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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 $Na_3[M(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=Ce–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 ± 0.0027 Å to 9.6787 ± 0.0015 Å while the value of c decreases from 28.410 ± 0.013 Å to 28.043 ± 0.006 Å. 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 ± 0.015 Å along the c axis and 0.137 ± 0.018 Å 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.*, $Na_3[M(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$, has previously been determined by the present author [1] 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 Nd>Gd>Yb. To get more accurate M–O and O–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.[1] Single crystals of NDG and YDG wer mounted along their b axes and preliminary Weissenberg photographs were taken with Cu$K\alpha$ radiation. The samples chosen for further investigation had a stout prismatic habit with the approximate dimensions $0.1 \times 0.2 \times 0.1$ mm^3 and $0.2 \times 0.4 \times 0.2$ 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 Mo$K\alpha$ radiation. The take-off angle was 6°. 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 ω scan techniques. The scan rate was 1°/min for 3° 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° was used. Coincidence losses were negligible and the pulse height discrimination levels were set for approximately a 90 % window centered on the Mo$K\alpha$ 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

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

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 μ is 20.2 cm^{-1} for NDG and 34.2 cm^{-1} for YDG. The transmission coefficients, evaluated by numerical integration, 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°C with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) in a Guinier focusing camera. Lead nitrate (cubic, $a = 7.8568$ Å) 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 $R32$.[2] 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,[3] 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*.[4] Those given by Cromer *et al.*[5] 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.[6]

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

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

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

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 nonhydrogen 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 e/Å^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 [7]), DRF, DATAP2, LALS, DISTAN, ORFFE, ORTEP, and PLANE.[8]

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

Atom	M=Nd			M=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 $\exp[-(h^2\beta_{11}+hk\beta_{12}+\cdots)]$. Root-mean-square components R_i along principal axes of the ellipsoids of thermal vibration calculated from the values of β_{ij} are also given.

A. NDG

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1/Å	R_2/Å	R_3/Å
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	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1/Å	R_2/Å	R_3/Å
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:

(i) $x-y,\bar{y},\bar{z}$ (ii) $\bar{y},x-y,z$ (iii) $y,x,\bar{z}$
(iv) $y-x,\bar{x},z$ (v) $\bar{x},y-x,\bar{z}$ (vi) $1-y,1+x-y,z$

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	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$	h	k	l	$\|F_o\|$	$\|F_c\|$	$\|F_o\|$	$\|F_c\|$
10	0	-14	54	53	87	85	4	0	22	68	66	91	92	9	-1	-24	56	67	96	94	3	-1	-20	50	51	58	58
10	0	-11	35	35	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	-8	41	37	49	47	4	0	28	77	76	107	111	8	-1	-18	40	44	64	66	3	-1	-26	96	99	114	117
10	0	-6	76	76	91	95	4	0	31	53	49	58	62	8	-1	-15	64	66	88	88	3	-1	-29	73	75	99	104
10	0	-2	72	67	83	84	4	0	34	44	50			8	-1	-12	79	75	96	94	3	-1	-32	50	56	73	75
10	0	1	37	33	47	51	3	0	33	62	59	90	88	8	-1	-9	96	102	130	130	3	-1	-35	61	60	69	75
10	0	4	55	51	79	82	3	0	30	75	71	125	97	8	-1	-6	63	62	85	82	2	-1	-36	45	43		
10	0	7	52	53	70	73	3	0	27	62	65	83	82	8	-1	-3	64	65	91	91	2	-1	-33	69	61	84	82
10	0	10	71	65	92	87	3	0	24	133	133	191	169	8	-1	0	119	119	148	149	2	-1	-30	72	74	84	83
10	0	13			21	21	3	0	21	109	110	134	125	8	-1	3	77	77	100	99	2	-1	-27	62	59	89	89
9	0	21	85	79			3	0	18	134	131	169	164	8	-1	6	78	79	97	97	2	-1	-24	84	86	114	116
9	0	18	45	43	65	65	3	0	15	14	26	43	42	8	-1	9	114	117	144	145	2	-1	-21	157	155	176	181
9	0	15	35	36	62	66	3	0	12	87	99	132	138	8	-1	12	71	75	109	108	2	-1	-18	82	82	111	110
9	0	12	61	56	83	83	3	0	9	81	77	112	113	8	-1	15	27	37	54	57	2	-1	-15	126	128	157	164
9	0	9	62	58	74	75	3	0	6	356	364	346	359	8	-1	18	50	53	72	74	2	-1	-12	74	71	88	87
9	0	6	56	59	77	79	3	0	3	16	21	43	44	8	-1	21	86	84	103	104	2	-1	-9	236	237	246	272
9	0	3	58	63	102	103	3	0	0	220	228	253	269	8	-1	24	55	58	75	78	2	-1	-6	83	75	109	106
9	0	0	73	67	89	89	3	0	-3	240	228	262	251	7	-1	29	34	43	49	50	2	-1	-3	160	157	170	187
9	0	-3	18	20	34	36	3	0	-6	62	63	91	92	7	-1	26	64	63	80	83	2	-1	0	247	258	255	298
9	0	-6	67	69	88	90	3	0	-9	175	174	206	207	7	-1	23	68	60	84	82	11	-2	-14	57	60		
9	0	-9	90	87	121	118	3	0	-12	209	207	239	235	7	-1	20	45	43	65	64	11	-2	-11	46	48	63	62
9	0	-12	75	69	96	93	3	0	-15	73	67	95	91	7	-1	17	54	65	92	95	11	-2	-8	26	27	44	48
9	0	-15	60	59	94	90	3	0	-18	38	44	76	86	7	-1	14	123	128	171	166	11	-2	-5	45	59	76	79
9	0	-18	21	27	55	56	3	0	-21	114	113	134	131	7	-1	11	78	87	93	92	11	-2	-2	47	46	62	68
9	0	-21	54	47	53	57	3	0	-24	144	145	179	181	7	-1	8	24	27	36	38	11	-2	1	54	52	70	73
8	0	-25	63	74	81	81	3	0	-27	28	29	36	39	7	-1	5	113	112	151	149	11	-2	4	44	41	54	53
8	0	-22	38	36	67	68	3	0	-30	115	111	145	140	7	-1	2	101	105	140	136	11	-2	7	53	53	73	75
8	0	-19	58	50	81	81	3	0	-33	46	55	69	70	7	-1	-1	47	50	72	72	11	-2	10	57	53	79	83
8	0	-16	72	68	87	88	2	0	-34	28	30	38	39	7	-1	-4	115	114	144	141	11	-2	13	25	38	56	61
8	0	-13	75	75	82	84	2	0	-31	51	54	75	69	7	-1	-7	75	67	98	92	10	-2	18	9	40	50	49
8	0	-10	123	124	154	155	2	0	-28	89	93	165	121	7	-1	-10	85	80	104	97	10	-2	15	59	58	78	71
8	0	-7	82	83	104	105	2	0	-25	128	132	150	149	7	-1	-13	56	44	60	59	10	-2	12	63	56	84	75
8	0	-4	55	62	88	89	2	0	-22	29	21	45	38	7	-1	-16	114	110	150	146	10	-2	9	54	58	93	87
8	0	-1	43	42	81	85	2	0	-19	87	87	133	129	7	-1	-19	94	92	123	123	10	-2	6	37	44	70	65
8	0	2	73	70	106	106	2	0	-16	200	199	240	226	7	-1	-22	16	36	44	46	10	-2	3	59	62	78	75
8	0	5	161	162	187	195	2	0	-13	22	26	51	45	7	-1	-25	48	63	76	79	10	-2	0	103	96	111	116
8	0	8	68	69	88	89	2	0	-10	191	184	215	213	7	-1	-28	61	55	68	73	10	-2	-3	48	45	60	64
8	0	11	45	46	80	82	2	0	-7	199	211	252	236	6	-1	-29	45	44	63	65	10	-2	-6	36	33	58	57
8	0	14	68	68	92	93	2	0	-4	63	68	51	43	6	-1	-26	70	71	87	88	10	-2	-9	55	53	83	83
8	0	17	41	50	60	64	2	0	-1	90	93	62	54	6	-1	-23	67	70	95	94	10	-2	-12	60	51	75	77
8	0	20	71	72	83	87	2	0	2	210	211			6	-1	-20	48	56	78	77	10	-2	-15	56	62	73	78
8	0	23	73	79	95	95	2	0	5	459	461	401	486	6	-1	-17	72	80	106	107	10	-2	-18	23	36	41	42
7	0	28	61	60			2	0	8	19	17	22	22	6	-1	-14	124	126	157	154	9	-2	-22	41	39	58	58
7	0	25	57	61	66	61	2	0	11	165	172	199	209	6	-1	-11	88	86	113	110	9	-2	-19	57	60	73	76
7	0	22	48	44	66	62	2	0	14	122	124	167	167	6	-1	-8	21	18	7	8	9	-2	-16	59	65	77	79
7	0	19	77	82	111	116	2	0	17	34	23	57	55	6	-1	-5	209	205	243	234	9	-2	-13	33	35	62	62
7	0	16	101	102	131	129	2	0	20	110	108	121	121	6	-1	-2	89	89	116	118	9	-2	-10	58	62	85	87
7	0	13	8	12	44	44	2	0	23	96	95	127	124	6	-1	1	111	111	160	159	9	-2	-7	75	72	101	103
7	0	10	135	132	161	159	2	0	26	85	84	106	105	6	-1	4	89	90	126	126	9	-2	-4	83	82	104	108
7	0	7	59	67	69	69	2	0	29	19	23	37	37	6	-1	7	81	79	113	115	9	-2	-1	67	68	74	78
7	0	4	109	113	128	128	2	0	32	61	58	76	74	6	-1	10	60	63	84	85	9	-2	2	19	40	43	45
7	0	1	82	80	105	106	2	0	35	95	90	123	112	6	-1	13	84	85	101	100	9	-2	5	114	107	130	133
7	0	-2	114	110	161	163	1	0	34	82	77	112	108	6	-1	16	122	128	141	144	9	-2	8	40	38	67	71
7	0	-5	76	72	92	88	1	0	31	63	74	88	84	6	-1	19	103	108	148	149	9	-2	11	53	58	75	79
7	0	-8	66	66	90	92	1	0	28	70	74	94	93	6	-1	22	84	88	45	45	9	-2	14	67	77	94	101
7	0	-11	89	92	109	108	1	0	25	58	56	78	74	6	-1	25	60	58	71	73	9	-2	17	40	39	54	54
7	0	-14	120	116	149	145	1	0	22	60	64	90	93	6	-1	28	68	62	80	78	9	-2	20	44	43	49	56
7	0	-17	49	57	80	80	1	0	19	131	131	173	173	6	-1	31	68	62	79	80	9	-2	23	53	53	70	72
7	0	-20	53	63	99	96	1	0	16	239	237	266	269	5	-1	33	62	63	94	89	8	-2	25	64	68	88	84
7	0	-23	57	43	61	62	1	0	13	171	163	190	192	5	-1	30	70	76	96	91	8	-2	22	86	89	40	45
7	0	-26	77	76	86	80	1	0	10	22	24	48	48	5	-1	27	40	35	52	51	8	-2	19	63	64	97	86
6	0	-30	72	70	84	78	1	0	7	212	203	224	240	5	-1	24	83	78	114	110	8	-2	16	63	65	109	94
6	0	-27	34	28	26	28	1	0	4	196	209	211	258	5	-1	21	131	138	174	169	8	-2	13	54	69	113	99
6	0	-24	42	34	64	62	1	0	1	165	149			5	-1	18	48	50	67	67	8	-2	10	114	114	161	138
6	0	-21	68	66	89	91	1	0	-2			60	64	5	-1	15	88	102	142	139	8	-2	7	104	102	147	127
6	0	-18	93	96	122	120	1	0	-5			245	282	5	-1	12	93	97	135	132	8	-2	4	43	42	85	74
6	0	-15	93	94	130	127	1	0	-8	32	21	59	54	5	-1	9	124	130	173	169	8	-2	1	42	41	61	62
6	0	-12	122	120	154	150	1	0	-11	96	97	113	116	5	-1	6	128	126	157	149	8	-2	-2	81	84	100	95
6	0	-9	36	46	58	59	1	0	-14	259	269	292	300	5	-1	3	110	113	149	144	8	-2	-5	136	134	159	162
6	0	-6	69	74	89	90	1	0	-17	90	80	103	99	5	-1	0	207	206	253	248	8	-2	-8	44	48	69	69
6	0	-3	76	77	129	125	1	0	-20	123	121	160	159	5	-1	-3	156	134	163	154	8	-2	-11	73	72	84	83
6	0	0	182	186	223	227	1	0	-23	76	68	94	95	5	-1	-6	59	53	88	82	8	-2	-14	56	53	77	76
6	0	3	69	69	86	82	1	0	-26	104	102	123	120	5	-1	-9	168	169	222	215	8	-2	-17	62	61	86	87
6	0	6	8	19	52	49	1	0	-29	90	87	116	116	5	-1	-12	104	105	134	128	8	-2	-20	76	73	90	91
6	0	9	36	29	53	52	1	0	-32	48	56	73	72	5	-1	-15	83	86	108	105	8	-2	-23	70	66	86	88
6	0	12	71	74	75	77	1	0	-35	101	91	119	116	5	-1	-18	66	73	102	104	8	-2	-26	51	52	72	77
6	0	15	111	115	126	127	0	0	-36	63	63	88	86	5	-1	-21	138	136	178	176	7	-2	-30	54	55		
6	0	18	87	86	128	131	0	0	-33	81	88	115	116	5	-1	-24	56	63	86	87	7	-2	-27	40	40	59	59
6	0	21	68	74	104	102	0	0	-30	161	157	185	181	5	-1	-27	101	48	67	66	7	-2	-24	71	68	90	89
6	0	24	53	63	83	85	0	0	-27			64	64	5	-1	-30	84	80	99	100	7	-2	-21	106	108	124	126
6	0	27	33	22	37	36	0	0	-24	31	30	61	63	5	-1	-33	111	54	68	75	7	-2	-18	58	66	86	86
6	0	30	92	78	97	95	0	0	-21	169	172	209	216	4	-1	-34	49	47	63	67	7	-2	-15	57	54	70	71
5	0	32	34	51	70	61	0	0	-18	191	189	227	230	4	-1	-31	68	66	75	84	7	-2	-12	56	53	75	75
5	0	29	45	54	82	74	0	0	-15	117	116	123	126	4	-1	-28	85	85	109	111	7	-2	-9	107	105	137	134
5	0	26	66	67	97	84	0	0	-12	112	117	141	152	4	-1	-25	79	83	92	98	7	-2	-6	62	63	94	81
5	0	23	52	56	96	87	0	0	-9	146	147	169	172	4	-1	-22	50	53	75	79	7	-2	-3	103	97	124	123
5	0	20	77	76	108	99	0	0	-6	47	44	61	92	4	-1	-19	103	104	131	134	7	-2	0	153	152	189	189
5	0	17	99	105	130	131	11	-1	9	54	54	82	79	4	-1	-16	191	190	211	215	7	-2	3	65	65	106	106
5	0	14	99	102	145	141	11	-1	6	43	38	49	52	4	-1	-13	27	25	52	49	7	-2	6	51	55	78	81
5	0	11	124	128	153	154	11	-1	3	7	37	53	55	4	-1	-10	236	228	271	272	7	-2	9	125	126	148	153
5	0	8	68	72	109	112	11	-1	0	50	62	88	92	4	-1	-7	153	152	178	176	7	-2	12	85	85	88	94
5	0	5	98	100	157	155	11	-1	-3	45	47	65	67	4	-1	-4	106	102	147	142	7	-2	15	87	93	105	110
5	0	2	143	138	177	176	11	-1	-6	45	47	56	59	4	-1	-1	108	108	150	147	7	-2	18	43	52	79	80
5	0	-1	138	153	190	185	11	-1	-9	34	50	64	64	4	-1	2	123	130	140	147	7	-2	21	81	82	104	107
5	0	-4	47	44	80	76	10	-1	-16	50	54	75	75	4	-1	5	226	228	236	244	7	-2	24	46	54	66	74
5	0	-7	78	69	123	123	10	-1	-13	42	35	60	56	4	-1	8	107	103	149	150	7	-2	27	41	40	47	49
5	0	-10	113	117	133	131	10	-1	-10	56	61	86	87	4	-1	11	130	137	165	171	7	-2	30	63	68	78	78
5	0	-13	58	50	77	77	10	-1	-7	58	53	68	72	4	-1	14	144	144	174	175	6	-2	32	61	47		
5	0	-16	134	138	171	166	10	-1	-4	34	44	58	64	4	-1	17	85	75	98	96	6	-2	29	47	55	78	77
5	0	-19	171	165	213	206	10	-1	-1	39	47	65	67	4	-1	20	88	92	110	114	6	-2	26	70	65	83	79
5	0	-22	40	30	56	55	10	-1	2	56	56	77	88	4	-1	23	83	88	104	103	6	-2	23	65	70	94	96
5	0	-25	64	61	89	97	10	-1	5	66	69	93	91	4	-1	26	134	131	167	164	6	-2	20	79	83	106	107
5	0	-28	66	61	84	82	10	-1	8	41	39	56	60	4	-1	29	45	47	76	78	6	-2	17	62	63	76	76
5	0	-31	68	59	72	70	10	-1	11	57	57	80	80	4	-1	32	54	50	67	69	6	-2	14	89	90	112	114
4	0	-32	70	65	84	85	10	-1	14	62	61	88	87	3	-1	34	45	43	60	58	6	-2	11	76	75	105	102
4	0	-29	46	50	70	70	10	-1	17	14	36	52	52	3	-1	31	88	66	94	97	6	-2	8	80	80	113	113
4	0	-26	93	91	120	120	9	-1	22	28	42	43	51	3	-1	28	79	81	111	105	6	-2	5	154	157	204	179
4	0	-23	123	123	148	148	9	-1	19	72	76	110	104	3	-1	25	93	88	112	105	6	-2	2	126	130	189	165
4	0	-20	106	108	134	132	9	-1	16	62	65	80	82	3	-1	22	38	33	50	45	6	-2	-1	125	125	152	148
4	0	-17	90	90	120	119	9	-1	13	18	28	42	43	3	-1	19	161	182	222	197	6	-2	-4	63	61	77	81
4	0	-14	206	197	247	243	9	-1	10	56	60	86	85	3	-1	16	78	78	99	95	6	-2	-7	132	133	161	164
4	0	-11	78	70	80	76	9	-1	7	93	95	132	132	3	-1	13	51	57	93	90	6	-2	-10	110	103	143	142
4	0	-8	116	113	172	163	9	-1	4	69	68	93	91	3	-1	10	196	194	239	235	6	-2	-13	54	50	77	77
4	0	-5	223	220	212	275	9	-1	1	57	55	78	79	3	-1	7	227	228	267	264	6	-2	-16	52	76	89	88
4	0	-2	145	144	172	170	9	-1	-2	51	49	79	76	3	-1	4	160	156	187	187	6	-2	-19	76	73	98	104
4	0	1	35	22	55	26	9	-1	-5	74	81	120	119	3	-1	1	52	53	77	77	6	-2	-22	45	49	57	61
4	0	4	245	243	275	283	9	-1	-8	45	53	71	75	3	-1	-2	151	140	182	169	6	-2	-25	76	80	89	97
4	0	7	115	106	139	129	9	-1	-11	88	84	112	113	3	-1	-5	182	185	222	220	6	-2	-28	67	72	88	94
4	0	10	247	252	263	272	9	-1	-14	84	81	110	110	3	-1	-8	103	98	129	122	6	-2	-31	40	44	52	61
4	0	13			148	145	9	-1	-17	35	45	59	63	3	-1	-11	217	210	242	236	5	-2	-32	36	37	89	49
4	0	16	128	121	151	154	9	-1	-20	34	36	40	42	3	-1	-14	122	120	161	159	5	-2	-29	57	56	77	79
4	0	19	124	129	149	154	9	-1	-23	58	52			3	-1	-17	51	43	64	63	5	-2	-26	83	86	104	108

Table 3. Continued.

h	k	l	NDG $\lvert F_o \rvert$	NDG $\lvert F_c \rvert$	YDG $\lvert F_o \rvert$	YDG $\lvert F_c \rvert$
5	-2	-23	76	72	96	96
5	-2	-20	35	34	50	49
5	-2	-17	69	72	95	94
5	-2	-14	169	163	196	198
5	-2	-11	87	87	113	115
5	-2	-8	92	90	117	115
5	-2	-5	222	221	256	261
5	-2	-2	62	58	70	71
5	-2	1	142	136	156	156
5	-2	4	101	96	115	121
5	-2	7	97	97	124	136
5	-2	10	72	74	94	104
5	-2	13	90	92	112	121
5	-2	16	104	108	128	134
5	-2	19	116	115	139	147
5	-2	22	49	54	60	63
5	-2	25	75	78	101	99
5	-2	28	64	66	92	95
5	-2	31	52	53	64	66
4	-2	33	39	53	70	75
4	-2	30	89	92	110	117
4	-2	27	52	52	71	73
4	-2	24	65	69	93	92
4	-2	21	122	121	141	140
4	-2	18	52	57	73	71
4	-2	15	109	114	139	135
4	-2	12	103	100	137	134
4	-2	9	144	150	189	190
4	-2	6	121	114	149	133
4	-2	3	154	158	202	189
4	-2	0	205	208	264	238
12	-3	6	41	50		
12	-3	3	27	30	43	41
12	-3	0	67	62	79	81
12	-3	-3	49	51	72	74
12	-3	-6	32	40		
11	-3	-16	65	60		
11	-3	-13	25	37	48	50
11	-3	-10	49	56	74	77
11	-3	-7	61	61	86	91
11	-3	-4	55	58	69	74
11	-3	-1	63	66	76	79
11	-3	2	67	64	84	87
11	-3	5	60	62	86	90
11	-3	8	29	34	51	51
11	-3	11	49	48	60	64
11	-3	14	66	70	92	100
10	-3	19	47	51	61	64
10	-3	16	73	73	91	92
10	-3	13	30	37	53	53
10	-3	10	56	57	82	81
10	-3	7	43	51	73	76
10	-3	4	76	77	95	96
10	-3	1	39	42	56	57
10	-3	-2	77	76	93	93
10	-3	-5	76	77	101	101
10	-3	-8	49	54	82	85
10	-3	-11	35	42	58	56
10	-3	-14	88	79	101	105
10	-3	-17	29	38	39	45
10	-3	-20	45	47	58	62
9	-3	-24	47	53	60	69
9	-3	-21	67	70	87	95
9	-3	-18	56	54	74	73
9	-3	-15	36	42	48	48
9	-3	-12	45	50	74	75
9	-3	-9	97	98	136	134
9	-3	-6	70	72	94	95
9	-3	-3	56	56	78	74
9	-3	0	104	107	146	145
9	-3	3	0	21	41	39
9	-3	6	30	37	42	43
9	-3	9	89	90	125	123
9	-3	12	67	77	100	107
9	-3	15	32	41	53	58
9	-3	18	51	49	56	62
9	-3	21	62	64	76	87
9	-3	24	53	50	60	67
8	-3	26	72	71	80	88
8	-3	23	65	62	82	84
8	-3	20	55	49	65	65
8	-3	17	45	40	66	64
8	-3	14	119	119	149	147
8	-3	11	125	121	147	148
8	-3	8	17	20	54	49
8	-3	5	108	112	146	140
8	-3	2	86	83	123	113
8	-3	-1	58	61	94	87
8	-3	-4	102	105	142	135
8	-3	-7	124	125	157	146
8	-3	-10	75	75	110	105
8	-3	-13	52	48	77	79
8	-3	-16	100	98	118	120
8	-3	-19	90	92	116	121
8	-3	-22	43	41	46	60
8	-3	-25	76	66	61	86
8	-3	-28	46	45		
7	-3	-29	44	46	27	61
7	-3	-26	78	78	63	105
7	-3	-23	68	72	78	100
7	-3	-20	96	95	109	113
7	-3	-17	46	39	46	45
7	-3	-14	150	141	182	182
7	-3	-11	102	97	133	130
7	-3	-8	67	68	99	90
7	-3	-5	134	127	179	160
7	-3	-2	135	136	184	167
7	-3	1	32	36	44	38
7	-3	4	102	99	135	127
7	-3	7	119	122	159	155
7	-3	10	116	114	152	150
7	-3	13	53	54	58	61
7	-3	16	142	141	154	165
7	-3	19	85	89	110	117
7	-3	22	50	47	59	66
7	-3	25	56	59	62	76
7	-3	28	74	73	69	102
6	-3	30	76	72	19	87
6	-3	27	23	36	25	53
6	-3	24	63	66	76	98
6	-3	21	121	125	124	137
6	-3	18	59	60	81	79
6	-3	15	63	56	78	78
6	-3	12	96	99	135	123
6	-3	9	121	123	167	151
6	-3	6	98	100	148	134
6	-3	3	17	19	30	26
6	-3	0	241	246	243	251
12	-4	7	51	51	70	73
12	-4	4	13	41	54	59
12	-4	1	47	50	73	72
12	-4	-2	43	49	72	75
12	-4	-5	80	78	110	107
12	-4	-8	30	36	60	57
11	-4	-15	34	46	58	66
11	-4	-12	51	57	82	80
11	-4	-9	61	66	81	79
11	-4	-6	58	58	71	72
11	-4	-3	44	44	54	57
11	-4	0	52	90	116	117
11	-4	3	47	51	69	71
11	-4	6	52	50	75	75
11	-4	9	62	59	78	80
11	-4	12	63	56	72	75
11	-4	15	69	52	70	74
10	-4	20	41	53	80	72
10	-4	17	46	44	65	62
10	-4	14	68	68	104	98
10	-4	11	60	59	77	77
10	-4	8	64	59	77	78
10	-4	5	89	86	108	104
10	-4	2	60	63	89	91
10	-4	-1	24	31	51	51
10	-4	-4	53	58	85	84
10	-4	-7	51	53	76	77
10	-4	-10	86	79	102	99
10	-4	-13	43	37	55	54
10	-4	-16	62	60	80	78
10	-4	-19	60	60	86	83
10	-4	-22	56	49		
9	-4	-23	62	65	86	87
9	-4	-20	42	49	63	66
9	-4	-17	27	41	63	63
9	-4	-14	59	70	97	98
9	-4	-11	88	88	119	113
9	-4	-8	0	21	44	42
9	-4	-5	127	116	166	165
9	-4	-2	97	96	134	132
9	-4	1	56	52	80	85
9	-4	4	76	78	97	99
9	-4	7	84	91	115	116
9	-4	10	69	73	94	95
9	-4	13	37	47	69	70
9	-4	16	73	73	97	102
9	-4	19	67	64	86	90
9	-4	22	39	29	34	41
9	-4	25	55	61	81	85
8	-4	27	51	53	73	73
8	-4	24	59	64	89	93
8	-4	21	72	70	88	91
8	-4	18	62	69	103	100
8	-4	15	100	96	126	127
8	-4	12	77	78	109	111
8	-4	9	108	110	152	150
8	-4	6	69	73	99	97
8	-4	3	72	83	109	106
8	-4	0	177	175	196	196
12	-5	11	54	49		
12	-5	8	0	35	46	47
12	-5	5	45	51	72	74
12	-5	2	53	53	76	79
12	-5	-1	33	56	83	82
12	-5	-4	36	47	65	68
12	-5	-7	49	51	71	69
12	-5	-10	54	51	71	68
11	-5	-17	59	44	63	62
11	-5	-14	53	63	91	87
11	-5	-11	50	52	73	70
11	-5	-8	19	33	41	43
11	-5	-5	66	74	94	93
11	-5	-2	50	50	73	71
11	-5	1	47	51	65	66
11	-5	4	67	65	85	85
11	-5	7	63	66	91	89
11	-5	10	44	55	84	78
11	-5	13	48	35	53	50
11	-5	16	52	60	89	84
10	-5	21	50	66	87	80
10	-5	18	48	45	60	65
10	-5	15	35	47	66	69
10	-5	12	37	47	61	65
10	-5	9	86	89	111	113
10	-5	6	40	49	60	62
10	-5	3	39	51	76	79
10	-5	0	80	75	104	104

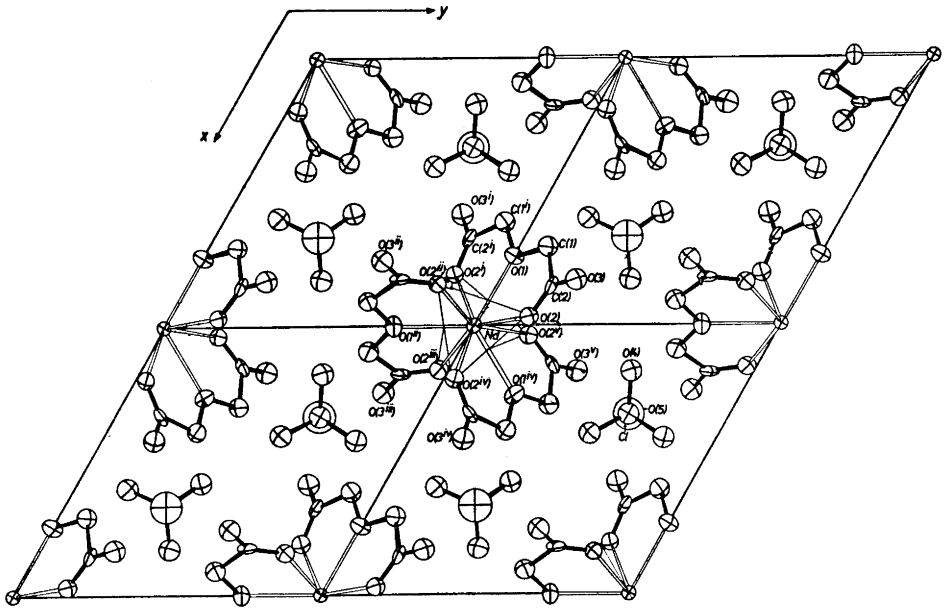

Fig. 1. A projection of NDG on (001) showing the layer around $z=0$ containing the tris(oxydiacetato) complexes and the perchlorate ions. The figure is drawn by the program ORTEP [8] representing the atoms by "thermal ellipsoids" scaled to include 50 % of the probability distribution.

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^{ii})	3.026 (9)	2.851 (8)
M—O(2)	2.428 (6)	2.339(6)	O(2)—O(2^{ii})	3.026(11)	2.924(11)
O(1)—O(2)	2.582 (8)	2.546(8)	O(2^{i})—O(2^{ii})	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^{i})	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^{vi})	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^{vi})	3.259(19)	3.157(20)
O(6)—O(3^{iv})	3.180(10)	3.150(10)	O(6)—O(2^{iv})	3.147 (9)	3.193 (9)
Angle			Angle		
O(2)—O(6)—O(3^{iv})	98.0(0.3)	94.8(0.3)	Na(1)—O(6)—O(4^{vi})	75.5(0.3)	75.2(0.3)
O(2)—O(6)—O(4^{vi})	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^{iv})	61.1(0.3)	58.2(0.3)	Na(2)—O(6)—O(3^{iv})	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^{vi})	152.9(0.3)	153.8(0.3)
Na(1)—O(6)—O(3^{iv})	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-

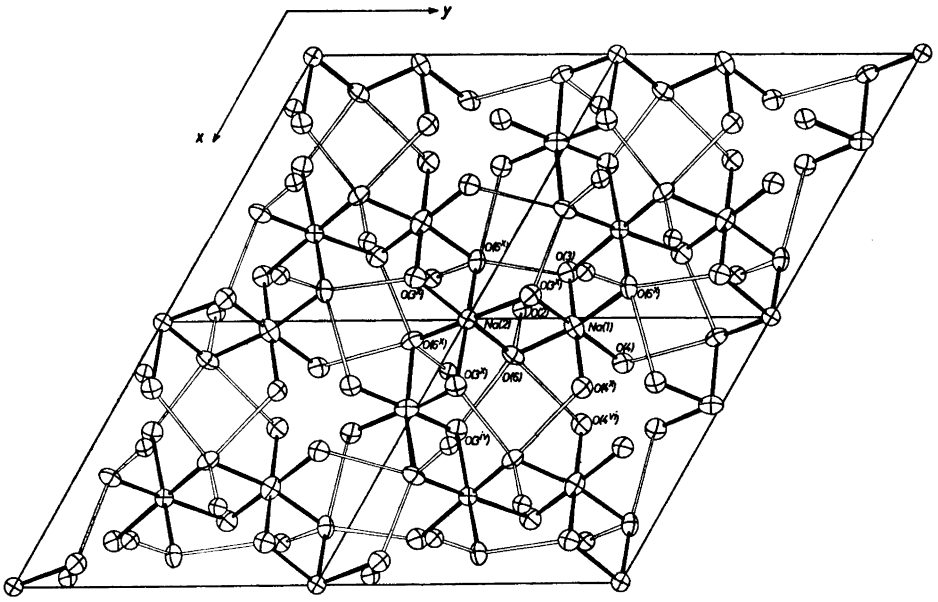

Fig. 2. A projection on (001) of the layer around $z=1/6$ in NDG showing the coordination around the sodium ions. Possible hydrogen bond distances, including O(6)–O(4^{vi}), are represented by unfilled sticks. Some symmetry-related sites not given in the text are designated by the superscript (x). The 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 $18.8\pm0.3°$ relative to each other in NDG but this angle has decreased to $13.3\pm0.3°$ in YDG. On the other hand the angle between M–O(2) and the *c* axis is only changed from $46.0\pm0.1°$ to $46.2\pm0.1°$. The distance between the triangular faces of the prism decreases from 3.371 ± 0.011 Å in NDG to 3.238 ± 0.011 Å 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^{i})	$\pm$0.044	$\pm$0.046
C(1), C(1^{i})	$\pm$0.063	$\pm$0.074	O(3), O(3^{i})	$\mp$0.089	$\mp$0.077
C(2), C(2^{i})	$\pm$0.061	$\pm$0.035	M	0.000	0.000

set, and with the expected distances and angles [1] 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.[9] 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^{iv}) and O(4^{vi}) in YDG. In NDG the distance O(6) – O(4^{vi}) might be too long, and in both compounds the angle O(2) – O(6) – O(2^{iv}) excludes a hydrogen bond between O(6) and O(2^{iv}). 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 $Na_3[M(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$, M=Ce–Lu.

M	a/Å	c/Å	V/Å^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

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

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.[10]

able 7. Observed and calculated values of $10^4 \cdot \sin^2\theta$ for the compounds $Na_3[M(C_4H_4O_5)_3] \cdot 2NaClO_4 \cdot 6H_2O$. The observed powder intensities of the neodynium compound are also given.

k	l	Ce obs	Ce calc	Pr obs	Pr calc	Nd obs	Nd calc	Sm obs	Sm calc	Eu obs	Eu calc	Gd obs	Gd calc	Tb obs	Tb calc	Dy obs	Dy calc	Ho obs	Ho calc	Er obs	Er calc	Tm obs	Tm calc	Yb obs	Yb calc	Lu obs	Lu calc	I_{obs} Nd
0	3	66	66	67	66	66	67	67	67	67	67	67	67	67	68	67	68	-	68	68	68	67	68	67	68	68	68	3
0	1	89	90	89	90	90	90	90	91	91	91	90	91	91	91	91	92	91	92	91	92	92	92	91	92	91	91	39
1	2	111	112	112	112	112	113	112	113	113	113	113	114	113	114	114	114	114	114	114	114	114	115	114	115	115	115	81
0	4	200	200	200	201	201	201	202	202	203	203	202	203	204	204	204	204	204	205	204	205	204	205	204	205	205	206	47
1	0	247	247	248	248	249	249	249	250	250	251	250	251	251	252	251	252	252	253	252	253	252	253	252	254	254	254	48
0	6	265	265	266	266	267	268	268	269	269	270	267	269	271	270	271	270	271	271	272	271	272	272	272	272	271	272	32
1	5		266		267		268		269		270		271		272		272		272		272		273		273		274	
1	3	313	313	312	314	315	315	316	317	317	318	319	318	319	319	319	320	320	320	321	321	320	321	321	322	320	322	20
2	1	335	337	338	339	339	340	341	341	342	343	344	342	344	343	344	344	346	346	345	346	344	345	345	346	347	346	9
0	2	358	359	359	360	361	361	362	363	362	364	367	364	367	366	366	366	368	367	367	367	368	367	368	368	369	369	22
0	7	441	443	444	445	446	446	448	448	450	450	452	450	453	452	452	452	455	453	453	454	454	454	456	454	457	455	24
2	4	446	447	449	449	451	450	453	452	454	454	457	454	457	456	456	456	459	457		457	456	457		459		459	
1	6	-	512	515	514	517	515	519	518	521	520	521	520	524	522	524	522	525	523	525	524	526	524	528	525	528	526	100
0	5	-	513		515		517		519		521		522		523		524		525		525		526		527		527	
0	9	602	596	598	598	600	600	601	602	605	606	606	606	606	608	606	608	608	609	609	610	609	610	608	611	610	612	3
2	2	606	606	608	608	610	610	612	613	614	615	615	615	616	617	617	618	618	619	618	620	622	620	621	622	623	622	15
2	7	691	690	694	692	698	694	701	698	698	700	703	701	-	703	704	704	705	705	708	706	708	707	709	708	708	709	18
1	4		694		697		699		702		704		705	707	707	708	708	708	710	711	710	713	711	712	712	712	713	
0	0	740	741	742	744	747	746	751	750	752	752	752	753	756	755	756	757	758	758	759	758	758	759	762	761	760	761	14
2	5	759	760	763	763	-	765	-	769	770	772	-	772	777	775	775	776	778	777	778	778	778	779	782	780	780	781	15
0	3	806	807	809	810	813	813	816	817	818	819	820	820	823	823	824	824	826	825	827	826	825	827	830	829	828	829	10
1	9	842	843	845	846	845	845	853	852	855	856	857	857	861	860	860	860	861	862	862	863	863	864	867	865	864	866	20
1	7	935	937	939	940	944	943	949	947	950	951	952	952	957	955	956	956	957	958	960	959	959	960	962	961	961	962	23
1	11	971	973	976	977	977	979	983	983	985	988	990	989	993	992	991	992	993	994	995	995	995	997	999	999	998	999	1
2	0	986	988	991	991	994	995	998	1000	1002	1002	1004	1004	1008	1007	1009	1009	1008	1010	1013	1011	1013	1012	1015	1014	1015	1015	4
0	6	1004	1006	1009	1010	1011	1013	1018	1018	1020	1021	1021	1022	1024	1025	1028	1027	1026	1028	1031	1029	1031	1030	1033	1032	1032	1033	20
2	8	1052	1047	-	1051	-	1054	-	1059	-	1063	-	1064	1067	1068	1068	1069	1070	1071	1072	1071	1076	1073	1078	1075	1077	1076	8
2	3		1054	-	1058	-	1061	-	1067	-	1070	1070	1071	1074	1074	1076	1076	1076	1078	1081	1079		1080	1085	1082	1082	1083	< 1
0	12	-	1060	-	1064	-	1067	-	1071	-	1076	-	1077	1083	1081	-	1081	1086	1083		1084		1086		1087		1088	
2	10	-	1066	1071	1069	1072	1072	1079	1077	1082	1081	1082	1083	1086	1086	1086	1087	1089	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	1100	1102	1102	1103	1102	1107	1104	1107	1106	1106	1107	3
1	2	1099	2000	1102	1104	1109	1107	1115	1113	1115	1116	1117	1117	1119	1121	1125	1123	1125	1125	1126	1125	1128	1126	1130	1129	1130	1130	4
3	4	1191	1198	1194	1192	1194	1196	1203	1202	1207	1206	1209	1207	1211	1211	1213	1213	1217	1215	1218	1216	1219	1217	1220	1219	1221	1221	4
0	11	1221	1220	1227	1224	1226	1228	1235	1233	1239	1238	1243	1240	1248	1244	1244	1244	1249	1247	1247	1248	1251	1250	1252	1251	1254	1252	3
2	6	1256	1253	1258	1257	1263	1261	1269	1268	1274	1271	1275	1273	1275	1277	1281	1279	1286	1281	1281	1282	1284	1283	1286	1286	1289	1287	18
1	5		1254		1259		1263		1269		1273		1274		1278		1280		1282		1283		1285		1287		1289	
1	12	1308	1307	-	1312	1313	1315	1320	1321	1328	1327	1325	1328	1330	1333	1331	1333	1334	1336	1339	1337	1340	1339	1342	1341	1343	1342	11
1	10	1313	1313	1316	1317	1322	1321	1328	1327	1333	1332	1333	1334	1336	1338	1338	1339	1341	1341	1344	1342	1347	1344	1348	1346	1348	1348	
0	1	1325	1324	1332	1329	1335	1333	1337	1341	1342	1344	1342	1345	1350	1352	1350	1352	1355	1354	1360	1355	1363	1357	1361	1360	1361	1361	3
0	13		1327		1331		1335		1340	1347	1346	1348	1348	1354	1353		1352		1355		1356		1358		1360		1362	
0	9	1342	1337	1344	1342	1347	1346	1353	1352	1359	1357	1360	1359	1364	1363	1365	1364	1370	1367	1367	1367	1366	1370	1374	1372	1373	1373	< 1
2	2	1350	1346	1354	1351	1356	1356	1363	1363	1364	1367	1366	1368	1369	1372	1376	1375	1377	1377	1378	1378	1378	1379	1384	1382	1386	1384	< 1
3	7	1435	1431	1438	1436	1439	1440	1445	1448	1455	1452	1456	1453	1457	1459	1460	1460	1462	1463	1463	1464	1466	1467	1468	1468	1472	1470	8
0	4		1435		1440	1444	1445	1454	1452		1456	1460	1458	1463	1462	1466	1465	1467	1467	1469	1468		1470	1472	1473		1474	
2	11	1468	1467	1472	1472	1476	1476	1484	1484	1490	1490	1489	1491	1495	1496	1497	1496	1498	1499	1501	1501	1502	1503	1507	1505	1509	1507	10
1	14		1525	1530	1531	1537	1535	1543	1540	1550	1548	1550	1550	1553	1556	1555	1555	1559	1558	1559	1560	1561	1562	1562	1564	1565	1566	5
1	8	1540	1541	1542	1547	-	1551	1560	1559	1566	1564	1566	1566	-	1571	1572	1573	1575	1576	1576	1577	1580	1579	1582	1582	1584	1583	1
2	1	1576	1571	1580	1577	1581	1582	1589	1591	1597	1594	1596	1596	1600	1601	1608	1605	1610	1607	1608	1608	1608	1610	1615	1613	1617	1615	1
2	13		1574		1579		1583		1590		1597		1599	1608	1605		1604		1608		1609	1613	1611		1614		1615	
2	9	1585	1584	1590	1590	1593	1594	1603	1602	1608	1608	1610	1610	-	1615	1617	1616	1620	1618	1619	1621	1621	1623	1623	1626	1625	1627	5
2	2	-	1593	1601	1599	-	1604	-	1611	-	1617	1619	1619	1619	1624	-	1627	-	1630		1631	-	1632	-	1636	-	1637	-
3	7	1676	1678	1682	1684	1692	1689	-	1698	-	1703	1708	1705	-	1710	-	1713	-	1715	1718	1717	1723	1719	1725	1722	1726	1724	1
2	4		1682	-	1688		1693	1705	1702	-	1707		1709	1717	1714	-	1717	1721	1720		1721		1723		1723		1728	
1	0	1731	1729	1736	1735	1739	1740	1753	1750	1757	1757	1755	1756	1764	1762	1764	1765	1770	1768	1767	1769	1770	1771	1773	1775	1780	1776	4
1	5	1749	1747	1756	1754	1760	1757	1768	1769	1776	1774	1776	1778	1780	1782	1784	1785	1788	1789	1788	1789	1787	1791	1793	1794	1798	1796	5
3	12	1800	1801	1811	1807	1814	1812	1825	1821	-	1828	-	1830	1839	1836	1840	1837	1844	1841	1844	1842	-	1845	1848	1848	1851	1850	10
3	10	-	1806		1813		1818		1827	-	1833	-	1835		1841	1844	1843	1849	1846	1850	1848	1849	1850	1853	1853	1857	1850	
1	11	1963	1961	1973	1958	1975	1974	1984	1983	1991	1990	1994	1993	1996	1999	2002	2001	2001	2004	2005	2006	2007	2008	2008	2012	2013	2014	9
3	16		1974		1978		1986		1987		1997	2001	1999	2008	2006		2005	2010	2009	2013	2011	2013	2014	2017	2016	2021	2019	
1	6	1994	1994	2000	2001	2010	2007	2016	2018	2020	2023	2022	2026	-	2032	2035	2035	2039	2039	2038	2040	2043	2042	2046	2046	2048	2048	3
2	14	2018	2019	2029	2026	2031	2032	2038	2041	2050	2049	2051	2052	-	2059	2058	2059	2061	2063	2060	2065	2068	2068	2071	2071	2074	2073	2
2	12	2051	2048	2063	2055	-	2061	-	2071	2084	2079	2087	2081	2093	2088	2094	2089	2096	2093	2096	2095	2099	2097	2099	2101	2106	2103	-
3	10		2053		2059	2068	2067	2079	2077		2084		2086		2093		2095		2099	2107	2101		2103		2109		2109	5
1	1	-	2065	2073	2073	2081	2079	2092	2091	-	2096	-	2098	-	2105	2111	2109	2112	2112	-	2113	-	2116	2112	2120	-	2122	< 1
3	2	-	2087	2094	2095	2102	2102	-	2113	-	2118	2118	2121	-	2127	-	2131	-	2135	-	2136	-	2138	-	2143	-	2145	< 1
1	11	-	2208	-	2216	-	2222	-	2233	-	2241	-	2243	-	2251	-	2253	-	2257	2255	2259	-	2261		2265	-	2268	-
3	17	-	2210	-	2218	-	2223	-	2233	-	2243	-	2246	-	2254	-	2253	-	2258		2260	2267	2266	-	2266	-	2269	-
3	16	2216	2214	-	2222	2231	2228	-	2237	-	2247	2253	2250	2258	2258	2261	2257	2265	2262	-	2264	2270	2267		2270	-	2273	4
3	0	2222	2230	2231	-	2238	-	2250	-	2256	-	2258	2265	-	2269	-	2273	-	2274	-	2277	-	2282	-	2284	-	2288	-
3	9	2318	2325	-	2333	2341	2340	2353	2353	2362	2360	2360	2362	-	2370	2373	2373	2378	2377	2376	2379	2384	2381	2384	2386	2388	2388	5

Because of the approximately parallel decrease in a and $c/3$ (*cf.* Fig. 3) it should be possible to use $\sqrt[3]{(V/Z)}$ as a "mean parameter" when the shrinking dimensions of the unit cell are compared with the lanthanoid contraction. Z is the number of lanthanoid ions per unit cell, and for the oxydiacetates $Z = 3$. One may look upon $\sqrt[3]{(V/Z)}$ as a "geometrical mean" of the lattice parameters per lanthanoid ion. Values of $\sqrt[3]{(V/Z)}$ and r are given in Table 8.

The coordination polyhedron of the tris(oxydiacetato)lanthanoidate ion is a distorted version of the mononuclear nona-aquo lanthanoid(III) complex in the compounds $[M(H_2O)_9](BrO_3)_3$, $M = La - Lu$. In this complex the co-ordinated water oxygen atoms form a symmetrically tricapped trigonal prism, *i.e.*, the idealised ground-state geometry for nine-coordination.[11] The crystal structure of the nona-aquo neodymium bromate was determined by Helmholtz.[12] The hexagonal cell contains two formula units. Because of the rather similar coordination geometry around the lanthanoid ion in the tris(oxydiacetato) and nona-aquo complexes one may compare the contraction

Table 8. Values of $\sqrt[3]{(V/Z)}$ for the two series of compounds $Na_3[M(C_4H_4O_5)_3]\cdot 2NaClO_3\cdot 6H_2O$ (denoted *O*) and $[M(H_2O)_9](BrO_3)_3$ (*B*) [13] compared with the crystal radii (*r*) of the trivalent lanthanoid ions.[10]

M	$\sqrt[3]{(V/Z)}$/Å		r/Å	M	$\sqrt[3]{(V/Z)}$/Å		r/Å
	O	*B*			*O*	*B*	
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 oxidiacetates and 0.01 for the bromates.

in the two series of compounds. Mayer and Glasner [13] 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

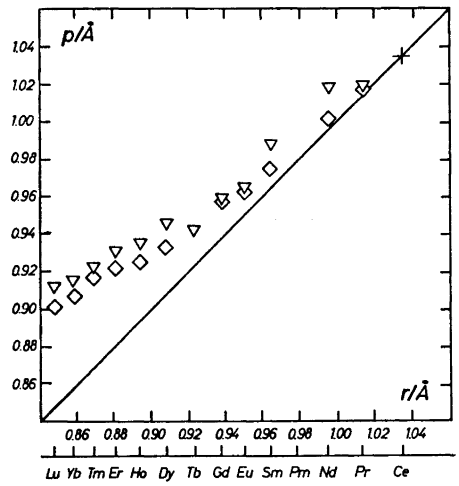

Fig. 3. Values of *p* of eqn. (1) with $q=a$ (◇) and $c/3$ (▽) plotted *versus* the crystal radius, *r*, of the trivalent lanthanoid ions. For comparison the line $p=r$ is included.

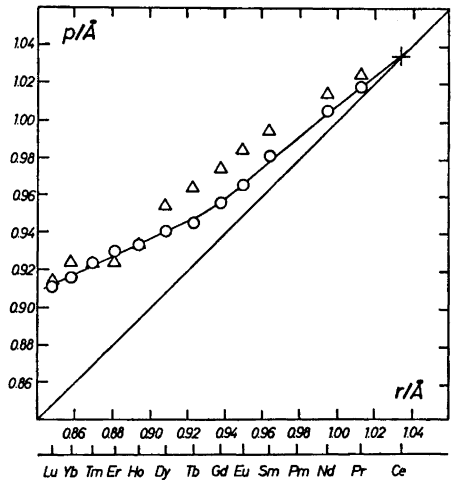

Fig. 4. Values of *p* with $q=\sqrt[3]{(V/Z)}$ for the oxydiacetate (○) and bromate (△) compounds plotted *versus* *r*. For comparison the line $p=r$ is included.

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 ± 0.015 Å along the *c* axis and 0.137 ± 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 ± 0.013 Å and 0.089 ± 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^{iii}) and O(2)–O(2^{ii}), have in YDG values compatible with twice the van der Waals radius of oxygen.[14] 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 ± 0.017 Å along the *c* axis and 0.210 ± 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 ± 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 reenforced 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 [15] and by Grenthe and

Hansson.[16] 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 $Na_3[M(C_4H_4O_5)_3]\cdot 2NaClO_4\cdot 6H_2O$, 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 $[M(H_2O)_9](BrO_3)_3$, M = La – Lu, have been reinvestigated using Guinier powder photographs.[17] 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.

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