The Bridging Tridentate-type Carboxylato Ligand in Isomorphous Guanidinium Di(μ-acetato)bis(triacetatoaqualanthanoidates(III)), $[(NH_2)_3C]_2$-$[M_2(CH_3CO_2)_8(H_2O)_2]$, (M=La, Ce, Pr, Nd, and Sm)

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The M-O bond lengths and some bond angles of the acetato ligands in the title compounds were compared with each other using their structural data as obtained by the single-crystal X-ray diffraction method. With the increase in the atomic number of the central metal atom, the length of the weakest M-O bond in the bridge increases, even though all the other M-O bonds are shortened. This fact can be explained as follows: as the number of ligating oxygen atoms around the central metal atom is almost at a maximum in these complexes, the sharing space of the tenth coordinating atom on the coordination sphere decreases when the radius of the central metal atom is shortened as a result of the lanthanoid contraction effect.

It has already been reported by some authors that the light and heavy lanthanoid complexes of the same ligand are often in different geometries around the central metal atom, where the coordination number of the former is higher than that of the latter.[1,2,3] Therefore, it is expected that, even in a series of isomorphous lanthanoid complexes, some bond lengths change systematically in the order of the atomic number of the central metal. For example, if the number of the coordinating atoms around the central metal atom is large, some ligating atom can be expected to leave farther from the center when the atomic number of the metal increases and its space on the coordination sphere decreases; however, no investigations of such a phenomenon yet been reported. Exact data about the problem are hard to obtain by the comparison of the structural data of only a few discrete members of the isomorphous complexes, especially those measured by different authors.

On the other hand, the structure of the carboxylato complexes is an interesting theme of research because of their complicated structures. As has been shown by Catterick, the ligands are in many types of coordination modes in the complexes.[4] They are classified as follows (some types of bonding are shown schematically in Fig. 1; the numbering scheme in the figure is also used in Table 4 and in its explanations); i) One metal atom is coordinated to one of the carboxyl oxygen atoms. ii) One metal atom is coordinated to each of the carboxyl oxygen atoms, thus forming four-membered chelate ring. iii) Two metal atoms are coordinated to each oxygen atom of a carboxyl group, bridged by the ligand. In this paper, the *Z, E* expression is used to show their conformation; if the other carboxyl oxygen and ligating metal atoms are bonded on the same side of a C-O bond of a carboxyl group, it is named *Z*, and if they are on different sides, it is shown by *E*. Therefore, the bridges are classified into these three groups; a) *Z, E*, b) *E, E*, and c) *Z, Z*, conformations, which correspond with the *syn-anti, anti-anti* and *syn-syn* classifications of Catterick respectively.[4] iv) One oxygen atom (O(1)) of a carboxylato chelate around a metal atom (M) is also bonded to another metal atom (M′), and, as a whole, the ligand acts as a tridentate. There are many examples of this iv type bridges in lanthanoid carboxylates.[5,6,7,9–18] Moreover, such bridging has also been reported in some manganese[19] and copper complexes,[20,21] as well as in calcium acetate.[22] In many cases, bridges of this type are deformed, and usually the O(1)-M bond is longer than O(2)-M or O(1)-M′; sometimes it is the longest M-O bond in the complex. Therefore, this bond may be removed first when the area of the coordination sphere decreases.

The change in some bond lengths and bond angles of the bridging carboxylato ligands can be expected to be affected not only by the change in the radius of the central metal atom, but also by the mutual steric interactions of the ligands. Therefore, in order to study the effect of the size of the central metal atom

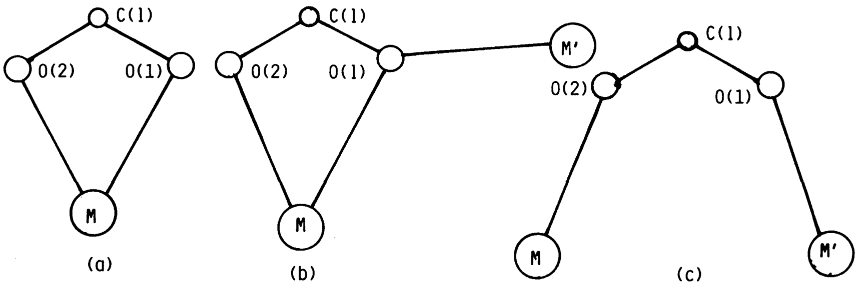

Fig. 1. Schematic presentation of ligands: a) chelating (type ii); b) tridentate type bridging (type iv); c) (*Z,Z*) type bridging (type iiic) carboxylate ligand.

on the coordination mode, avoiding the other steric influences, we have made a comparative structural study of the bridging acetato ligand, using the series of isomorphous complexes indicated in the title. Although Porai-Koshits has reported the structure of the cerium complex,[23] the data were not refined enough (R=0.177). Therefore, we have reinvestigated its structure, too.

Experimental

Synthesis of Guanidinium Di(μ-acetato)bis(triacetatoaqualanthanoidates(III)). The complexes in the title, where the metal is La, Ce, Pr, Nd, or Sm, were obtained by means of Canneri's method.[24] The crude product thus obtained was dissolved into water containing a little guanidinium acetate and then recrystallized by being left standing in a sillca-gel desiccator for several days. Although this synthetic method was also used in an attempt to obtain the same type of complexes of heavier lanthanoids, these attempts were not successful even when a large excess of guanidinium acetate was added; in these cases, only the guanidinium acetate and lanthanoid acetate (in their hydrated form) were precipitated separately. Anal. ($M_2C_{18}H_{40}O_{18}N_6$) M, C, H, N. (where M= La, Ce, Pr, Nd, or Sm).

Single-crystal X-ray Analysis. Crystals with dimensions of 0.3×0.3×0.4 mm³ of the lanthanum(III), cerium(III), and praseodymium(III), 0.4×0.4×0.3 mm³ of neodymium(III), and 0.3×0.3×0.3 mm³ of the samarium(III) complexes, were used for the measurement. All edges were ground off, but they were not shaped into spheres. They are isomorphous, and monoclinlc, with the space group $P2_1/n$; Z=2 for the formula $[(NH_2)_3C]_2[M_2(CH_3CO_2)_8(H_2O)_2]$. Other crystallographic data, some experimental conditions, and the final R values obtained by applying the anisotropic temperature factors,[25] are tabulated in Table 1.

The reflections were collected on a Rigaku AFC-6A automated four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation (0.7107 Å), at the scan speed 4° min⁻¹, by means of the θ-2θ scan technique. From the measured independent reflections, those with $(|F_o|)>3\sigma(|F_o|)$ were selected and were used for the calculations. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. All the calculations were carried out on a HITAC M-200H computer of the Computer Center of the University of Tokyo, using a local version of the UNICS program.[26] The atomic-scattering factors were taken from the table.[27]

Structure Determination. The structure of the lanthanum(III) complex was solved by the heavy-atom method. The positions of the central metal and some oxygen atoms were deduced from three-dimensional Patterson map, while all the other non-hydrogen atoms were found successively by repeated Fourier syntheses and by the block-diagonal least-squares method.

The structure of the other tetraacetato complexes were solved by assuming that their atomic coordinates were almost the same as those of the isomorphous lanthanum(III) complex. Therefore, at the first step, the final parameters for the lanthanum(III) complex were tentatively applied to them, and then they were refined as usual.

Results and Discussion

The final atomic parameters and their equivalent isotropic temperature factors are shown in Table 2, while some interatomic distances as well as bond angles are tabulated in Table 3. The perspective drawing of the complex around the central lanthanum atom, with the numbering scheme used in Tables 2 and 3, is shown in Fig. 2,[28] and the schematic bonding mode of the lanthanum(III) complex around a metal atom in Fig. 3.

The complex is in a dimer form. Each central-metal atom of the title complexes is deca-coordinated, being coordinated to ten oxygen atoms, and is in a distorted *cis*-bicapped cube (tetradecahedron) geometry including the weak M–O bonding from the bridging ligand. Each metal atom has three chelating acetato ligands, and each is bridged to the next metal atom by two "tridentate" acetato ligands.

In the titled complexes, as shown in Table 3, all the C–O bond lengths, as well as the O(nl)–C(nl)–O(n2) bond angles (where n=1, 2, 3, or 4), are not much different from each other, and they are almost the same as those of the other lanthanoid carboxylates.[5,6,11,12,15,18] All the M–O bond lengths of the same metal complex are about the same except for the long M–O(41), and the corresponding bond length of M–O(nn') (where n=1, 2, 3, or 4; n'=1 or 2) decreases depending on the order of the atomic number of the respective central metal, while that of M–O(41) increases in the same order.

Table 4 shows the selected bond lengths and bond angles of the coordinated carboxyl groups in the title complex as well as in some related lanthanoid carbox-

Table 1. Crystallographic data of the $[(NH_2)_3C]_2[M_2(CH_3CO_2)_8(H_2O)_2]$ complexes

M=	La	Ce	Pr	Nd	Sm
$a(l/\text{Å})$	18.398(8)	18.373(4)	18.364(9)	18.370(7)	18.409(4)
$b(l/\text{Å})$	8.524(2)	8.495(3)	8.458(3)	8.432(3)	8.405(2)
$c(l/\text{Å})$	11.003(5)	10.960(2)	10.931(5)	10.911(3)	10.830(3)
$\beta(\phi/°)$	106.60(4)	106.60(2)	106.65(3)	106.76(2)	106.92(1)
$U(v/\text{Å}^3)$	1653.7(12)	1637.3(8)	1626.6(12)	1618.3(10)	1603.2(7)
$D_m(d/\text{Mg m}^{-3})$	1.81(3)	1.83(3)	1.85(3)	1.89(3)	1.92(3)
$D_x(d/\text{Mg m}^{-3})$	1.82	1.84	1.86	1.88	1.92
$\mu(\text{Mo } K\alpha)(n/\text{mm}^{-1})$	2.62	2.85	3.04	3.28	3.76
F.W.	906.36	908.80	910.36	917.02	929.24
Number of reflections measured.	2068	2491	2471	2768	2589
Reflections used for the calculation	1801	2119	2150	2380	2198
Measured range $(\phi/°)$	3—42	3—46	3—46	3—48	3—47
R	0.030	0.032	0.037	0.033	0.030

TABLE 2. FINAL ATOMIC COORDINATES ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES, AND THEIR EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B_{eq}/Å^2)

1) Guanidinium di(μ-acetato)bis(triacetatoaqualanthanate(III))

Atom	x	y	z	B_{eq}/Å^{2} [a)]
La	5762.7(2)	3396.2(4)	4240.1(4)	1.8
O(W)	4440(3)	2190(5)	3912(5)	3.0
O(11)	6840(3)	4929(5)	3547(5)	3.2
O(12)	6420(3)	5965(5)	5043(4)	2.9
O(21)	5996(3)	820(5)	5623(5)	2.8
O(22)	6965(3)	2392(5)	5866(4)	2.5
O(31)	5343(3)	2038(7)	1991(5)	4.1
O(32)	6452(3)	1391(6)	3230(5)	3.6
O(41)	4615(3)	5761(5)	3821(4)	2.8
O(42)	5224(3)	5388(6)	2414(4)	3.3
N(1)	8063(3)	1073(7)	3900(6)	2.8
N(2)	9362(3)	1311(7)	4812(6)	2.9
N(3)	8536(4)	2219(7)	5901(6)	3.4
C(1)	8640(4)	1534(8)	4856(7)	2.7
C(11)	6809(4)	6058(9)	4262(7)	2.6
C(12)	7225(5)	7571(10)	4183(9)	5.1
C(21)	6680(4)	1146(8)	6135(7)	2.2
C(22)	7174(4)	35(9)	7117(8)	4.0
C(31)	5950(4)	1264(8)	2196(7)	2.8
C(32)	6060(5)	162(11)	1193(8)	5.0
C(41)	4726(4)	6079(8)	2771(7)	2.6
C(42)	4233(6)	7254(12)	1908(9)	6.1

2) Guanidinium di(μ-acetato)bis(triacetatoaquacerate(III))

Atom	x	y	z	B_{eq}/Å^{2} [a)]
Ce	5763.2(2)	3389.5(4)	4238.7(3)	1.7
O(W)	4445(3)	2196(6)	3896(5)	2.8
O(11)	6833(3)	4908(6)	3549(4)	3.1
O(12)	6413(3)	5949(6)	5042(4)	2.9
O(21)	5987(3)	823(6)	5604(4)	2.7
O(22)	6955(3)	2402(5)	5864(4)	2.4
O(31)	5343(3)	2051(7)	1991(5)	3.9
O(32)	6443(3)	1384(6)	3239(5)	3.3
O(41)	4607(3)	5781(6)	3828(4)	2.7
O(42)	5222(3)	5374(6)	2435(4)	3.0
N(1)	8060(3)	1067(8)	3906(6)	2.9
N(2)	9351(3)	1288(7)	4803(6)	2.8
N(3)	8531(3)	2211(8)	5895(6)	3.1
C(1)	8641(4)	1522(8)	4858(7)	2.3
C(11)	6804(4)	6041(8)	4259(7)	2.4
C(12)	7231(5)	7552(11)	4195(9)	4.8
C(21)	6671(4)	1143(8)	6132(6)	2.2
C(22)	7161(4)	33(10)	7111(8)	3.8
C(31)	5943(4)	1262(8)	2191(7)	2.5
C(32)	6062(5)	159(11)	1194(8)	4.8
C(41)	4725(4)	6084(8)	2780(6)	2.2
C(42)	4237(6)	7252(12)	1898(9)	5.6

3) Guanidinium di(μ-acetato)bis(triacetatoaquapraseodymate(III))

Atom	x	y	z	B_{eq}/Å^{2} [a)]
Pr	5764.2(2)	3381.0(5)	4238.3(4)	1.6
O(W)	4451(3)	2212(6)	3892(5)	2.6
O(11)	6830(3)	4872(7)	3547(5)	2.8
O(12)	6409(3)	5926(7)	5037(5)	2.7
O(21)	5977(3)	816(7)	5593(5)	2.7
O(22)	6949(3)	2405(6)	5856(5)	2.2
O(31)	5342(4)	2045(8)	1991(6)	4.0
O(32)	6441(3)	1373(7)	3251(6)	3.2
O(41)	4602(3)	5789(7)	3840(5)	2.7
O(42)	5222(3)	5358(7)	2451(3)	3.0
N(1)	8054(4)	1055(9)	3898(7)	2.9

N(2)	9346(4)	1269(8)	4796(6)	2.7
N(3)	8526(4)	2210(9)	5894(6)	2.9
C(1)	8641(4)	1506(9)	4856(7)	2.2
C(11)	6800(5)	6018(10)	4249(8)	2.6
C(12)	7228(6)	7522(12)	4193(11)	4.9
C(21)	6663(4)	1144(9)	6124(7)	2.1
C(22)	7158(5)	31(12)	7110(9)	3.7
C(31)	5944(4)	1256(9)	2194(8)	2.4
C(32)	6060(6)	155(12)	1197(9)	4.4
C(41)	4721(4)	6093(10)	2785(7)	2.0
C(42)	4235(7)	7283(14)	1902(10)	5.5

4) Guanidinium di(μ-acetato)bis(triacetatoaquaneodymate(III))

Atom	x	y	z	B_{eq}/Å^2 [a]
Nd	5766.3(2)	3369.3(4)	4237.5(3)	1.6
O(W)	4462(3)	2228(6)	3894(5)	2.5
O(11)	6821(3)	4862(6)	3536(5)	2.8
O(12)	6401(3)	5913(6)	5036(4)	2.5
O(21)	5974(3)	808(6)	5587(5)	2.5
O(22)	6944(3)	2397(6)	5852(4)	2.2
O(31)	5341(3)	2059(7)	1984(5)	4.0
O(32)	6436(3)	1367(6)	3251(5)	3.2
O(41)	4596(3)	5815(6)	3849(4)	2.7
O(42)	5215(3)	5343(6)	2467(5)	2.9
N(1)	8051(3)	1038(8)	3893(6)	2.8
N(2)	9343(3)	1251(7)	4790(6)	2.6
N(3)	8528(4)	2194(8)	5894(6)	2.9
C(1)	8637(4)	1493(8)	4853(7)	2.1
C(11)	6792(4)	6005(9)	4251(7)	2.3
C(12)	7226(5)	7512(11)	4200(9)	4.5
C(21)	6660(4)	1136(8)	6125(7)	2.1
C(22)	7152(5)	16(10)	7112(8)	3.5
C(31)	5940(4)	1249(9)	2197(7)	2.4
C(32)	6059(5)	149(12)	1189(8)	4.5
C(41)	4722(4)	6097(9)	2800(6)	2.1
C(42)	4253(6)	7290(13)	1908(9)	5.3

5) Guanidinium di(μ-acetato)bis(triacetatoaquasamarate(III))

Atom	x	y	z	B_{eq}/Å^2 [a]
Sm	5782.7(2)	3311.8(4)	4231.7(3)	1.8
O(W)	4474(3)	2257(6)	3866(5)	2.5
O(11)	6801(3)	4823(6)	3520(5)	2.9
O(12)	6390(3)	5856(6)	5045(5)	2.8
O(21)	5974(3)	750(6)	5555(5)	2.7
O(22)	6946(3)	2338(6)	5841(5)	2.4
O(31)	5351(3)	2076(7)	1945(6)	4.2
O(32)	6430(3)	1337(7)	3239(5)	3.3
O(41)	4566(3)	5914(7)	3883(5)	3.3
O(42)	5189(3)	5277(6)	2537(5)	3.0
N(1)	8037(3)	967(8)	3888(6)	2.9
N(2)	9328(3)	1199(8)	4760(6)	2.8
N(3)	8532(4)	2123(8)	5898(6)	3.0
C(1)	8634(4)	1432(8)	4845(7)	2.2
C(11)	6777(4)	5959(9)	4247(7)	2.4
C(12)	7204(6)	7484(11)	4210(10)	4.7
C(21)	6659(4)	1080(9)	6109(7)	2.3
C(22)	7142(5)	−27(10)	7122(8)	3.5
C(31)	5940(4)	1249(9)	2153(7)	2.4
C(32)	6075(5)	157(11)	1136(8)	4.4
C(41)	4712(4)	6113(9)	2844(7)	2.3
C(42)	4282(6)	7343(13)	1907(9)	5.7

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: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

TABLE 3. BOND LENGTHS AND BOND ANGLE OF THE COMPLEXES $[(NH_2)_3C]_2[M_2(CH_3CO_2)_8(H_2O)_2]$, WITH THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

Bond lengths M	La(l/Å)	Ce(l/Å)	Pr(l/Å)	Nd(l/Å)	Sm(l/Å)
M-O(11)	2.661(6)	2.634(6)	2.615(7)	2.605(6)	2.562(7)
M-O(12)	2.535(5)	2.512(5)	2.491(6)	2.477(5)	2.455(5)
M-O(21)	2.636(6)	2.607(6)	2.593(7)	2.579(6)	2.553(6)
M-O(22)	2.563(5)	2.539(5)	2.517(6)	2.501(5)	2.474(5)
M-O(31)	2.640(8)	2.621(9)	2.612(10)	2.602(9)	2.588(9)
M-O(32)	2.563(7)	2.539(7)	2.522(8)	2.507(7)	2.465(7)
M-O(41)	2.860(5)	2.880(5)	2.891(6)	2.919(5)	3.074(6)
M-O(42)	2.601(6)	2.571(6)	2.547(7)	2.529(7)	2.475(7)
M-O(41^{i})	2.529(8)	2.505(8)	2.483(9)	2.465(8)	2.401(9)
M-O(W)	2.570(5)	2.552(5)	2.533(6)	2.509(5)	2.488(5)
C(11)-O(11)	1.255(12)	1.248(11)	1.248(13)	1.251(12)	1.246(12)
C(11)-O(12)	1.268(14)	1.270(14)	1.272(16)	1.269(14)	1.274(14)
C(21)-O(21)	1.253(8)	1.254(8)	1.258(9)	1.258(8)	1.260(8)
C(21)-O(22)	1.258(9)	1.259(9)	1.260(11)	1.257(10)	1.253(10)
C(31)-O(31)	1.261(9)	1.256(9)	1.256(10)	1.258(10)	1.251(10)
C(31)-O(32)	1.248(11)	1.254(11)	1.255(13)	1.249(12)	1.259(12)
C(41)-O(41)	1.259(14)	1.254(14)	1.260(16)	1.254(14)	1.242(15)
C(41)-O(42)	1.244(11)	1.240(11)	1.249(12)	1.243(11)	1.244(11)
M···M^{i}	4.564(2)	4.563(1)	4.564(2)	4.577(1)	4.682(1)
Bond lengths M	La(ϕ/°)	Ce(ϕ/°)	Pr(ϕ/°)	Nd(ϕ/°)	Sm(ϕ/°)
O(11)-M-O(12)	49.88(17)	50.22(18)	50.57(20)	50.95(18)	51.64(19)
O(21)-M-O(22)	49.68(16)	50.07(17)	50.64(20)	50.83(18)	51.40(18)
O(31)-M-O(32)	49.4(2)	49.7(2)	49.9(2)	50.1(2)	50.6(2)
O(41)-M-O(42)	46.73(17)	46.53(17)	46.58(20)	46.28(18)	44.39(19)
O(41)-M-O(41^{i})	64.4(2)	64.3(2)	64.0(2)	63.8(2)	63.0(2)
O(W)-M-O(31)	71.4(2)	71.2(2)	71.2(2)	71.5(2)	72.0(2)
O(12)-M-O(21)	122.39(16)	122.39(16)	122.98(20)	123.17(18)	124.01(19)
O(21)-M-O(32)	71.1(2)	70.8(2)	70.7(2)	70.8(2)	70.9(2)
O(31)-M-O(42)	67.5(2)	67.4(2)	67.5(2)	67.2(2)	67.2(2)
M-O(41)-M^{i}	115.61(15)	115.67(16)	116.0(2)	116.20(17)	117.0(2)
O(11)-C(11)-O(12)	120.8(7)	120.6(7)	120.1(8)	120.6(7)	120.4(7)
O(21)-C(21)-O(22)	120.9(6)	120.2(7)	120.5(8)	120.3(7)	120.4(7)
O(31)-C(31)-O(32)	120.3(9)	119.5(9)	119.5(10)	119.5(9)	118.9(9)
O(41)-C(41)-O(42)	121.0(7)	121.0(7)	120.1(8)	120.7(8)	121.5(8)

Key to the symmetric operations: i: 1.0−x, 1.0−y, 1.0−z.

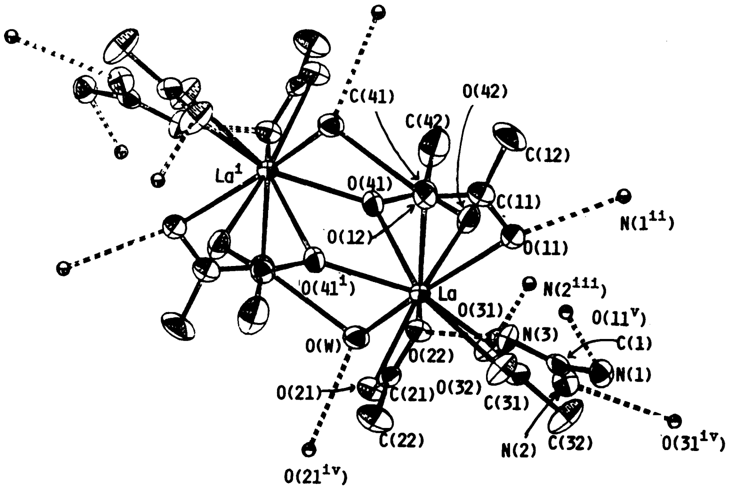

Fig. 2. A perspective drawing of $[(NH_2)_3C]_2[La_2(CH_3CO_2)_8(H_2O)_2]$ with the numbering scheme. Key to the symmetric operations: i, 1.0−x, 1.0−y, 1.0−z; ii, 1.5−x, 0.5+y, 0.5−z;, iii, −0.5+x, 0.5−y, −0.5+z; iv, 0.5+x, 0.5−y, 0.5+z; v, 1.5−x, −0.5+y, 0.5−z.

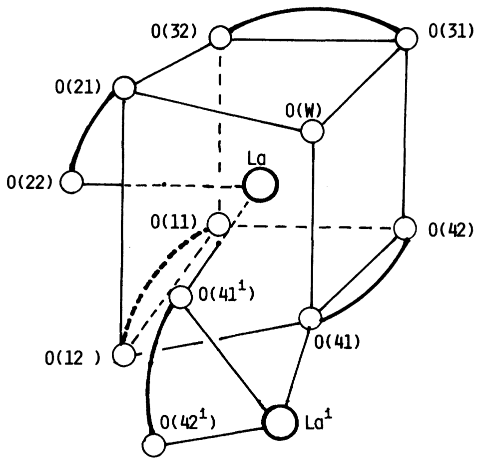

Fig. 3. Schematic presentation of the *cis*-bicapped cube geometry around a La(III) atom.

TABLE 4. THE INTERATOMIC DISTANCES AND BOND ANGLES OF SOME CARBOXYLATE LIGANDS

Type[a)]	Complex[b)]	Central metal	Average M-O[c)]	Elongation of M-O(1)[d)]	M-O(2) -C(1)	M-O(1) -C(1)	M′-O(1) -C(1)	Ref.[e)]
ch	1	Gd	2.468		93.9	92.8		5
ch	2	Ho	2.437		94.7	92.4		6
ch	3	Er	2.416		92.2	93.7		f
Z,E	4	Ho	2.341	62.5	140.3	61.8	145.2	8
Z,E	5	Er	2.336	63.8	142.2	60.4	146.4	8
E,E	4	Ho	2.388	89.9	130.3	18.8	133.7	8
E,E	5	Er	2.379	90.2	129.5	20.6	132.1	8
Z,Z	6	Pr	2.436	61.9	140.7	59.1	140.7	9
Z,Z	7	Ho	2.308	69.3	143.4	59.2	144.3	10
Z,Z	8	Sm	2.375	61.7	138.2	61.1	142.8	11
tri	18	Ca	2.475	−6.2	92.6	93.4	151.3	22
tri	1	Gd	2.439	5.4	97.8	92.9	151.7	5
tri	2	Ho	2.391	7.1	98.2	91.8	152.5	6
tri	3	Er	2.367	8.2	99.2	92.3	151.9	f
tri	9	Ce	2.591	−1.4	96.3	94.0	148.5	12
tri	10	Ce	2.497	7.6	99.7	89.3	168.6	13
tri	10	Ce	2.521	6.0	98.3	91.3	155.7	13
int	11	Nd	2.483	14.5	104.3	87.5	157.9	14
int	12	La	2.525	15.6	104.9	85.9	159.5	11
int	13	Pr	2.443	18.5	104.3	81.0	159.4	15
int	14	La	2.587	18.8	107.9	87.5	155.4	14
int	6	Pr	2.467	28.3	111.4	79.7	174.6	9
int	11	La	2.549	44.2	123.4	71.4	169.1	14
int	14	Nd	2.411	45.1	124.8	73.1	170.0	14
int	15	Er	2.292	58.2	136.0	70.3	157.9	16
int	7	Ho	2.306	53.5	128.6	68.4	164.6	9
int	16	Eu	2.391	63.1	140.3	62.5	152.6	17
int	17	Dy	2.260	66.3	138.8	60.8	163.3	18
	GL	La	2.563	11.6	102.6	89.7	150.3	
	GC	Ce	2.538	13.5	103.9	88.5	151.2	
	GP	Pr	2.515	15.0	105.2	88.2	151.2	
	GN	Nd	2.497	16.9	106.2	86.8	152.4	
	GS	Sm	2.438	26.1	111.9	82.3	156.3	

a) ch: chelate, tri: tridentate-type bridge, *E,E*, *E,Z*, and *Z,Z*: each type of bridge, int: intermediate of tri- and *Z,Z*-type bridges. b) The complexes including the respective ligands. 1, $[Gd_2(CH_3CO_2)_6(H_2O)_4]\cdot 4H_2O$; 2, $[Ho_2(CH_3CO_2)_6(H_2O)_4]\cdot 4H_2O$; 3, $[Er_2(CH_3CO_2)_6(H_2O)_4]\cdot 4H_2O$; 4, $[Ho(HCO_2)_3(H_2O)_2]_n$; 5, $[Er(HCO_2)_3(H_2O)_2]_n$; 6, $[Pr(CF_3CO_2)_3(H_2O)_3]_n$; 7, $[Ho(HL)_3(H_2O)_2]_n[Cr(NCS)_6]_n\cdot 2H_2O$ (HL=nicotic acid); 8, $[SmL_6(H_2O)_4]$; 9, $[Ce(CH_3CO_2)_3(H_2O)]_n$; 10, $[CeL'_3(H_2O)]_n$ (HL′=*m*-hydroxybenzoic acid); 11, $[LaL'_3(H_2O)_2]_n(HL')_n\cdot 2nH_2O$; 12, $[La_2L_6(H_2O)_4]$; 13, $[Pr_2L_6(H_2O)_4]$; 14, $[NdL'_3(H_2O)_2]_n(HL')_n\cdot 2nH_2O$; 15, $[ErL''_3(H_2O)_2]_n$ (HL″=isonicotic acid); 16, $[EuL''_2(H_2O)_4]_n(NO_3)_n$; 17, $[Dy_2L'''_6(H_2O)_4]$ (HL‴=*p*-aminobenzoic acid); 18, $[Ca(CH_3CO_2)_2(H_2O)]_n$; GL—GS, $[(NH_2)_3C]_2[M_2(CH_3CO_2)_8(H_2O)_2]$, where M of GL=La, GC=Ce, GP=Pr, GN=Nd, and GS=Sm. c) Average of the bond lengths of M-O(2) and M′-O(1). d) Each value (d) was obtained from the respective interatomic distance, l_1, l_2 or l_3, by means of the following equations: $d=\{(l_3-l_m)/l_m\}\times 100$ and $l_m=(l_1+l_2)/2$, where l_1=M-O(2), l=M′-O(1), and l_3=M-O(1). e) References. f) Although the structural data of this complex has already been reported by Porai-Koshits.[7)] These data are new ones obtained by the present authors.[28)]

ylates. The numbering scheme of the atoms used in the table as well as in its explanation presented below is shown in Fig. 1.

Typical examples of some bond lengths and bond angles of the four membered chelate ring of the lanthanoid carboxylates are shown in Table 4 as the "ch" group. In many cases, the two M-O-C bond angles are not the same; they are about 90 and 95° respectively, where the M-O, which is about 3% longer than the other one, has the larger M-O-C angle. Usually the planarity of the chelate ring is good, although there are some exceptions.

As shown in Table 4, the bridging ligands in lanthanoid formates (Complexes 4 and 5 in Table 4) have forms a little different from those of the other carboxylates. A special *Z,E*-type bridge is found in them, where the M-O(2)-C(1) (*Z*-side) and M′-O(1)-C(1) (*E*-side) bond angles are about 140 and 145° respectively, and where both the M and M′ atoms are almost on the carboxyl COO plane. The interatomic distance, M···O(1), from the *Z*-side metal to the *E*-side oxygen atom is about 3.8 Å, about 63% longer than the average of M-O(2) and M′-O(1), while the M···M′ distance is about 6.0 Å. Typical *E,E*-type bridges are found in the same formates. They are about symmetric, and the M-O(2)-C(1) and M′-O(2)-C(1) bond angles as well as the interatomic distances, M···O(1) and M′···O(2), are about the same; 129—132° and 4.51—4.53 Å respectively. The M···M′ distance is about 6.7 Å.

Typical examples of *Z,Z*-type bridge are shown as the *Z,Z* group in Table 4. As is shown in the table, this type of bridging is about symmetric in terms of bond lengths and bond angles: M–O(2) and M′–O(1); M···O(1) and M′···O(2); M–O(2)–C(1) and M′–O(1)–C(1), and M–O(1)–C(1) and M′–O(2)–C(1) are almost the same. However, in their real forms, M and M′ atoms are not strictly on the C(1), O(1), O(2) plane. The M···M′ distance is about 4.2···4.5 Å. As the M···O(1) distance is about 62% longer than the average of M–O(2) and M′–O(1), an effective bonding between them is not probable.

An idealized figure of the tridentate-type bridge, deduced from those of calcium acetate[22] and others, is shown in Fig. 1b; the ligand forms a chelate around the M atom, while another metal atom, M′, approaches the O(1) atom from the direction of the extension of O(2)···O(1); the M–O(2) and M′–O(1) bond lengths, as well as that of M–O(1) are not very different from each other; both of the metal atoms are almost on the carboxyl C(1), O(1), O(2) plane, and the expected C(1)–O(1)–M′ angle is about 150° (*E*-side). However, in many of the "tri"-type ligands shown in Table 4, M–O(2)–C(1) and M–O(1)–C(1) are each about 93—99°, the former commonly larger than the latter. The M–O(1) bond length is longer than M–O(2) or M′–O(1) by several per cent, the latter two being approximately the same, although M′–O(2) is much longer (more than 4 Å).

In the cases of more deformed tridentate-type bridges, they are classified separately in Table 4 as the "int"-group. They range from the one resembling a tridentate bridge to the one having almost the structure of the *Z,Z*-type bridge. In the "tri"-type bridge, the M′ atom is on the *E*-side, and in the *Z,Z*-type one, on the *Z*-side, although the C(1)–O(1)–M′ angle is about the same in both cases (140—150°). In the series of "int"-group members, the angle seems not to change in definite way, for the shift of the M′-atom position from the C(1), O(1), O(2) plane is irregular in them. On the other hand, the elongation of the M–O(1) length compared with the mean of the M–O(2) and M′–O(1) lengths increasing from 15 to 66%, the C(1)–O(2)–M bond angle increasing from 110 to 140°, and the C(1)–O(1)–M bond angle decreasing from 86 to 60°, they change in about the same order, while the position of the M′ atom moves from the *E* side to *Z* side, at least at the early stage of the series; their values of the typical tridentate- and the *Z,Z*-type bridges are 0 and 63%, 97 and 140°, and 92 and 60° respectively. Of course, there are some irregularities in some examples, especially when the positional deviations of the M and M′ atoms from the carboxyl C(1), O(1), O(2) plane are large. In the cases of the last four members of the "int"-group series, the elongation of the M–O(1) length is very large, almost the same as that of the *Z,Z*-type bridges, and no interaction between them can be expected; however, its symmetry in shape is not so good as in the *Z,Z*-type bridges.

The corresponding data from the ligands in the titled complexes are shown in the GL—GS column in Table 4. The bond lengths and bond angles of these complexes resemble those of the "int"-group ones. The deviations of their bond lengths and bond angles from the typical tridentate-type bridge are in the order of the increase on the atomic number of the central metal. Therefore, the bridge in the lanthanum complex has the most resemblance, and that of the samarium, the least similarity, to the tridentate bridge. However, even in the samarium complex, the elongation percentage of M–O(1) is about 26%, and the M–O(2)–C(1) and M–O(1)–C(1) angles are 111.9 and 82.3° respectively; these values correspond with those of some early members in the "int"-group series shown in the table. Therefore, the M–O(1) bonding of the titled complexes is expected to be effective, although such bond may be weaker than those of the typical tridentate ones and the bonds are weakened in the order of the atomic number of the central metal. As the geometrical environments of the bridge, except for the size of the central metal atom, are about the same in all these isomorphous complexes, this change in the M–O(1) length can be expected to be concerned mainly with the contraction of the central-metal atomic radius.

Although this is only one example, the authors have recognized that, in a series of lanthanoid complexes where the coordination number of the central metal atom is large, the weakest bonding is continuously weakened depending on the decrease in the coordination sphere; this fact can also be expressed by saying that the coordination number of the central metal atom of such complexes decreases continuously depending on the increase in the atomic number of the central metal.

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