

Structural Studies on the Rare Earth Carboxylates

13. The Crystal and Molecular Structure of Tetra-aquo Tris-oxalato Discandium(III) Dihydrate

EVA HANSSON

Physical Chemistry 1, Chemical Center, University of Lund, P. O. Box 740, S-220 07 Lund 7, Sweden

The crystal and molecular structure of the compound, $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, has been determined from three-dimensional, photographic, X-ray intensity data. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ and has the lattice parameters $a=6.189(1)$ Å, $b=6.523(1)$ Å, $c=9.957(2)$ Å, $\alpha=114.99(1)^\circ$, $\beta=95.03(1)^\circ$, and $\gamma=96.52(1)^\circ$. The crystal structure consists of layers containing an infinite scandium-oxalate network alternating with layers containing the water molecules. The scandium ion is eight-coordinated. It is surrounded by six carboxylic and two water oxygen atoms in an approximately dodecahedral arrangement. Each oxalate ion is coordinated to two scandium ions forming two chelates. The Sc-O bond distances are in the range 2.18–2.26 Å.

One aim of the present series of investigations is to study the influence of the decrease in ionic radius across the lanthanoid series, on the structures of some lanthanoid carboxylates. The structures of the corresponding scandium compounds are of interest in this respect since Sc(III) has a similar outer electron shell configuration to the trivalent lanthanoids but a considerably smaller ionic radius. The ionic radius of Sc(III) in eight coordination is 0.87 Å while the corresponding values for La(III) and Lu(III) are 1.18 Å and 0.97 Å, respectively.¹

The decrease of the size of the metal ion results for the compounds $\text{M}_2(\text{C}_2\text{O}_4)_3 \cdot n\text{H}_2\text{O}$ (M=lanthanoid) in a change of structure. Thus two groups of isotypic compounds are formed; one with $n \approx 10$ for M=La–Er, and the other with $n=6$ for M=Ho–Lu. $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$ is isotypic with the compounds of the latter group.

The structure of $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10.5\text{H}_2\text{O}$, abbreviated NDOX below, has been reported previously.²⁻⁴ In this paper the crystal and molecular structure of $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, abbreviated SCOX, is described.

Large single crystals of SCOX form easily. This is not the case for the corresponding lanthanoid compounds which are always twinned. A structure determination of the ytterbium compound is in progress and that structure will be given in a subsequent paper together with the lattice parameters of the compounds of the two groups.

EXPERIMENTAL

Preparation and analysis. SCOX was prepared according to Wylie.⁵ Dilute solutions of scandium perchlorate and oxalic acid were slowly added at the same rate to water maintained at 70°C. The precipitate was digested in the mother liquor at this temperature for about one week and then filtered and dried in air at room temperature. The compound was analysed for Sc, C, and H. The relative amounts found are compared with those calculated for $\text{Sc}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$, F.W. 462.0

	Sc	C	H	
Found	19.4	16.1	3.0	(%)
Calc.	19.5	15.6	2.6	(%)

Single crystal work. Two tabular single crystals, both of the approximate dimensions $0.1 \times 0.1 \times 0.03$ mm³ and mounted along a 0.1 mm edge, were used in recording the first five layers along [100] and [011], respectively. The directions refer to the *A*-centered cell given below. Weissenberg photographs were taken with Ni-filtered Cu-radiation. They were integrated in the first setting and non-integrated in the second one. 843 independent reflexions were recorded, representing about 70 % of the possible number in the investigated reciprocal region. The intensities of the reflexions were measured visually by comparison with a calibrated scale.

The linear absorption coefficient is 44 cm⁻¹. Because of this low value and the small crystals used no absorption correction was applied.

UNIT CELL AND SPACE GROUP

SCOX crystallizes in the Laue class $\bar{1}$. The possible space groups are thus $P\bar{1}$ (No. 1) and $P\bar{1}$ (No. 2).⁶ The structures of SCOX and NDOX are closely related. To elucidate this it is convenient to use a cell which becomes *A*-centered in the description of SCOX. The dimensions of the *A*-centered cell are given below together with those of the primitive cell. The transformation of indices from the *A*-centered to the primitive cell is given by the matrix $(0, -\frac{1}{2}, -\frac{1}{2} | 0, -\frac{1}{2}, \frac{1}{2} | -1, \frac{1}{2}, -\frac{1}{2})$. The values of the lattice parameters were refined from powder data obtained at room temperature by using a Guinier focusing camera and $\text{CuK}\alpha$ radiation, $\lambda = 1.54178$ Å.

<i>A</i> -centered cell	Primitive cell
$a = 9.317(2)$ Å, $\alpha = 93.04(1)^\circ$	$a = 6.189(1)$ Å, $\alpha = 114.98(1)^\circ$
$b = 8.468(2)$ Å, $\beta = 106.50(1)^\circ$	$b = 6.523(1)$ Å, $\beta = 95.03(1)^\circ$
$c = 9.489(2)$ Å, $\gamma = 86.27(2)^\circ$	$c = 9.957(2)$ Å, $\gamma = 96.52(1)^\circ$

The structure was assumed to be centrosymmetric and the subsequent calculations did not contradict this assumption. Thus the space group is $A\bar{1}$, the general position of which is fourfold: $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}) + x, y, z; \bar{x}, \bar{y}, \bar{z}$.

Table 1. Atomic parameters with estimated standard deviations in SCOX. The space group is $A\bar{1}$. The transformation of the positional parameters from the A -centered cell to the primitive cell is given by the matrix $(0, -1, -1, -1, -1, 1, -1, 0, 0)$. The anisotropic thermal parameters, β_{ij} , have been obtained by using the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + \dots)]$ and the root-mean-squares displacements along the principal axis of the thermal ellipsoids, R_i , have been calculated from the values of β_{ij} .

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$	$R_1/\text{Å}$	$R_2/\text{Å}$	$R_3/\text{Å}$
Sc		3064(2)	48(2)	1925(1)	42(2)	70(2)	41(2)	3(3)	10(2)	5(2)	0.161	0.121	0.143
O(1)	-COO-	1667(6)	-418(7)	-414(6)	50(6)	134(10)	74(7)	12(14)	6(11)	29(12)	0.223	0.135	0.189
O(2)	-COO-	690(6)	365(6)	1904(6)	56(7)	105(8)	66(6)	26(13)	16(11)	14(11)	0.203	0.140	0.175
O(3)	-COO-	3997(7)	1531(6)	627(6)	92(7)	68(7)	80(6)	24(14)	71(12)	13(10)	0.204	0.149	0.172
O(4)	-COO-	4512(6)	-1560(6)	860(5)	73(7)	87(8)	56(6)	8(13)	44(11)	-3(10)	0.185	0.147	0.168
O(5)	-COO-	5451(6)	93(6)	3344(8)	74(7)	75(7)	56(6)	7(13)	28(10)	11(9)	0.181	0.151	0.163
O(6)	-COO-	3076(6)	23(6)	4308(5)	52(6)	110(8)	58(6)	23(13)	-12(10)	18(10)	0.206	0.121	0.184
O(7)	H ₂ O	2682(7)	2625(7)	2412(6)	93(8)	92(8)	88(7)	11(14)	86(13)	-16(11)	0.207	0.153	0.195
O(8)	H ₂ O	228(11)	-1574(13)	4368(11)	134(12)	302(22)	208(16)	-138(29)	-9(23)	56(28)	0.357	0.207	0.299
O(9)	H ₂ O	2516(7)	-2399(6)	2161(6)	85(8)	85(8)	90(7)	19(14)	23(13)	22(11)	0.210	0.161	0.191
C(1)		282(9)	-244(10)	-674(8)	62(9)	105(12)	69(9)	12(20)	-1(16)	-9(15)	0.211	0.144	0.180
C(2)		4869(9)	893(8)	-86(7)	70(9)	73(11)	47(8)	17(18)	9(15)	3(13)	0.189	0.135	0.155
C(3)		5690(8)	14(9)	4739(7)	55(9)	80(10)	51(7)	21(18)	6(14)	8(13)	0.184	0.129	0.159

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The positions of all non-hydrogen atoms, except the uncoordinated water oxygen O(8) (notations, *cf.* Table 1), were deduced from the vector maps obtained in a three-dimensional Patterson synthesis. A difference synthesis based upon the positions of the located atoms revealed the position of O(8).

The preliminary atomic coordinates and isotropic temperature factors were then improved together with the inter-layer scale factors by full-matrix, least squares refinement. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with weights, w , chosen according to Cruickshank.⁷ An analysis of the weighting scheme used is given in Table 2. The atomic scattering factors for the neutral

Table 2. Analysis of the weighting scheme $w = 1/(3.0 + |F_o| + 0.03|F_o|^2 + 0.001|F_o|^3)$. The averages, $w\Delta^2$, where $\Delta = |F_o| - |F_c|$, are normalized.

Interval $ F_o $	Number of reflexions	$\overline{w\Delta^2}$	Interval $\sin \theta$	Number of reflexions	$\overline{w\Delta^2}$
0 - 12	84	1.20	0.00 - 0.37	73	1.75
12 - 15	84	1.02	0.37 - 0.47	77	0.56
15 - 18	84	0.91	0.47 - 0.54	71	1.57
18 - 21	84	0.91	0.54 - 0.59	66	1.32
21 - 24	85	1.08	0.59 - 0.64	60	1.06
24 - 28	84	1.06	0.64 - 0.68	46	0.71
28 - 32	84	1.16	0.68 - 0.71	45	1.02
32 - 40	84	0.74	0.71 - 0.74	46	0.61
40 - 52	84	1.00	0.74 - 0.77	51	0.84
52 - 149	85	0.93	0.77 - 0.80	45	0.57

atoms were for O and C taken from *International Tables*⁸ and for Sc from Cromer *et al.*⁹

After three cycles of refinement the values of the conventional discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ were 0.084 and 0.102 for the integrated and non-integrated materials, respectively. The data were then brought together and three more cycles resulted in $R = 0.091$ while the weighted R -factor $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ had converged to 0.127.

Further refinement using anisotropic thermal parameters for (i) Sc, (ii) Sc and O(8), and (iii) all non-hydrogen atoms resulted in the following R -values: (i) $R = 0.086$, $wR = 0.121$, (ii) $R = 0.083$, $wR = 0.116$, and (iii) $R = 0.076$, $wR = 0.104$, and it was considered reasonable to assign anisotropic temperature factors to all non-hydrogen atoms. The over-all scale factor was refined in these calculations.

The shifts in all parameters were less than 1 % of their estimated standard deviations in the last cycle of refinement. The final atomic parameters with their estimated standard deviations are given in Table 1.

It was not possible to locate the hydrogen atoms in the structure. Regions of positive electron density in the vicinity of the water oxygens were observed in the electron density maps of a difference synthesis based upon the positions

of the non-hydrogen atoms and calculated using data obeying the condition $\sin \theta/\lambda < 0.5$. The highest density, about $0.6 \text{ e}/\text{\AA}^3$, was found in the region between the uncoordinated water oxygen O(8) and its nearest neighbour, the water oxygen O(9), but there were no distinct peaks and attempts to refine hydrogen atoms in geometrically and chemically reasonable positions were not successful.

A final difference synthesis including all F_o showed a slowly varying electron density, less than $1 \text{ e}/\text{\AA}^3$ in all regions. The observed and calculated structure factors are compared in Table 3.

All computations were performed on the UNIVAC 1108 computer at Lund, Sweden, using the programs DRF, LALS, DISTAN, PLANE and ORTEP.¹⁰

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The superscripts (i)–(x) are used to indicate the following equivalent sites in the structure:

	x, y, z	(iii)	$1 - x, \bar{y}, 1 - z$	(vii)	$1 + x, y, z$
(i)	$x, \frac{1}{2} + y, \frac{1}{2} + z$	(iv)	$1 - x, \bar{y}, \bar{z}$	(viii)	$1 + x, \frac{1}{2} + y, \frac{1}{2} + z$
(ii)	$x, -\frac{1}{2} + y, \frac{1}{2} + z$	(v)	$1 - x, \frac{1}{2} - y, \frac{1}{2} - z$	(ix)	$1 + x, -\frac{1}{2} + y, \frac{1}{2} + z$
		(vi)	$1 - x, -\frac{1}{2} - y, \frac{1}{2} - z$	(x)	$\bar{x}, \bar{y}, \bar{z}$

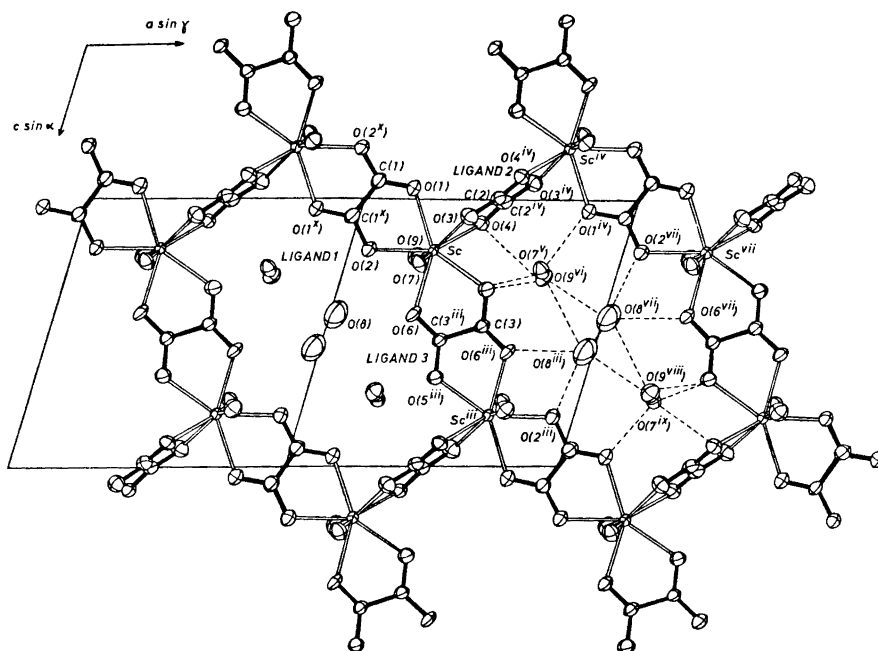


Fig. 1. A part of the scandium-oxalate layer around $y=0$ projected along b , and with $-0.30 \leq y \leq 0.30$, *i.e.*, the water oxygen atoms above and below the layer are included. The possible hydrogen bond distances are marked with dashes. The figure is drawn by the program ORTEP¹⁰ representing the atoms by "thermal ellipsoids" scaled to include 50% of the probability distribution.

where x, y, z are the atomic coordinates given in Table 1. The notations of the atoms forming the three structurally independent oxalate ions referred to as ligand 1, ligand 2, and ligand 3, respectively, are shown in Fig. 1.

The structure of SCOX is composed of scandium-oxalate layers around $y=0$ and $y=\frac{1}{2}$. Fig. 1 shows the layer around $y=0$ projected along b . The metal ion is coordinated by three oxalate ions—two approximately in the plane $y=0$ (ligands 1 and 3) and the third one (ligand 2) approximately perpendicular to that plane—forming three five-membered chelate rings. Each oxalate ion acts as a bridge between two metal ions, in such a way that rings containing six metal and six oxalate ions are formed. Each scandium ion is a member of three such rings. The resulting two-dimensional network is very similar to that formed in NDOX.

Adjacent layers are related by the translation $(0, \frac{1}{2}, \frac{1}{2})$ placing oxalate ions (*i.e.* ligand 1) directly above and below the centre of a metal-ligand ring. This feature is most easily imagined by looking at Fig. 1. The water molecules are situated in the cavities formed.

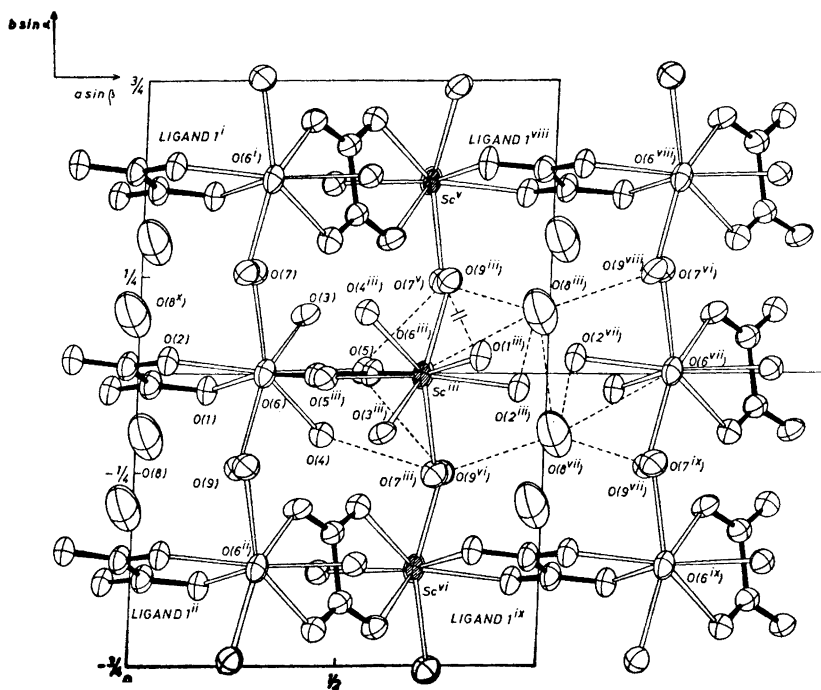


Fig. 2. The structure of SCOX projected along c . All oxygen atoms coordinated to the scandium ions included are shown but for clarity complete oxalate ions are shown only around $(0,0,0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(\frac{3}{2}, 0, 0)$, $(0, \pm \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \pm \frac{1}{2}, \frac{1}{2})$, $(1, \pm \frac{1}{2}, \frac{1}{2})$, and $(\frac{3}{2}, \pm \frac{1}{2}, \frac{1}{2})$. Ligand 1^{viii} and ligand 1^{ix} are situated directly above and below $(1, 0, \frac{1}{2})$. The possible hydrogen bond distances are denoted by dashed lines. The line between O(7^v) and O(1ⁱⁱⁱ) is broken to indicate that the distance is to O(1^{iv}) in the cell behind. The figure is drawn as Fig. 1.

Table 4. Selected interatomic distances (Å) and angles (°) with their estimated standard deviations.

A. Within the coordination polyhedron			
Sc-O(1)	2.259(6)	O(3)-O(6)	3.242(8)
Sc-O(2)	2.206(6)	O(3)-O(7)	2.471(8)
Sc-O(3)	2.184(6)	O(4)-O(5)	2.634(7)
Sc-O(4)	2.257(6)	O(4)-O(9)	2.658(9)
Sc-O(5)	2.251(6)	O(5)-O(6)	2.625(8)
Sc-O(6)	2.258(6)	O(5)-O(7)	3.198(8)
Sc-O(7)	2.233(6)	O(5)-O(9)	3.457(8)
Sc-O(9)	2.205(6)	O(6)-O(7)	2.854(9)
O(1)-O(2)	2.648(8)	O(6)-O(9)	2.782(8)
O(1)-O(3)	2.739(8)	O(3)-Sc-O(4)	72.9(2)
O(1)-O(4)	2.716(8)	O(2)-Sc-O(6)	74.7(2)
O(1)-O(7)	3.590(8)	O(1)-Sc-O(5)	142.4(2)
O(1)-O(9)	2.924(9)	O(7)-Sc-O(9)	147.4(2)
O(2)-O(6)	2.708(8)	O(5)-Sc-O(9)	101.7(2)
O(2)-O(7)	2.685(8)	O(4)-Sc-O(6)	125.4(2)
O(2)-O(9)	2.782(8)	O(1)-Sc-O(7)	106.1(2)
O(3)-O(4)	2.640(8)	O(2)-Sc-O(3)	121.0(2)
O(3)-O(5)	2.850(8)		
B. Within ligand 1			
C(1)-C(1 ^x)	1.537(16)	O(1)-C(1)-O(2)	127.5(8)
C(1)-O(1)	1.244(10)	O(1)-C(1)-C(1 ^x)	115.2(9)
C(1)-O(2)	1.265(10)	O(2)-C(1)-C(1 ^x)	117.3(9)
C. Within ligand 2			
C(2)-C(2 ^{iv})	1.527(15)	O(3)-C(2)-O(4)	127.1(7)
C(2)-O(3)	1.272(10)	O(3)-C(2)-C(2 ^{iv})	113.8(8)
C(2)-O(4)	1.233(10)	O(4)-C(2)-C(2 ^{iv})	119.1(9)
D. Within ligand 3			
C(3)-C(3 ⁱⁱⁱ)	1.513(15)	O(5)-C(3)-O(6)	127.6(7)
C(3)-O(5)	1.279(9)	O(5)-C(3)-C(3 ⁱⁱⁱ)	115.3(8)
C(3)-O(6)	1.243(9)	O(6)-C(3)-C(3 ⁱⁱⁱ)	117.1(8)
E. Possible hydrogen bonds			
O(7 ^v)-O(1 ^{iv})	2.905(8)	O(8 ^{vii})-O(9 ^{vi})	2.734(12)
O(7 ^v)-O(5)	2.931(8)	O(8 ^{vii})-O(8 ⁱⁱⁱ)	2.932(23)
		O(8 ^{vii})-O(2 ^{vii})	3.065(12)
O(9 ^{vi})-O(5)	2.977(8)	O(8 ^{vii})-O(6 ^{vii})	3.070(12)
O(9 ^{vi})-O(4)	2.982(9)	O(8 ^{vii})-O(7 ^{ix})	3.205(12)

The packing of the layers is illustrated in Fig. 2 which shows the structure projected along c . Hydrogen bonds *via* the water molecules hold the layers together, and the way of packing is almost the same as that found in NDOX.

The coordination polyhedron. The scandium ion is coordinated by three oxalate ions bonded as chelates, and two water molecules. Thus the coordination number is eight. Distances and angles of interest for the description of the coordination polyhedron are given in Table 4 A.

The Sc–O bond distances range from 2.18 to 2.26 Å. The mean value, 2.23 Å, is identical with the mean values found in the compounds ScVO_4 ¹¹ and ScPO_4 ¹² where the scandium ion is also eight-coordinated. The Sc–O bond distance may also be compared to the averaged Zr–O bond distance of 2.20 Å in the compound $\text{Na}_4\text{Zr}(\text{C}_2\text{O}_4)_4 \cdot 3\text{H}_2\text{O}$ ¹³ which contains mononuclear $\text{Zr}(\text{C}_2\text{O}_4)_4^{4-}$ complexes. Taking the difference in ionic radius into account ($r_{\text{Sc(III)}} = 0.87$ Å, $r_{\text{Zr(IV)}} = 0.84$ Å¹) the agreement is good.

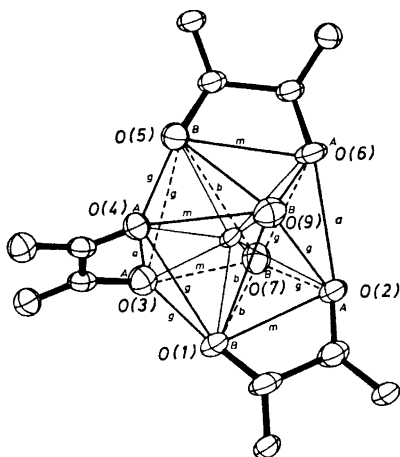


Fig. 3. The coordination around the scandium ion with the dodecahedron outlined. The figure is drawn as Fig. 1.

The coordination polyhedron is shown in Fig. 3 as a distorted dodecahedron. It might also be described as a distorted square antiprism with the square faces formed by O(5), O(6), O(9), O(4) and O(3), O(7), O(2), O(1), respectively. Comparison with the hard sphere models¹⁴ of the two polyhedra shows that the deviations from the ideal dodecahedron are somewhat less than those from the ideal square antiprism.

Following the notation of Hoard and Silverton¹⁴ as indicated in Fig. 3 and taking all Sc–O bond distances equal to the mean value, 2.23 Å, the ideal dodecahedron has $a = m = g = 2.68$ Å, $b = 3.35$ Å, $\theta_A = 36.9^\circ$, and $\theta_B = 69.5^\circ$. θ_A and θ_B are the angles which the metal-ligand bonds M–A and M–B form with the $\bar{4}$ -axis, respectively. The mean values of these parameters found in SCOX are $a = 2.67$ Å, $m = 2.60$ Å, $g = 2.76$ Å, $b = 3.29$ Å, $\theta_A = 37^\circ$, and $\theta_B = 73^\circ$. An increase in θ_B from the ideal value by a few degrees is commonly found in dodecahedral complexes and can also be predicted by calculations of the total ligand-ligand repulsive energies.^{14,15} Another feature commonly

found for dodecahedral complexes is a significant difference between the M–A and M–B bond lengths. Even though there are significant differences in length between the longest and shortest Sc–O bonds they cannot be divided into two groups in this way.

The scandium ion is situated very near the planes formed by the oxalate ions (*cf.* Table 5), and thus the three five-membered rings are approximately planar. The deviations of the scandium and oxygen atoms from the mean trapezoidal planes are given in Table 6 and it is seen that the scandium ion is approximately in these planes, too.

Table 5. The deviations in Å of the scandium ion and ligand atoms from the respective least squares planes through the ligands. The lower signs refer to the superscripted atoms.

Ligand 1		Ligand 2		Ligand 3	
Atoms	Distance	Atoms	Distance	Atoms	Distance
C(1),C(1 ^x)	± 0.015	C(2),C(2 ^{iv})	± 0.002	C(3),C(3 ⁱⁱⁱ)	± 0.000
O(1),O(1 ^x)	∓ 0.004	O(3),O(3 ^{iv})	∓ 0.001	O(5),O(5 ⁱⁱⁱ)	∓ 0.001
O(2),O(2 ^x)	± 0.004	O(4),O(4 ^{iv})	± 0.001	O(6),O(6 ⁱⁱⁱ)	∓ 0.000
Sc	-0.107	Sc	-0.013	Sc	-0.088

Table 6. The deviations in Å from the mean trapezoidal planes of the scandium ion and the atoms defining the respective planes.

Atom	O(1)	O(2)	O(6)	O(5)	Sc
Distance	-0.126	0.201	-0.202	0.127	0.094
Atom	O(7)	O(3)	O(4)	O(9)	Sc
Distance	-0.132	0.211	-0.196	0.117	-0.046

In Fig. 4 the coordination geometry around Sc(III) is compared to that around Nd(III) in NDOX. For this purpose the most convenient description of the coordination polyhedron is the distorted bi-capped trigonal prism (hendecahedron) which is shown in the figure together with the tri-capped trigonal prism of NDOX.

There is no radical rearrangement of the ligands in going from nine- to eight-coordination. The water oxygen O(8) in NDOX disappears in SCOX and is substituted by the carboxylic oxygen O(1), previously situated in the equatorial plane of the prism. This change is accompanied by a further distortion of the trigonal prism in a way that makes the uncapped "rectangular" face considerably smaller than the other two. This is mainly accomplished by

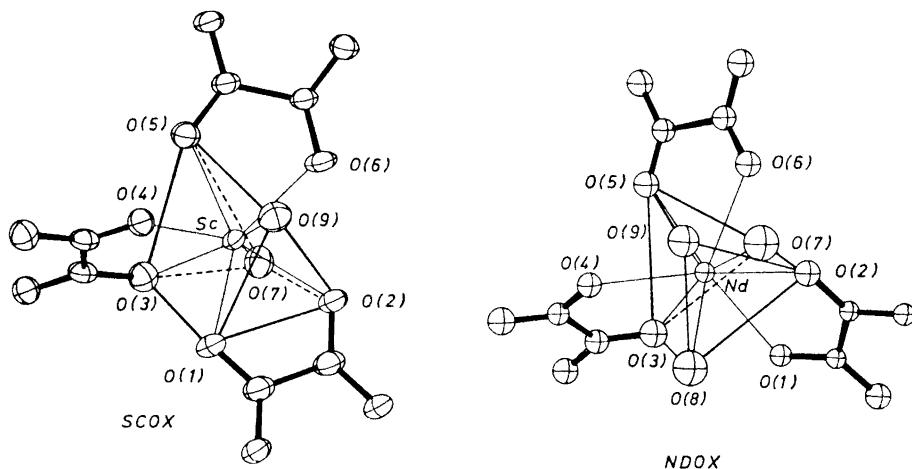


Fig. 4. The coordination polyhedra of NDOX and SCOX. The trigonal prism of NDOX is tri-capped and that of SCOX is bi-capped. The figure is drawn as Fig. 1.

increasing the angle between the two triangular faces; the distances from O(3), O(7), and O(5) to the plane defined by the atoms forming the opposite triangle are 2.73 Å, 2.57 Å, and 3.43 Å in SCOX as compared to 3.25 Å, 3.42 Å, and 3.67 Å in NDOX.

The averaged M–O bond distance decreases from 2.50 to 2.23 Å between NDOX and SCOX. The dimensions of the coordination polyhedron are accordingly reduced. The mean distance between the coordinated oxygen atoms, except distances between atoms belonging to the same ligand are 3.06 Å in NDOX and 2.82 Å in SCOX. In spite of the decrease in coordination number the crowding of oxygen atoms is larger around Sc than around Nd. There are a great number of O–O distances in the dodecahedron of SCOX which are shorter than 2.8 Å, *i.e.* twice the van der Waals radius of oxygen.¹⁶ The distance O(3)–O(7) is only 2.47 Å, which seems to be extremely short, and eight distances are in the range 2.64–2.78 Å. These facts indicate that the oxygen–oxygen repulsive forces in the polyhedron are large. As a matter of fact the coordination number eight is uncommon for Sc(III)¹⁷ and only two structures containing eight coordinated Sc(III) have been reported previously, *viz.* ScVO₄¹¹ and ScPO₄.¹²

The oxalate ions. The values of the bond distances and angles in the oxalate ions, given in Table 4 B, C and D, do not show any significant differences between the three independent ligands, and are in agreement with those found in other oxalate structures.^{18,13,19} The two “bites” are identical, and in this respect the oxalate ions of SCOX differ from those found in structures containing mononuclear oxalato complexes (*e.g.*, Na₄Zr(C₂O₄)₄·3H₂O,¹³ K₂[Pd(C₂O₄)₂]·4H₂O, and K₂[Pt(C₂O₄)₂]·2H₂O¹⁹) where the chelating “bite” tends to be considerably shorter than the other one.

The oxalate ions are planar within the limits of errors (*cf.* Table 5) as is almost invariably found. A frequently cited exception is the oxalate ion of

$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ²⁰ in which the two COO-groups are twisted with respect to each other around the C–C bond. The presence of a centre of symmetry in the three oxalate ions of SCOX excludes such a deviation from planarity in this compound.

Possible hydrogen bonds. The O–O distances suitable for hydrogen bond formation are given in Table 4 E. Distances between oxygen atoms belonging to the same coordination polyhedron are omitted since hydrogen bonds within the polyhedron seem improbable because of the expected large $\text{Sc}^{3+} - \text{H}^+$ repulsions.

The only distance short enough to clearly indicate a hydrogen bond is O(8^{vii})–O(9^{vi}) which is 2.73 Å, and it seems impossible to choose a most probable hydrogen bond system from the other distances. The C–O...O and O...O(water)...O angles involved are in the intervals 112–127° and 74–148°, respectively, except the angle C(2^{iv})–O(4)...O(9^{vi}) which is 90° and the angles O(4)...O(9^{vi})...O(5) and O(6^{vii})...O(8^{vii})...O(2^{vii}) which are both 52°. Hydrogen bonds have been shown to exist involving C–O...O acceptor angles in the range 100–160° ²¹ and O...O(water)...O donor angles in the range 60–150°. ²² Thus several hydrogen bond arrangements are geometrically possible and a disordered hydrogen bond system seems probable especially in view of the large values found for the thermal parameters of O(8) (*cf.* Table 1).

It may still be concluded that the hydrogen bonds form links between the metal-oxalate layers. This feature is shown in Fig. 2 where the distances given in Table 4 E are indicated by dashed lines. The distances O(7^v)–O(5), O(7^v)–O(1^{iv}), O(9^{vi})–O(4), and O(9^{vi})–O(5) are between water molecules coordinated to scandium ions in the layers at $y \approx \frac{1}{2}$ and $y \approx -\frac{1}{2}$, respectively, and carboxylic oxygen atoms in the layer at $y \approx 0$. The uncoordinated water molecule O(8^{vii}) is most probably bonded to O(9^{vi}) and is within hydrogen bond distance from the carboxylic oxygens O(2^{vii}) and O(6^{vii}) at $y \approx 0$, and the water oxygens O(8ⁱⁱⁱ) and O(7^{ix}).

The function of the uncoordinated water molecules is then to fill out the "free spaces" around $(0, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$ and to form additional hydrogen bonds between the metal-oxalate layers. This is just the role assumed for the uncoordinated water molecules in the structure of NDOX, where most of these water molecules could not be located, but the "free spaces", corresponding to those around $(0, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$ in SCOX, were found to be large enough to occlude them in a disordered way.

In NDOX all located water molecules have a carboxylic oxygen atom as possible hydrogen bond acceptor within 2.7–2.9 Å while in SCOX all possible hydrogen bond distances except O(8^{vii})–O(9^{vi}) are larger than 2.9 Å. Thus the hydrogen bonds of SCOX are rather weak as compared to those of NDOX and this feature may be one reason for the increased solubility of SCOX compared to NDOX.

I am indebted to Professor Ido Leden and Drs. Jörgen Albertsson, Karin Aurivillius and Ingmar Grenthe for many valuable discussions. I should also like to thank Professor Sture Frønaeus for placing the X-ray equipment at my disposal and for his kind interest in my work. This work is part of a research project supported by the *Swedish Natural Science Research Council*.

REFERENCES

1. Shannon, R. D. and Prewitt, C. T. *Acta Cryst.* **B 25** (1968) 925.
2. Hansson, E. and Albertsson, J. *Acta Chem. Scand.* **22** (1968) 1682.
3. Ollendorff, W. and Weigel, F. *Inorg. Nucl. Chem. Letters* **5** (1969) 263.
4. Hansson, E. *Acta Chem. Scand.* **24** (1970) 2969.
5. Wylie, A. W. *J. Chem. Soc.* **1947** 1687.
6. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. I.
7. Cruickshank, D. W. J. In Rollet, J. S., Ed., *Computing Methods in Crystallography*, Pergamon, Glasgow 1965, pp. 99–116.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
9. Cromer, D. T., Larsson, A. C. and Waber, J. T. *Acta Cryst.* **17** (1964) 1044.
10. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1206.
11. Milligan, W. O. and Vernon, L. W. *J. Phys. Chem.* **56** (1952) 145.
12. Mooney, R. C. L. *Acta Cryst.* **9** (1956) 677.
13. Glen, G. L., Silverton, J. V. and Hoard, J. L. *Inorg. Chem.* **2** (1963) 250.
14. Hoard, J. L. and Silverton, J. V. *Inorg. Chem.* **2** (1963) 235.
15. Kepert, D. L. *J. Chem. Soc.* **1965** 4736.
16. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca 1960, p. 260.
17. Lippard, S. J. *Progr. Inorg. Chem.* **8** (1967) 109.
18. Hodgson, D. J. and Ibers, J. A. *Acta Cryst.* **25** (1969) 469.
19. Krogmann, K. *Z. anorg. allgem. Chem.* **364** (1966) 188.
20. Robertson, J. H. *Acta Cryst.* **18** (1965) 410.
21. Nahringsbauer, I. *Abstracts of Uppsala Dissertations in Science* **157** (1970) 30.
22. Hamilton, W. C. and Ibers, J. A. *Hydrogen Bonding in Solids*, W. A. Benjamin, New York—Amsterdam 1968, p. 213.

Received July 14, 1971.