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Structural Studies on the Rare Earth Carboxylates

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

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The crystal and molecular structure of the triclinic compound $Yb_2(C_2O_4)_3.6H_2O$ has been determined from three-dimensional, photographic X-ray intensity data. The space group used is $A\bar{1}$. The lattice parameters are $a=9.611(2)$ Å, $b=8.457(2)$ Å, $c=9.778(2)$ Å, $\alpha=93.39(1)°$, $\beta=106.24(1)°$, and $\gamma=85.29(2)°$, and $Z=4$.

The structure is isotypic with that of $Sc_2(C_2O_4)_3.6H_2O$. A comparison of the two structures reveals that the change in size of the metal ion is accompanied by a distortion of the metal-oxalate network resulting in an almost unchanged hydrogen bond system in the two compounds.

The structure of the lanthanoid oxalate hexahydrates is closely related to that of the lanthanoid oxalate decahydrates. The variation of the unit cell dimensions through the lanthanoid series has been determined for the two types of hydrates. The lattice parameters of the various compounds have been calculated from powder data obtained with a Guinier-Hägg focusing camera.

Isomorphous rare earth oxalates of the composition $M_2(C_2O_4)_3.6H_2O$ are formed for M = Ho – Lu, Y, and Sc. The structure of $Sc_2(C_2O_4)_3.6H_2O$ (SCOX) has been determined previously.[1] The present investigation of the structure of $Yb_2(C_2O_4)_3.6H_2O$ (YBOX) has been undertaken in order to study the alterations of the structure that may be induced by an increase in size of the metal ion.

Similar investigations of the lanthanoid oxydiacetate[2] and hydroxyacetate[3] structures have revealed that the change in the metal-oxygen bond distances, caused by the change of metal ionic radius, is accompanied by distortions of the coordination polyhedron and of the ligands. Very small changes were found in the hydrogen bond distances shorter than 2.8 Å, indicating that the preservation of a favourable hydrogen bond system plays an important role in deciding the detailed geometry of hydrogen bonded lanthanoid carboxylate structures. In SCOX all hydrogen bond distances but one

are longer than 2.8 Å. Seven of them are in the range 2.8 – 3.1 Å. Hydrogen bonds in this range were not represented in the structures cited, and the present study may thus give more information about the importance of the hydrogen bonds in structures of this type.

The lighter elements of the lanthanoid series form isomorphous oxalates of the composition $M_2(C_2O_4)_3.10H_2O$. The crystal structure of these decahydrates is closely related to that of the hexahydrates as shown by a structural study of the neodymium compound (NDOX).[4–6] The unit cell dimensions of the compounds of the two series have been determined and are included in this paper.

EXPERIMENTAL

Preparation. The mixing of dilute solutions of oxalic acid and lanthanoid chloride at room temperature results in the precipitation of the decahydrate, $M_2(C_2O_4)_3.10H_2O$, for M = La – Ho while oxalates with a variety of hydration numbers are formed for M = Er – Lu. Increasing the temperature of precipitation above 90°C results in the formation of the hexahydrate, $M_2(C_2O_4)_3.6H_2O$ for M = Er – Lu and in a mixture of the deca- and hexahydrates for M = Ho. The lighter elements form the decahydrate also at this temperature. The pure hexahydrate with M = Ho is not obtained even from boiling solutions. The pure decahydrate with M = Er is precipitated at 50°C. The decahydrate with M = Tm is not formed at any temperature between 20 and 100°C.

The oxalates prepared in this way were all fine powders. They were identified by their X-ray powder patterns.

Large crystals of YBOX were prepared according to Weigel *et al.*[8] by saturating a boiling solution of 5 g oxalic acid in 100 ml 3 M sulphuric acid with the lanthanoid oxide and slowly cooling it to 0°C. With M = La – Ho this method results in large crystals of the decahydrate while the elements Er and Tm form the acid oxalate $MC_2O_4.HC_2O_4.3H_2O$. The structure of the latter solid has been determined by Steinfink and Brunton.[9]

The ranges of existence for the deca- and hexahydrates, respectively, indicated by the results of the preparations first described, agree with those found by Watanabe and Nagashima [10] in a recent study of the hydration number of $M_2(C_2O_4)_3.nH_2O$ as a function of the temperature of formation and the metal ionic radius for M = Dy – Lu, Y, and Sc.

Powder work. The powder photographs were taken at room temperature with a Guinier-Hägg focusing camera, using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Lead nitrate (cubic, $a = 7.8568$ Å) was used as internal standard.

The preliminary unit cell parameters for NDOX and SCOX obtained from Weissenberg and oscillation photographs were used for indexing the powder lines of the deca- and hexahydrates, respectively. The unit cell dimensions were least squares refined. The function minimized was $\sum w(\sin^2 \theta_o - \sin^2 \theta_c)^2$ with weights, $w = 1/\sin^2 2\theta_o$. The final unit cell dimensions with estimated standard deviations are given in Table 1. Tables of the observed powder patterns may be obtained from Department of Physical Chemistry, University of Lund, Sweden.

The lattice parameters of the decahydrates with M = La – Dy have been determined by several authors (see Ref. 6) and the values obtained in the present work agree with those previously reported, within the limits of errors.

Watanabe and Nagashima [10] give lattice parameters of $Er_2(C_2O_4)_3.10H_2O$ and $Sc_2(C_2O_4)_3.6H_2O$. For both compounds their values are significantly different from those obtained in the present work (see Table 1). Since no details are given of their method of recording the powder patterns or of the refinement of the parameters, it seems difficult to find a reason for the deviations.

Weissenberg work. The crystals of YBOX large enough for single crystal work are invariably twinned. The *b*-axis is common for the two parts and the Weissenberg photographs of a crystal mounted along this axis show two reciprocal lattices related to each other by a rotation 180° around *b*.

A tabular crystal of the approximate dimensions $0.05 \times 0.05 \times 0.02$ mm³ mounted along an 0.05 mm edge was used in recording the layers *h0l* – *h5l*. Non-integrated Weissen-

Table 1. Unit cell parameters (in Å and °) and volumes (in Å^3) for the rare earth oxalates $M_2(C_2O_4)_3.nH_2O$.

M	a	b	c	α	β	γ	V
A. The monolinic decahydrates							
Ce	11.780(3)	9.625(3)	10.401(3)		119.07(2)		1029.7
Nd	11.678(3)	9.652(3)	10.277(2)		118.92(2)		1013.9
Sm	11.577(2)	9.643(2)	10.169(2)		118.87(2)		994.2
Gd	11.516(2)	9.631(3)	10.081(3)		118.82(2)		979.6
Dy	11.433(2)	9.615(3)	9.988(3)		118.76(2)		962.5
Ho	11.393(3)	9.607(3)	9.955(3)		118.75(2)		955.2
Er [a]	11.359(2)	9.616(2)	9.940(2)		118.72(1)		952.1
B. The triclinic hexahydrates.							
Er	9.644(3)	8.457(3)	9.836(3)	93.54(1)	105.99(1)	85.05(3)	767.7
Tm	9.620(3)	8.458(3)	9.808(3)	93.44(1)	106.12(1)	85.13(3)	763.3
Yb	9.611(2)	8.457(2)	9.778(2)	93.39(1)	106.24(1)	85.29(2)	760.0
Lu	9.597(3)	8.455(2)	9.758(3)	93.42(1)	106.27(1)	85.41(2)	757.1
Sc[b]	9.317(2)	8.468(2)	9.489(2)	93.04(1)	106.50(1)	86.27(2)	715.9

[a] The values given by Watanabe and Nagashima[10] are $a=11.07(4)$ Å, $b=9.52(2)$ Å, $c=9.63(4)$ Å, and $\beta=118.6(2)°$.

[b] The values given by Watanabe and Nagashima, recalculated to the A-centered cell used in the present paper, are $a=9.252(5)$ Å, $b=8.418(5)$ Å, $c=9.446(5)$ Å, $\alpha=92.7(2)°$, $\beta=107.7(2)°$, and $\gamma=86.3(2)°$. The indexes of the two cells are related by $(h,k,l)=(1,0,0/0,-\frac{1}{2},\frac{1}{2}/0,\frac{1}{2},\frac{1}{2})$ $(h,'k',l')$ where h',k',l' refer to the A-centered cell.

berg photographs were taken with Cu$K\alpha$ radiation. The intensities of 828 independent reflexions, representing about 75 % of the possible number in the region investigated, were measured visually by comparison with a calibrated scale. Reflexions from both parts of the crystal were used and in this way all reflexions of a layer could be measured on the same half of the photograph.

The linear absorption coefficient is 238 cm^{-1}, but because of the twinning the intensities could not be corrected for absorption effects. Transmission factors calculated assuming the crystal to be a single crystal range from 0.25 to 0.57 and are for 97 % of the reflexions in the interval 0.35 – 0.55. Too long exposure to X-rays results in disintegration of the crystals and the use of Mo$K\alpha$ radiation was impossible.

REFINEMENT OF THE STRUCTURE

The space group used for the refinement and description of YBOX is $A\bar{1}$ with the general fourfold position $(0,\frac{1}{2},\frac{1}{2}) \pm (x,y,z,)$. The approximate positions of the 13 non-hydrogen atoms of the structure were known from the investigation of the isostructural compound SCOX.[1]

The preliminary atomic coordinates and isotropic temperature factors were improved together with the inter-layer scale factors by full matrix least squares refinement. The function minimized was $\sum w(|F_o|-|F_c|)^2$ with weights w chosen according to Cruickshank.[11] In addition, reflexions not obeying the condition $0.80 \leq |F_o|/|F_c| \leq 1.25$ were given zero weight. The value of $w\Delta^2$ is approximately constant between different $|F_o|$ and sin θ intervals (Table 2),

Table 2. Analysis of the weighting scheme $w = 1/(30 + |F_o| + 0.01|F_o|^2 + 0.001|F_o|^3)$. The averages, $\overline{w\Delta^2}$, 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 – 50	72	1.16	0.00 – 0.37	61	1.16
50 – 59	75	1.10	0.37 – 0.47	61	1.02
59 – 68	74	1.04	0.47 – 0.54	67	0.90
68 – 79	78	1.11	0.54 – 0.59	54	0.69
79 – 92	77	0.99	0.59 – 0.64	46	1.09
92 – 104	74	1.10	0.64 – 0.68	49	1.15
104 – 119	75	0.87	0.68 – 0.71	33	0.97
119 – 140	74	1.05	0.71 – 0.74	37	1.19
140 – 170	67	0.88	0.74 – 0.77	43	0.85
170 – 374	60	0.71	0.77 – 0.80	39	0.99

indicating that the weighting scheme used is reasonable. The atomic scattering factors for the neutral atoms were taken from *International Tables* [12] for O, and C and from Cromer *et al.*[13] for Yb.

After six cycles of refinement the R-factors $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{\frac{1}{2}}$ had converged to 0.118 and 0.103, respectively. Further refinement using anisotropic thermal parameters for Yb and an over-all scale factor resulted in $R = 0.114$ and $wR = 0.097$. In the last cycle of refinement the shifts in all parameters were less than 1 % of their

Table 3. Atomic parameters with estimated standard deviations for the compound $Yb_2(C_2O_4)_3.6H_2O$. The space group is $A\bar{1}$. The transformation of the positional parameters from the A-centered cell to the primitve cell is given by the matrix $(0,-1,-1/-1,-1,1/-1,0,0)$.

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B/Å^2
Yb	$-COO^-$	3072(1)	43(2)	1945(1)	(1.815)[a]
O(1)	$-COO^-$	1076(17)	−307(22)	−430(16)	1.6(2)
O(2)	$-COO^-$	638(13)	303(21)	1865(14)	1.0(2)
O(3)	$-COO^-$	4109(18)	1523(23)	662(17)	2.1(3)
O(4)	$-COO^-$	4561(14)	−1569(22)	833(14)	1.2(2)
O(5)	$-COO^-$	5517(19)	106(26)	3343(19)	2.4(3)
O(6)	$-COO^-$	3110(19)	71(25)	4424(18)	2.4(3)
O(7)	H_2O	2631(16)	2765(23)	2465(16)	1.8(3)
O(8)	H_2O	251(34)	−1520(41)	4312(33)	5.7(6)
O(9)	H_2O	2429(16)	−2525(23)	2100(16)	1.8(3)
C(1)		315(17)	−107(28)	−674(17)	0.6(3)
C(2)		4867(20)	839(29)	−50(17)	1.0(3)
C(3)		5662(17)	36(29)	4758(18)	0.8(3)

[a] The anisotropic thermal parameters for ytterbium, calculated from the expression $\exp[-(h^2\beta_{11} + hk\beta_{12} + \ldots)]$, are $\beta_{11} = 0.0058(1)$, $\beta_{22} = 0.0066(4)$, $\beta_{33} = 0.0045(1)$, $\beta_{12} = -0.0000(2)$, $\beta_{13} = 0.0029(1)$, and $\beta_{23} = 0.0001(2)$, resulting in root mean square displacements along the principal axis of the thermal ellipsoid, $R_1 = 0.163$ (Å), $R_2 = 0.141$ (Å), and $R_3 = 0.152$ (Å).

estimated standard deviations, and 102 reflexions did not obey the condition $0.80 \leq |F_o|/|F_c| \leq 1.25$.

The final atomic parameters with their estimated standard deviations are given in Table 3. Tables of the observed and calculated structure factors may be obtained from Department of Physical Chemistry, University of Lund, Sweden.

The electron density maps of a difference synthesis based upon the parameters given in Table 3 showed, except for a peak of about 4 $e/\text{Å}^3$ at the position of Yb, only spurious peaks $1-2$ $e/\text{Å}^3$ above a slightly varying background.

Programmes used. All computations were performed on the UNIVAC 1108 computer at Lund Sweden, using the programmes CELSIUS, DRF, LALS, DISTAN, PLANE, and ORTEP.[14]

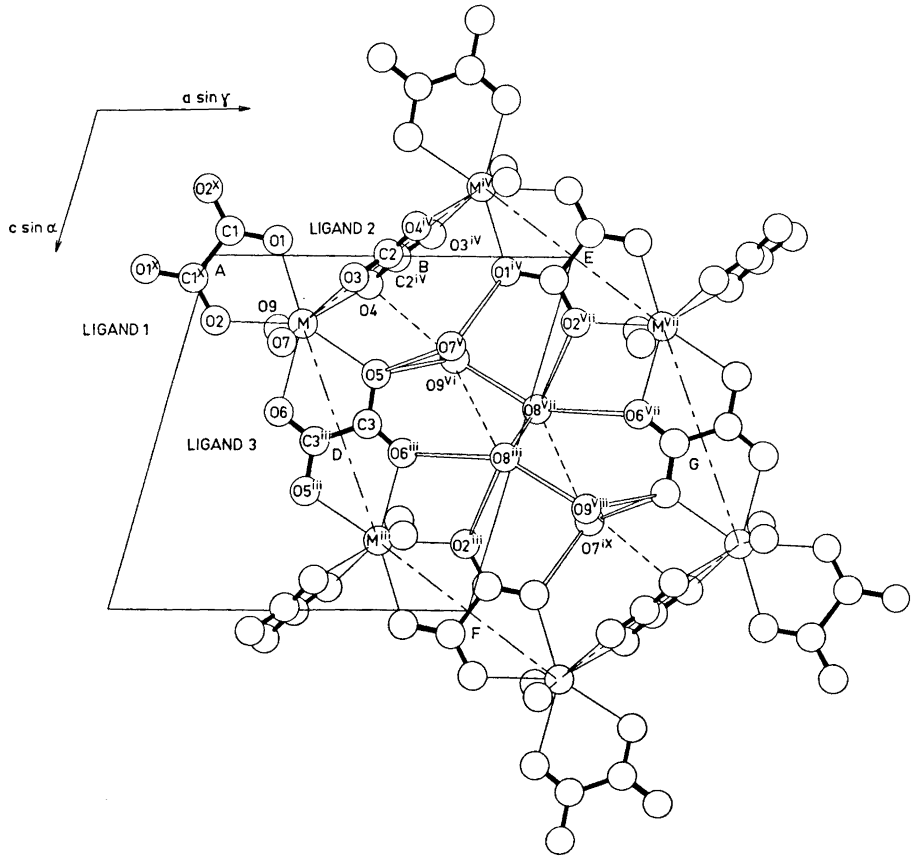

Fig. 1. Part of the metal-oxalate network around $y = 0$ in YBOX and SCOX. It is projected along the b-axis, with $-0.30 \leq y \leq 0.30$, *i.e.* the water oxygens immediately above and below the network are included. Metal-oxygen bonds are drawn as single lines and covalent bonds are filled. The hydrogen bonds probable in both structures are open while the additional possible hydrogen bond distances in SCOX are marked with dashes.

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

		Yb	Sc			Yb	Sc
A. The metal-oxalate network							
$M^{iv}-M^{vii}$		6.070(4)	5.844(3)	A−M−B		105.53(9)	106.14(5)
$M-M^{iv}$		6.000(3)	5.814(3)	A−M−D		146.45(4)	145.95(6)
$M-M^{iii}$		6.090(4)	5.928(3)	B−M−D		107.97(9)	107.84(5)
B. The coordination polyhedron							
M−O(1)		2.341(15)	2.259(6)	O(1)−O(2)	*m*	2.73(2)	2.648(8)
M−O(2)		2.313(13)	2.206(6)	O(1)−O(3)	*g*	2.80(2)	2.739(8)
M−O(3)		2.281(17)	2.184(6)	O(1)−O(4)	*g*	2.83(2)	2.716(1)
M−O(4)		2.342(15)	2.257(6)	O(1)−O(7)	*b*	3.69(2)	3.590(8)
M−O(5)		2.368(18)	2.251(6)	O(1)−O(9)	*b*	3.08(2)	2.924(9)
M−O(6)		2.413(17)	2.258(6)	O(2)−O(6)	*a*	2.94(2)	2.708(8)
M−O(7)		2.359(20)	2.233(6)	O(2)−O(7)	*g*	2.86(2)	2.685(8)
M−O(9)		2.325(19)	2.205(6)	O(2)−O(9)	*g*	2.82(2)	2.782(8)
O(3)−O(4)	*a*	2.62(3)	2.604(8)	O(3)−M−O(4)	$2\theta_A$	69.1(6)	72.9(2)
O(3)−O(5)	*g*	2.88(3)	2.850(8)	O(2)−M−O(6)	$2\theta_A$	76.8(5)	74.7(2)
O(3)−O(7)	*m*	2.68(3)	2.471(8)	O(1)−M−O(5)	$2\theta_B$	140.5(6)	142.4(2)
O(4)−O(5)	*g*	2.72(2)	2.634(7)	O(7)−M−O(9)	$2\theta_B$	145.9(5)	147.4(2)
O(4)−O(9)	*m*	2.86(2)	2.658(9)	A−M−O(7)		88.8(4)	89.3(2)
O(5)−O(6)	*m*	2.80(3)	2.625(8)	B−M−O(7)		104.3(4)	103.6(2)
O(5)−O(7)	*b*	3.38(3)	3.198(8)	D−M−O(7)		84.8(4)	84.8(2)
O(5)−O(9)	*b*	3.73(3)	3.457(8)	A−M−O(9)		76.5(4)	78.9(2)
O(6)−O(7)	*g*	2.99(3)	2.845(9)	B−M−O(9)		109.3(4)	108.8(2)
O(6)−O(9)	*g*	3.03(3)	2.782(8)	D−M−O(9)		90.8(4)	88.3(2)
C. Ligand 1.							
$C(1)-C(1^{x})$		1.59(3)	1.537(15)	O(1)−C(1)−O(2)		127(2)	127.5(8)
C(1)−O(1)		1.29(2)	1.244(10)	$O(1)-C(1)-C(1^{x})$		117(2)	115.2(9)
C(1)−O(2)		1.28(2)	1.256(10)	$O(2)-C(1)-C(1^{x})$		115(2)	117.3(9)
D. Ligand 2.							
$C(2)-C(2^{iv})$		1.43(5)	1.527(15)	O(3)−C(2)−O(4)		123(2)	127.1(7)
C(2)−O(3)		1.23(3)	1.272(10)	$O(3)-C(2)-C(2^{iv})$		118(2)	113.8(8)
C(2)−O(4)		1.27(2)	1.233(10)	$O(4)-C(2)-C(2^{iv})$		119(2)	119.1(9)
E. Ligand 3.							
$C(3)-C(3^{iii})$		1.48(3)	1.513(15)	O(5)−C(3)−O(6)		119(2)	127.6(7)
C(3)−O(5)		1.36(3)	1.279(9)	$O(5)-C(3)-C(3^{iii})$		119(2)	115.3(8)
C(3)−O(6)		1.23(2)	1.243(9)	$O(6)-C(3)-C(3^{iii})$		123(2)	117.1(8)
F. Possible hydrogen bonds.							
$O(7^{v})-O(1^{iv})$		2.85(2)	2.905(8)	$O(8^{vii})-O(9^{vi})$		2.72(4)	2.734(12)
$O(7^{v})-O(5)$		2.91(3)	2.931(8)	$O(8^{vii})-O(8^{iii})$		2.90(7)	2.932(23)
				$O(8^{vii})-O(2^{vii})$		3.04(4)	3.065(12)
$O(9^{vi})-O(5)$		2.93(3)	2.977(8)	$O(8^{vii})-O(6^{ii})$		3.12(4)	3.070(12)
$O(9^{vi})-O(4)$		3.10(2)	2.982(9)	$O(8^{vii})-O(7^{ix})$		3.34(4)	3.205(12)

DISCUSSION OF THE STRUCTURE

YBOX is isotypic with SCOX the structure of which has been described in detail in Ref. 1. In the present paper the numbering of the atoms and oxalate ions (see Table 3 and Fig. 1) is the same as that used in Ref. 1, as in the significance of the superscripts (i) – (x),* used to indicate equivalent sites in the structure.

The ratio $\sum Z^2_{\text{heavy}}/\sum Z^2_{\text{light}}$ is equal to 7 in YBOX. As a result of this high value the accuracy in the coordinates of the light atoms is fairly low. Fortunately the oxalate ions all have a centre of symmetry whose position may sometimes be used when comparing YBOX with SCOX. Some of these symmetry centres are denoted in the following way:

A: 0,0,0	B: $\frac{1}{2}$,0,0	D: $\frac{1}{2}$,0,$\frac{1}{2}$	E: 1,0,0
F: 1,0,1	G: $\frac{3}{2}$,0,$\frac{1}{2}$		

The structure is composed from almost planar metal-oxalate networks parallel to (010). Fig. 1 shows one of these networks projected along b and it is seen that the oxalate ions join the metal ions in a ring centered at (1,0$\frac{1}{2}$). The metal ions are situated at $\pm$ 0.04 Å from the plane $y = 0$. and the intra-ring M – M connecting lines form a hexagon, indicated by dash-dotted lines in Fig. 1, and with the dimensions given in Table 4A. Ligands 1 and 3 are almost in the plane $y = 0$ while ligand 2 is approximately perpendicular to that plane.

Adjacent networks are related by the translation (0,$\frac{1}{2}$,$\frac{1}{2}$) and are held together by hydrogen bonds formed by the three independent water molecules, which are situated between the networks. Two water molecules, O(7) and O(9), are coordinated to the metal ion while the third one, O(8), is hydrogen bonded in the structure. A stereoscopic view of the structure is given in Fig. 2.

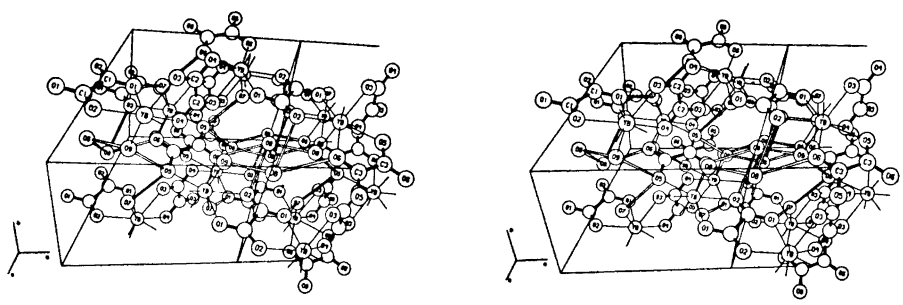

Fig. 2. A stereoscopic view of the YBOX structure drawn by using the program ORTEP. The bonds are indicated as in Fig. 1.

*	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)	$\bar{x},\bar{y},\bar{z}$

x,y,z are the atomic coordinates given in Table 3.

The coordination polyhedron. Each ytterbium ion is coordinated by three oxalate ions bonded as chelates and by two water molecules. The Yb – O bond distance is in average 2.34 Å, in agreement with the value 2.23 Å found in SCOX if the difference in metal ionic radius, 0.11 Å,[15] is taken into account.

The eight coordinated oxygens form a distorted $\bar{4}2m$ dodecahedron. The metal ion is approximately in the mean trapezoidal planes of this polyhedron (Table 5) and is also situated very near the planes of the oxalate ions (Table 6). In this respect, the situation is the same in YBOX and SCOX.

Table 5. The deviations in Å from the mean trapezoidal planes, of the central ion and the ligand atoms defining the respective planes.

	Yb	Sc		Yb	Sc
O(1)	−0.10	−0.126	O(7)	−0.12	−0.132
O(2)	0.15	0.201	O(3)	0.21	0.211
O(6)	−0.15	−0.202	O(4)	−0.20	−0.196
O(5)	0.10	0.127	O(9)	0.11	0.117
M	0.05	0.094	M	−0.08	−0.046

Table 6. The deviations in Å of the metal 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	
	Yb	Sc		Yb	Sc		Yb	Sc
C(1),C(1^{x})	∓0.05	±0.015	C(2),C(2^{iv})	∓0.01	±0.002	C(3),C(3^{iii})	±0.02	±0.000
O(1),O(1^{x})	±0.02	∓0.004	O(3),O(3^{iv})	±0.00	∓0.001	O(5),O(5^{iii})	±0.01	∓0.001
O(2),O(2^{x})	∓0.02	±0.004	O(4),O(4^{iv})	∓0.00	±0.001	O(6),O(6^{iii})	∓0.01	∓0.000
M	−0.03	−0.107	M	−0.11	−0.013	M	−0.17	−0.088

The dimensions of the dodecahedron are given in Table 4B, where the notation of the edges (a, m, g, b) and angles (θ_A, θ_B) are those used by Hoard and Silverton [16] in describing a dodecahedron. The mean distance between coordinated oxygens not belonging to the same oxalate ion is 2.97 Å. The corresponding value for SCOX is 2.82 Å. The number of O – O contacts shorter than 2.80 Å is two in YBOX and nine in SCOX. Thus, not surprisingly, the O – O repulsive forces seem to be less around Yb than around Sc.

In Table 7 the dimensions of the hard sphere model, HSM, of a dodecahedron around Yb(III) and Sc(III), respectively, are given and compared to the dimensions found in the structure determinations. In both structures the polyhedra show deviations in the average edge lengths and angles from the HSM, which are of the magnitude and sign theoretically predicted to minimize the ligand-ligand repulsive forces in a dodecahedron.[17] The ranges of the edge

Table 7. Mean dimensions of the dodecahedra formed by the eight coordinated oxygens in YBOX and SCOX. The corresponding hard sphere models, HSM, have been calculated using the mean M – O bond distance in the respective structures, *viz.* for YBOX 2.34 Å and for SCOX 2.23 Å.

	YBOX			SCOX		
	HSM	Mean	Range	HSM	Mean	Range
Edge (Å)						
a, m, g	2.81	2.83	2.62 – 3.03	2.68	2.70	2.47 – 2.85
b	3.51	3.47	3.08 – 3.73	3.35	3.29	2.92 – 3.59
Angle (°)						
θ_A	36.9	36.5	34.6 – 38.4	36.9	36.9	36.5 – 37.4
θ_B	69.5	71.6	70.3 – 73.0	69.5	72.5	71.2 – 73.4

lengths found are approximately equal in the two polyhedra. The variation in the angles θ_A and θ_B is larger in YBOX than in SCOX indicating that the YBOX-polyhedron may be somewhat less regular than that of SCOX.

The positions of the coordinated water molecules relative to the oxalate ions are illustrated by the angles formed by the bonds M – O(water) and the lines connecting M with the symmetry centre of the oxalate ions. These angles are included in Table 4B and it is seen that when going from SCOX to YBOX the position of O(9) is changed in a direction towards ligand 1 while that of O(7) is almost unchanged.

The oxalate ions. The three independent oxalate ions are planar within the limits of errors (*cf.* Table 6). The bond distances and angles are given in Table 4, C, D, and E. They do not differ significantly from those commonly found for oxalate ions (see, *e.g.*, Ref. 18). These features were also found in SCOX.

Nevertheless a comparison of the corresponding ligands in the two structures shows a significant decrease in the angle O(5) – C(3) – O(6^{iii}) by $9.1 \pm 1.7°$ in going from SCOX to YBOX and also significant changes in the "bites" of ligands 1 and 3; the distance O(1) – O(2) increases by 0.08 ± 0.02 Å and O(5) – O(6) by 0.17 ± 0.03 Å. A slight increase in this distance might have been expected as a result of the decreased van der Waals repulsions between the coordinated oxygens, but the value 2.80 Å found for O(5) – O(6) must be regarded with some suspicion in view of the values found in other oxalate structures. Thus in $K_2C_2O_4.H_2O$ [18] and $Li_2C_2O_4$ [19] where the oxalate ion is expected to interact relatively weakly with the metal ion, the "bites" are 2.707 and 2.675 Å, respectively. The values found in metal complexes are always smaller. The decrease seems to be more pronounced for oxalate ions in mononuclear complexes than for bridging oxalate ions, *i.e.* those forming two chelates, as judged from the values available in the literature, *viz.* for mononuclear complexes, $Zr(C_2O_4)_4^{4-}$: 2.55 – 2.58 Å,[20] $Pt(C_2O_4)_2^{2-}$: 2.61 – 2.65 Å,[21] $Pd(C_2O_4)_2^{2-}$: 2.63 Å,[21] $NbO(C_2O_4)_3^{3-}$: 2.51 – 2.58 Å,[22] and $Nb(O_2)_2(C_2O_4)_2^{3-}$: 2.59 – 2.60 Å,[23] and for bridges, SCOX: 2.63 – 2.65 Å,[1] NDOX: 2.65 – 2.67 Å,[6] and $NH_4Y(C_2O_4)_2.H_2O$: 2.67 – 2.70 Å.[24] An increase in this distance is found only for the non-chelating part of the oxalate ions in mononuclear complexes; 2.75 – 2.90 Å for the compounds mentioned above.

Hydrogen bonds. The possible hydrogen bond distances are given in Table 4 F. The hydrogen bonds form links between the metal oxalate layers, as is seen in Fig. 2 where the probable hydrogen bonds are indicated by open lines.

The hydrogen bond scheme outlined is very probable also in SCOX. An expected result of the expansion of the structure caused by the increased M – O bond distances in going from SCOX to YBOX might have been increased hydrogen bond distances, but they all remain constant within the limits of errors (Table 6F). Two distances included in Table 6F increase significantly, *viz.* $O(8^{vii}) - O(7^{ix})$ and $O(9^{vi}) - O(4)$. These are the least probable as hydrogen bonds in SCOX: $O(8^{vii}) - O(7^{ix})$ because of its length, 3.20 Å, and $O(9^{vi}) - O(4)$ because of the unfavourable angle $C(2^{iv}) - O(4) - O(9^{vi})$, which is 90°. Hydrogen bonds between these oxygens are still more improbable in YBOX and thus excluded from the hydrogen bond scheme.

The unit cell dimensions and the metal-oxalate network. In Fig. 3 the least squares refined values of *a*, *b*, and *c* for the various lanthanoid oxalate hexahydrates are plotted *versus* the crystal radius, *r*, of the lanthanoid ion.

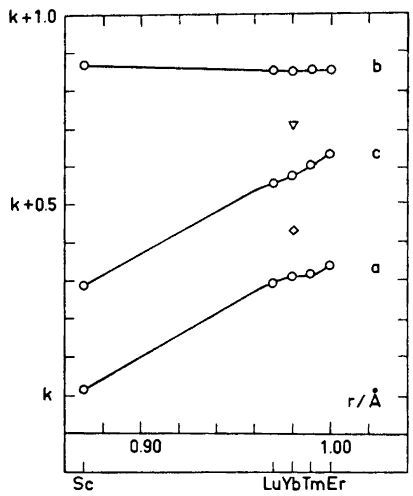

Fig. 3. The lattice parameters *a*, *b*, and *c* of the triclinic compounds $M_2(C_2O_4)_3.6H_2O$ with M = Er – Lu and Sc, plotted *versus* the crystal radius, *r*, of the trivalent metal ions in eight coordination. The values of *k* are, respectively, 9.3, 7.6, and 9.2. The values of *a* and *c* calculated for YBOX by using the model described in the text are denoted by ◇ and ▽, respectively.

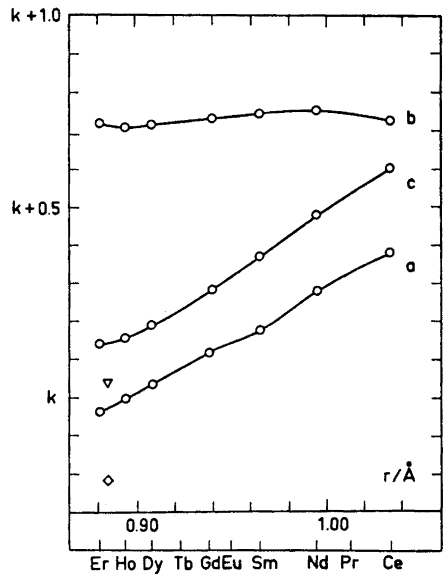

Fig. 4. The lattice parameters *a*, *b* and *c* of the monoclinic compounds $M_2(C_2O_4)_3.10H_2O$ with M = Ce – Er plotted *versus* the crystal radius, *r*, of the trivalent metal ions in six coordination. The values of *k* are, respectively, 11.4, 9.1, and 9.8. The values of *a* and *c* calculated for *r* = 0.885 Å by using the model described in the text and starting with NDOX are denoted by ◇ and ▽, respectively.

Expected changes in a and c in going from SCOX to YBOX may be calculated geometrically assuming the only change of the metal-oxalate network to be the increase in the M – O bond distances by 0.11 Å. Under this assumption the increase in the distance between adjacent metal ions in the ring is found to be 0.26 Å or 4.4 % of the mean value found for this distance in SCOX which is 5.86 Å. This means that all edges of the hexagon will increase by 4.4 % as will all distances between points on the hexagon. Especially the distances D – G and E – F (see Fig. 1), *i.e.* the cell edge lengths a and c, will increase by 4.4 %. The values of a and c calculated for YBOX in this way are included in Fig. 3 and it is obvious that the real values of these parameters are less than expected. This fact shows that the increase in the M – O bond distances is accompanied by changes of the metal-oxalate network that counteract its expansion.

The main features of this distortion of the network may be described by the dimensions of the metal-oxalate hexagon given in Table 4A. The changes in the M – M distances are all less than 0.26 Å. They are 0.23, 0.19, and 0.16 Å and correspond to increases in the M – O bond distances of 0.10, 0.08, and 0.07 Å for the ligands Nos. 1, 2, and 3, respectively. These values are within the limits of errors for those found for ligands 1 and 2 but not for ligand 3 (*cf.* Table 4B), a fact that indicates that the distortion of ligand 3 discussed on p. 831 may be real. There are also small changes in the hexagon angles resulting in a compression of the polygon along [10$\bar{1}$].

The distortions observed result in almost unchanged hydrogen bond distances between SCOX and YBOX. This indicates that the preservation of even this rather weak hydrogen bond system is of great importance for the stability of the structure.

The values of a, b, and c found for the lanthanoid oxalate decahydrates are plotted *versus* r in Fig. 4. The decahydrate structure is composed from metal-oxalate networks very similar to those of the hexahydrates. They are parallel to the ac-plane and joined together by hydrogen bonds. Values of a and c calculated for a 0.11 Å decrease of the M – O bond distances in NDOX, in the way described above, are included in Fig. 4. It is obvious that the change of metal ion even in this structure leads to distortions of the metal-oxalate network. In view of the findings for the hexahydrates and the structures mentioned in the introduction it seems reasonable to assume that also these distortions occur with preserved hydrogen bonds.

In both lanthanoid oxalate series the distance between adjacent metal-oxalate layers, *i.e.* the value of b, is almost independent of the size of the lanthanoid ion (Figs. 3 and 4). For the hexahydrates this distance seems to be determined by the close contact between ligands 2 and 3 of adjacent layers; the shortest nonbonded distance between the layers, O(3^{i}) – O(5), is 2.97 Å in YBOX and 3.00 Å in SCOX. No such close contacts were found in NDOX and since only 20 % of the uncoordinated water molecules of that structure have been located it seems meaningless to try to find a reason for the constant inter-layer distance for the decahydrates.

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