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The Structure of Tris(tetraphenyl imidodiphosphato)ytterbium(III)

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Abstract

The crystal structure of $C_{72}H_{60}N_3O_{18}P_6Yb$ has been determined by single-crystal X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/c$, with cell constants $a = 18.627$ (6), $b = 15.761$ (8), $c = 26.553$ (10) Å, $\beta = 113.76$ (2)°, $V = 7135$ (5) Å³, $Z = 4$, $D_c = 1.50$ Mg m⁻³. The structure was solved by Fourier and direct methods and refined by full-matrix least squares to an R factor of 0.051 for 7443 reflections including those below background. The structure consists of discrete $Yb\{N[PO(OC_6H_5)_2]_2\}_3$ molecules. The Yb atom is six coordinated. The low coordination number is due to the bulky ligands. The six O atoms of the three bidentate chelate rings form the coordination environment of the Yb^{3+} ion. The coordination polyhedron has virtual D_3 symmetry, more in the direction of a distorted octahedron than in the direction of a trigonal prism. The intrachelate O—O separation is 2.883 Å and the interchelate separation is 3.07–3.39 Å. The Yb atoms lie almost on a superposition lattice which has a quarter of the volume of the unit cell.

Introduction

Numerous structures of the complexes of rare-earth ions have been determined by X-ray diffraction in recent years, and their stereochemistry has been studied in detail (Moseley, 1975; Thompson, 1979). So far, a

large number of the investigations of such complexes in solution have been directed towards solvent-extraction separation. Neutral chelate complexes of tetraphenyl imidodiphosphate (idtph) with rare-earth ions of the type $Ln\{N[PO(OC_6H_5)_2]_2\}_3$ have been synthesized (Herrmann, Hoàng bá Nặng & Dreyer, 1979). We have carried out an X-ray structure analysis of the Yb complex, $Yb(idtph)_3$, in order to determine the structure, especially the exact coordination environment of the lanthanoid ions of such complexes in the solid state. We have started with the heavy rare-earth element Yb which has a small ionic radius. The relation of the stereochemistry of the structure to other information, e.g. extraction, IR, ³¹P NMR, ¹³C NMR and ¹H NMR measurements, will be discussed elsewhere. Moseley (1975) expected an octahedral environment with distortions towards a trigonal prism for the six-coordinate tris-bidentate rare-earth complexes. This was due to the decreasing 'bite' of the bidentate ligand. A six-coordinate Er complex, $Er(dpm)_3$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionato), with trigonal-prismatic coordination for Er has been reported by de Villers & Boeyens (1971).

Experimental

The compound (m.p. 503–508 K) was prepared according to the procedure of Herrmann, Hoàng bá Nặng & Dreyer (1979). Suitable crystals were obtained by recrystallization from alcohol. Preliminary X-ray

Table 1. *Positional* ($\times 10^4$) *and thermal* ($\times 10^3$) *parameters of the non-hydrogen atoms*

The Yb, P, O and N atoms were refined anisotropically, the C atoms isotropically. The values in parentheses are the e.s.d.'s.
 $U_{eq} = 1/3 \sin^2 \beta (U_{11} + U_{22} \sin^2 \beta + U_{33} + 2U_{13} \cos \beta)$.

	x	y	z	$U_{eq}/U_{iso} (\text{Å}^2)$
Yb	7564 (1)	2396 (1)	7454 (1)	34 (0)
P(1)	7209 (1)	2880 (2)	6106 (1)	37 (1)
P(2)	6341 (1)	1495 (1)	6220 (1)	39 (1)
P(3)	9200 (1)	1146 (2)	8015 (1)	42 (1)
P(4)	8032 (1)	731 (2)	8380 (1)	40 (1)
P(5)	6475 (1)	3942 (1)	7749 (1)	33 (1)
P(6)	8092 (1)	4246 (2)	8209 (1)	40 (1)
O(1)	7535 (3)	3048 (4)	6710 (2)	39 (3)
O(2)	6826 (4)	3735 (4)	5808 (2)	41 (3)
O(3)	7892 (4)	2803 (6)	5897 (2)	66 (3)
O(4)	6697 (3)	1578 (3)	6831 (2)	42 (3)
O(5)	6470 (3)	575 (3)	6038 (2)	46 (3)
O(6)	5412 (3)	1504 (3)	5999 (2)	55 (3)
O(7)	8639 (3)	1691 (3)	7572 (2)	49 (3)
O(8)	9656 (3)	519 (4)	7783 (2)	53 (2)
O(9)	9900 (3)	1738 (3)	8369 (2)	52 (3)
O(10)	7559 (3)	1486 (3)	8090 (2)	44 (3)
O(11)	7499 (3)	-63 (3)	8117 (2)	49 (3)
O(12)	8078 (3)	652 (3)	8981 (2)	46 (3)
O(13)	6582 (3)	3140 (3)	7486 (2)	40 (3)
O(14)	5914 (3)	4508 (3)	7255 (2)	41 (3)
O(15)	5944 (3)	3757 (3)	8070 (2)	45 (3)
O(16)	8252 (3)	3436 (3)	7984 (2)	47 (3)
O(17)	8663 (3)	4244 (4)	8838 (2)	54 (3)
O(18)	8428 (3)	5020 (4)	7993 (2)	53 (3)
N(1)	6627 (3)	2115 (4)	5885 (2)	45 (3)
N(2)	8867 (4)	641 (4)	8383 (3)	42 (3)
N(3)	7229 (3)	4433 (4)	8125 (2)	35 (3)
C(1)	6432 (5)	3804 (5)	5231 (3)	42 (2)
C(2)	5636 (5)	3766 (6)	5011 (4)	62 (2)
C(3)	5234 (6)	3862 (7)	4426 (4)	77 (3)
C(4)	5666 (6)	3974 (6)	4114 (4)	70 (2)
C(5)	6456 (6)	4027 (6)	4352 (4)	67 (2)
C(6)	6877 (5)	3937 (5)	4927 (3)	55 (2)
C(7)	8536 (5)	2241 (5)	6161 (3)	48 (2)
C(8)	8476 (5)	1438 (6)	5959 (4)	61 (2)
C(9)	9149 (6)	910 (6)	6211 (4)	77 (2)
C(10)	9809 (6)	1232 (7)	6636 (4)	78 (3)
C(11)	9838 (6)	2036 (6)	6817 (4)	74 (2)
C(12)	9179 (5)	2580 (6)	6580 (4)	64 (2)
C(13)	6206 (5)	-178 (5)	6191 (3)	44 (2)
C(14)	5775 (5)	-708 (6)	5756 (4)	64 (2)
C(15)	5524 (6)	-1506 (6)	5886 (4)	73 (2)
C(16)	5713 (5)	-1726 (6)	6427 (4)	68 (2)
C(17)	6147 (5)	-1168 (6)	6849 (4)	65 (2)
C(18)	6396 (5)	-385 (5)	6732 (3)	54 (2)
C(19)	4964 (5)	2245 (5)	5863 (3)	45 (2)
C(20)	5167 (5)	2955 (5)	6201 (3)	52 (2)
C(21)	4688 (5)	3672 (6)	6028 (4)	59 (2)
C(22)	4020 (5)	3674 (6)	5535 (4)	65 (2)
C(23)	3827 (5)	2938 (6)	5214 (4)	68 (2)
C(24)	4297 (5)	2213 (6)	5370 (4)	59 (2)
C(25)	9345 (5)	-162 (5)	7420 (3)	52 (2)
C(26)	8566 (5)	-285 (6)	7130 (4)	66 (2)
C(27)	8318 (6)	-980 (7)	6760 (4)	85 (3)
C(28)	8902 (7)	-1512 (8)	6699 (5)	94 (3)
C(29)	9674 (7)	-1351 (8)	7001 (5)	94 (3)
C(30)	9933 (6)	-674 (6)	7374 (4)	70 (2)
C(31)	10525 (5)	1497 (5)	8862 (3)	49 (2)
C(32)	10486 (5)	1760 (6)	9343 (4)	67 (2)

Table 1 (cont.)

	x	y	z	$U_{iso} (\text{Å}^2)$
C(33)	11142 (6)	1559 (7)	9838 (4)	86 (3)
C(34)	11764 (6)	1107 (7)	9825 (4)	86 (3)
C(35)	11774 (6)	849 (7)	9333 (5)	87 (3)
C(36)	11138 (6)	1061 (6)	8826 (4)	72 (2)
C(37)	7640 (4)	-888 (5)	8353 (3)	45 (2)
C(38)	8318 (5)	-1314 (6)	8401 (4)	60 (2)
C(39)	8396 (5)	-2154 (6)	8623 (4)	73 (2)
C(40)	7827 (6)	-2505 (6)	8765 (4)	75 (2)
C(41)	7166 (6)	-2042 (6)	8704 (4)	75 (2)
C(42)	7074 (5)	-1208 (6)	8504 (4)	60 (2)
C(43)	8554 (4)	1166 (5)	9423 (3)	46 (2)
C(44)	8430 (5)	2025 (6)	9409 (4)	63 (2)
C(45)	8886 (6)	2509 (7)	9878 (4)	78 (3)
C(46)	9416 (6)	2116 (7)	10330 (4)	77 (3)
C(47)	9545 (6)	1256 (7)	10342 (4)	81 (3)
C(48)	9103 (5)	743 (6)	9872 (4)	65 (2)
C(49)	5572 (5)	5249 (5)	7351 (2)	40 (2)
C(50)	5986 (5)	5993 (5)	7448 (3)	54 (2)
C(51)	5592 (6)	6736 (6)	7524 (4)	78 (2)
C(52)	4459 (6)	5927 (6)	7401 (4)	75 (2)
C(53)	4813 (5)	5185 (6)	7325 (3)	58 (2)
C(54)	4829 (6)	6663 (7)	7496 (5)	82 (3)
C(55)	6146 (4)	3906 (5)	8630 (3)	42 (2)
C(56)	5987 (5)	4688 (5)	8783 (3)	57 (2)
C(57)	6149 (6)	4807 (6)	9354 (4)	79 (3)
C(58)	6455 (5)	4129 (6)	9722 (4)	74 (2)
C(59)	6595 (6)	3362 (6)	9543 (4)	74 (2)
C(60)	6446 (5)	3226 (5)	8979 (3)	58 (2)
C(61)	8671 (4)	4883 (5)	9215 (4)	49 (2)
C(62)	9287 (5)	5463 (6)	9365 (4)	73 (2)
C(63)	9319 (6)	6035 (7)	9791 (4)	82 (3)
C(64)	8810 (7)	6023 (7)	10026 (4)	86 (3)
C(65)	8203 (7)	5439 (7)	9858 (5)	94 (3)
C(66)	8146 (5)	4838 (6)	9438 (4)	71 (2)
C(67)	7997 (4)	5484 (4)	7516 (3)	43 (2)
C(68)	8036 (5)	6365 (5)	7581 (3)	61 (2)
C(69)	7618 (6)	6852 (6)	7110 (4)	73 (2)
C(70)	7185 (6)	6485 (6)	6616 (4)	76 (2)
C(71)	7169 (5)	5596 (6)	6567 (4)	70 (2)
C(72)	7594 (5)	5088 (5)	7031 (3)	55 (2)

investigations using Weissenberg techniques indicated the space group $P2_1/c$. Three-dimensional single-crystal X-ray diffraction data were obtained on a Hilger & Watts four-circle automatic diffractometer controlled by a PDP-8 computer. Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ Å}$) and a graphite monochromator were used. The lattice parameters were obtained at room temperature (296 K) by a least-squares fit of 12 well centred reflections. Intensities were measured up to $2\theta = 42^\circ$ by a θ - 2θ scan technique over a range of 40 steps per reflection with a step size $\Delta\omega$ of 0.02° and 1 s per step. Backgrounds were measured during two 20 s counts made on each side of the scanning range. Two standard reflections were measured every 50 reflections. No significant decomposition of the crystal was noted. A total of 7457 unique reflections were measured including those not significantly above background. Scattering factors for the neutral atoms were taken from *International Tables for X-ray*

Crystallography (1974). A Lorentz-polarization correction was applied; no absorption correction was made ($\mu_{\text{MoK}\alpha} = 1.58 \text{ mm}^{-1}$) despite the comparatively large crystal size ($0.5 \times 0.6 \times 0.7 \text{ mm}$).

The Patterson method was used to determine the position of the Yb atom; *MULTAN 78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) was then employed. The positions of the P, N and O atoms were obtained from an *E* map. The almost special position of the Yb atom (0.75693, 0.23957, 0.74535) is close to the *c*-glide plane and the 2_1 screw axis. The $I(hkl)$ values imply that the reflections are systematically stronger for $l = 2n$ and for $h + k = 2n$. The *E* values were modified in the *MULTAN* program.

The positions of the remaining non-hydrogen atoms were obtained from electron density difference syntheses. Full-matrix least-squares refinement [*SHELX 76* (Sheldrick, 1976), using a BESM-6 computer] of the positional and thermal parameters of the non-hydrogen atoms converged to $R = 0.051$ ($R = \sum |F_o| - |F_c| / \sum |F_o|$). The Yb, P, O and N atoms were refined anisotropically, the C atoms isotropically. 7443 reflections were included in the final least-squares cycles; 14 strong reflections were omitted. The positions of all the H atoms of the phenyl rings were calculated assuming standard geometries. These atoms were not included in the refinement. The final positional and thermal parameters are listed in Table 1.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and some bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36963 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

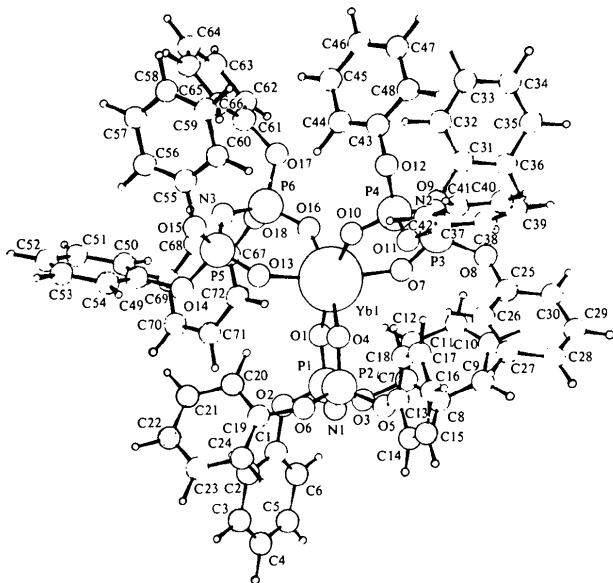


Fig. 1. View of a molecule of $\text{Yb}(\text{idtph})_3$, showing the numbering scheme of the atoms. H atoms are numbered according to the C atoms to which they are attached.

Discussion

Fig. 1 shows the numbering scheme for all atoms of the molecule. Table 2 gives some of the intramolecular bond lengths, Table 3 some of the bond angles. Fig. 2 shows a stereoscopic view of the molecule. Fig. 3 gives average values of related bond lengths and bond angles of the ligand.

The coordination polyhedron

$\text{Yb}(\text{idtph})_3$ is a six-coordinated tris-bidentate rare-earth complex with three bidentate idtph ligands. The

Table 2. Some bond distances (Å) with *e.s.d.*'s in parentheses

Yb—O(1)	2.209 (6)	P(6)—O(16)	1.490 (6)
Yb—O(4)	2.202 (4)	P(6)—O(17)	1.577 (5)
Yb—O(7)	2.199 (6)	P(6)—O(18)	1.580 (7)
Yb—O(10)	2.219 (6)	P(1)—N(1)	1.569 (7)
Yb—O(13)	2.204 (5)	P(2)—N(1)	1.554 (8)
Yb—O(16)	2.204 (5)	P(3)—N(2)	1.570 (8)
P(1)—O(1)	1.493 (6)	P(4)—N(2)	1.560 (8)
P(1)—O(2)	1.580 (6)	P(5)—N(3)	1.562 (6)
P(1)—O(3)	1.583 (10)	P(6)—N(3)	1.560 (7)
P(2)—O(4)	1.490 (5)	O(2)—C(1)	1.411 (9)
P(2)—O(5)	1.577 (6)	O(3)—C(7)	1.428 (11)
P(2)—O(6)	1.588 (6)	O(5)—C(13)	1.405 (10)
P(3)—O(7)	1.492 (5)	O(6)—C(19)	1.395 (9)
P(3)—O(8)	1.580 (7)	O(8)—C(25)	1.403 (10)
P(3)—O(9)	1.571 (5)	O(9)—C(31)	1.409 (8)
P(4)—O(10)	1.496 (5)	O(11)—C(37)	1.420 (9)
P(4)—O(11)	1.575 (6)	O(12)—C(43)	1.407 (8)
P(4)—O(12)	1.569 (6)	O(14)—C(49)	1.402 (10)
P(5)—O(13)	1.495 (6)	O(15)—C(55)	1.400 (9)
P(5)—O(14)	1.584 (5)	O(17)—C(61)	1.416 (10)
P(5)—O(15)	1.570 (7)	O(18)—C(67)	1.402 (8)

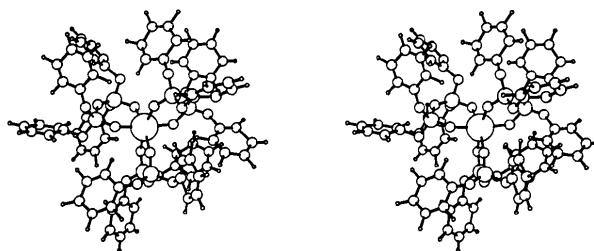


Fig. 2. A stereoscopic view of a molecule of $\text{Yb}(\text{idtph})_3$, down the direction of least atomic overlap (*PLUTO*; Motherwell, 1978).

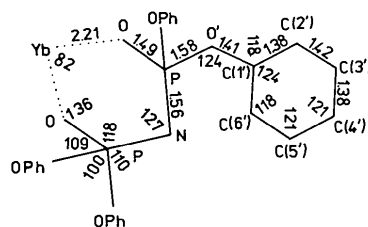


Fig. 3. Average bond lengths (Å) and average bond angles ($^\circ$) of the ligands. The individual values for all 12 phenyl substituents have been deposited.

Table 3. Some bond angles ($^{\circ}$) with e.s.d.'s in parentheses

O(1)—Yb—O(4)	81.7 (2)	O(14)—P(5)—O(15)	101.7 (3)
O(7)—Yb—O(10)	81.3 (2)	O(14)—P(5)—N(3)	111.9 (3)
O(13)—Yb—O(16)	81.8 (2)	O(15)—P(5)—N(3)	110.3 (3)
O(1)—P(1)—O(2)	107.0 (3)	O(16)—P(6)—O(17)	105.4 (3)
O(1)—P(1)—O(3)	110.7 (4)	O(16)—P(6)—O(18)	110.1 (4)
O(1)—P(1)—N(1)	117.3 (4)	O(16)—P(6)—N(3)	117.8 (3)
O(2)—P(1)—O(3)	98.9 (4)	O(17)—P(6)—O(18)	100.9 (3)
O(2)—P(1)—N(1)	111.3 (3)	O(17)—P(6)—N(3)	111.5 (4)
O(3)—P(1)—N(1)	110.0 (4)	O(18)—P(6)—N(3)	109.7 (3)
O(4)—P(2)—O(5)	111.0 (3)	Yb—O(1)—P(1)	137.0 (4)
O(4)—P(2)—O(6)	110.1 (4)	P(1)—O(2)—C(1)	122.8 (5)
O(4)—P(2)—N(1)	117.6 (3)	P(1)—O(3)—C(7)	120.7 (7)
O(5)—P(2)—O(6)	100.0 (3)	Yb—O(4)—P(2)	137.7 (4)
O(5)—P(2)—N(1)	105.8 (4)	P(2)—O(5)—C(13)	125.0 (6)
O(6)—P(2)—N(1)	110.9 (3)	P(2)—O(6)—C(19)	123.5 (5)
O(7)—P(3)—O(8)	111.7 (4)	Yb—O(7)—P(3)	135.4 (4)
O(7)—P(3)—O(9)	106.2 (3)	P(3)—O(8)—C(25)	127.4 (6)
O(7)—P(3)—N(2)	117.1 (4)	P(3)—O(9)—C(31)	124.8 (5)
O(8)—P(3)—O(9)	99.1 (3)	Yb—O(10)—P(4)	136.4 (4)
O(8)—P(3)—N(2)	109.6 (4)	P(4)—O(11)—C(37)	124.1 (4)
O(9)—P(3)—N(2)	111.6 (3)	P(4)—O(12)—C(43)	124.1 (6)
O(10)—P(4)—O(11)	105.6 (3)	Yb—O(13)—P(5)	137.4 (3)
O(10)—P(4)—O(12)	111.5 (4)	P(5)—O(14)—C(49)	121.1 (5)
O(10)—P(4)—N(2)	117.0 (4)	P(5)—O(15)—C(55)	125.9 (5)
O(11)—P(4)—O(12)	98.9 (3)	Yb—O(16)—P(6)	137.3 (3)
O(11)—P(4)—N(2)	112.2 (4)	P(6)—O(17)—C(61)	123.9 (5)
O(12)—P(4)—N(2)	110.0 (3)	P(6)—O(18)—C(67)	124.3 (5)
O(13)—P(5)—O(14)	104.9 (3)	P(1)—N(1)—P(2)	128.0 (4)
O(13)—P(5)—O(15)	109.1 (3)	P(3)—N(2)—P(4)	126.5 (4)
O(13)—P(5)—N(3)	117.6 (3)	P(5)—N(3)—P(6)	127.4 (4)

coordination number six, a rare value for lanthanoid complexes, is due to the very bulky ligands — especially the twelve phenyl groups per molecule. The steric factor is presumably the reason for the low coordination number. The coordination polyhedron of the Yb^{3+} ion is intermediate between the octahedral and a trigonal prism (Fig. 4). The virtual symmetry of the inner part of the molecule, consisting of the Yb^{3+} ion and the three chelate rings (but without the twelve phenyl rings), deviates slightly from D_3 symmetry. Fig. 4 is drawn perpendicular to the virtual threefold axis connecting the three chelate rings. To estimate the deviation from octahedral and trigonal-prismatic environments, we consider three types of O—O distances.

(1) The average intrachelate O—O distance; the 'average bite' is 2.88 (1) Å.

(2) The average distance of all O atoms connected by the virtual threefold axis is 3.15 (5) Å. These are the two triplets O(1), O(7) and O(16) in plane E_I and O(4), O(10) and O(13) in plane E_{II} . Both are nearly parallel to the plane of Fig. 4 and nearly perpendicular to the threefold axis (Table 4).

(3) The average interplanar O—O distance between the three pairs O(1), O(13); O(7), O(4); and O(16), O(10) of the two triplets is 3.32 (7) Å.

All three types are significantly different. The planes E_I and E_{II} are almost parallel with a dihedral angle of 2.0° . To bring the triangle O(1), O(7), O(16) in E_I into approximate coincidence with the triangle O(4), O(10), O(13) in E_{II} a clockwise average twist in Fig. 4 of 44.8° must be applied as compared to the 60° for octahedral coordination.

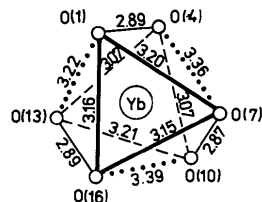


Fig. 4. Coordination polyhedron of the Yb atoms with virtual D_3 symmetry viewed down the virtual threefold axis through the Yb atom. (Distances are in Å.)

Table 4. Mean planes, dihedral angles between the planes and distances of atoms from the planes (Å)

E.s.d.'s are ~ 0.006 Å and 0.4° .

Plane E_I : O(1), O(7), O(16)
 Plane E_{II} : O(4), O(10), O(13)
 Plane E_{III} : P(1), P(2), O(1), O(4), N(1)
 Plane E_{IV} : P(3), P(4), O(7), O(10), N(2)
 Plane E_V : P(5), P(6), O(13), O(16), N(3)

	Distances of atoms from planes (Å)			Dihedral angles ($^{\circ}$)	
	E_{III}	E_{IV}	E_V	E_I, E_{II}	E_{III}, E_{IV}
P(1)	-0.022	—	—	—	2.0
P(2)	0.039	—	—	E_{III}, E_{IV}	76.8
P(3)	—	0.114	—	E_{III}, E_V	99.8
P(4)	—	-0.135	—	E_{IV}, E_V	81.4
P(5)	—	—	-0.016	—	—
P(6)	—	—	-0.050	—	—
O(1)	0.027	—	—	—	—
O(4)	-0.033	—	—	—	—
O(7)	—	-0.117	—	—	—
O(10)	—	0.124	—	—	—
O(13)	—	—	-0.006	—	—
O(16)	—	—	0.027	—	—
N(1)	-0.012	—	—	—	—
N(2)	—	0.014	—	—	—
N(3)	—	—	0.045	—	—

The coordination polyhedron of the Yb^{3+} ion is thus best described as a distorted octahedron (Kulpe, Seidel & Herrmann, 1981). The 'bite' is the most constant distance reflecting the fact that the chelate rings, and especially the geometry of the O polyhedron, are the most rigid elements in the molecule. The 'normalized bite', defined as the 'average bite' divided by the average Yb—O distance [2.20 (7) Å], is 1.305. The twelve phenyl rings do not have virtual D_3 symmetry.

The ligands

The chelate rings show only slight deviations from planarity (Table 4). The planes E_{III} and E_V show small, E_{IV} somewhat larger deviations.

The P—O bonds (1.49 Å) in the chelate ring are partial double bonds; the same holds for the P—N lengths (1.56 Å). The ligand part of the chelate ring may be considered to have a polymethine-like electron structure (Fig. 5). It is a trimethine-like structure with P and N atoms in the chain and O atoms as chain end-atoms (Dähne & Kulpe, 1977).

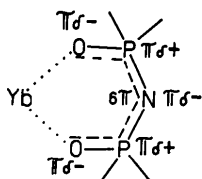


Fig. 5. Representation of the polymethine-like electron structure of the ligand part of the chelate ring. There are six delocalized π electrons over a polymethine chain consisting of five atoms.

The P—O(Ph) bond lengths (1.58 Å) are virtual single bonds. The same holds for the O'—C(1') bonds (1.41 Å), with a tendency towards shortening. The P atoms have a virtual tetrahedral environment.

In spite of the bulky molecule and the relatively large number of parameters to be determined there is some significance in the deviation of the phenyl-ring geometry from the ideal geometry of the aromatic state.

The phenyl ring seems to prefer certain ionic canonic structures with single bonds between the *ortho* and *meta* C atoms in the phenyl ring. Judging from the valence angles, C(1') seems to deviate slightly from sp^2 hybridization towards sp hybridization, and C(2') and C(5') deviate towards sp^3 .

Molecular packing

The structure consists of discrete Yb(idtph)₃ molecules with van der Waals contacts only. Because of the nearly special positions of the Yb atoms, they are arranged on a nearly regular lattice with a virtual superposition cell having a quarter of the volume of the unit cell of the structure. The primitive superposition cell has the translational periods: $a' = a$, $b' = (a/2) + (b/2)$, $c' = c/2$ (Fig. 6). This is equivalent to a C face-centred superposition cell with the translational periods $a'' = a$, $b'' = b$, $c'' = c/2$.

The asymmetric unit of the structure contains a whole molecule consisting of 100 non-hydrogen atoms.

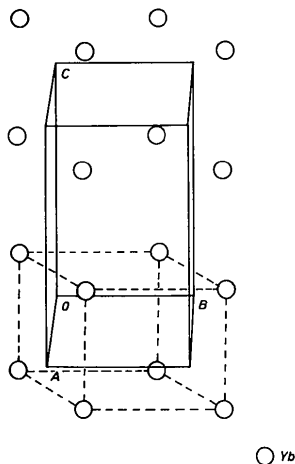


Fig. 6. View of the superposition lattice of the Yb atoms with the virtual translation periods $a' = a$, $b' = (a/2) + (b/2)$, $c' = c/2$. It is viewed down the a axis of the unit cell. The unit cell (full lines) and the primitive subcell (broken lines) are drawn.

The complexity of the asymmetric unit decreases considerably if, in addition to normal crystallographic symmetries, so called non-crystallographic symmetries are considered (Blow, 1976). Such a non-crystallographic symmetry, or partial symmetry, brings only a part of the crystal structure into coincidence with itself, or with another part of the structure. Groupoids are to be used instead of groups, for an adequate description of the symmetry (Fichtner, 1980). For Yb(idtph)₃, the symmetry of a molecule is described by a groupoid consisting of 13 parts (objects). The central part of the molecule forms one of the objects, the 12 phenyl rings the remaining ones. The central part consists of the 28 non-carbon and non-hydrogen atoms of the molecule. The symmetry of this part is approximately D_3 (32). A single phenyl ring has symmetry C_{2v} ($mm2$). The number of parameters necessary for the description of the structure drops considerably if partial symmetries are taken into account (Fichtner, 1981).

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