

Structural Studies on the Rare Earth Carboxylates

4. The Crystal and Molecular Structure of Orthorhombic Trisodium Tris(pyridine-2,6-dicarboxylato)ytterbiumate(III)-14-hydrate

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The structure of the orthorhombic tris(dipicolinato)ytterbiumate(III) compound $\text{Na}_3[\text{Yb}(\text{OCOC}_5\text{H}_3\text{NOCO})_3] \cdot 14\text{H}_2\text{O}$ has been determined from three-dimensional X-ray intensity data collected with the Weissenberg multiple-film technique. The compound crystallizes in the space group *Pnma* with the unit cell dimensions $a = 10.323 \pm 0.006 \text{ \AA}$, $b = 21.119 \pm 0.006 \text{ \AA}$, and $c = 16.581 \pm 0.003 \text{ \AA}$, $Z = 4$. The structure contains mononuclear tris(dipicolinato)ytterbiumate complexes. Each dipicolinate ion acts as a tridentate ligand forming two five-membered rings with the ytterbium ion which is thus nine-coordinated. The coordination polyhedron around the ytterbium ion can be described as a distorted trigonal prism of carboxylate oxygen atoms with the nitrogen atoms lying outside the approximately rectangular faces of the prism. The average value of both the Yb—O and Yb—N bond distances is $2.35 \pm 0.02 \text{ \AA}$. All Yb—Yb distances are very long, the shortest one is $9.76 \pm 0.01 \text{ \AA}$. The water oxygen atoms and the carboxylate oxygen atoms coordinated to the sodium ions form finite chains, each containing four octahedra connected by sharing edges. These chains are parallel to the *c* axis. Each sodium site has an occupation number of about $\frac{3}{4}$. The tris(dipicolinato)ytterbiumate complexes are held together by the sodium ions in layers perpendicular to the *c* axis. These layers are connected only by hydrogen bonds *via* the water molecules.

Grenthe¹ has determined the compositions and the relative amounts of the complexes formed in solution between the trivalent lanthanoid ions and the dipicolinate (or pyridine-2,6-dicarboxylate) ion, $\text{C}_5\text{H}_3\text{N}(\text{COO})_2^{2-}$. This species has three possible coordinating sites and presumably acts as a tridentate ligand. In solution the stable mononuclear complexes ML , ML_2 , and ML_3 are formed with all lanthanoids, suggesting that the central ion is at least nine-coordinated.

As a ligand the dipicolinate ion is very similar to the oxydiacetate ion. In the first paper of the present series² the crystal and molecular structure

of the oxydiacetate compounds $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, $\text{M}=\text{Ce-Lu}$, were reported. While the structures in that series are all isomorphous the situation is more complicated for the compounds containing the mononuclear tris(dipicolinato)lanthanoidate(III) complexes. The elements Ce-Dy give compounds with almost identical triclinic structures but depending upon the method of preparation, hexagonal, monoclinic, and orthorhombic phases have been obtained for the elements Dy-Lu.³ This paper is a report of the crystal and molecular structure of the orthorhombic compound trisodium tris(dipicolinato)ytterbiumate(III)-14-hydrate, $\text{Na}_3[\text{Yb}(\text{OCOC}_5\text{H}_3\text{NOCO})_3] \cdot 14\text{H}_2\text{O}$, which is referred to as ORTYB-DIPIC below.

EXPERIMENTAL

Preparation and analysis. Gelatinous ytterbium hydroxide (2 mmole) and pyridine-2,6-dicarboxylic acid (6 mmole) were dissolved in boiling water. Sodium hydroxide (about 6 ml 1 M) was added until the pH of the solution had a value near 7. Slow evaporation at room temperature gave prismatic, regularly grown crystals. Since they effloresced very rapidly they were stored in the mother liquor. Samples to be analysed were kept for at least 12 h at room temperature in an atmosphere saturated with water vapor. In this way the crystals could be preserved for at least one week before a change in the composition was detected. The compound was analysed for Yb, H_2O , Na, N, C, and H. (The last four elements by *Division of Analytical Chemistry*, University of Lund). The relative amounts found are compared with those calculated for $\text{Na}[\text{Yb}(\text{OCOC}_5\text{H}_3\text{NOCO})_3]14\text{H}_2\text{O}$, F.W. 989.6.

	Yb	Na	N	C	H	H_2O	
Found	16.9	7.2	4.3	25.9	3.8	26.6	(%)
Calc.	17.5	7.0	4.2	25.4	3.7	25.5	(%)

The results of the analyses are compatible with (15 ± 1) H_2O per Yb but since only 14 H_2O per Yb were found during the structure determination this latter amount seems to be correct.

Powder work. Powder photographs were taken at room temperature with $\text{CuK}\alpha$ radiation in a Guinier focusing camera ($\lambda=1.54178 \text{ \AA}$). Aluminium (cubic, $a=4.04934 \text{ \AA}$ at 21°C) was used as an internal standard. After grinding together with some mother liquor, the material was placed between plastic films during the exposure. To avoid errors due to film shrinkage a scale graduated in 0.1 mm was photographed on the films before their processing.

Single-crystal work. Freshly prepared single crystals of ORTYBDIPIC were mounted in capillaries together with mother liquor. Even then, they could only be used for X-ray work for about one week before disintegrating. The intensity data were recorded from three different crystals. They were all prismatic, elongated in the a direction, with the approximate dimensions $0.2 \times 0.1 \times 0.1 \text{ mm}^3$. Two of them were mounted along the a axis and employed for the layers $0kl-6kl$ and $7kl-9kl$, respectively. The third one was mounted along the b axis and the layers $h0l$ and $h1l$ were recorded. Several attempts to get more data along the b and c axes failed because of the long time needed to mount and adjust the crystals along other axes than a .

The intensity data were recorded with the non-integrated Weissenberg multiple-film technique. Ni-filtered Cu radiation was used. The intensities were estimated visually by comparison with a calibrated scale. All reflexions with $h+l \neq 2n$ are weak or absent. Furthermore, it was found that most reflexions with both h and l even and with $h/2+k \neq 2n$ were absent. Thus only 1285 independent reflexions were measured representing about 40 % of the possible number in the recorded reciprocal region. The linear absorption coefficient μ is 59 cm^{-1} . Because of this low value and the small crystals used, no absorption corrections were applied.

Table 1. X-Ray powder data for ORTYBDIPIC.

<i>hkl</i>	$10^4 \times \sin^2\theta$ (observed)	$10^4 \times \sin^2\theta$ (calculated)	<i>I</i> (observed)	<i>hkl</i>	$10^4 \times \sin^2\theta$ (observed)	$10^4 \times \sin^2\theta$ (calculated)	<i>I</i> (observed)
0 1 1	34.9	34.9	w	1 2 5	649.4	649.5	s
0 2 0	54.0	53.3	vs	0 3 5	662.0	660.3	w
1 0 1	76.9	77.4	vvvs	2 3 4	692.1	{688.8}	w
0 0 2	86.2	86.5	s	3 0 3		{696.5}	
1 1 1	89.8	90.7	vs	3 1 3	710.3	709.8	w
1 2 1	131.2	130.7	s	1 6 3	731.6	{730.0}	w
0 2 2	140.0	{139.8}	m	1 7 1		{730.3}	
0 3 1		{141.5}		1 5 4		{734.7}	
1 1 2	156.3	155.6	w	3 4 1	739.7	736.7	m
1 3 1	198.5	197.3	m	3 2 3	748.2	{749.7}	vw
0 1 3	207.3	207.9	w	2 5 3		{750.7}	
0 4 0	215.8	213.2	m	2 1 5	777.1	{776.8}	m
2 0 0	225.5	223.1	vvw	0 0 6		{778.2}	
2 1 0	234.5	236.4	w	1 7 2	796.5	795.1	vw
1 0 3	248.8	250.3	w	3 3 3	814.9	{816.4}	s
1 3 2	262.4	{262.1}	vvw	2 2 5		{816.8}	
1 1 3		{263.6}		0 2 6	832.0	831.5	m
2 2 0	276.0	276.4	m	3 1 4	861.9	861.1	vvw
1 4 1	293.2	290.6	s	4 0 0	889.1	892.3	m
2 2 1	297.4	{298.0}	w	3 4 3	909.1	909.6	m
0 4 2		{299.7}		0 8 2	934.3	939.2	w
1 2 3	302.1	303.6	s	4 2 0	944.5	945.6	w
0 3 3	316.3	314.5	vvw	1 3 6	955.1	953.8	w
2 1 2	321.2	322.9	w	2 4 5	975.8	{976.6}	m
2 3 0	343.7	{343.0}	vs	4 0 2		{778.7}	
0 0 4		{345.9}		1 8 2	995.5	995.0	w
2 2 2	361.0	362.8	vw	2 1 6	1012.0	1014.6	s
2 3 1	364.0	364.6	vvw	4 2 2	1033.5	1032.0	m
0 2 4	399.6	399.1	s	3 0 5	1041.9	1042.3	w
1 1 4	416.2	414.9	w	1 7 4	1053.4	{1054.5}	w
2 3 2	430.8	{429.5}	s	3 1 5		{1055.6}	
2 1 3		{430.9}		2 3 6	1122.1	1121.1	m
2 4 0	440.2	436.3	vw	4 4 2	1191.9	1191.9	
1 4 3	460.9	463.5	m	0 7 5	1194.4	{1193.3}	m,d
2 2 3	466.7	470.9	w	0 8 4		{1198.6}	
0 6 0	481.2	479.7	w	1 3 7	1236.0	{1234.8}	
3 0 1	523.8	523.5	w	4 0 4	1260.7	{1238.1}	m
3 1 1	535.5	{536.9}	m	0 6 6		1257.8	
2 3 3		{537.5}		4 2 4	1291.5	1291.4	w
0 1 5	550.5	553.7	vvw	2 9 1	1322.2	1323.9	w
0 6 2	561.9	566.1	vs	3 2 6		1333.4	
3 2 1	576.4	{576.8}	w	2 5 6	1338.3	{1334.3}	m,d
2 5 1		{577.8}		2 2 7		{1335.5}	
2 1 4	582.8	{582.2}	m	4 3 4	1360.9	1358.0	vw
1 5 3		{583.4}		0 0 8	1381.1	1383.4	m
1 0 5	596.9	596.2	vvw	2 9 2	1388.8	1388.8	vw
1 1 5	610.0	609.5	m	1 10 1	1407.9	1409.8	m
2 4 3	634.1	630.8	vw				

UNIT CELL AND SPACE GROUP

ORTYBDIPIC crystallizes in the orthorhombic system. The systematically absent reflexions are $0kl$: $k+l \neq 2n$, $h0l$: $h+l \neq 2n$, and $hk0$: $h \neq 2n$. The only possible space group is thus $Pnna$ (No. 52).⁴ The general positions of this space group are eightfold: $\pm(x, y, z; \frac{1}{2}-x, \bar{y}, z; x, \frac{1}{2}-y, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}+\bar{y}, \frac{1}{2}-z)$

Preliminary unit cell dimensions were obtained from Weissenberg and oscillation photographs. They were improved by a series of least-squares treatments of the powder data minimizing $\sum w(\sin^2\theta_o - \sin^2\theta_c)^2$ with weights $w=1/\sin^2 2\theta_o$. The observed powder pattern is given in Table 1. The following crystal data were obtained:

$$\begin{array}{ll} a = 10.323 \pm 0.006 \text{ \AA} & D_m = 1.7 \text{ g/cm}^3 \\ b = 21.119 \pm 0.006 \text{ \AA} & D_x = 1.74 \text{ g/cm}^3 \\ c = 16.581 \pm 0.003 \text{ \AA} & Z = 4 \\ V = 3615 \pm 2 \text{ \AA}^3 & \end{array}$$

The density D_m was estimated by flotation.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The special condition $h+l=2n$ limiting the strong reflexions of ORTYBDIPIC locates the ytterbium atoms in the positions $4(d)$, $\pm(x, \frac{1}{4}, \frac{1}{4}; \frac{1}{2}+x, \frac{1}{4}, \frac{3}{4})$, of the space group $Pnna$, *i.e.* on twofold axes. A linear Harker synthesis computed for $(u, \frac{1}{2}, \frac{1}{2})$ gave $x=0.12$. One could, however, have arrived at approximately the same value of x without reference to any Fourier summation. As noted above (p. 1214) most reflexions with both h and l even are absent if $h/2+k=2n+1$. Since the scattering power of ytterbium is much greater than that of the other atoms in the structure, this additional condition might depend upon the actual location of the ytterbium atoms. If both h and l are even the contribution to the structure factors of the heavy atoms in the positions $4(d)$ contains the factor $1 + \exp(\pi i(k-4hx))$ which is zero for $x=1/8$ when $h/2+k=2n+1$. When $h/2+k=2n$ and $x=1/8$ its value is 2. The great number of absent spectra thus depends both upon the fact that the heavy atoms are located in the positions $4(d)$ and that they approximately fit into a centered rectangular lattice with the dimensions $a/2$ and b when projected on the ab plane.

Omitting the reflexions with $h+l$ odd, the preliminary value $x=0.12$ for the ytterbium atoms was refined together with the isotropic temperature factor and the inter-layer scale factors in three cycles of least-squares treatment. A three-dimensional difference synthesis based upon the improved ytterbium positions was then computed. Two images of the structure, related by a mirror plane at $y=1/4$, appeared, as the reflexions with $h+l$ odd had to be omitted from the synthesis too. The carbon, nitrogen, and oxygen atoms belonging to one of the images of the dipicolinate complex were located in the electron density maps by using the assumption that the coordination geometry around the ytterbium atom in ORTYBDIPIC is similar to that of the tris(oxydiacetato)ytterbiumate(III) complex.² The approximately planar,

tridentate ligands should lie in the planes defined by the central ion and the diagonals of the "rectangular" faces of a distorted trigonal prism. This prism was first located and the remaining ligand atoms were then readily found in the presumed planes from known interatomic distances and angles.

A new difference synthesis was computed using the parameters of the image chosen for the dipicolinate complex. This time the reflexions with $h+l$ odd could be included. In the electron density maps thus obtained, the mirror plane at $y=1/4$ was removed but the peaks still appeared in pairs. Trial positions of the seven independent water oxygen atoms of $\text{Na}_3[\text{Yb}(\text{OCOC}_5\text{H}_3\text{NOCO})_3] \cdot 14\text{H}_2\text{O}$ were deduced by choosing the higher peak in each pair of related ones. Together with two independent carboxylate oxygens, O(2) and O(6), the water oxygens form limited chains of four octahedra along each of the twofold axes ($x = \pm 1/4, y = 0$; $x = \pm 1/4, y = 1/2$). Within each chain the octahedra are linked together by sharing edges. In the centre of each octahedron, *i.e.* in positions 4(c), and at distances of about 2.4 Å from the surrounding oxygen atoms a peak with the approximate height $3 \text{ e}/\text{Å}^3$ was found. Since there are only twelve sodium ions in the unit cell to be placed in these sixteen available sites, $3/4$ of an ion was placed in each. The positions chosen for the sodium ions and water oxygen atoms must belong to the same image of the structure as the dipicolinate complex, since this is the only choice in which four carboxylate oxygens per dipicolinate complex are within coordination distances from sodium sites. It should also be observed that in this case regular coordination polyhedra around each of the sodium sites are obtained.

The atomic coordinates and isotropic temperature factors of one of the two mirror-related trial structures of ORTYBDIPIC were improved together with the inter-layer scale factors by least-squares refinement. Because of the large number of parameters a diagonal approximation which allows for the correlation between the scale and temperature factors was used. A damping factor of 0.7 was applied to the shifts. In the quantity minimized, $\sum w(|F_o| - |F_c|)^2$, only observed reflexions with $0.50 \leq |F_o|/|F_c| \leq 2.00$ were included. The weighting scheme was chosen according to Cruickshank.⁵ After six cycles of refinement, the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ had converged to 0.105. All observed reflexions were included in the calculations of R . In the sixth cycle the shifts in the parameters were less than 1 % of the estimated standard deviations except for the temperature factor of the carbon atom C(3). This parameter will be discussed below (p. 1219). The atomic coordinates and isotropic temperature factors obtained in the sixth cycle are given in Table 2 together with their estimated standard deviations. The occupation numbers on the sodium sites have not been refined, but as the temperature factors of Na(1)—Na(4) are rather uniform, the assigned value of $3/4$ seems to be reasonable.

In the next step of the analysis six cycles of full-matrix least-squares refinement of the structure were computed. Only the scale factors and the parameters describing the ytterbium dipicolinate complex were varied in the first three cycles. In the latter three cycles the complex ion was fixed and the parameters of the sodium ions and the water oxygen atoms were varied. Neither refinement produced an improvement compared to the refinement of the complete structure using the diagonal approximation.

Table 2. Atomic parameters with estimated standard deviations in ORTYBDIPIC. The space group is *Pnma* (No. 52).^a *B* denotes the isotropic temperature factor.

Atom	Group	Position	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$B/\text{Å}^2$
Yb		4(<i>d</i>)	1228 (2)	2500	2500	2.9(0.1)
Na(1)		4(<i>c</i>)	2500	5000	1719(16)	4.8(0.5)
Na(2)		4(<i>c</i>)	2500	5000	3778(19)	6.8(0.7)
Na(3)		4(<i>c</i>)	2500	5000	5845(16)	4.3(0.5)
Na(4)		4(<i>c</i>)	2500	5000	7995(15)	4.4(0.5)
N(1)	C...N...C	4(<i>d</i>)	3482(29)	2500	2500	3.4(0.5)
C(1)	...CH...	8(<i>e</i>)	4324(28)	2995(12)	2260(14)	2.7(0.5)
C(2)	...CH...	8(<i>e</i>)	5576(29)	3048(13)	2254(15)	3.0(0.5)
C(3)	...CH...	4(<i>d</i>)	6141(71)	2500	2500	9.4(1.7)
C(4)	-COO ⁻	8(<i>e</i>)	3317(26)	3553(12)	2004(16)	2.6(0.5)
O(1)	-COO ⁻	8(<i>e</i>)	2175(18)	3439 (8)	2035(11)	3.1(0.4)
O(2)	-COO ⁻	8(<i>e</i>)	3887(20)	4056 (9)	1775(12)	4.1(0.4)
N(2)	C...N...C	8(<i>e</i>)	14(21)	2819(10)	1330(12)	2.4(0.4)
C(5)	...CH...	8(<i>e</i>)	216(27)	2522(17)	600(16)	3.7(0.5)
C(6)	...CH...	8(<i>e</i>)	-426(33)	2646(13)	-71(17)	3.8(0.7)
C(7)	...CH...	8(<i>e</i>)	-1495(39)	3100(16)	-12(21)	5.4(0.8)
C(8)	...CH...	8(<i>e</i>)	-1639(38)	3431(18)	697(25)	6.0(0.9)
C(9)	...CH...	8(<i>e</i>)	-942(24)	3251(11)	1354(14)	2.4(0.5)
C(10)	-COO ⁻	8(<i>e</i>)	1293(35)	2042(14)	633(19)	4.5(0.6)
C(11)	-COO ⁻	8(<i>e</i>)	-1018(26)	3529(11)	2216(14)	2.4(0.4)
O(3)	-COO ⁻	8(<i>e</i>)	1896(18)	2014 (8)	1310(10)	2.7(0.3)
O(4)	-COO ⁻	8(<i>e</i>)	1524(23)	1717(10)	26(13)	4.7(0.5)
O(5)	-COO ⁻	8(<i>e</i>)	-358(20)	3268 (9)	2722(11)	3.9(0.5)
O(6)	-COO ⁻	8(<i>e</i>)	-1795(20)	3986 (9)	2286(10)	3.6(0.4)
O(7)	H ₂ O	8(<i>e</i>)	1266(30)	4436(13)	751(19)	8.1(0.7)
O(8)	H ₂ O	8(<i>e</i>)	1208(24)	4601(11)	2824(14)	5.3(0.5)
O(9)	H ₂ O	8(<i>e</i>)	3857(26)	3935(12)	3938(16)	6.6(0.6)
O(10)	H ₂ O	8(<i>e</i>)	1119(26)	4613(11)	4772(16)	6.2(0.6)
O(11)	H ₂ O	8(<i>e</i>)	3516(26)	3921(11)	5813(16)	6.3(0.6)
O(12)	H ₂ O	8(<i>e</i>)	913(25)	4691(11)	9005(16)	5.9(0.6)
O(13)	H ₂ O	8(<i>e</i>)	986(25)	4614(12)	6840(16)	6.2(0.6)

As has been discussed above (pp. 1214 and 1216) about 60 % of the reflexions within the range covered by the Weissenberg photographs were not observed. Thus two additional cycles of least squares treatment were carried out including 2106 non-observed reflexions assigned the value $I_{o, \min}/2$. Reflexions not obeying the condition $0.33 \leq |F_o|/|F_c| \leq 3.00$ were given zero weight (827 in the second cycle). The resulting values of the positional parameters were nearly the same as before while the estimated standard deviations decreased because the number of "observations" increased from 1285 to 3391. The discrepancy index went up to $R=0.28$. The calculated structure factors indicated that only about 50 of the 2106 missing reflexions might have been of measurable intensity. Many non-observed reflexions instead showed calculated intensity values much smaller than the assigned one, $I_{o, \min}/2$. The rather large increase in R thus arises from the inclusion of a large number of small but incorrect values of $|F_o|$.

The temperature factor given in Table 2 for the carbon atom C(3) which is located on the same twofold axis as Yb and N(1), is much higher than those for the rest of the carbon atoms. The estimated standard deviation is also large and the shift obtained in the last cycle of refinement was 0.26 \AA^2 . When the non-observed intensity material was included, all temperature factors decreased and the following values were, *e.g.*, obtained for C(1)—C(4): $1.1 \pm 0.3 \text{ \AA}^2$, $1.2 \pm 0.3 \text{ \AA}^2$, $1.4 \pm 0.2 \text{ \AA}^2$, and $1.6 \pm 0.3 \text{ \AA}^2$, respectively. This indicates that the high value given in Table 2 for C(3) is artificial and arises mainly from the incompleteness of the set of structure factors used in the actual refinement.

The set of atomic parameters chosen to describe the structure of ORTYBDIPIC is that given in Table 2 and obtained in the first six cycles of diagonal refinement. It has not been possible to locate the hydrogen atoms in the structure. A three-dimensional difference synthesis based upon the parameters given in Table 2 showed only spurious peaks. The highest ones, about 3.5 e/\AA^3 , were situated at $(0, \frac{1}{4}, \frac{1}{4})$ and $(0.24, \frac{1}{4}, \frac{1}{4})$, *i.e.* symmetrically around the ytterbium site $(0.12, \frac{1}{4}, \frac{1}{4})$. In fact peaks were observed at $(nx, \frac{1}{4}, \frac{1}{4})$ and $(1-nx, \frac{1}{4}, \frac{1}{4})$ $x=0.12$, $n=0, 1, 2, \dots$ as is shown in Fig. 1. These

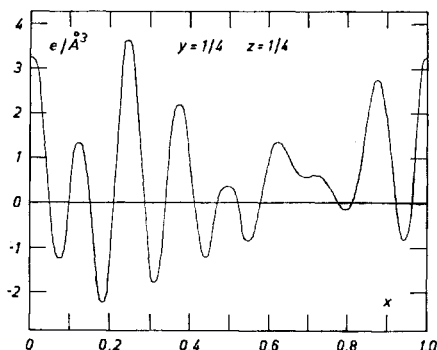


Fig. 1. The electron density along the twofold axis $y = \frac{1}{4}$, $z = \frac{1}{4}$ in the final three-dimensional difference synthesis.

Table 3. Analysis of the weighting scheme $w=1/(50+|F_o|+0.01|F_o|^2)$ used in the least-squares refinement of ORTYBDIPIC. The averages $w\Delta^2$ are normalized. $\Delta=|F_o|-|F_c|$.

Interval $ F_o $	Number of reflexions	$\overline{w\Delta^2}$	Interval $\sin\theta$	Number of reflexions	$\overline{w\Delta^2}$
0—43	123	1.10	0.00—0.42	252	1.07
43—53	128	0.97	0.42—0.53	186	0.83
53—59	127	1.07	0.53—0.60	144	0.82
59—66	128	1.06	0.60—0.66	121	1.46
66—72	127	0.93	0.66—0.71	123	1.10
72—82	128	1.01	0.71—0.76	115	0.94
82—97	128	0.94	0.76—0.80	84	1.27
97—114	129	1.10	0.80—0.84	74	1.01
114—149	127	0.78	0.84—0.87	45	0.44
149—579	129	1.05	0.87—0.90	42	1.04

Table 4. Observed and calculated structure factors.

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	h	k	l	F_o	F_c	h	k	l	F_o	F_c						
0	4	0	357	341	0	8	16	70	73	1	4	8	60	-56	2	8	1	47	-51	2	19	14	35	-42	3	3	9	14	-83	4	10	5	42	-43	
0	6	0	58	-66	1	6	0	69	70	2	8	0	73	-67	2	4	13	54	39	3	4	3	104	-86	4	2	6	175	-96	4	2	6	175	-96	
0	8	0	201	193	0	12	16	68	71	1	9	9	41	37	2	10	1	50	40	2	3	16	80	82	3	5	9	106	94	4	4	8	178	177	
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0	25	1	45	11	1	4	1	187	-194	1	18	9	75	53	2	21	2	66	67	2	12	20	40	-31	3	2	11	132	-116	4	10	8	139	132	
0	27	1	162	-158	1	6	1	152	153	2	20	9	53	-51	2	25	2	43	41	2	5	20	33	-35	4	4	11	90	80	4	14	8	125	116	
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0	14	2	115	119	1	11	1	171	175	1	10	10	52	-52	2	6	2	26	-24	3	4	163	168	3	9	11	71	-66	4	2	10	133	-134		
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0	8	4	140	143	1	3	2	58	30	1	13	11	69	69	2	21	4	60	-51	3	19	1	70	-74	3	22	13	72	-72	4	12	12	87	-83	
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0																																			

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	h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c	h	k	l	$ F_o $	F_c	
5	8	5	79	79	5	8	13	84	58	6	5	5	47	42	7	7	1	56	82	7	4	11	63	-54	9	8	1	64	-65	8	0	4	86	80	
5	9	5	90	94	5	9	13	96	59	6	8	5	47	42	7	8	1	60	78	7	5	11	70	-47	9	9	1	69	-82	9	0	6	81	-83	
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5	3	7	89	98	5	9	17	55	-42	6	3	8	107	-112	7	4	3	124	-118	8	14	0	69	-67	9	3	5	77	67	2	1	1	30	-36	
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5	6	7	73	78	5	3	17	53	39	6	9	8	121	121	7	8	3	53	-54	8	4	2	103	-128	9	6	5	81	77	2	1	4	223	-209	
5	7	7	81	104	5	4	17	52	-39	6	11	8	121	-118	7	8	5	62	-66	8	6	2	100	-124	9	0	7	57	44	2	1	5	189	162	
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5	16	7	77	-84	6	5	0	180	229	6	8	10	87	-75	7	2	5	108	-109	8	8	3	108	-109	9	0	8	200	206	3	1	3	190	-102	
5	17	7	69	-55	6	6	0	63	-60	6	11	10	78	75	7	3	5	72	72	8	10	4	127	-116	9	0	10	65	-58	3	4	4	60	-64	
5	2	9	116	-112	6	7	0	71	-71	6	13	10	69	-67	7	4	5	77	-74	8	12	4	91	71	9	0	12	96	119	3	1	5	210	173	
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5	4	9	61	56	6	11	0	105	-116	6	17	10	57	-48	7	6	5	68	-70	8	16	4	70	64	1	0	3	184	148	3	1	9	84	92	
5	5	9	89	86	6	13	0	78	87	6	19	10	48	47	7	7	5	45	30	8	2	6	97	105	1	0	5	94	-89	3	1	11	73	-82	
5	6	9	81	-84	6	14	0	114	-108	6	1	12	174	10	7	8	6	102	-107	8	4	8	6	102	-107	9	0	7	80	116	3	1	12	116	116
5	7	9	70	-66	6	15	0	71	65	6	3	12	103	-102	7	19	5	66	-68	8	6	6	113	100	1	0	9	147	-133	4	1	0	44	44	
5	8	9	55	55	6	19	0	62	-51	6	5	12	89	74	7	12	5	76	42	8	8	6	101	-89	2	0	4	70	51	4	1	2	75	2	
5	9	9	105	105	6	9	0	102	106	6	13	12	63	52	7	3	7	64	-62	8	4	8	71	84	3	0	2	184	-150	4	1	5	85	-95	
5	10	9	81	-80	6	3	2	126	147	6	9	12	83	77	7	14	5	83	-80	8	12	6	87	-72	3	0	1	108	-92	4	1	6	69	66	
5	11	9	94	-93	6	4	2	29	20	6	11	12	80	-78	7	2	7	90	93	8	14	6	81	61	3	0	3	107	103	4	1	8	65	47	
5	12	9	65	59	6	5	2	180	-153	6	13	12	63	-57	7	3	7	64	-62	8	16	6	67	-63	3	0	5	265	-244	4	1	5	132	-148	
5	13	9	105	98	6	6	2	35	38	6	15	12	56	-48	7	4	7	78	-70	8	4	7	80	-86	3	0	3	107	89	5	1	5	132	142	
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5	15	9	70	-67	6	8	2	109	-119	6	7	14	73	55	7	6	7	71	84	8	4	8	97	77	3	0	11	88	109	5	1	9	87	89	
5	3	10	49	-29	6	11	2	98	96	6	3	14	83	77	7	7	7	53	-55	8	6	8	106	-81	4	0	4	262	-254	6	2	2	118	-135	
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5	5	10	51	-28	6	15	2	117	111	6	7	14	73	55	7	9	7	60	54	8	10	8	108	-97	4	0	2	184	150	6	1	0	139	138	
5	6	11	55	-56	6	17	2	71	-77	6	9	14	75	65	7	10	7	75	75	8	12	8	73	66	4	0	4	262	-254	6	2	2	118	-135	
5	7	11	85	85	6	19	2	66	59	6	11	14	64	39	7	12	7	70	-64	8	14	8	53	-55	4	0	6	179	203	6	1	4	184	210	
5	8	11	95	84	6	21	2	113	111	6	13	14	64	39	7	14	7	69	63	8	16	8	63	-74	4	0	8	166	-152	6	1	5	143	-142	
5	9	11	73	-79	6	1	3	27	-19	6	15	14	46	42	7	17	7	51	32	8	2	10	112	98	4	0	10	95	104	6	1	8	116	132	
5	5	11	62	-69	6	2	3	33	-22	6	1	16	62	55	7	1	9	64	-65	8	4	10	91	-80	4	0	12	112	-146	6	1	10	87	-106	
5	6	11	74	-76	6	5	3	37	-32	6	3																								

DESCRIPTION OF THE STRUCTURE

The building blocks of the structure are (i) the mononuclear trisdipicolinato complex and (ii) the chain of four, edge-connected water-carboxylate oxygen octahedra around the sodium ions. In Fig. 2, a perspective

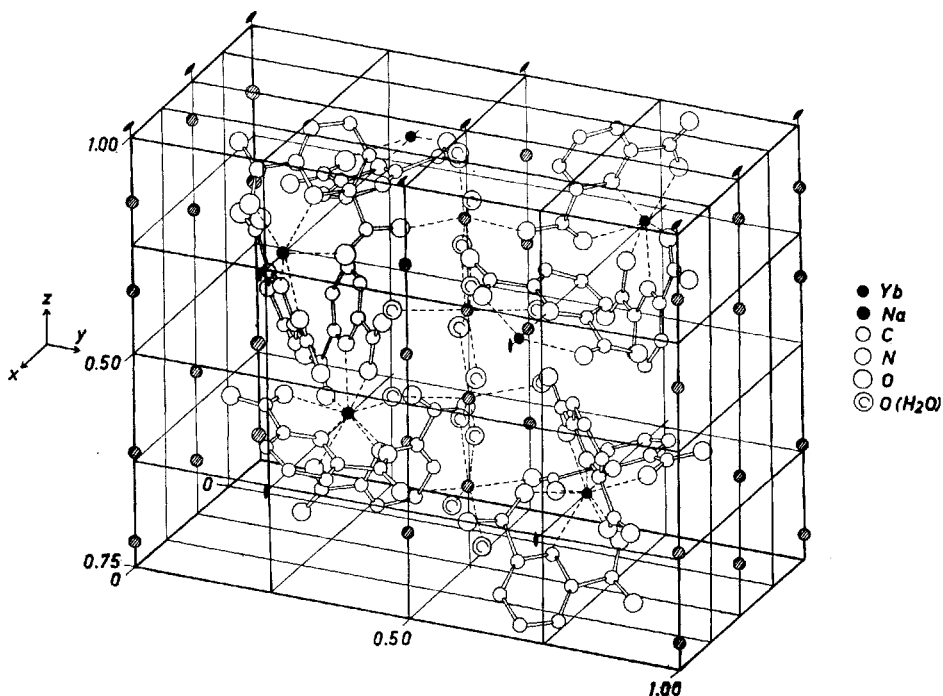


Fig. 2. The unit cell of ORTYBDIPIC. Only the water around the two-fold axis $x = \frac{1}{4}$, $y = \frac{1}{2}$ is shown.

drawing of the unit cell is shown. The dipicolinate complexes are held together by the sodium ions in layers which are perpendicular to the c axis and related by a glides. The ytterbium atoms lie in the planes $z = \frac{1}{4}$ and $z = \frac{3}{4}$. Within the layers each complex can be connected to four other complexes, as the O(2) and O(6) oxygen atoms are within coordination distances from sites belonging to the Na(1) and Na(4) positions. Since, on the average, one site is unoccupied in each "sodium chain" the layers are held together only by hydrogen bonds *via* the water molecules. This might be the reason for the rapid distintegration of the crystals when removed from the mother liquor.

When discussing the structure of ORTYBDIPIC the symmetry-related sites are designated by superscript (i)-(x) in the following way

	x, y, z	(i)	$x, \frac{1}{2} - y, \frac{1}{2} - z$	(ii)	$\frac{1}{2} - x, 1 - y, z$
(iii)	$\frac{1}{2} + x, y, 1 - z$	(iv)	$1 - x, 1 - y, 1 - z$	(v)	$\bar{x}, 1 - y, 1 - z$
(vi)	$x - \frac{1}{2}, y, 1 - z$	(vii)	$x, y, z - 1$	(viii)	$x, y, 1 + z$
(ix)	$\frac{1}{2} + x, y, \bar{z}$	(x)	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$		

where x, y, z are coordinates of the "crystal-chemical" unit given in Table 2.

The dipicolinato complex

The coordination polyhedron. The structure of the tris(dipicolinato)ytterbiumate(III) ion in ORTYBDIPIC is shown in Fig. 3. The ytterbium ion is

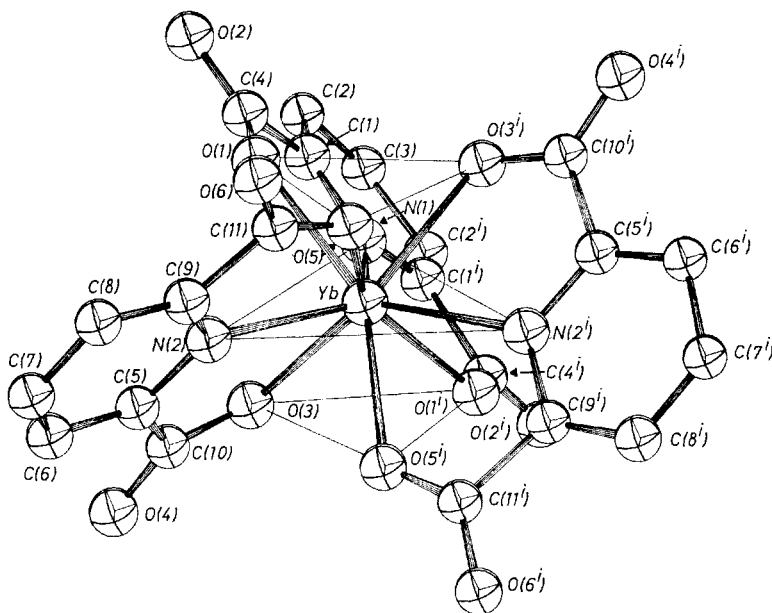


Fig. 3. The structure of $[\text{Yb}(\text{OCOC}_6\text{H}_3\text{NOCO})_3]^{3-}$ in ORTYBDIPIC drawn by the program ORTEP.⁹

nine-coordinated. The six carboxylate oxygens O(1), O(1ⁱ), O(3), O(3ⁱ), O(5), and O(5ⁱ) are at the corners of a distorted trigonal prism with the nitrogen atoms N(1), N(2), and N(2ⁱ) outside the centers of the "rectangular" faces. The main features of the complex are thus very similar to those of the tris-(oxydiacetato)lanthanoidate(III) group discussed in Ref. 2.

Selected distances in the coordination polyhedron are given in Table 5. The Yb—N(2) bond distance is 2.41 ± 0.02 Å, *i.e.* somewhat longer than the

Table 5. Selected interatomic distances (Å) and angles (°) with estimated standard deviations in the $[\text{Yb}(\text{OCOC}_2\text{H}_4\text{NOCO})_3]^{2-}$ group in ORTYBDIPIC.

A. The coordination polyhedron.

Distance		Distance	
Yb—N(1)	2.33 ± 0.03	O(5)—O(5 ¹)	3.33 ± 0.04
Yb—N(2)	2.41 ± 0.02	O(1)—N(1)	2.52 ± 0.02
Yb—O(1)	2.34 ± 0.02	O(3)—N(2)	2.58 ± 0.03
Yb—O(3)	2.33 ± 0.02	O(5)—N(2)	2.53 ± 0.03
Yb—O(5)	2.33 ± 0.02	O(1)—N(2)	2.84 ± 0.03
O(1)—O(3 ¹)	2.92 ± 0.03	O(3)—N(1)	2.76 ± 0.03
O(3 ¹)—O(5)	2.89 ± 0.03	O(5 ¹)—N(2)	2.81 ± 0.03
O(1)—O(5)	2.87 ± 0.03	N(1)—N(2)	4.12 ± 0.03
O(1)—O(3)	3.25 ± 0.03	N(2)—N(2 ¹)	4.11 ± 0.05

B. Ligand No. 1.

Distance		Angle	
N(1)—C(1)	1.42 ± 0.03	C(1)—N(1)—C(1 ¹)	104 ± 3
C(1)—C(2)	1.30 ± 0.04	N(1)—C(1)—C(2)	133 ± 3
C(2)—C(3)	1.36 ± 0.04	C(1)—C(2)—C(3)	111 ± 4
C(1)—C(4)	1.63 ± 0.04	C(2)—C(3)—C(2 ¹)	129 ± 6
C(4)—O(1)	1.20 ± 0.03	N(1)—C(1)—C(4)	102 ± 2
C(4)—O(2)	1.27 ± 0.03	C(2)—C(1)—C(4)	125 ± 2
N(1)—C(3)	2.75 ± 0.08	C(1)—C(4)—O(1)	118 ± 2
O(1)—O(2)	2.24 ± 0.03	C(1)—C(4)—O(2)	113 ± 2
		O(1)—C(4)—O(2)	129 ± 2

C. Ligand No. 2.

Distance		Angle	
N(2)—C(5)	1.38 ± 0.04	C(5)—N(2)—C(9)	116 ± 2
C(5)—C(6)	1.32 ± 0.04	N(2)—C(5)—C(6)	125 ± 3
C(6)—C(7)	1.47 ± 0.05	C(5)—C(6)—C(7)	117 ± 3
C(7)—C(8)	1.38 ± 0.05	C(6)—C(7)—C(8)	118 ± 3
C(8)—C(9)	1.36 ± 0.05	C(7)—C(8)—C(9)	119 ± 3
C(9)—N(2)	1.35 ± 0.03	C(8)—C(9)—N(2)	124 ± 3
C(5)—C(10)	1.51 ± 0.05	N(2)—C(5)—C(10)	113 ± 2
C(9)—C(11)	1.55 ± 0.03	C(6)—C(5)—C(10)	122 ± 3
C(10)—O(3)	1.28 ± 0.04	N(2)—C(9)—C(11)	108 ± 2
C(10)—O(4)	1.28 ± 0.04	C(8)—C(9)—C(11)	127 ± 3
C(11)—O(5)	1.21 ± 0.03	C(5)—C(10)—O(3)	115 ± 3
C(11)—O(6)	1.26 ± 0.03	C(5)—C(10)—O(4)	119 ± 3
N(2)—C(7)	2.78 ± 0.04	O(3)—C(10)—O(4)	126 ± 3
O(3)—O(4)	2.25 ± 0.03	C(9)—C(11)—O(5)	116 ± 2
O(5)—O(6)	2.24 ± 0.03	C(9)—C(11)—O(6)	114 ± 2
		O(5)—C(11)—O(6)	130 ± 2

Yb—N(1) and Yb—O bond distances which are all 2.33 ± 0.02 Å. The triangles O(1)O(3ⁱ)O(5) and N(1)N(2)N(2ⁱ) are equilateral within the limits of error. The six independent distances between adjacent coordinated atoms not belonging to the same ligand are in the range 2.76–2.92 Å thus indicating van der Waals contacts in the coordination polyhedron.⁹ Such contacts should impose a steric hindrance for the formation of the third dipicolinate complex with the heaviest lanthanoid ions. In solution such an increasing difficulty has been observed for the elements dysprosium to lutetium.¹⁰

The ligand. ORTYBDIPIC contains one and one-half independent ligand ions. Their atoms are designated in Fig. 4. Each dipicolinate ion acts as a tridentate ligand forming two five-membered rings with the ytterbium ion. Selected bond distances and angles of the two ligands are given in Table 5.

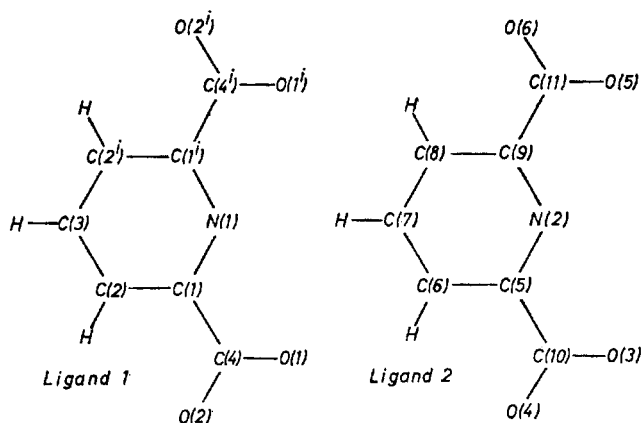


Fig. 4. Designation of the atoms in the two different dipicolinate ligands in ORTYBDIPIC.

Strahs and Dickerson have investigated the crystal structure of calcium dipicolinate tris-hydrate, CaDPA.¹¹ Due mainly to the low atomic number of calcium (20) compared to that of ytterbium (70) the set of interatomic distances and angles of the dipicolinate ion obtained from CaDPA have values nearer the expected ones than the set obtained from ORTYBDIPIC. The estimated standard deviations are also smaller than those of this paper but within the limits of error the two sets are, on the whole, compatible.

All carbon-oxygen bond lengths are approximately equal with a mean value of 1.24 Å in ORTYBDIPIC compared to 1.25 Å in CaDPA. In both compounds the carboxyl groups are attracted to the central ion; the angles N(1)—C(1)—C(4), N(2)—C(5)—C(10), and N(2)—C(9)—C(11) in ORTYBDIPIC are all significantly less than 120° as well as the corresponding angles of the dipicolinate ion in CaDPA.

The least-squares planes through the seven carbon atoms and the nitrogen atom of each ligand in ORTYBDIPIC have been calculated. As is shown in

Table 6, the carbon and nitrogen atoms are coplanar within 0.02 Å and 0.05 Å for the ligands Nos. 1 and 2, respectively. The carboxyl groups of ligand No. 2, O(3)—C(10)—O(4) and O(5)—C(11)—O(6), are twisted out of the ligand plane, O(5)—C(11)—O(6) to a significant degree. The ytterbium atom is not in the plane of ligand No. 2, but as it is located on the same twofold axis as N(1) and C(3), it lies in the plane of ligand No. 1.

The packing of the complex ions. The tris(dipicolinato)ytterbiumate complexes are located in layers perpendicular to the *b* axis with the ytterbium ions in the planes $y = \frac{1}{4}$ and $y = \frac{3}{4}$ (see Fig. 2). The "free space" distance between these layers is more than 4 Å. Within them each ligand of type 1 is surrounded by four ligands of type 2 from three adjacent complexes. All carbon-carbon packing distances are longer than 3.7 Å except the distance C(4)—C(7^{ix}) which is 3.44 ± 0.04 Å.

The large mononuclear complex in ORTYBDIPIC makes all ytterbium-ytterbium distances very long. The shortest one, Yb—Ybⁱⁱⁱ, is 9.76 ± 0.01 Å. Each lanthanoid ion is thus completely isolated from the other ones in this structure.

The coordination around sodium

The sodium ions. In Fig. 5 the coordination around the sodium sites at $y = \frac{1}{2}$ is shown. The sodium—oxygen bond distances and the sodium—sodium distances within the chain of four, connected oxygen octahedra around the sodium sites are given in Table 7. The sodium positions Na(1) and Na(3) are surrounded by oxygen atoms at almost equal distances, the average sodium-oxygen bond distance in these two octahedra being 2.43 Å. On the other hand, each Na(2) has two O(8) at 2.23 Å, two O(10) at 2.33 Å, and two O(9) at 2.66 Å. The distance Na(4)—O(13), 2.60 Å, also falls outside the normal range. The O—Na—O bond angles with adjacent oxygen atoms are all in the range 85—95° except O(6ⁱⁱⁱ)—Na(4)—O(12ⁱⁱ) and O(6ⁱⁱⁱ)—Na(4)—O(13) which are $100 \pm 1^\circ$ and $76 \pm 1^\circ$, respectively. Of the 24 different oxygen—oxygen "contact" distances within the "sodium chain" 22 have values between 3.20 and 3.64 Å. It is only the two distances O(6ⁱⁱⁱ)—O(13) and O(8)—O(8ⁱⁱ) that are shorter than 3.20 Å (see Table 8).

Possible hydrogen bonds. To get some idea about the hydrogen bonds in the structure all distances less than 3.20 Å between the water oxygen atoms and other oxygen atoms are listed in Table 8. The most probable hydrogen bonds are shown in Fig. 5 as dashed lines. Judging from the oxygen—oxygen distances the structure seems passably well held together along the *c* axis by hydrogen bonds.

The carboxylate oxygens O(1), O(3), and O(5) which are coordinated to ytterbium, might also be hydrogen bonded to the water oxygen atoms O(8), O(9), and O(11), respectively. The carboxylate oxygens O(2) and O(6) are coordinated to sodium. O(2) seems to form one hydrogen bond with O(12) but it is doubtful if O(6) takes part in any hydrogen bond. On the other hand the carboxylate oxygen O(4) which does not coordinate a metal ion might form two hydrogen bonds with the water oxygens O(10) and O(11). Each water oxygen, except possibly O(11), is within a hydrogen bond distance from another water oxygen atom.

Table 6. The deviations (in Å) of the ytterbium and ligand atoms from the least-squares planes through the ligand ions.

A. Ligand No. 1. The lower signs refer to the superscripted atoms.

Atom	Distance	Atom	Distance
N(1)	0.00	C(4), C(4 ⁱ)	0.00
C(1), C(1 ⁱ)	± 0.01	O(1), O(1 ⁱ)	± 0.04
C(2), C(2 ⁱ)	∓ 0.02	O(2), O(2 ⁱ)	∓ 0.01
C(3)	0.00	Yb	0.00

B. Ligand No. 2.

Atom	Distance	Atom	Distance
N(2)	0.00	C(11)	-0.01
C(5)	0.00	O(3)	0.09
C(6)	0.02	O(4)	-0.08
C(7)	-0.05	O(5)	-0.16
C(8)	0.05	O(6)	0.12
C(9)	-0.01	Yb	-0.13
C(10)	0.00		

Table 7. The sodium-oxygen bond distances and sodium-sodium distances (Å) with estimated standard deviations in ORTYBDIPIC.

Distance		Distance	
Na(1)-O(7)	2.37 ± 0.04	Na(3)-O(13)	2.41 ± 0.03
Na(1)-O(2)	2.46 ± 0.02	Na(4)-O(13)	2.60 ± 0.03
Na(1)-O(8)	2.42 ± 0.03	Na(4)-O(6 ⁱⁱⁱ)	2.31 ± 0.02
Na(2)-O(8)	2.23 ± 0.03	Na(4)-O(12)	2.43 ± 0.03
Na(2)-O(9)	2.66 ± 0.03	Na(1)-Na(2)	3.41 ± 0.04
Na(2)-O(10)	2.33 ± 0.03	Na(2)-Na(3)	3.43 ± 0.04
Na(3)-O(10)	2.42 ± 0.03	Na(3)-Na(4)	3.57 ± 0.04
Na(3)-O(11)	2.50 ± 0.03	Na(4)-Na(1 ^{viii})	6.17 ± 0.04

Table 8. Distances (Å) less than 3.20 Å between water oxygen atoms and other oxygen atoms in ORTYBDIPIC.

Distance		Distance	
O(7)-O(1)	3.14 ± 0.04	O(10)-O(4 ⁱ)	2.86 ± 0.03
O(7)-O(12 ^v)	2.94 ± 0.04	O(10)-O(10 ^v)	2.93 ± 0.03
O(8)-O(1)	2.96 ± 0.03	O(11)-O(4 ⁱ)	2.82 ± 0.03
O(8)-O(8 ⁱⁱ)	3.16 ± 0.05	O(11)-O(5 ⁱⁱⁱ)	3.03 ± 0.03
O(8)-O(13 ^v)	2.86 ± 0.04	O(11)-O(6 ⁱⁱⁱ)	3.17 ± 0.03
O(9)-O(3 ⁱ)	2.88 ± 0.03	O(12)-O(2 ^{vi})	2.80 ± 0.03
O(9)-O(11)	3.13 ± 0.04	O(12)-O(7 ^{viii})	2.97 ± 0.04
O(9)-O(13 ⁱⁱⁱ)	2.93 ± 0.04	O(13)-O(6 ⁱⁱⁱ)	3.02 ± 0.03

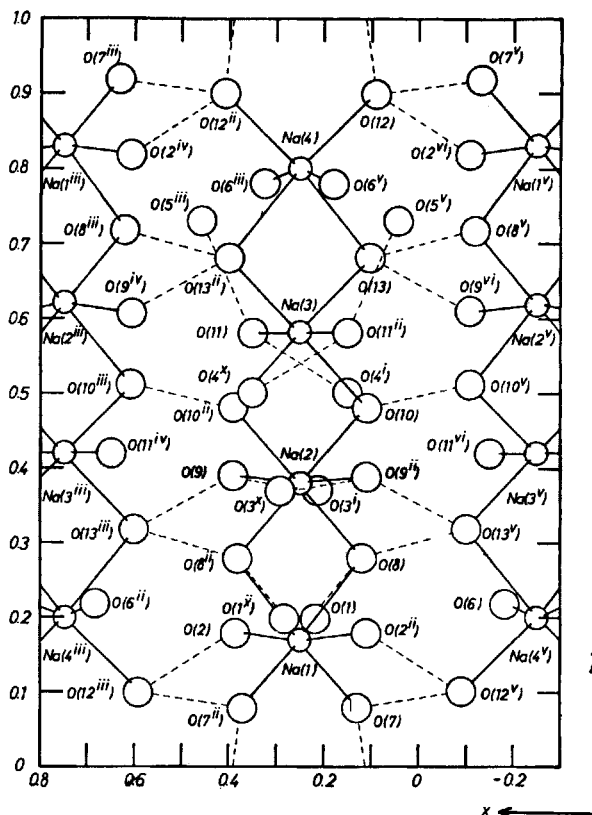


Fig. 5. The coordination around the sodium ions in the plane $y = \frac{1}{2}$ projected on this plane. Possible hydrogen bonds between the water oxygen atoms and other oxygens are shown as dashed lines.

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