

## Structural Studies on the Rare Earth Carboxylates

### 3. The Crystal and Molecular Structure of Tris-hydroxyacetato-gadolinium(III), $\text{Gd}(\text{HOCH}_2\text{COO})_3$

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The crystal and molecular structure of  $\text{Gd}(\text{HOCH}_2\text{COO})_3$  has been determined from three-dimensional X-ray intensity data. The crystals are orthorhombic with the space group  $Pna2_1$  and have the lattice parameters  $a=10.300(6)$  Å,  $b=11.250(4)$  Å and  $c=7.641(1)$  Å. The structure is a three-dimensional network formed by cross-linked metal ligand chains. The gadolinium atom is surrounded by nine coordinated oxygen atoms and the coordination polyhedron is based on a distorted trigonal prism. The ligands are bonded as chelates along the diagonals of the rectangular faces of the prism. Six of the coordination sites are occupied by the chelates and three by carboxylate oxygens from adjoining ligands.

In a previous communication<sup>1</sup> the crystal and molecular structure of hydroxyacetato-oxyacetato-aquo-erbium(III)monohydrate [ $\text{Er}(\text{HOCH}_2\text{COO})(\text{OCH}_2\text{COO})(\text{H}_2\text{O})\text{H}_2\text{O}$ ] was described. Compounds of this composition are formed by the rare earth elements from gadolinium to lutetium by hydrothermal treatment of corresponding tris-hydroxyacetates. In this paper the crystal and molecular structure of  $\text{Gd}(\text{HOCH}_2\text{COO})_3$  is described. The gadolinium compound was chosen for the study because it was the lanthanide tris-hydroxyacetate of which suitable single crystals were most easy to prepare.

#### EXPERIMENTAL

*Preparation of  $\text{Gd}(\text{HOCH}_2\text{COO})_3$ .* Tris-hydroxyacetato-gadolinium(III) was prepared according to Jantsch and Grünkraut.<sup>2</sup> The micro-crystalline precipitate was recrystallized from hot water and large crystals ( $0.1 \times 0.1 \times 0.1$  mm<sup>3</sup>) of the anhydrous<sup>3</sup> compound were obtained on cooling. (Found: Gd 40.1; C 18.3; H 2.5. Calc. for  $\text{GdC}_6\text{H}_9\text{O}_9$ : Gd 41.1; C 18.8; H 2.35). The analyses show that the percentages of gadolinium and carbon are lower, and that of hydrogen higher than expected. The density calculated with the formula  $\text{GdC}_6\text{H}_9\text{O}_9$  is  $2.87 \text{ g}\cdot\text{cm}^{-3}$ , which is lower than the measured value,  $3.04 \text{ g}\cdot\text{cm}^{-3}$  (*vide infra*). These facts indicate that the compound might contain water; 0.5 water per formula

unit gives calculated percentages of Gd, C, and H equal to 40.2, 18.36, and 2.55, respectively, while the calculated density is  $2.94 \text{ g}\cdot\text{cm}^{-3}$ .

*X-Ray diffraction work.* Non-integrated equi-inclination Weissenberg photographs were taken with  $\text{MoK}\alpha$  radiation using the multiple film technique (three films, separated by tin foils).

Two single crystals were used in recording the layers  $0kl-11kl$  and  $hk0-hk8$ , respectively. The first specimen was prismatic with height equal to 0.1 mm and all other edges equal to 0.2 mm each. The crystal was mounted perpendicular to the triangular faces along the 0.1 mm edges. The second specimen was tabular of the approximate dimensions  $0.1 \times 0.05 \times 0.2 \text{ mm}^3$  and was mounted along the 0.2 mm edge. 1216 independent reflexions were recorded. All intensities were measured visually by using a calibrated scale and no absorption correction was made because of the low linear absorption coefficient,  $79 \text{ cm}^{-1}$  for  $\text{MoK}\alpha$  radiation.

The intensity data were corrected for the Lorentz and polarization effects by using the data reduction and Fourier calculation programme DRF.<sup>4</sup> All computing work was carried out on the CD 3600 computer at Uppsala, Sweden.

*Table 1.* Powder data for  $\text{Gd}(\text{HOCH}_2\text{COO})_3$  taken with a Guinier focusing camera using  $\text{CuK}\alpha$  radiation.  $\text{Pb}(\text{NO}_3)_2$  has been used as internal standard for the determination of the camera constants.  $\text{Sin}^2\theta_{\text{calc}}$  has been computed using the final least-squares refined cell parameters:  $a = 10.300 \pm 0.006 \text{ (\AA)}$ ,  $b = 11.250 \pm 0.004 \text{ (\AA)}$ ,  $c = 7.641 \pm 0.001 \text{ (\AA)}$ .

$hkl$	$\text{sin}^2\theta_{\text{obs}} \times 10^4$	$\frac{\text{sin}^2\theta_{\text{obs}} - \text{sin}^2\theta_{\text{calc}}}{\times 10^4}$	observed intensity	$hkl$	$\text{sin}^2\theta_{\text{obs}} \times 10^4$	$\frac{\text{sin}^2\theta_{\text{obs}} - \text{sin}^2\theta_{\text{calc}}}{\times 10^4}$	observed intensity
1 0 1	157.9	0.4	vw	0 1 3	961.9	0.4	vvw
0 2 0	187.4	-0.1	m	1 0 3	973.0	2.5	w
1 1 1	204.8	0.4	vst	1 1 3	1018.0	0.6	st
2 0 0	224.9	1.2	m+	3 3 1	1028.2	1.3	w
2 1 0	271.9	1.3	m	2 4 1	1083.4	8.0	vvw
2 2 0	410.8	-0.4	w	3 2 2	1099.0	1.6	vvw
1 1 2	509.6	0.3	vvw	4 3 0	1317.9	1.1	m
0 3 1	521.5	-2.0	m	2 2 3	1325.9	0.1	m
0 2 2	592.5	-1.5	st	2 4 2	1379.5	-0.8	m+
3 0 1	605.3	0.3	m+	1 3 3	1392.5	0.0	st
2 0 2	630.0	-0.2	m+	3 1 3	1465.5	0.7	m+
3 1 1	651.5	-0.3	m-	3 2 3	1606.5	1.0	m-
2 1 2	676.5	-0.6	m+	0 0 4	1624.9	-1.1	w
2 3 1	747.3	0.0	m+	2 2 4	2034.1	-3.1	m+
3 2 1	792.7	0.2	m-	4 5 0	2062.9	-3.9	m+
2 2 2	817.6	-0.1	st	5 4 1	2245.8	-4.1	w

#### UNIT CELL AND SPACE GROUP

The crystals investigated are orthorhombic and approximate values of the lattice parameters were obtained from oscillation and Weissenberg photographs. They were refined from powder data as described previously.<sup>1</sup> The final refinement was based on the 32 reflexions given in Table 1 and by using these the following crystal data were obtained

$$\begin{array}{ll}
 a = 10.300(6) \text{ \AA} & Z = 4 \\
 b = 11.250(4) \text{ \AA} & D_{\text{m}} = 3.04 \text{ g}\cdot\text{cm}^{-3} \\
 c = 7.641(1) \text{ \AA} & D_{\text{x}} = 2.87 \text{ g}\cdot\text{cm}^{-3} \\
 V = 885.3(7) \text{ \AA}^3 & \mu = 79 \text{ cm}^{-1}(\text{MoK}\alpha)
 \end{array}$$

The density of the crystals,  $D_m$ , was determined by the displacement method.

The following conditions limit the possible reflexions:  $0kl$  present for  $k+l=2n$  and  $hk0$  present for  $h=2n$  and the space group is thus either  $Pnma$  or  $Pn2_1a$ .

The unit cell contains four formula units and the reflexions with  $h+l=2n$  and  $k=2n$  are strong and if  $Pnma$  is the correct space group then: a) The gadolinium atom must occupy the positions  $4a$  as the reflexions with  $h+l=2n$  and  $k=2n$  are strong, b) All carbon and oxygen atoms in at least one of the ligands must occupy the four-fold positions  $4c$  (on the mirror planes) because the unit-cell contains only four formula units and the ligand is known to be approximately planar.<sup>1</sup>

The shortest possible metal-oxygen distance is then equal to  $b/4$  i.e. 2.81 Å and most of the gadolinium-coordinated oxygen distances must be larger than this figure. Such large bond distances are unlikely in compounds of this type, cf. rare earth-oxygen bond distances in known structures.<sup>1,5,6</sup> The space group  $Pnma$  can thus be rejected and  $Pn2_1a$  or  $C_{2v}$ <sup>9</sup> is the most probable space group; it is called  $Pna2_1$  (No. 33) in the standard setting and the matrix of the transformation to this setting is 100/00-1/010. The coordinates of the equivalent sites in  $Pn2_1a$  are  $x, y, z; \bar{x}, \frac{1}{2}+y, \bar{z}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z; \frac{1}{2}+x, y, \frac{1}{2}-z$ .

This choice of space group was confirmed by the distribution of vectors<sup>7</sup> in a set of three-dimensional Patterson maps calculated in order to determine the location of the gadolinium atoms.

#### DETERMINATION AND REFINEMENT OF THE STRUCTURE

The  $x$  and  $z$  coordinates of the gadolinium atom were determined from Patterson maps calculated by using the programme DRF.<sup>4</sup> A zero value was assigned to the  $y$ -coordinate as there are no symmetry conditions limiting the choice of origin along this axis. 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.<sup>4</sup> A three-dimensional difference synthesis based on the gadolinium position was then calculated; in this way a spurious mirror plane running perpendicular to  $[001]$  and passing through the gadolinium position is introduced because the  $z$ -coordinate of Gd is very close to  $\frac{1}{2}$ . The positions of the nine oxygen atoms belonging to one enantiomorphous set were determined from these electron density maps, peak heights, and geometrical considerations (gadolinium-oxygen, and oxygen-oxygen distances) being used in the identification of the atoms. The carbon atoms were located in a new set of electron density maps obtained from a new difference synthesis by using the identified part of the structure.

The atomic scattering factors used in the Fourier calculations were those given for neutral carbon and oxygen in *International Tables*<sup>8</sup> and those for neutral gadolinium given by Cromer *et al.*<sup>9</sup>

The interlayer scale factors, the preliminary atomic coordinates, and the estimated temperature factors for all atoms were then improved by ten cycles of full-matrix least-squares refinement. All thermal parameters

except those for gadolinium were isotropic. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$  with weighting according to Cruickshank,<sup>10</sup> the average values of  $w(|F_o| - |F_c|)^2$  in different  $|F_o|$  and  $\sin \theta$  intervals were approximately constant (*cf.* Table 3) indicating that the weighting scheme used is satisfactory. The discrepancy index  $R$  was equal to 0.080 after the tenth cycle and the shifts in the parameters were then less than 1 % of their estimated standard deviations. The  $R$ -value has been computed by using the observed reflexions only.

A final difference synthesis calculated by using all refined parameters showed the presence of a large peak, approximately  $8 \text{ e}/\text{\AA}^3$ , at the position of the gadolinium atom. This peak was surrounded by a negative region with its minimum approximately  $-3 \text{ e}/\text{\AA}^3$ , situated at a radial distance of  $1.0\text{--}1.2 \text{ \AA}$  from the gadolinium atom. The other parts of the electron density maps consisted of small peaks,  $1\text{--}2 \text{ e}/\text{\AA}^3$  above a slowly varying background and none of these peaks were assignable to an oxygen of a possible water. If water is present (0.5 water per formula unit) it must be randomly distributed because the unit cell contains four formula units and the space group chosen has only four-fold positions.

The presence of the large peak at the gadolinium position indicates that the thermal parameters for this atom have been given too large values in the least-squares refinement. The peak has the same magnitude in the final dif-

Table 2. Coordinates and thermal parameters for the various atoms in  $\text{Gd}(\text{HOCH}_2\text{COO})_3$ . The space group is No 33  $Pna2_1$ . The anisotropic thermal parameters for gadolinium have been calculated from the expression:  $\exp[-(h^2\beta_{11} + hk\beta_{12} + \dots)]$ .

Atom	Group	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/\text{\AA}^2$
O(1)	COO(1) <sup>-</sup>	2039 (23)	3060 (21)	1326 (31)	1.71 (0.31)
O(2)	CO(2)O <sup>-</sup>	2022 (22)	1206 (21)	2561 (29)	1.42 (0.34)
O(3)	O(3)H	4450 (15)	1260 (13)	3436 (19)	0.55 (0.18)
C(1)	OC(1)O <sup>-</sup>	2610 (19)	2193 (16)	2135 (26)	0.39 (0.19)
C(2)	HOC(2)C	4030 (21)	2301 (19)	2663 (27)	0.86 (0.27)
O(4)	COO(4) <sup>-</sup>	4811 (10)	108 (16)	6875 (14)	0.76 (0.18)
O(5)	CO(5)O <sup>-</sup>	619 (16)	-10 (66)	5461 (23)	2.12 (0.23)
O(6)	O(6)H	2467 (12)	151 (13)	8203 (15)	0.79 (0.19)
C(3)	OC(3)O <sup>-</sup>	4723 (15)	13 (59)	8463 (19)	1.16 (0.19)
C(4)	HOC(4)C	3398 (19)	-236 (16)	9359 (26)	1.12 (0.27)
O(7)	COO(7) <sup>-</sup>	2993 (21)	3678 (19)	7801 (28)	1.17 (0.27)
O(8)	CO(8)O <sup>-</sup>	2856 (22)	2088 (20)	6037 (29)	1.56 (0.31)
O(9)	O(9)H	387 (23)	3810 (23)	8122 (34)	2.38 (0.44)
C(5)	OC(5)O	2376 (53)	3001 (44)	7059 (70)	3.58 (0.87)
C(6)	HOC(6)C	933 (27)	2811 (24)	7307 (35)	1.49 (0.39)
Gd		2921 (0.6)	0 (0)	4974 (1.2)	—
$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
18.5 (0.9)	16.8 (0.3)	28.3 (0.7)	-6.8 (3.3)	-4.5 (1.9)	-7.0 (5.7)

ference synthesis obtained by using the data for each setting separately and it does not seem possible that it is connected with an error in the recording procedure.

The final atomic parameters obtained by using the data from the two settings are given in Table 2 and the experimental and calculated structure factors are compared in Table 4.

The standard deviations of the atomic parameters are of the same magnitude as those found in a previous structure investigation<sup>1</sup> except for  $x, y, z$  coordinates of C(5) and the  $y$ -coordinate of O(5). Inspection of the correlation matrix showed that the  $x$ - and  $y$ -coordinates of C(5) had fairly large correlation coefficients (approximately 0.4) to some of the scale factors, while the  $z$ -coordinate had a large correlation,  $-0.32$ , to the  $y$ -coordinate of O(5).

Table 3. 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  $w = 1/(24.0 + |F_o| + 0.01 |F_o|^2 + 0.005 |F_o|^3)$ .

$ F_o $ interval	Number of reflexions	$w \cdot \Delta^2$	$\sin \theta$ interval	Number of reflexions	$w \cdot \Delta^2$
0—31	99	0.84	0.00—0.30	189	1.10
31—39	114	1.08	0.30—0.38	180	0.89
39—45	118	1.13	0.38—0.44	145	1.18
45—51	118	1.02	0.44—0.48	125	1.03
51—57	121	0.84	0.48—0.52	105	0.87
57—68	119	0.78	0.52—0.55	100	0.96
68—78	119	1.19	0.55—0.58	94	1.17
78—88	122	1.16	0.58—0.60	59	1.06
88—112	120	1.01	0.60—0.63	57	0.94
112—260	116	0.94	0.63—0.65	44	0.81

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Interatomic distances and angles were computed from the refined unit-cell dimensions and the final atomic parameters of Table 2 by using the programme DISTAN.<sup>4</sup> Distances and angles of interest in the following discussion are given in Table 5 together with their estimated standard deviations. In order to facilitate the description of the structure the symmetry related atoms have been given super-scripts with the following significance

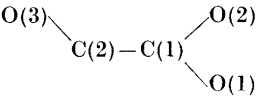
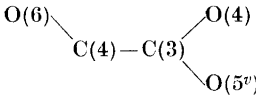
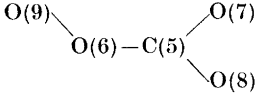
$$\begin{array}{ll}
 i & \frac{1}{2} + x, y, \frac{1}{2} - z \\
 ii & 1 - x, \frac{1}{2} + y, 1 - z \\
 iii & \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z \\
 iv & \frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z \\
 v & \frac{1}{2} + x, y, \frac{3}{2} - z \\
 vi & \frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z \\
 vii & \frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z \\
 viii & \frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z
 \end{array}$$

The structure is a three-dimensional network formed by cross-linked metal-ligand chains and these features are illustrated in the two projections of the structure along  $c$  and  $b$ , respectively, shown in Figs. 1 and 2. The approximately planar chains are formed in the following way





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

Within the coordination polyhedron			
Gd—O(1 <sup>vi</sup> )	2.42(2)	O(2) —O(8)	2.96(3)
Gd—O(2)	2.47(2)	O(1 <sup>vi</sup> ) —O(5)	3.31(6)
Gd—O(3)	2.42(2)	O(4) —O(8)	3.07(3)
Gd—O(4)	2.43(1)	O(2) —O(9 <sup>vii</sup> )	3.70(3)
Gd—O(5)	2.40(2)	O(3) —O(9 <sup>vii</sup> )	2.77(3)
Gd—O(6)	2.52(1)	O(3) —O(8)	2.74(3)
Gd—O(7 <sup>vii</sup> )	2.42(2)	O(3) —O(4)	2.95(3)
Gd—O(8)	2.49(2)	O(6) —O(1 <sup>vi</sup> )	2.80(3)
Gd—O(9 <sup>vii</sup> )	2.61(2)	O(6) —O(8)	2.77(3)
O(1 <sup>vi</sup> ) —O(9 <sup>vii</sup> )	3.10(4)	O(6) —O(5)	2.84(2)
O(1 <sup>vi</sup> ) —O(4)	3.02(3)	O(7) —O(1 <sup>vi</sup> )	2.95(3)
O(4) —O(9 <sup>vii</sup> )	3.22(3)	O(7) —O(2)	2.85(3)
O(5) —O(2)	2.98(4)	O(7) —O(5)	2.89(5)
O(5) —O(8)	3.33(6)		
			
Within the first ligand			
C(1)—O(1)	1.30(3)	∠O(1)—C(1)—O(2)	123(2)
C(1)—O(2)	1.30(3)	∠O(1)—C(1)—C(2)	120(2)
C(1)—C(2)	1.52(3)	∠O(2)—C(1)—C(2)	117(2)
C(2)—O(3)	1.38(3)	∠O(3)—C(2)—C(1)	110(2)
			
Within the second ligand			
C(3)—O(4)	1.22(2)	∠O(4) —C(3)—O(5 <sup>v</sup> )	127(2)
C(3)—O(5)	1.24(2)	∠O(5 <sup>v</sup> ) —C(3)—C(4)	111(2)
C(3)—C(4)	1.55(3)	∠O(4) —C(3)—C(4)	121(2)
C(4)—O(6)	1.37(2)	∠O(6) —C(4)—C(3)	106(2)
			
Within the third ligand			
C(5)—O(7)	1.14(6)	∠O(7) —C(5)—O(8)	125(5)
C(5)—O(8)	1.38(6)	∠O(8) —C(5)—C(6)	109(4)
C(5)—C(6)	1.51(6)	∠O(7) —C(5)—C(6)	125(4)
C(6)—O(9)	1.40(4)	∠O(9) —C(6)—C(5)	110(3)
Possible hydrogen bonds			
O(2 <sup>i</sup> ) —O(3)	2.76(3)	∠O(2 <sup>i</sup> ) —O(3) —C(2)	102(1)
O(4) —O(6 <sup>v</sup> )	2.74(3)	∠O(4) —O(6 <sup>v</sup> ) —C(4 <sup>v</sup> )	135(1)
O(8) —O(6)	2.77(3)	∠O(8) —O(6) —C(4)	122(1)
O(1 <sup>vi</sup> ) —O(6)	2.80(3)	∠O(1 <sup>vi</sup> ) —O(6) —C(4)	86(1)
O(7) —O(9 <sup>v</sup> )	2.57(3)	∠O(7) —O(9 <sup>v</sup> ) —C(6 <sup>v</sup> )	103(2)



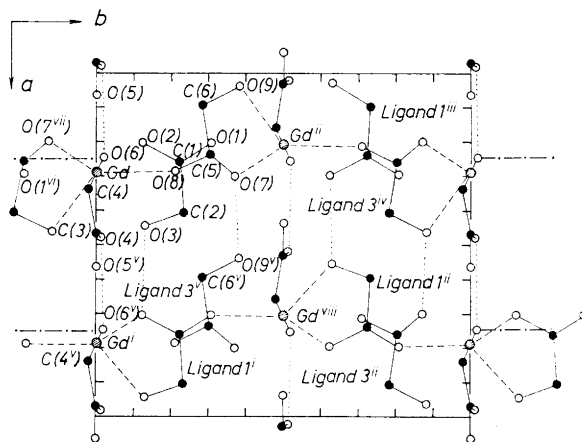


Fig. 1. Projection of the structure along  $c$ . The gadolinium, carbon, and oxygen atoms are denoted by striped, black, and white circles, respectively. The symbols used for symmetry related atoms are explained on p. 1756. Bonds within the ligands are full-drawn, metal-oxygen bonds are dashed, and hydrogen bonds are dotted.

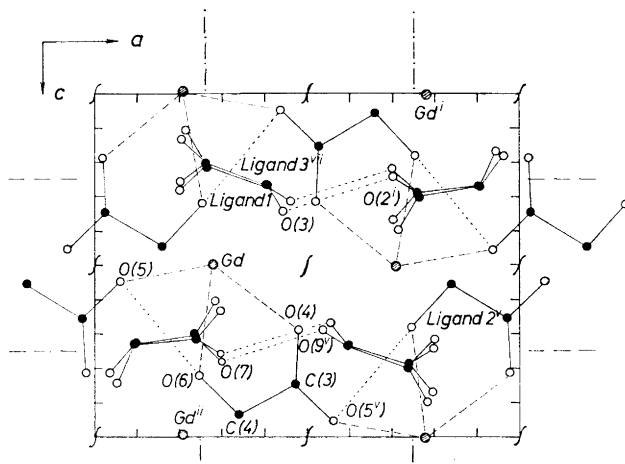


Fig. 2. Projection of the structure along  $b$ . The symbols used are the same as in the previous figure.

$a$ . Ligand  $1^i$ , formed by  $O(1^i)$ ,  $O(2^i)$ ,  $O(3^i)$ ,  $C(1^i)$  and  $C(2^i)$  (cf. Fig. 1), forms a chelate by coordination of  $O(2^i)$  and  $O(3^i)$  to  $Gd^i$ , while the remaining carboxylate oxygen  $O(1^i)$  is bonded to  $Gd^{viii}$ . The  $n$ -glide plane transforms Ligand  $1^i$  to Ligand  $1^{ii}$ , where  $O(2^{ii})$  and  $O(3^{ii})$  are coordinated to  $Gd^{viii}$ . By repetition of this symmetry operation a chain running parallel with  $[0\bar{1}1]$  is formed. The symmetry related Ligand 1, Ligand  $1^{iii}$  etc. form in the same way a chain parallel with  $[011]$ .

b. Ligand 3, formed by O(7), O(8), O(9), C(5), and C(6), also gives rise to two sets of metal-ligand chains (*vide* Fig. 1). The chains are formed by application of  $n$  to the symmetry related Ligand 3 and Ligand 3<sup>*n*</sup> and the chains are running parallel with [0 $\bar{1}$ 1] and [011], respectively.

c. The bonding of the remaining ligand, Ligand 2, is best illustrated in Fig. 2: a chelate is formed by coordination of O(4) and O(6) to Gd. Two sets of approximately planar metal-ligand chains, running parallel with [100] are obtained by applying the symmetry operations  $2_1$  and  $a$  to Ligand 2.

The chains formed by the three ligands intersect at the metal sites and the gadolinium atom is thus coordinated by nine oxygen atoms. The chains are also cross-linked by hydrogen bonds and these features will be discussed later.

*The coordination polyhedron.* A parallel projection of the coordination polyhedron drawn by using the programme ORTEP,<sup>4</sup> is given in Fig. 3. The nine oxygen atoms which surround each gadolinium atom form a polyhedron based on a distorted trigonal prism similar to the type previously described.<sup>5</sup> The ligands are bonded as chelates along the diagonals of the rectangular faces of the prism; the points of attachment are at the corners of the prism and outside the midpoints of the rectangular faces, O(3), O(6), and O(7<sup>*iii*</sup>) in Fig. 3. The chelates use six of the coordination sites, while the

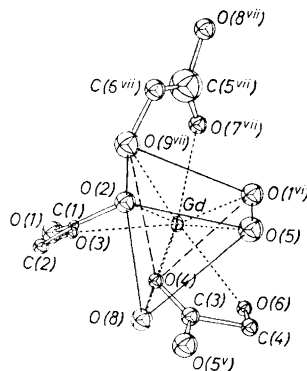


Fig. 3. A parallel projection of the structure drawn by using the programme ORTEP.<sup>4</sup> The distorted trigonal prism is outlined and the various metal-oxygen bonds are dotted.

remaining three are occupied by three carboxylate oxygens from adjoining ligands. The various metal-oxygen bond distances are given in Table 5 and the values agree with those found by Albertsson<sup>5</sup> in a tris-oxidiacetato-gadolinium complex. The distances from carboxylate and ether oxygens to gadolinium are  $2.41 \pm 0.01$  Å and  $2.49 \pm 0.03$  Å, respectively, in this complex.

The trigonal prism is distorted and the distortion is mainly caused by the fact that the two triangular faces are not parallel; the distances between the corresponding corners of opposite triangles are 3.07 Å, 3.31 Å and 3.70 Å, respectively (*cf.* Table 5).

Some of the distances between neighbouring oxygen atoms in the coordination polyhedron are so small that it is reasonable to assume that they are in van der Waals contact, *e.g.* the distances O(3)—O(9<sup>*iii*</sup>), O(3)—O(8), O(6)—O(8),

O(6)—O(1<sup>vi</sup>), O(6)—O(5), and O(7<sup>vii</sup>)—O(2) are 2.77 Å, 2.74 Å, 2.77 Å, 2.80 Å, 2.84 Å, and 2.85 Å, respectively. These figures are approximately twice the estimated value of the van der Waals radius of oxygen, (1.40±0.05) Å.<sup>11</sup>

The dimensions of the coordination polyhedron are decreasing with decreasing ionic radius of the central atom and this decrease will force the oxygen atoms in contact even closer together. The net result is a decrease in stability of the structure.

The tris-hydroxyacetates have, as seen above, many oxygen-oxygen contacts. This is not the case in the rare earth trisglycolato dihydrates<sup>16</sup> or in the hydroxyacetato-oxyacetato compounds where, in the erbium compound for instance, only the distances O(2<sup>iii</sup>)—O(1) and O(2<sup>iii</sup>)—O(5<sup>ii</sup>) are close enough (2.72 Å and 2.85 Å, respectively) for such a contact. The short O(3<sup>iii</sup>)—O(3<sup>vi</sup>) distance, 2.53 Å, in compounds of this type is connected with the special type of bonding for O(3).<sup>1</sup> A transition from tris-hydroxyacetate to tris-hydroxyacetato dihydrate or hydroxyacetate-oxyacetate must now be followed by a decrease in van der Waals repulsion and this decrease must be largest for the elements with the smallest ionic radius. The experimental finding<sup>1</sup> that it is only rare earths with the smallest ionic radii which form tris-glycolato dihydrates and hydroxyacetato-oxyacetato complexes can thus be explained.

A decrease in stability caused by oxygen-oxygen van der Waals contacts is not unique for the tris-hydroxyacetato compounds, but is probably of importance in a number of rare earth complexes. Steric effects observable in the formation of tris-oxydiacetato and tris-2,6-pyridinodicarboxylato complexes will be discussed along these lines in forthcoming publications.<sup>12</sup>

Table 6. The deviation in Å of the gadolinium and ligand atoms from the least-squares plane formed by the C—COO group in each ligand.

Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
Gd	-0.819	Gd	0.098	Gd <sup>ii</sup>	-0.326
O(1)	-0.003	O(4)	0.008	O(7)	-0.021
O(2)	-0.003	O(5 <sup>v</sup> )	0.007	O(8)	-0.015
O(3)	0.062	O(6)	-0.425	O(9)	0.248
C(1)	0.009	C(3)	-0.021	C(5)	0.049
C(2)	-0.002	C(4)	0.005	C(6)	-0.013

*The ligands.* The three organic ligands are approximately planar (*cf.* Table 6) and some intermolecular distances and angles are given in Table 5. Corresponding distances and angles within the three ligands are not significantly different from one another (as judged by the *t*-test<sup>10</sup>), or from the values found in other glycolato complexes.<sup>1,13</sup> The uncertainty in the C(5) position is fairly large which results in large standard deviations for some of the interatomic distances within Ligand 3. The difference in distance between

C(5)—O(7) and C(5)—O(8),  $1.14 \pm 0.06$  Å and  $1.38 \pm 0.06$  Å, respectively, may because of this not be significant ( $t=2.5$ ).

*Possible hydrogen bonds.* The hydrogen atoms in the three hydroxy groups are all hydrogen bonded. The angle H—O—C is approximately  $109^\circ$ <sup>14,15</sup> and if a linear hydrogen bond is formed the angle O—O—C must be close to this figure. Hydrogen bonded oxygen—oxygen distances are expected to fall in the range 2.5—3.0 Å. From these criteria it is obvious that only one possible hydrogen bond can be formed by each of Ligand 1 and Ligand 3. These bonds are formed between O(3)—O(2<sup>i</sup>) and between O(7)—O(9<sup>v</sup>) and have bond distances  $2.76 \pm 0.03$  Å and  $2.56 \pm 0.03$  Å, respectively. The angles O(2<sup>i</sup>)—O(3)—C(2) and O(7)—O(9<sup>v</sup>)—C(6<sup>v</sup>) are  $101 \pm 1^\circ$  and  $103 \pm 2^\circ$ , respectively, and thus the hydrogen bonds formed must be approximately linear.

Hydrogen bonds might be formed by Ligand 2, between either O(6̄)—O(8), O(6)—O(1<sup>vi</sup>) or O(4)—O(6<sup>v</sup>). The corresponding bond distances are  $2.77 \pm 0.03$  Å,  $2.80 \pm 0.03$  Å, and  $2.74 \pm 0.03$  Å, respectively, while the angles O(8)—O(6)—C(4), O(1<sup>vi</sup>)—O(6)—C(4) and O(4)—O(6<sup>v</sup>)—C(4<sup>v</sup>) are  $122 \pm 1^\circ$ ,  $86 \pm 1^\circ$ , and  $135 \pm 1^\circ$ , respectively. The hydrogen bond is probably formed between O(4) and O(6<sup>v</sup>) because the hydroxy hydrogen will then lie approximately at a position expected in a glycolate molecule; the large angle indicates that a bent hydrogen bond is formed.

This series of crystal structure determinations has been started with two aims; one is to obtain information on the bonding (coordination geometries, coordination numbers, and bond distances) of complexes in the solid state, the other is to obtain correlations between properties of complexes in the solid state and in solution. In a following communication the nature of the rare earth—glycolate bonds in solution will be discussed by using infrared data obtained from rare earth glycolate solutions and from solid complexes of known structure.

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