear polymeric form, respective pairs of side-by-side metal atoms are linked only with one carboxylate ion.[9]

From these results, we deduced that the size of the central metal ion as well as the substituted groups on the carboxylato ligands are the reasons for forming such a variety of the linkages in the polymeric structure.

This time, we have obtained the chloroacetates of a series of the lanthanoid elements, which were expected to have some characteristic structures. Moreover, the type of complexes indicated in the title could be obtained only for lanthanum(III) to europium(III), while gadolinium(III) and heavier lanthanoids did not give isomorphous complexes. Therefore, some effect of the central metal-ionic size to its structure is also expected to be found even in the series of the isomorphous complexes, as in cases of the tetraacetatolanthanoidates(III),[4] and of lanthanoid(III) *m*-hydroxybenzoates.[3] For these reasons, the authors have tried to determine the structures of the series of the complexes by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Neodymium(III) Chloroacetate, $[\{Nd(ClCH_2CO_2)_3\}_3(H_2O)_5]$, and Its Isomorphous Complexes. Freshly obtained neodymium(III) hydroxide, by mixing solutions of neodymium(III) chloride hexahydrate (0.72 g, 2.0 mmol) and excess sodium hydroxide, was mixed with chloroacetic acid (0.57 g, 6.0 mmol). After stirring several minutes, the obtained aqueous solution was filtered and the filtrate was left standing for several days in a silica gel desiccator; care was taken that the solution did not become dry. The deposited crystals were filtered off and washed with a small portion of water. They were then dried in open air overnight and kept in a sealed bottle, where they remained stable. Yield: 0.55 g, 60%. Some additional lot, about 0.2 g, was obtained from the residual mother liquor, which almost had the same purity.

By applying the same synthetic technique, lanthanum(III), praseodymium(III), and europium(III) salts, which are apparently isomorphous with each other, were obtained almost in the same yield. Anal. ($M_3C_{18}H_{28}O_{23}Cl_9$) M, C, H. (where M=La, Pr, Nd, or Eu).

When this synthetic method was applied to obtain gadolinium(III) or heavier lanthanoid(III) salts, triclinic-type crystals were obtained instead. Chemical analyses showed that they also include 5/3 molecules of water per one metal atom and are isomorphous with each other.

Although our synthetic results regarding the title complexes are reproducible, the compositions as well as the crystallographic data (obtained by the X-ray powder diffraction method) of the lanthanoid(III) chloroacetates shown in a reference,[11] did not agree with our results. Probably, the crystallizing conditions and, consequently, the number of the included water molecules of the salts were different from each other.

Single-Crystal X-Ray Analysis. From the crystallographic data obtained by the single-crystal X-ray diffraction method, the lanthanum(III), praseodymium(III), neodymium(III), and europium(III) chloroacetates indicated in the title are apparently isomorphous, although (as shown later) there are some discrepancies in their detailed structures. They are monoclinic with the space group $P2_1/c$, $Z=4$ (for the title formula; twelve metal atoms are included in one unit cell). Their crystallographic data are shown in Table 1 and some other experimental conditions are tabulated in Table 2. The reflections shown in Table 2 were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation (scan speed was 4° min^{-1} (θ)), the ω—2θ scan technique being employed.

Structure Determination. The structure of the neodymium(III) complex was solved by the heavy-atom method. The positions of the metal and some ligated oxygen atoms were deduced from a three-dimensional Patterson map, while all the other non-hydrogen atoms were located by means of successive Fourier syntheses and refined by the block-diagonal least-squares method. In the last cycle of the refinement with anisotropic temperature factors for all atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The structures of the isomorphous complexes were solved by starting with the final parameters of the neodymium(III) complex and were refined in the same way. All of their parameters converged in the same grade.

All the calculations were carried out on a HITAC M-280H apparatus at the Computer Center of the University of Tokyo, using the local version of the UNICS program.[12] The atomic scattering factors were taken from Ref. 13.

Infrared Spectrum Measurements. Their infrared spectra were obtained by means of a JASCO 202-A grating infrared spectrophotometer, using Nujol or hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters of the complex are listed in Table 3 (1—3), while selected bond lengths and bond angles as well as some interatomic distances (which are thought to be the hydrogen-bonding types) are tabulated in Table 4.[14] A perspective drawings of the neodymium(III) complex around the metal atoms (Nd(1), Nd(2), and Nd(3)) as well as the numbering scheme of the atoms are shown in Figs. 1—3, and the crystal packing diagram in Fig. 4, respectively.

Table 1. Crystallographic Data of the Complexes $[\{M(ClCH_2CO_2)_3\}_3(H_2O)_5]_n$ (M=La, Pr, Nd, and Eu)

M=	La	Pr	Nd	Eu
F.W.	449.40	451.40	454.73	462.45
$a(l/\text{Å})$	14.918(4)	14.817(6)	14.805(4)	14.716(9)
$b(l/\text{Å})$	18.972(5)	18.825(5)	18.765(4)	18.671(4)
$c(l/\text{Å})$	14.514(6)	14.421(6)	14.403(5)	14.365(6)
$\beta(\phi/°)$	95.18(3)	95.11(3)	95.13(3)	95.36(4)
$U(v/\text{Å}^3)$	4091(3)	4002(3)	3986(2)	3930(3)
$D_m(d/\text{Mg m}^{-3})$	2.19(3)	2.23(3)	2.24(3)	2.34(3)
$D_x(d/\text{Mg m}^{-3})$	2.19	2.25	2.27	2.35
$\mu(\text{Mo }K\alpha)$ (n/mm^{-1})	3.18	4.28	4.57	5.45

Table 2. Some Experimental Conditions to Obtain the Reflection Intensities

Metal	La	Nd	Eu
Number of reflections measured	7500	7310	7205
Reflections used for the calculation[a)]	5527	5874	5693
Measured range $(2\theta/°)$	3—50	3—50	3—50
R[b)]	0.043	0.037	0.049
R_{weight}[b)]	0.052	0.050	0.059
Size of the crystal (v/mm^3)	0.15×0.15×0.3	0.3×0.3×0.25	0.3×0.3×0.3
Scan width $(\theta/°)$	$1.04+0.5\tan\theta$	$1.12+0.5\tan\theta$	$1.05+0.5\tan\theta$
S[c)]	2.157	2.547	3.322

a) Reflections with $|F_o|>3\sigma(|F_o|)$ were used. b) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_{\text{weight}}=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, where $w=1/[\{\sigma(|F_o|)\}^2+(F_{\text{weight}}\times F_o)^2]$, $F_{\text{weight}}=0.015$. c) $S=[\sum w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o=number of reflections, N_p=number of parameters.

Table 3. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) of Non-Hydrogen Atoms, with Estimated Standard Deviations in Parentheses

3.1. Lanthanum Complex

Atom	*x*	*y*	*z*	B_{eq}/Å^2 [a]
La(1)	4254.9(3)	898.6(2)	481.5(3)	1.6_4
La(2)	716.0(3)	4080.1(2)	297.0(3)	1.6_6
La(3)	2384.3(3)	2568.6(2)	1915.7(3)	1.6_5
O(11)	5036(4)	271(3)	1919(4)	2.8_9
O(12)	3562(4)	296(3)	1866(4)	3.0_1
O(13)	2619(4)	889(4)	79(5)	3.3_0
O(14)	1924(4)	1829(3)	575(4)	2.7_8
O(15)	4204(4)	−386(3)	78(4)	2.2_7
O(16)	4161(4)	−1452(3)	−491(5)	3.2_0
O(21)	−110(4)	5048(3)	997(4)	2.6_1
O(22)	−1170(4)	5730(3)	1442(4)	2.9_3
O(23)	1355(5)	4209(4)	1968(5)	3.8_1
O(24)	2686(4)	3812(3)	2511(4)	2.9_8
O(25)	929(4)	6137(4)	5(5)	3.6_1
O(26)	1688(4)	5142(3)	321(5)	2.7_8
O(31)	2206(4)	3496(3)	477(4)	2.2_4
O(32)	3570(4)	3152(3)	902(4)	2.7_5
O(33)	4009(4)	1819(3)	1656(4)	2.0_3
O(34)	3946(4)	2561(3)	2807(4)	2.3_8
O(35)	598(4)	2962(3)	1197(5)	3.3_0
O(36)	771(4)	2284(4)	2409(4)	3.3_4
C(11)	4290(7)	73(4)	2211(6)	2.6_0
C(12)	4395(9)	−477(6)	2977(8)	4.7_3
C(13)	1934(6)	1256(5)	184(6)	2.2_2
C(14)	1085(6)	933(6)	−303(9)	4.5_0
C(15)	3799(6)	−964(4)	−88(6)	2.1_4
C(16)	2880(7)	−1011(5)	262(8)	3.6_1
C(21)	−670(6)	5214(5)	1570(6)	2.6_0
C(22)	−683(10)	4696(9)	2374(10)	7.5_7
C(23)	2092(6)	4276(5)	2411(6)	2.5_0
C(24)	2357(7)	4967(5)	2909(8)	3.9_0
C(25)	1615(6)	5794(5)	286(7)	2.5_6
C(26)	2421(7)	6265(5)	580(9)	4.0_2
C(31)	3043(5)	3530(4)	415(5)	1.7_0
C(32)	3338(6)	4052(5)	−274(7)	3.2_5
C(33)	4386(6)	2171(4)	2322(6)	2.0_9
C(34)	5386(6)	2096(6)	2463(7)	3.7_5
C(35)	284(5)	2598(5)	1812(6)	2.2_8
C(36)	−728(6)	2537(7)	1740(7)	4.2_3
Cl(11)	3343(4)	−776(3)	3285(3)	9.4_8
Cl(12)	74(2)	1318(2)	24(3)	5.8_6
Cl(13)	2333(2)	−1821(2)	−21(3)	5.1_8
Cl(21)	−1286(4)	4932(3)	3236(3)	10.6_7
Cl(22)	1490(3)	5595(2)	2867(3)	8.7_8
Cl(23)	3383(2)	5777(2)	1018(3)	5.0_7
Cl(31)	4496(2)	3986(2)	−427(2)	4.9_0
Cl(32)	5867(2)	2601(2)	3417(2)	4.8_3
Cl(33)	−1154(2)	2666(3)	2817(3)	8.3_7
O(W1)	4031(4)	2117(3)	−308(4)	2.8_2
O(W2)	607(5)	2959(3)	−743(4)	3.2_8
O(W3)	2412(4)	1317(3)	2513(4)	2.6_3
O(W4)	2284(5)	2617(4)	3672(4)	3.7_7
O(W5)	4132(4)	854(3)	−1258(4)	2.8_3

3.2. Neodymium Complex

Atom	*x*	*y*	*z*	B_{eq}/Å^2 [a]
Nd(1)	4257.0(3)	898.4(2)	475.5(3)	1.5_1
Nd(2)	711.7(3)	4089.3(2)	283.0(3)	1.5_8
Nd(3)	2410.4(3)	2572.1(2)	1921.5(3)	1.7_0
O(11)	5046(4)	294(3)	1889(4)	2.5_1
O(12)	3577(4)	298(3)	1835(4)	2.7_4
O(13)	2646(4)	914(3)	116(4)	2.9_1
O(14)	1927(4)	1868(3)	590(4)	2.5_2
O(15)	4214(4)	−368(3)	78(4)	2.2_8
O(16)	4193(4)	−1452(3)	−466(4)	2.7_6
O(21)	−137(4)	5023(3)	967(4)	2.6_6
O(22)	−1172(4)	5727(3)	1441(4)	2.8_1
O(23)	1327(4)	4227(4)	1945(4)	3.7_1
O(24)	2653(4)	3801(3)	2495(4)	2.7_7
O(25)	896(4)	6137(3)	100(6)	4.5_3
O(26)	1680(3)	5128(3)	353(4)	2.7_0
O(31)	2172(3)	3505(3)	487(4)	2.1_8
O(32)	3537(3)	3144(3)	895(4)	2.3_9
O(33)	4018(4)	1804(3)	1635(3)	2.0_8
O(34)	3944(4)	2568(3)	2780(3)	2.3_9
O(35)	526(6)	3007(4)	1182(5)	5.3_8
O(36)	815(4)	2326(4)	2369(4)	4.1_7
C(11)	4315(6)	80(4)	2178(5)	2.5_0
C(12)	4429(8)	−475(5)	2952(7)	4.4_5
C(13)	1950(5)	1289(4)	203(5)	2.0_0
C(14)	1090(6)	960(5)	−309(7)	3.8_0
C(15)	3817(5)	−963(4)	−88(5)	1.8_8
C(16)	2876(6)	−1015(5)	253(7)	3.4_1
C(21)	−682(6)	5196(4)	1560(6)	2.5_1
C(22)	−699(8)	4686(7)	2376(8)	6.1_3
C(23)	2057(5)	4275(5)	2402(5)	2.4_7
C(24)	2330(7)	4960(5)	2926(7)	3.8_4
C(25)	1598(5)	5782(4)	344(6)	2.8_5
C(26)	2402(6)	6266(5)	610(8)	4.1_3
C(31)	3015(5)	3537(4)	413(5)	1.7_2
C(32)	3318(6)	4053(5)	−279(6)	3.1_1
C(33)	4397(5)	2169(4)	2294(5)	1.8_0
C(34)	5392(6)	2104(5)	2440(6)	3.6_5
C(35)	270(5)	2633(4)	1789(5)	2.3_5
C(36)	−732(7)	2504(7)	1783(9)	5.6_7
Cl(11)	3380(3)	−773(2)	3298(3)	8.0_3
Cl(12)	78(2)	1328(2)	31(3)	5.4_6
Cl(13)	2336(2)	−1829(1)	−44(2)	4.9_3
Cl(21)	−1302(3)	4931(2)	3250(3)	8.9_2
Cl(22)	1464(3)	5601(2)	2892(3)	8.5_9
Cl(23)	3385(2)	5779(2)	1033(2)	4.9_8
Cl(31)	4485(2)	3977(2)	−431(2)	4.8_7
Cl(32)	5872(2)	2613(2)	3409(2)	4.6_2
Cl(33)	−1137(2)	2697(3)	2855(3)	8.0_2
O(W1)	4034(4)	2102(3)	−298(4)	2.5_6
O(W2)	634(4)	2969(3)	−730(4)	3.2_5
O(W3)	2417(4)	1334(3)	2493(4)	2.4_8
O(W4)	2285(4)	2601(4)	3651(4)	3.4_5
O(W5)	4122(4)	850(3)	−1239(4)	2.7_0

Table 3. Continued.

3.3. Europium Complex

Atom	x	y	z	B_{eq}/Å$^{2\,a)}$	Atom	x	y	z	B_{eq}/Å$^{2\,a)}$
Eu(1)	4255.1(3)	903.4(2)	462.5(3)	1.4_3	C(21)	−725(7)	5174(6)	1552(7)	2.0_7
Eu(2)	677.9(3)	4095.2(3)	292.7(3)	1.4_8	C(22)	−742(10)	4676(8)	2364(9)	4.3_5
Eu(3)	2494.4(3)	2556.2(3)	1905.3(3)	1.4_6	C(23)	2054(7)	4248(5)	2394(7)	2.1_0
O(11)	5058(5)	307(4)	1856(5)	2.1_3	C(24)	2326(8)	4933(6)	2918(8)	2.8_5
O(12)	3573(5)	308(4)	1804(5)	2.6_1	C(25)	1550(7)	5769(6)	529(8)	2.2_6
O(13)	2665(5)	933(4)	121(6)	2.7_4	C(26)	2388(8)	6253(7)	739(11)	3.9_0
O(14)	1943(5)	1905(4)	541(5)	2.4_4	C(31)	2958(6)	3533(5)	403(7)	1.6_3
O(15)	4201(5)	−351(4)	85(5)	2.3_6	C(32)	3255(7)	4066(6)	−290(8)	2.5_9
O(16)	4222(5)	−1437(4)	−455(5)	2.6_9	C(33)	4440(7)	2173(5)	2281(7)	1.7_8
O(21)	−249(4)	4949(4)	927(5)	1.9_0	C(34)	5461(7)	2110(7)	2395(9)	3.6_4
O(22)	−1150(5)	5743(4)	1442(5)	2.6_1	C(35)	172(7)	2738(6)	1768(7)	2.2_7
O(23)	1299(5)	4188(4)	1935(5)	2.5_5	C(36)	−569(8)	2284(8)	2142(10)	4.5_2
O(24)	2663(5)	3765(4)	2483(5)	2.2_4	Cl(11)	3397(3)	−755(3)	3299(4)	7.1_3
O(25)	823(5)	6113(4)	454(6)	2.7_1	Cl(12)	76(2)	1295(2)	88(3)	5.4_3
O(26)	1664(5)	5111(4)	449(5)	2.3_1	Cl(13)	2345(2)	−1839(2)	−118(3)	5.1_6
O(31)	2117(4)	3493(4)	495(5)	1.9_0	Cl(21)	−1280(4)	4958(3)	3287(3)	8.3_6
O(32)	3519(4)	3141(4)	869(5)	2.1_9	Cl(22)	1418(3)	5554(2)	2934(3)	6.0_2
O(33)	4036(4)	1801(4)	1613(4)	1.8_7	Cl(23)	3408(2)	5773(2)	1046(3)	4.7_9
O(34)	3993(5)	2563(4)	2769(5)	2.3_0	Cl(31)	4420(2)	3989(2)	−459(3)	4.8_8
O(35)	−46(7)	3224(5)	1212(7)	4.6_4	Cl(32)	5932(2)	2615(2)	3391(3)	4.4_7
O(36)	958(6)	2552(5)	2032(8)	4.7_7	Cl(33)	−1165(4)	2765(3)	2892(5)	10.9_6
C(11)	4322(8)	92(5)	2156(7)	2.3_2	O(W1)	4020(5)	2097(4)	−307(5)	2.4_0
C(12)	4446(10)	−450(7)	2941(9)	3.8_4	O(W2)	622(5)	2903(4)	−555(6)	3.4_7
C(13)	1961(7)	1307(5)	180(7)	2.0_5	O(W3)	2406(5)	1338(4)	2442(5)	2.4_0
C(14)	1101(8)	964(7)	−300(10)	3.9_4	O(W4)	2270(6)	2559(5)	3590(5)	3.5_1
C(15)	3819(7)	−951(5)	−85(7)	1.8_7	O(W5)	4126(5)	853(4)	−1227(5)	2.5_8
C(16)	2884(8)	−1032(7)	215(10)	3.7_1					

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$. The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

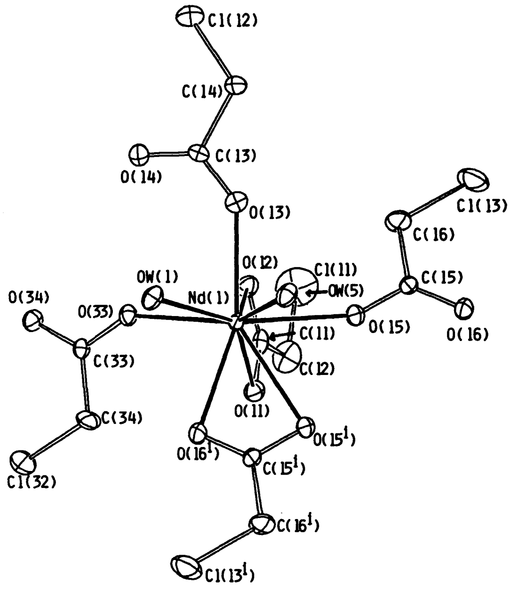


Fig. 1. A perspective drawing of the complex around Nd(1) atom with the numbering scheme of the atoms.

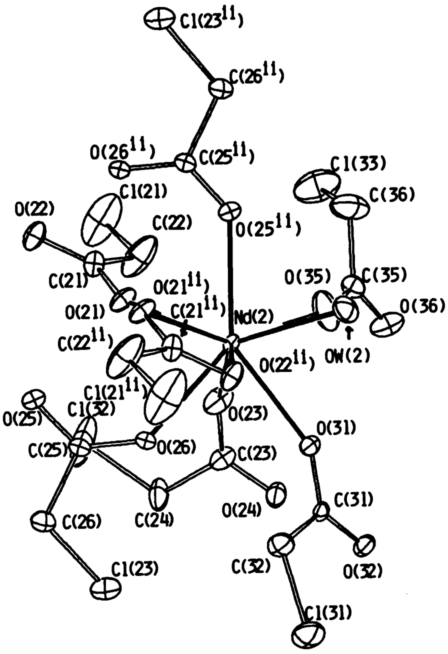


Fig. 2. A perspective drawing of the complex around Nd(2) atom with the numbering scheme of the atoms.

Schematic presentations to show the coordination geometries of the ligating atoms around the Nd(1), Nd(2), and Nd(3) atoms are shown in Figs. 5.1, 5.2, and 5.3. As shown in these figures, in the neodymium(III) complex, Nd(1) and Nd(2) atoms are approximately in a tricapped trigonal prism geometry. The Nd(3) atom is regarded as being in a monocapped square-antiprism geometry,[15] however other than these nine oxygen atoms, another oxygen atom, O(35), also approaches the metal atom above one side face of the square-antiprism, Nd(3)···O(35)=3.009(8) Å, although the distance is much longer than the other Nd–O bond lengths of this complex.[15]

As shown in Table 5, the average of eighteen Nd–O bond lengths around the Nd(1) and Nd(2) atoms is 2.493 Å, while that of nine Nd–O bond lengths around the Nd(3) atom is 2.553 Å. The former is about the same as the sum of the radii of the tervalent Nd (Coordination number (CN)=9) and O (Valence (Val)=2−, CN=2) ions, 2.51 Å;[16] however the latter is too long. It is rather near to the sum of the Nd(CN=10) and O ions, 2.56 Å (see the footnote g of Table 5). Concerning their lengths, the Nd–O bonds around the Nd(3) atom are like those of ten-coordination. This fact is probably because the O(35) atom, which is not very far from the coordination area around the metal atom, giving some steric hindrance effect to the other coordinated ligands.

The respective Nd–O bond lengths around the Nd(1) or Nd(2), and Nd(3) atoms are distributed in the ranges shown in Table 5 by the ratios of the maximum and minimum values to the average lengths, respectively. In the high-coordination-number geometries, such a discrepancy regarding the respective M–O bond lengths around one metal atom is sometimes found.

The coordinating carboxylate ions found in the neodymium(III) complex are classified into three groups, depending on their forms (as previously shown in Ref. 4). The **A**-, **B**-, and **C**-type ions (as

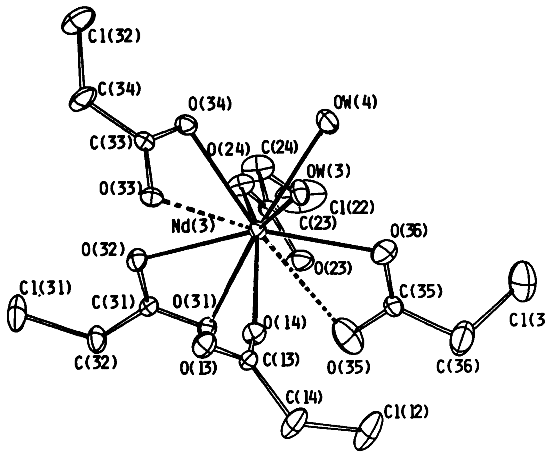


Fig. 3. A perspective drawing of the complex around Nd(3) atom with the numbering scheme of the atoms.

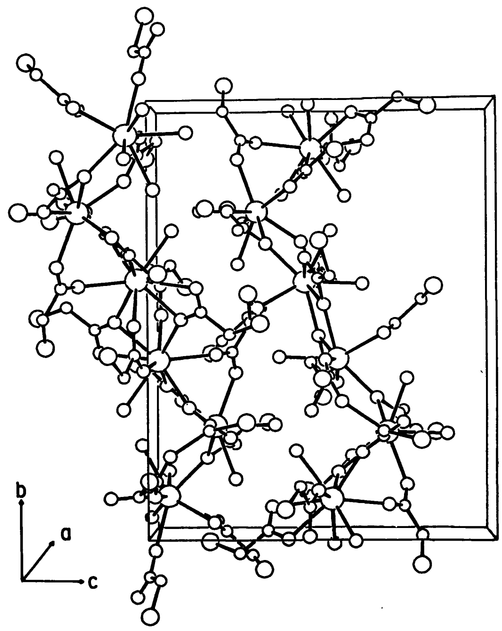
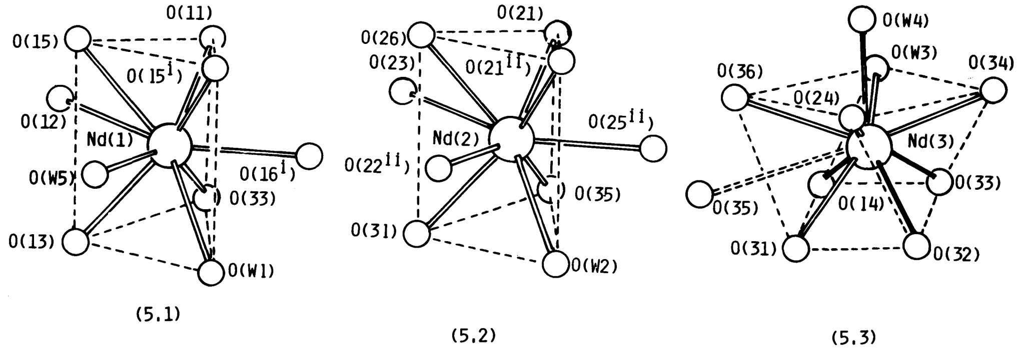


Fig. 4. Crystal packing diagram of the neodymium(III) complex.



(5.1) (5.2) (5.3)

Fig. 5. Schematic presentation of the complex with the numbering scheme of the ligating atoms: 5.1, 5.2, and 5.3 show the coordination geometries around Nd(1), Nd(2), and Nd(3), respectively.

Table 4. Interatomic Distances and Bond Angles of the Complexes, with the Standard Deviations in Parentheses

M	La(l/Å)	Nd(l/Å)	Eu(l/Å)	M	La(ϕ/°)	Nd(ϕ/°)	Eu(ϕ/°)
M(1$^{\mathrm{i}}$)···M(1)	4.368(1)	4.315(1)	4.301(1)	O(33)-M(1)-O(16$^{\mathrm{i}}$)	84.4(2)	84.48(18)	84.3(2)
M(1)···M(3)	4.817(1)	4.764(1)	4.641(2)	O(16$^{\mathrm{i}}$)-M(1)-O(W1)	73.8(2)	73.27(18)	74.0(2)
M(3)···M(2)	4.345(1)	4.352(1)	4.429(2)	O(W1)-M(1)-O(33)	69.9(2)	69.93(18)	70.1(3)
M(2)···M(2$^{\mathrm{ii}}$)	4.142(1)	4.060(1)	3.974(1)	O(11)-M(1)-O(13)	123.7(2)	124.08(19)	124.6(3)
M(3)···M(2$^{\mathrm{iii}}$)	6.501(2)	6.455(2)	6.539(2)	O(13)-M(1)-O(W5)	77.0(2)	78.1(2)	78.9(3)
M(1)···M(3$^{\mathrm{iv}}$)	6.358(2)	6.278(2)	6.215(2)	O(W5)-M(i)-O(11)	141.5(2)	141.5(2)	140.9(3)
M(1)-O(11)	2.586(7)	2.524(6)	2.490(8)	O(12)-M(1)-O(15$^{\mathrm{i}}$)	118.9(2)	118.10(19)	117.7(3)
M(1)-O(12)	2.605(8)	2.544(7)	2.513(9)	O(15$^{\mathrm{i}}$)-M(1)-O(15)	65.53(18)	64.63(17)	64.5(2)
M(1)-O(13)	2.457(6)	2.395(5)	2.346(7)	O(15)-M(1)-O(12)	75.4(2)	75.26(19)	74.6(3)
M(1)-O(15)	2.505(6)	2.445(5)	2.404(7)	O(11)-M(1)-O(33)	81.6(2)	81.10(19)	81.0(3)
M(1$^{\mathrm{i}}$)-O(15)	2.688(6)	2.660(6)	2.679(8)	O(12)-M(1)-O(33)	71.7(2)	71.9(2)	72.0(3)
M(1$^{\mathrm{i}}$)-O(16)	2.584(6)	2.520(5)	2.454(7)	O(11)-M(1)-O(12)	50.0(2)	50.7(2)	51.7(3)
M(1)-O(33)	2.491(6)	2.430(6)	2.396(7)	O(21)-M(2)-O(21$^{\mathrm{ii}}$)	70.9(2)	70.2(2)	70.9(3)
M(1)-O(W1)	2.587(6)	2.527(6)	2.497(7)	O(21$^{\mathrm{ii}}$)-M(2)-O(26)	70.0(2)	70.17(19)	67.4(2)
M(1)-O(W5)	2.516(8)	2.461(7)	2.419(9)	O(26)-M(2)-O(21)	72.8(2)	74.12(19)	78.1(2)
M(2)-O(21)	2.479(6)	2.416(6)	2.337(7)	O(23)-M(2)-O(25$^{\mathrm{ii}}$)	117.6(2)	120.1(2)	133.4(3)
M(2)-O(23)	2.536(9)	2.498(8)	2.456(9)	O(25$^{\mathrm{ii}}$)-M(2)-O(22$^{\mathrm{ii}}$)	100.6(2)	97.9(2)	84.8(3)
M(2)-O(26)	2.480(6)	2.417(5)	2.386(7)	O(22$^{\mathrm{ii}}$)-M(2)-O(23)	141.1(3)	141.3(2)	141.6(3)
M(2$^{\mathrm{ii}}$)-O(21)	2.603(7)	2.543(6)	2.539(8)	O(35)-M(2)-O(W2)	66.9(2)	67.4(2)	71.0(3)
M(2$^{\mathrm{ii}}$)-O(22)	2.696(8)	2.656(7)	2.666(9)	O(W2)-M(2)-O(31)	72.8(2)	71.98(19)	68.5(3)
M(2$^{\mathrm{ii}}$)-O(25)	2.488(6)	2.432(6)	2.395(7)	O(31)-M(2)-O(35)	70.8(2)	72.5(2)	92.7(3)
M(2)-O(31)	2.477(5)	2.419(5)	2.391(6)	O(21)-M(2)-O(23)	72.2(2)	72.1(2)	75.9(3)
M(2)-O(35)	2.505(8)	2.437(8)	2.407(11)	O(21)-M(2)-O(35)	110.6(2)	107.5(2)	86.7(3)
M(2)-O(W2)	2.605(7)	2.556(7)	2.535(9)	O(14)-M(3)-O(W3)	74.3(2)	74.84(19)	75.9(3)
M(3)-O(14)	2.447(7)	2.385(6)	2.383(8)	O(14)-M(3)-O(31)	76.1(2)	74.65(19)	71.5(3)
M(3)-O(24)	2.539(6)	2.464(6)	2.410(7)	O(31)-M(3)-O(24)	70.3(2)	69.88(18)	70.0(2)
M(3)-O(31)	2.725(7)	2.707(6)	2.694(8)	O(32)-M(3)-O(34)	70.1(2)	71.07(18)	70.0(2)
M(3)-O(32)	2.644(7)	2.562(6)	2.470(8)	O(34)-M(3)-O(W4)	68.3(2)	69.7(2)	72.4(3)
M(3)-O(34)	2.561(6)	2.486(5)	2.427(7)	O(W4)-M(3)-O(36)	66.5(2)	66.5(2)	72.5(3)
M(3)-O(36)	2.628(7)	2.546(7)	2.285(9)	O(24)-M(3)-O(32)	72.1(2)	73.66(19)	75.2(3)
M(3)-O(W3)	2.526(6)	2.464(5)	2.409(7)	O(32)-M(3)-O(W3)	126.4(2)	127.18(18)	131.6(3)
M(3)-O(W4)	2.569(9)	2.515(8)	2.473(10)	O(W3)-M(3)-O(36)	72.6(2)	73.8(2)	83.6(3)
M(3)-O(33)	2.865(6)	2.845(5)	2.736(7)	O(36)-M(3)-O(24)	103.7(2)	101.3(2)	92.7(3)
M(3)-O(35)	2.872(7)	3.009(8)	3.978(10)	M(1)-O(11)-C(11)	93.5(6)	93.5(5)	93.4(6)
O(11)-C(11)	1.283(12)	1.260(11)	1.267(14)	M(1)-O(12)-C(11)	93.9(6)	93.4(5)	93.1(7)
O(12)-C(11)	1.229(12)	1.228(10)	1.237(13)	M(1)-O(13)-C(13)	140.1(6)	142.2(5)	144.1(7)
O(13)-C(13)	1.257(11)	1.263(9)	1.259(13)	M(3)-O(14)-M(13)	149.4(7)	147.1(6)	142.1(8)
O(14)-C(13)	1.227(11)	1.222(10)	1.231(13)	M(2)-O(23)-C(23)	138.7(7)	139.1(6)	138.6(8)
O(15)-C(15)	1.265(10)	1.273(9)	1.267(12)	M(3)-O(24)-C(23)	120.9(6)	123.3(5)	125.6(7)
O(16)-C(15)	1.245(12)	1.227(10)	1.231(13)	M(2$^{\mathrm{ii}}$)-O(25)-C(25)	137.5(6)	137.7(5)	134.8(7)
O(21)-C(21)	1.270(13)	1.269(12)	1.261(15)	M(2)-O(26)-C(25)	139.4(6)	138.1(5)	134.9(7)
O(22)-C(21)	1.235(11)	1.237(10)	1.236(13)	M(2)-O(21)-C(21)	146.3(6)	147.7(6)	152.7(7)
O(23)-C(23)	1.229(12)	1.217(10)	1.242(13)	M(2$^{\mathrm{ii}}$)-O(21)-C(21)	96.2(6)	96.7(5)	98.0(7)
O(24)-C(23)	1.248(11)	1.252(10)	1.268(12)	M(2$^{\mathrm{ii}}$)-O(21)-M(2)	109.1(3)	109.9(3)	109.1(3)
O(25)-C(25)	1.248(11)	1.257(10)	1.244(12)	M(2$^{\mathrm{ii}}$)-O(22)-C(21)	92.7(6)	92.1(5)	92.1(7)
O(26)-C(25)	1.243(11)	1.233(10)	1.246(13)	M(1)-O(15)-C(15)	153.1(5)	153.9(5)	155.4(7)
O(31)-C(31)	1.261(10)	1.263(9)	1.259(12)	M(1$^{\mathrm{i}}$)-O(15)-C(15)	92.0(5)	90.4(4)	88.7(6)
O(32)-C(31)	1.237(10)	1.235(9)	1.251(12)	M(1)-O(15)-M(1$^{\mathrm{i}}$)	114.5(2)	115.4(2)	115.5(3)
O(33)-C(33)	1.263(11)	1.262(10)	1.285(13)	M(1$^{\mathrm{i}}$)-O(16)-C(15)	97.5(5)	98.2(5)	100.4(6)
O(34)-C(33)	1.249(11)	1.258(10)	1.242(14)	M(2)-O(31)-C(31)	148.6(5)	147.9(5)	145.8(6)
O(35)-C(35)	1.252(13)	1.208(12)	1.231(15)	M(3)-O(31)-C(31)	93.4(5)	91.9(4)	89.0(6)
O(36)-C(35)	1.232(12)	1.248(11)	1.234(13)	M(2)-O(31)-M(3)	113.2(2)	116.1(2)	121.0(3)
O(W4)···O(W2$^{\mathrm{iii}}$)	2.926(10)	2.882(9)	2.948(13)	M(3)-O(32)-C(31)	98.0(5)	99.6(5)	99.8(6)
O(34)···O(W1$^{\mathrm{iii}}$)	2.795(10)	2.829(9)	2.832(12)	M(1)-O(33)-C(33)	144.2(6)	144.6(5)	144.2(7)
O(W4)···O(W1$^{\mathrm{iii}}$)	2.923(10)	2.934(8)	2.964(11)	M(3)-O(33)-C(33)	87.7(5)	86.4(4)	85.5(6)
O(36)···O(W2$^{\mathrm{iii}}$)	2.754(12)	2.830(11)	3.647(17)	M(3)-O(33)-M(1)	128.1(2)	129.0(2)	129.3(3)
O(W5)···O(24$^{\mathrm{iv}}$)	2.738(10)	2.788(8)	2.799(11)	M(3)-O(34)-C(33)	102.6(6)	103.5(5)	102.2(7)
				M(2)-O(35)-C(35)	152.5(6)	157.8(7)	138.8(9)
				M(3)-O(35)-C(35)	89.5(6)	85.8(6)	54.9(6)
				M(2)-O(35)-M(3)	107.6(2)	105.6(3)	84.0(3)
				M(3)-O(36)-C(35)	101.9(6)	107.8(6)	151.8(9)

Key to the symmetry operations: i, $1-x$, $-y$, $-z$; ii, $-x$, $1-y$, $-z$; iii, x, $0.5-y$, $0.5+z$; iv, x, $0.5-y$, $-0.5+z$.

follows) are schematically given in Fig. 6.

(**A**) Chelating ion: The ion **11**,[17] belongs to this group. Its COM and CO′M angles are 93.5(3) and 93.4(5)°, which are normal (in the range of 90—95°) for this group ions.[4]

(**B**) *Z,Z*-Type bridging bidentate ions: (*syn-syn* type bridge according to the classification by Chatteric.[18]) The ions **12**, **22**, and **23** belong to this group. In the standard form of this type ion, 2(M-O′)/(M-O+M′-O′) is about 1.6—1.7, the angles MO′C and M′OC, and COM and CO′M′ are about 60 and 135—150°, respectively. The bond lengths and angles of these ions are found to be in the normal ranges, respectively, although C(23)-O(24)-Nd(3) is an exception (123.3(5)°).

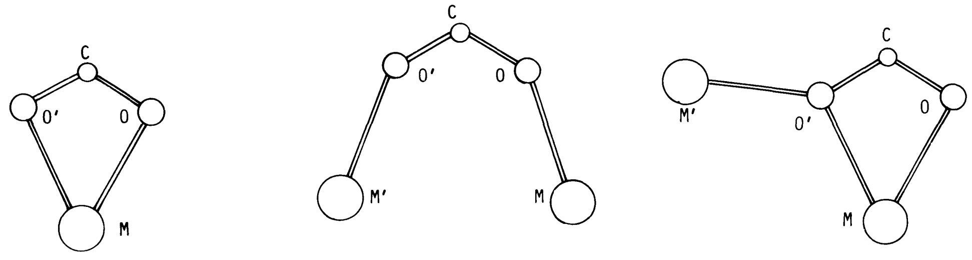
Table 5. The Comparison of the Metal-Oxygen Bondings of the Complexes

Metal	La	Nd	Eu
$\text{M-O}_{\text{calc(CN=9)}}$ b)	2.57	2.51	2.47
$\text{M-O}_{\text{calc(CN=10)}}$ b)	2.62	(2.56) g)	(2.52) g)
$\text{M-O}_{\text{av(M(1), M(2))}}$ c)	2.54_9	2.49_3	2.46_2
$\text{M-O}_{\text{av(M(3), 9)}}$ d)	2.61_2	2.55_3	2.47_6
$\text{M-O}_{\text{av(M(3), 10)}}$ d)	2.63_8	2.59_8	2.62_7
$\text{M-O}_{\text{min(M(1), M(2))}}/\text{M-O}_{\text{av(M(1), M(2))}}$ e)	0.96	0.97	0.95
$\text{M-O}_{\text{max(M(1), M(2))}}/\text{M-O}_{\text{av(M(1), M(2))}}$ e)	1.06	1.07	1.09
$\text{M-O}_{\text{min(M(3))}}/\text{M-O}_{\text{av(M(3), 9)}}$ f)	0.94	0.93	0.92
$\text{M(3)-O(35)}/\text{M-O}_{\text{av(M(3), 10)}}$ f)	1.09	1.16	1.51
$\text{M(3)-O(33)}/\text{M-O}_{\text{av(M(3), 9)}}$ f)	1.09	1.11	1.11

b) The sum of the Shannon's ionic radii.[16] The valence of the central metal is 3+, and its coordination number *n* is shown by CN=*n*. c) Average of the 18 M-O bond lengths around M(1) and M(2) atoms. d) Average of written numbers of the M-O bond lengths around M(3) atom. (In the case of 9, M(3)-O(35) one is rejected.) e) The shortest (shown by min) or the longest (shown by max) M-O bond length around the M(1) and M(2) atoms is divided by the average of all the M-O bond lengths around the metal atoms. f) The written bond length is divided by the average M-O bond length around M(3) atom, where "av(M(3), 9)" means the average of nine M-O bond lengths excluding M(3)-O(35), while "av(M(3), 10)" that of all ten bond lengths around the metal atom. g) As Shannon did not give the ionic radii of neodymium(III) and europium(III) in ten-coordination, the values 0.05 Å longer than the corresponding nine-coordination radii are tentatively adopted.

(**C**) Tridentate-type bridging ions: (One oxygen atom of a carboxylato chelate around a metal atom is also bonded to another metal atom, consequently as a whole the ligand acts as a tridentate.) Ions **21**, **13**, **31**, **32**, and **33** are the members. In the typical form, the bond lengths (M-O, M-O′, and M′-O′) as well as the bond angles (MOC and MO′C, about 90—100°) are about the same, respectively, and the angle M′O′C is in the range 140—150°. Bonds O′-M′ and C-O are at the opposite sides of the C-O′ bond from each other. As previously shown,[4] many of the actually found ligands of this type are deformed from the ideal shape. When it deforms, the M-O′ length as well as the COM angle increase, while the CO′M angle decreases. In this complex, the type of ligands deforms approximately in the given order. Their bond lengths and bond angles are compared with each other in Table 6, where the corresponding data regarding those of the lanthanum(III) and europium(III) complexes are also shown. As shown in the Table, for ion **21** of the neodymium(III) complex (which is almost in the standard form) the M-O′ length is not much different from that of M-O and M′-O′ and angles MOC and MO′C are within the normal range. On the other hand, in cases of the other deformed ligands, the bond lengths and bond angles deviate as mentioned above. The deformation in the form of the tridentate-type ligand is thought to tend toward the *Z,E*-type bidentate one (where M-O and C-O′ bonds are at the same side of the C-O bond, while M′-O′ and C-O bonds are at the opposite sides of the C-O′ bond from each other, respectively). Angles COM and CO′M′ are in the range 140—145° (CO′M is about 60°) and M-O′ length is about 1.6- to 1.7-times the average of the M-O and M′-O′ lengths in standard *Z,E*-type bidentate ion.[4] Therefore, even the most deviated ion, **33**, of the neodymium(III) complex is far from the normal *Z,E*-type bidentate.

The coordination type of the respective carboxylate ions, their bridging positions as well as the number of the intermetallic bridges are schematically shown in Fig. 7. As shown in this figure, the pairs of the



(A) (B) (C)

Fig. 6. Schematic presentation of the three types of ligands.

neodymium(III) atoms, Nd(1^{i}) and Nd(1), Nd(1) and Nd(3), Nd(3) and Nd(2), and Nd(2) and Nd(2^{ii}) (where the key to the symmetry operations: i, $1-x$, $-y$, $-z$; ii, $-x$, $1-y$, $-z$) are bridged by: two **C**-type ions; one **B**-and one **C**-type ion; one **B**-, one **C**- and one extremely deformed **C**-type ion; and two **B**- and two **C**-type ions, respectively. The respective inter-metal-atomic distances are: 4.315(1), 4.764(1), 4.352(1), and 4.060(1) Å. Therefore, judging from these data, the effect of a **C**-type bridge to shorten the intermetallic distance is greater than that of a **B**-type bridge.

Thus, the metal atoms in the complex are arranged in the order of ···Nd(1^{i})···Nd(1)···Nd(3)···Nd(2)···Nd(2^{ii})···, approximately along [-110] axis, although in a zig-zag way. The next chain on the *z*-axis direction, ···Nd(1^{iv})···Nd(1^{iii})···Nd(3^{iii})···Nd(2^{iii})···Nd(2^{v})···, (where the key to the symmetry operations: iii, x, $0.5-y$, $0.5+z$; iv $1-x$ $0.5+y$, $0.5-z$; v, $-x$, $-0.5+y$, $0.5-z$), is laid along [110] axis. Thus, the polymeric chains along both axes are aligned alternately. Between these side-by-side chains, no coordinated carboxylato bridges are found, though some hydrogen bondings are expected to exist (as shown by some interatomic distances in Table 4).

The structures of the lanthanum(III) and europium(III) complexes resemble that of the neodymium(III) complex. However, there are some differences between them (mentioned below) regarding their detailed structures.

In the lanthanum(III) complex, an average of eighteen La–O bond lengths around the La(1) and La(2) atoms is 2.549 Å; this is slightly shorter than the

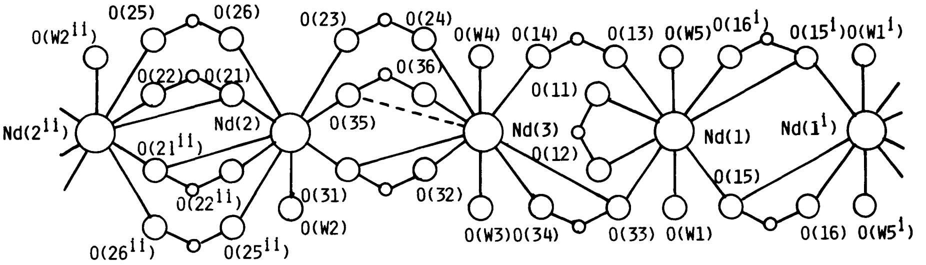


Fig. 7. Schematic presentation of the bridgings between the metal atoms. (Key to the symmetric operations: i, $1.0-x$, $-y$, $-z$; ii, $-x$, $1.0-y$, $-z$).

Table 6. Some Comparative Data about Interatomic Distances and Bond Angles of Tridentate-Type Ligands of the Complexes[h)]

Lanthanum(III) Complex

Ligand	21	11	31	32	33
(M-O+M′-O′)/2	2.588	2.545	2.561	2.526	2.567
2(M′-O)/(M-O+M′-O′)	1.02	1.06	1.06	1.13	1.12
MOC(ϕ/°)	92.7(6)	97.5(5)	98.0(5)	102.6(6)	101.9(6)
MO′C(ϕ/°)	96.2(6)	92.0(5)	93.4(5)	87.7(5)	89.5(6)
M′O′C(ϕ/°)	146.3(6)	153.1(5)	148.6(5)	144.2(6)	152.5(6)

Neodymium(III) Complex

Ligand	21	11	31	32	33
(M-O+M′-O′)/2	2.536	2.483	2.491	2.458	2.492
2(M′-O)/(M-O+M′-O′)	1.00	1.07	1.09	1.16	1.21
MOC(ϕ/°)	92.1(5)	98.2(5)	99.6(5)	103.5(5)	107.8(6)
MO′C(ϕ/°)	96.7(5)	90.4(4)	91.9(4)	86.4(4)	85.8(6)
M′O′C(ϕ/°)	147.7(6)	153.9(5)	147.9(5)	144.6(5)	157.8(7)

Europium(III) Complex

Ligand	21	11	31	32	33
(M-O+M′-O′)/2	2.502	2.429	2.431	2.412	2.346
2(M′-O)/(M-O+M′-O′)	1.01	1.10	1.11	1.13	1.70
MOC(ϕ/°)	92.1(7)	100.4(6)	99.8(6)	102.2	151.8(9)
MO′C(ϕ/°)	98.0(7)	88.7(6)	89.0(6)	85.5(6)	54 9(6)
M′O′C(ϕ/°)	152.7(7)	155.4(7)	145.8(6)	144.2(7)	138.8(9)

h) The nominations of the atoms shown in this Table are the same as those of Fig. 6(C).

sum of the tervalent La(CN=9) and O ionic radii, 2.57 Å.[16] The average of ten La–O bond lengths, including La(3)–O(35), around the La(3) atom is 2.638 Å; this is almost the same as the sum of the tervalent La(CN=10) and O ionic radii, 2.62 Å[16] (the average of nine La–O lengths, excluding La(3)–O(35), is 2.612 Å, which is not much different from the latter sum, too).

The corresponding La–O bonds, except La(3)–O(35), are all longer than the respective Nd–O bonds; the differences between them are in the range of 0.028—0.068 Å around the M(1) and M(2) atoms, and 0.017—0.082 Å around the M(3) atom. The relatively long La(3)–O(35) distance is, on the contrary, 0.137 Å shorter than that of the neodymium(III) complex. Even other than this bond, La(1^{i})–O(15), La(3)–O(31), and La(3)–O(33), which are relatively long, are also not very elongated when the central metal atom is changed from neodymium(III) to lanthanum(III). Consequently, the range between the shortest and the longest M–O bond lengths of the lanthanum(III) complex is widened in the neodymium(III) complex (Table 5).

Table 6 gives a comparison of the respective tridentate-type ions of the neodymium(III) complex with the corresponding ones of lanthanum(III) complex; the deviations from the ideal values of the relative M–O′ lengths, and of the MOC as well as MO′C angles are a little greater in the neodymium(III) complex.

As the ionic radius of the neodymium(III) is shorter than that of lanthanum(III), due to the lanthanoid contraction effect, the spherical area around the neodymium(III) atom to be occupied by the ligating atoms is smaller than that of the lanthanum(III) ion. Therefore, in the neodymium (III) complex, there are more steric interactions between the ligating atoms and between the ligand molecules. These steric hindrance effects work unequally on the respective ligands. Consequently, the respective M–O bond lengths do not decrease equally, and the M–O bond lengths of the neodymium(III) complex disperse over a wider range.

Of course, even in the lanthanum(III) complex, as the restrictions such as the bonding directions of the respective ligating atoms, and the definite distance between each pair of the oxygen atoms of the same ligand still remain, the discrepancy of the respective La–O bond lengths and the deformation of the coordination geometries around the respective metal atoms are also found.

Although the disproportional changes of several M–O bond lengths are found when the central metal atom of the lanthanum(III) complex is substituted by the neodymium(III) atom; no change of the bonding type of the ligands is found. This kind of the unequal bond-length change in a series of the isomorphous complexes was also reported in a series of guanidinium tetraacetatolanthanoidates(III).[4]

In the europium(III) complex, an average eighteen Eu–O bond lengths around the Eu(1) and Eu(2) atoms is 2.462 Å; this is about the same as the sum of the tervalent Eu(CN=9) and O ionic radii: 2.47 Å.[16] However, the differences between the respective Eu–O and the corresponding Nd–O bond lengths distribute over a wider range than those between the Nd–O and La–O lengths: 0.079—−0.019 Å (negative value means that the Eu–O is longer). The relatively long Nd–O bonds, such as Nd(1^{i})–O(15) and Nd(2^{ii})–O(25), are rather elongated in the europium(III) complex. On the other hand, some M–O bonds other than the elongated type of the same ligand are greatly shortened: M(1^{i})–O(16) and M(2)–O(21) are the examples.

The Eu(3) atom is regarded as being nine-coordinated. The average of the nine Eu–O bond lengths around it is 2.476 Å; this is about the same as the sum of the radii of tervalent Eu(CN=9) and O ions. No such discrepancy, as was found in the lanthanum(III) or the neodymium(III) complexes, was recognized. From this aspect, the Eu(3) atom is in pure nine-coordination geometry. Around the Eu(3) atom, except Eu(3)–O(35), all the Eu–O lengths are shorter than the corresponding Nd–O lengths of the neodymium(III) complex by 0.002 to 0.261 Å.

The general tendency of the change of the M–O bond lengths around the Eu(3) atom is about the same as that around the Eu(1) and Eu(2) atoms, although in more drastic way. The distance Eu(3)···O(35) is 0.969 Å longer than that of the neodymium(III) complex; consequently the O(35) atom of the europium(III) complex is perfectly out of the bonding distance. Moreover, it is thought to be even out of the sterically affecting region around the metal atom. On the other hand, the bond Eu(3)–O(36) is extremely short, 2.285(9) Å, although almost the same short Nd–O bond (2.312(10) Å) was already found in another polymeric-type carboxylato complex of neodymium(III).[2] Such disproportional changes of the M–O bond lengths of the same ligands are also found in ions **31**, and **32**. As shown in Table 4 (compared with the corresponding ions of the neodymium(III) complex), in the ion **31** the shorter bond is very shortened, while the longer one is shortened only a little, in the europium(III) complex. On the other hand, in the ion **32** the longer bond is more shortened.

According to the data shown in Table 6, four tridentate-type ions (except **33**) of the europium(III) complex are found to be in the forms approximately the same as the corresponding ones of the neodymium(III) or lanthanum(III) complexes; the grade of their deviations from the respective values of the standard types are not much different from those of the former two complexes.

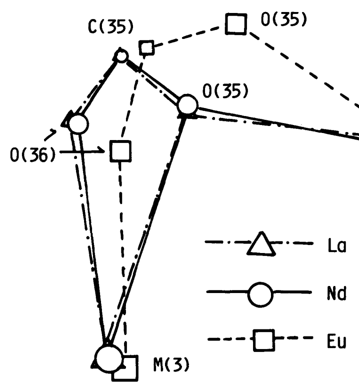


Fig. 8. The projection of **33** and the bonded metal atoms of the complexes to the (001) plane. The origin of the unit cell, the a-axis, and the scaling in length are taken commonly.

On the other hand (as shown in Fig. 8) in ion **33** of the europium(III) complex, bonds O(35)–Eu(2) and O(36)–C(35) are at the same side of bond C(35)–O(35) (*Z*-type), while the corresponding bonds of the neodymium(III) and lanthanum(III) complexes are at the opposite sides of the C(35)–O(35) bond from each other (*E*-type). As shown in Table 6, in the europium(III) complex, the bond length ratio 2(M–O′)/(M–O+M′–O′), and the bond angles C(35)–O(36)–Eu(3) (COM) and C(35)–O(35)–Eu(2) (CO′M′) are in the respective standard ranges of the *Z,Z*-type ion, while in those of the other two complexes the values are in the range of the tridentate-type ion, although they are a little deviated.

Thus, in the europium(III) complex, there are not only the unequal change of the respective M–O bond lengths, but also the change of the type of the coordinating ligand, depending on the change of the atomic number (i.e., the ionic size of the central metal atom). This is the first example of this kind of the discrepancy of the structure in the series of the apparently isomorphous lanthanoid complexes.

Such change of the M–O bond lengths in the complex of the smaller size metal causes some stress on the coordination geometry around the metal atom; also, the degree of the stress should affect the stability of the complex. As a result, in an europium(III) complex, the modification of the ligand form also took place, although its apparent crystal system did not change yet.

The infrared spectra of the series of the complexes were examined, and we found continuous changes in the intensities of the ν_{as}(COO) peaks as well as of the splitting of the ν_{s}(COO) band, depending on the increase of the metal atomic number.

The main peak of the ν_{as}(COO) band of lanthanum(III) and praseodymium(III) complexes appeared at about 1580 cm^{-1}, together with small shoulders at about 1565 and 1605 cm^{-1}, while in the neodymium(III) complex, both of the 1565 and 1580 cm^{-1} peaks were dominant (former one is stronger). On the other hand, in the europium(III) complex, only the 1565 cm^{-1} peak was dominant together with a new small peak at 1650 cm^{-1}; no shoulders could be recognized at 1580 and 1605 cm^{-1}.

The ν_{s}(COO) band of the lanthanum(III) and praseodymium(III) complexes appears at 1415 cm^{-1} as a broad peak, while in the neodymium(III) and europium(III) complexes, the peak splits clearly into three equal height ones at 1396, 1420, and 1440 cm^{-1}.

Although at present, it is impossible to assign these peaks exactly, at least we can deduce that there are some changes in the bonding modes (not only the continuous change of bond strengths) of the carboxylate ions. This depends on the increase in the atomic number of the central metal atom; this fact may correspond with the X-ray analysis results mentioned above.

The authors wish to thank Shin-Etsu Chemical Ind. Co. Ltd., for presenting us with the highly pure lanthanoid oxides.

References

1) R. C. Mehrotra and R. Bohra, "Metal Carboxylates," Academic Press, London, U. K. (1983), p. 757, and references cited in it.

2) S. Kondo, M. Shimoi, A. Ouchi, and T. Takeuchi, *Bull. Chem. Soc. Jpn.*, **55**, 2840 (1982).

3) Y. Koizumi, H. Sawase, Y. Suzuki, T. Takeuchi, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 1809 (1984).

4) H. Sawase, Y. Koizumi, Y. Suzuki, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2730 (1984), and the references cited in it.

5) M. S. Khiyalov, I. R. Amiraslanov, Kh. S. Mamedov, and E. M. Movsmov, *Koord. Khim.*, **7**, 445 (1981).

6) J. W. Bats, R. Kalus, and H. Fuess, *Acta Crystallogr., Sect. B*, **35**, 1225 (1979).

7) G. G. Sadikov, G. A. Kukina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **8**, 551 (1967).

8) G. G. Sadikov, G. A. Kukina, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **12**, 859 (1971).

9) A. Ouchi, M. Shimoi, and S. Kondo, *Bull. Chem Soc. Jpn.*, **58**, 1053 (1985).

10) A. S. Antsyshkina, M. A. Porai-Koshits, I. V. Ar-Khangel'ski, and L. A. Butman, *Koord. Khim.*, **2**, 565 (1976).

11) E. R. Birmingham, "Rare Earth Element Coordination Compounds, D5," of Gmelin's Handbook of Inorganic Chemistry, 8th ed (1984), p. 61.

12) "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallograghic Society of Japan, Tokyo (1967).

13) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.

14) Some additional data regarding bond lengths and bond angles, the final thermal parameters, and the final F_o–F_c tables are deposited as Document 8709 at the office of the editor of Bull. Chem. Soc. Jpn.

15) Although in many papers each coordination geometry (where the coordination number is higher than 7) around the lanthanoid or such heavy metal atom is approximated to some type, generally it is only an approximation and it is deformed from the ideal shape. Some other geometry may also be applicable in place of the written one. In the title complex, for the geometry of Nd(1) and Nd(2) atoms, the tricapped trigonal-prism is thought to be the best approximation, although they are deformed. When the geometry is assumed as schematically shown in Fig. 5 as 5.1 and 5.2, the dihedral angles between the side rectangulars are within the range of 55.8 to 63.5°, while those between the planes of the both end triangles and of the side rectangulars are within the range of 77.4 to 99.2°. The dihedral angles between two end triangle planes are 21.2 and 17.0°. Around the Nd(3) atom, if the O(33) and O(35) atoms are rejected, the coordination geometry of the metal atom is regarded as a deformed dodecahedron, where the atoms [O(32), O(34), O(W4), and O(36)] and [O(24), O(31), O(14), and O(W3)] are on the apexes of the both trapezia, respectively. Moreover, if only the O(35) is rejected, a tricapped trigonal-prism geometry can be adopted, where both end triangles are [O(36), O(W3), and O(14)] and [O(24), O(32), and O(34)], while O(W4), O(33), and O(31) are capped above the respective faces.

However, as the O(35) atom only in the lanthanum(III) complex is not very far from the metal atom (compared with the other ligated oxygen atoms), it is preferable to adopt a common structure available to all three complexes which includes the O(35) atom. In the two above-mentioned geometries, we cannot give any reasonable position around the assumed polyhedron to the O(35) atom. On the other hand, if we assume the *cis*-bicapped square-antiprism geometry around the M(3) atom, we can consider it reasonable as a cap above one side face, although the geometry is deformed to some grade. Moreover, as the monocapped square-antiprism is a more common geometry, we can imagine an additional capping atom above a side face, O(35), is less strongly ligated.

16) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976). The presented ionic radii are as follows (the valence of the metals is 3+, and of oxygen ion 2−; the coordination numbers of the metal ions (8, 9, or 10) are shown by the respective numbers (unit is in *l*/Å): r_{La}, 8=1.160, 9=1.216, 10=1.27 Å; r_{Nd}, 8=1.109, 9=1.163 Å; r_{Eu}, 8=1.066, 9=1.120 Å; r_{O}, 2=1.35 Å.

17) Hereafter, each carboxylate ion is numbered according to that of the chlorine atom in it; ions ***n*1**, ***n*2**, and ***n*3** (where *n*=1, 2, and 3) include the carboxylato group atoms of C(n1), O(n1), O(n2); C(n3), O(n3), O(n4); and C(n5), O(n5), O(n6), respectively.

18) J. Chatteric and P. Thornton, "Advances in Inorganic Chemistry and Radiochemistry," Academic Press, New York (1977), Vol. 20, p. 291.