The Crystal and Molecular Structures of the Scandium(III) and Yttrium(III) Chloroacetates, $[Sc(ClCH_2CO_2)_3]_n$ and $[Y_3(ClCH_2CO_2)_9(H_2O)_4]_n \cdot nH_2O$

Yoshihiko SUGITA, Yoshiyuki OHKI,† Yasuo SUZUKI,† and Akira OUCHI*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Higashi-Mita, Tama-ku, Kawasaki, Kanagawa 214
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Synopsis. The crystal and molecular structures of the titled scandium(III) (**1**) and yttrium(III) chloroacetates (**2**) were determined by the single-crystal X-ray diffraction method. **1** is monoclinic, with the space group $P2_1/n$, a=12.148(4), b=8.860(5), c=11.028(4) Å, and β=103.31(3)°. In **1**, the metal atom has the hexa-coordinated octahedral geometry, and any pair of the neighboring metal atoms are bridged by three bidentate carboxylate ions, forming an infinite chain. **2** is isomorphous with the heavy lanthanoid salts, $[Ln_3(ClCH_2CO_2)_9(H_2O)_4]_n \cdot nH_2O$ (Ln=Gd—Yb), and its crystal structure closely resembles that of the erbium(III) complex.

We have previously reported on the complicated structures of the series of light and heavy lanthanoid(III) chloroacetates.[1,2] Although it is well-known that the properties of the scandium(III) and yttrium(III) complexes resemble those of the lanthanoids(III)[3,4] there are not much structural data about their carboxylates; moreover, the data regarding complexes synthesized under the same conditions as those for the corresponding lanthanoid complexes are rare.

The structural data of scandium(III) formate is the sole example;[5] its metal atoms are in the hexa-coordinated octahedral geometry, and are bridged by the anions forming a two-dimensional polymeric form. Therefore, it is desirable to obtain more structural data concerning the scandium complexes in order to clarify whether their coordination numbers are always six or not, and to determine its polymeric form.

The yttrium(III) formate dihydrate[6,7] and yttrium(III) acetate tetrahydrate[8] are known to be isomorphous with the corresponding heavy lanthanoid salts.[6,9,10,11] If the yttrium and heavy lanthanoids always give complexes isomorphous with each other, the high coordination number and the complicated bridging found in the lanthanoid complexes should not be due to the 4f-orbitals of the latters.

Therefore, we have synthesized the scandium(III) and yttrium(III) chloroacetates, $Sc(ClCH_2CO_2)_3$ (**1**) and $[Y_3(ClCH_2CO_2)_3(H_2O)_4]_n \cdot nH_2O$ (**2**), under synthetic conditions almost the same as that for the lanthanoid salts.

Experimental

Syntheses of the Scandium(III) and Yttrium(III) Chloroacetates. Scandium(III) hydroxide (obtained from 0.193 g (1.0 mmol) of Sc_2O_3) was dissolved into an aqueous solution of chloroacetic acid (0.59 g (6.2 mmol) into 10 cm³ of water). The solution was filtered off, left standing in a silica-gel desiccator for several days until 2/3 of the water was evaporated off; crystals of **1** were deposited. Yield: 0.33 g (51%). The yttrium salt, **2**, was obtained almost in the same way starting from 0.229 g (1.0 mmol) of Y_2O_3 and chloroacetic acid (0.59 g, 6.2 mmol). Yield, 0.61 g (75%). Found; Sc, 13.77; C, 22.11; H, 1.58%; Calcd for $ScC_6H_6O_6Cl_3$, Sc, 13.81; C, 22.15; H, 1.86%. Found; Y, 22.15; C, 17.50; H, 2.31%; Calcd for $Y_3C_{18}H_{28}O_{23}Cl_9$; Y, 22.26; C, 18.04; H, 2.36%.

X-Ray Structure Analysis. Crystallographic data and some experimental conditions for obtaining their intensities are tabulated in Table 1. The intensities were collected on a Rigaku AFC-6A automated 4-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation, a ω—2θ scan technique being employed (the scan speed was 4° min^{-1} (θ)).

The structure of the scandium complex was solved by the heavy-atom method. In the case of the yttrium salt, the structure was solved starting with the final parameters of the erbium complex, $[Er_3(ClCH_2CO_2)_9(H_2O)_4]_n \cdot nH_2O$,[2] and were refined as usual.

In both cases, all the hydrogen atoms were fixed at the calculated positions (C–H=1.08 Å), B_{iso}=8.00 Å² being given.

All the calculations were carried out on a HITAC M-682H

Table 1. Crystallographic Data and Various Experimental Conditions to Obtain the Reflection Intensities

Complex	**1**	**2**
F.W. (n=1)	325.42	1198.20
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a(l/Å)	12.148(4)	13.349(12)
b(l/Å)	8.860(5)	13.691(10)
c(l/Å)	11.028(4)	12.126(8)
α(ϕ/°)	90	96.62(6)
β(ϕ/°)	103.31(3)	100.64(7)
γ(ϕ/°)	90	67.35(6)
U(v/Å³)	1155.1(9)	2008(3)
Z	4	6
D_m(d/Mg m^{-3})	1.86(3)	1.95(3)
D_x(d/Mg cm^{-3})	1.87	1.98
μ(Mo $K\alpha$) (n/mm^{-1})	1.34	5.13
N_m[a]	3292	7173
N_c[b]	1400	4481
R[c]	0.069	0.072
V_c[d]	0.3×0.15×0.10	0.3×0.2×0.14
S_W[e]	1.12+0.5 tanθ	1.08+0.5 tanθ
S_R[f]	3—55	3—50

a) Number of reflections measured. b) Reflections used for the calculation (reflections of $|F_o| > 3\sigma(|F_o|)$). c) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. d) Size of crystals ($v$/mm³). e) Scan width ($\theta$/°). f) Scan range ($2\theta$/°).

apparatus 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 liquid paraffin and hexachloro-1,3-butadiene mull.

Results and Discussion

The final parameters and their equivalent thermal parameters of **1** are listed in Table 2.[14]

In **1**, the metal atom has an octahedral coordination by six oxygen atoms of six different anions (Fig. 1); the octahedral geometry is not much deformed.[15] The mean Sc–O distance is 2.075 Å (Table 3), not far from the sum of the Shannon's ionic radii of Sc and O, 2.10 Å.[16] The metal atoms are laid along the b-axis in a zig-zag way, and any pair of side-by-side metal atoms are bridged by three carboxylate ions, where all carboxylate ions act as *Z,Z*-type bidentate (Fig. 2).[17] Such a type of the triple carboxylate ion bridging is rarely found, even in any other metal complexes. The three oxygen atoms (O(11), O(21), and O(31)) of the respective three carboxylate ions bridging to the one side next metal atom are in an *fac*-configuration (Fig. 1). The carboxylato carbon and oxygen atoms (C(**n1**), O(**n1**), and O(**n2**)) of each carboxylato bridge, together with the metal atoms Sc and Sc^{ii},[18] are approximately on each plane. The average deviations of the atoms from the respective planes are: **11**, 0.065; **21**, 0.131; and **31**, 0.027 Å. The dihedral angles between them are: **11**—**21**, 114.2; **11**—**31**, 56.7; **21**—**31**, 57.5°.[19] Although all of the bridging ions are approximately the *Z,Z*-type, angles C(11)-O(12)-Sc^{ii} (164.1(5)°) and C(31)-O(31)-Sc (171.6(7)°) are larger than, and C(11)-O(11)-Sc (133.8(5)°) and C(31)-O(32)-Sc^{ii} (131.8(6)°) are smaller than the standard value (145—150°) of the type of bridge[14,17] On the other hand, although ion **21** has almost a normal C-O-Sc angle, the planarity of the Sc-O-C-O-S^{ii} plane is not good. Relatively short Sc-O(12^{i}) and Sc-O(31) bonds are found where

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

Atom	x	y	z	B_{eq}/Å^2 a)
Sc	2769.5(12)	1573.8(14)	2379.3(13)	1.9$_6$
O(11)	4219(4)	2914(5)	2853(5)	2.5$_3$
O(12)	3629(4)	5236(5)	3112(5)	3.0$_6$
O(21)	2207(5)	2908(5)	803(5)	3.0$_5$
O(22)	1591(4)	5233(5)	1057(4)	2.7$_3$
O(31)	1920(4)	2889(5)	3390(5)	2.9$_7$
O(32)	1387(4)	5222(5)	3682(5)	3.1$_7$
C(11)	4387(6)	4281(8)	3113(6)	2.2$_5$
C(12)	5612(6)	4756(8)	3444(7)	2.7$_0$
C(21)	1811(6)	4158(8)	423(7)	2.1$_6$
C(22)	1502(8)	4452(9)	−979(7)	3.6$_2$
C(31)	1401(6)	3818(7)	3874(7)	2.2$_1$
C(32)	753(8)	3332(9)	4809(9)	4.6$_8$
Cl(11)	5822(2)	6642(2)	3938(2)	4.2$_7$
Cl(21)	2333(2)	3426(3)	−1799(2)	5.0$_7$
Cl(31)	836(3)	1395(3)	5111(3)	6.0$_4$

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

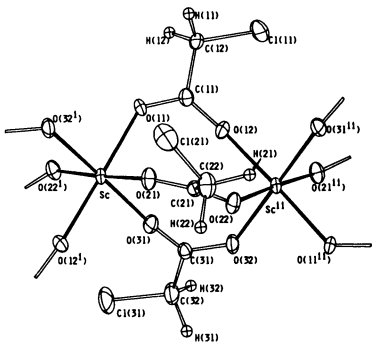

Fig. 1. A perspective drawing of the scandium(III) complex showing the metal atoms and the bridging carboxylate ions.

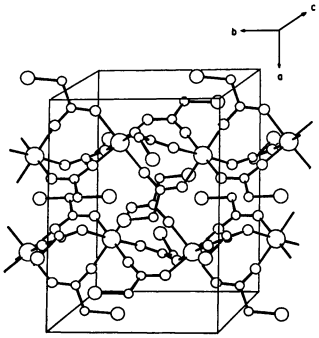

Fig. 2. Crystal packing diagram of the scandium(III) complex.

Table 3. Bond Lengths and Bond Angles of the Scandium Complex with the Standard Deviations in Parentheses[18]

Bond length	(l/Å)	Bond length	(l/Å)	Bond length	(l/Å)
Sc-O(11)	2.088(5)	Sc-O(21)	2.083(7)	Sc-O(31)	2.048(7)
Sc-O(12^{i})	2.040(5)	Sc(22^{i})	2.091(7)	Sc-O(32^{i})	2.099(7)
O(11)-C(11)	1.251(8)	O(12)-C(11)	1.250(9)	O(21)-C(21)	1.241(9)
O(22)-C(21)	1.246(11)	O(31)-C(31)	1.230(11)	O(32)-C(31)	1.262(8)
Sc···Sc^{ii}	4.495(4)				
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
O(11)-Sc-O(21)	89.0(2)	O(11)-Sc-O(31)	92.4(2)	O(11)-Sc-O(12^{i})	178.7(2)
O(11)-Sc-O(22^{i})	89.1(2)	O(11)-Sc-O(32^{i})	88.4(2)	O(21)-Sc-O(31)	91.2(3)
O(21)-Sc-O(22^{i})	177.3(3)	O(31)-Sc-O(12^{i})	88.9(2)	O(31)-Sc-O(32^{i})	178.9(3)

Table 4. Selected Bond Lengths of the Yttrium Complex with the Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)	Bond length	(l/Å)
Y(1)-O(11)	2.388(10)	Y(1)-O(12)	2.455(9)	Y(1)-O(13)	2.391(9)
Y(1)-O(14)	2.551(9)	Y(1)-O(15)	2.233(8)	Y(1)-O(23)	2.219(12)
Y(1)-O(W1)	2.288(10)	Y(1)-O(14^{i})	2.322(10)	Y(2)-O(12)	2.354(9)
Y(2)-O(16)	2.383(7)	Y(2)-O(21)	2.300(12)	Y(2)-O(24)	2.305(12)
Y(2)-O(25)	2.310(8)	Y(2)-O(31)	2.270(9)	Y(2)-O(W2)	2.401(9)
Y(2)-O(W5)	2.511(10)	Y(3)-O(22)	2.241(11)	Y(3)-O(33)	2.281(9)
Y(3)-O(26)	2.238(8)	Y(3)-O(31)	2.764(10)	Y(3)-O(32)	2.401(9)
Y(3)-O(33^{ii})	2.845(10)	Y(3)-O(34^{ii})	2.402(11)	Y(3)-O(35)	2.334(13)
Y(3)-O(W4)	2.420(8)	Y(1^{i})···Y(1)	4.057(3)	Y(1)-Y(2)	4.246(4)
Y(2)···Y(3)	4.326(4)	Y(3)···Y(3^{ii})	4.309(4)		

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

the C-O-Sc angles of the oxygen atoms are large.[18,19] Therefore, in the case of the chloroacetate, scandium makes a polymeric complex like the heavier IIIA elements; however, its coordination number is six, not so high as yttrium and the lanthanoids. This fact is probably due to its small ionic radius.

The structure of **2** is isomorphous with heavy lanthanoid salts, $[Ln_3(ClCH_2CO_2)_9(H_2O)_4]_n \cdot nH_2O$, (Ln=Gd—Yb).[2] The Shannon's ionic radius of the yttrium ion resemble those of holmium and erbium.[16] The bond lengths and angles of the yttrium salt (Table 4) are not so much different from the corresponding values of the latter salts.[2] The average of the 25 Y-O bond lengths of **2** is 0.012 Å longer than that of the Er-O bonds of the erbium complex,[2] reflecting a longer ionic radius, Y(1.019 Å), than that of Er(1.004 Å) (where the valence of the metal atoms is 3+, and the coordination number is 8).[16]

Therefore, we deduce from these results that both yttrium and the lanthanoids form the same complicated polimeric-type carboxylate complexes; 4f electrons are not greatly related with the characteristic structures.

In the infrared spectrum of **1**, the ν_{as}(COO) and ν_s(COO) bands appear as singlets at 1565 and 1442 cm^{-1}, and do not split as those of the lanthanoid salts. These peaks probably correspond with bands of the *Z,Z*-type bridging carboxylate ion.[17] The general feature as well as the wavenumbers of the ν_{as}(COO) and ν_s(COO) bands of **2**(which appear at 1662, 1627, 1595, 1572 (strongest); and 1442 and 1399 cm^{-1}, respectively) are approximately similar to those of the erbium salt.[2]

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14) "Final thermal parameters of the non-hydrogen atoms, the positional parameters of **2** and those of the hydrogen atoms of **1**, final F_o–F_c tables of **1** and **2**, and some of their additional data for the bond lengths and angles are deposited as Document No. 8748 at the office of the Editor of the Bull. Chem. Soc. Jpn.
15) Average of the six edge lengths of two triangles is 2.950 (2.922—2.985) Å, and the average of their six angles is 60.16 (58.95—61.08)°. The dihedral angle between the O(11), O(21), O(31), and the O(12^{i}), O(22^{i}), O(32^{i}) planes is 0.19°.
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18) Key to the symmetry operations of the scandium complex: i, 0.5−x, −0.5+y, 0.5−z; ii, 0.5−x, 0.5+y, 0.5−z.
19) From now on, each carboxylate ion of **1** is numbered by the number of each carboxylate carbon atom in it: **11**, **21**, and **31**.