

## Structural Studies on the Rare Earth Carboxylates

## 6. A Reinvestigation of Trisodium-tris(oxydiacetato)lanthanoidate(III)

## Di(sodium Perchlorate) Hexahydrate

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The unit cell dimensions of the isostructural series of lanthanoid oxydiacetate compounds  $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{M}=\text{Ce}-\text{Lu}$ , have been determined using powder photographs obtained with a Guinier focusing camera. The crystals are trigonal with the space group (No. 155) and with  $Z=3$ . Between the cerium and lutetium compounds the value of  $a$  decreases from  $9.8117 \pm 0.0027 \text{ \AA}$  to  $9.6787 \pm 0.0015 \text{ \AA}$  while the value of  $c$  decreases from  $28.410 \pm 0.013 \text{ \AA}$  to  $28.043 \pm 0.006 \text{ \AA}$ . The previously determined atomic parameters of the neodymium and ytterbium compounds have been refined by least-squares methods using three-dimensional X-ray intensity data newly collected with an automatic single crystal diffractometer. The coordination polyhedron around the nine-coordinated lanthanoid ion is found to decrease  $0.133 \pm 0.015 \text{ \AA}$  along the  $c$  axis and  $0.137 \pm 0.018 \text{ \AA}$  along the  $a$  and  $b$  axes between the neodymium and ytterbium compounds. The contraction thus imposed on the unit cell dimensions is obstructed through the whole series by the other parts of the structure. For the heaviest lanthanoid ions this trend is reenforced by van der Waals contacts between the oxygen atoms coordinated to the lanthanoid ion.

The structure of the isomorphous neodymium, gadolinium, and ytterbium oxydiacetate (or diglycolate) compounds of the composition trisodium-tris(oxydiacetato)lanthanoidate(III) di(sodium perchlorate) hexahydrate, *i.e.*,  $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ , has previously been determined by the present author<sup>1</sup> from three-dimensional intensity data recorded with the Weissenberg multiple film technique. Although the general features of the structure were obtained, the main purpose of that investigation was not reached: the dimensions of the coordination polyhedron around the lanthanoid ions could not be determined accurately enough to reveal the expected decrease in the order  $\text{Nd} > \text{Gd} > \text{Yb}$ . To get more accurate  $\text{M}-\text{O}$  and  $\text{O}-\text{O}$  distances than the "photographic" ones, the neodymium and ytterbium compounds,

referred to as NDG and YDG below, have been reinvestigated with an automatic single crystal diffractometer.

All lanthanoid compounds of the composition stated above have the same structure. The second aim of the present investigation is to study the variation of the unit cell dimensions in this isostructural series as a function of the crystal radius of the trivalent lanthanoid ion and to correlate the results with the now obtained single crystal measurements.

### EXPERIMENTAL

*Single crystal work.* The compounds were prepared from the appropriate lanthanoid perchlorates and sodium oxydiacetate as described before.<sup>1</sup> Single crystals of NDG and YDG were mounted along their *b* axes and preliminary Weissenberg photographs were taken with  $\text{CuK}\alpha$  radiation. The samples chosen for further investigation had a stout prismatic habit with the approximate dimensions  $0.1 \times 0.2 \times 0.1 \text{ mm}^3$  and  $0.2 \times 0.4 \times 0.2 \text{ mm}^3$  for NDG and YDG, respectively. They were elongated in the *b* direction.

The intensity data were collected with an automatic single crystal diffractometer of type PAILRED using  $\text{MoK}\alpha$  radiation. The take-off angle was  $6^\circ$ . The radiation was made monochromatic by reflexion from the (200) plane of a lithium fluoride crystal. The data were collected by the equi-inclination and  $\omega$  scan techniques. The scan rate was  $1^\circ/\text{min}$  for  $3^\circ$  scan ranges. Stationary background counts,  $B_1$  and  $B_2$ , of 1 min were taken at each end of the scan interval. All measured backgrounds fulfilled the condition  $0.5 < B_1/B_2 < 2.0$ . A counter aperture size of  $2^\circ$  was used. Coincidence losses were negligible and the pulse height discrimination levels were set for approximately a 90% window centered on the  $\text{MoK}\alpha$  peak. As a check an electronic stability during the period of data collection the intensities of standard reflexions were measured at regular intervals. No systematic change in these standards was observed.

The intensities of all independent reflexions within the copper sphere ( $\sin \theta < 0.4610$ ) were measured. The total number of independent reflexions collected was 698 for NDG and 683 for YDG. The corrected integrated peak counts  $I$  were calculated from the eqn.

$$I = C - t_c(B_1 + B_2)/2t_b$$

where  $C$  is the total integrated peak count obtained in time  $t_c$ , and  $t_b$  is the time for each of the background counts. The corrected intensities were assigned standard deviations according to the formula

$$\sigma(I) = [C + t_c^2(B_1 + B_2)/4t_b^2 + (kI)^2]^{1/2}$$

The value of  $k$  was selected as 0.03. The effect of the term  $(kI)^2$  is to weight down strong reflexions.

The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz, polarization, and absorption factors. The linear absorption coefficient  $\mu$  is  $20.2 \text{ cm}^{-1}$  for NDG and  $34.2 \text{ cm}^{-1}$  for YDG. The transmission coefficients, evaluated by numerical integration,<sup>2</sup> were found to range from 0.83 to 0.88 for the sample of NDG and from 0.52 to 0.59 for the sample of YDG. No corrections for extinction effects were applied.

*Powder work.* Powder photographs were taken at  $20^\circ\text{C}$  with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in a Guinier focusing camera. Lead nitrate (cubic,  $a = 7.8568 \text{ \AA}$ ) was used as an internal standard. A scale graduated in 0.1 mm was photographed on the films before their processing. All lanthanoid oxydiacetates except the promethium compound were investigated. The intensities of the powder reflexions were measured for the neodymium compound with a commercial Philips diffractometer using Ni-filtered Cu radiation.

### THE REFINEMENT OF THE STRUCTURE

The isostructural lanthanoid oxydiacetate compounds crystallize in the trigonal space group  $R\bar{3}2$ .<sup>2</sup> The general positions of this space group are

eighteenfold. The structure contains twelve independent nonhydrogen atoms. Their positional and thermal parameters in NDG and YDG were improved by fullmatrix least-squares refinements. The initial values were taken from Ref. 1. In the function minimized

$$\sum w(|F_o| - |F_c|)^2$$

only reflexions with  $0.80 \leq |F_o|/|F_c| \leq 1.25$  were included. The following weighting schemes, chosen according to Hughes,<sup>3</sup> were applied in the preliminary refinements

$$1/\sqrt{w} = (A \text{ if } |F_o| \leq A, \text{ else } |F_o|)$$

with  $A = 100$  for NDG and  $120$  for YDG.

The atomic scattering factors used in the calculations were those for C, N, O, Na, and Cl given in *International Tables*.<sup>4</sup> Those given by Cromer *et al.*<sup>5</sup> were used for the lanthanoid atoms. The scattering factors of the lanthanoid, chlorine, and sodium atoms were corrected for anomalous dispersion using the corrections  $\Delta f'$  and  $\Delta f''$  tabulated by Cromer.<sup>6</sup>

The convergence of the refinements was followed by the usual discrepancy indices

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$wR = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Reflexions assigned zero weight are included in the calculation of  $R$ .

There are two possible absolute configurations of NDG and YDG. They are related, *e.g.*, by a mirror plane at  $x - 2y = 0$ . With one of them the following three cases were refined for both compounds.

- (a) All atoms have isotropic temperature factors.
- (b) Only the lanthanoid atom has an anisotropic temperature factor.
- (c) All atoms have anisotropic temperature factors.

These refinements converged to the following discrepancy indices for NDG

	(a)	(b)	(c)
$R$	0.0761	0.0674	0.0587
$wR$	0.0682	0.0610	0.0536

It thus seems reasonable to assign anisotropic temperature factors to all non-hydrogen atoms. Since the other absolute configuration of NDG converged to  $R(c) = 0.0676$  and  $wR(c) = 0.0591$  the first one tried is most probably correct if no systematic errors are present and the weighting scheme is correctly chosen. As mentioned below (p. 3530) it is doubtful if these conditions are obeyed but the first tried configuration of NDG was used for further work.

The weighting scheme was changed to  $w = 1/\sigma^2(|F_o|)$  for reflexions obeying the conditions  $I > 3\sigma(I)$  and  $0.80 \leq |F_o|/|F_c| \leq 1.25$ , other reflexions were given zero weights. Three more cycles of least-squares refinement resulted in  $R(c) = 0.0613$  and  $wR(c) = 0.0450$ . The shifts in the parameters were less than 1% of the estimated standard deviations in the last cycle. A three-dimensional difference synthesis showed only a slowly varying background, the highest

peak being about  $0.7 \text{ e}/\text{\AA}^3$ . It was not possible to locate the hydrogen atoms in the structure.

The same absolute configuration of YDG as the one chosen for NDG converged to the following discrepancy indices in the refinements (a)–(c)

	(a)	(b)	(c)
$R$	0.0697	0.0667	0.0590
$wR$	0.0645	0.0623	0.0540

Anisotropic temperature factors were assigned to all non-hydrogen atoms in YDG too. The other possible configuration converged to  $R(a)=0.0842$ ,  $wR(a)=0.0756$  and, consequently, the first one tried was used for further work. Three more cycles of least-squares refinements with the weighting scheme changed as for NDG gave  $R(c)=0.0593$ ,  $wR(c)=0.0536$ . After the last cycle the shifts in the parameters were less than 1 % of the estimated standard deviations.

Of the 25 reflexions given zero weights in the last cycle of the refinement of YDG only 2 had  $I \leq 3\sigma(I)$ . Due to the small volume of the crystal of NDG, 87 reflexions had  $I \leq 3\sigma(I)$ , while a total of 109 were given zero weights. None of the applied weighting schemes seemed to be appropriate; strong reflexions were given too heavy weights. This incorrect weighting might have resulted in somewhat low values of the estimated standard deviations, *e.g.*, in the interatomic distances and angles.

The ultimate positional parameters with estimated standard deviations for all non-hydrogen atoms in NDG and YDG are given in Table 1, and the thermal parameters together with the root-mean-square components along principal axes of the ellipsoids of thermal vibration are given in Table 2. Observed and calculated structure factors are compared in Table 3.

All computations were performed on the CD 3600 computer in Uppsala, Sweden, using the programs PELLE (a program for correction of PAILRED data <sup>7</sup>), DRF, DATAP2, LALS, DISTAN, ORFFE, ORTEP, and PLANE.<sup>8</sup>

Table 1. Positional parameters with estimated standard deviations in NDG and YDG. The space group is  $R32$  (No. 155).<sup>3</sup>

Atom	M=Nd			M <sub>2</sub> =Yb		
	$x$	$y$	$z$	$x$	$y$	$z$
M	0	0	0	0	0	0
Na(1)	0.0354 (8)	0.3687 (8)	1/6	0.0373 (7)	0.3707 (7)	1/6
Na(2)	0	0	0.2000(2)	0	0	0.2018(2)
O(1)	-0.2580(10)	0	0	-0.2511 (9)	0	0
O(2)	-0.0337 (8)	0.1595 (7)	0.0595(2)	-0.0234 (7)	0.1615 (7)	0.0577(2)
O(3)	-0.1706 (8)	0.2460 (8)	0.1009(2)	-0.1549 (8)	0.2542 (9)	0.0993(2)
O(4)	0.1736 (9)	0.5961(21)	0.1131(3)	0.1723(11)	0.6009(23)	0.1127(3)
O(5)	1/3	2/3	0.0455(4)	1/3	2/3	0.0452(4)
O(6)	0.1403 (9)	0.2179 (9)	0.1420(2)	0.1466 (8)	0.2195(10)	0.1426(2)
C(1)	-0.2946(13)	0.0926(13)	0.0324(3)	-0.2818(12)	0.0959(12)	0.0316(3)
C(2)	-0.1486(24)	0.1775(24)	0.0656(2)	-0.1425(17)	0.1791(17)	0.0650(3)
Cl	1/3	2/3	0.0956(1)	1/3	2/3	0.0952(1)

Table 2. Anisotropic temperature factor parameters  $\beta_{ij} \times 10^4$  with estimated standard deviations. The expression used is  $\exp[-(h^2\beta_{11} + hk\beta_{12} + \dots)]$ . Root-mean-square components  $R_i$  along principal axes of the ellipsoids of thermal vibration calculated from the values of  $\beta_{ij}$  are also given.

## A. NDG

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1/\text{\AA}$	$R_2/\text{\AA}$	$R_3/\text{\AA}$
Nd	50 (1)	50 (1)	3(1)	50 (1)	0	0	0.110	0.135	0.135
Na(1)	162(10)	162(10)	17(1)	218(22)	5(3)	-5 (3)	0.192	0.256	0.266
Na(2)	94 (5)	94 (5)	7(1)	94 (5)	0	0	0.169	0.185	0.185
O(1)	88(12)	123(27)	6(1)	123(27)	-11(4)	-22 (8)	0.133	0.167	0.227
O(2)	88(11)	95(11)	6(1)	90(18)	6(5)	-13 (5)	0.136	0.180	0.211
O(3)	128(16)	147(18)	10(1)	139(31)	17(5)	-22 (6)	0.142	0.222	0.266
O(4)	121(12)	208(28)	22(1)	167(48)	26(7)	19(16)	0.194	0.272	0.312
O(5)	298(21)	298(21)	11(2)	298(21)	0	0	0.212	0.329	0.329
O(6)	109(18)	169(13)	10(1)	178(21)	-2(5)	-14 (6)	0.169	0.198	0.253
C(1)	101(18)	111(18)	10(1)	99(31)	-2(8)	-25 (8)	0.158	0.192	0.239
C(2)	99(33)	28(18)	7(1)	40(41)	9(9)	-7 (8)	0.094	0.158	0.215
Cl	124 (4)	124 (4)	8(1)	124 (4)	0	0	0.180	0.212	0.212

## B. YDG

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$R_1/\text{\AA}$	$R_2/\text{\AA}$	$R_3/\text{\AA}$
Yb	37 (1)	37 (1)	2(0)	37 (1)	0	0	0.089	0.114	0.114
Na(1)	123 (8)	123 (8)	11(1)	164(17)	1(2)	-1 (2)	0.173	0.210	0.221
Na(2)	77 (5)	77 (5)	7(1)	77 (5)	0	0	0.165	0.167	0.167
O(1)	67 (9)	61(19)	3(1)	61(19)	-5(3)	-10 (6)	0.096	0.155	0.158
O(2)	61 (9)	74 (9)	5(1)	74(15)	-6(4)	12 (4)	0.124	0.142	0.176
O(3)	94(10)	110(11)	7(1)	119(17)	-4(4)	-26 (4)	0.121	0.179	0.224
O(4)	100(11)	139(21)	18(1)	100(29)	21(6)	16(11)	0.179	0.231	0.276
O(5)	289(22)	289(22)	5(1)	289(22)	0	0	0.141	0.320	0.320
O(6)	99(13)	140(13)	6(1)	141(18)	3(5)	-8 (5)	0.142	0.182	0.225
C(1)	73(13)	102(15)	9(1)	122(24)	-18(7)	-36 (7)	0.108	0.139	0.243
C(2)	62(22)	54(20)	4(1)	64(40)	10(6)	-11 (6)	0.106	0.136	0.162
Cl	96 (3)	96 (3)	7(1)	96 (3)	0	0	0.167	0.185	0.185

## DISCUSSION OF THE STRUCTURE

An outline of the structure was given in Ref. 1. In this section the result of the present investigation and that of Ref. 1 are compared and the differences between NDG and YDG are discussed. Some symmetry-related sites in the structure are designated below by superscripts (i)–(vi) in the following way:

$$\begin{array}{lll}
 \text{(i)} & x-y, \bar{y}, \bar{z} & \text{(ii)} \quad \bar{y}, x-y, z & \text{(iii)} \quad y, x, \bar{z} \\
 \text{(iv)} & y-x, \bar{x}, z & \text{(v)} \quad \bar{x}, y-x, \bar{z} & \text{(vi)} \quad 1-y, 1+x-y, z
 \end{array}$$

where  $x, y, z$  are the coordinates of the "crystal-chemical" unit given in Table 1. Selected interatomic distances and angles with estimated standard deviations are given in Table 4.

Table 3. Observed and calculated structure factors for the isostructural compounds NDG and YDG.

NDG				YDG				NDG				YDG				NDG				YDG				NDG				YDG																													
h	k	l	F <sub>o</sub>	F <sub>c</sub>	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	F <sub>o</sub>	F <sub>c</sub>																							
10	0	-14	84	53	87	85	4	0	22	68	66	91	92	9	-1	-24	56	67	86	94	3	-1	-20	50	51	58	59	10	0	-11	36	32	53	51	4	0	25	92	92	115	119	8	-1	-21	81	77	100	103	3	-1	-23	113	111	141	144		
10	0	-11	36	32	53	51	4	0	22	77	76	107	111	8	-1	-19	40	44	64	66	3	-1	-26	96	99	114	117	10	0	-6	76	91	91	91	4	0	31	53	49	58	62	8	-1	-15	64	66	88	88	3	-1	-29	73	75	99	104		
10	0	-6	76	91	91	91	4	0	34	44	50			8	-1	-12	79	75	96	94	3	-1	-32	50	56	73	75	10	0	-1	72	67	123	124	4	0	34	44	50			8	-1	-12	79	75	96	94	3	-1	-32	50	56	73	75		
10	0	-1	72	67	123	124	4	0	31	53	49	58	62	8	-1	-9	96	102	130	130	3	-1	-35	61	60	69	75	10	0	1	37	73	47	51	3	0	24	62	59	90	80	8	-1	-9	96	102	130	130	3	-1	-35	61	60	69	75		
10	0	1	37	73	47	51	3	0	30	75	71	125	97	8	-1	-6	63	62	85	82	2	-1	-36	45	43	84	83	10	0	4	55	51	79	82	3	0	24	75	71	125	97	8	-1	-6	63	62	85	82	2	-1	-36	45	43	84	83		
10	0	4	55	51	79	82	3	0	18	139	131	169	164	8	-1	-3	64	65	91	91	2	-1	-33	68	61	84	82	10	0	10	71	65	92	87	3	0	24	139	131	169	164	8	-1	-3	64	65	91	91	2	-1	-33	68	61	84	82		
10	0	10	71	65	92	87	3	0	15	14	26	43	42	8	-1	9	114	117	144	145	2	-1	-21	157	155	178	181	10	0	13	81	75	99	92	3	0	21	109	110	134	125	8	-1	9	114	117	144	145	2	-1	-21	157	155	178	181		
10	0	13	81	75	99	92	3	0	12	87	99	132	138	8	-1	12	71	75	109	108	2	-1	-18	82	82	111	110	10	0	18	94	88	111	104	3	0	12	87	99	132	138	8	-1	12	71	75	109	108	2	-1	-18	82	82	111	110		
10	0	18	94	88	111	104	3	0	8	81	77	112	113	8	-1	15	27	37	54	57	2	-1	-15	136	138	157	164	10	0	21	108	102	129	124	4	0	8	81	77	112	113	8	-1	15	27	37	54	57	2	-1	-15	136	138	157	164		
10	0	21	108	102	129	124	4	0	6	356	364	346	359	8	-1	18	50	53	72	74	2	-1	-12	74	71	88	87	10	0	21	85	79	103	97	3	0	6	356	364	346	359	8	-1	18	50	53	72	74	2	-1	-12	74	71	88	87		
10	0	21	85	79	103	97	3	0	3	16	21	43	44	8	-1	21	86	84	103	104	2	-1	-9	236	237	246	272	10	0	21	85	79	103	97	3	0	3	16	21	43	44	8	-1	21	86	84	103	104	2	-1	-9	236	237	246	272		
10	0	21	85	79	103	97	3	0	3	240	228	262	251	7	-1	24	106	107	138	138	2	-1	-12	82	82	111	110	10	0	21	85	79	103	97	3	0	3	240	228	262	251	7	-1	24	106	107	138	138	2	-1	-12	82	82	111	110		
10	0	21	85	79	103	97	3	0	-3	16	21	43	44	7	-1	26	64	63	80	83	2	-1	0	247	258	255	292	10	0	21	85	79	103	97	3	0	-3	16	21	43	44	8	-1	26	64	63	80	83	2	-1	0	247	258	255	292		
10	0	-3	16	21	43	44	8	-1	0	-18	20	28	205	207	7	-1	14	123	128	174	166	11	-2	-11	46	48	63	62	10	0	-3	16	21	43	44	8	-1	0	-18	20	28	205	207	7	-1	14	123	128	174	166	11	-2	-11	46	48	63	62
10	0	-18	20	28	205	207	7	-1	15	73	67	95	91	7	-1	-7	54	65	92	95	11	-2	-8	26	27	42	48	10	0	-12	75	69	93	3	0	15	73	67	95	91	7	-1	-7	54	65	92	95	11	-2	-8	26	27	42	48			
10	0	-12	75	69	93	3	0	-15	73	67	95	91	7	-1	-7	54	65	92	95	11	-2	-8	26	27	42	48	10	0	-12	75	69	93	3	0	-15	73	67	95	91	7	-1	-7	54	65	92	95	11	-2	-8	26	27	42	48				
10	0	-15	73	67	95	91	7	-1	-11	78	87	93	92	7	-1	8	24	27	36	38	11	-2	1	54	52	70	73	10	0	-21	84	81	3	0	-24	144	145	179	181	7	-1	8	24	27	36	38	11	-2	1	54	52	70	73				
10	0	-21	84	81	3	0	-24	144	145	179	181	7	-1	8	24	27	36	38	11	-2	1	54	52	70	73	10	0	-21	84	81	3	0	-24	144	145	179	181	7	-1	8	24	27	36	38	11	-2	1	54	52	70	73						
10	0	-24	144	145	179	181	7	-1	2	101	105	140	136	11	-2	1	101	105	140	136	11	-2	1	44	41	44	43	10	0	-25	83	74	88	8	0	-22	38	36	111	110	11	-2	1	101	105	140	136	11	-2	1	44	41	44	43			
10	0	-25	83	74	88	8	0	-33	44	41	44	43	11	-2	1	-1	-1	47	50	72	72	11	-2	10	57	53	79	83	10	0	-19	58	50	81	81	3	0	-33	44	41	44	43	11	-2	1	-1	-1	47	50	72	72						
10	0	-19	58	50	81	81	3	0	-34	44	41	43	11	-2	1	-4	114	144	141	11	-2	1	13	13	13	13	10	0	-16	72	68	80	86	2	0	-16	72	68	80	86	2	0	-16	72	68	80	86	2	0	-16	72	68	80	86			
10	0	-16	72	68	80	86	2	0	-34	44	41	43	11	-2	1	-4	114	144	141	11	-2	1	13	13	13	13	10	0	-16	72	68	80	86	2	0	-16	72	68	80	86	2	0	-16	72	68	80	86	2	0	-16	72	68	80	86			
10	0	-13	75	69	93	3	0	-28	89	93	165	121	7	-1	-10	85	80	104	97	10	-2	15	59	58	78	71	10	0	-13	75	69	93	3	0	-28	89	93	165	121	7	-1	-10	85	80	104	97	10	-2	15	59	58	78	71				
10	0	-28	89	93	165	121	7	-1	-25	128	132	150	149	7	-1	-10	36	46	59	60	10	-2	12	63	56	84	75	10	0	-7	82	83	104	105	2	0	-25	128	132	150	149	7	-1	-10	36	46	59	60	10	-2	12	63	56	84	75		
10	0	-7	82	83	104	105	2	0	-25	128	132	150	149	7	-1	-10	36	46	59	60	10	-2	12	63	56	84	75	10	0	-7	82	83	104	105	2	0	-25	128	132	150	149	7	-1	-10	36	46	59	60	10	-2	12	63	56	84	75		
10	0	-25	128	132	150	149	7	-1	-19	87	93	133	123	7	-1	-19	94	92	123	123	10	-2	6	37	44	70	65	10	0	-1	43	42	41	85	2	0	-19	87	93	133	123	7	-1	-19	94	92	123	123	10	-2	6	37	44	70	65		
10	0	-1	43	42	41	85	2	0	-19	87	93	133	123	7	-1	-22	116	116	146	146	10	-2	3	59	62	78	75	10	0	-1	43	42	41	85	2	0	-19	87	93	133	123	7	-1	-22	116	116	146	146	10	-2	3	59	62	78	75		
10	0	2	73	70	106	106	2	0	-17	200	199	240	226	7	-1	-5	128	128	178	178	9	-2	16	59	65	77	73	10	0	2	73	70	106	106	2	0	-17	200	199	240	226	7	-1	-5	128	128	178	178	9	-2	16	59	65	77	73		
10	0	2	73	70	106	106	2	0	-13	223	224	282	269	7	-1	-20	81	81	110	110	9	-2	16	59	65	77	73	10	0	2	73	70	106	106	2	0	-13	223	224	282	269	7	-1	-20	81	81	110	110	9	-2	16	59	65	77	73		
10	0	-13	223	224	282	269	7	-1	-10	191	184	215	213	7	-1	-20	61	55	68	73	10	-2	3	48	45	60	64	10	0	2	73	70	106	106	2	0	-10	191	184	215	213	7	-1	-20	61	55	68	73	10	-2	3	48	45	60	64		
10	0	2	73	70	106	106	2	0	-7	199	211	252	238	7	-1	-29	45	44	63	65	10	-2	-6	36	33	58	57	10	0	2	73	70	106	106																							

Table 3. Continued.

h	k	NDG			YDG			h	k	l	NDG			YDG			h	k	l	NDG			YDG						
		$ F_o $	$ F_c $	$ F_d $	$ F_o $	$ F_c $	$ F_d $				$ F_o $	$ F_c $	$ F_d $	$ F_o $	$ F_c $	$ F_d $				$ F_o $	$ F_c $	$ F_d $	$ F_o $	$ F_c $	$ F_d $	$ F_o $	$ F_c $	$ F_d $	
5	-2	-33	76	72	96	96	10	-3	-2	77	76	93	93	7	-3	4	102	99	135	127	9	-4	-17	27	41	63	63		
5	-2	-20	35	34	50	49	10	-3	-5	76	77	101	101	7	-3	7	119	122	159	155	9	-4	-14	59	70	97	98		
5	-2	-17	69	72	95	94	10	-3	-8	49	54	82	85	7	-3	10	116	114	152	150	9	-4	-11	89	119	113	88		
5	-2	-14	169	163	196	190	10	-3	-11	35	42	58	56	7	-3	13	53	54	58	61	5	-4	-8	0	21	44	42		
5	-2	-11	87	87	113	115	10	-3	-14	88	79	101	105	7	-3	16	142	141	154	165	9	-4	-5	127	136	166	165		
5	-2	-8	92	90	117	115	10	-3	-17	29	38	39	45	7	-3	19	85	89	110	117	9	-4	-2	97	96	134	132		
5	-2	-5	222	221	256	261	10	-3	-20	45	47	58	62	7	-3	22	50	47	59	66	9	-4	1	56	52	80	85		
5	-2	-2	62	58	70	71	9	-3	-24	47	53	60	69	7	-3	25	56	59	62	76	9	-4	4	76	78	97	99		
5	-2	1	142	136	156	156	9	-3	-21	67	70	87	95	7	-3	28	74	73	68	102	9	-4	7	84	91	115	116		
5	-2	4	101	96	115	121	9	-3	-18	56	54	74	73	6	-3	30	76	72	19	87	9	-4	10	68	73	94	95		
5	-2	7	97	97	124	136	9	-3	-15	36	42	48	48	6	-3	27	23	36	25	53	9	-4	13	37	47	69	70		
5	-2	10	72	74	94	104	9	-3	-12	45	50	74	75	6	-3	24	83	66	76	98	9	-4	16	73	73	97	102		
5	-2	13	90	82	112	121	9	-3	-9	97	98	116	134	6	-3	21	121	125	124	137	9	-4	19	67	84	86	90		
5	-2	16	104	108	128	134	9	-3	-6	70	72	94	95	5	-3	18	59	60	81	79	9	-4	22	39	29	34	41		
5	-2	19	116	115	139	147	9	-3	-3	56	56	78	74	6	-3	15	63	56	78	78	9	-4	25	55	61	81	85		
5	-2	22	49	54	60	63	9	-3	0	104	107	146	145	6	-3	12	96	99	135	123	8	-4	19	67	84	86	90		
5	-2	25	75	78	101	99	9	-3	3	60	21	41	39	6	-3	9	121	123	167	151	8	-4	24	59	64	89	93		
5	-2	28	64	66	92	95	9	-3	6	30	37	42	43	6	-3	6	90	100	148	134	8	-4	21	72	70	88	91		
5	-2	31	52	53	64	66	9	-3	9	89	90	125	123	6	-3	3	17	19	30	26	8	-4	18	62	69	103	100		
4	-2	33	38	53	70	75	9	-3	12	87	77	100	107	6	-3	0	241	246	243	251	8	-4	15	100	96	126	127		
4	-2	36	61	62	82	85	9	-3	15	32	41	53	58	12	-4	7	51	51	70	73	8	-4	12	77	78	109	111		
4	-2	39	52	52	71	73	9	-3	18	51	49	56	62	12	-4	4	13	41	54	59	8	-4	9	108	110	152	150		
4	-2	42	65	69	93	92	9	-3	21	63	64	76	77	12	-4	1	47	50	73	72	8	-4	6	69	73	99	97		
4	-2	45	122	121	141	140	9	-3	24	53	50	60	67	12	-4	-2	43	49	72	75	8	-4	3	72	83	109	106		
4	-2	48	18	32	37	73	71	8	-3	26	72	71	80	88	12	-4	-5	80	78	110	107	8	-4	0	175	196	196		
4	-2	51	109	114	139	135	8	-3	29	65	62	82	84	12	-4	-8	30	36	60	57	12	-5	11	54	49	46	47		
4	-2	54	103	100	137	134	8	-3	32	55	49	65	65	11	-4	-15	34	46	88	66	12	-5	8	0	35	46	47		
4	-2	57	144	150	189	190	8	-3	35	45	40	65	64	11	-4	-12	51	57	82	60	12	-5	5	45	51	72	74		
4	-2	60	121	114	169	133	8	-3	38	14	119	119	149	147	11	-4	-9	61	66	81	79	12	-5	2	53	53	76	79	
4	-2	63	154	158	202	189	8	-3	41	11	125	121	147	148	11	-4	-6	59	58	71	72	12	-5	-1	33	36	83	82	
4	-2	66	205	208	264	238	8	-3	44	8	137	20	54	49	11	-4	-3	44	44	54	57	12	-5	-4	36	47	65	68	
12	-3	6	41	50	59	59	8	-3	5	108	112	148	140	11	-4	0	92	90	116	117	12	-5	-7	49	51	71	69		
12	-3	9	27	30	43	41	8	-3	8	3	26	33	33	11	-4	3	47	51	69	71	12	-5	-10	54	51	71	68		
12	-3	12	67	62	79	81	8	-3	11	58	61	94	87	11	-4	6	52	50	75	75	11	-5	-17	59	44	63	62		
12	-3	15	49	51	72	74	8	-3	14	102	105	142	135	11	-4	9	62	59	78	80	11	-5	-14	53	63	91	87		
12	-3	18	6	32	40	40	8	-3	17	7	124	125	157	146	11	-4	12	63	56	72	75	11	-5	-11	50	52	73	70	
11	-3	16	65	60	80	80	8	-3	20	10	75	75	113	105	11	-4	15	69	59	74	11	-5	-8	19	23	41	43		
11	-3	19	12	25	37	48	50	8	-3	23	11	52	48	10	-4	20	41	53	80	72	11	-5	-5	66	74	94	93		
11	-3	22	10	49	56	74	77	8	-3	26	100	98	118	120	10	-4	17	46	44	65	62	11	-5	-2	30	50	73	71	
11	-3	25	81	61	86	91	91	8	-3	29	19	92	116	121	10	-4	14	66	68	104	98	11	-5	1	47	51	65	66	
11	-3	28	55	58	69	74	74	8	-3	32	43	41	46	60	10	-4	11	60	59	77	77	11	-5	4	67	65	85	85	
11	-3	31	63	66	76	79	79	8	-3	35	25	26	61	86	10	-4	8	64	59	77	78	11	-5	7	83	86	91	89	
11	-3	34	67	64	84	87	87	8	-3	38	28	46	45	45	10	-4	5	89	86	108	104	11	-5	10	44	55	84	78	
11	-3	37	68	70	92	100	96	8	-3	41	29	44	46	27	61	10	-4	8	63	89	91	11	-5	13	48	35	53	50	
11	-3	40	29	34	51	51	51	8	-3	44	26	78	78	63	105	10	-4	-1	24	31	51	51	11	-5	16	52	60	89	84
11	-3	43	49	48	60	64	64	7	-3	47	23	89	72	78	109	10	-4	-4	53	58	85	84	10	-5	21	38	66	87	63
11	-3	46	66	70	92	100	96	7	-3	50	20	96	95	159	113	10	-4	-16	62	60	80	78	10	-5	9	66	69	80	65
10	-3	49	47	51	61	64	64	7	-3	53	17	45	39	46	45	10	-4	-10	86	79	102	99	10	-5	15	35	47	66	89
10	-3	52	16	73	73	91	92	7	-3	56	14	150	141	182	182	10	-4	-13	43	37	55	54	10	-5	12	37	47	61	65
10	-3	55	13	30	37	53	53	7	-3	59	11	132	97	133	132	10	-4	-16	62	60	80	78	10	-5	9	66	69	111	113
10	-3	58	10	56	57	82	81	7	-3	62	8	67	68	99	90	10	-4	-19	60	60	86	83	10	-5	6	40	49	60	62
10	-3	61	7	43	51	73	76	7	-3	65	-5	134	127	179	160	10	-4	-22	56	49	63	63	10	-5	3	39	51	76	79
10	-3	64	78	77	95	94	94	7	-3	68	-2	135	136	194	167	9	-4	-23	62	65	86	87	10	-5	0	80	73	104	104
10	-3	67	1	39	42	56	57	7	-3	71	3	32	36	44	38	9	-4	-20	42	49	63	66	10	-5	0	80	73	104	104

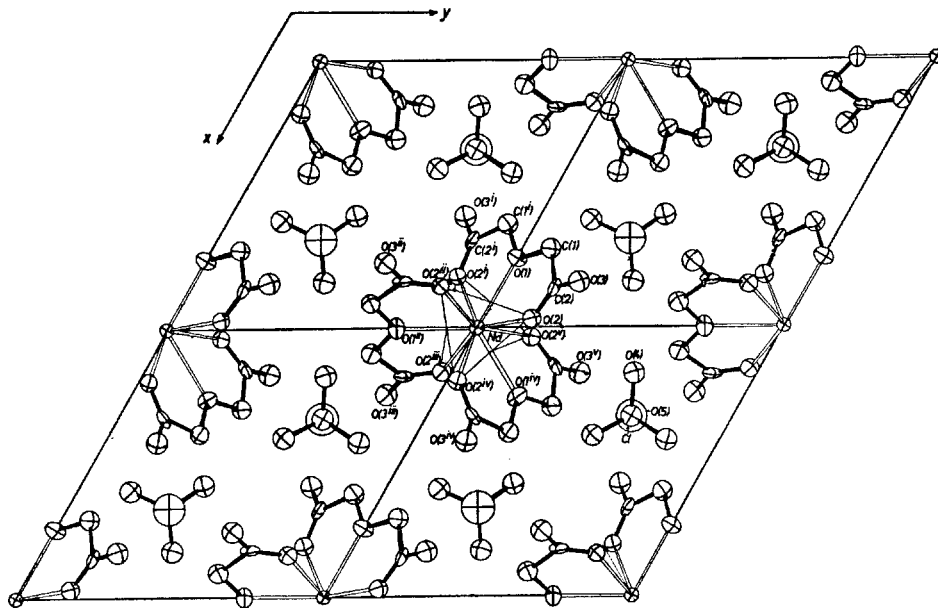


Fig. 1. A projection of NDG on (001) showing the layer around  $z=0$  containing the tris(oxydiacetato) complexes and the perchlorate ions. The figure is drawn by the program ORTEP<sup>3</sup> representing the atoms by "thermal ellipsoids" scaled to include 50 % of the probability distribution.

Table 4. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in NDG and YDG.

A. The coordination polyhedron around the lanthanoid ion.

Distance	Nd	Yb	Distance	Nd	Yb
M—O(1)	2.523(10)	2.431(9)	O(1)—O(2 <sup>ii</sup> )	3.026 (9)	2.851 (8)
M—O(2)	2.428 (6)	2.339(6)	O(2)—O(2 <sup>ii</sup> )	3.026(11)	2.924(11)
O(1)—O(2)	2.582 (8)	2.546(8)	O(2 <sup>i</sup> )—O(2 <sup>ii</sup> )	3.419(11)	3.262(11)

B. The ligand.

Distance	Nd	Yb	Angle	Nd	Yb
O(1)—C(1)	1.454(12)	1.419(11)	C(1)—O(1)—C(1 <sup>l</sup> )	112.2(1.0)	115.1(1.0)
C(1)—C(2)	1.557(20)	1.503(16)	O(1)—C(1)—C(2)	105.5(1.0)	108.3(0.9)
C(2)—O(2)	1.234(22)	1.264(16)	C(1)—C(2)—O(2)	119.8(1.2)	117.5(0.9)
C(2)—O(3)	1.281(16)	1.249(13)	C(1)—C(2)—O(3)	113.7(1.5)	118.1(1.2)
			O(2)—C(2)—O(3)	125.9(1.3)	124.3(1.0)

C. The sodium coordination.

Distance	Nd	Yb	Distance	Nd	Yb
Na(1)—O(3)	2.559 (8)	2.492 (7)	Na(1)—Na(2)	3.572(3)	3.562(3)
Na(1)—O(4)	2.463(15)	2.461(16)	Na(2)—O(3)	2.337(7)	2.390(7)
Na(1)—O(6)	2.287(10)	2.294(10)	Na(2)—O(6)	2.489(8)	2.504(8)

D. The perchlorate ion.

Distance	Nd	Yb	Angle	Nd	Yb
Cl—O(4)	1.444 (8)	1.444 (9)	O(4)—Cl—O(4 <sup>vi</sup> )	108.8(0.3)	109.1(0.4)
Cl—O(5)	1.418(12)	1.404(12)	O(4)—Cl—O(5)	110.1(0.3)	109.9(0.4)

E. Possible hydrogen bonds.

Distance	Nd	Yb	Distance	Nd	Yb
O(6)—O(2)	2.777 (9)	2.789 (8)	O(6)—O(4 <sup>vi</sup> )	3.259(19)	3.157(20)
O(6)—O(3 <sup>iv</sup> )	3.180(10)	3.150(10)	O(6)—O(2 <sup>iv</sup> )	3.147 (9)	3.193 (9)
Angle			Angle		
O(2)—O(6)—O(3 <sup>iv</sup> )	98.0(0.3)	94.8(0.3)	Na(1)—O(6)—O(4 <sup>vi</sup> )	75.5(0.3)	75.2(0.3)
O(2)—O(6)—O(4 <sup>vi</sup> )	94.8(0.3)	92.9(0.3)	Na(2)—O(6)—O(2)	111.1(0.3)	111.6(0.3)
O(2)—O(6)—O(2 <sup>iv</sup> )	61.1(0.3)	58.2(0.3)	Na(2)—O(6)—O(3 <sup>iv</sup> )	105.2(0.3)	105.1(0.3)
Na(1)—O(6)—O(2)	87.9(0.3)	88.0(0.3)	Na(2)—O(6)—O(4 <sup>vi</sup> )	152.9(0.3)	153.8(0.3)
Na(1)—O(6)—O(3 <sup>iv</sup> )	153.3(0.4)	156.3(0.4)			



The structure is composed of layers, perpendicular to the  $c$  axis, containing the mononuclear tris(oxydiacetato)lanthanoidate complexes and the perchlorate ions, Fig. 1, alternating with layers containing the sodium ions and water molecules, Fig. 2. As is seen in Table 4. A, there is a significant contrac-

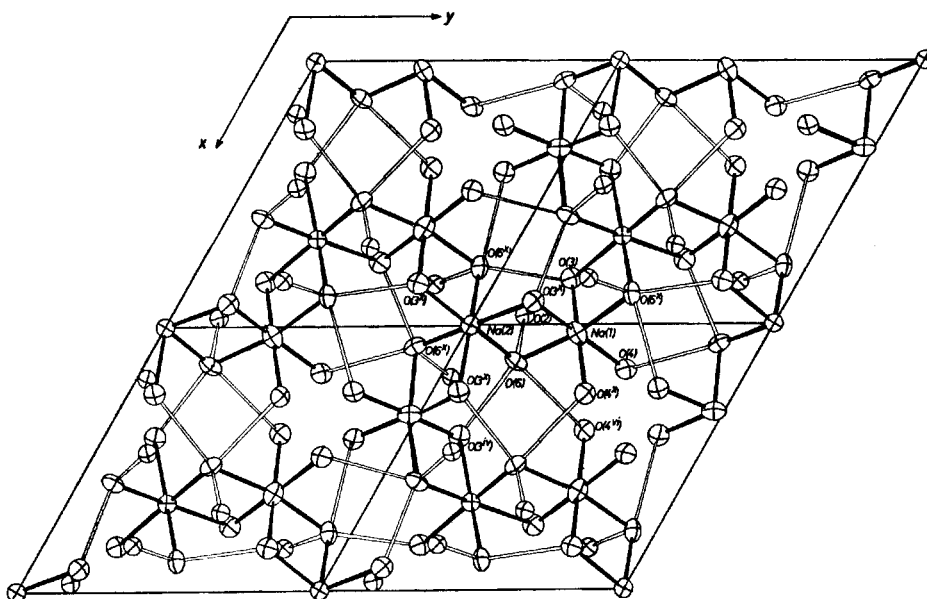


Fig. 2. A projection on (001) of the layer around  $z=1/6$  in NDG showing the coordination around the sodium ions. Possible hydrogen bond distances, including  $O(6) - O(4^{vi})$ , are represented by unfilled sticks. Some symmetry-related sites not given in the text are designated by the superscript (x). The figure is drawn as Fig. 1.

tion of the coordination polyhedron around the nine-coordinated lanthanoid ion between NDG and YDG. The smallest decrease is in the distance  $O(1) - O(2)$  where the atoms belong to the same ligand. The differences in both the  $M - O(1)$  and the  $M - O(2)$  bond distances between NDG and YDG are appreciably less than might be expected from the lanthanoid contraction (see below p. 3540). The triangular faces of the trigonal prism are rotated  $18.8 \pm 0.3^\circ$  relative to each other in NDG but this angle has decreased to  $13.3 \pm 0.3^\circ$  in YDG. On the other hand the angle between  $M - O(2)$  and the  $c$  axis is only changed from  $46.0 \pm 0.1^\circ$  to  $46.2 \pm 0.1^\circ$ . The distance between the triangular faces of the prism decreases from  $3.371 \pm 0.011 \text{ \AA}$  in NDG to  $3.238 \pm 0.011 \text{ \AA}$  in YDG.

The ligand is not much influenced by the change  $Nd - Yb$  (Table 4. B, Fig. 1). The deviations from the least-squares planes through the non-hydrogen atoms of the ligand in the two compounds are given in Table 5. The atoms are nearly coplanar. The distances and angles obtained for the ligand in the gadolinium compound were judged as the "best" set in Ref. 1. When comparing the sets obtained from NDG and YDG with each other, with the gadolinium

Table 5. The deviations (in Å) from the least-squares planes through the non-hydrogen atoms of the ligands in NDG and YDG. The lower sign refer to the superscripted atoms. O(1) and M are situated on the same twofold axis.

Atom	Nd	Yb	Atom	Nd	Yb
O(1)	0.000	0.000	O(2), O(2 <sup>i</sup> )	±0.044	±0.046
C(1), C(1 <sup>i</sup> )	±0.063	±0.074	O(3), O(3 <sup>i</sup> )	∓0.089	∓0.077
C(2), C(2 <sup>i</sup> )	±0.061	±0.035	M	0.000	0.000

set, and with the expected distances and angles<sup>1</sup> one may conclude that the ligand is slightly more distorted in NDG than in YDG.

The coordination around the sodium ions is shown in Fig. 2. The sodium-oxygen bond distances (Table 4.C) are almost the same as those given in Ref. 1. In both compounds the O–Na–O bond angles with adjacent oxygen atoms are in the range 81–107° and the twelve different oxygen–oxygen “contact” distances along the edges of the octahedra around Na(1) and Na(2) are in the range 3.24–3.99 Å.

The oxygen–chlorine bond lengths in the perchlorate ion (Table 4.D) are somewhat shorter than those given in the literature.<sup>9</sup> However, they are not corrected for thermal motion. Assuming riding motion (oxygen on chlorine) the following values were obtained

	NDG	YDG
Cl–O(4)	1.475 Å	1.468 Å
Cl–O(5)	1.462 Å	1.453 Å

These distances are in good agreement with those given in Ref. 9, and the differences between Cl–O(4) and Cl–O(5) are less than those in Table 4.D. The bond distances and bond angles are compatible with a tetrahedral perchlorate ion in both compounds.

In Table 4.E all distances less than 3.20 Å in YDG and NDG between the water oxygen atom O(6) and other oxygen atoms are listed. O(6)–O(2) is the only short distance and it has almost the same length in both compounds. Assuming a located, linear hydrogen bond between O(6) and O(2), the second hydrogen atom of O(6) may interact with O(3<sup>iv</sup>) and O(4<sup>vi</sup>) in YDG. In NDG the distance O(6)–O(4<sup>vi</sup>) might be too long, and in both compounds the angle O(2)–O(6)–O(2<sup>iv</sup>) excludes a hydrogen bond between O(6) and O(2<sup>iv</sup>). The possible hydrogen bond distances are shown in Fig. 2.

The refinements which were described in Ref. 1 converged to  $R=0.100$ , 0.089, and 0.087 for the neodymium, gadolinium, and ytterbium compounds, respectively. These values should be compared with the present ones:  $R=0.061$  for NDG and 0.059 for YDG. The estimated standard deviations are in the range 0.01–0.05 Å for distances and 1–3° for angles in the former case and are about halved in the latter. Even though the standard deviations may be somewhat low (*cf.* p. 3530), the essential aim of this investigation seems to be reached; the effect of the lanthanoid contraction on the tris(oxydiacetato)lanthanoidate group is established.

## THE VARIATION OF THE UNIT CELL DIMENSIONS

Approximate unit cell parameters were obtained from Weissenberg and oscillation photographs of the neodymium, gadolinium, and ytterbium oxydiacetate compounds. These parameters were used for a preliminary indexing of the powder photographs of the whole series of lanthanoid oxydiacetates. The unit cell dimensions were improved by least-squares treatments minimizing

$$\sum w(\sin^2\theta_o - \sin^2\theta_c)^2$$

with weights  $w = 1/\sin^2 2\theta_o$ . For each compound the powder lines were reindexed after each cycle of refinement. The final unit cell parameters and volumes with estimated standard deviations are given in Table 6. The observed values of  $\sin^2\theta$  for each compound are compared in Table 7 with those calculated in the last cycle of refinement.

Table 6. The unit cell parameters and volumes with estimated standard deviations of the trigonal compounds  $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_6)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{M} = \text{Ce} - \text{Lu}$ .

M	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
Ce	9.8117(27)	28.4099(126)	2368.6(1.3)
Pr	9.7935(15)	28.3629 (78)	2355.9(0.7)
Nd	9.7781(13)	28.3266 (56)	2345.5(0.5)
Sm	9.7510(16)	28.2687 (76)	2327.7(0.8)
Eu	9.7391(18)	28.2012 (74)	2316.5(0.9)
Gd	9.7343(17)	28.1822 (76)	2312.7(0.8)
Tb	9.7187(18)	28.1338 (73)	2301.3(0.9)
Dy	9.7092(12)	28.1423 (49)	2297.5(0.6)
Ho	9.7018(15)	28.1113 (64)	2291.5(0.7)
Er	9.6988(15)	28.0973 (60)	2288.9(0.7)
Tm	9.6940(18)	28.0759 (65)	2284.9(0.8)
Yb	9.6832(19)	28.0599 (74)	2278.5(0.9)
Lu	9.6787(15)	28.0428 (59)	2275.0(0.7)

The size of the trivalent ions is monotonously decreasing in the lanthanoid series. To prevent "rattling" of the heaviest central ions in the coordination polyhedron the size of the mononuclear tris(oxydiacetato) complex must decrease through the series (*cf.* Table 4.A) and thus influence the unit cell dimensions of the isostructural compounds.

In each unit cell of the structure there are three layers containing the tris(oxydiacetato) complexes. Since these layers are stacked along the  $c$  axis the decrease in the cell edge  $a$  through the lanthanoid series may be compared with the decrease in  $c/3$ . In Fig. 3 the quantities

$$p(\text{M}) = r(\text{Ce}) + q(\text{M}) - q(\text{Ce}) \quad (1)$$

for the different lanthanoid oxydiacetates represented by M and with  $q = a$  and  $c/3$ , respectively, are plotted *versus* the set of empirical crystal radii  $r$  for the lanthanoid ions determined by Templeton and Dauben.<sup>10</sup>

Table 7. Observed and calculated values of  $10^4 \cdot \sin^2\theta$  for the compounds  $\text{Na}_3[\text{M}(\text{C}_2\text{H}_3\text{O}_2)_6] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ . The observed powder intensities of the neodymium compound are also given.

k	l	Ce		Pr		Nd		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu		Obs	Nd		
		obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc				
0	3	66	66	67	66	67	67	67	67	67	67	67	67	67	68	67	68	67	68	68	68	67	68	67	68	68	68	3			
0	1	89	90	89	90	90	90	90	91	91	91	91	91	91	92	91	92	91	92	91	92	92	92	91	92	91	91	3			
1	2	111	112	112	112	112	113	113	113	113	113	113	114	114	114	114	114	114	114	114	114	114	115	115	115	115	115	3			
0	4	200	200	200	201	201	201	202	202	203	203	203	204	204	204	204	204	204	205	204	205	204	205	204	205	205	205	4			
0	6	247	247	248	248	248	249	249	250	250	251	251	251	252	251	252	252	252	252	252	252	252	252	252	252	254	254	254	4		
1	0	265	265	266	266	266	267	267	268	268	268	269	269	270	267	269	271	271	271	271	271	271	271	271	271	272	272	272	4		
1	5	266	266	267	267	268	268	268	269	269	269	270	270	271	271	271	271	271	271	272	272	272	272	272	272	272	273	273	4		
3	1	313	313	312	314	315	315	316	317	317	318	319	319	319	319	320	320	320	321	321	321	321	321	321	321	322	322	320	20		
2	1	335	337	339	338	339	339	340	341	341	342	344	342	344	343	344	344	344	346	344	345	346	344	345	345	346	347	346	9		
0	2	358	358	359	359	361	361	362	363	362	364	367	364	367	366	366	366	366	367	367	367	367	367	367	367	368	368	369	22		
0	7	441	443	444	445	446	446	448	448	450	450	452	450	452	452	452	452	452	455	453	453	453	453	454	454	454	455	455	24		
2	4	446	447	449	449	451	450	453	452	454	454	457	454	457	456	456	456	456	457	457	457	457	457	457	457	458	458	459	24		
1	6	461	461	462	462	463	463	464	464	465	465	466	466	467	467	467	467	468	468	468	468	468	468	468	468	469	469	470	24		
0	5	513	513	515	514	517	517	519	519	521	521	522	524	523	524	524	525	525	525	525	525	525	525	525	526	526	527	527	100		
0	9	602	598	598	598	600	600	601	602	605	606	606	606	606	606	606	606	606	607	609	610	609	610	609	610	610	611	610	3		
2	2	606	606	608	608	610	610	611	611	614	615	615	615	616	616	616	616	616	617	619	619	618	620	620	620	621	621	621	622	15	
2	7	691	690	694	692	698	694	701	698	698	700	703	703	705	703	704	704	705	705	708	705	708	707	708	707	709	708	708	709	18	
1	4	693	694	697	697	699	697	702	702	704	705	705	707	707	707	708	708	710	710	710	711	710	711	710	711	711	712	712	713	18	
0	0	740	741	741	741	743	741	747	747	752	752	752	752	756	756	756	756	756	759	759	759	759	759	759	759	762	759	762	763	18	
0	5	759	760	763	763	765	765	769	769	772	772	772	772	775	775	775	776	776	777	778	778	778	778	778	778	779	780	780	781	15	
2	3	806	807	809	810	813	813	816	817	818	819	820	820	823	823	824	824	826	825	827	826	825	827	826	825	827	828	829	10		
1	9	842	843	845	846	848	848	851	852	855	855	855	856	861	860	860	860	861	862	862	863	863	863	863	863	864	865	866	866	20	
1	7	935	937	939	940	944	943	949	948	953	953	953	954	959	958	958	958	959	959	960	960	960	960	960	961	961	962	962	23		
1	11	971	973	976	977	979	979	983	983	988	988	990	989	993	992	993	992	993	994	993	994	993	994	993	994	993	994	999	998	9	
2	0	986	988	991	991	994	995	1000	1000	1002	1002	1004	1004	1008	1007	1009	1009	1008	1010	1013	1011	1013	1012	1013	1014	1015	1014	1015	1015	4	
0	6	1004	1006	1008	1010	1011	1011	1018	1018	1020	1021	1021	1022	1024	1025	1028	1027	1026	1028	1031	1029	1031	1030	1031	1032	1033	1033	1033	1033	20	
2	8	1052	1047	1051	1051	1054	1054	1059	1059	1063	1063	1064	1067	1068	1068	1069	1070	1071	1070	1071	1071	1071	1071	1071	1071	1071	1072	1073	1073	8	
0	12	1060	1060	1064	1064	1067	1067	1071	1071	1076	1076	1077	1077	1081	1081	1081	1081	1081	1081	1081	1081	1081	1081	1081	1081	1082	1082	1083	3		
2	10	1066	1071	1069	1072	1072	1073	1077	1082	1081	1082	1083	1083	1086	1086	1087	1086	1086	1087	1088	1089	1091	1090	1091	1091	1094	1093	1092	1094	3	
3	1	1078	1077	1083	1081	1083	1085	1089	1091	1093	1096	1095	1099	1098	1101	1101	1102	1102	1103	1102	1103	1104	1107	1104	1107	1106	1106	1107	1107	3	
3	1	1099	1090	1102	1104	1107	1107	1111	1111	1115	1114	1117	1117	1121	1121	1121	1121	1121	1125	1125	1128	1128	1128	1128	1128	1129	1129	1130	1130	4	
3	4	1191	1188	1194	1192	1194	1196	1203	1202	1207	1206	1209	1207	1211	1211	1211	1211	1211	1215	1216	1216	1217	1217	1217	1220	1219	1221	1221	4		
0	11	1223	1220	1227	1224	1228	1228	1235	1233	1238	1238	1243	1240	1248	1244	1244	1244	1248	1247	1247	1248	1251	1250	1252	1251	1251	1254	1252	3		
2	6	1234	1234	1237	1239	1243	1243	1249	1249	1254	1254	1257	1257	1261	1261	1261	1261	1261	1262	1262	1263	1264	1265	1265	1265	1266	1267	1268	18		
1	12	1308	1307	1312	1313	1315	1315	1320	1321	1328	1327	1325	1329	1330	1333	1333	1333	1334	1336	1339	1337	1340	1339	1342	1341	1343	1343	1343	11		
1	10	1313	1313	1316	1317	1320	1321	1328	1327	1335	1334	1336	1336	1340	1340	1340	1340	1343	1343	1343	1343	1343	1343	1343	1343	1344	1344	1348	1348	3	
0	1	1325	1324	1333	1332	1335	1333	1341	1341	1348	1344	1342	1345	1354	1350	1350	1352	1352	1353	1356	1355	1361	1357	1361	1360	1361	1361	1361	3		
0	13	1325	1327	1331	1331	1335	1335	1340	1340	1347	1346	1348	1348	1354	1353	1353	1352	1355	1355	1359	1358	1359	1360	1361	1362	1362	1362	1362	1		
0	9	1342	1337	1344	1342	1347	1346	1353	1352	1359	1358	1360	1360	1366	1365	1364	1364	1370	1367	1367	1367	1367	1367	1367	1367	1368	1368	1368	1		
2	4	1350	1346	1354	1351	1356	1356	1363	1363	1368	1368	1368	1372	1376	1375	1375	1377	1377	1378	1378	1378	1378	1378	1378	1378	1378	1378	1378	1		
3	7	1435	1433	1438	1436	1439	1440	1445	1448	1455	1452	1456	1453	1457	1459	1460	1460	1462	1463	1463	1464	1466	1466	1467	1468	1472	1470	1470	8		
2	4	1435	1435	1440	1444	1445	1454	1452	1455	1460	1458	1463	1462	1466	1465	1467	1467	1468	1468	1469	1469	1470	1470	1470	1471	1471	1471	1474	1474	3	
1	11	1468	1467	1472	1472	1476	1476	1484	1484	1490	1490	1489	1491	1495	1496	1497	1496	1498	1499	1502	1503	1507	1505	1507	1509	1509	1509	1509	1507	10	
1	14	1525	1530	1531	1537	1535	1543	1540	1550	1548	1550	1550	1553	1556	1555	1555	1555	1559	1558	1559	1560	1561	1562	1562	1564	1564	1565	1566	5		
1	9	1540	1541	1543	1547	1551	1540	1569	1568	1608	1608	1610	1610	1615	1615	1615	1616	1620	1619	1621	1621	1622	1623	1624	1624	1624	1624	1624	1		
2	13	1574	1574	1580	1577	1581	1582	1591	1589	1597	1597	1598	1601	1608	1605	1610	1608														

Table 8. Values of  $\sqrt[3]{(V/Z)}$  for the two series of compounds  $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_6)_3] \cdot 2\text{NaClO}_3 \cdot 6\text{H}_2\text{O}$  (denoted O) and  $[\text{M}(\text{H}_2\text{O})_9](\text{BrO}_3)_3$  (B)<sup>13</sup> compared with the crystal radii ( $r$ ) of the trivalent lanthanoid ions.<sup>10</sup>

M	$\frac{\sqrt[3]{(V/Z)}/\text{\AA}}{O}$	$\frac{\sqrt[3]{(V/Z)}/\text{\AA}}{B}$	$r/\text{\AA}$	M	$\frac{\sqrt[3]{(V/Z)}/\text{\AA}}{O}$	$\frac{\sqrt[3]{(V/Z)}/\text{\AA}}{B}$	$r/\text{\AA}$
Ce	9.242	7.44	1.034	Tb	9.154	7.37	0.932
Pr	9.226	7.43	1.013	Dy	9.149	7.36	0.908
Nd	9.213	7.42	0.995	Ho	9.141	7.34	0.984
Pm	—	—	0.979	Er	9.138	7.33	0.881
Sm	9.189	7.40	0.964	Tm	9.132	7.33	0.869
Eu	9.174	7.39	0.950	Yb	9.124	7.33	0.858
Gd	9.169	7.38	0.938	Lu	9.119	7.32	0.848

$\sigma \approx 0.002$  for the oxydiacetates and 0.01 for the bromates.

in the two series of compounds. Mayer and Glasner<sup>13</sup> have determined the unit cell dimensions of the lanthanoid bromates. Their data were obtained with Ni-filtered Cu radiation using a powder diffractometer. Since the decreases in  $a$  and  $c$  are rather parallel it seems reasonable to calculate values of  $\sqrt[3]{(V/Z)}$  for the bromate compounds. These values are given in Table 8 too.

The contraction of the oxydiacetate and bromate compounds are compared with the contraction of the trivalent ions Fig. 4. The quantities  $p$  of eqn. (1) with  $q = \sqrt[3]{(V/Z)}$  are plotted versus the crystal radii for both series. The oxydiacetates are divided in two groups. The decrease in  $\sqrt[3]{(V/Z)}$  is slightly less than

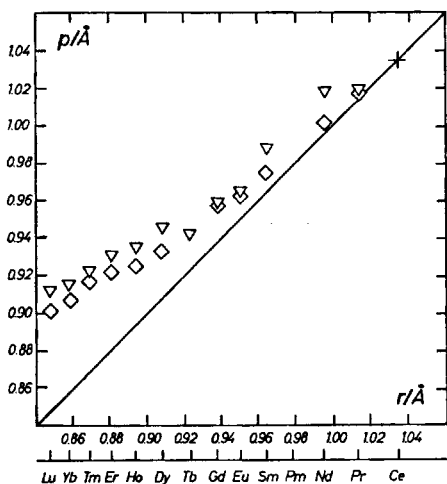


Fig. 3. Values of  $p$  of eqn. (1) with  $q = a$  (◊) and  $c/3$  (▽) plotted versus the crystal radius,  $r$ , of the trivalent lanthanoid ions. For comparison the line  $p=r$  is included.

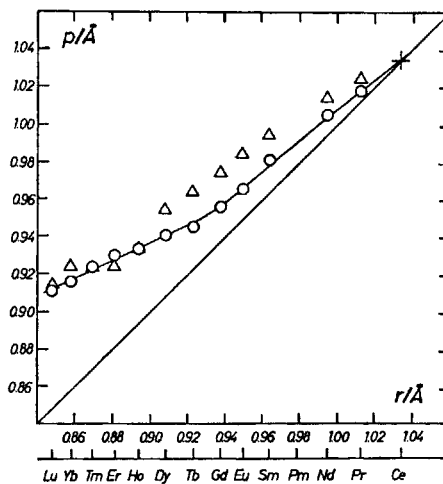


Fig. 4. Values of  $p$  with  $q = \sqrt[3]{(V/Z)}$  for the oxydiacetate (O) and bromate (Δ) compounds plotted versus  $r$ . For comparison the line  $p=r$  is included.

the decrease in crystal radius of the ions before gadolinium but is appreciably smaller than that for the heaviest ions. Taking the error in  $\sqrt[3]{(V/Z)}$  into account one might conclude that the bromates behave as the oxydiacetates.

#### THE EFFECT OF THE LANTHANOID CONTRACTION

The coordination polyhedron around the lanthanoid ion in the tris(oxydiacetato)complex shrinks  $0.133 \pm 0.015$  Å along the *c* axis and  $0.137 \pm 0.018$  Å along the *a* and *b* axes between NDG and YDG. The differences in the M–O(1) and M–O(2) bond distances are  $0.091 \pm 0.013$  Å and  $0.089 \pm 0.008$  Å, respectively. These latter values are appreciably less than the decrease in crystal radius, 0.137 Å. The distances between adjacent oxygen atoms coordinated to the lanthanoid ion but not belonging to the same ligand *i.e.* O(1)–O(2<sup>iii</sup>) and O(2)–O(2<sup>ii</sup>), have in YDG values compatible with twice the van der Waals radius of oxygen.<sup>14</sup> They are 2.851 Å and 2.924 Å, respectively. In NDG the corresponding lengths are both 3.026 Å.

In order to describe the contraction of the outer parts of the tris(oxydiacetato) complex it seems reasonable to look at the carboxylate oxygens O(3). They form a slightly irregular octahedron around the lanthanoid ion with edges in the interval 6.0–7.1 Å (see Fig. 1). The dimensions of this octahedron decrease  $0.144 \pm 0.017$  Å along the *c* axis and  $0.210 \pm 0.017$  Å along the *a* and *b* axes between NDG and YDG. The difference in the contraction of the coordination polyhedron and the O(3)-octahedron is, if real, a result of a change in the structure of the ligand between the two compounds (*cf.* p. 3535).

When the decrease in the dimensions of the complex ion is compared with the corresponding difference in  $\sqrt[3]{(V/Z)}$ ,  $0.089 \pm 0.003$  Å, it is found that the decrease in  $\sqrt[3]{(V/Z)}$  is not a direct measure of the contraction of the tris(oxydiacetato)lanthanoidate group. The layer containing the sodium ions and water molecules seems thus to partly obstruct the contraction imposed on the structure by the shrinking complex ion. This is corroborated by the distances Na(1)–Na(2), Na(1)–O(6), and Na(2)–O(6), which are almost unchanged between NDG and YDG as is seen in Table 4. C.

In view of the present single crystal measurements on NDG and YDG one may describe the trend in  $\sqrt[3]{(V/Z)}$  in the following way. With lanthanoid ions lighter than gadolinium the repulsive forces between the coordinated oxygen atoms of the tris(oxydiacetato) complex are small and the contraction of the complex ion is opposed mainly by the other parts of the structure. The trend thus imposed on  $\sqrt[3]{(V/Z)}$  is reinforced for the heaviest central ions by van der Waals repulsions between the coordinated oxygen atoms, resulting in a changed slope of  $p(M)$  in the region Gd–Dy as is seen in Fig. 4.

A further conclusion that might be reached is that the similarity between the bromate and oxydiacetate compounds shown in Fig. 4 does not necessarily depend on a similar contraction of the two coordination polyhedra through the lanthanoid series; it might as well be a result of small changes in other parts of the structure of the bromate compounds counteracting the contraction of the nona-aquo complex.

The thermodynamic data for the oxydiacetate complexes of the rare earth ions in water solution have been determined by Grenthe<sup>15</sup> and by Grenthe and

Hansson.<sup>16</sup> Their measurements indicate among other things increasing steric hindrance for the formation of the third complex with decreasing radius of the central ion. As the mononuclear tris(oxydiacetato) complexes are rather isolated and thus exposed only to weak interactions in the solid compounds  $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ , it is very probable that these complexes have almost the same structure in the solid state as in solution. Therefore, the result of the present investigation supports Grenthe and Hansson's interpretation of the thermodynamic solution data.

*Added in proof.* The unit cell dimensions of the bromate compounds  $[\text{M}(\text{H}_2\text{O})_6](\text{BrO}_3)_3$ ,  $\text{M} = \text{La} - \text{Lu}$ , have been reinvestigated using Guinier powder photographs.<sup>17</sup> It is found that  $(V/Z)^{1/3}$  is approximately a linear function of  $r$  and that the decrease in it is about 0.135 Å between the cerium and lutetium compounds.

I am indebted to Drs. Karin Aurivillius, Ingmar Grenthe, and Eva Hansson for useful discussions and valuable suggestions. I also wish to thank Professor Sture Fronæus for his kind interest and for the facilities he has put at my disposal. This work is part of a research project supported by the *Swedish Natural Science Research Council*.

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Received April 16, 1970.