Inorganica Chimica Acta, 132 (1987) 263–271

Synthesis and Characterization of a Ytterbium Complex with Diphenylacetylpyrazolone $Yb(DPAP)_3 \cdot (H_2O)_2 \cdot 3EtOH$

G. BOMBIERI

Istituto di Chimica Farmaceutica, Viale Abruzzi 42, 20131 Milan, Italy

A. POLO

Istituto di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti 4, 35100 Padua, Italy

JIA-FU WANG, JINGUANG WU and GUANG-XIAN XU

Chemistry Department, Peking University, Beijing, China

(Received November 5, 1986)

Abstract

Reaction of $YbCl_3$ with NH_4DPAP (HDPAP = 1,3-diphenyl-4-acetylpyrazol-5-one) in a 1:3 molar ratio results in the formation of the complex $Yb(DPAP)_3 \cdot (H_2O)_2 \cdot 3EtOH$, the crystal structure of which has been determined.

The compound crystallizes in the monoclinic system, space group $P2_1/n$ with $Z = 4$, unit cell parameters are $a = 16.067(2)$, $b = 22.254(3)$, $c = 15.297(2)$ Å and $\beta = 99.46(3)°$. The structure has been refined to $R = 0.0501$ ($R_w = 0.057$) for 7201 indepedent reflections.

The coordination polyhedron about the eight-coordinate ytterbium atom is a square antiprism. The three DPAP ligands are bidentate to the central metal ion, where two water molecules are also coordinated. The average bonding distances are $Yb-O_{(DPAP)} = 2.31(1)$ Å, $Yb-O_{(water)} = 2.36(1)$ Å. The complex has been further characterized by elemental analysis, TGA, DTA and IR spectroscopy.

Introduction

The chemistry of rare earth β-diketonates is developing very rapidly [1–5]. In particular, tris-acetylacetonate complexes with lanthanoid elements are known to form metastable trihydrates which decompose to stable monohydrates [6]; the dihydrate form for some of them can be obtained by recrystallization of the trihydrate form in ethanol [7]. In the solid state the structures of $Yb(acac)_3(H_2O)$ (Hacac = acetylacetone) [8], and of its hemibenzene solvate [9] are known, as well as the adduct with 4-amino-3-penten-2-one [10]. In these complexes, the Yb ion is hepta-coordinate with the three acac ligands chelated to the metal ion; the capped trigonal prism coordination polyhedron is completed with the coordination of the monodentate ligand. In the present investigation we have prepared a ytterbium complex $Yb(DPAP)_3 \cdot 2H_2O \cdot 3EtOH$, where HDPAP is a new ligand, 1,3-diphenyl-4-acetylpyrazol-5-one ($C_{17}H_{14}N_2O_2$). It was interesting to elucidate the physicochemical properties of the new complex as well as its crystal structure in order to ascertain which coordination number should be assigned to it: hepta-coordination as in the previously quoted examples, or something different because of the higher complexity of this new β-diketone ligand. The complex has also been characterized by elemental analyses, TGA, DTA and infrared spectra.

Experimental

Synthesis

When an aqueous solution of $YbCl_3$ reacted with $NH_4^+DPAP^-$ in molar ratio 1:3, at a final pH of 5, a precipitate was obtained immediately, which was recrystallized in ethanol, yielding colourless, transparent crystals. *Anal.* Calc. for $Yb(C_{17}H_{13}N_2O_2) \cdot (H_2O)_2 \cdot 3CH_3CH_2OH$: C, 58.0; N, 7.13; H, 5.17; Yb, 14.7. Found: C, 57.8; N, 7.18; H, 5.01; Yb, 14.7%.

IR Studies

The sample discs were prepared by mixing the compound with KBr (G.P.) or CsI (C.P.) for measuring median or far infrared spectra, respectively. The FT-IR spectra were recorded with a Nicolet-7199B infrared spectrometer.

X-ray Measurements and Structure Determination

The crystal and refinement data are summarized in Table I. $Yb(DPAP)_3 \cdot 2H_2O \cdot 3EtOH$ is in the form of white, transparent, irregular prisms.

A single crystal of 0.4 × 0.5 × 0.7 mm was lodged in a Lindemann glass capillary. It was centered on a

0020-1693/87/$3.50

TABLE I. Crystal Data

Formula	$C_{54}H_{54}N_6O_{9.5}Yb$
M	1110.09
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	16.067(2)
b (Å)	22.254(3)
c (Å)	15.297(2)
β (°)	99.46(3)
U (Å)	5395.2
Z	4
D_c (Mg m^{-3})	1.37
$F(000)$	2256
Radiation, λ (Å)	(Mo Kα(0.7107))
Reflection measured	10148
Scan method	$\theta/2\theta$
Scan speed (° min^{-1})	1.80
Scan width (°)	1.20
Background counts per second	10
$2\theta_{max}$ (°)	50
σ limit [$I > n\sigma(I)$]	$n = 3$
Unique observed reflection [$I > 3\sigma(I)$]	7201
Weighting scheme w	$2.0148[\sigma^2(F_o) + 0.001544(F_o)^2]^{-1}$
R ($R = [\Sigma\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$)	0.050
$R_w = \left[\frac{\Sigma w[\lvert F_o\rvert - \lvert F_c\rvert]^2}{\Sigma w\lvert F_o\rvert^2}\right]^{1/2}$	0.057
μ(Mo Kα) (cm^{-1})	16.91

four-circles Philips PW 1100 automated diffractometer with graphite monochromated Mo Kα radiation; the orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying the orientation angles ϕ and χ in the range of 120° each, the detector position varying between $\theta = 6°$ and $\theta = 9°$. For the determination of precise lattice parameters, 25 strong reflections with $8° < \theta < 16°$ were considered.

The intensities of the three standard reflections −4 4 6, −5 −2 6 and 2 −4 −4 were monitored every 180 min. There was no significant fluctuation in intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz-polarization effects and for absorption, following the method of North *et al.* [11]. The structure was solved using a three-dimensional Patterson and Fourier synthesis and was refined by a block matrix least-squares because of the large number of variables, with anisotropic thermal parameters only for the atoms belonging to the Yb coordination polyhedron and for the pyrazole atoms, and isotropic thermal parameters for the remaining non-hydrogen atoms. The phenyl rings were refined as rigid groups and were restricted to their normal geometry (D_{6h} symmetry, C–C 1.395 Å) using the group refinement procedure. Each ring was assigned six variable positional parameters and each ring carbon atom was assigned an individual isotropic thermal parameter. Hydrogen atom contributions (for the phenyl and methyl groups) were introduced in calculated positions ($d_{C-H} = 0.95$ Å and $U_{ISO} = 0.08$ Å^2). Some difficulties were experienced in the last stages of the refinement. In fact, the refinement of the $Yb(DPAP)_3 \cdot (H_2O)_2$ molecule reached convergency at $R = 0.065$. At this point a Fourier difference map failed to reveal clearly the EtOH atom positions as expected from the analytical formulation of the compound; instead about 9 residuals of the order of 2–3 e/Å3 were evidenced. They were interpreted as 1.5 statistically distributed ethanol molecules for the $Yb(DPAP)_3(H_2O)_2$ unit. The introduction of carbon and oxygen atoms in the positions indicated by the electron density residuals with population factors of 0.5 gave the most significant lowering of the R values: $R = 0.050$ and $R_w = 0.057$, but probably a more complex statistical distribution could be present. The anomalous dispersion terms [12] for Yb were taken into account in the refinement. Atomic scattering factors were taken from ref. 13.

Data processing and computation were carried out using the SHELX 76 program package [14].

Final positional parameters are presented in Table II. Thermal parameters, observed and calculated structure factors (X10) are available see 'Supplementary Material'.

Results and Discussion

Thermal Analysis

Figure 1 is a TG curve obtained by heating the compound on a thermobalance in flowing argon. The loss of weight begins at about 45.5 ℃; at the temperature of 190 ℃, the loss of water and ethanol of solvation is complete. At this stage the loss of weight of the sample is 15.5% (calc. 14.8%). The compound begins to melt at about 100 ℃ and completes melting at 160 ℃. Weight loss above 360 ℃ up to 770 ℃ can be mainly attributed to the decomposition of the ligand and, to a smaller extent, to the vaporization of the melting complex. The final product is a white powder of Yb_2O_3.

IR Spectra

There has been a great deal of work on infrared spectra of rare earth β-diketonates, but most are concerned with linear chain β-diketonates [15–20]. Only Okafor *et al.* [21] have reported on the IR spectra of pyrazolone-β-diketonate complexes.

We measured the FT-IR spectra of the title compound as well as the free ligand from 150 to 4000

TABLE II. Atomic Fractional Coordinates ($\times 10^4$) with e.s.d.s in Parentheses, and U_{eq} or U_{iso} ($\times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}[a] or U_{iso}
Yb	8021.9(1)	1398.1(1)	5330.9(2)	38.9(1)*
O7	7953(3)	390(2)	5851(3)	59(2)*
O8	6623(3)	1124(2)	4802(4)	64(2)*
O1	8493(3)	2000(2)	4323(3)	52(2)*
C1	8493(4)	2576(3)	4316(4)	45(2)*
N1	9061(3)	2900(3)	3946(4)	48(2)*
N2	8924(4)	3527(3)	4022(4)	52(2)*
C2	8253(4)	3580(3)	4414(4)	48(2)*
C3	7942(4)	3000(3)	4630(4)	46(2)*
C4	7295(4)	2809(3)	5085(5)	55(3)*
O2	7167(3)	2266(2)	5240(4)	59(2)*
C5	6683(6)	3247(4)	5382(7)	88(4)*
O3	9350(3)	1045(2)	5431(3)	44(1)*
C21	9736(4)	840(3)	4838(4)	40(2)*
N3	10599(3)	807(2)	4919(3)	42(2)*
N4	10850(3)	556(2)	4182(3)	47(2)*
C22	10148(4)	440(3)	3620(4)	42(2)*
C23	9415(4)	612(3)	3966(4)	41(2)*
C24	8542(4)	614(3)	3614(4)	41(2)*
O4	8005(2)	817(2)	4056(3)	47(1)*
C25	8242(4)	404(4)	2696(5)	65(2)*
O5	8845(3)	2048(2)	6259(3)	50(2)*
C41	8889(4)	2141(3)	7072(4)	44(2)*
N5	9496(3)	2504(3)	7551(4)	50(2)*
N6	9450(4)	2511(3)	8452(4)	58(2)*
C42	8802(4)	2158(3)	8530(4)	49(2)*
C43	8407(4)	1911(3)	7700(4)	43(2)*
C44	7744(4)	1508(3)	7456(4)	45(2)*
O6	7495(3)	1364(2)	6665(3)	54(2)*
C45	7307(5)	1201(4)	8118(6)	67(3)*
O9	1923(19)	6136(16)	1966(21)	218(12)
C61	1896(30)	5652(17)	2306(24)	238(22)
C62	1700(12)	5221(8)	1551(12)	78(5)
O10	344(18)	5518(13)	6861(19)	207(10)
C71	795(21)	5108(15)	7002(22)	152(11)
C72	389(28)	4817(20)	7783(27)	216(18)
O11	133(6)	3280(4)	9892(6)	55(2)
C81	−442(22)	3552(18)	10058(31)	198(17)
C82	−528(33)	4259(19)	10169(33)	253(22)
C7	10218(3)	2213(2)	3891(3)	60(2)
C8	10889(3)	2015(2)	3490(3)	74(2)
C9	11065(3)	2300(2)	2729(3)	80(2)
C10	10570(3)	2783(2)	2368(3)	86(3)
C11	9900(3)	2981(2)	2769(3)	72(2)
C6	9724(3)	2696(2)	3530(3)	50(2)
C13	7157(3)	4383(2)	4242(3)	62(2)
C14	6916(3)	4974(2)	4374(3)	67(2)
C15	7491(3)	5374(2)	4844(3)	75(2)
C16	8308(3)	5183(2)	5182(3)	84(3)
C17	8549(3)	4592(2)	5050(3)	75(2)
C12	7974(3)	4192(2)	4580(3)	52(2)
C27	11015(2)	1456(2)	6211(3)	58(2)
C28	11629(2)	1658(2)	6900(3)	64(2)
C29	12446(2)	1425(2)	7000(3)	76(2)
C30	12648(2)	991(2)	6411(3)	87(3)
C31	12033(2)	790(2)	5722(3)	72(2)
C26	11217(2)	1022(2)	5622(3)	45(1)
C33	10062(3)	−430(2)	2574(3)	56(2)
C34	10196(3)	−682(2)	1774(3)	63(2)
C35	10508(3)	−328(2)	1148(3)	75(2)
C36	10686(3)	278(2)	1321(3)	94(3)
C37	10552(3)	530(2)	2121(3)	77(2)
C32	10240(3)	176(2)	2747(3)	42(1)
C53	9181(3)	1831(2)	10109(3)	69(2)
C54	9018(3)	1801(2)	10976(3)	88(3)
C55	8268(3)	2036(2)	11181(3)	90(3)
C56	7682(3)	2300(2)	10520(3)	96(3)
C57	7845(3)	2330(2)	9653(3)	80(2)
C52	8595(3)	2096(2)	9448(3)	50(2)
C47	10870(3)	2995(2)	7816(2)	64(2)
C48	11485(3)	3349(2)	7521(2)	83(2)
C49	11356(3)	3565(2)	6653(2)	83(3)
C50	10613(3)	3427(2)	6080(2)	81(2)
C51	9998(3)	3073(2)	6374(2)	64(2)
C46	10126(3)	2857(2)	7242(2)	51(2)

[a] U_{eq} is denoted by an asterisk.

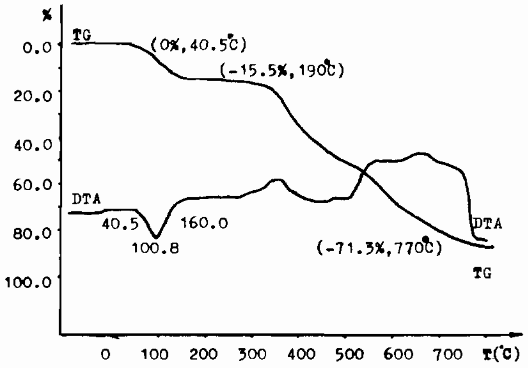


Fig. 1. The TG and DTA curves of $Yb(DPAP)_3 \cdot 2H_2O \cdot 3CH_3CH_2OH$.

cm^{-1}. Peaks at 1624 and 1546 cm^{-1} of the free ligand HDPAP, as shown in Fig. 2, are due to C=O vibration. As a result of coordination with Yb(III), they shift to 1615.9 and 1490 cm^{-1}, respectively, showing a slight weakening of the C=O bond. A broad peak at about 3400 cm^{-1} can be assigned to the O–H vibration of the coordinated water (see Fig. 3).

Although the far infrared spectra are usually due to the vibration of metal–ligand bonds, it is quite difficult to assign their peaks precisely. We only assign the peak at 401.4 cm^{-1} (Fig. 4) to the vibration of the Yb–O bond (between the metal and the ligand DPAP) by comparing Fig. 4 with the spectrum of the free ligand (see Fig. 5) and with spectra of a series of

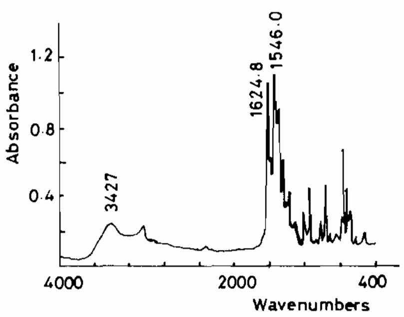


Fig. 2. The infrared spectrum of HDPAP.

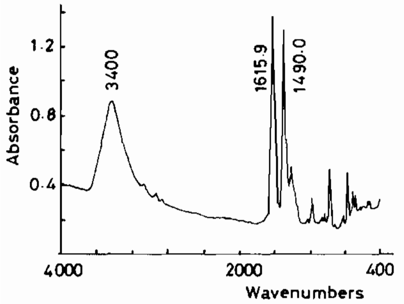


Fig. 3. The infrared spectrum of $Yb(DPAP)_3 \cdot 2H_2O \cdot 3CH_3CH_2OH$.

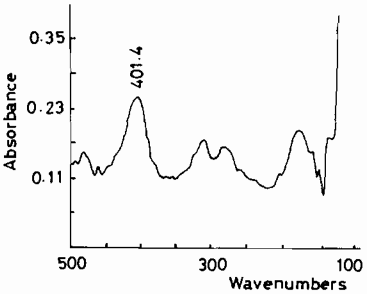


Fig. 4. The far infrared spectrum of $Yb(DPAP)_3 \cdot 2H_2O \cdot 3CH_3CH_3OH$.

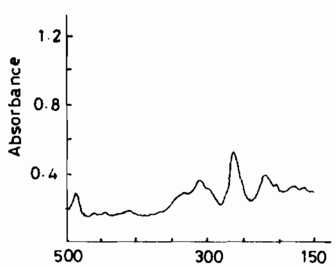


Fig. 5. The far infrared spectrum of HDPAP.

$Ln(DPAP)_3 \cdot mH_2O \cdot nEtOH$ complexes. The assignment of other peaks in the far IR spectrum of $Yb(DPAP)_3 \cdot 2H_2O \cdot 3EtOH$ will be done by a normal coordinate analysis to be reported later.

Crystal Structure

The crystal structure of the title compound consists of well separated molecules of $Yb(DPAP)_3 \cdot (H_2O)_2 \cdot 1.5EtOH$ which are packed in the monoclinic cell together with disordered ethanol molecules (see experimental section). A perspective view of a single molecule is shown in Fig. 6 together with the atom numbering scheme.

Bond distances and angles are given in Table III. The ytterbium ion is eight-coordinated to six oxygen atoms belonging to the three DPAP ligands and to two water molecules. The coordination geometry is a square-antiprism: one square plane is formed by O(1), O(2), O(4) and O(8) and the second square by O(3), O(5), O(6) and O(7).

In each square the corners are occupied by a chelating ligand, a water molecule and the fourth position by an oxygen of the third chelating ligand which connects the two squares as shown in Fig. 7. The DPAP ligands present a quasi-planar skeleton: the acetylpyrazolone moiety, with the Yb ion at distances from these planes of −0.781(1) Å for A, 0.479(1) Å for B and 0.285(1) Å for C ligands. The dihedral angles between the best mean planes are: AB angle = 76.2°, BC angle = 44.8° and AC angle = 65.2°. The phenyl rings are rotated from the plane of each skeleton in order to realise a rather compact packing (see Table IV) and in any case their hindering is ineffective on the first-coordination sphere. In fact, in the present case the coordination number is eight, while in the known structures with tris(acetylacetonate) ligands with less steric hindrance, the Yb ion is seven-coordinate, the seventh position being occupied by a monodentate ligand, water as in tris(acetylacetonato)aquaytterbium [8] and in the analogous benzene solvate [9], and acetylacetonimine in tris(acetylacetonato)-4-amino-3-penten-2-one [10]. The coordination geometry in these compounds approximates to a capped trigonal prism. The different hindering of the seventh ligand causes only different reciprocal positions of the chelating ligands; they bridge the triangular faces of the trigonal prism, while the third bridges one square face with the capping position in the aqua derivatives [8, 9], while in the acetylacetonimine adduct [10], two chelating ligands are on the two opposite triangular faces while the third again bridges one square face with the capping position.

In the present example with square antiprismatic geometry, among the five most likely geometrical isomers (see Scheme 1) compound **5** is that adopted by the title compound. (The other isomers arising from chelation on the diagonal sides of the squares are omitted because they are unfavourable on energetic grounds.) The known lanthanoid $(acac)_3$ structures $Y(acac)_3(OH_2)_2$ [22] and $La(acac)_3(OH_2)_2$ [23] depict octa-coordinate square antiprismatic structures of the type **2** (L indicates a monodentate ligand).

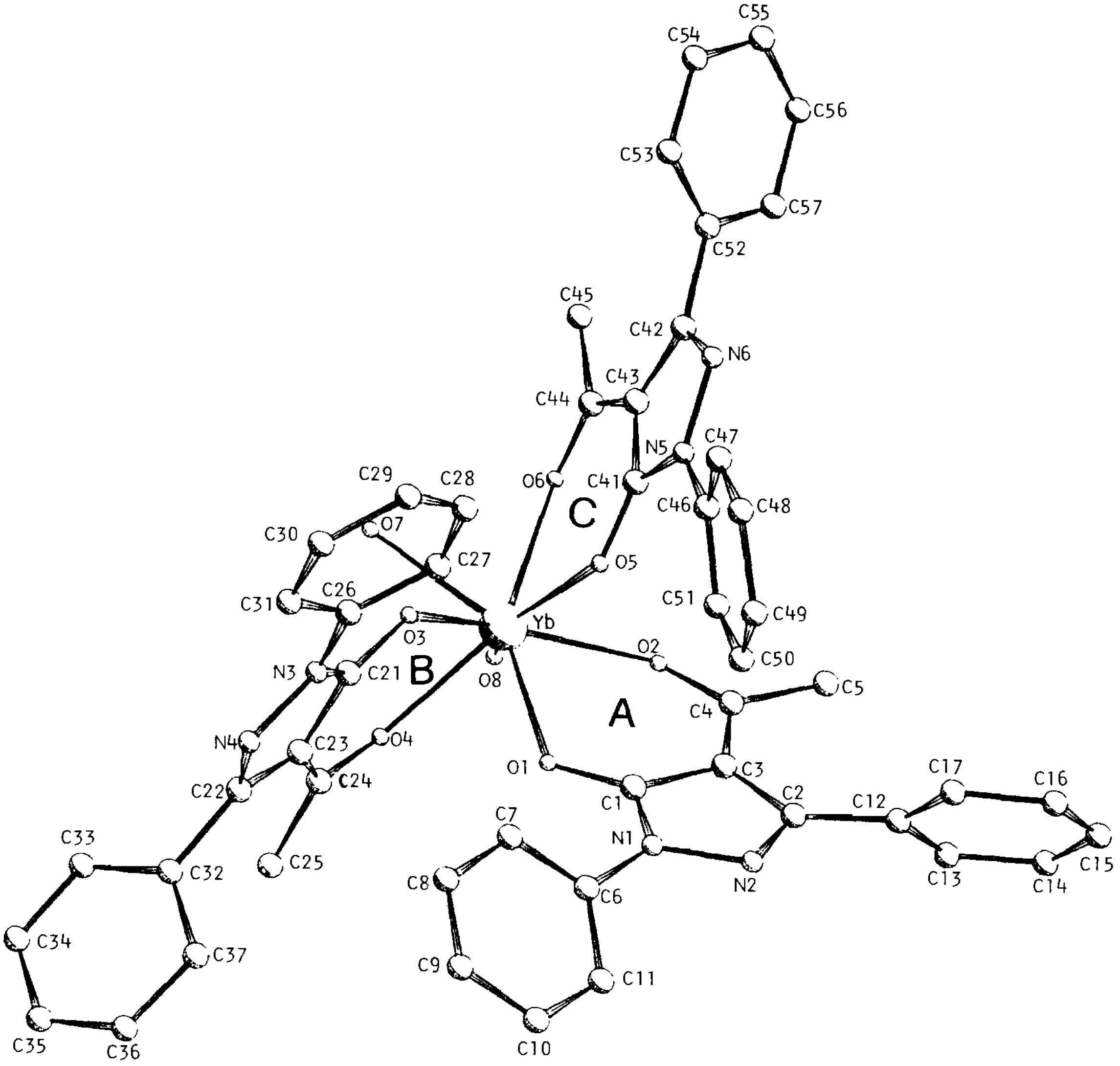


Fig. 6. A perspective view of the Yb(DPAP)$_3$(H$_2$O)$_2$ molecule.

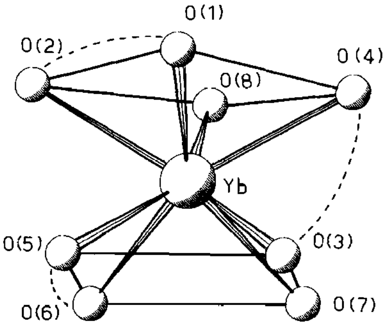
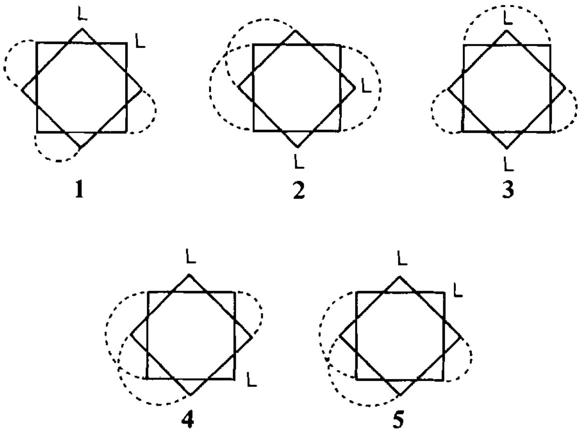


Fig. 7. Yb coordination polyhedron; shaded lines connect two oxygens of the same DPAP ligand.



Scheme 1.

TABLE III. Distances (Å) and Principal Angles (°) with e.s.d.s in Parentheses

Distances

Yb–O7	2.388(5)
Yb–O8	2.341(5)
Yb–O1	2.265(5)
Yb–O2	2.360(5)
Yb–O3	2.255(4)
Yb–O4	2.336(4)
Yb–O5	2.290(4)
Yb–O6	2.336(5)
O1–C1	1.282(8)
C1–N1	1.357(9)
C1–C3	1.429(10)
N1–N2	1.420(8)
N1–C6	1.403(8)
N2–C2	1.323(10)
C2–C3	1.441(9)
C2–C12	1.470(8)
C3–C4	1.408(10)
C4–O2	1.256(9)
C4–C5	1.507(13)
O3–C21	1.264(7)
C21–N3	1.374(7)
C21–C23	1.442(8)
N3–N4	1.378(8)
N3–C26	1.421(6)
N4–C22	1.327(7)
C22–C23	1.421(9)
C22–C32	1.487(7)
C23–C24	1.416(8)
C24–O4	1.264(8)
C24–C25	1.484(9)
O5–C41	1.250(8)
C41–N5	1.382(8)
C41–C43	1.425(9)
N5–N6	1.392(8)
N5–C46	1.421(8)
N6–C42	1.325(9)
C42–C43	1.434(8)
C42–C52	1.501(8)
C43–C44	1.395(9)
C44–O6	1.251(8)
C44–C45	1.490(11)

Angles

O5–Yb–O6	74.6(2)	C2–C12–C13	120.9(5)
O4–Yb–O6	139.0(2)	Yb–O3–C21	130.3(4)
O4–Yb–O5	142.5(2)	O3–C21–C23	130.4(6)
O3–Yb–O6	113.8(2)	O3–C21–N3	124.2(5)
O3–Yb–O5	74.6(2)	N3–C21–C23	105.4(5)
O3–Yb–O4	75.2(2)	C21–N3–C26	128.3(5)
O2–Yb–O6	77.7(2)	C21–N3–N4	112.1(5)
O2–Yb–O5	77.9(2)	N4–N3–C26	119.6(4)
O2–Yb–O4	118.5(2)	N3–N4–C22	106.1(5)
O2–Yb–O3	145.5(2)	N4–C22–C32	117.3(5)
O1–Yb–O6	145.4(2)	N4–C22–C23	112.0(5)
O1–Yb–O5	79.9(2)	C23–C22–C32	130.7(5)
O1–Yb–O4	73.7(2)	C21–C23–C22	104.4(5)
O1–Yb–O3	80.4(2)	C22–C23–C24	133.5(6)
O1–Yb–O2	74.5(2)	C21–C23–C24	122.2(5)
O8–Yb–O6	80.1(2)	C23–C24–C25	120.4(6)
O8–Yb–O5	143.4(2)	C23–C24–O4	121.2(5)
O8–Yb–O4	71.8(2)	O4–C24–C25	118.3(6)
O8–Yb–O3	140.9(2)	Yb–O4–C24	136.8(4)
O8–Yb–O2	71.1(2)	N3–C26–C31	119.1(4)
O8–Yb–O1	109.2(2)	N3–C26–C27	120.9(4)
O7–Yb–O6	68.6(2)	C22–C32–C37	119.6(4)
O7–Yb–O5	116.2(2)	C22–C32–C33	120.3(4)
O7–Yb–O4	76.3(2)	Yb–O5–C41	130.7(4)
O7–Yb–O3	75.3(2)	O5–C41–C43	131.5(6)
O7–Yb–O2	136.8(2)	O5–C41–N5	122.9(6)
O7–Yb–O1	145.2(2)	N5–C41–C43	105.5(5)
O7–Yb–O8	77.0(2)	C41–N5–C46	128.8(5)
Yb–O1–C1	126.7(4)	C41–N5–N6	112.5(5)
O1–C1–C3	131.0(6)	N6–N5–C46	118.7(5)
O1–C1–N1	122.3(6)	N5–N6–C42	104.8(5)
N1–C1–C3	106.6(6)	N6–C42–C52	116.0(6)
C1–N1–C6	129.0(5)	N6–C42–C43	112.7(6)
C1–N1–N2	111.3(5)	C43–C42–C52	131.2(6)
N2–N1–C6	119.6(5)	C41–C43–C42	104.4(6)
N1–N2–C2	105.8(5)	C42–C43–C44	133.7(6)
N2–C2–C12	117.0(6)	C41–C43–C44	121.8(6)
N2–C2–C3	111.3(6)	C43–C44–C45	122.5(6)
C3–C2–C12	131.6(6)	C43–C44–O6	122.1(6)
C1–C3–C2	104.9(6)	O6–C44–C45	115.4(6)
C2–C3–C4	134.0(6)	Yb–O6–C44	137.1(5)
C1–C3–C4	121.0(6)	C42–C52–C57	120.5(5)
C3–C4–C5	121.7(7)	C42–C52–C53	119.4(5)
C3–C4–O2	122.8(7)	N5–C46–C51	120.3(5)
O2–C4–C5	115.5(7)	N5–C46–C47	119.7(4)
Yb–O2–C4	133.4(5)	O9–C61–C62	105(3)
N1–C6–C11	120.3(5)	O10–C71–C72	98(3)
N1–C6–C7	119.7(4)	O11–C81–C82	128(3)
C2–C12–C17	119.1(5)		

The DPAP chelating mode is rather asymmetric, the ytterbium-to-carbonyl-oxygen distances being systematically longer on the side adjacent to the methyl group: Yb–$O_{av.}$ (2.344 Å) *vs.* Yb–$O_{av.}$ (2.267 Å). This asymmetric chelation was present also in previously studied structures such as the tris(acetylacetonate) monohydrate Yb derivatives [8, 9] and in the analogous acetylacetonimine derivative [10], but in the first two examples the high e.s.d.s in the bonds did not allow conclusive comments; in the third case the asymmetry was ascribed to the presence of intermolecular hydrogen bonding with the NH_2 group. Here the higher crowding around the Yb ion, consistent with the higher coordination number (from seven to eight), together with the close proximity of the methyl group to a coordinating oxygen, could be consistent with the observed lenthening also if electronic factors cannot in principle be ruled out. In fact, the two Yb–O_{water} bond distances of 2.388(5) (Yb–O(7)) and

TABLE IV. Least-squares Planes with Deviations (Å × 10^3) of the Relevant Atoms. The equations of the planes (× 10^3) in the direct space are in the form: $M1 \cdot x + M2 \cdot y + M3 \cdot z = D$

	M1	M2	M3	*D*
Plane 1 O(1), O(2), O(4), O(8) [O(1) 61(5), O(2) −78(5), O(4) −50(4), O(8) 82(5), Yb −1263(1)]	−385(1)	282(2)	−878(1)	−9382(19)
Plane 2 O(3), O(5), O(6), O(7) [O(3) −7(4), O(5) 8(4), O(6) −10(5), O(7) 10(5), Yb 1241(1)]	−421(1)	295(2)	−858(1)	−12089(15)
Skeleton A O(1), O(2), C(1), C(2), C(3), C(4), N(1), N(2) [O(1) 20(5), O(2) −39(5), C(1) 2(7), C(2) 28(7), C(3) 42(6), C(4) 20(7), N(1) −21(5), N(2) −31(6), Yb −78(1)]	−491(1)	−21(2)	−871(1)	−11958(13)
Phenyl A 1 C(6) ⟶ C(11)	−527(2)	−633(2)	−527(2)	−14590(20)
Phenyl A 2 C(12) ⟶ C(17)	448(2)	272(2)	−857(1)	1880(31)
Skeleton B O(3), O(4), C(21), C(22), C(23), C(24), N(3), N(4) [O(3) −26(4), O(4) 34(4), C(21) −17(6), C(22) −36(6), C(23) −40(6), C(24) −10(6), N(3) 48(5), N(4) 18(6), Yb 479(11)]	130(1)	921(1)	−368(2)	926(20)
Phenyl B 1 C(26) ⟶ C(31)	359(2)	721(1)	−593(1)	2575(36)
Phenyl B 2 C(32) ⟶ C(37)	−878(1)	239(2)	−414(2)	−15467(10)
Skeleton C O(5), O(6), C(41), C(42), C(43), C(44), N(5), N(6) [O(5) −23(5), O(6) 25(5), C(41) 16(6), C(42) −15(7), C(43) 10(6), C(44) −40(7), N(5) 27(6), N(6) 7(6), Yb −285(1)]	−593(1)	788(1)	−165(2)	−5442(20)
Phenyl C 1 C(46) ⟶ C(51)	486(2)	−822(1)	−298(2)	−1460(41)
Phenyl C 2 C(52) → C(57)	−418(2)	−887(1)	−199(2)	−11744(35)

Angles (°)

1–2	2.5(1)	A–C	65.2(1)	A–B	76.2(1)	B–C	44.8(1)
1–A	18.4(1)	1–B	57.8(1)				
2–C	51.4(1)	2–B	57.8(1)				
A–A1	40.0(1)	A–A2	58.9(1)	A1–A2	85.7(1)		
B–B1	21.8(1)	B–B2	75.0(1)	B1–B2	84.1(2)		
C–C1	27.6(1)	C–C2	65.3(1)	C1–C2	54.2(1)		

2.341(5) Å (Yb–O(8)) approximate the values of the longer Yb–O_{DPAP} distances, suggesting a higher electron density on O(1), O(3) and O(5) to be responsible for the shorter distances.

In any case, the average value for the Yb–O carbonyl distances of 2.305 Å is significantly longer than the average metal–oxygen distance of 2.23 Å found in the hepta-coordinate derivatives [8–10], due to the increase in the coordination number of Yb.

The ligand bites (average value 2.802 Å) are somewhat larger with respect to the values of 2.75 and 2.76 Å of the acetylacetonate ligands in the aqua [8, 9] and acetylacetonimine derivatives [10].

Packing

A projection of the unit cell content down the *b* crystal axis is shown in Fig. 8. The labelling O(9), O(10), O(11) represents the oxygens of the disordered ethanol molecules, which are disposed in the empty space of the structure, without any particular short contacts that could be considered as possible hydrogen bonds, except an O(8)···O(11)* contact distance of 2.76(1) Å. In this way the packing is

---

*At $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$.

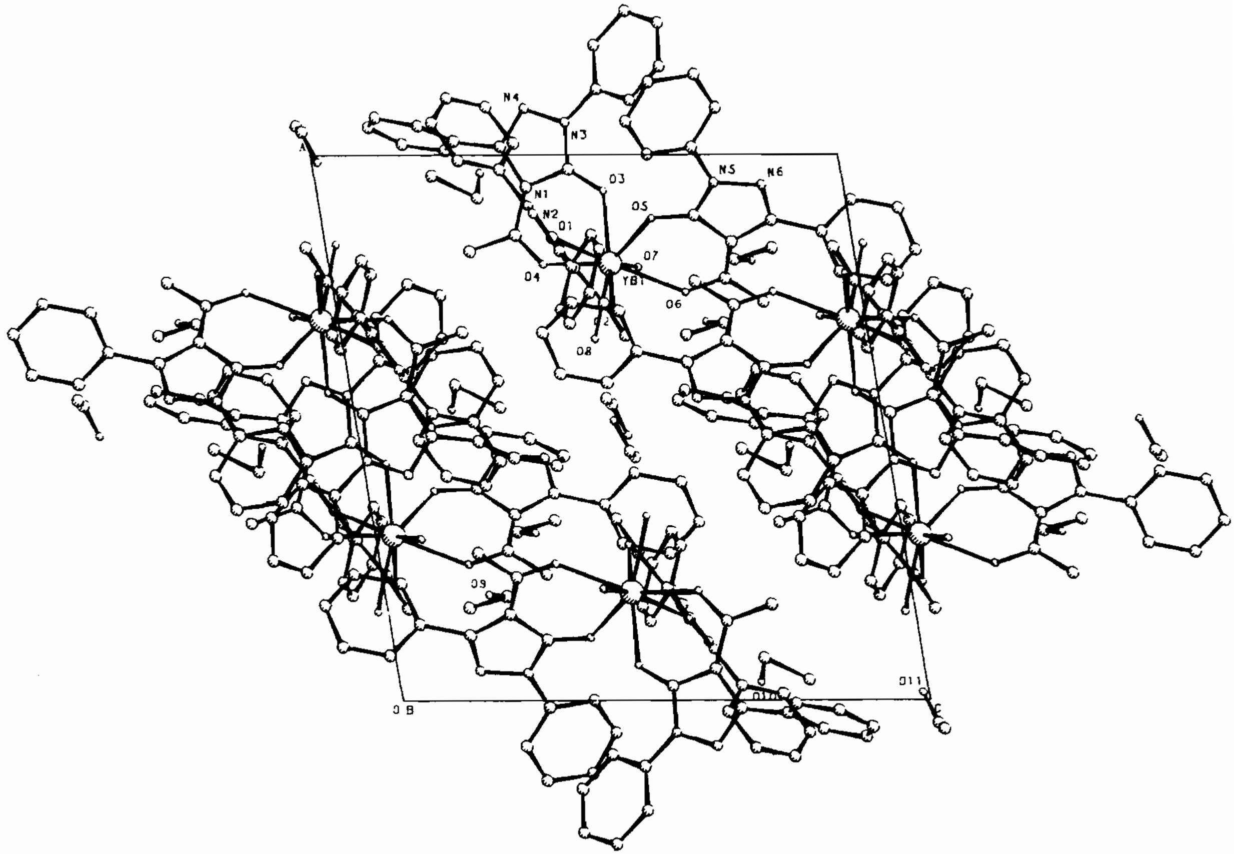


Fig. 8. Unit cell content down the *b* axis.

determined mainly by the normal van der Waals interactions and is consistent with the easy solvent loss.

Supplementary Material

Table A. Anisotropic and isotropic thermal parameters ($\times 10^3$) with e.s.d.s in parentheses. Table B. Fractional hydrogen coordinates ($\times 10^4$). These are available from author G.B. on request.

Acknowledgement

We thank Mrs. M. Magnabosco for technical assistance.

References

1 L. C. Thompson, in K. A. Gschneider Jr. and L. R. Eyring (eds.), 'Handbook of the Physics and Chemistry of Rare Earths', Vol. 3, North-Holland, Amsterdam, 1979, Chap. 25.
2 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal *beta*-Diketonates and Allied Derivatives', Academic Press, London, 1978.
3 R. C. Mehrotra, P. N. Kapoor and J. M. Batwara, *Coord. Chem. Rev., 31,* 67 (1980).
4 Shi Nai, Wu Jinguang, Xu Guang-Xian, Qian Jinzi, Yao Jia-xing, Fan Haifu, M. Kusunoki, N. Yasuoka and M. Kakudo, *J. Mol. Sci. (Wuhan, China), 2*(1), 9 (1984).
5 J. G. White, *Inorg. Chim. Acta, 16,* 159 (1976).
6 G. W. Pope, J. F. Steinbach and W. F. Wagner, *J. Inorg. Nucl. Chem., 20,* 304 (1961).
7 M. F. Richardson, W. F. Wagner and D. E. Sands, *Inorg. Chem., 7,* 2495 (1965).
8 J. A. Cunningham, D. E. Sands, W. F. Wagner and M. F. Richardson, *Inorg. Chem., 8,* 22 (1969).
9 E. D. Watkins, A. A. Cunningham, T. Phillips, D. E. Sands and W. F. Wagner, *Inorg. Chem., 8,* 29 (1969).
10 M. F. Richardson, P. W. R. Corfield, D. E. Sands and R. E. Sievers, *Inorg. Chem., 9,* 1632 (1970).
11 A. C. T. North, D. C. Philips and F. Matheus, *Acta Crystallogr., Sect. A, 24,* 351 (1968).
12 'International Tables for X-Ray Crystallography', Vol. 4, 2nd edn., Kynoch Press, Birmingham, 1974, p. 101.
13 G. M. Sheldrick, 'SHELX 76', University of Cambridge, 1976.
14 Liang Yingqiu, Liu Juzheng, Liu Guofa, Zhao Yongnian and Wang Yitian, *Chem. J. Chin. Univ., 2,* 97 (1981).
15 K. Nakamoto, 'IR and Raman Spectra of Inorganic Compounds', Interscience, New York, 1978.
16 S. Misumi and N. Iwasaki, *Bull. Chem. Soc. Jpn., 40,* 550 (1967).
17 Xu Guangzhi, Sun Jiabin, Wang Yuzhen, Li Zhipu and Tang Youqi, *Kexue Tongbao, 26,* 474 (1981) (in Chinese).

18 P. C. Mathur, S. S. L. Surana and S. P. Tandon, *Z. Naturforsch., Teil B, 30*, 207 (1975).

19 P. C. Metha, S. S. L. Surana and S. P. Tandon, *Can. J. Spectrosc., 18*, 55 (1973).

20 E. C. Okafor, *Polyhedron, 2*, 309 (1983); E. C. Okafor, *J. Inorg. Nucl. Chem., 42*, 1155 (1980); Liang Yingqiu, Zhao Yongnian, Fu Xingji, Chen Dian, Li Shengchong, *Kexue Tongbao, 29*, 210 (1984) (in Chinese).

21 J. A. Cunningham, D. E. Sands and W. F. Wagner, *Inorg. Chem., 6*, 99 (1967).

22 T. Phillips, D. E. Sands and W. F. Wagner, *Inorg. Chem., 7*, 2295 (1968).