

Structural Studies on the Rare Earth Carboxylates

1. The Crystal and Molecular Structure of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M} = \text{Nd, Gd, and Yb}$

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The crystal and molecular structures of the isostructural lanthanoid-oxydiacetate compounds $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M} = \text{Nd, Gd, and Yb}$, have been determined from three-dimensional X-ray intensity data. The crystals are trigonal with the space group $R\bar{3}2$ and the unit cell dimensions $a = 9.78, 9.73, 9.68 \text{ \AA}$ and $c = 28.33, 28.18, 28.06 \text{ \AA}$ for the neodymium, gadolinium, and ytterbium compounds, respectively. The oxydiacetate ion acts as a tridentate ligand forming two five-membered rings with the lanthanoid ion. The latter is nine-coordinated. Its coordination polyhedron is based upon a distorted trigonal prism of carboxylic oxygens with the ether oxygens lying on twofold axes outside the rectangular faces of the prism. The crystal structure is built up of layers containing the negatively charged trisoxydiacetatolanthanoid(III) complexes and the perchlorate ions alternating with layers containing the positive sodium ions and the water molecules.

In a research programme at this Institute a number of investigations dealing with the complex formation in solution between the rare earth ions and various carboxylate ligands have been carried out. In order to establish the coordination geometries, coordination numbers, and bond distances in complexes of this type a series of crystal structure analyses of rare earth carboxylates have been started.

Grenthe and Tobiasson¹ have determined the amounts and the compositions of the complexes formed in solution between various lanthanoids and the oxydiacetate ion, $\text{OCOCH}_2\text{OCH}_2\text{OCO}^{2-}$. Mononuclear complexes of high stability are formed and the maximum value of \bar{n} is three, *i.e.* only the species MA , MA_2 , and MA_3 are formed. The ligand has three possible coordinating groups and presumably acts as a tridentate ligand. The central lanthanoid ions must therefore be at least nine-coordinated.

A preliminary report of the molecular structure of the nine-coordinated complex $[\text{Nd}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]^{3-}$ has been published earlier.² The present paper deals with the determination and refinement of the complete structures of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M}=\text{Nd}$, Gd , and Yb .

EXPERIMENTAL

Preparation and analysis. The compounds $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ $\text{M}=\text{Nd}$, Gd , and Yb , were prepared by mixing water solutions of the respective lanthanoid perchlorate (5 mmole) and sodium oxydiacetate (15 mmole). Crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature. During the evaporation, the pH of the solution was maintained between 5 and 6 by the addition of perchloric acid. The ytterbium compound was analysed for ytterbium, sodium, carbon, and water. It contained: 17.6 % Yb, 11.6 % Na, 14.9 % C, and 10.9 % H_2O ; calc. for $\text{Na}_3[\text{Yb}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$: 17.5 % Yb, 11.6 % Na, 14.5 % C, and 10.9 % H_2O . Powder photographs of the neodymium, gadolinium, and ytterbium compounds were nearly identical. The former two preparations were only analysed for their lanthanoid contents. They contained 15.3 % Nd and 16.2 % Gd, respectively; calc. 15.0 % Nd and 16.1 % Gd. The perchlorate ion (originally discovered in the electron density maps during the structure determination) was identified by mixing strong solutions of the compounds and potassium nitrate. A white precipitate of potassium perchlorate was then formed.

When chloride, nitrate, or sulphate ions were used instead of perchlorate in the preparations of the ytterbium compound no double salts were obtained. All the resulting compounds were identical with that formed when calculated amounts of ytterbium oxide, oxydiacetic acid, and sodium hydroxide were mixed in water for the formation of $\text{Na}_3[\text{Yb}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot x\text{H}_2\text{O}$. Large crystals were obtained in the solutions by slow evaporation at $+4^\circ\text{C}$ but they very rapidly effloresced at normal room temperature even at a rather high humidity.

Single-crystal work. Oscillation and Weissenberg photographs were taken with $\text{CuK}\alpha$ radiation for the neodymium and ytterbium compounds and with $\text{MoK}\alpha$ radiation for the gadolinium compound. Preliminary photographs of the trigonal crystals were taken along [001]. The three-dimensional intensity data were then recorded from layers $h0l-h5l$ for the neodymium and the ytterbium structures, and $h0l-h10l$ for the gadolinium structure. Single crystal fragments of a somewhat irregular shape but with the approximative dimensions $0.05 \times 0.05 \times 0.15 \text{ mm}^3$ were used, mounted in the elongated direction. Non-integrated Weissenberg multiple-film technique was used. The intensities were estimated visually by comparison with a calibrated scale. 600 independent reflexions were measured for the neodymium compound and 475 for the ytterbium compound, representing ca. 90 and 70%, respectively, of the possible number in the recorded reciprocal region ($\text{CuK}\alpha$ radiation). The linear absorption coefficient μ is 151 and 89 cm^{-1} for the neodymium and ytterbium compound. For the gadolinium compound $\text{MoK}\alpha$ radiation was used with $\mu=25 \text{ cm}^{-1}$. 505 independent reflexions were measured, representing ca. 75 % of the possible number in the copper sphere. No reflexions were detected outside this region. Because of the relatively low absorption coefficients and the irregular shape of the used crystals no absorption corrections were applied in any of the three cases. The data were corrected for the Lorentz and polarization effects on the CD 3600 computer in Uppsala, Sweden, using the data reduction and Fourier calculation programme, DRE.³ The different layers were approximately brought to the same scale by a comparison of correlated $|F_0|$ values.

UNIT CELL AND SPACE GROUP

The compounds $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaCl}_4 \cdot 6\text{H}_2\text{O}$, $\text{M}=\text{Nd}$, Gd , and Yb , are isostructural. The crystals are trigonal. The unit-cell dimensions, given in Table 1, were obtained by a least-squares procedure on powder pho-

Table 1. Crystal data at 20°C for $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]\cdot 2\text{NaClO}_4\cdot 6\text{H}_2\text{O}$.

M	a (Å)	c (Å)	V (Å ³)	Density	
				calc.	obs.
Nd	9.7781 ± 0.0013	28.327 ± 0.006	2345.5	2.043	2.03
Gd	9.7343 ± 0.0017	28.182 ± 0.008	2312.7	2.099	2.02
Yb	9.6832 ± 0.0019	28.060 ± 0.007	2278.5	2.166	2.14

tographs taken with a Guinier focusing camera. This treatment will be described in a following paper.

With three formula units in the elementary cell, the calculated densities agree with the observed ones obtained by using the method of Archimedes, see Table 1.

The systematically absent spectra are hkl with $-h+k+l \neq 3n$ and the diffraction symmetry is $\bar{3}m$. The possible space groups are thus $R32$ (No. 155), $R3m$ (No. 160), and $R\bar{3}m$ (No. 166).⁴ Space group $R32$ is the only one compatible with a reasonable coordination polyhedron around the lanthanoide ions and was therefore chosen. The general positions of this space group are eighteenfold: $(0,0,0)$; $1/3, 2/3, 2/3$; $2/3, 1/3, 1/3$ + (x, y, z) ; $\bar{y}, x-y, z$; $y-x, \bar{x}, z$; y, x, \bar{z} ; $\bar{x}, y-x, \bar{z}$; $x-y, \bar{y}, \bar{z}$.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The first structure to be investigated was $\text{Na}_3[\text{Yb}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]\cdot 2\text{NaClO}_4\cdot 6\text{H}_2\text{O}$. Since there are three formula units in the elementary cell, the ytterbium atom could be placed in the threefold positions $3(a)$ $(0,0,0)$; $1/3, 2/3, 2/3$; $2/3, 1/3, 1/3$) of the space group $R32$. Ytterbium is the only heavy atom in the structure. A three-dimensional Fourier synthesis with $|F_o|$ as coefficients should thus approximately show the electron density together with its centre-symmetrical equivalent. Such a synthesis was calculated on the CD 3600 computer using the programme DRF.³ Fig. 1 gives a part of the result in a composite diagram showing the coordination around the ytterbium atom at the origin.

From geometrical considerations the oxygen and carbon atoms of the ligand molecule were located without difficulty in the electron density maps. The sodium ions in the sixfold positions of the space group $R32$ (denoted $\text{Na}^+(2)$) and the atoms in the perchlorate ion were also easily found. For the sodium ions in the ninefold positions $9(e)$ ($\text{Na}^+(1)$) and the water oxygen atoms (O(6)) it was uncertain which of the two centro-symmetrically related possibilities should be chosen. As a trial a sodium ion was placed in $(0.29, 0.29, 0.50)$ and an oxygen atom in $(0.46, 0.20, 0.475)$.

The preliminary atomic coordinates, isotropic temperature factors, and inter-layer scale factors were improved on the CD 3600 computer using the

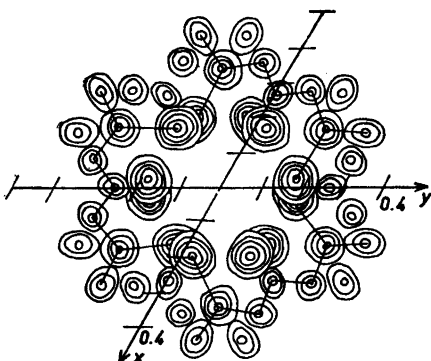


Fig. 1. Part of a three-dimensional Fourier synthesis with $|F_o|$ as coefficients in a composite diagram showing the coordination around the ytterbium atom at the origin and its centrosymmetrical equivalent. The contours are drawn at an interval of $1 \text{ e}/\text{\AA}^3$, the zero contour being omitted.

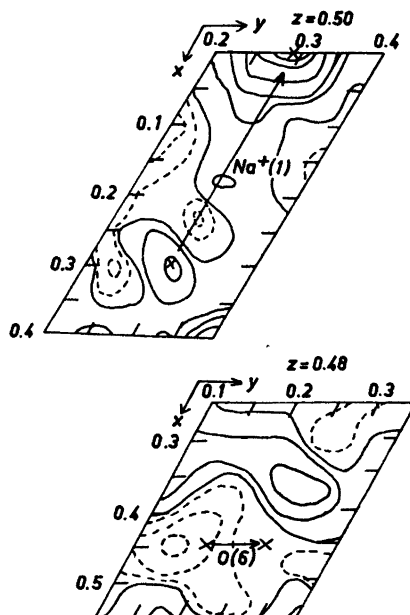


Fig. 2. The environments of the trial and final positions of $\text{Na}^+(1)$ and $\text{O}(6)$ in a three-dimensional difference synthesis after the preliminary refinement of the ytterbium structure. The contours are drawn at an interval of $0.3 \text{ e}/\text{\AA}^3$, negative values being dotted.

general full-matrix least-squares programme LALS.³ The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with the weighting scheme

$$w = 1 / (75 + |F_o| + 0.0055|F_o|^2 + 0.0001|F_o|^3)$$

Only reflexions with $0.80 \leq |F_o|/|F_c| \leq 1.25$ were included in the refinement. The total number of parameters varied was 41. After five cycles of refinement the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.094. Only the observed reflexions were considered.

At this stage angles and distances were calculated using the programme DISTAN.³ It was found that the sodium ion $\text{Na}^+(1)$ was coordinated only to four oxygen atoms. A three-dimensional $(F_o - F_c)$ synthesis was calculated. The environments of the trial positions of $\text{Na}^+(1)$ and $\text{O}(6)$ are shown in Fig. 2 together with those around the centro-symmetrically related ones. The maps do not clearly show that the atoms should be moved but, from a consideration of the coordination geometry around the sodium ions $\text{Na}^+(1)$ and $\text{Na}^+(2)$, the refined trial positions of $\text{Na}^+(1)$ and $\text{O}(6)$ were inverted. The ions $\text{Na}^+(1)$ and $\text{Na}^+(2)$ then have approximately octahedral

Table 2. Atomic parameters with estimated standard deviations in $\text{Na}_3[\text{M}(\text{O}(\text{COCH}_2\text{OCH}_2\text{OCO})_3)_2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}]$, $\text{M} = \text{Nd}$, Gd , and Yb . The space group is $R\bar{3}2$ (No. 155).^a B (Å^2) denotes the isotropic temperature factor.

Atom	Group	Posi- tions	The neodymium structure			The gadolinium structure			The ytterbium structure					
			$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	B
M	—	3(a)	0	0	0	1.1(0.1)	0	0	0	2.2(0.1)	0	0	0	0.5(0.1)
Na ⁺ (1)	—	9(e)	3017(22)	0	5000	6.5(0.4)	2984(14)	0	5000	4.6(0.2)	2975(22)	0	5000	5.1(0.4)
Na ⁺ (2)	—	6(c)	0	0	2001(4)	3.5(0.2)	0	0	2012(3)	2.9(0.1)	0	0	2015(4)	3.5(0.3)
O(1)	C—O—C	9(d)	7426(30)	0	0	5.1(0.6)	7441(19)	0	0	2.7(0.4)	7457(33)	0	0	4.4(0.7)
O(2)	—COO—	18(f)	6353(22)	4898(22)	3917(6)	4.4(0.3)	6380(16)	4950(16)	3926(4)	3.2(0.2)	6414(18)	4880(18)	3917(5)	2.2(0.2)
O(3)	—COO—	18(f)	5002(20)	5766(19)	4331(6)	4.3(0.4)	5114(17)	5887(16)	4325(5)	4.2(0.3)	5197(23)	5885(22)	4321(6)	3.8(0.4)
O(4)	ClO ₄ ⁻	18(f)	746(59)	1604(24)	4462(6)	6.7(0.4)	894(31)	1573(18)	4473(5)	5.3(0.3)	955(39)	1626(22)	4464(6)	4.8(0.4)
O(5)	ClO ₄ ⁻	6(c)	0	0	3768(13)	6.8(0.7)	0	0	3810(10)	6.6(0.6)	0	0	3809(12)	5.9(0.8)
O(6)	H ₂ O	18(f)	4424(33)	2444(40)	4765(9)	8.4(0.7)	4498(17)	2600(16)	4770(5)	4.1(0.3)	4488(22)	2605(20)	4772(5)	3.4(0.3)
C(1)	—CH ₃ —	18(f)	3697(30)	4216(32)	3656(9)	4.3(0.4)	3818(28)	4281(27)	3645(7)	4.4(0.4)	3821(27)	4206(28)	3653(7)	2.6(0.4)
C(2)	—COO—	18(f)	4923(36)	4879(36)	3984(6)	3.8(0.3)	5187(34)	5103(33)	3989(5)	3.2(0.3)	4943(39)	4787(39)	3995(6)	2.6(0.4)
Cl	ClO ₄ ⁻	18(f)	0	0	4286(3)	4.3(0.1)	0	0	4288(3)	4.0(0.1)	0	0	4288(3)	3.4(0.2)

environments of oxygen atoms. One cycle of refinement reduced the R value to 0.087 without changing either the new coordinates of $\text{Na}^+(1)$ and $\text{O}(6)$, or their earlier temperature factors appreciably. After five more cycles the shifts in all the parameters of the structure were less than 0.01 % of the estimated standard deviations. The R value did not change during these calculations.

A new three-dimensional difference synthesis showed only spurious peaks above a slowly varying background. The highest peak, *ca.* $3 \text{ e}/\text{\AA}^3$, was situated at the origin where a slight anisotropic effect for the ytterbium atom could be detected. No correction was applied for this effect. It does not seem possible

Table 3. Analysis of the weighting schemes. The averages $\overline{w(|F_o| - |F_c|)^2} = \overline{w\Delta^2}$ are normalized.

Interval $ F_o $	Number of reflexions	$\overline{w\Delta^2}$	Interval $\sin\theta$	Number of reflexions	$\overline{w\Delta^2}$
<i>The neodymium structure</i>					
0—47	50	1.10	0.00—0.42	51	1.16
47—53	57	0.95	0.42—0.53	50	1.10
53—58	59	0.51	0.53—0.60	51	0.89
58—63	57	0.87	0.60—0.66	44	1.07
63—69	60	0.93	0.66—0.71	44	1.27
69—77	58	0.96	0.71—0.76	45	1.17
77—91	57	1.22	0.76—0.80	44	0.91
91—107	58	0.97	0.80—0.84	38	0.70
107—131	55	1.30	0.84—0.87	40	0.92
131—410	56	1.18	0.87—0.90	44	0.80
<i>The gadolinium structure</i>					
0—43	44	0.59	0.00—0.21	69	1.00
43—49	46	0.83	0.21—0.26	61	1.15
49—53	45	0.86	0.26—0.30	64	0.82
53—58	44	1.17	0.30—0.33	58	0.98
58—64	47	1.11	0.33—0.36	53	0.93
64—74	49	1.05	0.36—0.38	53	0.91
74—94	49	1.17	0.38—0.40	46	1.11
94—111	51	1.17	0.40—0.42	34	1.02
111—150	51	0.74	0.42—0.43	23	0.92
150—370	50	1.30	0.43—0.45	10	1.17
<i>The ytterbium structure</i>					
0—61	36	1.31	0.00—0.42	54	0.99
61—73	45	0.94	0.42—0.53	48	1.00
73—81	44	0.53	0.53—0.60	45	0.84
81—87	47	1.05	0.60—0.66	46	0.82
87—98	46	0.78	0.66—0.71	32	0.99
98—107	48	1.02	0.71—0.76	34	0.90
107—120	46	1.26	0.76—0.80	32	1.03
120—137	47	0.97	0.80—0.84	28	1.23
137—167	45	1.14	0.84—0.87	29	1.29
167—459	47	1.00	0.87—0.90	21	0.92

Table 4. Observed and calculated structure factors for the three isostructural compounds Na3[M(OCO2OCH2OCO)3]·2NaClO4·6H2O, M=Nd, Gd, and Yb. For the gadolinium structure the planes with k=6-10 have always h<k and are transformed to planes with k≤5.

Table with 12 columns (h k l for Nd, Gd, Yb) and 12 rows of numerical data representing structure factors for each element.

Table 5. Selected interatomic distances (in Å) with estimated standard deviations in the structures of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M}=\text{Nd}$, Gd , and Yb .

Distance	Nd	Gd	Yb
M—3O(1)	2.52 ± 0.03	2.49 ± 0.03	2.46 ± 0.03
M—6O(2)	2.37 ± 0.02	2.41 ± 0.01	2.31 ± 0.02
O(1)—2C(1)	1.44 ± 0.03	1.40 ± 0.02	1.36 ± 0.03
C(1)—C(2)	1.40 ± 0.04	1.51 ± 0.03	1.34 ± 0.03
C(2)—O(2)	1.40 ± 0.04	1.26 ± 0.03	1.40 ± 0.04
C(2)—O(3)	1.29 ± 0.03	1.24 ± 0.03	1.33 ± 0.03
O(1)—2C(2)	2.26 ± 0.02	2.38 ± 0.02	2.22 ± 0.02
C(1)—C(1)	2.36 ± 0.05	2.37 ± 0.04	2.31 ± 0.04
O(2)—O(3)	2.23 ± 0.03	2.18 ± 0.02	2.18 ± 0.02
$\text{Na}^+(1)$ —2O(3)	2.54 ± 0.02	2.49 ± 0.02	2.45 ± 0.02
$\text{Na}^+(1)$ —2O(4)	2.40 ± 0.04	2.46 ± 0.02	2.46 ± 0.03
$\text{Na}^+(1)$ —2O(6)	2.18 ± 0.03	2.30 ± 0.01	2.29 ± 0.02
$\text{Na}^+(2)$ —3O(3)	2.40 ± 0.02	2.40 ± 0.02	2.46 ± 0.02
$\text{Na}^+(2)$ —3O(6)	2.50 ± 0.03	2.47 ± 0.02	2.47 ± 0.02
$\text{Na}^+(1)$ —2 $\text{Na}^+(2)$	3.55 ± 0.01	3.56 ± 0.01	3.55 ± 0.01
Cl—3O(4)	1.45 ± 0.02	1.43 ± 0.02	1.46 ± 0.02
Cl—O(5)	1.47 ± 0.04	1.35 ± 0.03	1.35 ± 0.03
O(4)—2O(4)	2.35 ± 0.04	2.30 ± 0.03	2.37 ± 0.03
O(4)—O(5)	2.39 ± 0.04	2.29 ± 0.03	2.29 ± 0.03
O(6)—O(2)	2.79 ± 0.03	2.80 ± 0.02	2.80 ± 0.02
O(6)—O(3)	3.25 ± 0.03	3.20 ± 0.02	3.16 ± 0.02
O(6)—O(4)	3.38 ± 0.06	3.24 ± 0.03	3.18 ± 0.04
O(6)—O(2)	3.25 ± 0.03	3.20 ± 0.02	3.16 ± 0.02
O(6)—2O(6)	3.31 ± 0.05	3.22 ± 0.03	3.22 ± 0.03

pared in Table 4. Distances and angles of interest in the three structures are given in Tables 5 and 6. The standard deviations were calculated with the programme DISTAN from the estimated standard deviations of the atomic coordinates and unit cell dimensions.⁵

DISCUSSION OF THE STRUCTURE

The structure of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M}=\text{Nd}$, Gd , and Yb , can be described as composed of layers, perpendicular to the c axis, containing the negatively charged mononuclear oxydiacetate complexes and the perchlorate ions, alternating with layers containing the positive sodium ions and the water molecules. Fig. 3 shows the unit cell of the neodymium structure viewed along the b axis. The lanthanoid ions, the chlorine atoms, and the sodium ions $\text{Na}^+(2)$ lie on threefold axes while the sodium ions $\text{Na}^+(1)$ are located on twofold axes. The lanthanoid ion is nine-coordinated. The sodium ions are surrounded by distorted octahedrons of oxygen atoms. Details of the structure will be described below.

Table 6. Selected interatomic angles (°) with estimated standard deviations in the structures of $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]\cdot 2\text{NaClO}_4\cdot 6\text{H}_2\text{O}$, M=Nd, Gd, and Yb.

Angle	Nd	Gd	Yb
O(1)–M–O(2)	63 ± 1	64 ± 1	65 ± 1
	75 ± 1	74 ± 1	74 ± 1
	135 ± 1	135 ± 1	134 ± 1
O(2)–M–O(2)	77 ± 1	75 ± 1	75 ± 1
	90 ± 1	89 ± 1	91 ± 1
	126 ± 1	127 ± 1	129 ± 1
	150 ± 1	149 ± 1	149 ± 1
C(1)–O(1)–C(1); I	111 ± 3	116 ± 2	117 ± 3
O(1)–C(1)–O(3); II	106 ± 2	110 ± 2	110 ± 2
O(2)–C(2)–O(3); III	112 ± 2	122 ± 2	106 ± 2
C(1)–C(2)–O(2); IV	122 ± 2	118 ± 2	119 ± 2
C(1)–C(2)–O(3); V	125 ± 3	121 ± 2	128 ± 3
O(3)–Na ⁺ (1)–O(3)	104 ± 1	107 ± 1	108 ± 1
O(3)–Na ⁺ (1)–O(4)	85 ± 1	84 ± 1	83 ± 1
	171 ± 1	167 ± 1	167 ± 1
O(3)–Na ⁺ (1)–O(6)	88 ± 1	89 ± 1	87 ± 1
	86 ± 1	85 ± 1	87 ± 1
O(4)–Na ⁺ (1)–O(4)	87 ± 1	85 ± 1	87 ± 1
O(4)–Na ⁺ (1)–O(6)	97 ± 1	101 ± 1	102 ± 1
	90 ± 1	86 ± 1	86 ± 1
O(6)–Na ⁺ (1)–O(6)	170 ± 2	170 ± 1	170 ± 1
O(3)–Na ⁺ (2)–O(3)	105 ± 1	106 ± 1	107 ± 1
O(3)–Na ⁺ (2)–O(6)	86 ± 1	86 ± 1	86 ± 1
	163 ± 1	162 ± 1	161 ± 1
	83 ± 1	83 ± 1	83 ± 1
O(6)–Na ⁺ (2)–O(6)	83 ± 1	82 ± 1	82 ± 1
O(4)–Cl–O(4)	109 ± 1	107 ± 1	109 ± 1
O(4)–Cl–O(5)	110 ± 1	111 ± 1	110 ± 1

When comparing the distances and the angles of the three structures the usual convention is adopted: the significance of the difference between two experimental values \bar{x}_1 and \bar{x}_2 with estimated variances s_1^2 and s_2^2 is tested using the statistic

$$t = |\bar{x}_1 - \bar{x}_2| / (s_1^2 + s_2^2)^{1/2}$$

with the normal law.⁵ Since the estimated standard deviations may be too optimistic only highly significant differences are accepted ($t \geq 3.3$).

The oxydiacetate complex

The lanthanoid ion. Each lanthanoid ion is coordinated by six carboxylic oxygens O(2) and three ether oxygens O(1). The oxygen atoms O(2) are located at the corners of a distorted trigonal prism with the lanthanoid ion at the centre. The triangular faces of the prism are slightly rotated relative to each other. Twofold axes pass through the centres of the rectangular faces of the prism and the ether oxygens of the ligands occupy positions

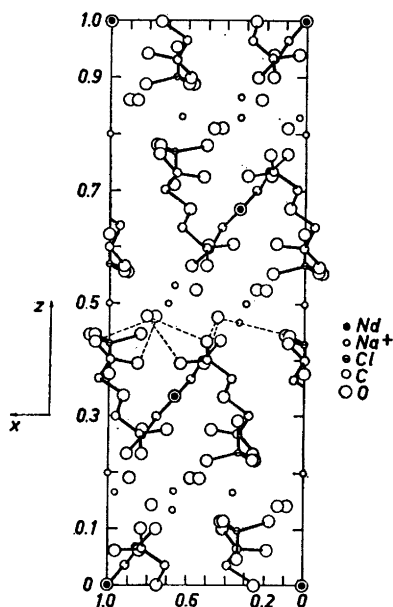


Fig. 3. The unit cell of $\text{Na}_3[\text{Nd}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ projected on (010). Possible hydrogen bonds are dotted.

on them. The symmetry of the complex is 32. The structure of $[\text{Yb}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]^{3-}$ is shown in Fig. 4. The neodymium and gadolinium complexes have almost exactly the same molecular structure. The coordination geometry is a distorted version of that of the $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$ complex in $[\text{Nd}(\text{H}_2\text{O})_9](\text{BrO}_3)_3$ which is based upon a regular trigonal prism.⁹

In all of the three oxydiacetate complexes the distance between the lanthanoid ion, M, and the carboxylic oxygen O(2) is significantly shorter than the distance between M and the ether oxygen O(1) (Table 5). The distances Nd—O(2) and Gd—O(2) are nearly the same and Gd—O(2) is appreciably longer than Yb—O(2). The distances M—O(1), although decreasing in the expected order Nd > Gd > Yb, are not significantly different in the three structures because of the errors involved. The same conclusion is reached when comparing the distances between the triangular faces of the coordination prism. They are 3.31 ± 0.02 , 3.34 ± 0.02 , and 3.28 ± 0.02 Å for the neodymium, gadolinium, and ytterbium structure, respectively. The edges of the triangular faces, O(2)—O(2), are 2.95 ± 0.03 , 3.00 ± 0.02 , and 2.83 ± 0.03 Å. From the experimental material it is thus not possible to ascribe the observed decrease in the unit cell dimensions to a corresponding decrease in the dimensions of the coordination polyhedron around the lanthanoid ion, although this correlation might be anticipated.

The ligand molecule. The oxydiacetate ion acts as a tridentate ligand and forms two identical five-membered rings with the lanthanoid ion. The bond distances and bond angles are given in Tables 5 and 6, respectively. The designation of the atoms and the angles is given in Fig. 5. The ligand molecule

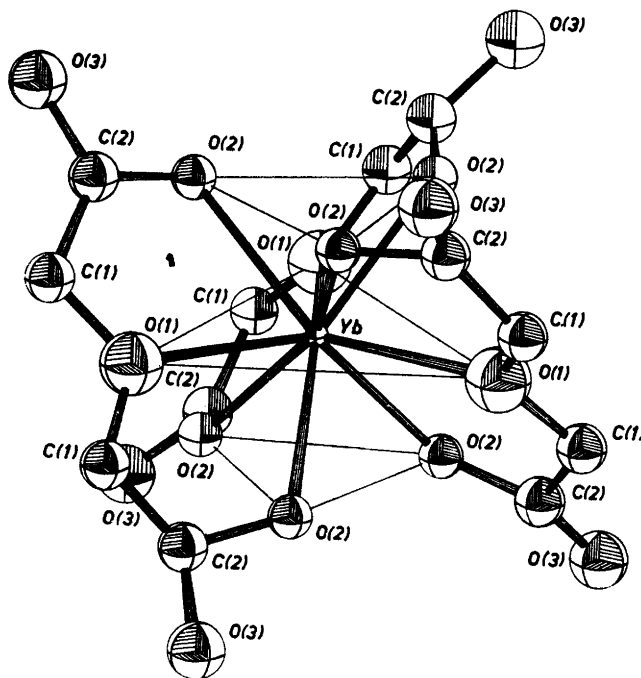


Fig. 4. The molecular structure of $[\text{Yb}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3]^{3-}$, drawn by the programme ORTEP.³ The atoms are represented by "thermal spheres" formally scaled to include 50 % of the probability distribution.

lies approximately in the plane defined by its two O(2) oxygen atoms and the lanthanoid ion. The equations of this plane in the three structures and the deviations of the ligand atoms from it are given in Table 7.

The ether oxygen—carbon bond length does not differ significantly from the usual single bond value 1.43 ± 0.02 Å in any of the three structures.¹⁰ On the other hand there are considerable differences in both the C(1)—C(2) and C(2)—O(2) distances. The C(1)—C(2) bond length is 1.34 ± 0.03 Å in the ytterbium structure, which is significantly different from the normal single bond value 1.50 Å found, *e.g.*, in thiodiacetic acid.¹¹ The C(2)—O(2) distance is 1.26 ± 0.03 Å in the gadolinium structure while the distance is

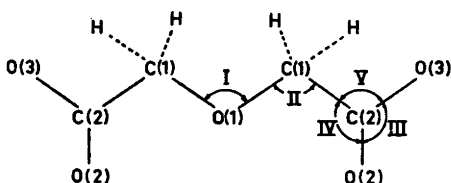


Fig. 5. Designation of atoms and angles in the oxydiacetate ion.

Table 7. The ligand plane defined by M and the two O(2).

7A. The equation of the plane. It is given in the form $\sum m_i x_i - d = 0$ where the direction cosines m_i are referred to orthogonal axes. Unit weights are given to the points defining the plane.

M	m_1	m_2	m_3	d
Nd	-0.0008	+0.7802	-0.6255	-3.708
Gd	-0.0008	+0.7746	-0.6324	-3.768
Yb	-0.0006	+0.7839	-0.6209	-3.619

7B. The deviations (in Å) of the ligand atoms from the plane.

Atom	Nd	Gd	Yb
O(1)	0.00	0.00	0.00
O(2)	—	—	—
O(3)	-0.16	-0.10	-0.04
C(1)	0.01	0.07	0.02
C(2)	-0.13	-0.01	-0.20

1.40 ± 0.04 Å in both the neodymium and ytterbium structures. In the gadolinium structure the C(2)—O(2) and C(2)—O(3) bond lengths are equal and in all the three structures the latter falls in the range expected for carboxylic C=O distances.¹²

Within the limits of error the angle C(1)—O(1)—C(1) is not different from the values normally found in ethers,¹⁰ and in all three structures the angle O(1)—C(1)—C(2) is compatible with the expected tetrahedral value. On the other hand the angle O(2)—C(2)—O(3) is significantly lower than 120° in

Table 8. The least-squares plane through the carboxylic group.

8A. The equation of the plane. See the legend to Table 7A.

M	m_1	m_2	m_3	d
Nd	-0.0293	+0.8277	-0.5604	-2.916
Gd	-0.0019	+0.8169	-0.5768	-2.979
Yb	-0.0082	+0.7997	-0.6003	-3.397

8B. The deviations (in Å) of the atoms from the plane.

Atom	Nd	Gd	Yb
C(1)	0.02	0.00	0.05
C(2)	-0.06	0.00	-0.14
O(2)	0.02	0.00	0.04
O(3)	0.02	0.00	0.05

the ytterbium and neodymium structures. The least-squares planes through the C—COO⁻ group in each structure (calculated with the programme PLANE³) are given in Table 8 together with the deviations of the atoms from it. The group is planar in the gadolinium structure.

The trivalent lanthanoid ions should influence the ligand molecule only slightly, if at all. In spite of this, it is only in the gadolinium structure that the distances and angles of the ligand molecule always have values near the expected ones. The intensity data were recorded with CuK α radiation for the neodymium and ytterbium compounds, while MoK α radiation was used for the gadolinium compound. Even if the true random errors are larger than those given in Tables 5 and 6, the differences in the ligand molecule between the gadolinium and the other two structures may still be indicative of a systematic error in the experimental material based on CuK α radiation. This is also indicated by the infrared spectra of the three compounds. They are almost equal and the ligand parts of them are not influenced by an exchange of the lanthanoid ion. A more detailed discussion of the spectrophotometric measurements will be given in a following paper.

The coordination around sodium

The sodium ions Na⁺(1) and Na⁺(2) are both at the centres of distorted octahedrons of oxygen atoms. Na⁺(1) is coordinated to carboxylic, perchlorate, and water oxygens (O(3), O(4), and O(6), respectively), two of each kind as it lies on a twofold axis. Na⁺(2) lies on a threefold axis and is surrounded by three O(3) and three O(6). Each Na⁺(2) is bridged to three Na⁺(1) by sharing O(3)—O(6) edges, while the latter sodium ion is connected to two Na⁺(2) ions. The coordination around a Na⁺(1)—Na⁺(2) couple in the neody-

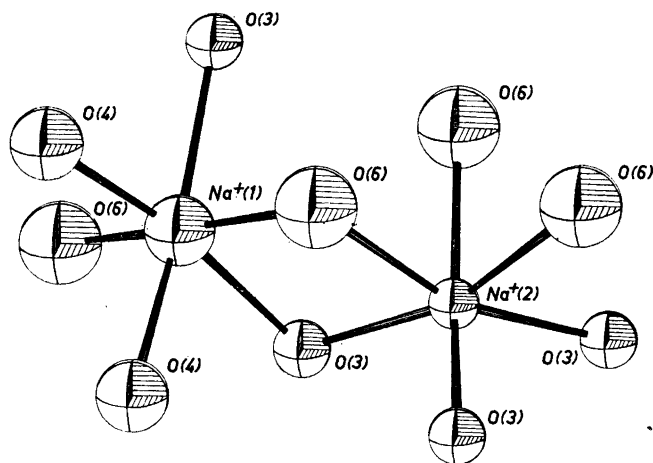


Fig. 6. The coordination around the sodium ions in the neodymium structure, drawn by the programme ORTEP.³ The atoms are represented as in Fig. 4.

mium structure is shown in Fig. 6. The sodium-coordinated oxygen distances are given in Table 5 and the bond angles in Table 6.

The $\text{Na}^+(1)-\text{O}(6)$ distance is always shorter than the distances between $\text{Na}^+(1)-\text{O}(3)$ and $\text{Na}^+(1)-\text{O}(4)$. In the neodymium structure it is very short, 2.18 ± 0.03 Å. In each structure, $\text{Na}^+(2)$ has the three O(3) and the three O(6) atoms at about 2.45 Å.

The perchlorate ion

Each perchlorate ion is composed of one Cl, one O(5), and three O(4). The O(4) oxygens are coordinated to $\text{Na}^+(1)$, while for O(5) the nearest non-hydrogen atoms are three C(1) at about 3.40 Å, not considering Cl and O(4). In the neodymium structure the Cl—O(4) and Cl—O(5) distances are both 1.46 Å. This bond length is compatible with those normally found in the literature.^{13,14} The perchlorate ion does not seem to be a regular tetrahedron in the gadolinium and ytterbium structures; the Cl—O(5) distances are short, 1.35 ± 0.03 Å, while the Cl—O(4) bond lengths have the more normal values 1.43 ± 0.02 and 1.46 ± 0.02 Å, respectively. The infrared spectra are, however, almost equal even in their perchlorate parts. Consequently there are no differences in the perchlorate ion between the three structures, and the two types of Cl—O bonds are most probably equal, as might be expected.

The distances given in Table 5, are not corrected for thermal motion. Assuming riding motion (oxygen on chlorine), a correction was applied to the perchlorate ion using the programme DISTAN. This correction produced only an insubstantial increase of at most one standard deviation, in all cases.

The water molecule

The shortest O(6)—O(2) distance, which in all cases was found to be 2.80 ± 0.02 Å, is the only one less than the distance 3.15 Å between the water oxygen atoms and another oxygen atom. If a linear hydrogen bond between O(6) and O(2) is assumed, then the second hydrogen atom may be described as forming a weak non-linear bond with an O(3) or an O(4) oxygen in the gadolinium and ytterbium structures, the angles O(2)—O(6)—O(3) and O(2)—O(6)—O(4) being about 95°. In the neodymium structure the actual O(4)—O(6) distance, 3.38 ± 0.06 Å, seems too long for any interaction. Some of the possible hydrogen bonds are shown as dotted line in Fig. 3.

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REFERENCES

1. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
2. Vannerberg, N.-G. and Albertsson, J. *Acta Chem. Scand.* **19** (1965) 1760.
3. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1206.

4. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1952, Vol. I.
5. Cruickshank, D. W. J. In Rollet, J. S. *Computing Methods in Crystallography*, Pergamon, Glasgow 1965, pp. 99–116.
6. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
7. Cromer, D. T., Larson, A. C. and Waber, J. T. *Acta Cryst.* **17** (1964) 1044.
8. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
9. Helmholtz, L. J. *J. Am. Chem. Soc.* **61** (1939) 1544.
10. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1958.
11. Paul, S. *Acta Cryst.* **23** (1967) 491.
12. Higgs, M. A. and Sass, R. L. *Acta Cryst.* **16** (1963) 657.
13. Nordman, C. E. *Acta Cryst.* **15** (1962) 18.
14. Liminga, R. *Acta Chem. Scand.* **21** (1967) 1217.

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