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Structural Studies on the Rare Earth Carboxylates

2. The Crystal and Molecular Structure of Hydroxyacetato-oxyacetato-aquo-erbium(III) Monohydrate, $[Er(HOCH_2COO)(OCH_2COO)(H_2O)]\cdot H_2O$

INGMAR GRENTHE

Division of Physial Chemistry, University of Lund, Chemical Center, Box 740, S-220 07 Lund 7, Sweden

The preparation of rare earth glycolates of the composition $MC_4H_9O_8$, M=Gd–Lu, is described. The crystal and molecular structure of the erbium compound has been determined from three-dimensional X-ray intensity data. The crystals are monoclinic with the space group $P2_1/c$. The lattice parameters are: $a=6.173$ Å; $b=9.045$ Å; $c=14.654$ Å; $\beta=93.92°$; $Z=4$. The structure determination has shown that the compound has the formula $[Er(HOCH_2COO)(OCH_2COO)(H_2O)]\cdot H_2O$ and that the erbium atom is coordinated by eight oxygen atoms in an approximately dodecahedral arrangement. The crystal structure consists of a three-dimensional network built up of ligand-metal chains aligned along the *a* and *c* axis and crosslinked *via* erbium-oxygen and hydrogen bonds.

The crystal and molecular structure of two rare earth glycolate complexes, $[Er(HOCH_2COO)(OCH_2COO)(H_2O)]\cdot H_2O$ and $Gd(HOCH_2COO)_3$ will be described in this and a following communication. This study is part of a series of investigations of rare earth complexes in the solid state.[1]

When solid rare earth glycolates of the composition $M(HOCH_2COO)_3\cdot 2H_2O$ ($MC_6H_{13}O_{11}$) with M=Gd–Lu, are treated hydrothermally a new compound of the composition $MC_4H_9O_8$ is formed. The anions in the complex could either be one hydroxide and two glycolates or one glycolate and one oxyacetate. Hence the composition could be $M(OH)(HOCH_2COO)_2\cdot H_2O$ or $M(HOCH_2COO)(OCH_2COO)\cdot 2H_2O$. In this investigation the erbium compound, $ErC_4H_9O_8$, has been investigated by three-dimensional X-ray methods in order to determine the crystal and molecular structure of the compound and from this information establish the correct formula.

EXPERIMENTAL

Preparation of $ErC_4H_9O_8$. Erbium glycolate, $Er(HOCH_2COO)_3 \cdot 2H_2O$ was prepared as described by Jantsch and Grünkraut.[2] The micro-crystalline precipitate was washed with water and dried in air. Elemental analyses gave the following result: 38.3 % Er, 17.0 % C and 3.4 % H. Calc. for $Er(HOCH_2COO)_3 \cdot 2H_2O$: 39.0 % Er, 16.8 % C and 3.1 % H. The precipitate was treated hydrothermally in order to obtain larger crystals and 0.3 g precipitate and 10 ml water gave, after approximately one month at 90°C, a small amount of larger ($0.1 \times 0.1 \times 0.1$ mm^3) tabular single crystals. The crystals were analyzed and contained 13.5 % C and 2.6 % H, *i.e.* a new solid of the composition $ErC_4H_9O_8$ had been formed. The calculated percentages of carbon and hydrogen for this compound are 13.5 and 2.6. The pH of the mother liquor was approximately 3 after the hydrothermal treatment, *i.e.* hydrogen ions had been released. Some preliminary investigations on the stability and the rate of formation of various rare earth compounds of the composition $MC_4H_9O_8$ were now made. The $MC_6H_{13}O_{11}$ phase was changed to $MC_4H_9O_8$ only if the temperature was above 70°C. The rate of the phase transformation was dependent on the initial hydrogen-ion concentration in the aqueous phase — it increased with decreasing hydrogen-ion concentration. A complete transformation of $MC_6H_{13}O_{11}$ to large single crystals of $MC_4H_9O_8$ was obtained after less than one hour of hydrothermal treatment, if a small amount of sodium hydroxide was added to the initial solution as a "catalyst". The amount of sodium hydroxide is not essential as long as it is smaller than the amount of rare earth present.

Compounds of the type $MC_4H_9O_8$ seem to be formed only by the heavy lanthanoids (Gd—Lu).

X-Ray diffraction work. Non-integrated, equi-inclination Weissenberg photographs were taken with Ni-filtered Cu$K\alpha$ radiation for the layers $0kl$—$4kl$ and for $h0l$—$h5l$. Two different single crystals of thick tabular shape were used. The first had the approximate dimensions $0.025 \times 0.01 \times 0.09$ mm^3 and was mounted along [100] (the 0.09 mm edge), the second had the dimensions $0.1 \times 0.06 \times 0.12$ mm^3 and was mounted along the 0.12 mm edge. The intensities were measured visually by using the multi-film technique (4 films) and a calibrated scale. 1216 independent reflexions, about 80 % of those within the investigated reciprocal region, were measured. No absorption correction was applied to the intensity data because the crystals used were small and had a fairly low linear absorption coefficient ($\mu = 197$ cm^{-1}).

The intensity data were corrected for the Lorentz and polarization effects by using the data reduction and Fourier calculation programme, DRF.[3] All computing work was made on the CD 3600 computer at Uppsala, Sweden. The different layers were approximately brought to the same scale by comparison of $|F_o|$-values for the same reflexions in the two settings.

SPACE GROUP AND UNIT CELL

The crystals investigated are monoclinic and the following conditions limit the possible reflexions, $h0l$ present for $l = 2n$ and $0k0$ present for $k = 2n$. The only space group compatible with these conditions is no. 14 $P2_1/c$.

Approximate values of the lattice parameters were obtained from oscillation and Weissenberg photographs. They were refined from powder data obtained by using a Guinier focusing camera with Cu$K\alpha$ radiation. The camera constants were determined by using lead nitrate as an internal standard and the powder photograph was indexed by a comparison of $\sin^2\theta_{obs}$ with $\sin^2\theta_{calc}$. The final refinement was based on 24 reflexions (*cf.* Table 1), using the least-squares programme CELSIUS [3] with weights proportional to $1/\sin^2 2\theta$.

The crystal data are as follows

$a = 6.173 \pm 0.005$ Å; $Z = 4$
$b = 9.045 \pm 0.004$ Å; $D_m = 2.80 \pm 0.06$ g·cm^{-3}
$c = 14.654 \pm 0.005$ Å; $D_x = 2.88$ g·cm^{-3}
$\beta = 93.92° \pm 0.03°$; $\mu = 197$ cm^{-1} (Cu$K\alpha$)
$V = 816.3 \pm 0.8$ Å^3;

The density of the crystals, D_m, was determined by flotation.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

A trial position of the erbium atom was obtained from two two-dimensional Patterson projections, $P(vw)$ and $P(uw)$, respectively. The vector maps were computed using the programme DRF.[3]

The preliminary atomic coordinates, the isotropic temperature factor and the inter-layer scale factors were refined by using the full matrix least-squares programme LALS[3] on the three-dimensional intensity data. A three-dimensional difference synthesis based upon the improved erbium parameters was then calculated. The positions of the oxygen and carbon atoms of the

Table 1. Powder data for $ErC_4H_9O_8$ taken with a Guinier focusing camera using Cu$K\alpha$ radiation. $Pb(NO_3)_2$ has been used as internal standard for the determination of the camera constants. $\sin^2\theta_{calc}$ has been computed using the final least-squares refined cell parameters.

h k l	$\sin^2\theta_{obs} \times 10^4$	$\sin^2\theta_{obs} - \sin^2\theta_{calc} \times 10^4$	observed intensity
0 1 1	100.2	−0.1	vst
1 0 0	155.0	−1.4	st
0 1 2	184.4	0.8	m
1 1 0	230.1	1.2	vw
1 1 −1	246.1	−1.6	m
1 0 −2	248.5	−0.9	st
0 2 1	318.3	0.5	m
0 1 3	324.7	2.4	m
0 0 4	446.2	2.1	st
1 1 3	507.4	1.6	m
0 1 4	520.7	4.1	w
1 2 −2	534.9	−4.6	vvw
2 0 0	625.8	0.1	m
0 3 1	678.8	−1.6	m
2 1 0	697.6	−0.6	m
2 1 −1	709.0	1.0	m
2 2 −1	927.9	2.4	w
1 3 2	940.6	2.5	m
0 0 6	996.6	−2.6	w
2 3 0	1278.0	−0.4	m
0 4 3	1413.0	2.9	vw
3 0 −2	1464.0	−0.8	vw
2 3 −4	1651.9	1.5	st
1 3 6	1855.2	−7.2	w

ligands were located without difficulty from these electron density maps. Peak heights and geometrical considerations were used in the identification of the atoms. A second difference synthesis using the identified part of the structure gave the positions of the two remaining oxygen atoms. No attempt was made to locate the hydrogen atoms in the structure.

The preliminary interlayer scale factors, the atomic coordinates and isotropic temperature factors for all atoms were then improved by three cycles of least-squares refinement. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with weighting according to Cruickshank.[4] The atomic scattering factors used were those given for the neutral atoms in *International Tables* [5] and the scattering factors for erbium were corrected for anomalous dispersion.

A computation of interatomic angles and distances using the programme DISTAN [3] showed significant differences in the distances between erbium and its coordinated oxygen atoms and it was thus physically reasonable to use anisotropic thermal parameters for the erbium atom in a new least-squares refinement. After five cycles of refinement of all parameters, the discrepancy index $R=\sum||F_o|-|F_c||/|F_o|$ was equal to 0.087; only the observed reflexions were considered. The shifts in the parameters at the last cycle was less than 1 % of the estimated standard-deviations.

The refined parameters with their corresponding standard-deviations are given in Table 2. Table 3 gives the average values of $w(|F_o|-|F_c|)^2$ in different $|F_o|$ and sin θ intervals for the last cycle in the refinement. The fact that the average values are approximately the same in all intervals indicates that the weighting scheme used is satisfactory.

Table 2. Coordinates and thermal parameters with their corresponding standard deviations. The space group is No. 14. $P2_1/c$ and all atoms are in the general positions 4*e*. The anisotropic thermal parameters for erbium 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)	$COO(1)^-$	1396(16)	1594(13)	2656(7)	2.27(0.16)
O(2)	$CO(2)O^-$	325(18)	3930(13)	2849(8)	2.62(0.19)
O(3)	$-O(3)^-$	448(16)	3775(12)	4636(6)	1.96(0.16)
C(1)	$OC(1)O^-$	965(21)	2689(17)	3141(8)	2.03(0.21)
C(2)	OC(2)C	1147(23)	2521(20)	4185(10)	2.65(0.23)
O(4)	$COO(4)^-$	3926(15)	2267(12)	1018(6)	2.20(0.16)
O(5)	$CO(5)O^-$	7060(19)	1150(15)	1247(8)	2.85(0.21)
O(6)	$-O(6)H$	9455(17)	3388(13)	1064(7)	2.34(0.17)
C(3)	$OC(3)O^-$	5928(19)	2192(15)	1057(8)	1.77(0.19)
C(4)	OC(4)C	7156(30)	3554(24)	842(12)	3.68(0.33)
O(7)	$H_2O(7)$	6236(22)	4236(15)	3600(10)	3.81(0.25)
O(8)	$H_2O(8)$	6189(23)	1216(17)	3273(10)	4.03(0.25)
Er		766(1)	800(0.9)	1144(0.4)	

$\beta_{11}\times10^4$	$\beta_{22}\times10^4$	$\beta_{33}\times10^4$	$\beta_{12}\times10^4$	$\beta_{13}\times10^4$	$\beta_{13}\times10^4$
105(4)	47.5(1.1)	14.6(0.4)	5.5(2.3)	7.5(1.1)	0.5(0.9)

Table 3. Analysis of the weighting scheme. The averages w $(|F_o|-|F_c|)^2=w\Delta^2$ are normalized. The weighting scheme is equal to $w=1/(10.0+|F_o|+0.02|F_o|^2+0.002|F_o|^3)$.

$\|F_o\|$interval	Number of reflexions	$w\Delta^2$	sinθ interval	Number of reflexions	$w\Delta^2$
0— 19	100	0.64	0.00—0.39	92	1.27
19— 26	111	0.87	0.39—0.50	84	0.95
26— 31	110	0.94	0.50—0.57	98	0.96
31— 39	114	1.01	0.57—0.63	77	1.07
39— 46	117	1.22	0.63—0.67	89	0.78
46— 54	119	0.92	0.67—0.72	78	0.80
54— 63	118	1.10	0.72—0.75	73	1.19
63— 76	119	1.16	0.75—0.79	84	1.23
76— 95	119	1.15	0.79—0.82	70	0.89
95—243	119	0.99	0.82—0.85	66	0.85

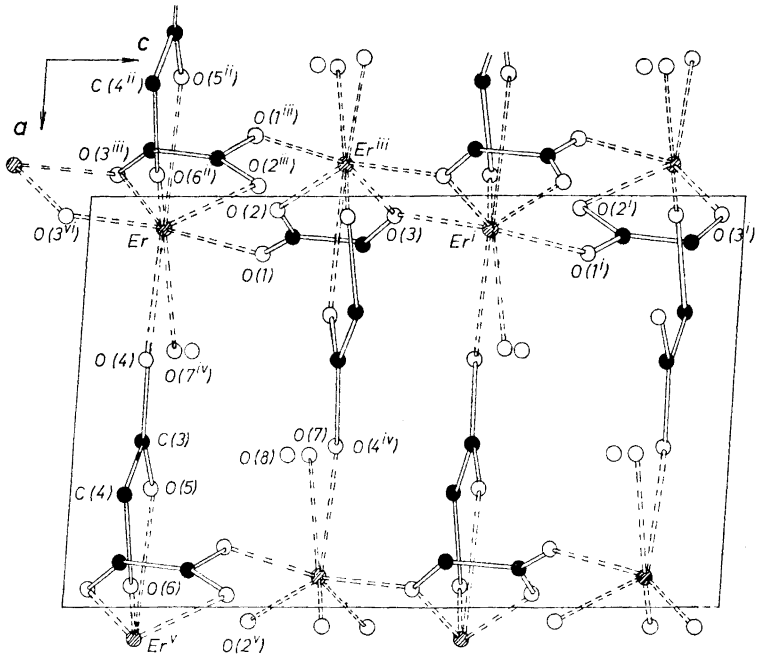

Fig. 1. A projection of the structure along [010]. Carbon atoms are black, oxygen atoms white and erbium atoms striped. Erbium—oxygen bonds are dashed and bonds within the ligands full-drawn. The various superscripts are defined on p. 1261.

Table 4. Observed and calculated structure factors.

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	0	4	242	275	1	0	12	98	109	1	6	-10	96	85	3	8	-4	47	46	4	6	-12	53	55
0	0	6	107	110	1	0	14	42	38	1	6	-8	90	90	3	8	-2	59	59	4	6	-10	29	29
0	0	8	131	148	1	0	16	55	55	1	6	-6	72	80	3	8	-1	39	35	4	6	-8	55	56
0	0	10	94	103	1	1	-17	56	37	1	6	-4	65	70	3	8	1	66	58	4	6	-6	74	67
0	0	12	75	83	1	1	-16	37	31	1	6	-2	71	77	3	8	2	54	47	4	6	-4	78	78
0	0	14	94	91	1	1	-15	49	43	1	6	0	86	96	3	8	4	25	21	4	6	-2	73	73
0	0	18	56	60	1	1	-13	69	75	1	6	2	55	50	3	8	5	44	44	4	6	0	44	40
0	1	1	156	161	1	1	-12	40	40	1	6	4	91	96	3	8	6	32	30	4	6	2	95	93
0	1	2	124	126	1	1	-11	82	85	1	6	6	22	21	3	8	9	47	44	4	6	3	31	26
0	1	3	109	110	1	1	-9	97	101	1	6	8	75	82	3	8	10	24	25	4	6	6	85	83
0	1	4	88	94	1	1	-8	29	23	1	6	9	25	23	3	9	-8	43	48	4	6	10	65	63
0	1	5	145	144	1	1	-7	56	53	1	6	12	69	67	3	9	-4	69	61	4	6	12	25	20
0	1	6	169	161	1	1	-6	64	66	1	6	14	31	26	3	9	0	55	56	4	7	-11	44	52
0	1	7	53	59	1	1	-5	86	102	1	7	-13	51	51	3	9	4	55	55	4	7	-10	27	29
0	1	8	63	70	1	1	-4	57	54	1	7	-11	27	20	3	9	6	20	24	4	7	-7	66	64
0	1	9	127	129	1	1	-1	151	186	1	7	-9	86	81	3	9	8	44	48	4	7	-3	81	78
0	1	10	58	55	1	1	0	45	43	1	7	-6	22	23	3	10	-6	16	19	4	7	0	43	39
0	1	11	25	29	1	1	1	65	68	1	7	-5	88	95	3	10	-5	48	53	4	7	1	74	72
0	1	12	55	60	1	1	2	44	38	1	7	-1	79	84	3	10	-3	26	30	4	7	3	39	30
0	1	13	88	96	1	1	3	123	139	1	7	3	86	91	3	10	-1	36	37	4	7	4	29	23
0	1	14	28	30	1	1	5	65	61	1	7	5	38	38	3	10	1	29	34	4	7	5	45	46
0	1	16	41	38	1	1	6	137	119	1	7	6	46	43	3	10	2	21	24	4	7	7	45	45
0	1	17	57	50	1	1	7	100	95	1	7	7	55	52	3	10	3	19	23	4	7	8	25	23
0	2	0	27	31	1	1	9	78	79	1	7	9	57	51	3	10	5	43	48	4	7	9	35	34
0	2	1	103	116	1	1	10	47	50	1	7	10	28	28	4	0	-16	55	61	4	8	-10	22	24
0	2	3	108	104	1	1	11	46	45	1	7	11	34	35	4	0	-12	60	64	4	8	-9	31	37
0	2	4	75	69	1	1	13	63	61	1	7	13	61	67	4	0	-10	42	41	4	8	-5	31	33
0	2	6	91	92	1	1	14	46	43	1	7	14	15	18	4	0	-8	69	81	4	8	-6	30	25
0	2	7	139	138	1	1	17	46	53	1	8	-13	16	19	4	0	-6	67	85	4	8	-5	42	43
0	2	8	67	72	1	2	-18	39	40	1	8	-11	47	43	4	0	-4	56	63	4	8	-2	57	45
0	2	9	25	27	1	2	-17	28	27	1	8	-10	45	45	4	0	-2	45	51	4	8	-1	44	44
0	2	11	71	83	1	2	-15	53	43	1	8	-8	26	30	4	0	0	27	33	4	8	1	28	26
0	2	12	43	51	1	2	-14	51	45	1	8	-7	59	53	4	0	2	61	73	4	8	2	32	30
0	2	13	76	76	1	2	-13	51	40	1	8	-6	47	41	4	0	4	34	34	4	8	3	43	46
0	2	18	30	28	1	2	-12	22	22	1	8	-4	45	44	4	0	6	112	114	4	8	5	25	26
0	3	2	144	150	1	2	-11	46	44	1	8	-3	26	24	4	0	10	90	78	4	8	6	33	34
0	3	3	22	23	1	2	-10	61	65	1	8	-2	41	39	4	0	12	34	35	4	8	7	28	28
0	3	4	68	56	1	2	-8	45	47	1	8	0	40	43	4	0	14	54	56	4	9	-6	53	58
0	3	5	14	14	1	2	-7	127	120	1	8	1	49	49	4	1	-18	56	52	4	9	-4	47	49
0	3	8	67	72	1	2	-6	74	74	1	8	2	38	33	4	1	-14	42	35	4	9	-3	28	28
0	3	10	67	74	1	2	-4	50	60	1	8	3	44	43	4	1	-13	28	24	4	9	-2	53	55
0	3	12	65	70	1	2	-3	129	118	1	8	4	74	66	4	1	-11	45	45	4	9	0	52	57
0	3	14	69	56	1	2	-2	109	99	1	8	5	54	49	4	1	-7	53	111	4	10	-1	31	41
0	3	16	57	53	1	2	-1	16	16	1	8	7	54	46	4	1	-6	27	29	4	10	1	16	13
0	3	18	30	32	1	2	0	78	80	1	8	8	52	52	4	1	-2	15	16					
0	4	0	139	130	1	2	1	137	122	1	8	9	41	37	4	1	-1	20	31	7	0	-8	34	38
0	4	1	82	78	1	2	2	49	47	1	8	10	35	38	4	1	0	35	57	7	0	-6	31	27
0	4	3	120	132	1	2	3	75	61	1	8	12	30	31	4	1	1	61	89	7	0	-4	48	56
0	4	5	82	64	1	2	4	94	92	1	9	-10	22	23	4	1	3	56	70	7	0	-2	35	32
0	4	6	17	15	1	2	5	112	113	1	9	-8	54	52	4	1	4	51	53	7	0	0	64	59
0	4	7	110	103	1	2	7	118	118	1	9	-6	44	43	4	1	5	84	93	7	0	2	12	10
0	4	8	54	57	1	2	8	87	90	1	9	-5	25	28	4	1	7	70	69	7	0	4	64	61
0	4	11	78	92	1	2	9	59	61	3	3	12	65	60	4	1	8	38	37	6	0	-12	42	45
0	4	15	79	68	1	2	10	22	23	3	3	14	65	61	4	1	9	37	32	6	0	-10	43	43
0	4	17	15	15	1	2	11	67	78	3	4	-16	19	18	4	1	11	71	63	6	0	-8	65	70
0	5	1	117	98	1	2	13	37	28	3	4	-15	72	68	4	1	15	40	46	6	0	-4	105	90
0	5	2	71	64	1	2	15	70	64	3	4	-9	81	85	4	2	-16	28	32	6	0	-2	17	17
0	5	3	69	60	1	2	16	24	25	3	4	-7	43	43	4	2	-15	36	36	6	0	0	100	93
0	5	5	93	87	1	3	-16	73	69	3	4	-6	58	52	4	2	-13	61	52	6	0	2	60	48
0	5	6	47	47	1	3	-12	99	110	3	4	-5	102	91	4	2	-12	52	48	6	0	4	81	82
0	5	7	29	33	1	3	-10	31	33	3	4	-3	68	64	4	2	-10	38	32	6	0	6	56	54
0	5	8	28	30	1	3	-9	31	39	3	4	-2	77	74	4	2	-9	83	81	6	0	8	43	41
0	5	9	85	94	1	3	-8	119	119	3	4	1	84	70	4	2	-8	46	47	6	0	10	53	47
0	5	10	58	58	1	3	-7	17	20	3	4	0	45	42	4	2	-6	66	59	5	0	-14	11	11
0	5	11	29	30	1	3	-6	137	126	3	4	1	91	91	4	2	-4	77	75	5	0	-12	58	59
0	5	12	39	34	1	3	-5	81	66	3	4	2	68	61	4	2	-3	39	35	5	0	-8	92	85
0	5	13	74	63	1	3	-4	82	72	3	4	3	43	46	4	2	-2	32	28	5	0	-6	24	27
0	5	14	22	20	1	3	-2	207	187	3	4	4	25	19	4	2	-1	61	64	5	0	-4	89	83
0	5	16	47	41	1	3	1	13	13	3	4	5	82	84	4	2	1	105	137	5	0	-2	30	35
0	6	0	164	148	1	3	2	229	212	3	4	6	53	55	4	2	2	46	47	5	0	0	71	74
0	6	2	18	18	1	3	3	23	22	3	4	9	82	85	4	2	3	63	71	5	0	2	51	55
0	6	3	28	30	1	3	6	188	192	3	4	12	33	32	4	2	5	59	69	5	0	4	47	52
0	6	4	132	132	1	3	10	81	90	3	4	13	57	55	4	2	6	69	76	5	0	6	80	81
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					1	5	10	76	81	3	8	-7	25	25	4	5	8	59	56					
					1	5	13	67	61	3	8	-6	36	36	4	5	11	39	36					
					1	5	14	45	40	3	8	-5	37	42	4	5	12	30	30					
					1	6	-14	38	54															

Table 4. Continued.

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	$\|F_o\|$	$\|F_c\|$
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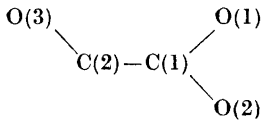
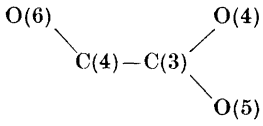
2	4	4	34	36	3	1	-11	38	70	7	2	7	26	30	5	4	-4	41	39					
2	4	5	106	117	3	1	-8	64	69	6	2	-12	26	26	5	4	-3	31	30					
2	4	6	42	45	3	1	-7	110	125	6	2	-11	43	43	5	4	-1	28	29					
2	4	7	32	30	3	1	-2	20	18	6	2	-8	29	29	5	4	3	29	26					
2	4	8	39	47	3	1	-1	82	117	6	2	-7	32	31	5	4	4	32	33					
2	4	9	84	91	3	1	0	69	106	6	2	-6	60	53	5	4	6	48	45					
2	4	11	35	31	3	1	1	57	66	6	2	-5	43	39	5	4	7	70	68					
2	4	12	49	47	3	1	2	38	38	6	2	-4	28	32	5	4	8	19	18					
2	4	13	42	43	3	1	3	116	120	6	2	-3	40	40	5	4	9	32	30					
2	4	15	47	45	3	1	4	42	34	6	2	-1	65	65	5	4	10	29	27					
2	5	-16	29	32	3	1	5	62	61	6	2	0	28	29	5	4	11	41	46					
2	5	-15	52	54	3	1	6	57	60	6	2	1	17	17	4	4	-12	23	22					
2	5	-13	30	26	3	1	7	119	125	6	2	3	65	65	4	4	-11	19	17					
2	5	-12	48	46	3	1	10	35	36	6	2	4	27	28	4	4	-10	23	21					
2	5	-11	54	49	3	1	11	95	97	6	2	6	17	18	4	4	6	24	27					
2	5	-9	45	48	3	1	15	57	56	6	2	7	23	23	4	4	11	27	28					
2	5	-8	55	54	3	2	-17	39	46	6	2	7	56	51	3	4	-14	21	23					
2	5	-7	58	60	3	2	-16	32	27	6	2	8	30	30	3	4	-12	17	16					
2	5	-5	91	82	3	2	-14	26	25	6	2	9	11	11	3	4	-11	16	16					
2	5	-4	96	95	3	2	-13	91	86	6	2	10	21	19	3	4	-10	21	21					
2	5	-3	49	47	3	2	-12	42	33	5	2	-14	10	10	3	4	-8	17	19					
2	5	-2	37	33	3	2	-10	41	39	5	2	-13	42	43	3	4	-4	12	13					
2	5	-1	104	106	3	2	-9	101	98	5	2	-12	48	45	3	4	8	19	18					
2	5	0	62	61	3	2	-8	28	28	5	2	-11	42	37	3	4	14	16	16					
2	5	2	69	65	3	2	-7	47	42	5	2	-9	78	76	2	4	-10	11	12					
2	5	3	95	95	3	2	-6	78	67	5	2	-8	62	56	2	4	-8	11	13					
2	5	4	58	57	3	2	-5	85	81	5	2	-7	55	48	2	4	10	16	9					
					3	2	-3	105	98	5	2	-5	75	73	1	4	8	47	54					
					3	2	-2	94	93	5	2	-4	54	58	1	4	12	54	52					
					3	2	1	120	126	5	2	-3	15	15										
					3	2	0	20	20															

Table 5. Selected bond distances (in Å) and angles with their corresponding standard deviations.

Distance in Å			Angle in degrees	
Er	$-Er^{iii}$	6.138 (2)		
Er^{i}	$-Er^{iii}$	3.720 (1)		
Within the coordination polyhedron				
Er	$-O(1)$	2.338(10)	$O(3^{vi})-O(3^{iii})-O(2^{iii})$	112.4(0.6)
Er	$-O(2^{iii})$	2.372(11)	$O(3^{iii})-O(2^{iii})-O(1)$	107.8(0.5)
Er	$-O(3^{iii})$	2.240 (9)	$O(5^{ii})-O(6^{ii})-O(4)$	106.5(0.5)
Er	$-O(3^{vi})$	2.261(10)	$O(6^{ii})-O(4)-O(7^{iv})$	106.6(0.5)
Er	$-O(4)$	2.378(10)		
Er	$-O(5^{ii})$	2.328(12)		
Er	$-O(6^{ii})$	2.476(12)		
Er	$-O(7^{iv})$	2.341(14)		
Within the first ligand				
C(1)	$-O(1)$	1.258(18)	O(1) $-C(1)-$ O(2)	125.8(1.2)
C(1)	$-O(2)$	1.255(19)	O(1) $-C(1)-$ C(2)	118.8(1.3)
C(1)	$-C(2)$	1.536(19)	O(2) $-C(1)-$ C(2)	115.4(1.3)
C(2)	$-O(3)$	1.396(19)	C(1) $-C(2)-$ O(3)	112.9(1.3)
Within the second ligand				
C(3)	$-O(4)$	1.237(15)	O(4) $-C(3)-$ O(5)	128.5(1.4)
C(3)	$-O(5)$	1.195(18)	O(4) $-C(3)-$ C(4)	117.8(1.3)
C(3)	$-C(4)$	1.491(24)	O(5) $-C(3)-$ C(4)	113.7(1.3)
C(4)	$-O(6)$	1.444(21)	C(3) $-C(4)-$ O(6)	111.9(1.5)
Possible hydrogen bond distances				
O(7)	$-O(2^{v})$	2.836(17)	$O(2^{v})-O(7)-O(4^{iv})$	102.6(0.5)
O(7)	$-O(4^{iv})$	2.800(17)	$O(8)-O(7)-O(2^{iv})$	80.6(0.5)
O(7)	$-O(8)$	2.772(21)	$O(8)-O(7)-O(4^{iv})$	176.8(0.7)
O(2)	$-O(6^{ii})$	2.683(15)	$O(2)-O(6^{ii})-C(4^{ii})$	109.3(0.9)
$O(3^{iii})$	$-O(6^{ii})$	2.959(15)	$O(3^{iii})-O(6^{ii})-C(4^{ii})$	99.0(0.9)

A new calculation of angles and distances was made from the refined unit-cell dimensions and atomic coordinates, and selected interatomic distances and angles are given in Table 5.

The final difference synthesis using the refined parameters only showed the presence of small peaks above a slowly varying background. The largest peak, 1.5 $e/Å^3$, was situated in the vicinity of O(8) where a slight anisotropic effect also could be detected. However, no conversion to anisotropic thermal parameters for O(8) was attempted.

The observed and calculated structure factors are compared in Table 4.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A projection of the structure along [010] is given in Fig. 1. In order to facilitate the description the symmetry related atoms are given superscripts of the following significance

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

The structure is a three-dimensional network built up of cross-linked erbium ligand chains. The first ligand, formed by O(1), O(2), O(3), C(1), and C(2), is aligned along the *c*-axis. Chains are formed by coordination of O(1) to Er, O(3) to Er^{i}, $O(1^{i})$ to Er^{i} *etc.* The second ligand is aligned along the *a*-axis and a chain is formed by coordination of O(4) to Er, O(5) and O(6) to Er^{v}, $O(4^{ii})$ to Er^{v} *etc.* The various chains are cross-linked by coordination to erbium (*cf.* Fig. 1) and *via* hydrogen bonding, probably between O(2) and $O(6^{ii})$ and between $O(2^{v})-O(7)-O(4^{iv})$; *vide* p. 1264.

O(7) can be part of: *a*, a coordinated water, in which case one of O(3) and O(6) must be an oxy-group ($R-O^{-}$); *b*, a coordinated hydroxide in which case both O(3) and O(6) belong to hydroxy-groups (R—OH).

The distances Er—O(3), Er—O(6) and Er—O(7), equal to 2.25 ± 0.01 Å, 2.48 ± 0.01 Å and 2.34 ± 0.01 Å, respectively, are of particular interest for the discussion of the formula of the $ErC_4H_9O_8$ compound. O(3) acts as a bridge between two erbium atoms, the Er—O(3) bond distances are in spite of this considerably shorter than the Er—O(6) distance (single bonded). This difference agrees well with the assumption that O(3) is negatively charged.

The acidity of the groups containing O(3), O(6), and O(7) will be strongly affected by coordination to erbium. O(3) is close to two metal atoms with a high charge density, while O(6) and O(7) are coordinated to only one metal atom. A hydrogen bonded to O(3) is thus exposed to a much stronger coulomb repulsion than a hydrogen bonded to any of the other two oxygen atoms, *i.e.* the ligand containing O(3) must be a much stronger acid than the one containing O(6). It is reasonable to assume that the effect of coordination is so large that the first ligand also turns out to be a stronger acid than a co-ordinated water.

It is then obvious that the formula of the $ErC_4H_9O_8$ compound is $[Er(HOCH_2COO)(OCH_2COO)(H_2O)]\cdot H_2O$, where one ligand, formed by O(1),

O(2), O(3), C(1), and C(2), is an oxy-acetate, the second ligand a hydroxy-acetate and the third ligand a water. The details of the structure will now be described.

The coordination polyhedron. The erbium atom is surrounded by eight coordinated oxygen atoms forming a distorted $\bar{4}2m$ dodecahedron. An analysis of the stereochemistry of eight-coordination has been given by Hoard and Silverton [6] and the subject has also been reviewed by Lippard.[7] It is convenient with a short description of the $\bar{4}2\ m$ dodecahedron for the following discussion. The nomenclature used will be the same as in Ref. 6.

A $\bar{4}2m$ dodecahedron consists of two equivalent trapezoids lying in mutually orthogonal mirror planes intersecting in $\bar{4}$. The full symmetry allows two sets of erbium-oxygen bond distances and four sets of edge lengths, *a*, *m*, *g*, and *b*, shown in Fig. 2. The shape of the dodecahedron is determined

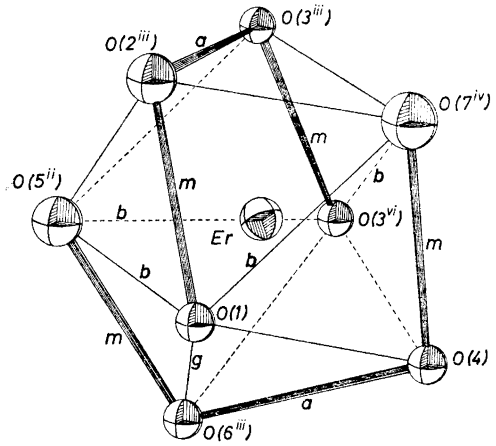


Fig. 2. The coordination polyhedron, drawn by using the programme ORTEP.[3] The atoms are represented by "thermal spheres" (or ellipsoide for the erbium atom), formally scaled to include 50% of the probability distribution. The two trapezoids forming the polyhedron are represented by the thick bond-sticks.

by two angles θ_A and θ_B, and the ratio between the two sets of erbium-oxygen bond distances. The angles θ_A and θ_B are equal to

$\angle[O(2^{iii})-Er-O(3^{iii})]/2$ or $\angle[O(4)-Er-O(6^{ii})]/2$, and
$\angle[O(5^{ii})-Er-O(7^{iv})]/2$ or $\angle[O(1)-Er-O(3^{vi})]/2$, respectively.

The angles can be calculated if the stereochemistry is determined mainly by ligand-ligand repulsion [6,8] and the values for θ_A and θ_B turn out to be 37° and 70°, respectively.

The coordination polyhedron in this structure can be obtained by distortion of a $\bar{4}2\ m$ dodecahedron. The distortions are fairly large in comparison with those found in the structures discussed by Lippard.[7] This is not unexpected because the coordination polyhedra in these structures occur as discrete units, formed of ligands of the same type where the various donor atoms belong to only one polyhedron. This is not the case in the $ErC_4H_9O_8$ structure because the polyhedra occur in pairs formed by sharing the $O(3^{iii})-O(3^{vi})$ edge, the ligands are not of the same type and the various donor atoms in

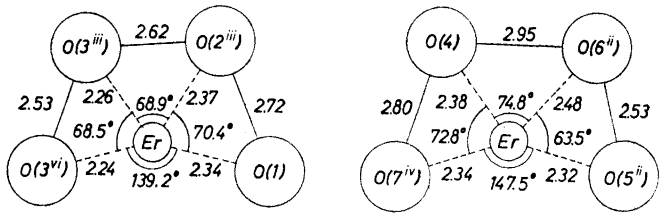


Fig. 3. Interatomic distances and angles within the coordination trapezoids.

the organic ligands are bonded in more than one polyhedron. The two organic ligands form chelates where one ligand spans the *a* edge of the first, and the other the *m* edge of the second trapezoid; *cf.* Fig. 3, it is obvious from this figure that the distances within the *a* and *m* sets are not equal. The angles θ_A and θ_B are also changed from the dodecahedral values, θ_A to 34.5° in one trapezoid and 37.4° in the other, θ_B to 73.2° and 69.5°, respectively. The trapezoids are distorted from planarity as shown in Table 6, where the distances of the coordinated oxygen atoms from the least-squares planes formed by the atoms in the two trapezoids are given. The calculation was done using the programme PLANES. As a result of these distortions three sets of significantly different erbium coordinated oxygen distances are obtained, as compared to at most two in the $\bar{4}2\,m$ dodecahedron.

Table 6. Least-squares planes for the ligands and the two trapezoids in the coordination polyhedron. The least-squares planes of the ligands are defined by the C—COO⁻ groups.

The equation of the various least-squares planes are expressed as $\sum m_i x_i - d = 0$ where the direction cosines m_i are referred to orthogonal axes. Unit weights are given to the points defining the plane.

Plane	m_1	m_2	m_3	d
O(1iii) —O(2iii) —O(3iii) —O(3vi)	−0.9827	−0.1840	−0.0220	−0.672
O(7iv) —O(4) —O(6ii) —O(5ii)	−0.0363	0.1625	−0.9860	−8.415
O(1) —O(2) —C(1) —C(2)	−0.9546	−0.2976	−0.0094	−1.031
O(4) —O(5) —C(3) —C(4)	0.0379	−0.2567	−0.9657	−1.876

The deviations in Å, of the various atoms from their corresponding least squares plane.

Atom	Distance,Å	Atom	Distance,Å	Atom	Distance,Å	Atom	Distance,Å
O(1)	−0.23	O(7iv)	−0.04	O(1)	0.006	O(4)	0.001
O(2iii)	0.33	O(4)	0.07	O(2)	0.005	O(5)	0.001
O(3iii)	−0.18	O(6ii)	−0.07	C(1)	−0.016	C(3)	−0.002
O(3vi)	0.08	O(5ii)	0.05	C(2)	0.004	C(4)	0.001
				O(3)	0.129	O(6)	−0.201

The ligands. Both organic ligands are approximately planar, with the oxy- and hydroxy-groups at the largest distance from the least-squares plane formed by the C—COO group; *vide* Table 6. The interatomic distances and angles in the two ligands are given in Table 5 and Fig. 4. Corresponding

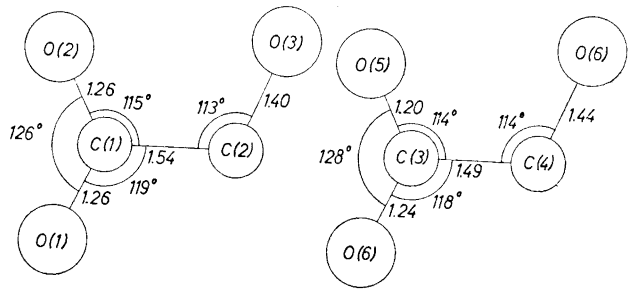


Fig. 4. Interatomic distances and angles within the ligands.

interatomic distances and angles within the ligands are not significantly different, and agree well with the corresponding figures found in other glycolate complexes.[9,10]

Possible hydrogen bonds. The various oxygen atoms which can be hydrogen bonded are listed in Table 5, with their corresponding interatomic distances. The distances $O(7)—O(2^{v})$ and $O(7)—O(4^{iv})$ are equal to 2.84 Å and 2.80 Å, respectively, and the angle $O(2^{v})—O(7)—O(4^{iv})$ is equal to 102,6°. This figure is very close to the H—O—H angle in water (104.5°), a fact which indicates that the hydrogen bonds formed are approximately linear. The distance O(7)—O(8) is equal to 2.77 Å, indicating that the second water molecule is hydrogen bonded to O(7). The remaining hydrogen on O(8) is not hydrogen bonded.

The angle $O(2)—O(6^{ii})—C(4^{ii})$ is equal to 109.3°, with the $O(2)—O(6^{ii})$ distance equal to 2.68 Å, and an approximately linear hydrogen bond can thus be formed between O(2) and $O(6^{ii})$. The $O(6^{ii})—O(3^{iii})$ distance, equal to 2.96 Å, and the angle $O(3^{iii})—O(6^{ii})—C(4^{ii})$, equal to 99.0°, are also reasonable if a hydrogen bond is formed between $O(6^{ii})$ and $O(3^{iii})$. As a stronger hydrogen bond can be formed between O(2) and $O(6^{ii})$ this is probably preferred.

A further discussion will be given in Part 4 of this series, where the crystal and molecular structure of tris-hydroxyacetato-gadolinium (III), will be described.

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