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Structural Studies on the Rare Earth Carboxylates

1. The Crystal and Molecular Structure of $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, M = Nd, Gd, and Yb

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The crystal and molecular structures of the isostructural lanthanoid-oxydiacetate compounds $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=Nd, Gd, and Yb, have been determined from three-dimensional X-ray intensity data. The crystals are trigonal with the space group $R32$ and the unit cell dimensions $a=9.78$, 9.73, 9.68 Å and $c=28.33$, 28.18, 28.06 Å 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 Tobiasson [1] have determined the amounts and the compositions of the complexes formed in solution between various lanthanoids and the oxydiacetate ion, $OCOCH_2OCH_2OCO^{2-}$. 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 $[Nd(OCOCH_2OCH_2OCO)_3]^{3-}$ has been published earlier.[2] The present paper deals with the determination and refinement of the complete structures of $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=Nd, Gd, and Yb.

EXPERIMENTAL

Preparation and analysis. The compounds $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$ M=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 $Na_3[Yb(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$: 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 $Na_3[Yb(OCOCH_2OCH_2OCO)_3]\cdot xH_2O$. Large crystals were obtained in the solutions by slow evaporation at +4°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 Cu$K\alpha$ radiation for the neodymium and ytterbium compounds and with Mo$K\alpha$ 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 $0.05\times 0.05\times 0.15$ 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 (Cu$K\alpha$ radiation). The linear absorption coefficient μ is 151 and 89 cm^{-1} for the neodymium and ytterbium compound. For the gadolinium compound Mo$K\alpha$ radiation was used with $\mu=25$ 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, DRF.[3] The different layers were approximately brought to the same scale by a comparison of correlated $|F_o|$ values.

UNIT CELL AND SPACE GROUP

The compounds $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaCl_4\cdot 6H_2O$, M=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 $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$.

M	a (Å)	c (Å)	V (Å^3)	Density calc. (g/cm^3)	Density obs. (g/cm^3)
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 $Na_3[Yb(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$. Since there are three formula units in the elementary cell, the ytterbium atom sould 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 $Na^+(2)$) and the atoms in the perchlorate ion were also easily found. For the sodium ions in the ninefold positions 9(e) ($Na^+(1)$) 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

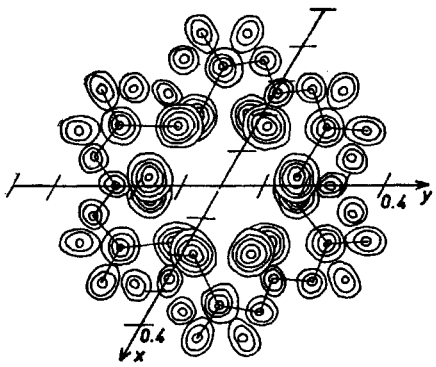


Fig. 1. Part of a three-dimensional Fourier synthesis with $|F_o|$ as coefficients in a composite diagram showing the coordination around the ytterbium atom at the origin and its centrosymmetrical equivalent. The contours are drawn at an interval of 1 e/Å^3, the zero contour being omitted.

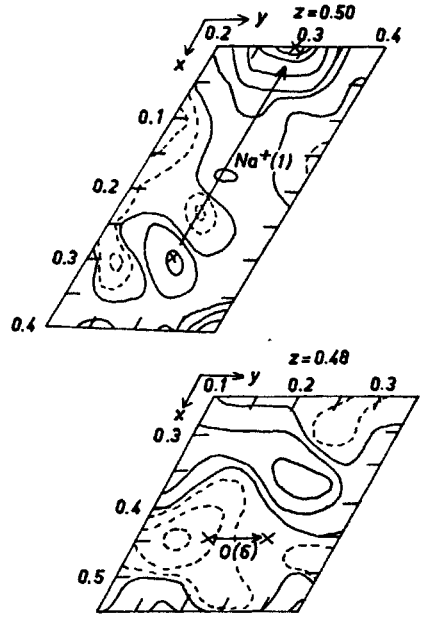


Fig. 2. The environments of the trial and final positions of $Na^+(1)$ and O(6) in a three-dimensional difference synthesis after the preliminary refinement of the ytterbium structure. The contours are drawn at an interval of 0.3 e/Å^3, negative values beeing dotted.

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 $0.80\leq|F_o|/|F_c|\leq1.25$ 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 $Na^+(1)$ was coordinated only to four oxygen atoms. A three-dimensional (F_o-F_c) synthesis was calculated. The environments of the trial positions of $Na^+(1)$ and 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 $Na^+(1)$ and $Na^+(2)$, the refined trial positions of $Na^+(1)$ and O(6) were inverted. The ions $Na^+(1)$ and $Na^+(2)$ then have approximately octahedral

Table 2. Atomic parameters with estimated standard deviations in $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=Nd, Gd, and Yb. The space group is $R32$ (No. 155).[4] B (Å^2) denotes the isotropic temperature factor.

Atom	Group	Positions	The neodymium structure				The gadolinium structure				The ytterbium structure			
			$x\times10^4$	$y\times10^4$	$z\times10^4$	B	$x\times10^4$	$y\times10^4$	$z\times10^4$	B	$x\times10^4$	$y\times10^4$	$z\times10^4$	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_2O	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)	$-CH_2-$	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 $Na^+(1)$ and 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 e/Å^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 sinθ	Number of reflexions	$\overline{w\Delta^2}$
		The neodymium structure			
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
		The gadolinium structure			
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
		The ytterbium structure			
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 $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, 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 $k\leq 5$.

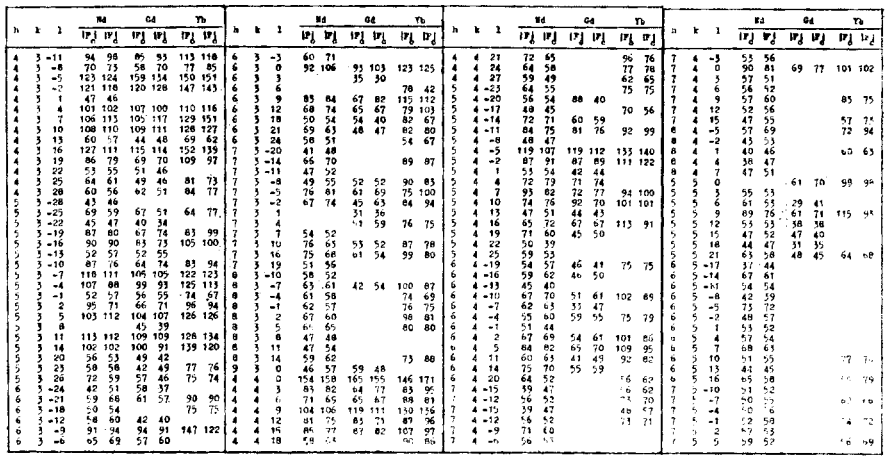
h	k	l	Nd $\|F_o\|$	Nd $\|F_c\|$	Gd $\|F_o\|$	Gd $\|F_c\|$	Yb $\|F_o\|$	Yb $\|F_c\|$
0	0	3	51	58			67	66
0	0	6	62	50	64	60	62	54
0	0	9	101	137	156	147	155	146
0	0	12	101	115	132	139	150	141
0	0	15	125	80	112	110	123	109
0	0	18	159	178	175	189	208	202
0	0	21			176	134	178	163
0	0	24	47	50			48	43
0	0	27	75	50			77	65
0	0	30	151	114	60	111		
1	0	-35			62	57	83	86
1	0	-32	58	51	45	36	56	[illegible]
1	0	-29	85	70	71	71	107	[illegible]
1	0	-26	100	85	89	77	106	[illegible]
1	0	-23	71	65	61	56		
1	0	-20	125	117	117	132	167	[illegible]
1	0	-17	81	80	77	66	93	81
1	0	-14	235	235	260	252	250	269
1	0	-11	104	104	93	105	103	105
1	0	-8	29	32	34	25	32	24
1	0	-5	204	225	226	242	227	247
1	0	-2	296	252			304	289
1	0	1	144	145			171	172
1	0	4	195	204			202	220
1	0	7	233	190	214	214	220	215
1	0	10	30	34	29	28	29	28
1	0	13	129	140	193	170	183	176
1	0	16	217	210	234	216	251	237
1	0	19	132	120	114	118	130	140
1	0	22	58	67	54	61	71	76
1	0	25	66	68	54	55	63	70
1	0	28	63	56	58	54	66	77
1	0	31	83	66	61	54		
1	0	34	62	61	61	57		
1	0	37			49	31		
2	0	-34	30	39				
2	0	-31	47	49	46	37	45	60
2	0	-28	89	82	83	73	114	105
2	0	-25	130	109	105	106	132	129
2	0	-19	104	94	94	65	134	114
2	0	-16	222	180	187	177	240	202
2	0	-13	29	32				
2	0	-10	199	169	199	185	195	195
2	0	-7	265	205	211	222	262	229
2	0	-4	82	82	47	66	55	64
2	0	-1	94	100	74	85	66	72
2	0	2	202	206	241	218	269	227
2	0	5	410	448	370	462	459	463
2	0	8	32	37				
2	0	11	190	160	173	170	194	180
2	0	14	126	126	114	123	144	145
2	0	17			40	43		
2	0	20	107	91	88	95	106	110
2	0	23	93	92	92	86	114	108
2	0	26	86	73	73	66	99	90
2	0	32	47	51	49	35		
2	0	35	84	70				
3	0	-33	46	53	52	59	51	60
3	0	-30	121	84	97	85	139	116
3	0	-27	46	43				
3	0	-24	130	108	125	113	150	134
3	0	-21	130	101	102	91	123	114
3	0	-18	50	45			57	59
3	0	-15	80	65	74	67	77	75
3	0	-12	200	193	210	195	254	205
3	0	-9	152	154	178	185	210	200
3	0	-6	73	71	69	70	70	70
3	0	-3	197	219	273	221	178	228
3	0	0	223	229	255	248	292	258
3	0	3			36	34		
3	0	6	395	338	344	338	320	344
3	0	9	98	91	97	92	105	104
3	0	12	93	91	96	112	111	122
3	0	18	122	104	134	124	155	139
3	0	21	113	92	94	86	108	108
3	0	24	131	112	120	117	121	141
3	0	27	55	57	42	36		
3	0	30	83	70	63	60	87	84
4	0	-32	59	53			77	69
4	0	-29	47	46				
4	0	-26	91	81	71	72	112	97
4	0	-23	117	98	110	99	120	127
4	0	-20	109	93	110	90	109	99
4	0	-17	82	181	90	82	99	104
4	0	-14	207	181	200	197	201	215
4	0	-11	78	70	56	51	60	59
4	0	-8	118	100	110	129	157	145
4	0	-5	222	224	238	240	260	255
4	0	-2	125	122	163	143	162	142
4	0	1			37	33		
4	0	4	220	213	280	241	267	258
4	0	7	119	114	108	100	135	125
4	0	10	210	230	218	240	278	249
4	0	13	108	98	116	111	133	128
4	0	16	118	110	124	109	126	118
4	0	19	117	108	117	116	123	129
4	0	22	65	63	54	59	77	79
4	0	25	76	75	75	72	105	95
4	0	28	78	70	67	66	94	88
4	0	31	48	48	100	105		
5	0	-31	50	53			45	63
5	0	-28	56	56	49	44	64	72
5	0	-25	58	61	61	56	70	79
5	0	-19	158	138	140	137	178	171
5	0	-16	127	115	121	120	133	146
5	0	-13	51	52	48	51	53	68
5	0	-10	120	120	100	105	110	115
5	0	-7	86	80	85	89	104	108
5	0	-4	42	49	47	47	60	59
5	0	-1	151	140	168	153	139	148
5	0	2	149	136	155	135	190	153
5	0	5	102	104	121	120	132	146
5	0	8	74	76	82	78	102	104
5	0	11	132	129	121	117	145	142
5	0	14	100	100	103	109	141	134
5	0	17	104	92	100	95	109	111
5	0	20	72	74	60	62	84	82
5	0	23	49	53	55	52	81	69
5	0	26	54	62			61	73
5	0	29	48	53			54	59
5	0	32	43	44				
6	0	-30	51	59	49	45		

h	k	l	Nd $\|F_o\|$	Nd $\|F_c\|$	Gd $\|F_o\|$	Gd $\|F_c\|$	Yb $\|F_o\|$	Yb $\|F_c\|$
6	0	-24					55	56
6	0	-21	62	67	50	54	57	81
6	0	-18	75	79	71	75	99	102
6	0	-15	90	91	76	86	105	116
6	0	-12	104	104	117	113	134	139
6	0	-9	42	50	36	32	42	46
6	0	-6	69	76	62	64		
6	0	-3	80	90	90	95	113	128
6	0	0	160	174	204	180	225	206
6	0	3	69	75	51	58	80	80
6	0	9	39	46	36	38		
6	0	12	67	73	151	153	67	70
6	0	15	90	82	117	105	161	132
6	0	18	72	76	79	81	135	120
6	0	21	72	76	54	60	95	93
6	0	24	68	60	45	48	71	70
6	0	30	61	61	53	55		
7	0	-26	63	62			61	69
7	0	-23	47	49				
7	0	-20	63	66	56	58	80	82
7	0	-17	62	62			62	86
7	0	-14	116	98	104	95	120	123
7	0	-11	69	77	71	78	100	96
7	0	-8	61	68	58	68	63	74
7	0	-5	71	82	67	69	74	85
7	0	-2	104	96	103	111	146	146
7	0	1	72	86	67	77	87	101
7	0	4	96	96	108	97	113	105
7	0	7	66	71	44	52	57	65
7	0	10	117	108	118	118	150	129
7	0	16	96	94	94	90	137	126
7	0	19	90	79	66	76		
7	0	22	44	48			43	54
7	0	25	53	50	56	38	41	59
8	0	-22	39	42			41	59
8	0	-19	40	57			69	73
8	0	-16	53	62	62	53	72	77
8	0	-13	72	72	55	56	71	77
8	0	-10	95	102	107	109	136	130
8	0	-7	75	78	62	72	90	88
8	0	-4	51	60	47	51	62	67
8	0	-1			47	54		
8	0	2	66	71	67	70	108	95
8	0	5	116	130	136	145	181	162
8	0	8	69	66	51	53	90	75
8	0	11			49	54	80	79
8	0	14	74	68	51	57	83	79
8	0	17	50	53	39	36		
8	0	20	56	64	54	58	74	82
8	0	23	70	63	68	57	74	82
9	0	-18	25	43			42	50
9	0	-15	51	60			82	80
9	0	-12	65	64	50	51	85	91
9	0	-9	77	79	62	72	108	113
9	0	-6	70	68	64	56	80	81
9	0	0	66	72	51	60	76	79
9	0	3	65	65	56	64	90	92
9	0	6	49	59	45	51	68	77
9	0	9	52	60	48	45	56	69
9	0	12	60	57	50	46		
9	0	15	48	47			53	54
9	0	18	38	44			53	54
9	0	21			65	56		
10	0	-11	27	46			38	65
10	0	-8	30	46				
10	0	-5	68	69	56	58	80	87
10	0	-2	54	63	50	49	70	70
10	0	4	47	55	43	43	68	75
10	0	7	40	61			50	76
10	0	10	50	59	52	51	73	75
1	1	0	257	247			228	264
1	1	3	157	134	159	144	135	156
1	1	6	74	35	85	71	112	65
1	1	9	204	208	232	235	253	228
1	1	12	46	87	78	79	84	93
1	1	15	124	111	134	130	161	148
1	1	18	91	97	104	95	113	121
1	1	21	150	126	135	126	168	150
1	1	24	65	77	84	70	97	93
1	1	27	55	45			57	63
1	1	30	56	63	55	50	75	73
1	1	33	59	50			65	69
2	1	-35	57	55				
2	1	-32	37	53			61	67
2	1	-29	78	64	59	56	90	83
2	1	-26	93	78	72	69	108	98
2	1	-23	47	76	103	95	137	122
2	1	-20	58	52	37	41	55	51
2	1	-17			48	50		
2	1	-14	123	125	120	123	164	142
2	1	-11	160	181	228	192	225	201
2	1	-8	103	88	95	92	130	107
2	1	-5	153	168	207	190	197	197
2	1	-2	132	143	178	151	154	149
2	1	1			62	57	59	57
2	1	4	155	149	185	174	160	181
2	1	7	240	156	220	215	230	216
2	1	10	196	175	203	199	217	208
2	1	13	57	25	47	42	73	55
2	1	16	77	87	86	78	93	93
2	1	19	159	141	157	145	164	167
2	1	22	53	47	33	29		
2	1	25	84	74	64	73	97	98
2	1	28	68	68	58	56	86	86
2	1	31	76	61	58	49	73	78
2	1	34	45	45				
3	1	-34	37	52				
3	1	-31	63	56	53	43	61	72
3	1	-28	76	69	71	64	94	95
3	1	-25	83	75	68	70	99	88
3	1	-22	44	31	37	36		
3	1	-19	98	100	98	92	107	108
3	1	-16	149	169	182	176	189	189
3	1	-13			27	39		
3	1	-10	221	205	265	228	266	251
3	1	-7	166	146	135	150	158	160
3	1	-4	100	116	121	122	125	143
3	1	-1	99	111	136	121	143	138
3	1	2	111	135	137	138	151	137
3	1	5	204	210	219	227	213	228
3	1	8	103	97	106	111	149	158
3	1	11	144	116	130	127	149	140

h	k	l	Nd $\|F_o\|$	Nd $\|F_c\|$	Gd $\|F_o\|$	Gd $\|F_c\|$	Yb $\|F_o\|$	Yb $\|F_c\|$
3	1	14	133	130	134	125	150	133
3	1	17	77	81	93	81	89	98
3	1	20	82	80	77	82	109	100
3	1	23	79	79	76	70		
3	1	26	110	101	114	104	125	137
3	1	29	62	53	49	38		
3	1	32	52	47				
3	1	35			53	45		
4	1	-33	44	49				
4	1	-30	82	66	66	59	62	86
4	1	-27	48	49				
4	1	-24	76	65	52	52		
4	1	-21	129	114	112	120	138	146
4	1	-18	80	71	60	69	81	95
4	1	-15	84	77	70	76	99	94
4	1	-12	97	110	111	110	115	126
4	1	-9	157	142	155	163	173	169
4	1	-6			62	61	69	75
4	1	-3	113	110	127	124	127	128
4	1	0	185	200	210	215	201	225
4	1	3	106	113	121	112	132	122
4	1	6	130	133	140	134	164	137
4	1	9	111	121	130	125	173	146
4	1	12	67	75	89	88	110	107
4	1	15	96	101	95	111	147	125
4	1	18	50	63	50	47		
4	1	21	107	109	122	111	147	125
4	1	24	72	77	74	67	106	96
4	1	27	45	40				
4	1	30	65	62	54	51	82	75
4	1	33	58	52				
5	1	-29	37	47			57	57
5	1	-26	66	61	52	48	74	78
5	1	-23	59	60	52	48	74	78
5	1	-20	56	53	55	50		
5	1	-17	60	51	53	58	129	75
5	1	-14	116	120	109	115	141	137
5	1	-11	83	91	73	77	91	102
5	1	-5	190	175	186	188	201	202
5	1	-2	84	96	70	81	103	108
5	1	1	106	103	104	120	140	147
5	1	4	91	82	88	82	109	96
5	1	7	87	73	70	74	94	99
5	1	10			66	73		
5	1	13	62	43	64	67	79	78
5	1	16	120	106	103	100	126	127
5	1	19	92	99	109	90	154	118
5	1	22			41	32		
5	1	25	55	55				
5	1	28	67	55	54	44	76	75
5	1	31	53	51	48	40		
6	1	-28	45	54				
6	1	-25	48	53	49	42	66	62
6	1	-19	74	85	75	79	104	108
6	1	-16	103	97	97	96	110	129
6	1	-13			34	34		
6	1	-10	79	82	56	75	81	89
6	1	-7	68	74	50	65	87	85
6	1	-4	112	97	102	100	121	130
6	1	-1			47	49		
6	1	2	93	103	96	103	120	133
6	1	5	112	110	102	106	132	129
6	1	8			28	28		
6	1	11	90	75	56	65		
6	1	14	140	110	117	110	157	142
6	1	17	64	54	51	50	99	85
6	1	20			41	40		
6	1	23			48	46		
6	1	26	47	57			82	69
7	1	-24	62	60	53	51		
7	1	-21	65	73	58	61	82	92
7	1	-18			39	36	79	68
7	1	-15	56	60	63	60	86	80
7	1	-12	69	63	47	57	90	73
7	1	-9	91	88	74	88	109	104
7	1	-6	59	68	49	55		
7	1	3	70	84	66	75	101	102
7	1	6	76	84	67	74	90	95
7	1	9	113	98	92	95	106	113
7	1	12	63	75	61	69	112	101
7	1	18	52	47	47	44		
7	1	21	87	73	63	65	107	89
7	1	24	54	55			72	64
8	1	-14	66	79	61	70	90	96
8	1	-11	63	71	55	67	105	93
8	1	-8	55	56	41	46	78	75
8	1	-5	87	78	58	71	104	93
8	1	-2			48	52	88	81
8	1	1	52	57	48	49		
8	1	4			53	51	96	88
8	1	7			63	84	133	119
8	1	10	59	64	52	52	83	77
8	1	16	62	66	53	51	70	72
8	1	19	75	64	59	61	82	89
8	1	25			48	41		
9	1	-13	47	44				
9	1	-10			53	50	71	87
9	1	-7	46	50	44	40	70	69
9	1	-1	45	50	45	39		
9	1	2	65	57	41	44	74	76
9	1	5	70	70	52	58	86	90
9	1	8			41	34		
9	1	11	61	56			81	68
9	1	14	52	60	46	49	75	77
10	1	0	49	63	56	51	69	82
2	2	0	163	230	216	214	188	224
2	2	3	137	158	202	183	149	195
2	2	6	118	62	98	93	95	90
2	2	9	142	143			161	166
2	2	12	114	96	81	99	121	125
2	2	15	116	115	115	114	123	127
2	2	18	65	62	57	51		
2	2	21	124	115	112	105	125	127
2	2	24	60	56	60	56	98	82
2	2	27	56	49	40	35		
2	2	30	76	77	75	67	114	99
2	2	33	48	55			68	70
3	2	-35			42	41		
3	2	-32	47	43			50	54
3	2	-29	62	56	53	44	59	68
3	2	-26	74	76	65	63	101	91
3	2	-23	64	64	61	61	82	84

h	k	l	Nd $\|F_o\|$	Nd $\|F_c\|$	Gd $\|F_o\|$	Gd $\|F_c\|$	Yb $\|F_o\|$	Yb $\|F_c\|$
3	2	-20			48	45		
3	2	-17			79	77	102	97
3	2	-14	145	148	184	150	174	179
3	2	-11	100	102	102	105	104	118
3	2	-8	94	83	74	78	97	100
3	2	-5	205	211	219	221	237	239
3	2	-2	59	29	38	38	62	56
3	2	1	126	132	150	147	135	155
3	2	4	104	98	91	93	90	101
3	2	7	89	103	113	106	118	127
3	2	10	76	79	104	85	98	99
3	2	13	98	99	103	90	101	111
3	2	16	107	105	105	97	109	122
3	2	19	112	109	128	113	120	134
3	2	22	54	59	37	37		
3	2	25	73	72	58	63	96	90
3	2	28	59	56	62	51	100	87
3	2	31	53	53				
4	2	-31	51	47				
4	2	-28	73	65	59	54	81	88
4	2	-25	81	74	66	61	89	87
4	2	-19	83	74	64	73	107	98
4	2	-16	81	85	61	62	88	81
4	2	-13	53	55	58	55		
4	2	-10	100	110	105	111	119	131
4	2	-7	122	118	125	124	140	152
4	2	-4	59	54	51	52		
4	2	-1	96	85	105	111	111	115
4	2	2	120	141	156	140	158	168
4	2	5	141	155	146	142	162	161
4	2	8	76	83	86	91	101	107
4	2	11	65	62	72	65	89	80
4	2	14	89	88	45	85	107	107
4	2	17	60	51	57	44		
4	2	20	87	79	78	73	98	99
4	2	23	58	66	59	56		
4	2	26	73	63	40	47		
4	2	29	37	46			73	67
5	2	-27	41	45				
5	2	-24	61	62	44	52	89	78
5	2	-21	88	86	71	78	113	106
5	2	-18	61	52	48	50	78	75
5	2	-15	61	72	54	53		
5	2	-12	56	66	47	50	81	79
5	2	-9	99	100	91	94	128	118
5	2	-6	65	63	65	69	77	84
5	2	-3	77	81	87	83	98	102
5	2	0	156	133	158	146	178	176
5	2	3	72	66	70	70	116	104
5	2	6	60	65	44	48		
5	2	9	123	113	108	116	152	137
5	2	12	70	61	56	59	89	73
5	2	15	91	80	83	76	98	92
5	2	18	66	53	34	40		
5	2	21	72	78	71	70	111	102
5	2	24	54	59	44	43		
5	2	27	41	44				
6	2	-26	51	50				
6	2	-23	61	62	59	51	86	80
6	2	-20	84	65	49	55	85	83
6	2	-17	58	61	46	52	94	85
6	2	-14	65	68	48	51	74	79
6	2	-11	72	74	55	60		
6	2	-8	61	56	38	42		
6	2	-5	120	126	114	127	157	151
6	2	-2	64	77	52	63	89	91
6	2	1			38	40		
6	2	4	60	46	31	45		
6	2	7	93	94	93	94	116	117
6	2	10	111	96	96	93	116	113
6	2	13	72	67	61	63	89	92
6	2	16	59	69	49	59	105	92
6	2	19	73	67	51	51		
6	2	25	78	62	52	52	81	80
7	2	-19	55	58			70	71
7	2	-16	75	64	57	50	83	78
7	2	-10	63	71	54	57	87	80
7	2	-7	78	73	63	65		
7	2	-4	93	82	57	74	81	103
7	2	-1	60	71	57	59	81	78
7	2	2	55	57	27	29		
7	2	5	101	94	88	96	125	123
7	2	8	54	52	39	37		
7	2	11	63	61	53	50		
7	2	14	79	74	72	67	105	94
7	2	20	48	50				
7	2	23	56	49				
8	2	-18					45	49
8	2	-15	61	58	56	47	65	72
8	2	-12	58	55	41	39	75	71
8	2	-9	51	58	43	48	75	76
8	2	-3	54	55	41	39		
8	2	0	84	78	72	64	120	112
8	2	3	59	58	43	44	81	66
8	2	6	53	47	39	36		
8	2	9	68	60	43	48	82	79
8	2	12	69	58	45	43	82	72
8	2	15	56	56	48	42		
9	2	-11					51	65
9	2	-8	46	37				
9	2	-5	50	58			76	69
9	2	-2	51	51			56	66
9	2	1	46	55			61	70
9	2	4	46	48				
9	2	7	47	57				
9	2	10	57	54			67	73
3	3	0	218	230	255	222	215	254
3	3	6	96	106	112	114	113	133
3	3	9	131	126	133	111	120	134
3	3	12	91	95	104	94	112	111
3	3	15	60	57	60	63	87	81
3	3	18	71	66	54	55	83	78
3	3	21	105	99	80	91	112	120
3	3	24	65	69	60	59	95	84
3	3	27	47	45				
3	3	30	62	61			73	71
4	3	-29	41	50			60	58
4	3	-26	80	69	78	64	98	92
4	3	-23	73	65	62	56	90	89
4	3	-20	95	76	87	77	96	97
4	3	-17	44	41				
4	3	-14	114	121	115	129	165	152

Table 4. Continued.



to locate the hydrogen atoms in the structure from the intensity data available. The ultimate atomic parameters are given in Table 2 together with their estimated standard deviations.[5] No attempt was made to determine the absolute configuration.

The refinements of the neodymium and gadolinium structures were then commenced using the final atomic parameters of the ytterbium structure. The weighting scheme for the neodymium structure was

$$w = 1/(60 + |F_o| + 0.0050|F_o|^2 + 0.0001|F_o|^3)$$

and for the gadolinium structure

$$w = 1/(75 + |F_o| + 0.0045|F_o|^2 + 0.0001|F_o|^3)$$

After four cycles of refinement the R value of the neodymium structure had been reduced to 0.100. Four more cycles reduced the shifts in all the parameters to less than 0.1 % of the estimated standard deviations without changing the R value further. The final R value of 0.089 for the gadolinium compound was reached after three cycles and five more cycles reduced the shifts to less than 0.01 % of the estimated standard deviations. Table 2 shows the final atomic parameters for both structures with their estimated standard deviations.

The weighting schemes were analysed for constancy of the average values of $w(|F_o|-|F_c|)^2$ between different intervals of the $|F_o|$ and sin θ values.[5] The analysis obtained in the last cycle of refinement for each structure is shown in Table 3. The weighting schemes seem as good as can be expected.

The atomic scattering factors used in the calculations were those for Na^+, Cl, O, and C given in the *International Tables*.[6] Those given by Cromer *et al.*,[7] corrected for anomalous dispersion,[8] were used for the lanthanoid atoms. Observed and calculated structure factors for the three structures are com-

Table 5. Selected interatomic distances (in Å) with estimated standard deviations in the structures of $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=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
$Na^+(1)$–2O(3)	2.54±0.02	2.49±0.02	2.45±0.02
$Na^+(1)$–2O(4)	2.40±0.04	2.46±0.02	2.46±0.03
$Na^+(1)$–2O(6)	2.18±0.03	2.30±0.01	2.29±0.02
$Na^+(2)$–3O(3)	2.40±0.02	2.40±0.02	2.46±0.02
$Na^+(2)$–3O(6)	2.50±0.03	2.47±0.02	2.47±0.02
$Na^+(1)$–2$Na^+(2)$	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 $Na_3[M(OCOCH_2OCH_2OCO)_3]_4\cdot 2NaClO_4\cdot 6H_2O$, M=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 $Na^+(2)$ lie on threefold axes while the sodium ions $Na^+(1)$ 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 $Na_3[M(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$, 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

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

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

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

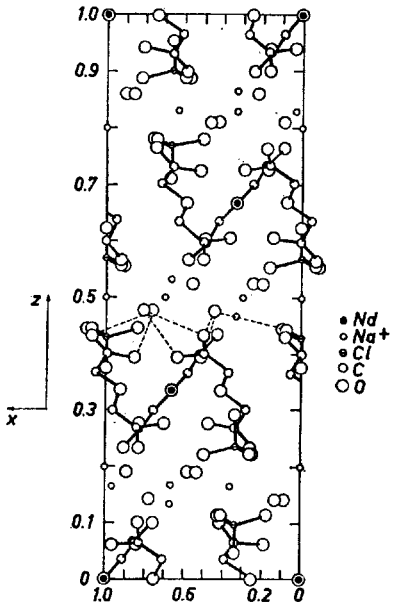


Fig. 3. The unit cell of $Na_3[Nd(OCOCH_2OCH_2OCO)_3]\cdot 2NaClO_4\cdot 6H_2O$ projected on (010). Possible hydrogen bonds are dotted.

on them. The symmetry of the complex is 32. The structure of $[Yb(OCOCH_2OCH_2OCO)_3]^{3-}$ 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 $[Nd(H_2O)_9]^{3+}$ complex in $[Nd(H_2O)_9](BrO_3)_3$ 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

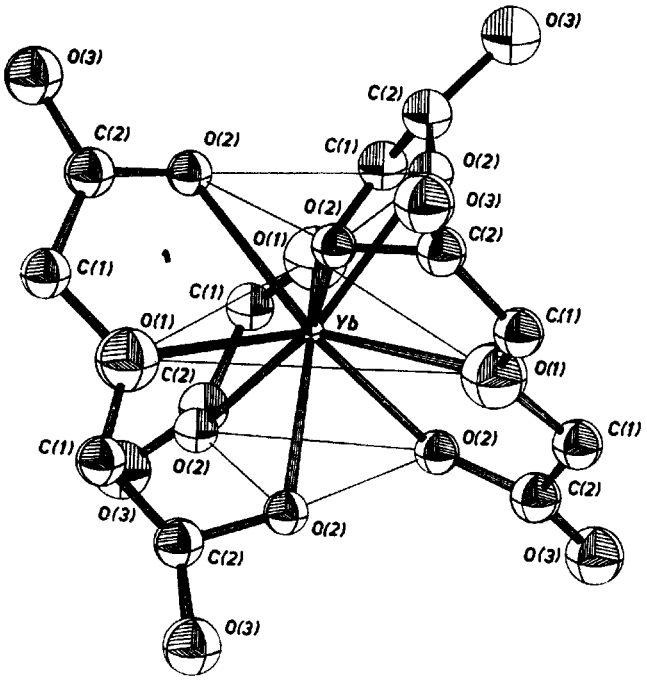


Fig. 4. The molecular structure of $[Yb(OCOCH_2OCH_2OCO)_3]^{3-}$, drawn by the programme ORTEP.[3] The atoms are represented by "thermal spheres" formally scaled to include 50 % of the probability distribution.

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

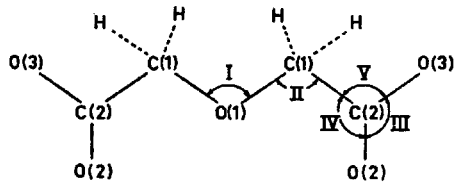


Fig. 5. Designation of atoms and angles in the oxydiacetate ion.

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 PLANE [3]) 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 Cu$K\alpha$ radiation for the neodymium and ytterbium compounds, while Mo$K\alpha$ 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 Cu$K\alpha$ 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-

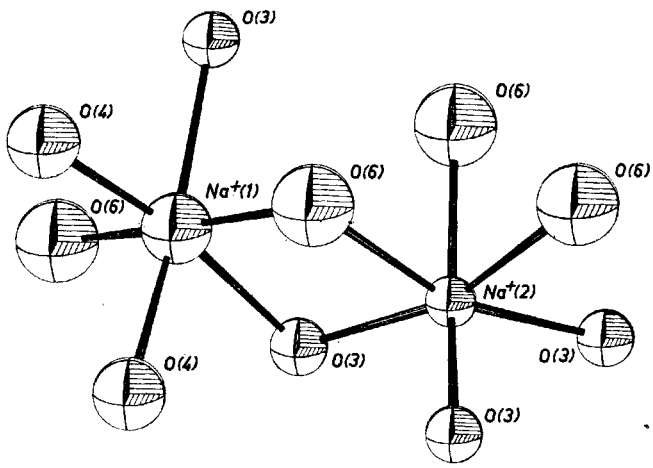


Fig. 6. The coordination around the sodium ions in the neodymium structure, drawn by the programme ORTEP.[3] The atoms are represented as in Fig. 4.

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 $Na^+(1)-O(6)$ distance is always shorter than the distances between $Na^+(1)-O(3)$ and $Na^+(1)-O(4)$. In the neodymium structure it is very short, 2.18 ± 0.03 Å. In each structure, $Na^+(2)$ 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 $Na^+(1)$, 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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