Structural Studies on the Rare Earth Carboxylates

14. A Structural Study of the Orthorhombic Trishydroxyacetates of Lanthanum(III) and Gadolinium(III)

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The structures of the orthorhombic tris-glycolates of lanthanum and gadolinium have been determined from three-dimensional X-ray intensity data, obtained by a linear single crystal diffractometer. The structures of both compounds have been described with a model using anisotropic thermal parameters on the heavy atom only. This model was refined to a final weighted R-value, equal to 0.043 and 0.035, in the lanthanum and gadolinium structures, respectively. A comparison of the corresponding interatomic bond distances indicates that the average metal − oxygen distances decrease approximately as the decrease in the ionic radius of the central ion. The change in size of the central ion also affects the oxygen − oxygen contact distances in the coordination polyhedron and the conformation of the ligands.

The metal-ligand bonds in lanthanoid(III) compounds involve little or no interaction between the metal $4f$ orbitals and the ligand orbitals.[1] There are, as a result of this, no pronounced directional bonds of the type found among the d-transition elements in rare earth complexes. Phenomenologically, one may often regard the structures of lanthanoid compounds as a result of the compromise between the achievement of spherical symmetry for the central ion and the minimization of ligand − ligand repulsions in the coordination sphere. For polydentate ligands one has also to take into account the geometrical constraints imposed by the geometry of the ligand and its possibility to form hydrogen or metal bonded networks.

The difference in energy between various coordination geometries in compounds of high coordination numbers is often quite small.[2] Hence, even small changes in any of the factors mentioned above are sufficient for the formation of a new phase. Examples of polymorphism are also frequent, *e.g.* the A, B, and C types of the rare earth sesquioxides, the orthorhombic [3] and monoclinic [4] rare earth tris-glycolates and the various rare earth dipicolinates,[5] described in previous parts of this series.

The present investigation has been made, mainly in order to investigate how a change in the size of the central ion within an isostructural series of compounds affects the coordination geometry and the conformation of the ligands. The main points of interest may be summarized as:

a. How are the packing of the oxygen donors in the coordination sphere and the oxygen − oxygen contact distances changed by a change of size of the central ion?

b. Are there any significant differences between the corresponding bond angles and distances within glycolate ligands in different crystallographic surroundings? How large is the variation in the conformation angle in the ligand? This angle is defined as the angle (the dihedral angle) between the projection of the C − O and the C − O(H) vectors viewed along the C − C vector. A discussion pertinent to these problems is found in part 8 of this series.[4]

c. Do possible conformation and packing changes among the ligands result in a change in the system of hydrogen bonds?

The compounds chosen for the study are the orthorhombic tris-glycolates of lanthanum and gadolinium, in the following abbreviated LAGLYC and GDGLYC, respectively. The crystal and molecular structure of the latter compound has been determined in part 3 of this series.[3]

The compounds studied contain approx. 41 % of a heavy atom, the ratios $Z^2_{heavy}/\sum Z^2_{light}$, being equal to 4 and 5, respectively. Hence, accurate determinations of the parameters for the light atoms are difficult. In order to obtain data of high accuracy, a single crystal diffractometer has been used in recording the various spectra for the X-ray structure determinations.

EXPERIMENTAL

Single crystal work. LAGLYC and GDGLYC were prepared as described before.[3,6] The habits and sizes of the crystals used are given in Table 1. Intensity data for the two compounds were collected at $25.0 \pm 0.2°C$ with an automatic linear single crystal diffractometer of type PAILRED. One LAGLYC crystal was used in recording a total of 1819 reflexions in the layers $0kl − 11kl$ and $h0l − h1l$. Two GDGLYC crystals were used in recording the layers $hk0 − hk7$ (1527 reflexions) and $h0l − h10l$ (1441 reflexions), respectively. In both structures the region sin $\theta \leq 0.80$ was investigated. Mo$K\alpha$ radiation was used. It was made monochromatic by reflexion in the (002) plane of a graphite crystal. The take-off angle was 6°. The pulse height discrimination levels were set for approximately a 95 % window, centered at the Mo$K\alpha$ peak. Coincidence losses were negligible, except for the four strongest reflexions in LAGLYC, where they amounted to at most 5 %. The electronic stability was checked by measuring the intensity of four standard reflexions for each layer. Only random variations, usually less than 3 %, were observed over a 24 h period. The counter aperture was 1.5° and the integrated intensities were determined by using the ω-scan technique. The scan speed was 1°/min and the scan ranges varied from 3° to 5°. The larger scan range was used in the vicinity of the ω-axis. Stationary background counts, B_1 and B_2, were measured for 10 sec in LAGLYC and 20 sec in GDGLYC, at both ends of each scan interval.

The corrected integrated peak counts, I, were calculated from the eqn.

$$I = C - t_c \frac{B_1 + B_2}{2\ t_B}$$

where C is the total integrated peak count obtained in a time t_c and t_B is the time for each of the background counts. The variances of the corrected intensities were estimated, using the expression

$$\sigma^2(I) = C + t_c^2(B_1 + B_2)/4t_B^2 + (0.025I)^2$$

Table 1. Unit cell parameters and volumes with their corresponding standard deviations for the various isostructural orthorhombic tris(hydroxyacetato) lanthanoid(III) compounds, $M(HOCH_2COO)_3$.

Central ion M	$a/Å$	$b/Å$	$c/Å$	$V/Å^3$
La	10.384(5)	11.564(4)	7.975(2)	957.5(4)
Ce	10.380(4)	11.541(3)	7.902(2)	946.7(4)
Pr	10.401(6)	11.527(4)	7.905(2)	947.7(4)
Nd	10.362(5)	11.411(3)	7.772(1)	918.9(3)
Sm	10.306(6)	11.335(4)	7.724(2)	902.4(4)
Eu	10.303(4)	11.306(5)	7.698(4)	896.7(5)
Gd	10.298(2)	11.275(2)	7.649(1)	888.1(5)
Tb	10.284(4)	11.247(4)	7.636(4)	883.2(5)

Table 2. Powder data for the orthorhombic rare earth tris-glycolates, $MC_6H_9O_9$. The observed values of $\sin^2\theta \times 10^4$ are denoted obs, while the corresponding quantities calculated from the least squares refined lattice parameters in Table 1 are denoted calc.

h k l	La obs	La calc	Ce obs	Ce calc	Pr obs	Pr calc	Nd obs	Nd calc	Sm obs	Sm calc	Eu obs	Eu calc	Gd obs	Gd calc	Intensity Gd	Tb obs	Tb calc
1 0 1	148.5	148.6	149.4	150.3	150.8	150.0	153.5	153.7	156.0	155.6	157.9	157.6	vw	157.6	158.1
0 2 0	176.9	177.8	178.2	178.5	180.3	178.9	180.3	182.6	185.6	185.0	187.4	187.0	m	187.7	187.9
1 1 1	195.7	193.0	194.7	194.9	196.7	194.8	200.5	199.4	203.1	201.8	204.8	204.4	vs	204.9	205.1
2 0 0	220.3	220.5	219.5	220.6	221.3	219.8	220.7	221.4	224.8	223.8	223.2	223.9	m+	223.7	224.7
2 1 0	264.6	264.9	263.7	265.3	265.3	264.5	268.6	267.0	270.2	270.1	269.1	270.4	m	271.8	271.7
2 2 0	398.5	398.2	399.8	399.1	401.6	398.7	405.3	404.0	409.5	408.8	409.5	409.9	w	413.1	412.7
2 2 1	498.3	491.7 / 493.4	499.6	494.3 / 496.7	490.9	493.8 / 497.7	498.1	502.3 / 509.2	505.5	508.4 / 515.9	509.6	510.2 / 518.7	vvw	515.4	514.6
0 3 1					–		512.1		513.5		521.8		m	528.1	524.8
1 3 1	550.6	548.5	552.4	551.9	559.0	552.6 / 559.3	565.8	564.5	–	571.9	–	574.7		–	578.4
0 2 2	554.1	551.6	558.6	559.1			–	576.1	586.3	583.4	588.6	587.1	s	596.6	595.6
3 0 1	590.9	589.5	591.9	591.6	595.7	589.5 / 600.1	600.0	596.5	602.6	603.1	606.3	604.2	m+	605.3	607.6
2 0 2	597.4	594.3	600.4	601.3			615.2	615.0	623.5	622.2	626.7	625.1	m+	630.0	632.4
1 2 2	608.5	606.7	613.8	614.3	607.5	614.2	631.7	631.5 / 632.2	640.2	639.4 / 640.1	643.1	643.1 / 642.4		–	649.3 / 651.8
2 3 0	–	620.4	621.3	622.2	621.9	622.3			649.3	649.4	650.7	650.7		653.9	647.6 / 654.6
3 1 1	634.5	634.0	634.3	636.2	628.3	634.2	643.9	642.2	670.4	668.5	672.4	671.6	m+	679.7	679.4
2 1 2	640.6	638.7	645.6	645.9	639.8	644.9	659.3	660.6							
0 4 0	711.0	711.1 / 713.9	714.7	713.8 / 717.3	–	715.7	728.3	730.3 / 730.6	759.6	740.1 / 739.7	743.3	743.9 / 742.6	m+	749.0	748.0 / 749.5
2 5 1					724.3	717.4									
2 2 2	776.4	772.0	778.6	779.8	775.2	779.0	796.8	797.5	806.1	807.2	812.8	811.1	s	822.8	820.3
4 0 0	882.6	881.9 / 885.5	881.4	882.6	888.5	879.0	890.3	886.6	891.2	895.2	894.6	895.8	m+	899.3	899.0
0 1 3			902.8	901.1	–	900.6			938.3	942.7 / 942.1	953.4	949.1	vvw	–	964.3
4 1 0	925.9	926.4	928.3	927.2	–	923.7	935.9	931.1 / 931.3	941.3	941.4	941.3	942.3	w	943.3	946.0
2 4 0	932.4	931.5	935.5	934.5	932.3	935.4	951.5	951.7	962.8	963.9	966.2	967.8	vvw	974.5	976.5
1 1 3	945.9	940.6	957.4	956.3	–	955.5	988.4	986.5 / 984.0	993.1	998.6 / 994.8	1010	1005	s	–	1020
4 0 1	976.0	975.4	975.9	977.8	971.6	974.1					993.3	996.1	vvw	999.0	1001
3 3 1	988.2	989.5	994.5	993.2	982.7	992.1	1010	1007	1019	1019	1023	1023	w	1025	1030
2 3 2	997.5	994.3	1002	1003	1002	1003	1027	1025	1042	1039	1045	1044	• –		1051	1055
3 2 2	–	1048	1051	1056				1074	1084	1087	1092	1091	vvw	1098	1101
4 2 0	–	1060	–	1061	1066	1058	1075	1074 / 1068	1079	1080	1080	1082	vvw	1086	1087
0 4 2	1091	1085	1098	1094	–	1096	1124	1124	1142	1139	1147	1145		–	1154	1159
0 5 1	1206	1204	1214	1211	–	1213	1239	1239	1256	1256	1260	1263		–	1270
1 5 1	1264	1260 / 1270	1271	1266 / 1279	1263	1277 / 1282	1297	1295 / 1302	1314	1312 / 1318	1318	1319 / 1323	m	1326	1326 / 1331
3 3 2								1296		1312		1314		1318	1317
1 3 3	1284	1282	1284	1284	–	1304	1330	1325	1345	1340	1344	1343	vs	1359	1354
4 1 2	1301	1300 / 1305	1308	1308	1319	1316	1346	1345	1366	1362	1370	1369	m+	1385	1384
2 4 2			1321	1315					1374	1380	1381	1386	s	1401	1399
2 5 0	1335	1332 / 1337	1340	1336	1332	1338	1382	1384	1404	1400	1410	1406	m-	1423	1423
3 0 3			1354	1353	1349	1350			1452	1446	1457	1453	m+	1470	1470
3 1 3	1389	1388	1397	1398	1392	1395	1430	1429		1479	–	1483		–	1495
4 2 2	–	1433	1444	1442	–	1438	1464	1462	–	1479	1500	1490			
5 0 1	1471	1471	1474	1474 / 1479	1480	1469 / 1478	1486	1482	1500	1498	1499	1500	m	1504	1503
2 3 3	–	1461					–	1518	–	1537	1549	1537		1566	1565
0 0 4	–	1495	–	1523	1526	1522 / 1529	–	1574	1603	1594	–	1604	w	1625	1625 / 1631
3 2 3	1509	1515	–	1531			1568	1566	1588	1585	1595	1592	m-	1606	1605
1 1 4	–	1595	1600	1606	1610	1610	1645	1643	1663	1665	–	1707	m+	1689	1683
0 6 0	1604	1600 / 1607	1630	1625	1629	1626	1671	1671 / 1675	–	1692	1674	1674		–	1718 / 1728
1 4 3			–	1622	–	1621			–	1696	–	1702	1722	m-	–	1725
4 3 2	1650	1656	1665	1665	1665	1662	1693	1690	1710	1710	1716	1715		–	1730
2 5 2	1701	1705	1719	1717	1726	1718	1753	1756	1783	1779	–	1787		–	1810
1 6 1	1746	1748	1759	1756	–	1760	1795	1797	–	1821	–	1830	w	1850	1841 / 1850
2 4 3	1774	1773	1795	1791	–	1791	–	1837	–	1860	–	1870		–	1886 / 1894
2 2 4	–	1893	1914	1922	–	1920	1976	1978	2007	2002 / 2014	–	2014	m+	2034	2036 / 2043
6 0 0	1979	1984	1980	1986	–	1978	–	1993			2025	2016		–	2018 / 2025
6 1 0	2031	2029	2032	2030	2015	2022	2031	2038	2058	2060	2059	2062	m+	2063	2064 / 2070	2070
3 6 1	2184	2189	2191	2198	2207	2200 / 2210	–	2240	2267	2268	2281	2278		–	2289 / 2299
2 6 2	2200	2194	2203	2207	2226	2210 / 2229	–	2258	2288	2287 / 2295	–	2299		–	2313 / 2324
5 0 3	2222	2219	2244	2236			2423	2259	2458	2459	2463	2302		2323	2315 / 2322
6 1 2	2406	2403	2418	2411	2402	2403 / 2401	2459	2432 / 2460	2480	2489	2493	2463 / 2500	w	2482	2477 / 2530
4 0 4	2372	2377	–	2405							–	2522		–	2530
1 0 5	2388	2391	–	2434	2432	2432	–	2515	2539	2546	–	2563		–	2595	2604

All intensities were corrected with the Lorentz, polarization, and absorption factors. The linear absorption coefficients and the range of the transmission factors are given in Table 3.

Powder work Powder photographs were taken at room temperature with a Guinier-Hägg camera, using CuKα radiation. Lead nitrate (cubic, $a = 7.8568$ Å) was used as an internal standard. The least-squares refined lattice parameters for the isomorphous orthorhombic Mglyc$_3$ phases ($M = $ La $-$ Tb) are given in Table 1 and the observed and calculated values of sin$^2\theta$ in Table 2.

REFINEMENT OF THE STRUCTURES

LAGLYC and GDGLYC are isostructural. The space group is $Pn2_1a$ with the general fourfold positions $(x,y,z;\ \bar{x},\frac{1}{2}+y,\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z;\ \frac{1}{2}+x,y,\frac{1}{2}-z)$. Preliminary values of the atomic parameters for the refinement of the 16 non-hydrogen atoms were obtained from Ref. 3. The atomic scattering factors used were taken from *International Tables* [8] (oxygen and carbon) and from Cromer *et al.*[7] (lanthanum and gadolinium). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights w were equal to $1/\sigma^2 (|F_o|)$ for reflexions obeying the conditions $I > 3\sigma(I)$ and $0.80 \leq |F_o|/|F_c| \leq 1.25$; other reflexions were

Table 3. Data on the crystals used for the structure determination of LAGLYC and GDGLYC and the course of the refinement of the two structures. The values of R and wR are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2/\sum w |F_o|^2]^{1/2}$, respectively.

	LAGLYC a-axis	GDGLYC b-axis	GDGLYC c-axis	GDGLYC Both settings averaged
Habit of the crystal	Approx. spherical	Tabular (100)	Tabular (100)	—
Approximate dimensions	Radius 0.15 mm	0.09 × 0.09 × × 0.03 mm	0.15 × 0.15 × 0.035 mm^3	—
μ/cm^{-1}	45.7	82.3	82.3	—
Range of transmission factors	0.57 − 0.61	0.33 − 0.55	0.17 − 0.50	—
Total number of independent reflexions recorded for sin $\theta < 0.80$	1819	1441	1527	1785
No. of reflexions with $I \leq 3\sigma(I)$	239	316	372	570
No. of reflexions with $I \leq 0$	35	106	118	89
Isotropic refinement, individual scale factors				
R (all reflexions)	0.0463	0.0664	0.0610	—
ωR	0.0440	0.0518	0.0469	—
No. of reflexions with $\omega \neq 0$	1516	978	1035	—
Refinement with anisotropic thermal parameters on the metal atom and an over-all scale factor				
R	0.0460	0.0617	0.0573	0.0522
ωR	0.0432	0.0464	0.0402	0.0352
No. of reflexions with $\omega \neq 0$	1512	982	977	1190
Anisotropic refinement of all atoms				
R	0.0408	—	—	—
ωR	0.0383	—	—	—
No. of reflexions with $\omega \neq 0$	1530	—	—	—

Table 4. Coordinates and thermal parameters for the various atoms in the orthorhombic LAGLYC and GDGLYC structures. The space group is $Pna2_1$ and the anisotropic thermal parameters for lanthanum and gadolinium have been calculated from the expression: $\exp[-(h^2\beta_{11}+hk\beta_{12}+\ldots)]$.

Atom	Group	$x \times 10^4$		$y \times 10^4$		$z \times 10^4$		$B/\text{Å}^2$	
		La	Gd	La	Gd	La	Gd	La	Gd
O(1)	COO⁻	1997(6)	2030(11)	1364(6)	1244(11)	2750(8)	2554(17)	1.27(10)	1.81(22)
O(2)	COO⁻	2092(7)	2024(10)	2996(7)	2995(10)	1271(10)	1275(14)	1.94(12)	1.42(17)
O(3)	−OH	4540(6)	4509(9)	1314(6)	1304(8)	3428(7)	3514(12)	1.48(10)	1.54(17)
C(1)	COO⁻	2722(10)	2622(16)	2183(9)	2218(14)	2083(12)	2152(25)	1.43(16)	0.91(29)
C(2)	COH	4044(7)	4040(11)	2321(6)	2244(11)	2593(8)	2401(16)	0.91(9)	0.88(18)
O(4)	COO⁻	4784(3)	4804(4)	72(8)	86(11)	6950(4)	6858(6)	1.21(6)	1.15(10)
O(5)	COO⁻	5599(4)	5672(5)	135(5)	−129(8)	9538(5)	9523(7)	1.54(7)	1.12(10)
O(6)	−OH	2412(4)	2453(5)	158(5)	149(8)	8107(5)	8156(7)	1.49(7)	1.37(10)
C(3)	COO⁻	4672(5)	4736(6)	56(11)	54(20)	8527(5)	8478(9)	1.27(7)	1.17(12)
C(4)	COH	3376(6)	3436(8)	244(5)	−255(8)	9277(8)	9360(12)	1.65(10)	1.41(15)
O(7)	COO⁻	2041(6)	1968(9)	−1273(6)	−1327(9)	2504(8)	2803(13)	1.17(9)	0.86(15)
O(8)	COO⁻	2180(6)	2180(11)	−2895(7)	−2959(12)	996(9)	1071(16)	1.65(10)	2.24(24)
O(9)	−OH	4487(6)	4454(7)	−1222(5)	−1182(7)	3148(7)	3205(11)	1.16(9)	0.67(12)
C(5)	COO⁻	2560(10)	2546(18)	−2194(9)	−2156(15)	2028(11)	2046(29)	1.27(15)	1.48(36)
C(6)	COH	4046(10)	4035(13)	−2239(9)	−2376(11)	2272(12)	2696(18)	2.39(17)	1.46(25)
M		2912(0.2)	2922(0.3)	0(0)	0(0)	4391(0.2)	4973(0.6)	−	−

	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
La	16.7(3)	13.3(2)	30.1(3)	−3.5(1.2)	0.2(3)	4.6(1.1)
Gd	12.1(4)	14.4(3)	27.1(4)	−1.0(1.0)	0.5(3)	3.8(1.1)

given zero weight. The convergence was followed by the usual discrepancy indices R and wR, defined in Table 3, where details of the various models used in the refinements are also given. The refined atomic parameters with their estimated standard deviations are given in Table 4. Tables of observed and calculated structure factors may be obtained from the Department of Physical Chemistry at the University of Lund. A final difference synthesis, calculated by using the refined parameters given in Table 4, showed the presence

Table 5. Analysis of the weighting schemes for the LAGLYC and the GDGLYC (b-axis data) structures. The averages of $(|F_o|-|F_c|)^2 = w\Delta^2$ are normalized and the weights are estimated from the Poisson statistics of the counting data (p. 1481).

$|F_o|$ interval LAGLYC	Number of reflexions	$\overline{w\Delta^2}$	$|F_o|$ interval GDGLYC	Number of reflexions	$\overline{w\Delta^2}$
0.0 − 9.3	90	0.29	0.0 − 14.4	80	0.26
9.3 − 13.1	128	0.60	14.4 − 20.3	93	0.38
13.1 − 16.9	141	0.87	20.3 − 29.3	99	0.93
16.9 − 22.3	143	1.16	29.3 − 42.2	97	1.28
22.3 − 28.6	148	1.51	42.2 − 55.8	98	1.10
28.6 − 36.3	144	1.57	55.8 − 67.8	98	0.74
36.3 − 46.5	148	0.93	67.8 − 81.6	101	1.19
46.5 − 59.7	174	1.02	81.6 − 94.6	104	1.09
59.7 − 80.3	194	0.62	94.6 − 117.6	104	0.75
80.3 − 234.8	195	1.44	117.6 − 234.4	103	2.27

of a peak equal to $3e/\text{Å}^3$ at the central ion sites in both structures. The other parts of the electron density maps showed only small spurious peaks, at most $0.5\ e/\text{Å}^3$, above a smooth background.

An examination of the values of $\overline{w\varDelta^2}$ between different $|F_0|$-intervals (Table 5) indicates that the weighting procedure used is not entirely satisfactory. Hence, the estimated standard deviations given in Table 4 may be too small. The weight analysis indicates the occurrence of systematic errors in the measurements. In the *Single Crystal Intensity Measurement Project Report* [9,10] of the International Union of Crystallography it has been shown, that serious instrumental malfunctions may occur with linear diffractometers, causing a systematic error in the structure factors with increasing angle of inclination (see Ref. 9, p. 13). However, no error of this type seems to be present in our diffractometer, as judged by the fact, that intensity data, obtained from two different settings, only showed small random variations, of the order $2-3$ %, between the $|F_0|$-values of the same reflexions.

The scale factors for the various layers were improved in the first stage of the refinement. The relative values thus obtained agreed within $2-3$ % with those calculated from data in the second setting. The covariance between the scale factors and the anisotropic thermal parameters is usually large. The anisotropic thermal parameters are also more sensitive towards systematic errors than the positional parameters. In order to investigate the effect of the first factor, two series of anisotropic refinements of all atoms and an overall scale factor were tried on the LAGLYC data. The relative scale-factors for the various layers, obtained from the isotropic refinement, were varied at random within $2-3$ % between the two refinements. Examination of the two sets of parameters showed that the coordinates for all atoms and the anisotropic thermal parameters for lanthanum, in general, had changed less than one standard deviation with the change of scale. On the other hand, the β_{ij}-values (especially β_{11}) of some of the light atoms had changed with 50 %. Hence, it was concluded, that no physically meaningful model of the structure with anisotropic thermal parameters on the light atoms could be used.

A fairly large number of the reflexions recorded have zero weight (Table 3). Most of these have $h+l=2n+1$ and $I\leq3\sigma(I)$. This is due to the value of z for the heavy atom, which is close to $\frac{1}{4}$. Hence, its contribution to the structure factor is small for the reflexions, obeying the above condition.

The experimental data were not corrected for extinction as there was no significant difference between the $|F_0|$ and $|F_c|$ values for strong reflexions at low values of sin θ.

Programmes used. All computing work was carried out on the UNIVAC 1108 Computer at Lund, Sweden, using the programmes DRF, DATAP2, LALS, DISTAN, PLANES, ORTEP, and CELSIUS.[11]

DISCUSSION

Selected interatomic distances and angles for the LAGLYC and GDGLYC structures are given in Table 6. A stereoscopic view of the two structures is given in Fig. 1. Some symmetry-related sites have been given superscripts of the following significance

(i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$ (iv) $\frac{1}{2}+x, y, \frac{1}{2}-z$

(ii) $-\frac{1}{2}+x, y, \frac{1}{2}-z$ (v) $\frac{1}{2}+x, 1+y, \frac{1}{2}-z$

(iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$

where x, y, z are coordinates of the crystal-chemical unit, given in Table 4. A description of the GDGLYC structure, based on photographic intensity data, has been given in part 3.[3] The parameters, obtained by photographic and diffractometer methods in general, agree within $3\times\sqrt{\sigma_1^2+\sigma_2^2}$, where σ_1 and σ_2 are the estimated standard deviations, obtained by the two methods. One exception is the x-coordinate of O(9). However, the diffractometer data give a bond length to gadolinium for this atom, which is in better accordance with the other $Gd-O$ distances than was the case with the photographic data.

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

Within the coordination polyhedra					La	Gd
	La	Gd				
M – O(1)	2.533(7)	2.466(11)	O(2^i) – O(5^{ii})		3.505(9)	3.234(13)
M – O(2^i)	2.552(8)	2.494(12)	O(1) – O(9)		3.966(9)	3.732(14)
M – O(3)	2.569(7)	2.463(9)	O(4) – O(8^{iii})		3.203(10)	3.061(16)
M – O(4)	2.525(4)	2.417(5)	O(3) – O(4)		3.164(8)	2.915(12)
M – O(5^{ii})	2.444(4)	2.353(5)	O(3) – O(8^{iii})		2.865(9)	2.744(15)
M – O(6)	2.592(4)	2.486(6)	O(3) – O(9)		2.941(9)	2.807(12)
M – O(7)	2.594(7)	2.438(10)	O(6) – O(2^i)		2.943(10)	2.868(14)
M – O(8^{iii})	2.580(8)	2.447(14)	O(6) – O(5^{ii})		2.828(6)	2.766(7)
M – O(9)	2.587(6)	2.467(8)	O(6) – O(8^{iii})		2.843(9)	2.686(16)
O(1) – O(5^{iii})	2.967(8)	3.055(14)	O(7) – O(1)		3.056(10)	2.899(15)
O(1) – O(8^{iii})	2.858(9)	2.947(18)	O(7) – O(2^i)		3.248(10)	2.949(15)
O(5^{ii}) – O(8^{iii})	3.271(9)	3.326(15)	O(7) – O(5^{ii})		3.234(8)	2.788(12)
O(2^i) – O(4)	3.139(11)	3.045(15)	∠O(1) – M – O(3)		63.8(2)	64.8(3)
O(2^i) – O(9)	3.116(10)	2.946(13)	∠O(4) – M – O(6)		61.9(1)	64.5(2)
O(4) – O(9)	3.395(7)	3.156(11)	∠O(7) – M – O(9)		60.0(2)	63.6(3)

Within ligand 1					La	Gd
	La	Gd				
C(1) – O(1)	1.322(12)	1.262(20)	∠O(1) – C(1) – O(2)		115.3(9)	118.9(15)
C(1) – O(2)	1.315(13)	1.291(20)	∠O(1) – C(1) – C(2)		120.6(8)	117.0(13)
C(1) – C(2)	1.441(13)	1.473(20)	∠O(2) – C(1) – C(2)		122.3(9)	122.6(14)
C(2) – O(3)	1.437(10)	1.440(15)	∠O(3) – C(2) – C(1)		112.5(7)	113.2(11)
O(1) – O(3)	2.696(10)	2.657(15)				

Within ligand 2					La	Gd
	La	Gd				
C(3) – O(4)	1.263(5)	1.240(9)	∠O(4) – C(3) – O(5)		124.5(5)	126.2(7)
C(3) – O(5)	1.259(6)	1.269(9)	∠O(4) – C(3) – C(4)		118.8(5)	119.5(7)
C(3) – C(4)	1.489(8)	1.539(12)	∠O(5) – C(3) – C(4)		115.0(5)	110.5(8)
C(4) – O(6)	1.372(8)	1.441(11)	∠O(6) – C(4) – C(3)		112.0(5)	105.1(7)
O(4) – O(6)	2.632(6)	2.618(7)				

Within ligand 3					La	Gd
	La	Gd				
C(5) – O(7)	1.252(12)	1.249(21)	∠O(7) – C(5) – O(8)		129.0(10)	133.0(18)
C(5) – O(8)	1.222(12)	1.230(23)	∠O(7) – C(5) – C(6)		114.7(9)	114.9(15)
C(5) – C(6)	1.556(15)	1.630(23)	∠O(8) – C(5) – C(6)		112.6(9)	111.2(14)
C(6) – O(9)	1.443(12)	1.464(15)	∠O(9) – C(6) – C(5)		110.3(8)	102.7(10)
O(7) – O(9)	2.591(9)	2.584(12)				

Possible hydrogen bonds					La	Gd
	La	Gd				
O(3) – O(1^{iv})	2.719(9)	2.723(15)	∠C(2) – O(3) – O(1^{iv})		104.0(2)	99.3(7)
			∠C(1^{iv}) – O(1^{iv}) – O(3)		114.3(6)	111.0(10)
O(6) – O(4^{ii})	2.731(6)	2.729(7)	∠C(4) – O(6) – O(4^{ii})		137.9(4)	134.2(5)
			∠C(3^{ii}) – O(4^{ii}) – O(6)		96.3(3)	93.5(4)
O(9) – O(7^v)	2.704(9)	2.706(12)	∠C(6) – O(9) – O(7^v)		112.5(6)	98.7(7)
			∠C(5^v) – O(7^v) – O(9)		101.6(6)	111.7(11)
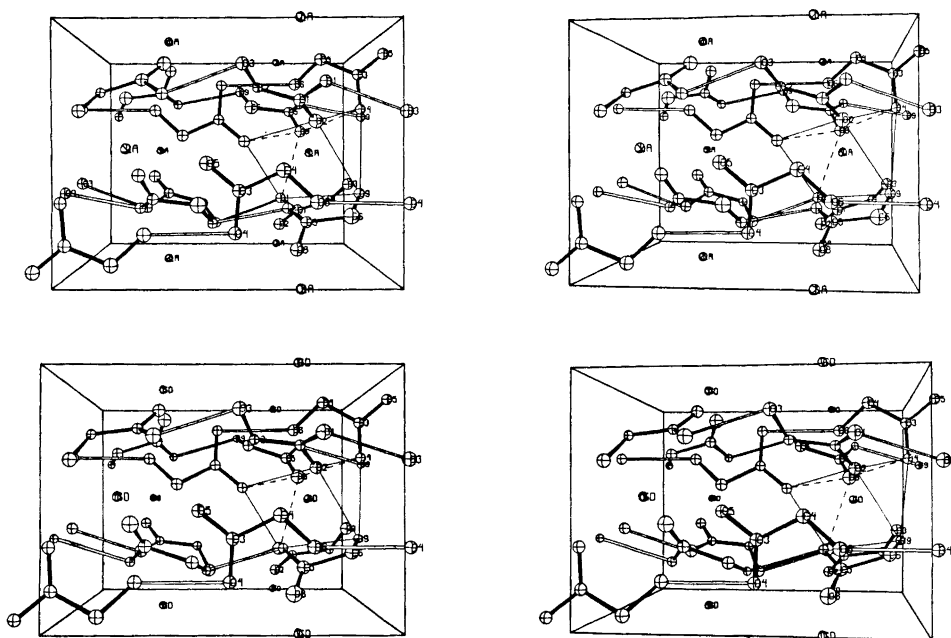
Fig. 1. Stereoscopic view of the LAGLYC and GDGLYC structures. The stick bonds be-
tween the ligand atoms are filled and those between possible hydrogen bonded atoms are
unfilled. The picture has been drawn by using the program ORTEP and the atoms are
represented by thermal spheres (or ellipsoids for the heavy atoms), formally scaled to
include 50 % of the probability distribution.

The average metal − oxygen bond distances decrease from 2.55_2 Å in
LAGLYC to 2.44_9 Å in GDGLYC. This change is approximately equal to the
decrease in the ionic radius of the two central ions (0.12 Å). The average
oxygen − oxygen contact distances in the coordination polyhedron also decrease
with decreasing size of the central ion, the averages in the two compounds being
3.05_8 Å and 2.92_6 Å, respectively. The decrease is considerably larger for the
distances above 3.1 Å than for those below, the averages being 0.22 Å and 0.03 Å,
respectively. Some of the shorter oxygen − oxygen contact distances actually
increase from LAGLYC to GDGLYC. This finding is a satisfactory piece of
experimental evidence for the importance of oxygen − oxygen repulsions in
deciding the geometry of solid rare earth complexes, a point, which has been
discussed before by Albertsson [12] and by the present author.[13] The change
in size of the central ion does not result in any significant changes in the
distances between the two oxygen donors in the chelate ring (the ligand bite).
The conformation of the ligand is instead changed in order to fit into the dif-
ferent crystallographic surroundings; a change wich is most noticeable in the
conformation angle. The differences in conformation are most easily seen
in Fig. 1 and in Table 7. The various conformations are a result both of dif-
ferences between corresponding bond angles in the various ligands and of

Table 7. The deviation in Å of the central ion and ligand atoms from the least-squares planes, formed by the equatorial oxygens and the C—COO groups, respectively. The conformation angle in the various ligands has also been included in the last line of the table.

Atom	Equatorial plane La	Gd	Atom	Ligand 1 La	Gd	Atom	Ligand 2 La	Gd	Atom	Ligand 3 La	Gd
M	− 0.025	− 0.012	M	− 0.412	− 0.826	M	− 0.078	0.215	M	− 0.554	− 0.117
O(3)	0	0	O(1)	− 0.027	0.023	O(4)	0.027	0.044	O(7)	0.041	− 0.020
O(7)	0	0	O(2)	− 0.028	0.025	O(5)	0.027	0.039	O(8)	0.042	− 0.020
O(9)	0	0	C(1)	0.082	− 0.070	C(3)	− 0.075	− 0.113	C(5)	− 0.110	0.053
			C(2)	− 0.027	0.021	C(4)	0.021	0.030	C(6)	0.027	− 0.012
			O(3)	0.154	− 0.178	O(6)	− 0.083	− 0.353	O(9)	0.187	0.603

Conformation angle	O(1)—C(1)—C(2)—O(3)		O(4)—C(3)—C(4)—O(6)		O(7)—C(5)—C(6)—O(9)	
	17.7	2.8	− 13.6	29.0	5.1	30.9

"inversion" of the atoms in the least-squares plane, formed by the C − COO group.

Some of the corresponding interatomic bond distances in the ligands, mainly the C − C distances, are significantly different from one another as judged by the *t*-test. These differences might well be artefacts, brought about by the presence of systematic errors in the data, as mentioned on p. 1484. Most of the bond distances within the ligands show, on the whole, a satisfactory agreement between one another, *i.e.* a change in size of the central ion does not seem to result in any significant changes in the *intra*-ligand bond distances.

Hydrogen bonding and unit cell dimensions. The hydrogen bond scheme is outlined in Table 6 and in Fig. 1. There are only small differences between the various hydrogen bonded oxygen − oxygen distances in the two structures and the change in packing and conformation of the ligands do not result in any significant changes in the hydrogen bonds. One might even guess, that the preservation of an energetically favourable network of hydrogen bonds is as important for the conformation of the ligand as the size of the central ion (*cf.* part 8, p. 3358).

The symmetry related ligands are connected by hydrogen bonds as shown in Fig. 1. All ligands are aligned along the *a* axis, inclined approximately 30°, 90°, and 150° to the *ab* plane. A decrease in the metal − oxygen bond distances moves the ligands closer to the central ion and results in a larger decrease in *b* and *c* than in *a* for decreasing radius of the central ion (*cf.* Table 1). The smaller decrease in *a* is due to the alignment of the ligands along this axis in connection with the near constancy of the ligand dimensions and the hydrogen bonded oxygen − oxygen distances.

COMPARISON BETWEEN DIFFERENT GLYCOLATE STRUCTURES

The ligands in solid complexes may often be approximated as rigid bodies with some rotational freedom around the single bonds, *i.e.* the carbon − carbon bond in the glycolate ion. The experimental values of bond distances and an-

Table 8. Ranges and means of the various interatomic distances and angles within the glycolate ion, obtained by X-ray structure determinations of various solid glycolate compounds.

	C— C Bond in Å	C— O Bond in Å	C— O(H) Bond in Å	Ligand bite in Å	Sum of angles around the carboxylate carbon
Potassium[14] and rubidium [15] hydrogen	$1.511 - 1.519$	$1.241 - 1.264$	$1.418 - 1.426$	$2.687 - 2.733$	359.9
bisglycolates	1.51_5	1.24_8	1.42_3	2.71_0	359.9
Copper(II) glycolate[1]	—	$1.24 - 1.27$	—	—	—
	1.53	1.25_5	1.43	2.57	359.9
Europium tris-glycolate[8]	$1.48 - 1.58$	$1.27 - 1.36$	$1.41 - 1.46$	$2.66 - 2.72$	360
	1.52	1.32	1.43	2.69	360
Hydroxyacetato-oxy- acetato-aquo- erbium(III) hydrate[17]	$1.49 - 1.54$	$1.20 - 1.26$	—	—	$359 - 360$
	1.51	1.24	1.44	2.54	360
Erbium tris-glycolate dihydrate [18]	$1.48 - 1.54$	$1.24 - 1.32$	$1.36 - 1.50$	$2.54 - 2.57$	$359 - 360$
	1.52	1.27	1.44	2.56	360
Lanthanum and gado- linium tris-glycolates	$1.441 - 1.630$	$1.222 - 1.322$	$1.372 - 1.464$	$2.584 - 2.696$	$356.2 - 358.5$
	1.52_1	1.26_4	1.43_3	2.63_0	358.3

gles, available in the literature on this ligand, are given in Table 8. These data indicate that the rigid body approximation is a fairly good model for the description of glycolate ions in crystallographic different surroundings.

Planar ligands are found in the Cu, K, Rb, and Eu (two ligands) compounds. The data from the alkali compounds, where the metal-ligand interactions are expected to be weaker than those in the other compounds, might indicate, that the planar form is the energetically favoured one for the "free" glycolate ion. The observed deviations from planarity are mainly caused by a twist of the hydroxy — oxygen from the C—COO plane, approximately 4° in ERGLYC[17] and at most 20° in GDGLYC. The conformation differences among the C—COO groups in LAGLYC and GDGLYC have been mentioned previously.

The ligand bite in the rare earth glycolate complexes is significantly shorter in eight- than in nine-coordinated complexes, 2.54 Å and 2.65 Å, respectively. This difference may be due to a larger average attraction between the metal and the donor atoms in the former compounds. Another result of this increased attraction is a shortening of the average metal — oxygen bond distance in the eight-coordinated complexes.

The orthorhombic rare earth tris-glycolate phases are thermodynamically more stable than the corresponding monoclinic phases (at 25°C and 1 atm) for the elements La — Sm, while the opposite is true for Eu — Tb. It is tempting to speculate over the possible structural causes of these differences in relative stability. The average oxygen — oxygen contact distances are approximately the same in the two structures as exemplified by the monoclinic EUGLYC and the orthorhombic GDGLYC. Hence, differences in the oxygen — oxygen repulsions do not seem to be the deciding factor for the relative stability of

the two phases. This may instead be determined by differences in the planarity of the ligands and in the hydrogen bonded oxygen – oxygen distances between the two structure types, *e.g.*, the average hydrogen bonded oxygen – oxygen distance is 0.10 Å shorter in GDGLYC than in EUGLYC.

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