

Structural Studies on the Rare Earth Carboxylates

11. On the Crystal Structure of Hexagonal Trisodium Tris(pyridine-2,6-dicarboxylato)ytterbate(III) Mono(sodium perchlorate) Decahydrate

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A model of the crystal and molecular structure of $\text{Na}_3[\text{Yb}(\text{C}_7\text{H}_3\text{NO}_4)_3]\cdot\text{NaClO}_4\cdot 10\text{H}_2\text{O}$ has been proposed from three-dimensional X-ray intensity data collected with the Weissenberg multi-film technique. The compound crystallizes in space group $P62c$ with $Z=2$. The elements Ho-Lu from isomorphous compounds. The unit cell dimensions are $a=10.4155(19)$ and $10.3651(7)$ Å, $c=18.3709(50)$ and $18.3501(20)$ Å for the holmium and lutetium compound, respectively. In the mononuclear tris(pyridine-2,6-dicarboxylato) complexes the lanthanoid ions are surrounded by six carboxylate oxygen and three nitrogen atoms which form a distorted tri-capped trigonal prism. The Yb-O and Yb-N bond distances are 2.38 and 2.43 Å, respectively. Together with statistically distributed sodium ions and water molecules the lanthanoid complexes form an infinite chain along the c axis. These chains are connected by hydrogen bonds *via* sodium coordination polyhedra attached to the chains. Four of the ten water molecules and the perchlorate oxygen atoms have not been located but are assumed to occupy disordered positions in the fairly wide tunnels of the structure. The proposed model has been refined to a conventional R factor of 0.076.

This paper is a report of the crystal and molecular structure of the hexagonal ytterbium pyridine-2,6-dicarboxylate (or dipicolinate) compound trisodium tris(dipicolinato)ytterbate(III) mono(sodium perchlorate) decahydrate, $\text{Na}_3[\text{Yb}(\text{C}_7\text{H}_3\text{NO}_4)_3]\cdot\text{NaClO}_4\cdot 10\text{H}_2\text{O}$, referred to as HEXYBDIPIC below. It is thus part of the systematic study of the crystal structures of some sodium salts of the mononuclear tris(dipicolinato)- and tris(oxydiacetato)lanthanoidate complexes undertaken at this laboratory.

The structures of the orthorhombic and monoclinic ytterbium dipicolinates $\text{Na}_3[\text{Yb}(\text{C}_7\text{H}_3\text{NO}_4)_3]\cdot n\text{H}_2\text{O}$ have been reported earlier.^{1,2} The orthorhombic phase has $n=14$ and is denoted ORTYBDIPIC while the monoclinic phase

has $n = 13$. It is denoted MONYBDIPIC. In a following paper the structure of the triclinic lanthanoid dipicolinate phase represented by $\text{Na}_3\text{Nd}(\text{C}_7\text{H}_3\text{NO}_4)_3 \cdot 15\text{H}_2\text{O}$ (NDP) will be reported.

The hexagonal phase is formed by the elements Ho–Lu. A second aim of the present investigation is to study the variation of the unit cell dimensions in this isostructural series.

EXPERIMENTAL

The hexagonal lanthanoid dipicolinates $\text{Na}_3[\text{M}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, M = Ho–Lu, were prepared by mixing water solutions of the lanthanoid perchlorates and disodium dipicolinate in the molar ratio 1:3. The pH of the resulting solutions had values near 7. Slow evaporation at room temperature gave crystals with the habit of hexagonal prisms, which were stored in the mother liquor to prevent efflorescing. The ytterbium compound HEXYBDIPIC was analysed for Yb, Na, N, C, H, Cl, and H_2O as described for ORTYBDIPIC.¹ The relative amounts found are compared with those calculated for $\text{Na}_3[\text{Yb}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, F.W. 1039.9.

	Yb	Na	N	C	H	Cl	H_2O	
Found	16.5	8.6	4.0	24.5	2.9	3.5	17.3	(%)
Calc.	16.6	8.8	4.0	24.2	2.8	3.4	17.3	(%)

In the structure determination only 6 H_2O per Yb were located. The perchlorate ion was detected by infrared spectrophotometry. Comparison with a calibration curve obtained using known amounts of sodium perchlorate in potassium bromide gave 9.1 % ClO_4^- in the compound, the calculated amount is 9.6 %.

The holmium, erbium, thulium, and lutetium compounds prepared as described above gave the same powder pattern as HEXYBDIPIC. One of the holmium samples crystallized in the monoclinic phase described before,² but when these crystals had been stored in their mother liquor about a week they had changed to the hexagonal phase.

Powder photographs were taken as described for ORTYBDIPIC in a Guinier-Hägg focusing camera (XDC 700, manufactured by IRD, Bromma, Sweden) using $\text{CrK}\alpha_1$ radiation ($\lambda = 2.28962 \text{ \AA}$).

A freshly prepared single crystal of HEXYBDIPIC was mounted along the b axis in a capillary together with mother liquor. It had the approximate dimensions $0.10 \times 0.10 \times 0.15 \text{ mm}^3$ and was elongated in the c direction. The intensities $h0l - h6l$ were recorded with non-integrated Weissenberg multi-film technique. Zr-filtered Mo-radiation was used. The intensities were measured visually by comparison with a calibrated scale. Most reflexions with $l \neq 2n$ were absent or weak. 583 independent intensities were measured.

The intensity data were corrected for Lorentz and polarization effects. The linear absorption coefficient, μ , is 30 cm^{-1} . Because of this low value and the small crystals used, no absorption corrections were applied. The different layers were brought to approximately the same scale by a comparison of correlated $|F_0|$ values.

UNIT CELL AND SPACE GROUP

HEXYBDIPIC, and thus the isomorphous Ho–Lu dipicolinates, crystallize in the Laue class $6/mmm$. The only systematically absent reflexions are hhl : $l \neq 2n$. These conditions were controlled using three different single crystals. The possible space groups are thus $P6_3mc$ (No. 186), $P\bar{6}2c$ (No. 190), and $P6_3/mmc$ (No. 194).³

The unit cell dimensions of all the hexagonal compounds were obtained from powder data as described before.² The observed powder patterns are

Table 1. X-Ray powder data: observed and calculated values of $10^3 \times \sin^2 \theta$ for the compounds $\text{Na}_3[\text{M}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, $\text{M} = \text{Ho} - \text{Lu}$. The observed powder intensities of the ytterbium compound are also given.

h	k	l	Ho		Er		Tm		Yb		Lu		I_{obs} Yb
			obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	
0	0	2	1536	1553	1554	1554	1557	1556	1559	1556	1556	1557	s
2	0	0	1597	1611	1615	1615	1621	1621	1624	1624	1627	1626	vvs
1	0	1	1983	1989	1989	2003	2011	2010	2017	2013	2013	2016	w
1	0	2	3136	3164	3152	3168	3179	3178	3151	3180	3181	3183	s
1	1	0	4807	4832	4845	4843	4858	4864	4873	4871	4877	4879	m
1	0	3	5083	5105	5105	5110	5116	5123	5129	5126	5124	5129	vw
0	0	4	6185	6213	6217	6214	6221	6226	6238	6226	6223	6227	w
1	1	2	6357	6386	6394	6397	6417	6420	6426	6428	6431	6436	vw
2	0	0	6419	6443	6452	6458	6463	6485	6495	6495	6504	6506	w
2	0	1	6804	6831	6842	6846	6873	6874	6885	6884	6892	6895	s
1	0	4	7800	7824	7824	7829	7841	7847	7851	7849	7853	7854	s
2	0	2	7972	7996	8010	8012	8032	8041	8059	8052	8058	8063	s
2	0	3	9912	9938	9949	9954	9979	9987	9998	9997	10005	10009	s
1	1	4	11026	11045	11056	11058	11081	11089	11097	11097	11104	11107	m
2	1	0	11271	11276	11303	11304	11342	11348	11370	11367	11384	11385	s
1	0	5	11271	11318	11303	11324	11342	11349	11370	11351	11384	11356	m
2	1	1	11642	11664	11688	11690	11726	11737	11752	11756	11775	11775	w
2	0	4	12642	12656	12657	12672	12697	12710	12717	12721	12724	12733	vs
2	1	2	12808	12829	12853	12855	12893	12905	12906	12923	12944	12942	w
3	0	0	14497	14497	14530	14530	14591	14591	14614	14614	14638	14638	w
1	1	5	14484	14540	14553	14553	14580	14591	14623	14599	14626	14609	vw
2	1	3	14763	14770	14790	14797	14852	14850	14870	14864	14895	14888	vw
1	0	6	15582	15590	15590	15597	15631	15629	15649	15641	15666	15638	vvs
3	0	2	16025	16050	16081	16084	16158	16147	16195	16171	16210	16195	w
2	0	5	16168	16151	16181	16181	16158	16212	16223	16223	16230	16236	w
2	1	4	17477	17488	17498	17516	17570	17574	17601	17592	17619	17613	m
3	0	3	17987	17992	18027	18026	18099	18093	18111	18116	18137	18141	vw
1	1	6	18806	18811	18826	18826	18868	18879	18883	18879	18851	18891	m
2	2	0	19331	19330	19385	19374	19451	19454	19463	19486	19517	19518	vw
2	0	6	20409	20422	20455	20440	20497	20492	20513	20503	20512	20517	vvs
3	0	4	20703	20710	20749	20745	20795	20816	20848	20840	20830	20865	m
2	2	2	-	20883	-	20928	-	21011	-	21042	-	21075	m
3	1	0	20930	20940	20991	20988	21050	21076	21078	21109	21101	21144	m
2	1	5	-	20983	-	21011	-	21076	-	21094	-	21115	-
3	1	1	21337	21329	21396	21377	21469	21465	21510	21498	21525	21534	vvs
3	1	2	22512	22494	22540	22542	22632	22632	22670	22666	22709	22701	-
0	0	8	24869	24851	24895	24858	24905	24902	-	-	24898	24909	s
2	1	6	25284	25254	25299	25284	25341	25355	25354	25374	25397	25397	m
2	2	4	25553	25542	-	-	25670	25680	25723	25711	25746	25745	vw
4	0	0	-	-	-	-	-	-	25976	25981	-	-	vvs
1	0	8	26498	26462	26463	26472	26531	26524	26527	26526	26528	26533	vw
3	1	4	2718	27153	27208	27203	27299	27301	27348	27335	27376	27372	m
4	0	2	27360	27326	27390	27386	27469	27496	27534	27537	27598	27581	m
3	0	6	28505	28476	28511	28513	28607	28598	28612	28622	28653	28650	vw
1	1	8	28705	28684	28705	28701	28782	28766	28751	28774	28788	28788	vvs

Table 2. The unit cell parameters and volumes with estimated standard deviations of the hexagonal compounds $\text{Na}_3[\text{M}(\text{C}_7\text{H}_3\text{NO}_4)_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, $\text{M} = \text{Ho} - \text{Lu}$.

M	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
Ho	10.4155(19)	18.3709(50)	1725.9(0.8)
Er	10.4036(08)	18.3699(21)	1721.9(0.3)
Tm	10.3833(07)	18.3528(19)	1713.6(0.3)
Yb	10.3736(10)	18.3523(27)	1710.3(0.4)
Lu	10.3651(07)	18.3501(20)	1707.3(0.3)

given in Table 1. The unit cell dimensions with estimated standard deviations are given in Table 2. For HEXYBDIPIC the density 2.0 g/cm^3 was estimated by flotation. With two formula units in the cell the calculated density is 2.03 g/cm^3 .

THE DETERMINATION AND REFINEMENT OF THE STRUCTURE

The most probable symmetry of the central ion in the tris(dipicolinato) complex is 32 , which is the symmetry of the central ion in the corresponding

tris(oxydiacetato) group (*cf.* Ref. 4). This fact and the special condition $l = 2n$ limiting the strong reflexions of HEXYBDIPIC makes space group $P6_2c$ the only one compatible with a reasonable coordination polyhedron around the lanthanoid ions. Thus, they should be located at $(0,0,0; 0,0,1/2)$, *i.e.*, in the positions $2(a)$ of this space group. An F_o -synthesis was computed using these sites. The electron density maps obtained showed two centro-symmetrically related images of the structure. The non-hydrogen atoms belonging to one of the images of the tris(dipicolinato) complex were located using the known interatomic distances and angles.¹ Trial positions of a sodium ion (denoted Na(1)) and of two water oxygen atoms (O(3) and O(4)) were obtained in the mirror plane $z = 1/4$, *i.e.*, in positions $6(h)$. A series of full-matrix least-squares refinements of the deduced parameters was computed. The discrepancy indices $R = \sum(|F_o| - |F_c|) / \sum|F_o|$ and $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ converged to the values $R = 0.103$ and $wR = 0.115$. The carbon atom C(3) located in position $6(g)$ was found to oscillate with $\Delta x = \pm 0.03$ during the refinement, this oscillation being coupled to an oscillation of the temperature factor of C(3). The correlation coefficient is -0.59 . To avoid difficulties due to this behaviour of C(3) it was held fixed at the reasonable value $x = 0.5000$ in position $6(g)$ during the following calculations.

The elemental and infrared analyses of HEXYBDIPIC clearly show it to contain 1 mol sodium perchlorate per mol ytterbium. Two sodium ions (denoted Na(2)) and two chlorine atoms should thus be placed in the unit cell. As neither of the two species could be located in the remaining twofold positions $2(b) - 2(d)$ a statistical distribution of them, *e.g.*, among the fourfold positions of the space group, was assumed. A three-dimensional difference synthesis revealed a peak of the approximate height $9.5 \text{ e}/\text{\AA}^3$ at $(0,0,0.20)$, *i.e.*, in the position $4(e)$. This gives a distance of about 1.8 \AA between the peak at $(0,0,0.20)$ and the mirror-related one at $(0,0,0.30)$. Inspection of the F_o -synthesis showed that the maximum corresponding to O(3) was in fact located at $z = 0.27$ (with a mirror-related peak at $z = 0.23$) and not at the mirror plane. The peak at $(0,0,0.20)$ was thus found to be situated near the centre of an approximate octahedron composed of the three carboxylate oxygen atoms O(1) and three O(3) at $z = 0.27$, while the peak at $(0,0,0.30)$ is surrounded by the mirror-related octahedron. O(1) is coordinated to ytterbium. Thus, half a sodium ion (Na(2)) was placed in position $4(e)$ and half a water oxygen atom (O(3)) in position $12(i)$. The distances Na(2) - O(1) and Na(2) - O(3) are 2.6 and 2.4 \AA , respectively.

A refinement of the tris(dipicolinato) complex, the sodium ions, and of the water oxygen atoms O(3) and O(4) converged to $R = 0.095$, $wR = 0.102$. The positions of two perchlorate ions and of eight water oxygen atoms had now to be located in the unit cell.

Two peaks with the approximate height $9 \text{ e}/\text{\AA}^3$ at $(1/3, 2/3, 0.15)$ and $(2/3, 1/3, 0.15)$ are available for chlorine (positions $4(f)$). In each of these positions half a chlorine atom can be refined. Using the first position an isotropic temperature factor $B = 3.45 \text{ \AA}^2$ is obtained for chlorine together with $R = 0.076$ and $wR = 0.091$, while the second one gives $B = 3.57$, $R = 0.084$, and $wR = 0.091$. If an occupancy number of $1/4$ is used for both positions and both are simultaneously included in the refinement, it is not possible to refine the chlorine

at (2/3,1/3,0.15). Using these facts and considering the possibilities of packing the perchlorate ion in the structure, a chlorine atom was placed at (1/3,2/3,0.15) with occupancy 1/2.

A new three-dimensional difference synthesis was computed. The highest peak, $2.5 \text{ e}/\text{\AA}^3$, was situated at (0,0,0.03), indicating a slight anisotropic motion of the ytterbium ion, but since a refinement using anisotropic temperature factors for the ytterbium atom gave no better values of R and wR than before, its vibration was still treated as isotropic. Beside the ytterbium peak the only maxima above the background were located in position 12(*i*) with coordinates (0.20,0.50,0.15), *i.e.*, on the same z level as the chlorine atom and about 1.59 Å from it. The height is $2 \text{ e}/\text{\AA}^3$. It is obvious that no perchlorate oxygen atom could be located at this peak. If the remaining oxygen atoms were situated at ordered positions the 583 measured independent intensities most probably should suffice to determine these positions too, even with an occupancy of 1/2 as should be the case for the perchlorate oxygen atoms. The actual appearance of the difference synthesis is thus taken to indicate that the perchlorate ion as well as the missing water molecules are disordered. One possible assumption regarding the perchlorate ion seems to be that it can rotate without any restriction around the chlorine atom. In spite of the impossibility of elucidating the structure further, one may notice the rather good fit between the measured structure factors and those calculated for the proposed incomplete model of the structure. In a last attempt to refine the position of C(3) its x -coordinate was released. The atom still oscillated around $x=0.50$ with $\Delta x = \pm 0.02$. Hence, a location of C(3) in position 6(*g*) with $x=0.5000$ was regarded as the best possible choice. The discrepancy indices finally obtained are $R=0.076$, $wR=0.091$. In the last cycle of refinement not including the x -coordinate of C(3) the shifts in the parameters were less than 5 % of the estimated standard deviations. Table 3 gives the final atomic positions and the isotropic temperature factors.

Table 3. Atomic parameters with estimated standard deviations in HEXYBDIPIC. The space group is $F\bar{6}2c$ (No. 190).^a B denotes the isotropic temperature factor.

Atom	Position	Occupancy	x	y	z	$B/\text{\AA}^2$
Yb	2(<i>a</i>)	1	0	0	0	1.1(0.1)
Na(1)	6(<i>h</i>)	1	0.3615(18)	-0.0249(18)	1/4	3.4(0.3)
Na(2)	4(<i>e</i>)	1/2	0	0	0.2007(16)	3.9(0.5)
N	6(<i>g</i>)	1	0.2339(25)	0.2339(25)	0	2.6(0.4)
C(1)	12(<i>i</i>)	1	0.3388(30)	0.2575(29)	0.0492(14)	2.9(0.4)
C(2)	12(<i>i</i>)	1	0.4694(30)	0.3900(33)	0.0524(14)	3.2(0.4)
C(3)	6(<i>g</i>)	1	0.5000	0.5000	0	2.9(0.4)
C(4)	12(<i>i</i>)	1	0.2960(22)	0.1330(30)	0.1018(09)	2.2(0.3)
O(1)	12(<i>i</i>)	1	0.1744(16)	0.0222(15)	0.0903(07)	1.9(0.2)
O(2)	12(<i>i</i>)	1	0.3830(19)	0.1453(18)	0.1519(09)	2.7(0.3)
O(3)	12(<i>i</i>)	1/2	0.0886(32)	-0.1296(31)	0.2699(11)	2.2(0.5)
O(4)	6(<i>m</i>)	1	0.6159(35)	0.0942(33)	1/4	3.6(0.5)
Cl	4(<i>f</i>)	1/2	1/3	-1/3	0.1530(11)	3.4(0.3)

Table 4. Observed and calculated structure factors of HEXYBDIPIC. The 12 reflexions not obeying the condition $0.67 \leq |F_o|/|F_c| \leq 1.50$ are denoted by asterisks.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	203	184	0	0	22	41	40	3	1	9	29	12*	2	2	4	122	102
0	0	10	24	33	0	0	24	43	35	3	1	10	109	102	2	2	6	152	167
0	0	12	177	174	7	0	0	77	77	3	1	12	52	54	2	2	8	93	103
0	0	14	33	57	7	0	1	20	27	3	1	14	70	70	2	2	10	97	96
0	0	16	55	57	7	0	2	84	83	3	1	16	69	70	2	2	12	70	69
0	0	18	69	66	7	0	4	37	39	3	1	18	58	62	2	2	14	80	85
0	0	20	124	119	7	0	5	31	27	3	1	20	52	49	2	2	16	57	58
0	0	22	62	62	7	0	6	49	59	3	1	22	39	41	2	2	18	67	70
0	0	24	47	44	7	0	8	61	62	4	1	0	150	150	2	2	22	41	39
0	0	26	42	35	7	0	9	26	22	4	1	1	22	26	3	2	0	129	132
1	0	5	62	20*	7	0	10	102	103	4	1	1	22	26	3	2	0	129	132
1	0	6	61	65	7	0	12	35	62	4	1	2	102	93	3	2	1	34	40
1	0	8	107	97	7	0	14	49	49	4	1	4	102	103	3	2	2	50	59
1	0	10	179	162	7	0	16	30	33	4	1	5	33	20	3	2	4	137	131
1	0	12	65	90	7	0	18	45	38	4	1	6	107	116	3	2	5	51	33
1	0	14	75	79	7	0	20	43	40	4	1	8	76	79	3	2	6	62	69
1	0	16	56	49	7	0	22	42	30	4	1	9	29	29	3	2	8	101	97
1	0	18	54	57	8	0	0	105	110	4	1	10	76	76	3	2	10	91	92
1	0	20	53	55	8	0	2	50	57	4	1	11	26	25	3	2	12	70	70
1	0	22	57	59	8	0	4	86	87	4	1	12	71	75	3	2	14	50	45
1	0	24	39	40	8	0	6	67	71	4	1	14	82	78	3	2	16	75	79
2	0	3	111	117	8	0	8	76	80	4	1	16	56	57	3	2	18	46	53
2	0	4	241	216	8	0	10	47	51	4	1	18	50	52	3	2	20	39	47
2	0	5	51	55	8	0	12	65	67	4	1	20	45	51	3	2	22	38	38
2	0	6	60	63	8	0	14	43	54	4	1	22	43	40	4	2	0	119	106
2	0	7	112	104	8	0	16	54	51	4	1	24	42	37	4	2	1	42	36
2	0	9	22	14*	8	0	13	43	41	5	1	0	118	123	4	2	2	96	95
2	0	10	100	96	8	0	20	45	45	5	1	2	99	89	4	2	3	25	19
2	0	11	25	20	9	0	0	46	56	5	1	4	84	78	4	2	4	113	101
2	0	12	65	70	9	0	2	50	53	5	1	5	45	45	4	2	5	24	21
2	0	14	62	67	9	0	4	65	68	5	1	6	64	65	4	2	6	112	107
2	0	16	97	97	9	0	6	69	73	5	1	8	58	61	4	2	8	76	74
2	0	18	30	53	9	0	8	49	54	5	1	9	28	17*	4	2	10	95	97
2	0	20	49	53	9	0	10	42	48	5	1	10	88	79	4	2	12	59	62
2	0	22	44	45	9	0	12	40	42	5	1	12	74	70	4	2	14	75	77
2	0	24	47	49	9	0	14	45	52	5	1	14	55	59	4	2	16	55	55
2	0	26	42	31	9	0	16	43	42	5	1	16	49	49	4	2	18	58	53
3	0	1	125	126	9	0	18	41	40	5	1	18	30	41	4	2	20	40	41
3	0	2	89	76	10	0	0	49	49	5	1	20	50	47	4	2	22	39	44
3	0	3	89	55*	10	0	2	50	49	5	1	22	41	42	5	2	0	115	108
3	0	4	176	151	10	0	4	55	66	5	1	24	43	37	5	2	1	27	26
3	0	5	36	36	10	0	6	51	49	6	1	0	97	98	5	2	2	76	79
3	0	7	109	122	10	0	8	44	52	6	1	2	103	102	5	2	4	68	69
3	0	7	24	19	10	0	10	49	50	6	1	4	67	65	5	2	6	81	81
3	0	8	104	97	10	0	12	42	41	6	1	6	44	40	5	2	8	52	53
3	0	9	26	26	10	0	14	40	39	6	1	8	46	46	5	2	10	49	53
3	0	10	89	89	10	0	16	42	43	6	1	10	94	93	5	2	12	62	56
3	0	12	61	76	11	0	0	41	44	6	1	12	53	53	5	2	14	54	61
3	0	13	36	14*	11	0	2	41	46	6	1	14	41	43	5	2	16	48	44
3	0	14	67	67	11	0	4	49	50	6	1	16	39	46	5	2	18	43	44
3	0	16	60	82	11	0	6	36	34	6	1	18	38	42	5	2	20	49	45
3	0	18	47	56	11	0	8	39	33	6	1	20	43	43	5	2	22	44	37
3	0	20	55	59	11	0	10	40	37	7	1	0	97	89	5	2	24	42	33
3	0	22	41	33	11	0	12	41	33	7	1	2	60	64	6	2	0	75	70
3	0	24	52	43	12	0	0	43	49	7	1	4	50	55	6	2	2	83	74
3	0	26	42	33	12	0	2	47	49	7	1	6	76	73	6	2	4	92	89
4	0	1	43	46	12	0	4	44	34	7	1	8	59	60	6	2	6	62	60
4	0	2	170	159	12	0	6	44	42	7	1	10	55	59	6	2	8	72	68
4	0	3	21	20	12	0	8	41	33	7	1	12	48	54	6	2	10	75	70
4	0	4	139	142	12	0	10	42	36	7	1	14	55	56	6	2	12	54	59
4	0	5	20	20	13	0	0	46	47	7	1	16	38	39	6	2	14	48	51
4	0	6	101	109	13	0	2	42	35	7	1	18	39	39	6	2	16	55	56
4	0	7	20	20	13	0	4	39	31	7	1	20	45	41	6	2	18	41	40
4	0	8	63	67	13	0	6	47	40	8	1	2	63	66	6	2	20	39	40
4	0	9	87	87	1	1	8	146	141	8	1	2	53	61	7	2	0	32	30
4	0	10	25	22	1	1	8	69	82	8	1	4	76	79	7	2	2	59	61
4	0	10	131	134	1	1	10	114	120	8	1	6	62	64	7	2	4	56	65
4	0	12	74	71	1	1	12	61	62	8	1	8	52	52	7	2	6	60	71
4	0	14	91	90	1	1	14	93	92	8	1	10	50	47	7	2	8	49	49
4	0	16	77	79	1	1	16	51	52	8	1	12	40	41	7	2	10	55	63
4	0	18	67	62	1	1	18	51	50	8	1	14	45	46	7	2	12	41	41
4	0	20	47	46	1	1	20	38	42	8	1	16	47	50	7	2	14	51	51
4	0	24	49	45	1	1	22	41	45	8	1	18	41	41	7	2	16	48	45
5	0	1	130	130	1	1	26	45	36	9	1	0	37	45	7	2	18	42	37
5	0	2	70	75	2	1	0	110	96	9	1	4	38	59	8	2	2	54	55
5	0	4	100	97	2	1	1	49	35	9	1	6	55	56	8	2	4	70	70
5	0	6	63	63	2	1	2	66	66	9	1	8	43	48	8	2	6	62	58
5	0	7	30	24	2	1	3	44	32	9	1	10	53	52	8	2	8	52	55
5	0	8	93	90	2	1	4	47	40	9	1	12	38	37	8	2	10	45	43
5	0	10	60	60	2	1	5	75	79	9	1	14	40	41	8	2	12	39	42
5	0	11	26	16*	2	1	6	150	144	9	1	16	45	39	8	2	14	45	45
5	0	12	102	94	2	1	9	92	83	10	1	0	57	55	8	2	16	39	45
5	0	14	43	40	2	1	10	52	72	10	1	2	40	39	9	2	0	53	59
5	0	16	50	58	2	1	12	40	41	10	1	4	37	37	9	2	2	45	42
5	0	18	35	30	2	1	11	26	25	10	1	6	49	50	9	2	4	38	42
5	0	20	49	49	2	1	12	59	61	10	1	8	39	45	9	2	6	30	40
5	0	24	41	40	2	1	13	26	13*	10	1	10	39	37	9	2	8	43	47
5	0	22	69	69	2	1	16	67	69	10	1	12	41	40	9	2	10		

Table 4. Continued.

h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $
3	3	4	111	103	6	3	14	53	54	4	4	16	50	51	6	5	7	42	40
3	3	6	98	79	6	3	18	41	38	4	4	20	40	43	6	5	4	60	50
3	3	8	96	93	6	3	16	47	43	4	4	18	40	40	6	5	6	40	42
3	3	10	64	60	6	3	20	36	40	5	4	11	74	69	6	5	8	44	45
3	3	12	68	71	7	3	0	46	47	5	4	4	69	76	6	5	10	30	47
3	3	14	67	62	7	3	2	47	50	5	4	6	74	73	6	5	12	44	45
3	3	16	55	52	7	3	4	56	57	5	4	8	59	60	7	5	0	45	52
3	3	18	40	46	7	3	6	65	62	5	4	10	77	73	7	5	2	41	43
3	3	20	36	41	7	3	8	42	49	5	4	12	41	46	7	5	4	46	45
3	3	22	35	33	7	3	10	52	52	5	4	14	43	45	7	5	6	42	43
4	3	0	88	91	7	3	12	38	42	5	4	16	49	50	7	5	8	46	43
4	3	1	33	32	7	3	14	40	45	5	4	18	47	46	7	5	10	45	47
4	3	2	86	69	7	3	16	30	40	6	4	0	74	71	7	5	12	42	42
4	3	4	103	100	8	3	0	62	58	6	4	2	70	67	8	5	0	40	56
4	3	5	23	19	8	3	2	47	51	6	4	4	65	63	8	5	2	41	41
4	3	6	59	83	8	3	4	56	58	6	4	6	73	68	8	5	4	41	39
4	3	8	59	64	8	3	6	41	37	6	4	8	57	54	8	5	6	42	45
4	3	10	48	58	8	3	8	41	45	6	4	10	54	53	9	5	0	45	44
4	3	11	29	24	8	3	10	43	46	6	4	12	54	53	9	5	2	45	36
4	3	12	51	52	8	3	12	37	36	6	4	14	47	47	9	5	4	45	36
4	3	14	62	64	8	3	14	38	32	6	4	16	45	44	9	5	6	47	40
4	3	16	57	56	8	3	16	36	39	7	4	0	52	57	9	5	8	44	37
4	3	18	46	49	9	3	0	56	52	7	4	2	41	43	10	5	0	63	61
4	3	20	37	39	9	3	2	48	50	7	4	4	49	46	10	5	2	53	51
4	3	22	36	37	9	3	4	39	38	7	4	6	54	55	10	5	4	50	46
5	3	0	79	70	9	3	6	47	46	7	4	8	43	48	10	5	6	43	46
5	3	2	61	59	9	3	8	44	39	7	4	10	40	44	10	5	8	37	43
5	3	4	86	89	9	3	10	49	45	7	4	12	36	46	10	5	10	45	48
5	3	6	76	71	9	3	12	43	36	8	4	0	52	56	10	5	12	42	43
5	3	8	79	75	10	3	0	36	36	8	4	2	52	57	10	5	14	37	41
5	3	10	72	70	10	3	2	38	40	8	4	4	52	54	10	5	16	40	50
5	3	12	62	60	10	3	4	42	42	8	4	6	45	47	10	5	18	44	42
5	3	14	51	50	10	3	6	35	36	8	4	8	42	44	10	5	20	36	39
5	3	16	35	36	11	3	0	37	33	8	4	10	47	51	10	5	22	35	32
5	3	18	36	40	11	3	2	37	33	8	4	12	47	51	10	5	24	39	39
5	3	20	36	36	4	4	0	95	84	5	5	0	67	70	10	5	26	40	43
5	3	0	91	80	4	4	2	65	80	5	5	2	70	64	10	5	28	40	44
6	3	2	56	56	4	4	4	92	86	5	5	4	57	60	10	5	30	40	41
6	3	4	57	57	4	4	6	113	104	5	5	6	54	57	10	5	32	40	39
6	3	5	24	25	4	4	8	69	84	5	5	8	50	51	10	5	34	37	36
6	3	6	62	81	4	4	10	102	86	5	5	10	51	51	10	5	36	36	35
6	3	8	62	57	4	4	12	79	67	5	5	12	41	44	9	6	0	35	27
6	3	10	41	42	4	4	14	56	64	6	5	0	54	55	9	6	2	35	29
6	3	12	51	51	4	4	16	51	50	6	5	2	54	55	9	6	4	33	36

The quantity minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. The weights w were calculated according to the expression $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$. An analysis of the weighting scheme suggested suitable values for a , c , and d . In the last cycle of refinement the values $a = 48$, $c = 0.00833$, and $d = 0.0001$ were used. Reflexions not obeying the condition $0.67 \leq |F_o|/|F_c| \leq 1.50$ were given zero weight. The atomic scattering factors used in the calculations were taken from the *International Tables*⁵ (Cl, Na⁺, O, N, and C) and from Cromer *et al.*⁶ (Yb). Observed and calculated structure factors are compared in Table 4.

Selected interatomic distances and angles in the structure are given in Table 5. The standard deviations are calculated from the estimated standard deviations of the atomic coordinates and the unit cell dimensions.

The computations were performed on the computers CDC 3600 in Uppsala and UNIVAC 1108 in Lund using the programs PIRUM,⁷ CELSIUS, DRF, LALS, DISTAN, PLANE, and ORTEP.⁸

DESCRIPTION OF THE STRUCTURE

The mononuclear tris(dipicolinato)ytterbate complexes in HEXYBDIPIC are located in mirror-related layers perpendicular to the c axis with the ytterbium ions in the planes $z = 0$ and $z = 1/2$. The layer around $z = 0$ is shown in Fig. 1. The lanthanoid complexes are held together in an infinite chain

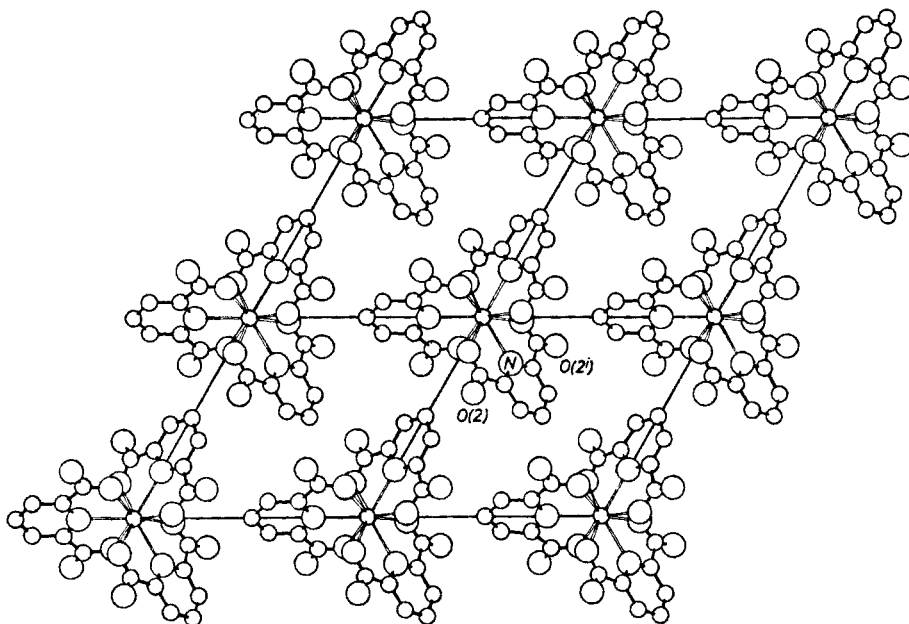


Fig. 1. A projection of HEXYBDIPIC on (001) showing the layer around $z=0$ containing the tris(dipicolinato) complexes. Figs. 1, 2, and 3 are drawn with the program ORTEP, written by C. K. Johnson, Oak Ridge.

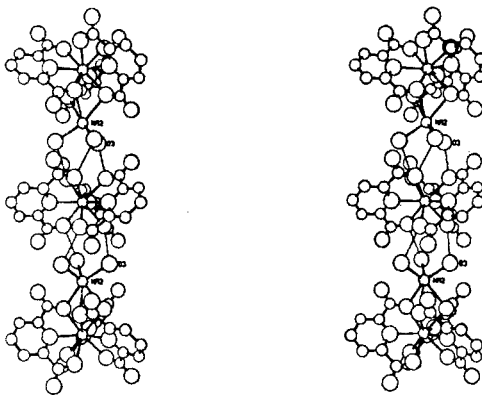


Fig. 2. A stereoscopic pair of drawings showing the chain composed of the tris(dipicolinato) complexes, the sodium ions Na(2), and the water oxygen atoms O(3).

along the c axis. This chain is composed of the complex ions, the sodium ions Na(2), and the water molecules containing the oxygen atoms O(3). The central ions of the complexes are located at $(0,0,0)$ and $(0,0,1/2)$. There are two sodium

ions Na(2) per unit cell. One of these may either be situated at (0,0,0.20) with three O(3) at $z=0.27$ or at (0,0,0.30) with the three O(3) at $z=0.23$. In the same way and independent of the location of the first Na(2) the second may either be situated at (0,0,0.70) with three O(3) at $z=0.77$ or at (0,0,0.80) with three O(3) at $z=0.73$. The chains are held together by coordination of O(1) and O(3) to Na(2) and by hydrogen bonds between O(3) and O(1). In Fig. 2, a part of a chain is shown in a stereoscopic view.

The chains are connected with each other by hydrogen bonds in the following way. The coordination polyhedra around the sodium ions Na(1) are attached to the Na(2) polyhedra by sharing the corner O(3) and by the bonds Na(1)–O(2) and Na(2)–O(1) *via* the carboxylate group O(1)C(4)O(2). The Na(1) coordination polyhedra attached to one chain are connected to the Na(1) polyhedra attached to adjacent chains by hydrogen bonds O(4)–O(2). The sodium ions with their coordination polyhedra are located in layers around $z=1/4$ and $z=3/4$. In Fig. 3 such a layer is shown.

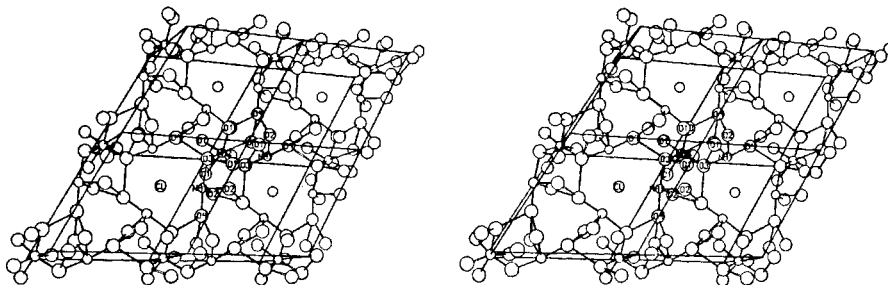


Fig. 3. A stereoscopic pair of drawings showing the layer around $z=1/4$ (the box is drawn between $z=0$ and $z=1/2$). The sodium-oxygen bonds are filled, the possible hydrogen bonds are open.

Around the sixfold inversion axes $x=1/3$, $y=2/3$ and $x=2/3$, $y=1/3$ there are fairly wide tunnels in the structure. In these tunnels the disordered perchlorate ions are located with the chlorine atoms at the positions 4(*f*), (1/3, 2/3, 0.15), with occupancy 1/2. Presumably, most of the eight water molecules per unit cell which are not found in the structure determination might also be occluded in these channels.^{2,9}

In a following paper of this series dealing with the structure of the triclinic compound NDP, the four investigated lanthanoid dipicolinate compounds ORT-, MON-, and HEXYBDIPIC, and NDP will be compared. Hence, no references are made to the other dipicolinate compounds in the following discussion.

Some symmetry-related sites in the structure of HEXYBDIPIC are designated below by superscripts (i)–(vi) in the following way.

- | | | |
|--------------------------|------------------------|-------------------------------|
| (i) y, x, \bar{z} | (ii) $\bar{y}, x-y, z$ | (iii) $x-y, \bar{y}, \bar{z}$ |
| (iv) $\bar{y}, x-y-1, z$ | (v) $1-y, x-y, z$ | (vi) $x, y, 1/2-z$ |

where x, y, z are coordinates of the "crystal-chemical" unit given in Table 3.

Table 5. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in HEXYBDIPIC.

A. The ytterbium coordination polyhedron

Distance		Distance	
Yb—O(1)	2.38(1)	N—O(1 ⁱⁱ)	2.88(2)
Yb—N	2.43(3)	O(1)—O(1 ⁱⁱ)	2.96(3)
N—O(1)	2.57(2)	O(1)—O(1 ⁱⁱⁱ)	3.34(3)

B. The ligand

Distance		Angle	
N—C(1)	1.34(3)	C(1)—N—C(1 ⁱ)	120(3)
C(1)—C(2)	1.37(4)	N—C(1)—C(2)	121(2)
C(2)—C(3)	1.40(3)	C(1)—C(2)—C(3)	120(2)
C(1)—C(4)	1.49(4)	C(2)—C(3)—C(2 ⁱ)	117(2)
C(4)—O(1)	1.23(3)	N—C(1)—C(4)	115(2)
C(4)—O(2)	1.25(3)	C(2)—C(1)—C(4)	124(2)
O(1)—O(2)	2.20(2)	C(1)—C(4)—O(1)	115(2)
N—C(3)	2.76(3)	C(1)—C(4)—O(2)	120(2)
		O(1)—C(4)—O(2)	125(2)

C. The sodium coordination

Distance		Distance	
Na(1)—O(2)	2.45(2)	Na(2)—O(1)	2.65(3)
Na(1)—O(3)	2.50(3)	Na(2)—O(3)	2.35(3)
Na(1)—O(4)	2.29(4)	Na(1)—Na(2)	3.99(2)

D. Possible hydrogen bond distances

Distance	
O(3)—O(1 ^{vi})	2.91(3)
O(3)—O(4 ^{iv})	3.16(4)
O(4)—O(2 ^v)	2.81(3)

The ytterbium coordination polyhedron. The ytterbium ion in HEXYBDIPIC is surrounded by a distorted tri-capped trigonal prism of oxygen and nitrogen atoms. The carboxylate oxygen atoms O(1) are in the corners of the prism and the nitrogen atoms of the pyridine rings in the equatorial plane. The triangular faces of the prism are rotated 10° relative to each other. The distance between these faces is 3.31 ± 0.03 Å. The symmetry of the central ion in the tris(dipicolinato) complex is $\bar{3}2$. Selected distances in the coordination polyhedron are given in Table 5 A.

The ligand. Each of the three ligands in the complex forms two identical five-membered rings with the ytterbium ion. The bond angles Yb—O(1)—C(4)

and $\text{Yb}-\text{N}-\text{C}(1)$ are $126 \pm 1^\circ$ and $120 \pm 1^\circ$, respectively. The atoms of the ligand are designated in Fig. 4. The bond distances and angles are given in Table 5 B. The dimensions of the different dipicolinate ions found in the present series of investigation are discussed in a following paper dealing with NDP. The least-squares plane through the seven carbon atoms and the nitrogen atom of the ligand has been calculated. As is shown in Table 6 these atoms are coplanar within 0.03 \AA . Within the limits of error the carboxylate oxygen atoms lie in the same plane.

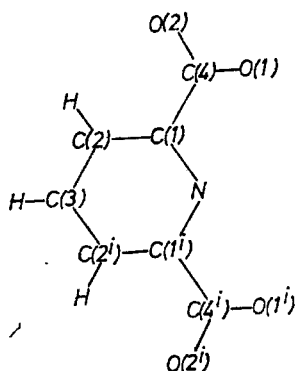


Fig. 4. Designation of the atoms in the dipicolinate ligand.

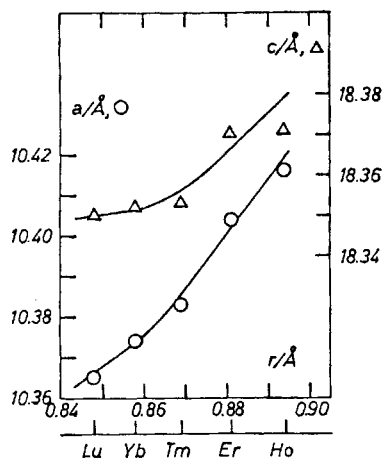


Fig. 5. The unit cell dimensions of the hexagonal compounds $\text{Na}_3[\text{M}(\text{C}_5\text{H}_7\text{NO}_4)_3] \cdot \text{NaClO}_4 \cdot 10\text{H}_2\text{O}$, $\text{M} = \text{Ho}-\text{Lu}$, plotted versus the crystal radius r of the trivalent lanthanoid ions.

The packing of the complex ions. The large mononuclear tris(dipicolinato) complex makes the ytterbium-ytterbium distances very long. The shortest distance is $\text{Yb}-\text{Yb}^{\text{vi}}$, which is 9.18 \AA . The carbon-carbon packing distances

Table 6. The deviation (in Å) from the least-squares plane through the seven carbon atoms and the nitrogen atom of the ligand. The lower signs refer to the superscripted atoms. N, C(3), and Yb are situated on the same twofold axis.

Atom	Distance	Atom	Distance
N	0.00	C(4), C(4')	± 0.01
C(1), C(1')	± 0.02	O(1), O(1')	± 0.06
C(2), C(2')	∓ 0.03	O(2), O(2')	∓ 0.03
C(3)	0.00	Yb	0.00

within a layer of complex ions are all longer than 3.50 Å. The separation distance between the layers is 3.60 Å.

The sodium coordination polyhedra. The sodium ion Na(2) is surrounded by the oxygen atoms O(1) and O(3) in an approximately octahedral configuration. Only the four oxygen atoms O(2), O(2^{vi}), O(3), and O(4) are found to be coordinated to Na(1). As is seen in Fig. 3, one may consider them as being located at four of the six corners of a distorted octahedron. It is thus probable that some of the disordered water molecules and perchlorate ions interact with Na(1). In this connection it should be observed that the maximum obtained at (0.20, 0.50, 0.15) in the last difference synthesis (see p. 1009) is situated 2.45 Å from Na(1), *i.e.*, within a reasonable sodium-oxygen coordination distance. This peak and the mirror-related one at (0.20, 0.50, 0.35) are near the unoccupied corners of the Na(1) octahedron.

The sodium-oxygen bond distances and the distance between the bridged Na(1) and Na(2) are given in Table 5 C. The distance Na(2)–O(1) is rather long. The different oxygen-oxygen “contact” distances along the edges of the sodium coordination polyhedra are in the range 3.26–4.02 Å, except the distance O(1)–O(1ⁱⁱ), also belonging to the ytterbium coordination polyhedron, which is 2.96 ± 0.03 Å (*cf.* Table 5 A). The O–Na–O bond angles with adjacent oxygen atoms lie in the interval 83–107° except O(1)–Na(2)–O(1ⁱⁱ) which is $68 \pm 1^\circ$.

Possible hydrogen bonds. Eight out of the 20 water molecules in the unit cell of HEXYBDIPIC are disordered. These water molecules most probably interact with each other, with the disordered perchlorate ions, and with the ordered oxygen atoms by forming hydrogen bonds. Thus only some of the possibilities of hydrogen bonding in the structure could be outlined. The three bond distances less than 3.20 Å which are given in Table 5 D and shown in Figs. 2 and 3 obey conditions similar to those given for the hydrogen bond system in Ref. 2.

The variation of the unit cell dimensions. In Fig. 5 the unit cell dimensions of the hexagonal Ho–Lu compounds are plotted *versus* the set of empirical crystal radii, r , for the lanthanoid ions determined by Templeton and Dauben.¹⁰ In each unit cell there are two layers containing the tris(dipicolinato) complexes. These layers are stacked along the c axis. Because of that, and in accordance with the previously investigated lanthanoid oxydiacetate compounds $\text{Na}_3[\text{M}(\text{C}_4\text{H}_4\text{O}_5)_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$,⁴ one might expect an approximately parallel decrease in a and $c/2$ when going from Ho to Lu. Instead, the decrease in c is much smaller than that in a , as is shown in Fig. 5. The reasons for this behaviour cannot be elucidated until single crystal data are available for at least two of the hexagonal compounds. The increased resistance to the lanthanoid contraction, which is shown by the compounds formed with the heaviest ions, may depend upon van der Waals repulsions in the coordination polyhedra around these small ions.⁴ In the ytterbium polyhedron (*cf.* Table 5 A) the distance N–O(1ⁱⁱ) agrees with the sum of the van der Waals radii of the atoms,¹¹ while the other independent contact distance between coordinated atoms not belonging to the same ligand, *i.e.*, O(1)–O(1ⁱⁱ), has a somewhat larger value.

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