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Structural Studies on the Rare Earth Carboxylates

9. The Crystal and Molecular Structure of Tris(hydroxyacetato)-erbium(III) Dihydrate, $Er(HOCH_2COO)_3.2H_2O$

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The crystal and molecular structure of tris(hydroxyacetato)-erbium(III) dihydrate has been determined from three-dimensional X-ray intensity data. The compound was chosen as a representative for an isostructural series of compounds of the general composition $M(HOCH_2COO)_3.2H_2O$ formed by the rare earth elements from terbium to lutetium. The monoclinic crystals belong to the space group $P2/c$. Unit cell dimensions of all the isostructural compounds have been calculated from powder data obtained with a Guinier–Hägg focusing camera.

There are two non-equivalent metal atoms in the structure. They are located on two-fold axes and are each coordinated by eight oxygen atoms forming distorted dodecahedra. One metal-ion is coordinated by four hydroxyacetate ligands forming a discrete anionic complex $[M(HOCH_2COO)_4^-]$, the other by two hydroxyacetates and four waters forming a discrete cationic complex $[M(HOCH_2COO)_2(H_2O)_4^+]$. The complexes are joined by hydrogen bonds and form layers parallel to the *ab* plane. The layers are bonded to one another by hydrogen bonds.

The structures of a number of rare earth glycolate complexes have been described in previous communications in this series.[1–3] The present study deals with lanthanoid glycolates of the composition $M(HOCH_2COO)_3.2H_2O$, formed by the elements from gadolinium to lutetium. All of these compounds except the gadolinium one are isostructural. The erbium compound, in the following called Erglyc, was chosen as a representative of this series and its crystal and molecular structure was determined from three-dimensional X-ray intensity data.

EXPERIMENTAL

Preparation of rare earth tris-glycolato dihydrates, $M(HOCH_2COO)_3.2H_2O$. Microcrystalline rare earth tris-glycolato dihydrates were prepared as described by Jantsch and Grünkraut.[4] Crystals of the erbium compound, suitable for single crystal X-ray

work, were prepared hydrothermally in the following way: 5 g of the compound and 10 ml 0.5 M perchloric acid were heated for one week at 180°C in a sealed, thick-walled glass tube. The temperature was then slowly decreased (approx. 10°C/24 h) to room temperature. The large increase in solubility obtained by heating the acid solution was essential for obtaining large crystals. The use of an acid liquid phase has the additional advantage of preventing the formation of erbium hydroxyacetato-oxyacetate.[1]

The crystals formed after the hydrothermal treatment were needle-shaped and cleft fairly easily along a plane parallel to the needle axis.

Elemental analyses gave the following result (%):

	Er	C	H	H_2O
Found	38.9	17.0	3.4	8.57
Calc.	39.0	16.8	3.1	8.40

The calculated values refer to the composition $ErC_6H_{13}O_{11}$. The water content was determined by heating a sample in a stream of dry nitrogen at 160°C. The sample decomposed at temperatures above 225°C. The other rare earth tris-glycolato dihydrates were analysed for the metal content only. The observed values agreed in all cases within 0.3 % with those expected for $MC_6H_{13}O_{11}$.

X-Ray diffraction work. Equi-inclination Weissenberg photographs were taken with Zr filtered Mo-radiation using the multi-film technique (three films separated by tin foils). One single crystal was used in recording the layers $h0l-h8l$ and $hk0$. The crystal was prismatic b and had the dimensions $0.04 \times 0.35 \times 0.08$ mm^3, where the b axis is aligned along the 0.35 mm edge. 2679 reflexions were recorded, 1911 of which were within the copper reflexion sphere, corresponding to about 70 % of the possible number. All intensities were estimated visually by using a calibrated scale. The linear absorption coefficient was 76 cm^{-1} and the intensities were corrected for absorption. The transmission factors, evaluated by numerical integration, were in the range $0.57-0.75$.

The powder data were obtained at 25°C by using a Guinier-Hägg focusing camera and Cu$K\alpha$ radiation. Lead nitrate (cubic $a=7.857$ Å at 25°C) was used as an internal standard.

The computing work was carried out on the CDC 3600 computer in Uppsala, Sweden, and the UNIVAC 1108 in Lund, Sweden. The programmes used were CELSIUS, DRF, DATAP2, LALS, DISTAN, PLANES and ORTEP.[5]

UNIT CELL AND SPACE GROUP

The space group and the approximate cell parameters of Erglyc were determined from oscillation and Weissenberg photographs. The crystals are monoclinic and the only condition limiting possible reflexions is $h0l$ absent for $l=2n+1$, indicating Pc and $P2/c$ as probable space groups.

The preliminary cell parameters for Erglyc were used for indexing the powder photographs for all the other compounds. The unit cell dimensions were then improved by least-squares refinement as described in Ref. 1.

The intensity distribution found in the powder photograph of $GdC_6H_{13}O_{11}$ differed from those in the other solids. This fact indicates that the gadolinium compound is not isostructural with the corresponding Tb – Lu phases. Nevertheless, the powder photograph could be indexed on the basis of a monoclinic unit cell with dimensions close to those of the other $MC_6H_{13}O_{11}$ solids.

The final unit cell parameters for all rare earth tris-glycolato dihydrates, with their corresponding standard deviations, are given in Table 1. A comparison of the observed values of $\sin^2\theta$ with those calculated in the last cycle of refinement is given in Table 2.

Table 1. Unit cell parameters and volumes of the monoclinic tris(hydroxyacetato)-lanthanoid(III) dihydrates, $M(HOCH_2COO)_3.2H_2O$. All compounds except the gadolinium one are isostructural.

M	a/Å	b/Å	c/Å	β/deg	V/Å^3
Gd	14.906 (13)	5.864 (3)	13.273 (4)	97.14 (2)	1151 (2)
Tb	15.102 (21)	5.827 (1)	13.360 (3)	96.39 (2)	1169 (2)
Dy	15.074 (17)	5.823 (1)	13.332 (3)	96.58 (2)	1163 (1)
Ho	15.020 (14)	5.812 (1)	13.293 (3)	96.50 (2)	1153 (1)
Er	14.935 (10)	5.809 (1)	13.271 (2)	96.28 (1)	1144 (1)
Tm	14.946 (15)	5.799 (1)	13.245 (3)	96.51 (2)	1141 (1)
Yb	14.980 (13)	5.795 (1)	13.242 (3)	96.46 (1)	1142 (1)
Lu	14.960 (13)	5.795 (1)	13.214 (3)	96.50 (2)	1138 (1)

The number of formula units per unit cell, as determined from the density of the crystals, were equal to four in all compounds.

DETERMINATION AND REFINEMENT OF THE TRIS(HYDROXYACETATO)-ERBIUM(III) DIHYDRATE STRUCTURE

The positions of the erbium atoms were deduced from a three-dimensional Patterson synthesis. There are two non-equivalent erbium atoms in the structure. They are located on the two-fold axes, the positions $2e$ and $2f$, if $P2/c$ is the correct space group, and in two general positions if the space group is Pc. The centro-symmetric space group requires two-fold symmetry in the coordination polyhedra and the most probable arrangement of the ligands is obtained when one erbium atom is coordinated by two, and the other by four chelate bonded glycolate ions. Arrangements where ligands act as bridges between the non-equivalent erbium atoms are less probable because of the long distance, 7.93 Å, between these atoms. There are no symmetry restrictions on the type of coordination in the non-centrosymmetric space group.

The positions of all carbon and oxygen atoms were obtained from the first difference synthesis. This showed that the erbium atoms were coordinated by two and four chelate bonded ligands, respectively. Hence the refinement of the structure was started by using the space group $P2/c$.

The inter-layer scale factors and the preliminary atomic parameters were improved by full-matrix, least-squares refinement. The quantity $\sum w(|F_o| - |F_c|)^2$ with weighting according to Cruickshank [6] was minimized. Only reflexions with $0.80 < |F_o|/|F_c| < 1.25$ were included in the refinement. The atomic scattering factors for the neutral atoms were taken from *International Tables* [7] (oxygen and carbon) and from Cromer *et al.*[8] (erbium).

After four cycles of refinement the discrepancy index $R = \sum||F_o| - |F_c||/|F_o|$ had converged to 0.121 while the value of $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{\frac{1}{2}}$ was 0.130. Three additional cycles of refinement using anisotropic thermal parameters for the erbium atoms gave $R = 0.094$ and $wR = 0.096$, respectively. This decrease in wR was considered significant and the parameters obtained in the last cycle of this refinement are given in Table 3. Observed and calculated

Table 2. Powder data for the monoclinic tris(hydroxyacetato)rare earth(III) dihydrates. The quantities given are the observed and calculated values of $\sin^2\theta \times 10^4$, where the calculated values have been obtained from the refined lattice parameters given in Table 1.

h	k	l	Tb		Dy		Ho		Er		Tm		Yb		Lu		Intensity
			obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	Er
2	0	0	106.4	105.5	105.8	106.0	105.7	106.7	106.5	107.9	107.1	107.8	107.4	107.3	106.9	107.6	vs
0	0	2	135.2	134.8	135.0	135.5	135.4	136.3	136.2	136.6	136.7	137.3	137.6	137.3	138.0	137.9	s
0	1	0	174.1	175.0	175.0	175.2	175.5	176.0	175.8	176.1	176.5	176.7	176.9	177.0	177.0	177.0	vw
1	1	0	202.7	201.4	201.8	201.8	202.1	202.6	202.2	203.1	203.7	203.7	202.9	203.8	203.9	203.9	vw
2	0	-2	212.5	213.8	214.4	214.1	213.8	215.7	216.3	217.9	216.2	217.5	216.1	217.3	216.6	217.9	m
1	1	-1	229.0	228.5	229.1	228.8	228.5	229.9	230.3	230.6	230.8	231.9	230.5	231.3	231.2	231.5	s
1	1	1	242.6	241.7	243.0	242.5	242.1	243.5	243.3	243.9	244.4	244.9	245.0	245.0	244.7	245.2	vs
2	0	2	267.2	267.0	269.1	269.0	269.1	270.3	271.9	271.0	271.9	272.6	273.5	271.9	272.2	273.1	m
2	1	-1	300.6	301.0	300.2	301.4	299.6	303.1	300.8	304.8	305.0	305.0	304.7	304.9	303.7	305.3	vw
1	1	-2	322.9	322.9	320.7	323.5	323.4	325.3	324.9	326.4	326.3	327.2	325.6	327.5	327.5	328.0	vw
1	1	2	346.0	349.5	-	351.0		352.6	-	353.0	-	354.5	-	354.7		355.3	
3	0	2	411.0	412.1	412.8	415.3	419.2	417.4	419.9	419.1	421.7	421.2	416.8	419.7	419.9	421.4	m
3	1	0		412.5		413.8		416.1		418.8		419.2		418.3		419.0	
3	1	-1	427.5	426.3	426.7	427.0	430.0	429.7	434.2	433.0	435.2	432.9	432.2	432.2	435.1	432.9	s
3	1	1	470.1	466.1	472.0	468.3	468.0	470.7	-	472.9	-	473.8	473.5	473.2	-	473.9	
1	1	-3	489.9	484.9	490.8	486.1	490.4	488.8	490.1	490.5	488.3	492.0	492.4	492.3	497.4	493.6	vw
4	0	-2	506.4	503.7	506.4	504.7	511.0	508.6	518.0	514.9	516.2	513.3	513.2	511.8	516.1	513.2	s
0	2	0	703.2	700.0	701.0	701.0	702.8	703.8	706.6	704.5	706.3	706.9	708.6	707.9	708.3	707.9	m
0	2	1	736.8	733.7	733.5	734.9	734.7	737.9	738.8	738.7	742.5	741.2	742.6	742.2	741.9	742.4	m-
3	1	3	-	776.1	782.4	780.6	783.3	784.1	786.8	786.0	791.5	790.1	789.1	788.8	790.7	791.4	vw
2	2	0	807.0	805.6	810.0	807.0	810.7	810.6	810.4	812.4	814.2	814.7	816.2	815.2	813.4	815.5	vw
0	2	2	834.4	834.8	835.4	836.5	840.2	840.1	843.0	841.1	846.2	844.1	846.6	845.2	847.5	845.8	w
2	2	1	848.6	852.5	854.4	854.6	859.3	858.3	860.4	859.8	863.6	862.8	861.2	863.2	862.1	863.8	w
2	2	-2	911.9	914.6	914.6	915.0	919.7	919.6	922.5	922.4	920.4	924.4	922.4	925.2	922.6	925.8	w
3	2	-1	948.1	951.3	954.2	952.8	956.4	957.6	958.8	961.4	964.0	963.1	965.8	963.1	966.7	963.8	vw
0	2	3	1000	1003	1007	1006	1011	1010	1013	1012	1017	1016	1018	1017	1022	1018	m-
1	1	5	1076	1077	1082	1083	1087	1088	1097	1090	1097	1096	1095	1096	1099	1100	vvw
4	2	0	1121	1122	1124	1125	1131	1131	1132	1136	-	1138	-	1137	-	1138	vvw
4	2	1	1180	1182	-	1186	-	1192	1194	1197	1195	1199	-	1198	1201	1200	vw
4	2	-2	1203	1204	1204	1206	1212	1212	1212	1219	1218	1220	1220	1220	1219	1221	m
0	2	4	1236	1239	1242	1243	1252	1249	1250	1251	1258	1256	1258	1257	1260	1260	m
2	2	4	1291	1292	1289	1294	1298	1301	1305	1306	1307	1309	1307	1310	1310	1312	w
2	0	6	1401	1399	1407	1408	1415	1415	1414	1417	1428	1424	-	1424	1427	1430	vw
1	1	6	1453	1455	1460	1463	1465	1470	1471	1472	1476	1480	1475	1480	1485	1485	w
4	2	3	1501	1505	1510	1512	1520	1519	1524	1523	-	1528	-	1527	-	1530	m
0	2	5	-	1543	1552	1548	1560	1556	1560	1558	-	1564	-	1566	1577	1570	w
1	3	0	1604	1601	1603	1604	1610	1610	1610	1612	1617	1617	1620	1620	1618	1620	m
1	3	-1	1633	1628	1633	1631	1641	1638	-	1640	-	1645	-	1647	-	1647	
1	3	1	-	1642	-	1644	-	1651	1655	1651	1655	1658	1662	1661	1662	1661	w
1	3	2	1754	1750	1753	1753	1763	1760	1763	1762	1766	1768	-	1770	1775	1771	w
1	3	4	2175	2168	2176	2173	2181	2183	2185	2185	2198	2193	-	2196	2201	2199	vvw

Table 3. Coordinates and thermal parameters with their corresponding standard deviations for the various atoms in $Er(HOCH_2COO)_3.2H_2O$. The anisotropic thermal parameters for the erbium atoms have been calculated from the expression: $\exp-[h^2\beta_{11}+hk\beta_{12}+\cdots]$.

Atom	Group	$x\times10^4$	$y\times10^4$	$z\times10^4$	B/Å^2
O(1)	$-COO^-$	1445 (7)	875 (17)	2154 (8)	3.17 (17)
O(2)	$-COO^-$	2848 (11)	1983 (21)	1902 (10)	4.12 (23)
O(3)	$-OH$	772 (8)	4945 (16)	2005 (8)	3.11 (16)
C(1)	$-COO^-$	1995 (11)	2408 (22)	1999 (11)	3.05 (20)
C(2)	$-COH$	1677 (11)	4905 (21)	1943 (10)	3.07 (20)
O(4)	$-COO^-$	247 (7)	−1364 (15)	3558 (8)	2.73 (15)
O(5)	$-COO^-$	1265 (10)	−3143 (19)	4677 (10)	3.70 (20)
O(6)	$-OH$	770 (8)	2702 (16)	4023 (8)	3.05 (16)
C(3)	$-COO^-$	901 (11)	−1409 (21)	4261 (11)	3.01 (20)
C(4)	$-COH$	1306 (10)	919 (21)	4643 (11)	3.00 (20)
O(7)	$-COO^-$	4547 (7)	199 (14)	3394 (7)	2.69 (14)
O(8)	$-COO^-$	3663 (9)	1922 (16)	4429 (9)	3.09 (17)
O(9)	$-OH$	4009 (8)	−3872 (17)	3682 (8)	3.17 (16)
C(5)	$-COO^-$	3953 (10)	162 (19)	4034 (10)	2.78 (18)
C(6)	$-COH$	3540 (11)	−2092 (20)	4206 (11)	2.94 (20)
O(10)	H_2O	3635 (8)	−1790 (15)	1540 (8)	2.85 (16)
O(11)	H_2O	4370 (7)	4017 (15)	1646 (7)	2.79 (15)
Er(1)		0 (0)	1701 (1)	2500 (0)	
Er(2)		5000 (0)	−2875 (1)	2500 (0)	

$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{23}\times10^4$
14.5 (4)	161 (10)	36.0 (5)	0 (0)	8.3 (6)	0 (0)
15.3 (4)	159 (10)	32.9 (5)	0 (0)	19.0 (6)	0 (0)

Table 4. Analysis of the weighting scheme. The averages $w(|F_o|-|F_c|)^2=w\cdot\Delta^2$ are normalized and the weighting scheme is equal to $w=1/(15.0+|F_o|+0.03|F_o|^2+0.00045\,|F_o|^3)$.

$\lvert F_o\rvert$ interval	Number of reflexions	$w\Delta^2$	sin θ interval	Number of reflexions	$w\Delta^2$
0 – 18	214	0.71	0.00 – 0.28	356	1.06
18 – 24	237	0.80	0.28 – 0.35	368	1.04
24 – 28	243	1.04	0.35 – 0.40	340	1.14
28 – 33	243	1.05	0.40 – 0.44	326	1.17
33 – 37	252	0.96	0.44 – 0.48	314	1.02
37 – 45	246	1.20	0.48 – 0.51	247	1.10
45 – 54	257	1.00	0.51 – 0.53	201	0.93
54 – 69	253	1.05	0.53 – 0.56	131	1.00
69 – 94	253	1.15	0.56 – 0.58	70	0.89
94 – 272	242	1.05	0.58 – 0.60	39	0.65

Table 5. Observed and calculated absolute values of structure factors in the Erglyc structure. Reflexions with $1.25 < |F_o|/|F_c| < 0.80$ are denoted with an asterisk.

h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$
-26	0	-2	48	41	14	0	10	59	59	3	1	3	214	180	-1	1	8	72	74	1	1	19	36	35
-28	0	-2	64	52 *	16	0	10	58	51	4	1	3	32	31	0	1	8	16	18	2	1	19	37	29 *
-24	0	0	56	44 *	-22	0	12	42	36	5	1	3	257	209 *	1	1	8	63	71	-22	2	-1	37	35
-22	0	0	64	58	-20	0	12	62	55	7	1	3	240	188 *	2	1	8	29	31	-20	2	0	41	41
-20	0	0	76	67	-18	0	12	58	62	8	1	3	35	31	3	1	8	44	48	-22	2	0	36	36
-18	0	0	83	71	-16	0	12	71	66	9	1	3	131	136	4	1	8	45	59	-20	2	0	46	42
-16	0	0	111	97	-14	0	12	83	80	11	1	3	110	124	5	1	8	57	60	-18	2	0	42	44
-14	0	0	130	137	-12	0	12	97	94	13	1	3	93	96	7	1	8	48	49	-16	2	0	75	67
-12	0	0	118	122	-10	0	12	97	70	15	1	3	93	91	9	1	8	29	21 *	-14	2	0	191	91
-11	0	0	41	30 *	-8	0	12	96	89	17	1	3	65	56	10	1	8	33	31	-13	2	0	35	38
-10	0	0	136	144	-6	0	12	99	99	19	1	3	55	58	-23	1	9	44	45	-12	2	0	74	78
-8	0	0	232	198	-4	0	12	103	112	21	1	3	47	51	-21	1	9	58	55 *	-10	2	0	196	110
-6	0	0	219	165	-2	0	12	107	108	-19	1	4	37	34	-19	1	9	45	67 *	-9	2	0	25	26
-4	0	0	56	47	0	0	12	83	94	-17	1	4	32	31	-17	1	9	82	71	-8	2	0	166	138
-2	0	0	58	51	2	0	12	92	107	-15	1	4	35	36	-15	1	9	80	79	-7	2	0	168	78
0	0	0	78	74	4	0	12	97	91	-14	1	4	34	29	-13	1	9	112	99	-6	2	0	197	144 *
2	0	0	122	99	6	0	12	87	67 *	-13	1	4	42	45	-11	1	9	95	99	-5	2	0	61	54 *
4	0	0	109	125	8	0	12	73	60	-12	1	4	28	26	-9	1	9	97	105	-4	2	1	176	135
6	0	0	149	125	10	0	12	60	58	-11	1	4	22	21	-7	1	9	117	117	-22	2	1	36	34
8	0	0	127	138	12	0	12	53	46	-10	1	4	19	18	-6	1	9	19	22	-20	2	1	41	46
11	0	0	43	31 *	14	0	12	52	40 *	-9	1	4	34	40	-5	1	9	139	145	-18	2	1	59	54
10	0	0	180	165	-20	0	14	42	40 *	-7	1	4	132	121	-3	1	9	121	127	-16	2	1	58	58
8	0	0	138	134	-18	0	14	75	59 *	-5	1	4	141	120	-1	1	9	120	110	-14	2	1	67	62
6	0	0	256	246	-16	0	14	62	67	-4	1	4	15	9 *	0	1	9	42	44	-12	2	1	64	72
4	0	0	35	35	-14	0	14	65	61	-3	1	4	98	75	1	1	9	147	122	-10	2	1	106	107
2	0	0	206	181	-12	0	14	51	53	-2	1	4	28	28	2	1	9	18	20	-9	2	1	155	125
0	0	0	46	45	-10	0	14	69	76	-1	1	4	58	58 *	3	1	9	103	110	-8	2	1	30	35
-2	0	0	105	103	-8	0	14	76	68	0	1	4	19	12 *	5	1	9	72	79	-7	2	1	140	112
-4	0	0	83	87	-6	0	14	68	68	1	1	4	91	80 *	7	1	9	87	88	-6	2	1	88	76
-6	0	0	122	140	-4	0	14	92	83	2	1	4	16	16 *	9	1	9	103	110	-5	2	1	214	167 *
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8	0	8	53	56																				
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12	0	8																						

Table 5. Continued.

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9	2	6	22	19
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12	2	6	79	73
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6	2	10	69	78
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6	3	1	91	76
7	3	1	57	44 *
8	3	1	57	52
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13	3	1	30	32
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-9	3	2	119	108
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3	3	2	189	145 *
5	3	2	167	120 *
6	3	2	14	14
7	3	2	122	116
8	3	2	24	25
9	3	2	77	84
11	3	2	93	85
13	3	2	74	76
15	3	2	66	66
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19	3	2	43	44
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-16	3	3	34	25 *
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-14	3	3	29	34
-13	3	3	41	32 *
-12	3	3	50	52
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2	3	3	105	84
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4	3	3	35	37
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9	3	3	45	49
10	3	3	46	52
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11	3	4	70	74
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0	3	5	61	63
1	3	5	54	51
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8	3	5	57	56
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-9	3	6	117	118
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h	k	l	$\|F_o\|$	$\|F_c\|$
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9	3	6	85	94
11	3	6	67	74
13	3	6	62	63
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17	3	6	46	45
19	3	6	38	40
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-15	3	7	32	37
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-12	3	7	43	42
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-9	3	7	52	59
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7	3	7	45	50
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10	3	7	27	28
11	3	7	37	36
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7	3	8	90	86
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15	3	8	45	47
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3	3	9	45	49
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3	3	10	82	99
5	3	10	72	74
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9	3	10	45	53
11	3	10	41	46
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-16	3	11	32	25 *
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-10	3	11	31	31
-9	3	11	33	37
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-5	3	11	28	28
-4	3	11	39	42
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0	3	11	35	35

h	k	l	$\|F_o\|$	$\|F_c\|$
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7	3	11	31	30
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5	3	12	55	53
7	3	12	51	48
9	3	12	45	46
11	3	12	37	35
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-10	3	13	28	24
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1	3	14	50	44
3	3	14	51	45
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7	3	14	39	39
9	3	14	34	37
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-5	3	15	28	29
-3	3	15	30	20 *
3	3	15	29	22 *
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1	3	16	32	34
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-7	3	17	31	23 *
-9	3	18	33	29
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-7	4	0	101	86
-5	4	0	86	76
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2	4	1	109	113
4	4	1	165	130 *
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7	4	1	21	19
8	4	1	91	90
10	4	1	93	94
12	4	1	83	76
14	4	1	67	66
16	4	1	64	63
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-9	4	2	51	51
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4	4	2	26	22
5	4	2	100	75 *
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7	4	2	65	66
9	4	2	50	57
11	4	2	32	31
13	4	2	27	28
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Table 5. Continued.

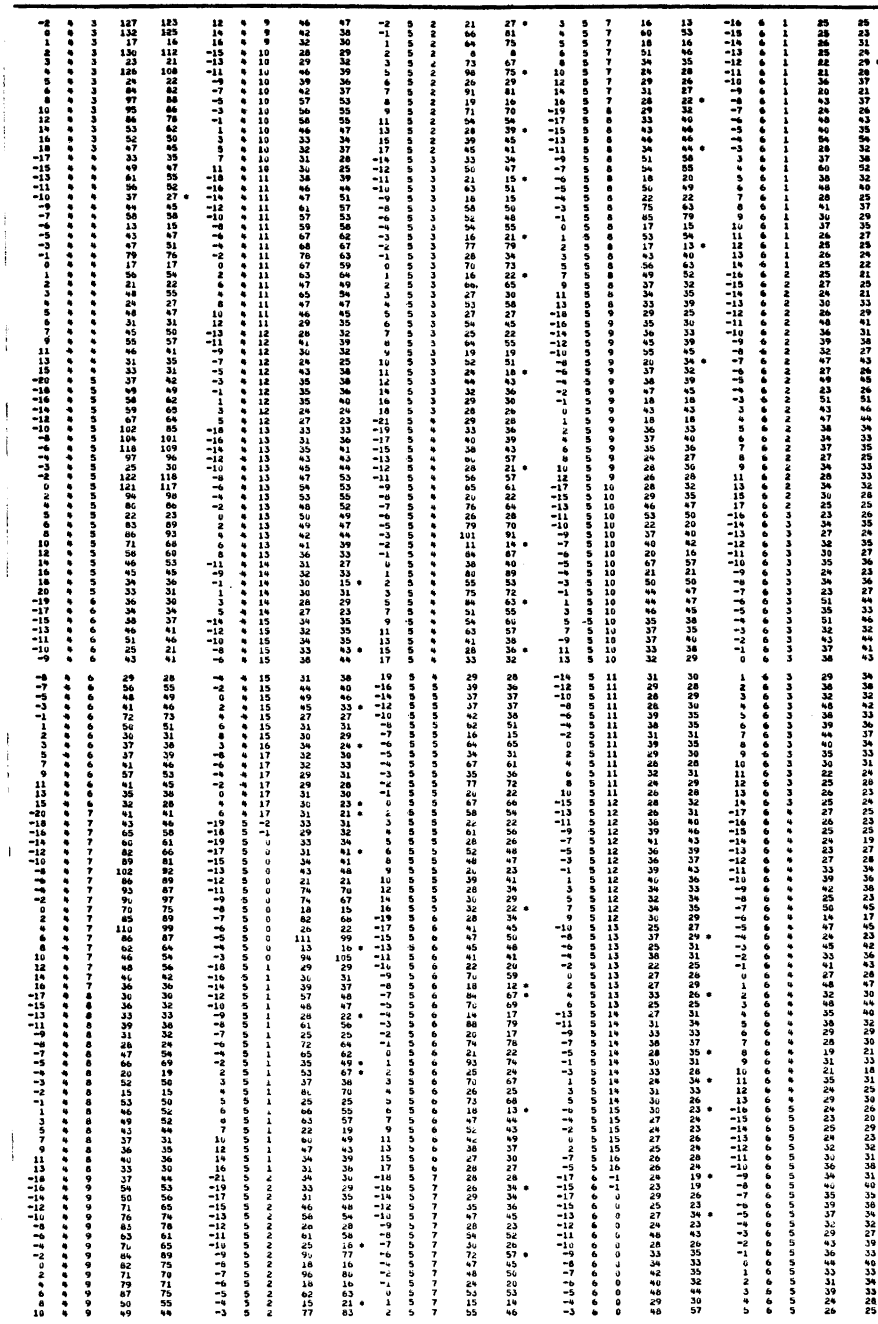

Table 5. Continued.

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8 6 5	38	39	0 6 11	35	36	-9 7 4	15	11 *	-15 7 9	18	16	13 8 3	23	23
9 6 5	27	29 *	1 6 11	19	21	-8 7 4	42	37	-13 7 9	16	19	15 8 3	16	19
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-11 6 6	24	30 *	-6 6 12	21	16 *	-1 7 4	16	16	-5 7 9	16	16	-4 8 4	16	17
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4 6 7	34	36	4 7 1	32	32	15 7 5	18	25	2 7 11	20	18	-15 8 7	19	24
5 6 7	26	24	5 7 1	31	27	-18 7 6	20	20	3 7 11	17	15	-13 8 7	26	24
6 6 7	34	34	6 7 1	17	16	-16 7 6	21	22	4 7 11	15	13	-11 8 7	24	25
7 6 7	25	28	7 7 1	32	28	-15 7 6	20	17	-12 7 12	21	22	-9 8 7	25	25
8 6 7	22	19 *	8 7 1	24	22	-14 7 6	20	25 *	-10 7 12	23	25	-7 8 7	24	27
9 6 7	27	27	9 7 1	22	21	-13 7 6	16	11 *	-8 7 12	17	21	-5 8 7	29	28
12 6 7	23	27	10 7 1	27	24	-12 7 6	28	30	-7 7 12	16	9 *	-3 8 7	35	33
-15 6 8	24	25	11 7 1	25	21	-11 7 6	16	16	-6 7 12	18	19	-1 8 7	37	36
-14 6 8	22	14 *	12 7 1	17	17	-10 7 6	31	33	-5 7 12	15	11 *	1 8 7	30	30
-11 6 8	42	25	13 7 1	22	19	-9 7 6	23	23	-4 7 12	19	21	3 8 7	28	28
-10 6 8	24	21	14 7 1	19	17	-8 7 6	32	31	-3 7 12	15	14	5 8 7	26	27
-9 6 8	35	38	-18 7 2	22	21 *	-7 7 6	27	27	-1 7 12	15	12 *	9 8 7	21	20
-8 6 8	29	26	-16 7 2	29	28	-6 7 6	21	21	0 7 12	27	27	11 8 7	17	20
-7 6 8	30	30	-14 7 2	29	29	-4 7 6	33	32	2 7 12	23	21	13 8 7	17	18
-6 6 8	26	29	-13 7 2	15	13	-3 7 6	28	28	3 7 12	17	12 *	15 8 7	17	15
-5 6 8	28	27	-12 7 2	25	26	-2 7 6	39	38	4 7 12	20	17	-14 8 8	16	12 *
-4 6 8	25	27	-11 7 2	14	14	-1 7 6	10	10	-18 7 14	19	17	-12 8 8	18	17
-3 6 8	29	31	-10 7 2	31	28	0 7 6	48	35	-17 7 14	17	12 *	-10 8 8	16	13
-2 6 8	24	23	-9 7 2	16	15	1 7 6	18	19	-15 7 14	18	18	-8 8 8	16	14
-1 6 8	36	36	-8 7 2	46	40	2 7 6	29	28	-14 7 14	16	16	-6 8 8	17	17
0 6 8	17	21	-7 7 2	19	16	3 7 6	18	16	-12 7 14	16	16	-4 8 8	16	16
1 6 8	31	30	-6 7 2	42	40	4 7 6	31	31	-10 7 14	18	18	-2 8 8	13	14
2 6 8	25	24	-5 7 2	9	10	5 7 6	14	16	-8 7 14	16	17	0 8 8	15	15
3 6 8	34	34	-4 7 2	45	44	6 7 6	25	28 *	-19 8 -1	18	16	2 8 8	14	16
4 6 8	27	28	-3 7 2	9	10	7 7 6	19	15 *	-17 8 -1	21	20	4 8 8	13	14
5 6 8	24	43 *	-2 7 2	36	50 *	8 7 6	23	26	-14 8 0	16	16	6 8 8	13	11
6 6 8	22	20	1 7 2	26	29 *	10 7 6	23	32	-12 8 0	14	11	-15 8 9	19	20
7 6 8	32	35	2 7 2	28	34	12 7 6	23	26	-10 8 0	14	13	-13 8 9	18	22
8 6 8	20	18	3 7 2	18	20	14 7 6	21	19	-8 8 0	28	24	-11 8 9	24	23
9 6 8	23	26	4 7 2	40	38	-17 7 7	20	14 *	-7 8 0	11	6 *	-9 8 9	22	24
-15 6 9	24	21	5 7 2	20	20	-16 7 7	20	14 *	-6 8 0	27	23	-7 8 9	24	25
-14 6 9	24	24	6 7 2	49	39 *	-15 7 7	21	17	-5 8 0	15	17	-5 8 9	23	25
-13 6 9	23	22	7 7 2	20	18	-14 7 7	18	13 *	-19 8 1	19	16	-3 8 9	25	26
-12 6 9	24	27	8 7 2	38	35	-13 7 7	16	15	-17 8 1	19	19	-1 8 9	30	28
-11 6 9	25	23	10 7 2	30	30	-12 7 7	15	13	-15 8 1	23	21	1 8 9	24	24
-10 6 9	32	27	11 7 2	15	15	-11 7 7	18	18	-13 8 1	24	25	3 8 9	17	20
-9 6 9	22	23	12 7 2	24	25	-10 7 7	19	19	-11 8 1	36	29	5 8 9	21	22
-8 6 9	35	34	13 7 2	19	17	-9 7 7	25	23	-9 8 1	40	34	7 8 9	23	22
-7 6 9	30	29	14 7 2	18	21	-8 7 7	24	21	-7 8 1	46	34	9 8 9	17	20
-6 6 9	35	34	16 7 2	18	18	-7 7 7	24	25	-5 8 1	34	34	11 8 9	18	19
-5 6 9	21	26 *	-17 7 3	18	18	-6 7 7	19	19	-3 8 1	31	37	-8 8 10	14	11 *
-4 6 9	29	32	-16 7 3	21	17	-5 7 7	23	23	-1 8 1	34	35	-6 8 10	14	10 *
-3 6 9	29	29	-15 7 3	21	16	-4 7 7	18	18	0 8 1	34	32	-4 8 10	14	13
-2 6 9	34	36	-14 7 3	18	17	-3 7 7	17	18	2 8 1	36	33	0 8 10	16	16
-1 6 9	20	23	-13 7 3	17	17	-2 7 7	23	25	4 8 1	26	30	2 8 10	14	10 *
0 6 9	28	33	-12 7 3	21	20	-1 7 7	20	22	6 8 1	22	25	-15 8 11	16	17
1 6 9	17	17	-11 7 3	28	25	0 7 7	27	23	8 8 1	16	21	-13 8 11	19	18
2 6 9	34	33	-10 7 3	23	22	1 7 7	24	24	-12 8 2	11	16	-11 8 11	19	18
3 6 9	21	19	-9 7 3	30	28	2 7 7	13	15	-10 8 2	19	19	-9 8 11	24	22
4 6 9	31	31	-8 7 3	23	20	3 7 7	24	25	-8 8 2	17	17	-7 8 11	25	25
5 6 9	20	21	-7 7 3	17	17	4 7 7	20	24 *	-7 8 2	12	8 *	-5 8 11	24	23
6 6 9	23	32 *	-6 7 3	21	21	5 7 7	24	28	-6 8 2	18	17	-3 8 11	24	18
7 6 9	20	19	-5 7 3	22	22	6 7 7	16	17	-4 8 2	19	20	-1 8 11	17	19
8 6 9	21	20	-4 7 3	15	18	7 7 7	21	23	-2 8 2	16	23 *	1 8 11	20	21
9 6 9	24	27	-3 7 3	32	36	8 7 7	22	19	0 8 2	16	17 *	3 8 11	21	19
-11 6 10	24	24	-2 7 3	19	22	9 7 7	21	20	2 8 2	11	12	5 8 11	16	19
-9 6 10	24	31 *	-1 7 3	34	34	10 7 7	18	16	4 8 2	24	22	7 8 11	17	19
-8 6 10	22	23	0 7 3	21	23	-16 7 8	22	23	6 8 2	11	8 *	9 8 11	17	11 *
-7 6 10	25	24	1 7 3	24	27	-14 7 8	26	25	8 8 2	19	18	11 8 12	15	11 *
-6 6 10	28	26	2 7 3	24	27	-12 7 8	19	22	10 8 2	20	19	13 8 12	14	11
-5 6 10	22	23	3 7 3	17	20	-11 7 8	17	14	12 8 2	17	14	-15 8 13	20	15 *
-4 6 10	28	27	4 7 3	33	31	-10 7 8	26	24	14 8 2	17	14	-13 8 13	16	16
-3 6 10	24	24	5 7 3	21	21	-9 7 8	21	21	-19 8 3	18	17	-11 8 13	17	16
-2 6 10	27	29	6 7 3	28	24	-8 7 8	26	24	-17 8 3	19	20	-9 8 13	16	14
-1 6 10	23	24	7 7 3	29	25	-7 7 8	19	20	-15 8 3	21	22	-7 8 13	17	18
0 6 10	28	29	8 7 3	20	22	-6 7 8	33	33	-13 8 3	23	23	-5 8 13	15	18
1 6 10	18	16	9 7 3	23	22	-5 7 8	15	15	-11 8 3	23	23	-3 8 13	15	16
2 6 10	32	32	10 7 3	15	14	-4 7 8	31	30	-9 8 3	41	34	-1 8 13	15	15
3 6 10	18	15	11 7 3	16	21	-3 7 8	10	7	-7 8 3	36	34	1 8 13	15	16
4 6 10	30	26	12 7 3	30	30	-2 7 8	35	34	-5 8 3	32	32	3 8 13	16	16
5 6 10	20	20	13 7 3	19	21	-1 7 8	12	10	-3 8 3	32	36	5 8 13	16	17
6 6 10	21	24	14 7 3	17	17	0 7 8	36	36	-1 8 3	33	40	7 8 13	16	14
-12 6 11	27	29	15 7 3	18	17	1 7 8	16	16	1 8 3	33	33	9 8 13	16	16
-10 6 11	24	25	-18 7 4	26	23	2 7 8	28	24	3 8 3	25	33 *	-7 8 15	16	14
-8 6 11	21	23	-16 7 4	23	24	3 7 8	15	15	5 8 3	8	6 *	-5 8 15	16	15
-6 6 11	26	26	-14 7 4	21	27	4 7 8	29	27	7 8 3	35	34	-3 8 15	16	15
-4 6 11	23	22	-13 7 4	25	18 *	6 7 8	27	29	9 8 3	36	35	-1 8 15	16	15
-2 6 11	36	32	-12 7 4	38	31	8 7 8	23	23	11 8 3	33	32	1 8 15	15	15

structure factors are compared in Table 5. The value of R was obtained by using all the observed reflexions, while the value of wR was obtained from the 2450 reflexions where $0.80 < |F_o|/|F_c| < 1.25$.

295 of the 2679 observed reflexions had the lowest intensity on the calibrated scale. 80 of these had $|F_o|/|F_c|$ values outside the range $0.80-1.25$. The difficulty of getting a good estimate of the weakest intensities thus seems to be one reason for the fairly large number of reflexions (229) deleted in the least-squares refinement. The shifts in the parameters were less than 5 % of their estimated standard deviations in the last cycle of the refinement.

The weighting scheme used was satisfactory as indicated by the near constancy of the averages of $w(|F_o|-|F_c|)^2$ between different $|F_o|$ and sin θ intervals (*cf.* Table 4).

A least-squares refinement with anisotropic thermal parameters on all atoms was also tried and gave values of R and wR equal to 0.094 and 0.093, respectively. The positional parameters and their standard deviations were very nearly the same as those found in the isotropic refinement. The improvement in the R-value was not considered large enough to warrant the use of anisotropic thermal parameters on the light atoms in the final description of the structure.

The choice of the space group was tested by a least-squares refinement using the space group Pc. The initial values of the positional parameters were obtained from the first difference synthesis by a transformation of the origin. The refinement was made by using a diagonal approximation which allows for the correlation between the scale and the temperature factors. The discrepancy indices R and wR were 0.118 and 0.130, respectively, after eight cycles of refinement with isotropic thermal parameters for all atoms. Transformation of the thermal parameters for the erbium atoms to anisotropic form, followed by three additional cycles of refinement improved both discrepancy indices to 0.094. The final positional parameters were, apart from the shift of origin, within two standard deviations the same whether the non-centrosymmetric or the centrosymmetric space group was used. Hence, there are no reasons for preferring the former to the latter.

A final difference synthesis was calculated by using the refined parameters given in Table 3. The electron density maps showed the presence of peaks equal to 2.5 $e/Å^3$ at the erbium atom positions, above a slightly varying background.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances and angles of interest for the following description are given with their corresponding standard deviations in Table 6. Symmetry related atoms have been given superscripts of the following significance

i	$-x,\ y,\ \frac{1}{2}-z$	iv	$1-x,\ y,\ \frac{1}{2}-z$
ii	$x,\ 1+y,\ z$	v	$x,\ -y,\ -\frac{1}{2}+z$
iii	$x,\ -y,\ \frac{1}{2}+z$		

where x, y, z are the coordinates of the crystal-chemical unit given in Table 3.

The coordination polyhedra. The two non-equivalent erbium atoms are bonded in discrete eight-coordinated complexes in the structure. One erbium

Table 6. Selected bond distances (in Å) and angles with their corresponding standard deviations.

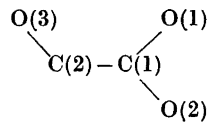
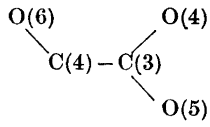
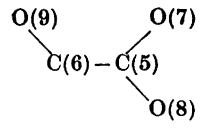
Distances and angles within the coordination polyhedra			
Er1 – O(1)	2.30 (1)	∠Er1 – O(1) – C(1)	122.2 (9)
Er1 – O(3)	2.34 (1)	∠Er1 – O(3) – C(2)	121.7 (8)
Er1 – O(4)	2.27 (1)	∠Er1 – O(4) – C(3)	121.9 (8)
Er1 – O(6)	2.29 (1)	∠Er1 – O(6) – C(4)	119.7 (7)
O(1) – O(4)	3.01 (2)	∠O(1) – Er1 – O(1^{i})	156.0 (5)
O(1) – O(4^{i})	2.91 (1)	∠O(6) – Er1 – O(6^{i})	150.5 (5)
O(1) – O(6)	2.97 (1)	∠O(3) – Er1 – O(3^{i})	72.8 (5)
O(1) – O(6^{i})	3.66 (2)	∠O(4) – Er1 – O(4^{i})	76.9 (5)
O(3) – O(3^{i})	2.78 (2)		
O(3) – O(6)	2.98 (2)		
O(3) – O(6^{i})	2.86 (2)		
O(4) – O(4^{i})	2.83 (2)		
Er2 – O(7)	2.29 (1)	∠Er2 – O(7) – C(5)	126.2 (7)
Er2 – O(9)	2.34 (1)	∠Er2 – O(9) – C(6)	120.8 (8)
Er2 – O(10)	2.37 (1)	∠O(9) – Er2 – O(9^{iv})	151.4 (5)
Er2 – O(11)	2.28 (1)	∠O(10) – Er2 – O(10^{iv})	149.1 (4)
O(7) – O(10)	2.92 (1)	∠O(11) – Er2 – O(11^{iv})	75.3 (5)
O(7) – O(10^{iv})	2.94 (2)	∠O(7) – Er2 – O(7^{iv})	77.3 (5)
O(7) – O(7^{iv})	2.86 (2)		
O(9) – O(10)	3.08 (1)		
O(9) – O(10^{iv})	3.76 (2)		
O(9) – O(11)	3.07 (1)		
O(9) – O(11^{iv})	2.79 (1)		
O(11) – O(11^{iv})	2.78 (2)		
O(10) – O(11)	2.67 (1)		
Distances and angles within ligand 1			
C(1) – O(1)	1.24 (2)	∠O(1) – C(1) – O(2)	123.0 (13)
C(1) – O(2)	1.32 (2)	∠O(1) – C(1) – C(2)	118.8 (14)
C(1) – C(2)	1.53 (2)	∠O(2) – C(1) – C(2)	118.2 (13)
C(2) – O(3)	1.36 (2)	∠O(3) – C(2) – C(1)	108.5 (11)
O(1) – O(3)	2.57 (1)		
Distances and angles within ligand 2			
C(3) – O(4)	1.27 (2)	∠O(4) – C(3) – O(5)	127.1 (13)
C(3) – O(5)	1.24 (2)	∠O(4) – C(3) – C(4)	117.6 (11)
C(3) – C(4)	1.54 (2)	∠O(5) – C(3) – C(4)	115.3 (13)
C(4) – O(6)	1.50 (2)	∠O(6) – C(4) – C(3)	105.0 (11)
O(4) – O(6)	2.54 (1)		

Table 6. Continued.

Distances and angles within ligand 3			
C(5)–O(7)	1.29 (2)	∠O(7)–C(5)–O(8)	123.8 (11)
C(5)–O(8)	1.25 (2)	∠O(7)–C(5)–C(6)	116.4 (11)
C(5)–C(6)	1.48 (2)	∠O(8)–C(5)–C(6)	119.4 (13)
C(6)–O(9)	1.47 (2)	∠O(9)–C(6)–C(5)	108.8 (12)
O(7)–O(9)	2.54 (1)		
Possible hydrogen bonds			
O(3)–O(4^{ii})	2.69 (1)	∠C(2)–O(3)–O(4^{ii})	122.0 (8)
		∠C(3^{ii})–O(4^{ii})–O(3)	123.5 (8)
O(6)–O(5^{ii})	2.64 (1)	∠C(4)–O(6)–O(5^{ii})	109.7 (8)
		∠C(3^{ii})–O(5^{ii})–O(6)	120.1 (11)
O(9^{ii})–O(8)	2.71 (1)	∠C(6^{ii})–O(9^{ii})–O(8)	110.0 (8)
		∠C(5)–O(8)–O(9^{ii})	119.7 (9)
O(10)–O(2)	2.56 (2)	∠O(2)–O(10)–O(8^{v})	105.6 (5)
O(10)–O(8)	2.81 (2)	∠C(1)–O(2)–O(10)	130.4 (10)
		∠C(5)–O(8)–O(10)	116.1 (9)
O(10)–O(11)	2.67 (1)	∠O(2)–O(10)–O(11)	165.2 (6)
O(11^{ii})–O(2)	2.62 (2)	∠O(2)–O(11^{ii})–O(7^{iv})	99.2 (4)
O(11^{ii})–O(7^{iv})	2.75 (1)	∠C(1)–O(2)–O(11^{ii})	142.3 (10)
		∠C(5^{iv})–O(7^{iv})–O(11^{ii})	118.3 (7)

atom, Er 1, is coordinated by four glycolate ligands in an anionic complex $[Er(HOCH_2COO)_4^-]$, the other, Er 2, in a cationic complex $[Er(HOCH_2COO)_2(H_2O)_4^+]$ formed by coordination of two glycolate and four water ligands.

The complexes form hydrogen bonded chains (p. 3735, and Fig. 1) running parallel to *b* through the structure. The chains obtained by the anionic and cationic species are centered at $x=0$, $z=1/4$; $x=0$, $z=3/4$ and $x=1/2$, $z=1/4$; $x=1/2$, $z=3/4$, respectively. The two sets of chains are linked to one another by hydrogen bonds (p. 3735) and form in this way layers parallel to the *ab* plane at *z* equal to 1/4 and 3/4. A stereo projection of the layer centered at $z=1/4$ and a projection perpendicular to *b* are shown in Figs. 1 and 2, respectively.

The eight coordinated oxygen atoms form a distorted dodecahedron. The most obvious deviation from the ideal $\bar{4}2m$ shape is the non-planarity of the two trapetzoids forming the dodecahedra; *e.g.* O(6) and O(6^{i}) are ± 0.64 Å from the plane formed by Er 1, O(4), and O(4^{i}), (Table 7). Parallel projections of the two coordination polyhedra are shown in Fig. 3.

All glycolate ligands are bonded as chelates along the *m*-edges of the two dodecahedra (see Ref. 1, p. 1262, for the notation of the edges). The same coordination sites were also found in the $ErC_4H_9O_8$ structure described in a previous communication.[1] The average erbium-oxygen bond distance is 2.31 ± 0.02 Å in both the coordination polyhedra. This quantity is in good

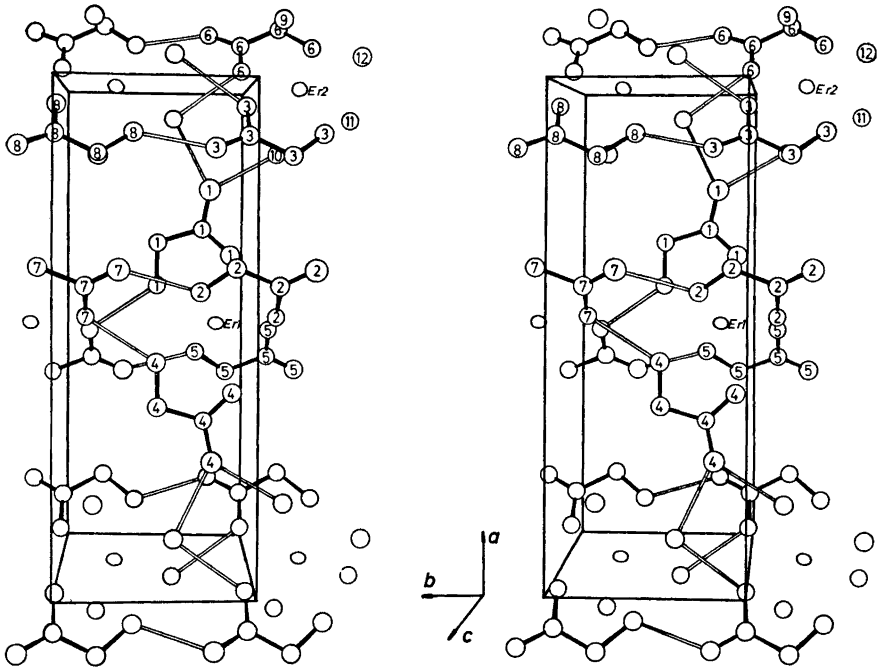


Fig. 1. Stereoprojection of a layer centered at $z = 1/4$ in the Erglyc structure. 1 and 4 denote the various atoms in ligand 1 and ligand 1^{i}. 2, 5, and 7 denote ligands 2, 2^{i}, and 2^{ii}, respectively. 3, 6, and 8 denote ligands 3, 3^{iv}, and 3^{ii}. 10 and 9 denote the water oxygens O(10) and O(10^{iv}), while 11 and 12 denote O(11) and O(11^{iv}). The bond sticks between the ligand atoms are filled and those between possible hydrogen bonded atoms are unfilled.

agreement with the corresponding bond distances found in other eight-coordinated structures of rare earths with ionic radius close to that of erbium.[9–11] The carbon – oxygen – erbium angles within the chelates are all close to 120°, the average being $(122 \pm 2)°$.

A comparison between the glycolato complexes formed by the elements La – Gd and Gd – Lu shows a change in coordination geometry as well as coordination number between the two series of compounds. A possible explanation to this fact might be the following. Within an isostructural series of rare earth glycolates, *e.g.* the orthorhombic trisglycolates, the average distances between the coordinated oxygen atoms which do not belong to the same ligand decrease with decreasing ionic radius of the central ion. This results in increased oxygen-oxygen repulsions and presumably a decrease in stability of the solid. The fact that the thermodynamically most stable compounds of the heavy lanthanides have a coordination number of eight and, as a result of this, larger average oxygen-oxygen distances than in a possible nine-coordinated complex is in keeping with this.

The ligands. Most of the corresponding distances and angles within the three glycolate ligands are not significantly different from one another or

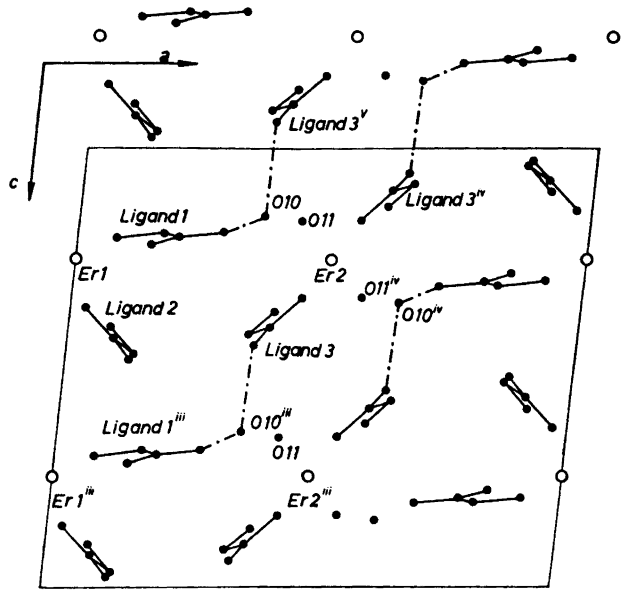


Fig. 2. Projection of the Erglyc structure perpendicular to *b*. The interlayer hydrogen bonds connect the water-oxygen O(10) with ligand 3v *etc.*

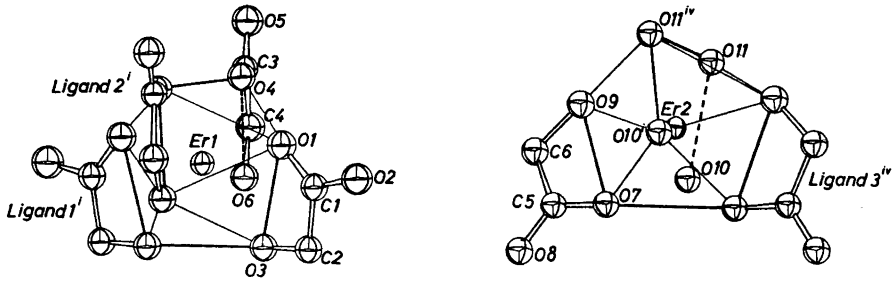


Fig. 3. A parallel projection of the coordination polyhedra around Er 1 and Er 2 drawn by using the program ORTEP. The atoms are represented by "thermal spheres" (or ellipsoids for the erbium atoms), formally scaled to include 50 % of the probability distribution.

from the values found in other glycolate complexes. One distance, C(4) – O(6), is 1.50 Å and is longer than the average value, 1.42 Å, found between carbon and hydroxy oxygen in a large number of glycolate compounds (Refs. 1 – 3, 12 – 14). There does not seem to be a structural reason for this deviation and it is presumably due to experimental shortcomings.

The C – COO-group is approximately planar in the three ligands (Table 7), while the hydroxy oxygen is twisted approximately 0.10 Å out of this plane.

Table 7. The deviation in Å of the erbium and ligand atoms from least-squares planes in the coordination polyhedra and in the ligands. These planes are in the ligands formed by the C–COO groups.

Atom	Distance in Å	Atom	Distance in Å	Atom	Distance in Å
O(1)	0.005	O(4)	−0.006	O(7)	0.006
O(2)	0.005	O(5)	−0.007	O(8)	0.006
C(1)	−0.015	C(3)	0.018	C(5)	−0.016
C(2)	0.004	C(4)	−0.005	C(6)	0.005
O(3)	−0.086	O(6)	0.105	O(9)	−0.094
Er1	0.235	Er1	0.803	Er2	0.171

The planarity of the trapetzoids defining the coordination polyhedra

Er1	0.000	Er1	0.000	Er2	0.000	Er2	0.000
O(4)	0.000	O(3)	0.000	O(7)	0.000	O(11)	0.000
O(4^{i})	0.000	O(3^{i})	0.000	O(7^{iv})	0.000	O(11^{iv})	0.000
O(6)	0.635	O(1)	0.644	O(9)	0.519	O(10)	1.285
O(6^{i})	−0.635	O(1^{i})	−0.644	O(9^{iv})	−0.519	O(10^{iv})	−1.285

Possible hydrogen bonds. Several oxygen–oxygen distances are compatible with the formation of a hydrogen bond (*cf.* Table 6). The most probable hydrogen bond scheme is outlined in Fig. 1 and was obtained from considerations of the oxygen–oxygen and the estimated hydrogen–erbium distances in the structure. Hydrogen bonding between oxygen atoms belonging to the same coordination polyhedron is not probable and has not been included in Table 6. The hydrogen bond donor and acceptor angles (–O(H)···O, and C–O···(H)O, respectively) were used as auxiliary criteria, with due consideration to the fairly large variations found in these quantities.[15,16]

All hydroxy and water hydrogens participate in hydrogen bonds. O(3) in Ligand 1 is hydrogen bonded to the carboxylate oxygen O(4^{ii}) in Ligand 2^{ii}. Ligands 2 and 3 and their translation equivalents form chains aligned along *b* by hydrogen bonding of O(6) to O(5^{ii}) and O(9^{ii}) to O(8). The hydroxyoxygen hydrogen bond donor angles lie in the range 110–120°, while the carboxylate hydrogen bond acceptor angles have values near 120°, the average is equal to (121 ± 1)°. These quantities are in good agreement with the corresponding values in other hydrogen bonded structures (Ref. 16, pp. 27 and 29).

It is difficult to suggest the most probable hydrogen bond scheme for the coordinated water molecules. One possible bond scheme is the following.

The coordinated water O(10) is hydrogen bonded to O(2) and O(8^{v}). The angle O(2)–O(10)–O(8^{v}) is 106.5°, very close to the bond angle in water, 104.5°. The bond O(2)–O(10) is one of the *intra*-layer links between the cationic and the anionic ligand chains mentioned previously. O(8^{v})–O(10) forms the only *inter*-layer link (Fig. 2). The layers in the structure are thus held together by only one hydrogen bond per crystallographic unit. The easy cleavage of the crystals along *b* might be explained by this fact.

The second of the coordinated water molecules, O(11^{ii}), forms two hydrogen bonds, one to O(2) and the other to O(7^{iv}) or O(10^{ii}). The hydrogen atom

would lie very near the erbium atom if the bond is formed between O(11^{ii}) and O(10^{ii}). Hence, the most favourable bond scheme seems to be obtained when O(11^{ii}) is bonded to O(2) and O(7^{iv}). The angle O(2)–O(11^{ii})–O(7^{iv}) has a value of 99.6°, in good agreement with the bond angle in water.

Most of the other hydrogen bond alternatives lead to short (approx. 2.4 Å) erbium–hydrogen distances. In the bond scheme suggested, the corresponding distances are estimated to approx. 3 Å.

Remarks on the variation of the lattice parameters. Single crystal data have been obtained for only one compound and it is thus impossible to decide how changes in packing and in the dimensions of the coordination polyhedra influence the lattice parameters. The decrease in unit cell volume with decreasing ionic radius of the central ion is considerably smaller for the elements after erbium than for those before (Table 1). This fact may be due to a smaller shrinkage of the coordination polyhedra due to increased oxygen–oxygen repulsions as discussed by Albertsson [17] and also in parts 2 and 3 of this series.[2,3]

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