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The Crystal and Molecular Structure of Heavy Lanthanoid(III) Chloroacetates in the Hydrated Form, $[M_3(ClCH_2CO_2)_9(H_2O)_4]_n \cdot nH_2O$ (M=Gd, Dy, Er, and Yb)

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The crystal and molecular structures of the chloroacetato complexes of gadolinium(III), erbium(III), and ytterbium(III) indicated in the title were determined by the single-crystal X-ray diffraction method. In addition to these three complexes, the isomorphous dysprosium(III) salt was also obtained. Their chemical composition, $M_3L_9 \cdot 5H_2O$ (where M=Gd, Dy, Er, or Yb; HL=chloroacetic acid), is the same as that of the light lanthanoid(III) (La—Eu) chloroacetates, though the latter crystals are monoclinic. The cell constants of the ytterbium(III) salt, for example, are: triclinic, space group $P\bar{1}$, a=13.278(10), b=13.624(6), c=12.067(4) Å α=96.62(3), β=100.68(5), γ=67.40(4)°, Z=2 (including 6 metal atoms). There are three kinds of crystallographically independent metal atoms; Yb(1), Yb(2), and Yb(3): Yb(1) and Yb(2) are octa-coordinated (square-antiprism geometry) and Yb(3) is ennea-coordinated (monocapped square-antiprism geometry). Two oxygen atoms around the last type of the metal atom are the more separated in the higher atomic-number lanthanoid(III) complex, while the other M–O bond lengths decrease, depending on the increase of the metal atomic number. The metal atoms are bridged by carboxylate ions in a chair form along the [111] axis, though in a way different from that of the light lanthanoid(III) complexes.

The variety of the coordination geometries of the central metal atom as well as the carboxylate ions in the lanthanoid carboxylate complexes are one of the interesting thème of structural chemistry.[1] Among them, chloroacetates of light lanthanoid(III) (La through Eu) were found to have a complicated linear polymeric structure bridged by carboxylate ions.[2]

Using the same synthetic technique, the chloroacetates of heavy lanthanoid(III) (Gd through Yb) in the hydrated form were obtained. From a preliminary check of their single crystals by the X-ray diffraction method, they were found to be isomorphous with each other since their cell constants resemble each other. However, their crystal system is triclinic, not monoclinic like that of the light lanthanoid(III) salts, though the results of their chemical analyses show that the heavy and light lanthanoid(III) chloroacetates have the same chemical composition: $ML_3 \cdot 5/3\ H_2O$ (where M=Gd, Dy, Er, or Yb, as well as La, Pr, Nd, or Eu; HL=chloroacetic acid).[2]

It was recognized in many other cases that the crystals of the complexes of the heavy and light lanthanoids(III) are different from each other, even when the used synthetic technique is the same. For example, in the case of acetates, the cerium(III) salt is in a linear polymeric structure, while the holmium(III) salt is in a dimer form.[3,4] In cases of the Lewis base (L′) adducts of tris(O,O'-dialkyl dithiophosphato)lanthanoid(III) ($Ln(R_2dtp)_3$), light and heavy lanthanoids(III) gave $[Ln(R_2dtp)_3L'_2]$ and $[Ln(R_2dtp)_2L'_3][R_2dtp]$ type complexes, respectively. The border of both series of complexes exists between praseodymium and neodymium in the case of the triphenylphosphine oxide adducts,[5] and at gadolinium in the case of the benzamide adducts (both types of adducts were obtained for gadolinium).[6,7]

Therefore, it is interesting to examine the difference in the structures between the light and heavy lanthanoid(III) complexes of the same ligand; we have determined the crystal and molecular structures of the latter complexes by the X-ray diffraction technique using their single crystals.

Experimental

Synthesis of Ytterbium(III) Chloroacetate, $[Yb_3(ClCH_2CO_2)_9(H_2O)_4] \cdot H_2O$, and Its Isomorphous Complexes. The synthetic technique is about the same as that for the neodymium(III) salt.[2] Ytterbium(III) hydroxide was obtained by mixing aqueous solutions of ytterbium(III) chloride (obtained by dissolving ytterbium(III) oxide (Yb_2O_3, 0.39 g, 1.0 mmol) in excess of hydrochloric acid), and of excess sodium hydroxide. After the ytterbium hydroxide and chloroacetic acid (0.57 g, 6.0 mmol) were mixed and stirred for several minutes, the obtained solution was filtered and the filtrate was left standing in a silica gel desiccator for several days. About two-thirds of the water was removed and crystals were deposited. They were first separated and dried in the open air overnight and then kept in a sealed glass bottle. They were stable there at least for several months. Yield: 0.75 g, 78%.

Applying the same technique, gadolinium(III), dysprosium(III), and erbium(III) salts, which were isomorphous with each other, were obtained in about the same yield. Anal. ($M_3L_9 \cdot 5H_2O = M_3C_{18}H_{28}O_{23}Cl_9$), M, C, H (where M=Gd, Dy, Er, or Yb).

It was reported that the number of water molecules in the lanthanoid chloroacetates $ML_3 \cdot n'H_2O$ were: n'=4 for the Ho salt, 5 for the Er salt, and 3 for the Tm, Yb and Lu salts.[8] However, according to our synthetic method, only one type of crystal, $M_3L_9 \cdot 5H_2O$, could be obtained for the heavy lanthanoids(III).

Single-Crystal X-Ray Analysis. The crystals used for the analysis were obtained by the above-mentioned syntheses. From the crystallographic data obtained by the single-crystal X-ray diffraction technique, the four above-mentioned chloroacetates were all found to be isomorphous with each other. They are triclinic with the space group of $P\bar{1}$, $Z=2$ (for the title formula with $n=1$; six metal atoms are included in a unit cell).

Their crystallographic data are given in Table 1 and some experimental conditions to obtain the intensity data are tabulated in Table 2. The reflections were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation (the scan speed was 4° min^{-1} (θ)), using the ω—2θ scan technique.

Structure Determination. The structure of the ytterbium(III) complex was solved by the heavy-atom method. The positions of the metal and some oxygen atoms were deduced from a three-dimensional Patterson map; the other non-hydrogen atoms were located successively by repeated Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by a block-diagonal least-squares method. At the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The structures of the isomorphous complexes were solved starting with the final parameters of the ytterbium(III) complex, and were refined in the same way. All the hydrogen atoms were fixed at the calculated positions assuming their C-H bond lengths to be 1.08 Å and their B_{iso}'s to be 8.0.

As shown in Table 3, the temperature factors of Cl(22), Cl(31), Cl(32), and Cl(33) atoms of all the complexes are large, and the apparent bond lengths of their C(36)-Cl(33) are a little too short. Attempts to determine the disorders of these atoms (i.e., to divide each atomic position into two with respective appropriate occupancy factors for them) were not successful; all the trials did not give any improvement to their temperature factors and to their R value. It is likely that these atoms are distributed in a wide region around the most probable position. Thus, these chlorine atoms as well as some carbon atoms of the ligands which take their positions far from the central metal atom are not well fixed; such position ambiguity regarding some ligand atoms was often encountered in structure determinations of some lanthanoid(III) complexes.[2,6,7,9–11)]

All the calculations were carried out on a HITAC M-680H at the Computer Center of the University of Tokyo using a 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 202A grating infrared spectrophotometer using Nujol and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters and their equivalent thermal parameters of the complexes are listed in

Table 1. Crystallographic Data of the Complexes $[M_3(ClCH_2CO_2)_9(H_2O)_4]_n\cdot nH_2O$ (M=Gd, Dy, Er, and Yb)

M=	Gd	Dy	Er	Yb
F.W. ($n=1$)	1403.24	1419.00	1433.27	1450.61
$a(l/\text{Å})$	13.428(6)	13.418(12)	13.333(5)	13.278(10)
$b(l/\text{Å})$	13.736(6)	13.722(17)	13.671(4)	13.624(6)
$c(l/\text{Å})$	12.185(5)	12.162(11)	12.111(3)	12.067(4)
$\alpha(\phi/°)$	96.55(4)	96.63(9)	96.65(2)	96.62(3)
$\beta(\phi/°)$	100.65(4)	100.72(8)	100.67(3)	100.68(5)
$\gamma(\phi/°)$	67.23(3)	67.13(7)	67.35(2)	67.40(4)
$U(v/\text{Å}^3)$	2034.3(16)	2025(4)	1999.6(11)	1978(2)
$D_m(d/\text{Mg m}^{-3})$	2.29(3)	2.31(3)	2.39(3)	2.41(3)
$D_x(d/\text{Mg m}^{-3})$	2.29	2.33	2.38	2.44
$\mu(\text{Mo } K\alpha)(n/\text{mm}^{-1})$	5.65	6.36	7.16	8.09

Table 2. Some Experimental Conditions to Obtain the Reflection Intensities

Metal	Gd	Er	Yb
Number of reflections measured	7211	6957	7038
Reflections used for the calculation[a)]	6104	5978	5952
Measured range ($2\theta/°$)	3—50	3—50	3—50
R[b)]	0.050	0.063	0.045
R_{weight}[b)]	0.061	0.075	0.054
Size of the crystal (v/mm^3)	0.3×0.25×0.2	0.3×0.2×0.15	0.3×0.25×0.25
Scan width ($\theta/°$)	$1.04+0.5\tan\theta$	$1.20+0.5\tan\theta$	$1.15+0.5\tan\theta$
S[c)]	1.696	2.115	1.592

a) Reflections with $|F_o|>3\sigma(|F_o|)$ were used. b) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_{\text{weight}}=[\Sigma(|F_o|-F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w=1/[\{\Sigma(|F_o|)\}^2+(F_{\text{weight}}\times F_o)^2]$, $F_{\text{weight}}=0.020$. c) $S=[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o= number of reflections, N_p=number of parameters.

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

3.1 Gadolinium Complex					3.2 Erbium Complex				
Atom	x	y	z	B_{ep}/Å^2 a)	Atom	x	y	z	B_{eq}/Å^2 a)
Gd(1)	573.6(4)	712.9(4)	1406.1(4)	2.1_7	Er(1)	568.8(5)	703.8(5)	1401.4(5)	2.0_8
Gd(2)	3043.5(4)	1647.4(3)	3411.1(4)	2.0_7	Er(2)	3048.6(5)	1638.6(5)	3394.5(5)	2.0_7
Gd(3)	4855.8(4)	3719.5(3)	3871.4(4)	2.0_7	Er(3)	4859.5(5)	3715.7(5)	3843.0(5)	2.1_9
O(11)	2045(6)	−123(7)	286(7)	3.9_2	O(11)	2007(9)	−111(10)	294(9)	4.1_3
O(12)	2476(5)	663(5)	1834(6)	2.8_0	O(12)	2452(7)	675(7)	1866(8)	2.5_2
O(13)	1337(7)	−1047(6)	2105(6)	3.8_2	O(13)	1304(9)	−1017(8)	2102(9)	3.6_0
O(14)	318(6)	−965(5)	462(6)	2.6_6	O(14)	277(8)	−935(7)	456(8)	2.7_1
O(15)	113(7)	2488(6)	1306(7)	4.0_1	O(15)	149(9)	2425(8)	1285(9)	3.5_7
O(16)	1319(6)	2925(5)	2598(6)	3.1_4	O(16)	1336(8)	2893(8)	2607(9)	3.0_8
O(21)	3350(6)	2320(6)	1873(6)	3.4_3	O(21)	3351(9)	2302(8)	1876(8)	3.3_4
O(22)	3729(7)	3773(6)	2220(7)	4.2_2	O(22)	3750(10)	3759(8)	2206(9)	3.9_3
O(23)	722(9)	1101(7)	3256(7)	5.4_2	O(23)	654(11)	1087(9)	3211(9)	4.5_9
O(24)	1748(6)	1730(7)	4529(7)	4.4_2	O(24)	1778(9)	1670(9)	4445(9)	3.8_7
O(25)	4887(6)	626(6)	3204(7)	3.5_0	O(25)	4858(8)	685(8)	3216(9)	3.2_8
O(26)	5514(7)	1927(6)	3591(7)	3.9_7	O(26)	5548(9)	1961(7)	3580(9)	3.5_3
O(31)	3095(6)	3286(5)	4129(6)	2.8_0	O(31)	3108(8)	3250(7)	4096(8)	2.8_9
O(32)	3104(6)	4862(5)	4479(7)	3.3_1	O(32)	3144(9)	4814(8)	4431(9)	3.5_6
O(33)	4775(6)	5465(5)	3944(6)	3.1_6	O(33)	4782(8)	5423(7)	3925(9)	3.0_9
O(34)	5038(6)	6939(5)	4288(6)	3.0_2	O(34)	5052(8)	6879(8)	4353(8)	3.1_0
O(35)	5850(7)	3683(7)	2415(7)	4.4_0	O(35)	5830(10)	3673(10)	2399(10)	4.4_3
O(36)	7505(7)	2463(7)	2710(7)	4.4_9	O(36)	7516(10)	2467(10)	2721(10)	4.5_4
C(11)	2728(8)	145(8)	946(9)	2.8_6	C(11)	2702(11)	170(11)	976(11)	2.3_5
C(12)	3859(9)	−110(10)	714(11)	4.3_7	C(12)	3859(13)	−129(15)	735(15)	4.4_2
C(13)	888(9)	−1486(8)	1297(9)	2.9_9	C(13)	864(12)	−1460(11)	1299(12)	2.8_5
C(14)	995(11)	−2596(9)	1313(10)	4.3_9	C(14)	986(16)	−2584(12)	1302(15)	4.5_7
C(15)	523(8)	3125(7)	1856(9)	2.6_2	C(15)	553(12)	3100(11)	1828(12)	2.8_2
C(16)	−109(11)	4249(9)	1488(12)	4.4_4	C(16)	−76(15)	4215(12)	1446(16)	4.2_5
C(21)	3344(9)	3181(9)	1592(10)	3.3_0	C(21)	3363(12)	3147(12)	1593(13)	3.0_5
C(22)	2901(12)	3507(11)	419(10)	4.9_9	C(22)	2913(18)	3501(16)	384(15)	5.4_4
C(23)	955(9)	1489(9)	4209(9)	3.1_9	C(23)	940(12)	1477(11)	4176(12)	2.7_9
C(24)	138(14)	1637(17)	4977(15)	8.1_6	C(24)	141(17)	1655(20)	4975(18)	6.6_2
C(25)	5629(8)	986(7)	3307(8)	2.3_9	C(25)	5628(11)	1038(11)	3317(11)	2.5_1
C(26)	6768(9)	278(8)	3133(10)	3.3_4	C(26)	6755(13)	285(12)	3139(14)	3.4_3
C(31)	2671(8)	4218(8)	4490(8)	2.5_3	C(31)	2683(11)	4186(11)	4451(12)	2.8_9
C(32)	1629(11)	4496(11)	4958(12)	5.2_6	C(32)	1629(15)	4479(15)	4917(16)	5.1_0
C(33)	4909(8)	6223(7)	3627(8)	2.3_3	C(33)	4916(11)	6190(11)	3608(12)	2.5_9
C(34)	4903(13)	6246(11)	2415(10)	5.2_5	C(34)	4913(20)	6252(16)	2421(15)	5.9_1
C(35)	6750(11)	3117(9)	2150(11)	4.4_9	C(35)	6727(16)	3113(13)	2125(15)	4.4_0
C(36)	6919(19)	3231(15)	992(16)	9.5_2	C(36)	6939(27)	3181(21)	925(23)	9.3_3
Cl(11)	4246(3)	−1108(3)	−352(3)	4.8_2	Cl(11)	4235(4)	−1102(4)	−333(4)	4.7_5
Cl(12)	2037(4)	−3334(3)	2336(4)	6.5_2	Cl(12)	2026(5)	−3314(4)	2348(5)	6.3_4
Cl(13)	578(4)	5105(3)	1969(4)	7.1_9	Cl(13)	589(5)	5085(4)	1952(5)	6.7_1
Cl(21)	2093(4)	2854(4)	−357(3)	7.3_6	Cl(21)	2097(5)	2842(5)	−384(4)	7.3_3
Cl(22)	343(8)	2311(11)	6198(7)	22.2	Cl(22)	405(9)	2386(12)	6193(8)	17.7
Cl(23)	6837(3)	−951(2)	2454(3)	5.5_5	Cl(23)	6806(4)	−946(3)	2456(4)	5.3_2
Cl(31)	1413(5)	5522(5)	5955(5)	11.8	Cl(31)	1460(7)	5500(7)	5963(7)	12.0
Cl(32)	5316(9)	7182(6)	2048(4)	18.7	Cl(32)	5368(13)	7182(8)	2102(6)	19.6
Cl(33)	6546(9)	4320(5)	465(6)	17.1	Cl(33)	6556(13)	4322(7)	458(8)	17.8
O(W1)	−1172(6)	874(7)	1658(7)	4.1_6	O(W1)	−1153(9)	891(9)	1649(9)	4.0_0
O(W2)	3594(6)	−116(6)	4062(7)	3.8_0	O(W2)	3618(9)	−102(8)	4008(9)	3.6_6
O(W3)	2364(8)	8803(7)	4301(7)	4.9_7	O(W3)	2390(11)	8798(10)	4322(10)	4.9_4
O(W4)	6809(5)	3200(5)	4674(6)	2.7_8	O(W4)	6760(8)	3237(7)	4667(8)	2.6_8
O(W5)	4082(7)	1529(6)	5382(6)	3.5_5	O(W5)	4075(9)	1522(8)	5344(8)	3.3_9

Table 3. Continued.

3.3 Ytterbium Complex

Atom	x	y	z	$B_{eq}/Å^2$ a)	Atom	x	y	z	$B_{eq}/Å^2$ a)
Yb(1)	568.8(3)	702.3(3)	1398.7(4)	1.6_6	C(21)	3362(8)	3135(8)	1595(10)	2.4_3
Yb(2)	3047.3(3)	1636.5(3)	3385.3(4)	1.6_9	C(22)	2921(12)	3486(10)	405(11)	3.9_8
Yb(3)	4862.6(4)	3714.8(3)	3828.7(4)	1.8_5	C(23)	929(8)	1469(8)	4141(10)	2.5_8
O(11)	2010(6)	−108(7)	307(6)	3.1_6	C(24)	144(13)	1663(15)	4981(13)	5.8_3
O(12)	2438(5)	689(5)	1879(6)	2.2_5	C(25)	5629(8)	1043(7)	3315(8)	1.9_1
O(13)	1318(7)	−1020(5)	2096(7)	2.9_4	C(26)	6764(9)	277(8)	3138(10)	2.7_9
O(14)	271(6)	−930(5)	451(6)	2.3_7	C(31)	2669(8)	4170(8)	4433(9)	2.0_8
O(15)	143(7)	2421(6)	1282(7)	3.0_3	C(32)	1614(11)	4498(12)	4912(13)	4.9_9
O(16)	1341(6)	2877(5)	2599(7)	2.5_7	C(33)	4928(7)	6182(7)	3653(8)	1.6_7
O(21)	3333(7)	2295(6)	1866(6)	2.8_9	C(34)	4920(13)	6248(10)	2428(11)	4.4_4
O(22)	3740(7)	3739(6)	2215(7)	3.4_2	C(35)	6743(11)	3102(9)	2116(11)	3.7_2
O(23)	660(7)	1071(6)	3207(7)	3.4_0	C(36)	6948(20)	3201(15)	942(16)	8.6_1
O(24)	1793(6)	1660(7)	4440(6)	3.0_0	Cl(11)	4236(3)	−1111(3)	−328(3)	4.2_3
O(25)	4854(6)	706(6)	3211(7)	2.8_5	Cl(12)	2032(3)	−3310(3)	2349(4)	5.5_5
O(26)	5561(6)	1966(6)	3587(7)	2.9_2	Cl(13)	591(4)	5078(3)	1938(4)	5.8_0
O(31)	3105(6)	3217(5)	4090(6)	2.6_3	Cl(21)	2094(4)	2843(4)	−393(3)	6.5_8
O(32)	3148(6)	4795(5)	4420(6)	2.5_2	Cl(22)	415(6)	2419(8)	6189(5)	14.0
O(33)	4781(6)	5401(6)	3898(7)	2.9_9	Cl(23)	6801(3)	−942(2)	2459(3)	4.6_2
O(34)	5058(6)	6865(6)	4370(6)	2.5_3	Cl(31)	1476(5)	5482(5)	5965(5)	10.6
O(35)	5827(7)	3664(7)	2383(7)	3.9_4	Cl(32)	5403(9)	7186(6)	2127(5)	17.3
O(36)	7521(7)	2468(7)	2723(8)	4.0_7	Cl(33)	6575(9)	4326(5)	454(6)	16.0
C(11)	2703(8)	154(8)	964(9)	2.1_0	O(W1)	−1140(6)	874(7)	1651(7)	3.2_0
C(12)	3855(10)	−120(10)	751(11)	3.8_2	O(W2)	3630(6)	−112(6)	3988(7)	3.2_5
C(13)	870(9)	−1460(8)	1304(9)	2.4_6	O(W3)	2389(8)	8798(7)	4315(7)	4.0_6
C(14)	980(11)	−2578(8)	1315(11)	3.8_2	O(W4)	6746(6)	3265(5)	4662(6)	2.4_6
C(15)	565(8)	3070(7)	1844(9)	2.2_3	O(W5)	4075(7)	1514(6)	5342(6)	3.0_7
C(16)	−107(11)	4206(8)	1441(12)	3.5_8					

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

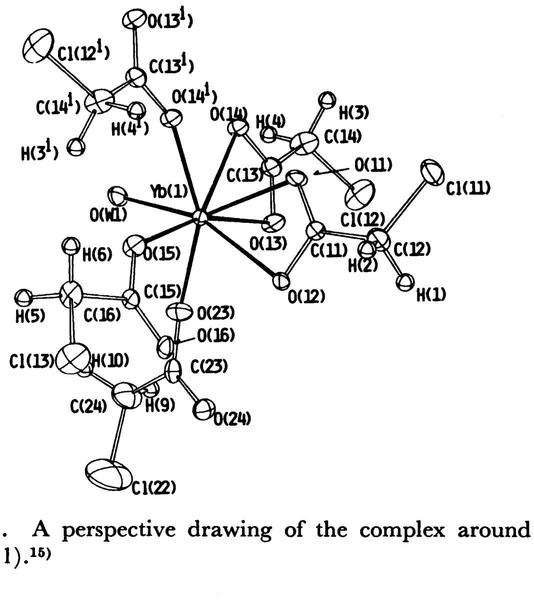


Fig. 1. A perspective drawing of the complex around Yb(1).[15]

Table 3 (3.1—3.3), while selected bond lengths and angles are given in Table 4.[14] Perspective drawings of the ytterbium(III) complex around the metal atoms (Yb(1), Yb(2), and Yb(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.

Schematic presentations of the coordination geometries of the ligating atoms around the Yb(1), Yb(2), and Yb(3) atoms are shown in Fig. 5 (5.1—5.3), respectively.

The structures of these complexes are completely different from those of the light lanthanoid(III) complexes, as mentioned in the following paragraph.

In these complexes, one water oxygen atom is not coordinated to any metal atoms, though all of the water molecules are coordinated in the light lanthanoid(III) salts. The coordination numbers of the metal atoms of the title complexes are smaller than those of the light lanthanoid(III) ones; there are two octa- and one ennea-coordinated metal atoms in the former complexes, while two ennea- and one deca- (or ennea-) coordinated metal atoms in the latter complexes.

The Yb(1) and Yb(2) atoms are octa-coordinated (square-antiprism geometry) while the Yb(3) atom is ennea-coordinated (monocapped square-antiprism geo-

Table 4. Interatomic Distances and Bond Angles of the Complexes, with the Standard Deviations in Parentheses[15)]

M	Gd(l/Å)	Er(l/Å)	Yb(l/Å)	M	Gd(ϕ/°)	Er(ϕ/°)	Yb(ϕ/°)
M(1$^{\mathrm{i}}$)…M(1)	4.009(2)	4.044(2)	4.023(2)	O(11)-M(1)-O(12)	52.0(3)	53.4(4)	53.7(3)
M(1)…M(2)	4.266(2)	4.240(2)	4.218(3)	O(12)-M(1)-O(15)	84.0(3)	82.9(4)	82.7(3)
M(2)…M(3)	4.339(2)	4.316(2)	4.305(2)	O(15)-M(1)-O(14$^{\mathrm{i}}$)	79.3(3)	79.3(4)	79.3(3)
M(3)…M(3$^{\mathrm{ii}}$)	4.306(2)	4.321(2)	4.325(2)	O(11)-M(1)-O(14$^{\mathrm{i}}$)	75.7(3)	74.3(4)	74.6(3)
M(1)-O(11)	2.443(10)	2.383(14)	2.365(9)	O(13)-M(1)-O(14)	52.0(3)	53.0(4)	53.3(3)
M(1)-O(12)	2.487(8)	2.456(10)	2.436(8)	O(14)-M(1)-O(W1)	74.3(3)	74.3(4)	73.9(3)
M(1)-O(13)	2.419(8)	2.365(11)	2.356(8)	O(W1)-M(1)-O(23)	81.6(4)	79.4(5)	79.3(4)
M(1)-O(14)	2.572(8)	2.529(10)	2.516(8)	O(13)-M(1)-O(23)	79.7(4)	79.3(5)	78.9(3)
M(1)-O(15)	2.284(8)	2.215(11)	2.203(8)	O(12)-M(2)-O(16)	77.5(3)	77.0(4)	76.3(3)
M(1)-O(23)	2.246(11)	2.186(15)	2.174(11)	O(16)-M(2)-O(24)	73.7(3)	73.2(4)	73.5(3)
M(1)-O(W1)	2.342(9)	2.283(13)	2.264(9)	O(24)-M(2)-O(W2)	73.6(3)	73.7(5)	73.9(3)
M(1)-O(14$^{\mathrm{i}}$)	2.364(9)	2.320(12)	2.301(9)	O(12)-M(2)-O(W2)	75.3(3)	74.6(4)	74.5(3)
M(2)-O(12)	2.401(8)	2.343(11)	2.311(8)	O(21)-M(2)-O(25)	74.8(3)	74.5(4)	74.6(3)
M(2)-O(16)	2.413(7)	2.371(9)	2.349(7)	O(25)-M(2)-O(W5)	75.5(3)	74.6(4)	74.5(3)
M(2)-O(21)	2.346(11)	2.304(15)	2.282(11)	O(W5)-M(2)-O(31)	68.4(3)	68.6(4)	68.4(3)
M(2)-O(24)	2.362(12)	2.285(15)	2.265(11)	O(21)-M(2)-O(31)	77.4(3)	77.1(5)	77.9(3)
M(2)-O(25)	2.371(7)	2.296(10)	2.279(7)	O(22)-M(3)-O(26)	86.6(3)	87.5(4)	87.6(3)
M(2)-O(31)	2.341(7)	2.293(10)	2.246(8)	O(26)-M(3)-O(W4)	77.2(2)	76.6(3)	76.9(3)
M(2)-O(W2)	2.425(9)	2.366(12)	2.361(8)	O(W4)-M(3)-O(33)	87.3(2)	86.6(4)	86.2(3)
M(2)-O(W5)	2.533(9)	2.489(13)	2.488(10)	O(22)-M(3)-O(33)	97.7(3)	98.0(4)	98.6(3)
M(3)-O(22)	2.273(10)	2.235(13)	2.217(10)	O(31)-M(3)-O(32)	48.9(3)	49.1(4)	49.3(3)
M(3)-O(33)	2.350(8)	2.287(11)	2.250(8)	O(22)-M(3)-O(35)	72.7(4)	72.1(5)	72.9(4)
M(3)-O(26)	2.279(7)	2.221(9)	2.206(7)	O(26)-M(3)-O(35)	84.8(3)	83.9(5)	83.8(4)
M(3)-O(31)	2.730(9)	2.721(13)	2.748(10)	O(33)-M(3)-O(35)	77.2(3)	77.8(5)	77.9(4)
M(3)-O(32)	2.463(8)	2.388(11)	2.375(8)	O(W4)-M(3)-O(35)	71.7(3)	73.1(5)	73.5(4)
M(3)-O(33$^{\mathrm{ii}}$)	2.802(9)	2.853(13)	2.897(10)	O(32)-M(3)-O(34$^{\mathrm{ii}}$)	76.3(3)	75.3(4)	74.6(3)
M(3)-O(34$^{\mathrm{ii}}$)	2.472(10)	2.385(14)	2.368(8)	O(33$^{\mathrm{ii}}$)-M(3)-O(34$^{\mathrm{ii}}$)	48.1(3)	47.3(4)	47.1(3)
M(3)-O(35)	2.396(12)	2.343(17)	2.329(12)	O(31)-M(3)-O(34$^{\mathrm{ii}}$)	65.0(3)	65.0(4)	64.6(3)
M(3)-O(W4)	2.471(7)	2.405(10)	2.382(7)	C(35)-O(35)-M(3)	135.6(10)	136.1(15)	135.9(10)
C(11)-O(11)	1.243(15)	1.27(2)	1.232(15)	C(15)-O(15)-M(1)	131.7(7)	133.6(10)	131.7(7)
C(11)-O(12)	1.251(16)	1.24(2)	1.278(16)	C(15)-O(16)-M(2)	147.9(7)	147.3(9)	147.3(7)
C(13)-O(13)	1.275(16)	1.26(2)	1.248(16)	C(23)-O(23)-M(1)	162.0(11)	158.1(14)	157.4(10)
C(13)-O(14)	1.260(15)	1.27(2)	1.281(15)	C(23)-O(24)-M(2)	125.2(10)	130.7(13)	129.2(9)
C(15)-O(15)	1.273(15)	1.30(2)	1.287(15)	C(21)-O(21)-M(2)	138.7(9)	139.3(13)	138.8(9)
C(15)-O(16)	1.228(14)	1.236(19)	1.208(14)	C(21)-O(22)-M(3)	139.0(9)	137.8(12)	139.2(9)
C(21)-O(21)	1.265(17)	1.25(2)	1.243(16)	C(25)-O(25)-M(2)	124.7(7)	127.3(10)	128.7(7)
C(21)-O(22)	1.245(16)	1.25(2)	1.235(16)	C(25)-O(26)-M(3)	165.1(7)	162.1(9)	160.9(7)
C(23)-O(23)	1.259(18)	1.28(2)	1.245(17)	C(11)-O(11)-M(1)	95.0(8)	94.3(10)	95.8(8)
C(23)-O(24)	1.219(16)	1.22(2)	1.252(15)	C(11)-O(12)-M(1)	92.7(7)	91.7(10)	91.2(7)
C(25)-O(25)	1.256(15)	1.27(2)	1.261(15)	M(1)-O(12)-M(2)	121.6(3)	124.1(5)	125.4(3)
C(25)-O(26)	1.256(13)	1.233(18)	1.234(13)	C(13)-O(13)-M(1)	97.3(7)	97.5(10)	97.5(7)
C(31)-O(31)	1.248(12)	1.243(17)	1.257(12)	C(13)-O(14)-M(1$^{\mathrm{i}}$)	156.2(8)	155.7(11)	155.7(8)
C(31)-O(32)	1.234(15)	1.24(2)	1.246(15)	M(1)-O(14)-M(1$^{\mathrm{i}}$)	112.2(3)	113.0(4)	113.2(3)
C(33)-O(33)	1.236(15)	1.24(2)	1.229(15)	C(31)-O(31)-M(2)	153.4(7)	153.1(10)	153.2(8)
C(33)-O(34)	1.244(14)	1.27(2)	1.235(14)	C(31)-O(32)-M(3)	101.3(7)	103.6(10)	104.7(7)
C(35)-O(35)	1.237(16)	1.23(2)	1.240(16)	M(2)-O(31)-M(3)	117.5(3)	118.5(4)	118.8(3)
C(35)-O(36)	1.216(15)	1.25(2)	1.237(15)	C(31)-O(31)-M(3)	88.1(6)	87.2(9)	86.4(6)
O(36)…O(W4)	2.677(15)	2.68(2)	2.676(15)	C(33)-O(33)-M(3)	155.8(7)	155.8(11)	159.2(8)
O(34)…O(W5$^{\mathrm{ii}}$)	2.746(13)	2.808(18)	2.820(13)	C(33)-O(33)-M(3$^{\mathrm{ii}}$)	87.0(7)	86.4(10)	82.3(7)
O(W3)…O(W4$^{\mathrm{ii}}$)	2.875(12)	2.892(17)	2.922(14)	C(33)-O(34)-M(3$^{\mathrm{ii}}$)	102.7(7)	108.6(11)	108.1(8)
O(W1)…O(36$^{\mathrm{iii}}$)	2.602(12)	2.595(17)	2.605(13)	M(3)-O(33)-M(3$^{\mathrm{ii}}$)	113.1(4)	113.9(5)	113.7(4)
O(W3)…O(13$^{\mathrm{iv}}$)	2.765(15)	2.80(2)	2.778(15)				
O(W3)…O(W2$^{\mathrm{iv}}$)	2.682(16)	2.71(2)	2.708(16)				
O(W2)…O(W5$^{\mathrm{v}}$)	2.965(10)	2.951(14)	2.925(10)				

metry). Table 4 compares the gadolinium(III), erbium(III), and ytterbium(III) complexes with each other. It can be seen that the respective M–O bond lengths, except for M(3)–O(31), and M(3)–O(33$^{\text{ii}}$),[15] decrease in the order of the metal atomic number, due to a decrease in the metal atomic radius.

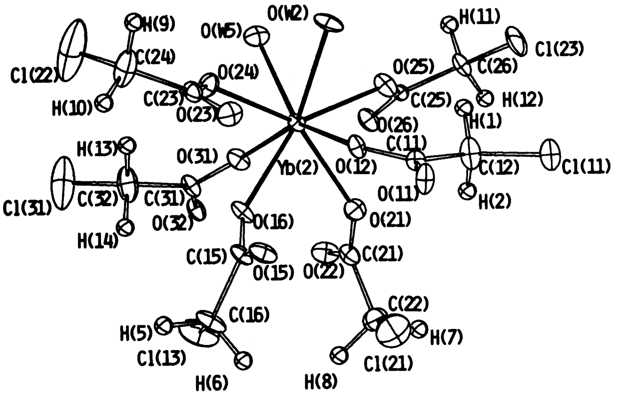


Fig. 2. A perspective drawing of the complex around Yb(2).[15]

The observed lengths of the M–O bonds of these complexes are distributed relatively over a wide range; no clear difference between the lengths to the carboxylato oxygen and to the water oxygen atoms could be found. The average M–O bond lengths around M(1) and M(2) atoms are 2.397(2.246—2.572), 2.343(2.186—2.529), and 2.325(2.174—2.516) Å for the gadolinium, erbium, and ytterbium complexes, respectively. These are comparable to the respective sums of Shannon's ionic radii of the metals (Valence(Val)=3+, Coordination number(CN)=8) and oxygen (Val=2–, CN=2); the calculated M–O bond lengths, where M=Gd, Er, and Yb, are 2.40, 2.35, and 2.34 Å in the order.[16]

The average of the nine M–O bond lengths around the M(3) atom is 2.471(2.273—2.802), 2.426(2.221—2.853), and 2.419(2.206—2.897) Å, for the gadolinium, erbium, and ytterbium complexes, respectively. These

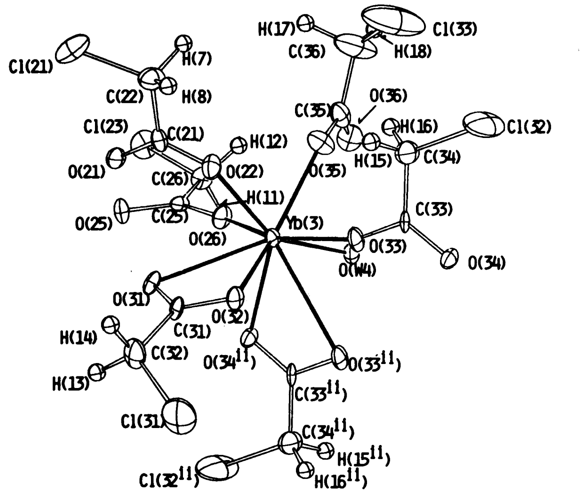


Fig. 3. A perspective drawing of the complex around Yb(3).[15]

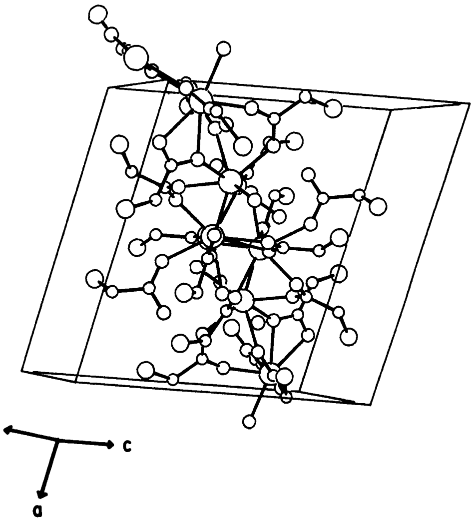
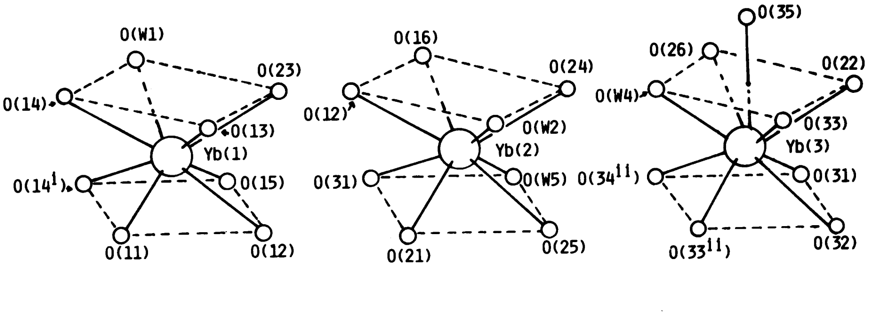


Fig. 4. Crystal packing diagram of the complex.



(5.1) (5.2) (5.3)

Fig. 5. Schematic presentation of the complex with the numbering scheme of the ligated oxygen atoms: 5.1, 5.2, and 5.3 show the coordination geometries around Yb(1), Yb(2), and Yb(3) atoms, respectively.[15]

are slightly longer than the respective sums of the ionic radii of metal(Val=3+, CN=9) and oxygen; the calculated M–O bond lengths, where M=Gd, Er, and Yb, are 2.46, 2.41, and 2.39 Å.16) Except for the two long bonds, M(3)–O(31) and M(3)–O(33$^{\mathrm{ii}}$), the average lengths of the other seven M–O bonds around the M(3) atom are 2.394, 2.337, and 2.318 Å, respectively, for the three complexes. These are much longer than the respective sums of the ionic radii of the metal (Val=3+, CN=7) and oxygen; 2.35, 2.295, and 2.275 Å for M=Gd, Er, and Yb. Consequently, around the M(3) atom, it is better to adopt the ennea-coordination geometry.

In the series of lanthanoid(III) elements, its ionic radius decreases depending on the increase of their atomic number due to the lanthanoid contraction effect. Therefore, the coordination area to be occupied by the ligating atoms around each metal atom decreases depending on the increase of the atomic number, too. In such case, the weakly ligating atoms, such as O(31) and O(33$^{\mathrm{ii}}$), are kept further away than the other coordinating atoms, while the other M–O lengths decrease.2)

All the carboxylate ions in the complex are coordinated to the metal atoms, and their coordination geometries are classified into three types (as follows). The chelating-type ions, found in the light lanthanoid(III) salts, were not found in the heavy lanthanoid(III) complexes, while the unidentate-type ions were not found in the former.

(**A**) Unidentate type: The ion **35**,17) is type one. The O(35) atom is ligated to the M(3) atom, while the O(36) atom is not coordinated to any metal atom; but it is hydrogen-bonded with a water oxygen atom, O(W4), which is ligated to the M(3) atom. The bond lengths O(35)–C(35) and O(36)–C(35) are not very different from each other, and the C=O double bond of the carboxyl group is probably not very localized.

(**B**) *Z,Z*-Type bidentate bridging type: Ions **15**, **21**, **23**, and **25** are members.17) Although the MOC angles of this type ion in the standard form should be in the range 140—150°, some of the determined angles of the title complexes are out of the range, and the differences between both the M–O bond lengths of the same ligands are relatively large: in the ytterbium(III) complex, for example, they are in the range 0.065—0.146 Å. Therefore, the deformation of this type ion is thought to be greater than those of the light lanthanoid(III) complexes.

(**C**) Tridentate type:18) The ideal form of this type ion is that the carboxyl group COO′ makes a chelate ring with a metal atom M. At the same time, one oxygen atom, O′, approaches another metal atom, M′. Ions **11**, **13**, **31**, and **33**,17) are members (where the more deformed one is written the later). In the most deformed ones, **31** and **33**,17) the M–O′ bond lengths are much longer than M–O or M′–O′ bond lengths of the complex. However, as shown in Table 4, their MOC angles are in the range 101—109°, while the angles MO′C are in the range 82—89°. Therefore, their deformations are not the range-out ones of this type ion. The change of the coordination type, found in an europium(III) complex in the series of light lanthanoid(III) complexes,2) could not be found.

Respective types and numbers of the bridges between the metal atoms are schematically shown in Fig. 6, and the intermetallic distances are shown in Table 4. As shown in the Figure, the pairs of metal atoms, M(1$^{\mathrm{i}}$)···M(1) and M(3)···M(3$^{\mathrm{ii}}$) are bridged by two tridentate type ions, while M(1)···M(2) and M(2)···M(3) by one tridentate type and two *Z,Z*-type bidentate bridging type ions, respectively. No clear relation was found between the numbers as well as the types of the bridging ions and the intermetallic distances.

The metal atoms are lined in a linear polymeric chain of Yb(1$^{\mathrm{i}}$)···Yb(1)···Yb(2)···Yb(3)···Yb(3$^{\mathrm{ii}}$)···, which spans approximately along [111] axis. Thus, in the heavy lanthanoid(III) complexes, all the polymeric chains are parallel, though in the light lanthanoid(III) salts, two kinds of the lines along [110] and [−110] are alternately placed. As shown in Table 4, there are some hydrogen bondings through a coordinated water oxygen and O(36) as well as

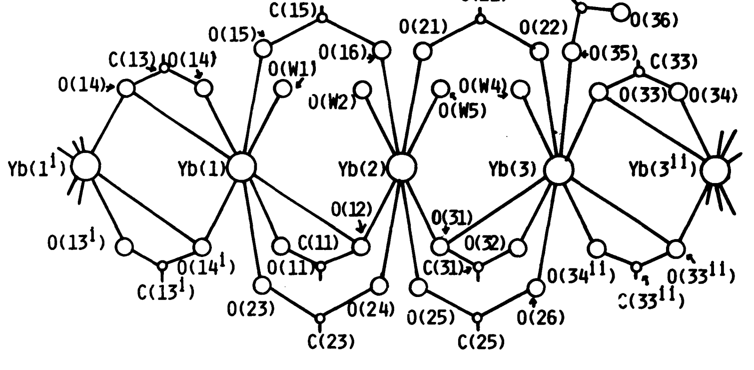


Fig. 6. Schematic presentation of the bridgings between the metal atoms.15)

O(W3) atoms to the side-by-side chains; however, no carboxylato bridgings between them were found.

This kind of the complicated bridging is also found in various other lanthanoid(III) carboxylates.[2,19]

The general feature of the infrared spectra of the gadolinium, dysprosium, erbium, and ytterbium chloroacetates are about the same, although it is different from those of the light lanthanoid(III) chloroacetates.[2] As the ν_{as}(COO) band, two strong peaks appeared at 1570 and 1620 cm^{-1}, with smaller peaks at 1620—1630 and at 1650—1660 cm^{-1}. As the ν_s(COO) band, two strong peaks appeared at 1398 and 1440 cm^{-1}, with two shoulders at both sides of the main peaks. The maximum wavenumbers of these peaks of the four complexes are not very different from each other.

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References

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

2) T. Imai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **60**, 159 (1987).

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

4) W. Bats, R. Kalus, and H. Fuess, *Acta Crystallogr., Sect. B*, **35**, 1225 (1977).

5) A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.*, **1976**, 2466.

6) K. Nagai, R. Nakamura, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2725 (1984).

7) R. Nakamura, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2919 (1984).

8) L. M. Vdovina and O. V. Dubinina, *Zh. Neorg. Khim.*, **28**, 76 (1983); E. R. Birnbaum, "Gmelin's Handbook of Inorganic Chemistry," 8th ed, System No. 39, Part D5 (1984), p. 65.

9) Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **58**, 1593 (1985).

10) T. Imai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **59**, 669 (1986).

11) T. Imai, M. Nakamura, K. Nagai, Y. Ohki, Y. Suzuki, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc Jpn.*, **59**, 2115 (1986).

12) "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic 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 of bond lengths, the final thermal parameters, and the final F_o—F_c tables are deposited as Document No. 8708 at the office of the Editor of Bull. Chem. Soc. Jpn.

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

16) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976). (r_{Gd}(Val=3+), CN=7, 1.00, CN=8, 1.053, CN=9, 1.107; r_{Er}(Val=3+), CN=7, 0.945, CN=8, 1.004, CN=9, 1.062; r_{Yb}(Val=3+), CN=7, 0.925, CN=8, 0.985, CN=9, 1.042; r_O(Val=2−), CN=2, 1.35 Å.

17) Each carboxylate ion is numbered by that of the chlorine atom in it; the ions ***n*1**, ***n*2**, and ***n*3** (where n=1, 2, or 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) H. Sawase, Y. Koizumi, Y. Suzuki, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2730 (1984).

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