Strzyżewska & Tosik, 1983), the distance corresponding to N(1)—C(8) is 1·31 (1) Å [1·323 (2) Å in the title compound]; however, the distance corresponding to N(1)—C(2) is somewhat longer [1·543 (9) Å compared to 1·397 (2) Å].

The authors are indebted to Mr S. Gorter for performing the X-ray data collection and to Mr A. J. Kinneging for helpful discussions.

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Structure of Diaquatriglutaratodineodymium(III) Dihydrate

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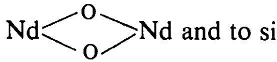
(*Received* 31 *January* 1986; *accepted* 9 *May* 1986)

Abstract. $[Nd_2(C_5H_6O_4)_3(H_2O)_2].2H_2O$, $M_r = 750{\cdot}84$, monoclinic, $C2/c$, $a = 8{\cdot}061\ (2)$, $b = 15{\cdot}080\ (3)$, $c = 19{\cdot}740\ (3)$ Å, $\beta = 93{\cdot}70\ (4)°$, $V = 2394{\cdot}6\ (7)$ Å^3, $Z = 4$, $D_m = 2{\cdot}10\ (1)$, $D_x = 2{\cdot}082\ (1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 4{\cdot}38$ mm^{-1}, $F(000) = 1456$, $T = 297$ K, $R = 0{\cdot}033$ for 2525 reflections. Complex possesses twofold (C_2) symmetry. The coordination polyhedron of the Nd ions comprises eight O atoms from glutarate ions and one from a water molecule. Each Nd ion is linked to two Nd ions by oxygen bridges of type  and to six other ones by glutarate ions $[NdOOC(CH_2)_3COONd]$, forming a three-dimensional polymeric structure. Nd—O distances are 2·425 (6)–2·665 (6) Å.

Introduction. Recently we have published spectroscopic and crystal structure data for lanthanide complexes with amino acids (Legendziewicz, Huskowska, Strek & Jeżowska-Trzebiatowska, 1981; Legendziewicz, Huskowska, Waskowska & Argay, 1984; Legendziewicz, Huskowska, Argay & Waskowska, 1984; Legendziewicz, Głowiak, Huskowska & Dao-Cong-Ngoan, 1985). From our spectroscopic studies it follows that in the case of dicarboxylic amino acids the mode of bonding with Ln^{III} ions depends upon the chain length of the amino acid molecules. We have now begun a study of the crystal structures of lanthanide compounds with dicarboxylic amino acids (Głowiak, Legendziewicz, Dao-Cong-Ngoan & Huskowska, 1986) and dicarboxylic acid analogues of the respective amino acids. Our goal in the present work was the determination of the coordination mode of the glutaric acid molecule (analogue of glutamic acid) with Nd^{III} and the dependence of the bonding upon the chain length of the carboxylic acid molecule.

The above problems are important since lanthanide ions are widely applied as metal probes in studies of the calcium bonding of proteins and of other biological systems.

Experimental. Rose-coloured crystals obtained from aqueous solution, dimensions 0·25 × 0·3 × 0·4 mm; D_m by flotation in chloroform/ethylene bromide. Space group determination based on Weissenberg photographs; cell parameters by least-squares orientation matrix program using 15 reflections in the range $23 < 2\theta < 30°$. Syntex $P2_1$ diffractometer, graphite monochromator; 2749 unique reflections measured; $2\theta_{\max} = 55{\cdot}0°$; variable θ–2θ scan, scan rate 2·0–

0108-2701/86/111494-03$01.50

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2) *for the non-*H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	B_{eq}
Nd	0·25443 (5)	0·03773 (3)	0·01188 (2)	1·10 (3)
O(1)	−0·0133 (7)	0·0449 (4)	0·0621 (3)	1·7 (4)
O(2)	−0·2683 (7)	0·0492 (4)	0·0942 (3)	2·3 (5)
O(3)	−0·0148 (6)	0·4198 (4)	0·0340 (3)	1·7 (4)
O(4)	−0·2664 (6)	0·3836 (4)	0·0607 (3)	2·0 (4)
O(5)	0·3457 (8)	0·0552 (4)	0·1328 (3)	2·1 (5)
O(6)	0·3323 (7)	0·1774 (4)	0·0740 (3)	1·9 (4)
O*W*(1)	0·1133 (8)	0·1485 (4)	0·0616 (4)	2·3 (5)
O*W*(2)	0·1085 (26)	0·4056 (8)	0·2001 (7)	11·9 (21)
C(1)	−0·1212 (9)	0·0743 (5)	0·1019 (4)	1·3 (5)
C(2)	−0·0720 (10)	0·1407 (5)	0·1553 (5)	1·7 (6)
C(3)	−0·1405 (11)	0·2341 (6)	0·1354 (5)	2·2 (7)
C(4)	−0·0516 (11)	0·2743 (5)	0·0779 (5)	2·4 (7)
C(5)	−0·1159 (9)	0·3637 (5)	0·0573 (5)	1·5 (5)
C(6)	0·3663 (9)	0·1372 (6)	0·1298 (5)	1·5 (6)
C(7)	0·4261 (11)	0·1905 (6)	0·1921 (5)	1·9 (6)
C(8)	0·5	0·1331 (8)	0·25	2·0 (9)

29·3° min^{-1}, depending on intensity; two standards (136, 26$\bar{3}$) with intensity variations ±3% measured every 50 reflections; 2525 reflections with $I > 1{\cdot}96\sigma(I)$ used for structure determination; index range h 0 to 10, k 0 to 19, l −25 to 25. Absorption correction not applied; Nd positions derived from three-dimensional Patterson map; remaining non-hydrogen atoms from difference syntheses; H atoms (excluding those bonded to water O) generated from assumed geometries (C—H 1·0 Å); full-matrix least-squares refinement, minimizing $\sum w(|F_o|-|F_c|)^2$, $w = 1/\sigma^2(F)$; anisotropic thermal factors for non-H atoms; $R = 0{\cdot}033$, $wR = 0{\cdot}041$, $S = 4{\cdot}452$; max. $\Delta/\sigma = 0{\cdot}056$; max. and min. heights in final difference Fourier map 0·45 and −0·25 e Å^{-3}. Final atomic parameters are given in Table 1.* Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Crystallographic calculations performed on a NOVA 1200 computer using the *XTL/XTLE* programs (Syntex, 1976).

Discussion. The bond distances and angles with their e.s.d.'s are shown in Table 2. The Nd ions are nine-coordinated. Each Nd ion is coordinated by eight carboxylate O atoms derived from five deprotonated glutaric acid molecules and by one water O (see Figs. 1 and 2).

There are two crystallographically independent glutarate ligands in the structure. Ligand 1 lies in general positions, while ligand 2 possesses crystallographic twofold symmetry.

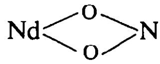
Table 2. *Selected interatomic distances* (Å), *angles* (°) *and torsion angles* (°) *with estimated standard deviations*

Nd—Nd$^{\mathrm{i}}$	4·254 (1)	Nd—O(3$^{\mathrm{iv}}$)	2·590 (5)
Nd—Nd$^{\mathrm{ii}}$	4·175 (1)	Nd—O(4$^{\mathrm{iv}}$)	2·526 (6)
Nd—O(1)	2·435 (6)	Nd—O(5)	2·467 (7)
Nd—O(1$^{\mathrm{i}}$)	2·665 (6)	Nd—O(6)	2·497 (6)
Nd—O(2$^{\mathrm{i}}$)	2·479 (7)	Nd—O*W*(1)	2·444 (7)
Nd—O(3$^{\mathrm{iii}}$)	2·425 (6)		
C(1)—O(1)	1·288 (10)	C(1)—O(2)	1·246 (10)
C(1)—C(2)	1·488 (12)	C(2)—C(3)	1·554 (12)
C(3)—C(4)	1·508 (14)	C(4)—C(5)	1·492 (12)
C(5)—O(3)	1·281 (10)	C(5)—O(4)	1·255 (9)
C(6)—O(6)	1·272 (11)	C(6)—O(5)	1·250 (10)
C(6)—C(7)	1·521 (13)	C(7)—C(8)	1·524 (11)
O(6)—Nd—O(5)	52·1 (2)	O(6)—Nd—O*W*(1)	78·9 (2)
O(5)—Nd—O(3$^{\mathrm{iv}}$)	75·2 (2)	O(1$^{\mathrm{i}}$)—Nd—O*W*(1)	72·5 (2)
O(3$^{\mathrm{iv}}$)—Nd—O(1$^{\mathrm{i}}$)	105·2 (2)	O(5)—Nd—O*W*(1)	126·9 (2)
O(3$^{\mathrm{iii}}$)—Nd—O(4$^{\mathrm{iv}}$)	117·8 (2)	O(4$^{\mathrm{iv}}$)—Nd—O*W*(1)	144·6 (2)
O(1)—C(1)—O(2)	119·7 (7)	O(5)—C(6)—O(6)	119·4 (8)
C(2)—C(1)—O(1)	120·3 (7)	C(7)—C(6)—O(5)	121·4 (8)
C(2)—C(1)—O(2)	120·0 (7)	C(7)—C(6)—O(6)	119·1 (7)
C(1)—C(2)—C(3)	110·9 (7)	C(6)—C(7)—C(8)	113·2 (7)
C(2)—C(3)—C(4)	112·1 (8)	O(3)—C(5)—O(4)	120·1 (7)
C(4)—C(5)—O(3)	118·5 (7)	C(4)—C(5)—O(4)	121·4 (8)
C(3)—C(4)—C(5)	113·3 (8)		
O(1)—C(1)—C(2)—C(3)	105·9 (9)	O(5)—C(6)—C(7)—C(8)	15·4 (8)
O(2)—C(1)—C(2)—C(3)	−71·8 (8)	O(6)—C(6)—C(7)—C(8)	−166·5 (7)
O(3)—C(5)—C(4)—C(3)	149·0 (9)	C(6)—C(7)—C(8)—C(7$^{\mathrm{xi}}$)	174·1 (7)
O(4)—C(5)—C(4)—C(3)	−33·0 (10)	C(2)—C(3)—C(4)—C(5)	179·5 (9)
C(1)—C(2)—C(3)—C(4)	−71·2 (10)		

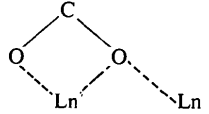
Superscripts i–xi are used to indicate the following equivalent sites in the structure: (i) $-x, -y, -z$; (ii) $1-x, -y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $\frac{1}{2}+x, -\frac{1}{2}+y, z$; (v) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vi) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$; (vii) $-\frac{1}{2}+x, \frac{1}{2}+y, z$; (viii) $\frac{1}{2}+x, -\frac{1}{2}+y, z$; (ix) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (x) $\frac{1}{2}-x, -\frac{1}{2}-y, -z$; (xi) $1-x, y, \frac{1}{2}-z$.

Both carboxylate groups of ligand 1 [atoms O(1)—C(1)—O(2) and O(3)—C(5)—O(4)] are coordinated to Nd ions as in mode [*A*]. As illustrated in Fig. 1, in the layer parallel to (001), each Nd ion is linked to six symmetry-related Nd ions along directions: [110] Nd$^{\mathrm{vi}}$—Nd—Nd$^{\mathrm{v}}$, [1$\bar{1}$0] Nd$^{\mathrm{viii}}$—Nd—Nd$^{\mathrm{vii}}$ and [010] Nd$^{\mathrm{x}}$—Nd—Nd$^{\mathrm{ix}}$ by ligand 1 (superscripts are defined in Table 2).

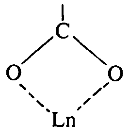
In addition each Nd is linked to two other Nd ions, Nd$^{\mathrm{i}}$—Nd—Nd$^{\mathrm{ii}}$ by symmetric oxygen bridges of the type



along the x axis. There are two different Nd···Nd distances in these oxygen bridges: 4·175 (1) and 4·254 (1) Å, caused by differences in the Nd—O bonding distances of the bridging oxygens, O(1) 2·435 (6) and 2·665 (6) Å and O(3) 2·425 (6) and 2·590 (5) Å.



[*A*]



[*B*]

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* Lists of structure amplitudes, anisotropic thermal parameters, calculated H-atom parameters and the results of least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43040 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The carboxylate groups of ligand 2 coordinate with Nd as in mode [*B*]. Each ligand of this type connects a pair of Nd ions along [101] [Nd—Nd^{xi}]. The Nd–glutarate bridges built in this way link adjacent (001) structural layers to form a three-dimensional polymeric structure. A stereoscopic view of the packing has been deposited.

The conformations of ligand 1 and ligand 2 are different. The carbon chain of ligand 2 has a *trans* conformation and is planar, with torsion angle C(6)—C(7)—C(8)—C(7^{xi}) 174·1 (7)°. The remaining torsion angles for both ligands are given in Table 2. However, the bond distances and valence angles in each ligand agree with those found in the free glutaric acid molecule (Morrison & Robertson, 1949). All the C—COO groups are planar within the limits of experimental error.

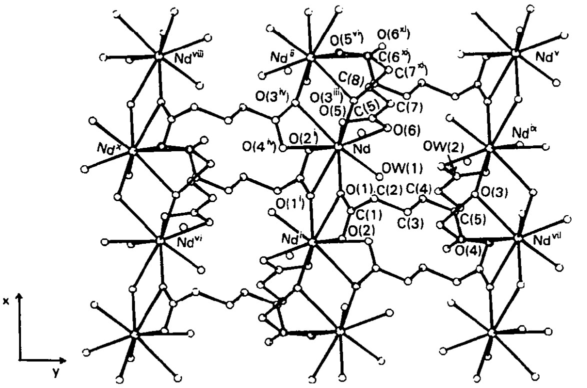

Fig. 1. The structural layer parallel to (001) showing the atom numbering.

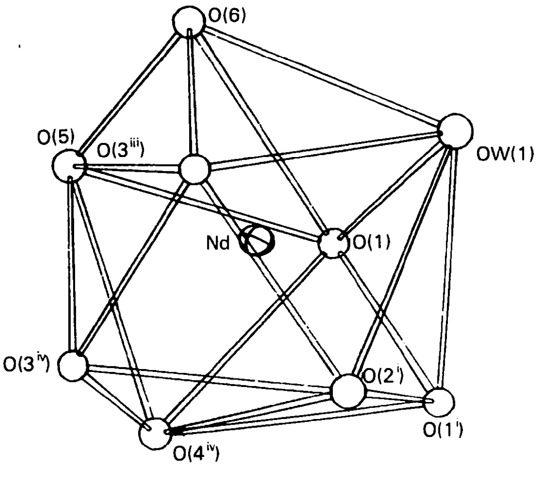

Fig. 2. The neodymium coordination polyhedron.

The structure of the title compound is similar to the polymeric structure of hexaaquafumaratodimaleatodineodymium hexahydrate (Hansson & Thornqwist, 1975), where each carboxylate group is bonded to different Nd ions. Our spectroscopic results (Legendziewicz *et al.,* 1981) indicated that glutamic acid is also bonded with lanthanide ions in a similar way. On the other hand aspartic acid is believed to coordinate by formation of a seven-membered ring with lanthanide ions (the two carboxylate groups of the acid bonded to one lanthanide ion). Thus the bonding mode of dicarboxylic acids is expected to depend on the carbon-chain length and on the nature of the bonding (presence or absence of double bonds) within the carbon chain.

The geometry of the coordination polyhedron is intermediate between a tri-capped trigonal prism and a mono-capped square antiprism (Fig. 2). The triangular faces of the prism are made up of atoms O(1), O(5), O(4^{iv}) and O*W*(1), O(3^{iii}), O(2^{i}). The angle between these faces is 9·3 (9)° and the perpendicular distances from O(1), O(5), O(4^{iv}) to this plane are −3·02 (1), −3·53 (1) and −3·25 (1) Å, respectively. The distances from the Nd ion to these faces are 1·700 (4) and −1·580 (4) Å. The 'square' faces of the antiprism are formed by O(1), O(5), O(3^{iii}), O*W*(1) and O(3^{iv}), O(2^{i}), O(1^{i}), O(4^{iv}). The angle between these 'square' faces is 4·9 (9)°. A list of deviations of atoms from the least-squares planes of the trigonal prism and the square antiprism has been deposited.

This work was supported by the Polish Academy of Sciences.

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