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- (31) The greater electron-withdrawing power of the  $C_6F_5$  and  $C_6Cl_5$  substituents vs. that of the  $C_6H_5$  and  $CF_3$  substituents in lowering the  $\pi$ - and  $\pi^*$ -orbital energies of the olefin-like acetylene ligands relative to the  $4d[Rh]$  levels is expected from a consideration of their overall inductive and resonance electronic effects.
- (32) Atomic charges derived via potential models from the measurements by x-ray photoelectron spectroscopy (ESCA) of the core-electron bind-

- ing-energy shifts of carbon and fluorine 1s levels of various fluorinated hydrocarbons including trifluoromethylbenzenes indicate that the carbon atom adjacent to the  $CF_3$  group is negative in agreement with theoretical predictions.<sup>33</sup> It was concluded<sup>33a</sup> that the  $CF_3$  group is actually an electron donor and that the well-known inductive effect of  $CF_3$  results not because  $CF_3$  withdraws electrons from its neighbors but because the positive dipole of  $CF_3$  creates a positive potential on the adjacent atoms.
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## Crystal Structures of Aquotris(salicylato)samarium(III) and Aquotris(salicylato)americium(III)<sup>1</sup>

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Two isostructural compounds  $(C_7H_5O_3)_3Sm \cdot H_2O$  and  $(C_7H_5O_3)_3Am \cdot H_2O$  are monoclinic, space group  $P2_1/c$ , and have unit-cell dimensions:  $a = 13.641$  (3) Å,  $b = 6.752$  (1) Å,  $c = 24.202$  (7) Å,  $\beta = 113.24$  (2)° and  $a = 13.69$  (2) Å,  $b = 6.762$  (2) Å,  $c = 24.14$  (1) Å,  $\beta = 112.89$  (5)°, respectively;  $Z = 4$ . Heavy-atom methods were used to determine the structure from x-ray diffraction data. Refinement of parameters by least-squares methods was carried out using 3280 observations on the Sm compound and 1401 on the Am. The  $R_F$  values obtained were 0.037 and 0.055 for the two refinements. There are no discrete molecules of the complex in the crystal; instead each metal ion is linked to six different salicylato ions through a variety of dentation modes in which both the carboxylate and phenolic oxygen atoms participate. Cross-linking of metal ions produces endless chains along the  $b$  axis and only van der Waals contacts exist between the chains. A total of eight oxygen atoms from the salicylato ligands plus one from a water molecule comprise the metal coordination. There is also evidence for some hydrogen bonding among the ligands. The bonding pattern within the salicylato ions is the same for all three independent ligands. It is characterized by equivalence of bond lengths to carboxylate oxygen atoms, by distortion of the benzene ring from hexagonal symmetry, by a short C-C bond to the carboxyl group, and by a short C-O bond to the hydroxyl group. Except for the carboxyl group, which is ionized, the molecular shape is the same as for salicylic acid. Analogous compounds containing La and Nd were shown to have this structure also.

### Introduction

Previous work with salicylato complexes of trivalent lanthanides and actinides has been concerned with their formation in solution, their stability constants, and their solubility products. The first solid compounds of the type being considered here were obtained<sup>2,3</sup> from slightly acid solutions and were assigned the formula  $(C_7H_5O_3)_3La \cdot 1.5H_2O$  and  $(C_7H_5O_3)_3Pu \cdot 1.5H_2O$ . Later studies<sup>4,5</sup> showed that, in slightly basic solutions, two-thirds of the phenolic H atoms could be ionized from the ligands and two complex compounds involving the divalent salicylato ion were made:  $NaLa(C_7H_4O_3)(C_7H_5O_3)_2$  and  $NaLa(C_7H_4O_3)_2$ . Solution studies<sup>6,7</sup> of  $Nd^{3+}$  ions with salicylato (*o*-hydroxybenzoate) and *p*-hydroxybenzoate ions showed differences in solubility which were attributed, respectively, to cyclic and linear attachment of the ligands. A recent study<sup>8</sup> of the stability constants of salicylato complexes of several lanthanide elements assumes that there are no polynuclear species in solution. An understanding of all these observations should be enhanced by knowledge of the structure of the complex molecule and we undertook the determination described here for this purpose.

The study of complexation of lanthanide and actinide elements by salicylato ions is important also because the bonding in such complexes can serve as a very simple model for the interaction of these elements with humic materials in the natural environment. These materials are products of plant decomposition and are characterized chemically as complex polymers containing benzene rings with varying numbers of carboxyl and hydroxyl groups attached in a wide variety of combinations.<sup>9</sup> The salicylato ion,  $(C_7H_5O_3)^-$ , contains both the carboxylic and hydroxy functional groups, and complexes

with it must show bonding typical of the more complicated, natural materials.

Only a few crystal structures containing the salicylato ion have been determined. In all of these the metal is copper; in two cases the salicylato ion is linked to it through the carboxyl group, one<sup>10</sup> in monodentate and one<sup>11</sup> in bidentate fashion; in the third<sup>12</sup> some ions are linked to (different) metal ions by both the carboxylic and phenolic O atoms. A precise description of the structure of salicylic acid itself is available also.<sup>13</sup>

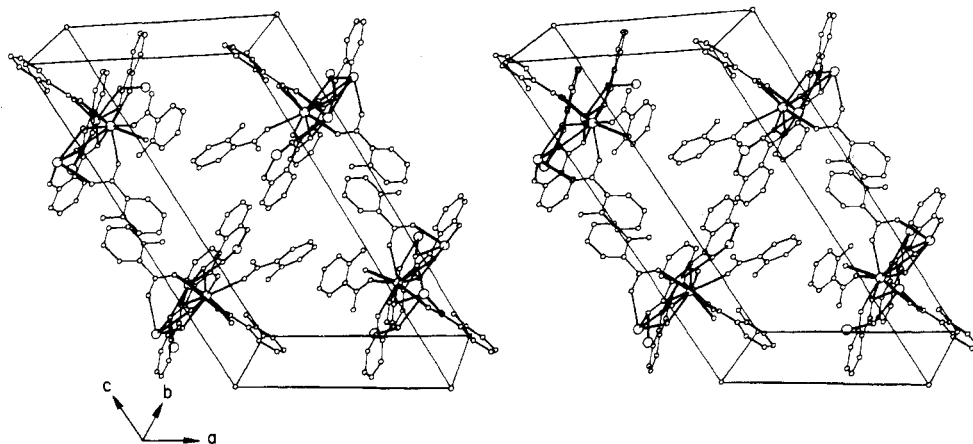
### Experimental Section

**Preparation of Compounds.** Aquotris(salicylato)samarium(III) was made by reaction of  $SmCl_3$  and  $Na(C_7H_5O_3)$  in aqueous ethanol. To increase crystal size of the product the components were allowed to diffuse together through a separate layer of aqueous ethanol. Colorless needles up to several millimeters in length were obtained. Analysis for salicylate was carried out by converting the ion to salicylic acid on a Dowex 50 resin column, eluting with 1:1 aqueous ethanol, and titrating the eluate with standard base. The equivalent weight found was 187.5; that calculated for  $(C_7H_5O_3)_3Sm \cdot H_2O$  is 193.2.

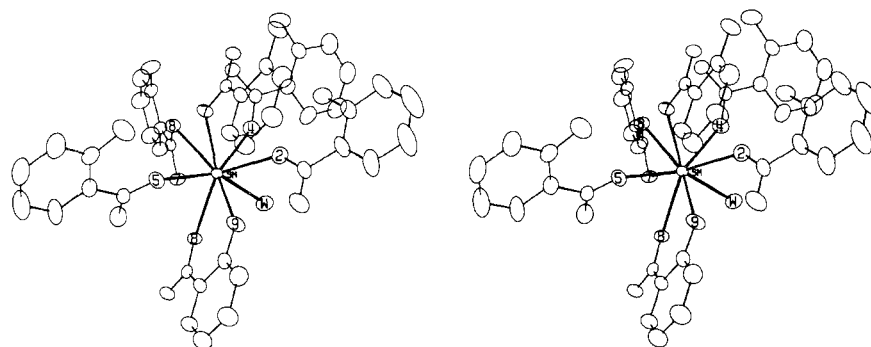
Aquotris(salicylato)americium(III) was made by diffusion together of aqueous solutions of  $Na(C_7H_5O_3)$  and  $Am(NO_3)_3$  over a period of a few days. The latter solution was prepared from  $^{243}AmO_2$  by dissolution in concentrated  $HNO_3$ . Pale yellow-pink needles were formed. No elemental analysis was done because the x-ray diffraction pattern showed isomorphism with the Sm analogue.

Aquotris(salicylato)lanthanum(III) was prepared in the manner described by Zvyagintsev and Sudarikov.<sup>2</sup> At a pH between 3 and 7,  $La(NO_3)_3$  and  $Na(C_7H_5O_3)$  were mixed to yield fine, white needles of the compound. No attempt was made at increasing crystal size because these were adequate for identification purposes.

Aquotris(salicylato)neodymium(III) was made as pale violet crystals by diffusing together neutral solutions of  $NdCl_3$  and  $Na(C_7H_5O_3)$ .



**Figure 1.** Stereoscopic view of one unit cell of the structure with some additional metal ions shown to indicate the cross-linking which produces chains along *b*. Metal ions are represented by the larger circles, and heavy lines bond them to oxygen atoms.



**Figure 2.** Stereoscopic view of the ligands which coordinate a single Sm (or Am) ion. Sufficient numbering of oxygen atoms is added to make all atoms identifiable with the aid of Figure 3.

Needles large enough for single-crystal x-ray diffraction were obtained and were identified by this means.

**X-Ray Diffraction.** Precession photographs of each of the four salicylato complexes showed that they are isomorphous and are of monoclinic symmetry with the needle axis parallel to *b*. Systematic absences are uniquely indicative of space group  $P2_1/c$  ( $h0l, l$  odd;  $0k0, k$  odd). Unit-cell dimensions were obtained from these photographs and, in the case of the Sm and Am compounds, refined by the use of 12 carefully centered reflections measured with a four-circle diffractometer. The lattice parameters and calculated densities are shown in Table I. The density of  $(C_7H_5O_3)_3Sm \cdot H_2O$  was measured by flotation to be  $1.88 \pm 0.06 \text{ g cm}^{-3}$ .

For collection of intensity data a needle of  $(C_7H_5O_3)_3Sm \cdot H_2O$  measuring about  $0.040 \times 0.010 \times 0.014 \text{ cm}$  and a needle of  $(C_7H_5O_3)_3Am \cdot H_2O$  of about  $0.091 \times 0.013 \times 0.005 \text{ cm}$  were used. Each was mounted on a computer-controlled four-circle Picker diffractometer with the crystal *b* axis nearly parallel to the  $\phi$  axis. The radioactive isotope was contained by sealing the latter crystal in a thin-walled glass tube. Niobium-filtered Mo  $K\alpha$  x rays ( $\lambda 0.70926 \text{ \AA}$ ) were employed at a takeoff angle of  $2^\circ$ , and the reflections were measured by  $\theta-2\theta$  scanning over a range of  $0.8^\circ$  at the minimum  $2\theta$  and  $1.6^\circ$  at the maximum to follow the  $\alpha_1, \alpha_2$  dispersion. A receiving aperture  $3 \times 3 \text{ mm}$  at  $21 \text{ cm}$  from the crystal was used for the Sm compound and an aperture of  $6 \times 6 \text{ mm}$  was used at the same distance for the Am-containing crystal, which had a greater mosaic spread. All independent reflections having  $2\theta < 50^\circ$  were measured in the first case; but because the Am compound was known to be isostructural with the Sm analogue and a structure determination was not needed, only about half as many reflections were measured for it. A single reference reflection was measured hourly in each case; its observed intensity fluctuated by  $\sim 2\%$  about the mean value in both cases, but in the case of the Am compound it also showed a net decline of about 8% over the 4-day period of data collection. This decline is attributed to crystal deterioration caused by  $\alpha$  irradiation, a phenomenon commonly found in crystals containing  $\alpha$ -emitting actinides and organic ligands.

**Table I**

Metal	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	$\beta$ , deg	$d_{\text{calcd}}^{\text{---}}$ ( <i>Z</i> = 4), g $\text{cm}^{-3}$	<i>T</i> , $^\circ\text{C}$
La	13.86	6.89	23.93	112.9	1.79	
Nd	13.69	6.81	24.10	113.0	1.84	
Am	13.69 (2)	6.762 (2)	24.14 (1)	112.89 (5)	2.169	25
Sm	13.641 (3)	6.752 (1)	24.202 (7)	113.24 (2)	1.880	24

**Determination and Refinement of the Structure.** Absorption corrections were made to the observed intensities using transmission factors calculated<sup>14</sup> on the basis of measured planes bounding the crystals and linear absorption coefficients<sup>16</sup> of  $27.5 \text{ cm}^{-1}$  for  $(C_7H_5O_3)_3Sm \cdot H_2O$  and  $36.0 \text{ cm}^{-1}$  for  $(C_7H_5O_3)_3Am \cdot H_2O$ . In the former, crystal transmission factors ranged from 0.71 to 0.80 and in the latter from 0.63 to 0.85. Application of these factors and the Lorentz and polarization corrections, followed by normalization to values of the reference reflection interpolated between measurements, converted the observed intensities to relative squared structure factors,  $F_o^2$ . There were 3280 values greater than  $\sigma$  for  $(C_7H_5O_3)_3Sm \cdot H_2O$  and 1401 for  $(C_7H_5O_3)_3Am \cdot H_2O$ . In the refinement, the variances of these observations were assumed to be  $\sigma^2(F_o^2) = \sigma_c^2 + (0.03F_o^2)^2$ , where  $\sigma_c^2$  is the variance attributed to counting statistics.

A Patterson map was calculated using the data from  $(C_7H_5O_3)_3Sm \cdot H_2O$ , and from it the coordinates of the Sm atom in a general fourfold equipoint of  $P2_1/c$  were readily determined. Phases calculated from this atom were employed with the  $F_o$  data to compute an electron density map. In it were found maxima for each of the 10 oxygen and 21 carbon atoms of the asymmetric unit; these also occupy general positions. At this point the degree of hydration actually was ascertained, since the analytical data were not definitive. The hydrogen atoms were not located.

The atomic coordinates and anisotropic thermal parameters of all nonhydrogen atoms were refined by the method of least squares. The

Table II. Positional and Thermal Parameters of the Samarium Complex (Upper Values) and of the Americium Complex (Lower Values)<sup>a</sup>

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Sm	1010.9 (2)	1558.6 (4)	2707.0 (1)	21.3 (2)	60 (1)	8.7 (1)	-0.6 (3)	4.6 (1)	2.4 (2)
Am	1015.9 (7)	1511 (1)	2703.1 (4)	33.9 (6)	47 (2)	9.3 (2)	0 (2)	4.5 (2)	3 (1)
O(1)	5978 (3)	-2875 (7)	1331 (2)	42 (3)	214 (12)	23 (1)	18 (5)	0 (1)	-32 (3)
	5981 (13)	-2926 (26)	1331 (8)						
O(2)	7331 (3)	-1485 (6)	2070 (2)	29 (2)	156 (10)	16 (1)	6 (4)	4 (1)	-5 (3)
	7292 (10)	-1518 (28)	2071 (6)						
O(3)	7043 (3)	1622 (6)	2569 (2)	49 (3)	168 (11)	27 (1)	-18 (5)	13 (2)	-22 (3)
	7056 (12)	1549 (31)	2574 (7)						
O(4)	-815 (3)	-1514 (6)	3180 (2)	51 (3)	164 (10)	17 (1)	-24 (5)	14 (1)	-23 (3)
	-810 (11)	-1538 (30)	3198 (7)						
O(5)	207 (3)	1153 (5)	3408 (2)	56 (3)	120 (9)	15 (1)	-12 (4)	17 (1)	-2 (2)
	228 (12)	1075 (23)	3440 (7)						
O(6)	-178 (4)	3895 (6)	4054 (2)	108 (5)	146 (11)	26 (1)	-33 (6)	31 (2)	-16 (3)
	-139 (15)	3840 (26)	4087 (8)						
O(7)	-703 (3)	-88 (5)	1946 (2)	38 (2)	84 (8)	12 (1)	6 (4)	6 (1)	-3 (2)
	-679 (11)	-123 (22)	1930 (7)						
O(8)	-878 (3)	2936 (5)	2189 (2)	31 (2)	91 (8)	12 (1)	-4 (3)	4 (1)	-7 (2)
	-924 (12)	2893 (20)	2184 (7)						
O(9)	-2499 (3)	5119 (6)	1456 (2)	43 (3)	121 (9)	16 (1)	15 (4)	3 (1)	-13 (2)
	-2532 (12)	5027 (24)	1464 (7)						
O(W)	1848 (3)	-16 (6)	2108 (2)	65 (3)	145 (10)	20 (1)	29 (5)	22 (2)	8 (3)
	1816 (13)	-57 (25)	2074 (7)						
C(1)	6350 (4)	-1555 (9)	1719 (3)	37 (4)	135 (14)	14 (1)	20 (6)	10 (2)	3 (4)
	6339 (17)	-1628 (44)	1720 (10)						
C(2)	5632 (5)	24 (9)	1756 (3)	50 (4)	170 (16)	13 (1)	35 (7)	12 (2)	2 (4)
	5647 (20)	-21 (40)	1762 (11)						
C(3)	6010 (5)	1591 (9)	2168 (3)	55 (4)	143 (15)	19 (2)	22 (7)	20 (2)	6 (4)
	6012 (18)	1528 (47)	2164 (11)						
C(4)	5341 (6)	3117 (11)	2171 (4)	86 (6)	223 (20)	27 (2)	48 (9)	26 (3)	-4 (5)
	5361 (23)	3132 (46)	2177 (13)						
C(5)	4259 (7)	3041 (15)	1761 (4)	96 (8)	416 (31)	29 (2)	122 (13)	16 (3)	-4 (7)
	4265 (27)	3003 (54)	1778 (15)						
C(6)	3876 (6)	1459 (15)	1382 (4)	62 (6)	457 (32)	22 (2)	95 (11)	6 (3)	-15 (7)
	3881 (22)	1390 (62)	1374 (13)						
C(7)	4548 (5)	-54 (2)	1371 (3)	40 (4)	337 (24)	17 (2)	57 (9)	5 (2)	-4 (5)
	4562 (20)	-75 (47)	1377 (12)						
C(8)	-461 (4)	-4 (8)	3483 (2)	30 (3)	121 (13)	10 (1)	-2 (6)	7 (2)	-3 (3)
	-470 (18)	28 (36)	3500 (10)						
C(9)	-832 (4)	517 (9)	3966 (2)	35 (4)	161 (15)	10 (1)	-11 (6)	6 (2)	-7 (4)
	-836 (18)	550 (40)	3972 (10)						
C(10)	-685 (5)	2420 (9)	4224 (3)	43 (4)	152 (15)	15 (1)	3 (6)	10 (2)	-12 (4)
	-667 (20)	2367 (40)	4255 (11)						
C(11)	-1083 (6)	2891 (12)	4660 (3)	62 (5)	295 (23)	17 (2)	-6 (9)	17 (3)	-14 (5)
	-1049 (23)	2833 (44)	4703 (12)						
C(12)	-1580 (6)	1430 (13)	4858 (3)	63 (5)	338 (25)	20 (2)	-11 (10)	22 (3)	-17 (6)
	-1582 (20)	1407 (58)	4876 (11)						
C(13)	-1704 (6)	-491 (13)	4622 (3)	87 (6)	339 (24)	23 (2)	-66 (11)	31 (3)	-29 (6)
	-1753 (24)	-455 (51)	4614 (13)						
C(14)	-1346 (6)	-934 (11)	4180 (3)	65 (5)	265 (21)	19 (2)	-47 (8)	24 (2)	-20 (5)
	-1353 (21)	-895 (42)	4183 (12)						
C(15)	-1212 (4)	1530 (8)	1818 (2)	25 (3)	82 (11)	11 (1)	2 (5)	9 (2)	5 (3)
	-1207 (15)	1541 (42)	1815 (9)						
C(16)	-2143 (4)	1740 (8)	1242 (2)	32 (3)	99 (12)	10 (1)	7 (5)	8 (2)	-1 (3)
	-2162 (16)	1707 (39)	1250 (9)						
C(17)	-2748 (4)	3532 (8)	1091 (2)	26 (3)	132 (13)	10 (1)	10 (6)	5 (2)	1 (3)
	-2747 (15)	3498 (44)	1108 (9)						
C(18)	-3652 (5)	3632 (10)	548 (3)	39 (4)	205 (17)	11 (1)	2 (7)	2 (2)	-4 (4)
	-3676 (17)	3648 (45)	555 (10)						
C(19)	-3946 (5)	2006 (10)	163 (3)	51 (5)	191 (17)	11 (1)	8 (7)	2 (2)	-9 (4)
	-3981 (20)	1966 (36)	158 (11)						
C(20)	-3340 (5)	270 (10)	304 (3)	47 (4)	184 (17)	12 (1)	3 (7)	4 (2)	-14 (4)
	-3344 (20)	230 (41)	302 (11)						
C(21)	-2454 (5)	155 (9)	839 (3)	43 (4)	127 (14)	12 (1)	-1 (6)	7 (2)	-10 (3)
	-2431 (19)	96 (37)	833 (11)						

<sup>a</sup> All values are multiplied by  $10^4$ . The number in parentheses is the standard error in the last place of the accompanying entry. Temperature factors are of the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$ . The water molecule is designated O(W).

function minimized was  $\sum w(F_o^2 - F_c^2)^2$ , in which  $w = 1/\sigma^2(F_o^2)$  and  $F_c$  is the calculated structure factor. Atomic scattering factors<sup>17</sup> for neutral atoms were used, and the heavy-atom contributions were corrected for the  $\Delta f'$  and  $\Delta f''$  components of anomalous dispersion.<sup>16</sup> Convergence was rapid and the agreement index,  $R = \sum |F_o| - |F_c| / \sum |F_o|$ , reached a value of 0.037. The standard deviation of an observation of unit weight,  $\sigma_1$ , was 1.55.

After completion of this refinement, the data collected for  $(C_7H_5O_3)_3Am \cdot H_2O$  were used to carry out the same refinement process

for its structure. Because of the smaller number and somewhat less precise values of these data, the refinement was not quite as satisfactory. Although convergence was rapid, several temperature factors of C and O atoms shifted to nonpositive definite values. Refining with isotropic temperature factors on all of the light atoms produced convergence with  $B$  values ranging from 1.4 to 7.5  $\text{\AA}^2$  and an  $R$  of 0.059. It was decided that the refined temperature factors for  $(C_7H_5O_3)_3Sm \cdot H_2O$  were probably nearer the true values, and in the final stage of refinement they were used and only the  $\beta$ 's of the Am

Table III. Bond Lengths and Standard Errors (Å)

Bond	Sm	Am	Bond	Sm	Am
M -O(5)	2.371 (4)	2.431 (15)	C(1)-C(2)	1.475 (8)	1.47 (3)
-O(W)	2.418 (4)	2.434 (16)	C(2)-C(3)	1.403 (9)	1.41 (3)
-O(4)	2.433 (4)	2.465 (16)	C(3)-C(4)	1.381 (10)	1.36 (4)
-O(8)	2.473 (4)	2.470 (14)	C(4)-C(5)	1.369 (12)	1.42 (4)
-O(9)	2.434 (4)	2.471 (16)	C(5)-C(6)	1.418 (12)	1.44 (4)
-O(2)	2.488 (4)	2.541 (15)	C(6)-C(7)	1.379 (9)	1.41 (4)
-O(7)	2.508 (4)	2.548 (15)	C(7)-C(2)	1.404 (9)	1.38 (3)
-O'(7)	2.588 (3)	2.592 (15)	C(8)-C(9)	1.487 (8)	1.45 (3)
-O'(8)	2.555 (3)	2.630 (15)	C(9)-C(10)	1.408 (8)	1.38 (3)
C(1)-O(1)	1.248 (7)	1.24 (3)	C(10)-C(11)	1.402 (9)	1.41 (3)
-O(2)	1.272 (6)	1.25 (2)	C(11)-C(12)	1.385 (10)	1.37 (4)
C(3)-O(3)	1.360 (7)	1.39 (3)	C(12)-C(13)	1.400 (11)	1.39 (4)
C(8)-O(4)	1.238 (6)	1.27 (3)	C(13)-C(14)	1.372 (9)	1.38 (3)
-O(5)	1.266 (6)	1.24 (2)	C(14)-C(9)	1.418 (9)	1.41 (3)
C(10)-O(6)	1.365 (8)	1.38 (3)	C(15)-C(16)	1.476 (7)	1.48 (3)
C(15)-O(7)	1.266 (6)	1.31 (3)	C(16)-C(17)	1.428 (7)	1.42 (3)
-O(8)	1.262 (6)	1.23 (3)	C(17)-C(18)	1.404 (8)	1.44 (3)
C(17)-O(9)	1.344 (7)	1.30 (3)	C(18)-C(19)	1.393 (8)	1.44 (3)
			C(19)-C(20)	1.398 (9)	1.42 (3)
			C(20)-C(21)	1.381 (8)	1.40 (3)
			C(21)-C(16)	1.397 (8)	1.43 (3)

Table IV. Bond Angles and Standard Errors (deg)

Angle	Sm	Am	Angle	Sm	Am
O(1)-C(1)-O(2)	122.6 (5)	124 (2)	O(6)-C(10)-C(11)	117.0 (6)	117 (2)
O(1)-C(1)-C(2)	118.6 (5)	120 (2)	C(9)-C(10)-C(11)	120.8 (6)	123 (3)
O(2)-C(1)-C(2)	118.8 (5)	116 (2)	C(10)-C(11)-C(12)	119.1 (7)	119 (3)
C(1)-C(2)-C(3)	121.4 (5)	123 (2)	C(11)-C(12)-C(13)	121.1 (6)	121 (2)
C(1)-C(2)-C(7)	118.9 (6)	118 (2)	C(12)-C(13)-C(14)	119.7 (7)	119 (3)
C(3)-C(2)-C(7)	119.8 (6)	119 (2)	C(13)-C(14)-C(9)	121.0 (7)	122 (3)
C(2)-C(3)-O(3)	120.4 (5)	120 (2)	O(7)-C(15)-O(8)	117.8 (4)	120 (2)
C(2)-C(3)-C(4)	120.5 (6)	123 (2)	O(7)-C(15)-C(16)	119.9 (5)	119 (2)
O(3)-C(3)-C(4)	119.1 (6)	117 (3)	O(8)-C(15)-C(16)	122.3 (5)	122 (2)
C(3)-C(4)-C(5)	118.5 (7)	116 (3)	C(15)-C(16)-C(21)	119.8 (5)	119 (2)
C(4)-C(5)-C(6)	120.9 (7)	121 (3)	C(15)-C(16)-C(17)	121.2 (5)	120 (2)
C(5)-C(6)-C(7)	120.7 (7)	119 (3)	C(21)-C(16)-C(17)	119.0 (5)	121 (2)
C(6)-C(7)-C(2)	119.5 (7)	122 (3)	C(16)-C(17)-O(9)	122.4 (5)	124 (2)
O(4)-C(8)-O(5)	123.9 (5)	122 (2)	C(16)-C(17)-C(18)	119.1 (5)	120 (2)
O(4)-C(8)-C(9)	119.1 (5)	119 (2)	O(9)-C(17)-C(18)	118.5 (5)	116 (2)
O(5)-C(8)-C(9)	117.0 (5)	118 (2)	C(17)-C(18)-C(19)	120.2 (6)	119 (2)
C(8)-C(9)-C(10)	122.1 (5)	124 (2)	C(18)-C(19)-C(20)	120.7 (5)	120 (2)
C(8)-C(9)-C(14)	119.7 (5)	119 (2)	C(19)-C(20)-C(21)	119.4 (5)	121 (2)
C(14)-C(9)-C(10)	118.1 (5)	117 (2)	C(20)-C(21)-C(16)	121.6 (5)	119 (2)
C(9)-C(10)-O(6)	122.2 (5)	120 (2)			

Table V. Displacement, in Å, from Least-Squares Planes through the Benzene Rings

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	O(1)	O(2)	O(3)
Plane 1, Sm	0.095	0.023	-0.007	-0.015	0.020	-0.033	-0.018	0.174	0.117	-0.072
Plane 1, Am	0.066	0.015	-0.004	0.000	-0.006	0.017	-0.021	0.166	0.078	-0.093
	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	O(4)	O(5)	O(6)
Plane 2, Sm	-0.039	-0.010	0.018	-0.011	-0.004	0.012	-0.005	-0.368	0.277	0.044
Plane 2, Am	-0.040	-0.025	0.012	0.002	-0.003	-0.011	0.025	-0.298	0.298	0.008
	C(15)	C(16)	C(17)	C(18)	C(19)	C(20)	C(21)	O(7)	O(8)	O(9)
Plane 3, Sm	0.060	0.009	-0.008	-0.001	0.009	-0.007	-0.002	0.100	0.290	0.003
Plane 3, Am	0.032	0.032	-0.012	-0.014	0.020	-0.001	-0.026	0.061	0.051	0.016

Equations of the Planes<sup>a</sup>

1, Sm:  $7.28x + 3.33y - 20.4z - 0.507 = 0$

1, Am:  $7.23x + 3.33y - 20.3z - 0.476 = 0$

2, Sm:  $8.94x - 1.82y + 9.43z - 2.91 = 0$

2, Am:  $8.81x - 2.10y + 9.50z - 2.95 = 0$

3, Sm:  $-11.15x - 2.33y + 18.1z - 4.22 = 0$

3, Am:  $-11.06x - 2.44y + 18.0z - 4.19 = 0$

<sup>a</sup>  $x$ ,  $y$ , and  $z$  are crystal coordinates.

atom varied, along with all the positional parameters. The latter did not, in this treatment or in the case when isotropic temperature factors were used, change by more than  $\sigma$  from the values attained when all  $\beta$ 's were allowed to vary. The agreement index reached was 0.055

and  $\sigma_1$  was 1.74 in this case. A listing of observed and calculated structure factors on an absolute scale is available elsewhere.<sup>18</sup>

In Table II are listed the refined parameters of both compounds. Tables III and IV present the bond lengths and angles and their

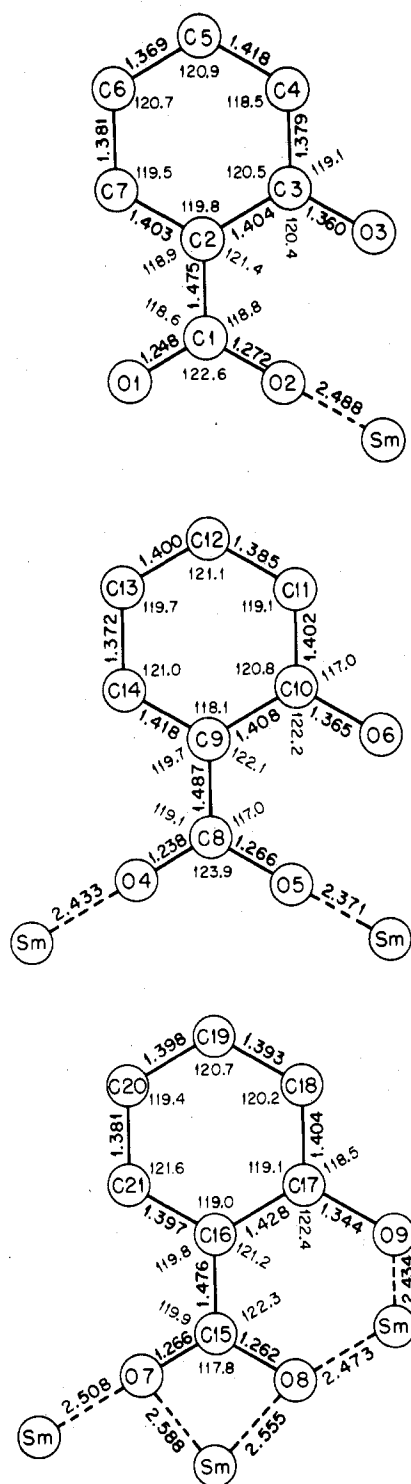


Figure 3. Schematic representation of the three independent salicylato ions in  $(C_7H_5O_3)_3Sm \cdot H_2O$  showing the numbering sequence as well as bond lengths and angles. The standard errors of these plus all of the values for  $(C_7H_5O_3)_3Am \cdot H_2O$  are given in Tables III and IV.

standard deviations calculated from the parameters of Table II.

### Discussion

The overall structure is portrayed in Figure 1 and a detailed look at the metal ion coordination is found in Figure 2. There are no discrete molecules of the salicylato complex in the crystal structure. Each metal ion is bonded to the oxygen atoms of six salicylato ions and to one water molecule. One salicylato ion is bidentate through its carboxyl group, another is bidentate through a combination of carboxylic and phenolic

oxygens, and four are monodentate through carboxylic oxygens. There is extensive cross-linking by the attachment of two of the independent salicylato ions to more than one metal ion. The ion containing C(1) through C(7) is terminal (see Figure 3), but the ion containing C(8) through C(14) has its carboxyl group, O(4) and O(5), attached to two different metal ions. The ion containing C(15) through C(21) is linked to three different metal ions; in it O(7) and O(8) are attached to one metal ion, O(7) is also bonded to a second metal ion, and O(8) and O(9) are bonded to a third. The cross-linking produces endless chains along  $b$  (see Figure 1); these are held together only by van der Waals forces between them, and many C-C and C-O contacts exist between chains at about 3.7 Å. Macroscopic evidence of this structural feature is found in the easy cleavage of the needlelike crystals into other needles of smaller cross section.

The sharing of the anions between cations is, of course, necessary because of the need for high coordination numbers ( $\sim 9$ ) for these large-radius cations (Sm, 0.964 Å; Am, 0.984 Å) and the limitations of stoichiometry and molecular geometry. It is curious that a single  $H_2O$  molecule is included in the coordination polyhedron although there is available another oxygen from the carboxyl group of the terminal salicylato ion.

Bond lengths and angles are given in Tables III and IV, and Figures 2 and 3 aid in visualizing their places in the structure. The lengths quoted in the following discussion are for the Sm complex; the (similar) values for the Am complex can be found in Tables III and IV. The pattern of bonding within the salicylato ions themselves is the same for all three independent ions. It is characterized by the equivalence of the bond lengths to the two carboxylate O atoms, by a short C-C bond to the carboxyl group, a short C-O bond to the hydroxyl group, and possibly a distortion of the benzene ring from hexagonal symmetry (deviations from equivalence of the C-C bonds within the hexagonal rings are only marginally significant, but the shortened exterior C-C and C-O bonds are real). This is the same molecular shape as was found for salicylic acid<sup>13</sup> except, of course, for the nonequivalent bonds in the nonionized carboxylic acid group of that molecule. These bonding peculiarities, found also in 2-amino-3-methylbenzoic acid,<sup>19</sup> were attributed previously to appreciable contribution of a quinoid structure to the resonance state of these organic molecules. Values for C-OH bond lengths ( $\sim 1.45$  Å), when not affected by resonance, can be seen in the malato ion<sup>20</sup> or in the citrato ion.<sup>21</sup> Typical values for ionized carboxyl groups with C-O lengths of  $\sim 1.25$  Å are also found in these two structures.

In Table V are listed the displacements of the atoms of the salicylato ions from the best plane through the benzene ring of each. Planarity is quite good except for the carboxylate O atoms which are subject to the influence of the metal ion to which they are bonded.

Although H atoms were not located in this work, the existence of some hydrogen bonds can be inferred. For the two independent salicylato ions not involved in cyclic chelation the phenolic H atoms probably form intramolecular H bonds to carboxylic O atoms as in salicylic acid. The interatomic distances involved are O(2)···O(3) = 2.527 (6) Å and O(5)···O(6) = 2.608 (6) Å. (The third phenolic H atom is discussed below.) From a consideration of the position of the water molecule in relation to its near O neighbors, it seems most likely that the H atoms form H bonds with an O(3) atom and possibly an O(6) atom of different salicylato ions along the chain. Distances from O(W) to these atoms are 2.668 (6) and 2.929 (7) Å, respectively, and the O(6)-O(W)-O(3) angle is 101.8 (2)°.

By showing that these complexes all are isomorphous we have established that they have the same stoichiometry,

namely,  $(C_7H_5O_3)_3M \cdot H_2O$  where  $M = La, Nd, Sm,$  or  $Am$ . This had been found previously only for the case of  $Nd$ . The formula for the  $Pu$  complex is probably the same because our findings have covered the range of ionic size which includes  $Pu^{3+}$ ; we have not, however, been able to produce the compound despite numerous attempts using the published method.<sup>3</sup>

The kinds of linkages found in the crystal between salicylato and metal ions are relevant to the previous work with stability constants and also suggest the type of interaction which these ions have with humic materials. The chains of metal ions sharing common organic ligands raise the possibility that in solution the molecules are also polynuclear. The presence of numerous types of configurations by which the ligands are attached to the metal not only confirms the cyclic mode of chelation suggested for salicylato ions but also includes many endwise attachments which were proposed to be the case for *p*-hydroxybenzoate ligands. The phenolic hydrogen atom is not expected to be ionized in solutions with  $pH < 7$ , and the structural evidence tends to confirm this. The one  $OH, O(9)$ , that is chelated to the metal would seem most likely to be ionized, if any. Evidence that the  $H$  atom is *not* ionized is that (1) the  $C-OH$  bond is of normal length and equivalent to that in the other salicylato ions, (2) there is a very short  $O(9) \cdots O(1)$  contact of 2.399 Å to another ligand, and (3) the  $C-O \cdots O$  angle is  $112.7(3)^\circ$  which is typical for a phenolic  $C-O-H$  angle.

**Registry No.**  $(C_7H_5O_3)_3Sm \cdot H_2O$ , 61026-21-9;  $(C_7H_5O_3)_3Am \cdot H_2O$ , 61026-23-1;  $(C_7H_5O_3)_3Nd \cdot H_2O$ , 61026-25-3;  $(C_7H_5O_3)_3La \cdot H_2O$ , 61026-27-5.

**Supplementary Material Available:** Tables of observed and cal-

culated structure factors (16 pages). Ordering information is given on any current masthead page.

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## Metal-Metal Bonding in Reduced Scandium Halides. Synthesis and Crystal Structure of Scandium Monochloride<sup>1</sup>

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The synthesis of a number of reduced scandium chlorides is achieved by reaction of excess metal with  $ScCl_3$  in sealed Ta tubing above  $877^\circ C$  for periods of weeks to months. Extreme conditions are necessary because of both the kinetic problems of forming extended metal-metal bonded structures and the fact that  $ScCl_{1.5}$  effectively blocks further reaction on metal surfaces below this temperature. Single-crystal x-ray diffraction data showed that a gray-black laminar phase was  $ScCl$  with a sheet structure consisting of close-packed homoatomic layers sequenced  $Cl-Sc-Sc-Cl$  along  $[001]$  ( $R\bar{3}m$ , trigonal cell;  $a = 3.473(2)$  Å,  $c = 26.71(4)$  Å,  $Z = 6$ ;  $R = 0.088$ ,  $R_w = 0.101$  for 79 independent reflections taken with  $Mo K\alpha$  radiation). The phase is thus polytypic (ignoring the difference in metal atom) with  $ZrCl$  and isostructural with  $ZrBr$  even though there are only two-thirds as many electrons for bonding the double-metal sheets of scandium. The general occurrence of metal-metal bonding in clusters, ribbons, and sheets in transition metal groups 3–5 is considered.

### Introduction

Since 1963 a series of publications reporting and disputing the existence of solid, lower chlorides of scandium has appeared. Polyachenok and Novikov<sup>2a</sup> first reported a relatively large amount of reaction of the metal with the liquid  $ScCl_3$  and the formation of the solid phases  $ScCl_{2.67}$  and  $ScCl_2$ , although the means whereby these compositions were established was not given. Corbett and Ramsey<sup>2b</sup> disputed these results based on thermal analysis data, suggesting the earlier results had been perturbed by reaction with the silica container. In a subsequent publication McCollum and co-workers<sup>3</sup> reported on the preparation of solid  $ScCl_{1.5}$ , scandium sesquichloride, as well as  $ScBr_{1.5}$ , both of which could be prepared

at elevated temperatures when proper attention was paid to avoiding blockage of the metal surface by product. Subsequent efforts to prepare single crystals of  $ScCl_{1.5}$  have revealed a complex and unpredicted<sup>4</sup> chemistry in the  $Sc-ScCl_3$  system. This paper notes some of the chemistry in the region  $2.0 \geq Cl:Sc \geq 1.0$  and reports on the single-crystal structure of the stoichiometric monochloride,  $ScCl$ .

### Experimental Section

**Materials.** The metal used had been distilled in tantalum and had typical major impurity levels (atomic ppm) of 70 Fe, 250 Ta, <30 individual rare earths, and <800 each C, O, F. Thin foil strips for reduction of  $ScCl_3$  were made from cold-rolled scandium sheet which was cut into pieces (4 cm × 1 cm × 0.12 cm), annealed at  $750^\circ C$