

**The Crystal and Molecular Structure of a Europium Shift Reagent Complex,
the Dipyridine Adduct of
Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III), $\text{Eu}(\text{dpm})_3(\text{py})_2$**

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The crystal structure of the dipyridine adduct of tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III), $\text{Eu}(\text{dpm})_3(\text{py})_2$, has been determined so that the principal features of its paramagnetically shifted n.m.r. spectrum could be calculated. The crystals form as triclinic parallelepipeds in space group $P\bar{1}$ with $a = 13.611$ (5), $b = 17.306$ (4), $c = 10.493$ (7) Å, $\alpha = 93.33$ (3), $\beta = 105.20$ (5), and $\gamma = 94.75$ (4)°, with two molecules per unit cell. All unique reflections for which $2\theta < 50^\circ$ were observed using graphite monochromatized Mo $K\alpha$ radiation and a pulse-height analyzer. The structure was refined by large-block diagonal least-squares methods, using 6840 observed reflections, to an R index of 0.039. Most hydrogen atoms were located, and the remainder have been included at their calculated positions. The $\text{Eu}(\text{dpm})_3(\text{py})_2$ molecule contains a near twofold axis, and the coordination sphere is best described as a square antiprism. Eu(III) lies 0.3 to 0.4 Å out of the molecular planes of four of the five ligands. Because of the low symmetry of the complex, two geometric factors are needed to account for the observed n.m.r. shifts.

Introduction

Since the discovery by Hinckley (1969) of lanthanide shift reagents, their use has become widespread. The potential for deducing the structural details of substrate molecules coordinated to $\text{Ln}(\text{dpm})_3$ complexes (Ln is lanthanide; dpm is dipivalomethanato or 2,2,6,6-tetramethylheptane-3,5-dionato) has led several authors to postulate various correlations between the induced shifts and various structural parameters (Sievers, 1972). The most successful treatments have been those which relate the observed shifts to a geometric factor $G(r, \theta)$ given as $(3 \cos^2 \theta - 1)/r^3$ (Horrocks & Sipe, 1971). This geometric factor occurs in one form of the dipolar shift equation, which is valid only for molecules with axial (n -fold, $n \geq 3$) symmetry. Consideration of the known crystal structures of pertinent lanthanide complexes (Horrocks, Sipe & Lubner, 1971; Erasmus & Boeyens, 1971; Cunningham, Sands & Wagner, 1967; Phillips, Sands & Wagner, 1968) argues against threefold symmetry, and illustrates the need for accurate structural information for shift reagent adducts. Since the most widely used complexes have been those of $\text{Eu}(\text{dpm})_3$ and since the crystallization of the dipyridine adduct had been reported, $\text{Eu}(\text{dpm})_3(\text{py})_2$ (py is pyridine) was selected for study by X-ray diffraction techniques (Cramer & Seff, 1972).

Collection and reduction of intensity data

Clear colorless crystals of $\text{Eu}(\text{dpm})_3(\text{py})_2$ formed readily from a saturated pyridine solution of $\text{Eu}(\text{dpm})_3$. A single crystal, a parallelepiped with the dimensions $0.028 \times 0.020 \times 0.033$ cm, was selected and was lodged and sealed in a thin-walled capillary tube. A volume of mother liquor approximately equal to that of the crystal

was included in such a way that the crystal was entirely bathed in liquid throughout data collection.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda = 0.70926$ Å; $K\alpha_2$, $\lambda = 0.71354$ Å) and with a pulse-height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants were determined three times during the course of data collection by least-squares methods from the centered angular coordinates of fifteen intense reflections with 2θ values up to 11.7° . Each time, under computer control, the angular coordinates for the center of each peak were determined. The cell constants at 20°C are: $a = 13.611$ (5), $b = 17.306$ (4), $c = 10.493$ (7) Å, $\alpha = 98.33$ (3), $\beta = 105.20$ (5) and $\gamma = 94.75$ (4)°; $V = 2333$ (2) Å³ and $\rho_c = 1.224$ g.cm⁻³. The density was not successfully measured by flotation because of the pronounced instability of the complex. Still, the density measurements indicated that $Z = 2$. Hinckley (1971) had previously determined b and had assigned the space group $P\bar{1}$.

Diffraction intensities were collected for 997 consecutive hours by the $\theta-2\theta$ scan technique at a scan rate which varied from 0.5° per min (in 2θ) to 24° per min in such a way that more time was spent on weaker reflections to improve their standard deviations. Most reflections were observed at the slowest scan rate. All 8312 unique reciprocal lattice points for which $2\theta < 50^\circ$ were examined. The scan range varied from 1.63° at $2\theta = 3^\circ$ to 1.92° at $2\theta = 50^\circ$. A time equal to half the scan time for each reflection was spent counting the background at each end of the scan range. Two check reflections, which were measured periodically during data collection, showed an average total decrease in intensity of 8.2%, and an approximate correction for this effect was made.

Table 1 (cont.)

A large table of numerical data with multiple columns and rows, containing various numbers and symbols.

Table 1 (cont.)

Table with multiple columns of numerical data, likely representing coordinates or parameters for a complex structure. The table is organized into several vertical sections, each with its own set of column headers. The data is presented in a grid-like format with varying column widths and some text annotations interspersed.

Table 1 (cont.)

A large table with multiple columns and rows of numerical data, organized into sections labeled with '10, k=...' and '11, k=...'. Each section contains several columns of numbers, some with signs and subscripts, representing statistical or mathematical data points.

All were well formed and showed a peak height of at least $0.3 \text{ e.}\text{\AA}^{-3}$. The positions of the 13 pyridine and methine hydrogen atoms were calculated from the appropriate carbon atom coordinates assuming planar geometries and a 1.08 \AA C-H bond length. These agreed well with the observed positions and were included in the final calculation of the structure factors and error functions. The latter, based on observed reflections only, are $R_1=0.039$ and $R_2=0.040$. The

Table 2. *Final nonhydrogen positional parameters and their standard deviations*

Values are given $\times 10^4$. See Fig. 1 for the identities of the atoms. The e.s.d. is in the units of the least significant digit given for the corresponding parameter.

	$x, \sigma(x)$	$y, \sigma(y)$	$z, \sigma(z)$
Eu(1)	2493 (1)	2486 (1)	2080 (1)
O(2)	2635 (3)	3772 (2)	1717 (3)
O(3)	2997 (2)	3326 (2)	4177 (3)
O(4)	4082 (2)	2119 (2)	3211 (3)
O(5)	2572 (2)	1167 (2)	1148 (3)
O(6)	1318 (2)	2298 (2)	-0072 (3)
O(7)	0885 (2)	2709 (2)	2308 (3)
N(8)	1951 (3)	1530 (2)	3601 (4)
N(9)	3751 (3)	2616 (2)	0555 (4)
C(10)	3034 (8)	4992 (4)	0438 (7)
C(11)	2808 (9)	5934 (4)	2307 (10)
C(12)	1310 (5)	4991 (4)	0885 (9)
C(13)	2464 (5)	5096 (3)	1517 (6)
C(14)	2690 (3)	4456 (2)	2370 (4)
C(15)	2885 (4)	4616 (2)	3745 (5)
C(16)	3039 (3)	4052 (2)	4582 (4)
C(17)	3257 (5)	4313 (4)	6103 (5)
C(18)	3442 (15)	3629 (6)	6828 (8)
C(19)	2342 (12)	4667 (12)	6382 (9)
C(20)	4132 (15)	4976 (10)	6604 (10)
C(21)	6245 (7)	2300 (11)	3822 (17)
C(22)	5547 (7)	1878 (8)	5547 (8)
C(23)	6175 (9)	0905 (8)	4112 (12)
C(24)	5636 (5)	1638 (4)	4161 (7)
C(25)	4547 (3)	1525 (3)	3160 (4)
C(26)	4147 (4)	0814 (3)	2314 (5)
C(27)	3186 (4)	0663 (3)	1366 (5)
C(28)	2802 (6)	-0155 (3)	0498 (8)
C(29)	1770 (15)	-0407 (8)	0584 (24)
C(30)	3620 (14)	-0712 (6)	0657 (19)
C(31)	2633 (17)	-0040 (7)	-0976 (12)
C(32)	0703 (12)	1880 (10)	-2740 (7)
C(33)	-1022 (7)	2144 (10)	-2700 (8)
C(34)	0232 (13)	3247 (7)	-2374 (9)
C(35)	0087 (5)	2397 (4)	-2096 (5)
C(36)	0435 (3)	2462 (2)	-0561 (4)
C(37)	-0218 (3)	2711 (3)	0203 (4)
C(38)	0029 (3)	2817 (3)	1591 (4)
C(39)	-0725 (4)	3084 (4)	2372 (6)
C(40)	-0790 (7)	2499 (7)	3308 (9)
C(41)	-1808 (5)	3113 (6)	1493 (7)
C(42)	-0290 (7)	3906 (6)	3134 (12)
C(43)	1084 (7)	1040 (5)	3094 (11)
C(44)	0814 (8)	0459 (7)	3741 (13)
C(45)	1467 (9)	0355 (6)	4924 (11)
C(46)	2343 (9)	0859 (6)	5462 (11)
C(47)	2560 (7)	1441 (5)	4779 (8)
C(48)	3674 (6)	2106 (5)	-0546 (8)
C(49)	4411 (7)	2109 (6)	-1248 (7)
C(50)	5242 (7)	2671 (7)	-0784 (10)
C(51)	5323 (7)	3198 (7)	0336 (11)
C(52)	4563 (6)	3159 (5)	0989 (9)

'goodness of fit', $\{[\sum w(F_o - |F_c|)^2]/(m-s)\}^{1/2}$, is 0.96. The number of reflections (6840) is m , and s (469) is the total number of variables in the least-squares calculations. The standard deviation of the electron density on the final Fourier function was $0.1 \text{ e.}\text{\AA}^{-3}$; difference peaks as large as $1.1 \text{ e.}\text{\AA}^{-3}$ appeared in the vicinity of those methyl groups with the largest thermal parameters.

The observed and calculated structure factors are presented in Table 1. Tables 2, 3 and 4 give the positional and thermal parameters of the structure and their standard deviations. Molecular dimensions are given in Table 5. The molecule, without hydrogen atoms, is shown in Fig. 1. Figs. 2 and 3 together demonstrate the entire molecule in stereoviews produced by ORTEP (Johnson, 1965).

The full-matrix least-squares program used (UCLALS4) was that of Gantzel, Sparks & Trueblood [ACA Library (old) no. 317, modified], which minimizes $\sum w(\Delta F)^2$; the weights used were the reciprocal squares of σ , the standard deviation for each observation. Atomic scattering factor for Eu^0 , O^0 , N^0 , C^0 (valence) (*International Tables for X-ray Crystallography*, 1962), and H (bonded) (Stewart, Davidson & Simpson, 1965) were used. The first was decreased by 0.3 to 0.4 e to account for the real part of the anomalous dispersion correction. In the last cycle of least-squares refinement, nearly all shifts were less than their standard deviations. All parameters appeared to be converging well so that further refinement was not expected to significantly alter any parameter.

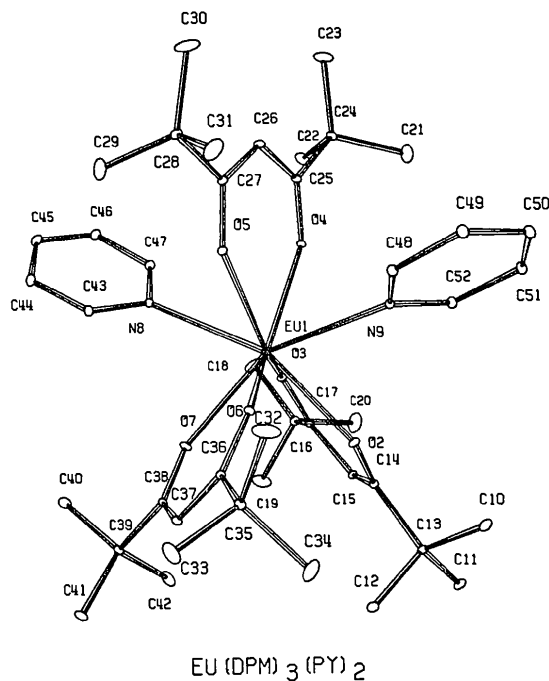


Fig. 1. $\text{Eu}(\text{dpm})_3(\text{py})_2$, with all nonhydrogen atoms shown and labelled. Ellipsoids of 1% probability are used.

Discussion

Examination of Table 6 and Fig. 4 shows that the co-ordination polyhedron about the Eu(III) ion is best described as a square antiprism according to the criteria of Lippard & Russ (1968). The largest deviation from the plane of the square face formed by O(2), O(3), O(4) and N(9) is 0.022 Å at N(9) and the average deviation is 0.018 Å; for the other square face, formed by O(5), O(6), O(7) and N(8), the largest deviation from

the plane is 0.073 Å at N(8) and the average deviation is 0.055 Å. The square faces are inclined with respect to each other at an angle of 4.2°. In contrast, the deviations from the best trapezoidal planes of a dodecahedron are much larger, ranging from 0.21 Å to 0.53 Å and averaging 0.44 Å for the O(2), O(7), N(8), N(9) least-squares plane and 0.329 Å for the O(3), O(4), O(5), O(6) plane, while the dihedral angle between them is 86.4°. The average length of the square edges of the antiprism is $s=2.869$ Å and of the lateral edges

Table 3. *Thermal vibration parameters and their standard deviations*

The b are $\times 10^4$. See Fig. 1 for the identities of the atoms. The e.s.d. is in the units of the least significant digit given for the corresponding parameter. The temperature factor = $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Eu(1)	51 (1)	28 (1)	80 (1)	21 (1)	29 (1)	11 (1)
O(2)	126 (3)	33 (1)	89 (3)	38 (3)	65 (5)	23 (3)
O(3)	78 (2)	34 (1)	88 (3)	26 (2)	34 (4)	17 (3)
O(4)	58 (2)	38 (1)	109 (3)	27 (2)	30 (4)	5 (3)
O(5)	69 (2)	30 (1)	120 (3)	15 (2)	38 (4)	3 (3)
O(6)	61 (2)	47 (1)	87 (3)	29 (2)	36 (4)	6 (3)
O(7)	62 (2)	74 (2)	97 (3)	62 (3)	44 (4)	33 (4)
N(8)	73 (3)	43 (1)	148 (5)	25 (3)	88 (6)	39 (4)
N(9)	64 (2)	40 (1)	129 (4)	12 (3)	62 (5)	30 (4)
C(10)	181 (8)	59 (3)	163 (7)	56 (8)	169 (13)	94 (8)
C(11)	142 (7)	35 (2)	178 (9)	11 (7)	44 (14)	45 (7)
C(12)	95 (4)	58 (3)	232 (11)	23 (6)	3 (11)	100 (9)
C(13)	82 (4)	33 (2)	123 (6)	12 (4)	29 (8)	31 (5)
C(14)	67 (3)	30 (1)	104 (4)	16 (3)	42 (5)	15 (4)
C(15)	86 (3)	31 (1)	107 (4)	20 (3)	42 (6)	8 (4)
C(16)	56 (2)	37 (2)	87 (4)	18 (3)	27 (5)	7 (4)
C(17)	93 (4)	47 (2)	90 (5)	26 (5)	31 (7)	3 (5)
C(18)	469 (24)	82 (4)	117 (7)	174 (17)	160 (21)	59 (9)
C(19)	275 (15)	233 (13)	132 (9)	310 (24)	193 (19)	70 (17)
C(20)	319 (20)	151 (10)	138 (9)	-195 (23)	-62 (21)	19 (15)
C(21)	73 (5)	200 (12)	509 (27)	-49 (12)	-85 (18)	-378 (32)
C(22)	103 (6)	139 (7)	156 (8)	81 (11)	-21 (11)	-14 (12)
C(23)	146 (8)	125 (7)	287 (16)	180 (13)	-78 (18)	-44 (16)
C(24)	66 (3)	68 (3)	139 (7)	54 (5)	38 (8)	32 (7)
C(25)	64 (3)	48 (2)	106 (4)	44 (4)	51 (6)	28 (4)
C(26)	90 (4)	44 (2)	146 (6)	62 (4)	48 (7)	17 (5)
C(27)	89 (3)	32 (1)	127 (5)	26 (4)	79 (7)	15 (4)
C(28)	19 (6)	35 (2)	173 (8)	28 (5)	83 (11)	-1 (6)
C(29)	284 (18)	78 (5)	709 (50)	-167 (17)	572 (53)	-257 (28)
C(30)	306 (19)	72 (4)	562 (33)	163 (16)	-113 (40)	-189 (19)
C(31)	410 (25)	77 (5)	233 (13)	-57 (17)	167 (29)	-128 (14)
C(32)	312 (15)	206 (10)	103 (7)	354 (21)	6 (15)	-38 (12)
C(33)	104 (6)	225 (10)	111 (7)	-1 (12)	-7 (10)	57 (13)
C(34)	327 (17)	95 (5)	142 (9)	-67 (15)	100 (20)	89 (11)
C(35)	73 (4)	52 (2)	96 (5)	20 (5)	36 (7)	16 (5)
C(36)	59 (3)	34 (1)	91 (4)	6 (3)	23 (5)	15 (4)
C(37)	57 (3)	52 (2)	99 (4)	34 (4)	24 (5)	31 (4)
C(38)	51 (2)	43 (2)	104 (4)	22 (3)	37 (5)	27 (4)
C(39)	60 (3)	56 (2)	120 (6)	36 (4)	60 (7)	23 (6)
C(40)	136 (7)	133 (6)	228 (10)	139 (10)	239 (15)	194 (14)
C(41)	72 (4)	104 (5)	175 (8)	84 (7)	88 (9)	71 (10)
C(42)	103 (6)	99 (5)	353 (17)	21 (8)	178 (17)	-170 (16)
C(43)	84 (5)	51 (3)	241 (11)	-3 (6)	113 (11)	26 (10)
C(44)	131 (6)	58 (4)	329 (15)	-19 (8)	230 (13)	37 (12)
C(45)	193 (7)	59 (3)	301 (10)	55 (8)	315 (11)	113 (9)
C(46)	143 (7)	70 (4)	227 (10)	42 (9)	166 (13)	113 (9)
C(47)	102 (5)	55 (3)	160 (7)	37 (6)	103 (10)	64 (8)
C(48)	92 (4)	51 (3)	138 (7)	13 (6)	100 (8)	15 (7)
C(49)	119 (6)	73 (4)	155 (5)	24 (8)	148 (8)	34 (7)
C(50)	95 (5)	87 (4)	193 (9)	37 (8)	136 (10)	88 (10)
C(51)	78 (4)	72 (4)	235 (11)	-4 (7)	100 (11)	74 (11)
C(52)	71 (4)	53 (3)	175 (9)	-12 (6)	59 (10)	17 (8)

is $l = 3.078 \text{ \AA}$ yielding an l/s ratio of 1.07 which is close to the value for an ideal square antiprism, 1.06, quoted by Hoard & Silverton (1963). The largest deviations of l and s values from their averages are found on the edges bounded by the chelate 'bites'.

Table 4. *Hydrogen atom positions and assigned thermal parameters*

The serial number used to designate a hydrogen atom is the same as that of the carbon atom to which it is bonded. Fractional coordinates $\times 10^4$ are given. Atoms whose positions were calculated are indicated.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(10A)	2860	4425	0	7.5
H(10B)	2810	5310	-260	7.5
H(10C)	3850	5230	1150	7.5
H(11A)	2750	6320	1725	6.7
H(11B)	3600	6010	2810	6.7
H(11C)	2390	5940	2810	6.7
H(12A)	1250	4460	475	7.5
H(12B)	940	5070	1550	7.5
H(12C)	940	5390	310	7.5
H(15)	3075	5230	4160	4.6
H(18A)	3440	3830	7810	11.3
H(18B)*	4145	3426	6701	11.3
H(18C)*	2863	3144	6284	11.3
H(19A)	2760	4840	7500	12.0
H(19B)*	2150	5131	5811	12.0
H(19C)*	1671	4232	6085	12.0
H(20A)	4060	4920	7500	13.5
H(20B)*	4789	4826	6269	13.5
H(20C)*	3945	5483	6142	13.5
H(21A)	6090	2660	3900	12.3
H(21B)*	6404	2083	2897	12.3
H(21C)	6775	2340	4590	12.3
H(22A)	5050	1360	5880	9.5
H(22B)	6200	1950	5990	9.5
H(22C)	5210	2270	5725	9.5
H(23A)	6875	1000	4850	10.4
H(23B)	6200	625	3125	10.4
H(23C)*	5723	468	4394	10.4
H(26)	4590	350	2550	5.6
H(29A)*	1241	9	291	14.7
H(29B)	2190	-390	1560	14.7
H(29C)*	1422	-949	-92	14.7
H(30A)	3390	-1170	0	16.2
H(30B)*	4326	-371	673	16.2
H(30C)*	3818	-787	1694	16.2
H(31A)	2198	-625	-1562	12.7
H(31B)*	3371	115	-1135	12.7
H(31C)*	2231	467	-1120	12.7
H(32A)	310	1660	-3750	11.0
H(32B)*	1437	2221	-2598	11.0
H(32C)*	886	1429	-2135	11.0
H(33A)	-1200	2100	-3438	10.4
H(33B)	-1510	2270	-2350	10.4
H(33C)*	-1136	1599	-2606	10.4
H(34A)	260	3200	-3275	10.5
H(34B)*	883	3561	-1588	10.5
H(34C)*	-363	3548	-2090	10.5
H(37)	-840	2890	-220	4.6
H(40A)	-1250	2580	3440	8.4
H(40B)*	-31	2524	3977	8.4
H(40C)*	-568	1956	2887	8.4
H(41A)	-1975	2580	940	7.3
H(41B)	-2188	3280	2190	7.3
H(41C)	-1775	3360	675	7.3
H(42A)*	410	3750	3750	9.7
H(42B)	-775	4060	3600	9.7
H(42C)*	-179	4275	2426	9.7

Table 4 (cont.)

H(43)	675	1170	2240	6.8
H(44)	312	156	3437	8.8
H(45)	1250	-80	5313	9.1
H(46)	2600	780	6300	8.1
H(47)	3125	1800	5050	6.0
H(48)	3125	1640	-790	5.6
H(49)	4375	1640	-1925	7.2
H(50)	5675	2580	-1250	7.6
H(51)	5930	3590	940	7.4
H(52)	4525	3510	1600	6.1

The parameters of the least-squares planes of the β -diketonate chelate rings are given in Table 7. The sum of internal angles for the O(2)-O(3), O(4)-O(5), and O(6)-O(7) rings are respectively 717.8, 719.8 and 718.0° compared with 720.0° for planar six-membered rings. The Eu(III) ion lies in the plane of the chelate which bridges the square faces, but the other two chelates exhibit the often-noted folding about the O-O line (Cotton & Wood, 1964) such that the chelate plane makes an angle of 10.2° with the O(2)Eu(1)O(3) plane and 9.9° with the O(6)Eu(1)O(7) plane. The 'bite' distance, 2.767 Å, for the bridging chelate is somewhat larger than those of the non-bridging chelates: 2.738 for O(2)-O(3) and 2.730 Å for O(6)-O(7).

While the pyridine ring geometries are normal, the

Table 5. *Molecular dimensions*

Bond lengths			
Eu(1)-O(2)	2.312 (3) Å	C(17)-C(18)	1.502 (12) Å
Eu(1)-O(3)	2.354 (3)	C(17)-C(19)	1.508 (18)
Eu(1)-O(4)	2.364 (3)	C(17)-C(20)	1.510 (20)
Eu(1)-O(5)	2.372 (3)	C(24)-C(21)	1.497 (18)
Eu(1)-O(6)	2.360 (3)	C(24)-C(22)	1.492 (11)
Eu(1)-O(7)	2.320 (3)	C(24)-C(23)	1.519 (15)
		C(28)-C(29)	1.466 (21)
Eu(1)-N(8)	2.647 (4)	C(28)-C(30)	1.524 (17)
Eu(1)-N(9)	2.651 (4)	C(28)-C(31)	1.548 (14)
		C(35)-C(32)	1.486 (16)
O(2)-C(14)	1.265 (5)	C(35)-C(33)	1.477 (11)
O(3)-C(16)	1.258 (5)	C(35)-C(34)	1.547 (13)
O(4)-C(25)	1.253 (6)	C(39)-C(40)	1.521 (12)
O(5)-C(27)	1.261 (6)	C(39)-C(41)	1.529 (9)
O(6)-C(36)	1.250 (5)	C(39)-C(42)	1.516 (12)
O(7)-C(38)	1.255 (5)		
		N(8)-C(43)	1.330 (10)
C(14)-C(15)	1.378 (6)	N(8)-C(47)	1.333 (10)
C(15)-C(16)	1.398 (6)	N(9)-C(48)	1.323 (9)
C(25)-C(26)	1.385 (7)	N(9)-C(52)	1.323 (9)
C(26)-C(27)	1.397 (8)		
C(36)-C(37)	1.398 (6)	C(43)-C(44)	1.370 (15)
C(37)-C(38)	1.387 (6)	C(44)-C(45)	1.370 (17)
		C(45)-C(46)	1.353 (16)
C(13)-C(14)	1.525 (7)	C(46)-C(47)	1.374 (14)
C(16)-C(17)	1.535 (6)	C(48)-C(49)	1.392 (12)
C(24)-C(25)	1.553 (8)	C(49)-C(50)	1.361 (14)
C(27)-C(28)	1.536 (8)	C(50)-C(51)	1.353 (15)
C(25)-C(36)	1.540 (6)	C(51)-C(52)	1.384 (13)
C(38)-C(39)	1.533 (7)		
C(13)-C(10)	1.530 (10)		
C(13)-C(11)	1.531 (10)		
C(13)-C(12)	1.520 (9)		

Table 5 (*cont.*)

Bond angles			
Eu(1)–O(2)–C(14)	137.9 (3) ^o	C(43)–N(8)–C(47)	117.7 (6) ^o
Eu(1)–O(3)–C(16)	135.8 (3)	C(48)–N(9)–C(52)	118.0 (6)
Eu(1)–O(4)–C(25)	137.4 (3)		
Eu(1)–O(5)–C(27)	136.9 (3)	N(8)–C(43)–C(44)	122.0 (10)
Eu(1)–O(6)–C(36)	136.4 (3)	N(8)–C(47)–C(46)	123.0 (8)
Eu(1)–O(7)–C(38)	138.7 (3)	N(9)–C(48)–C(49)	123.0 (8)
		N(9)–C(52)–C(51)	122.0 (8)
Eu(1)–N(8)–C(43)	118.3 (5)		
Eu(1)–N(8)–C(47)	123.4 (4)	C(43)–C(44)–C(45)	119.5 (10)
Eu(1)–N(9)–C(48)	122.9 (4)	C(44)–C(45)–C(46)	118.9 (10)
Eu(1)–N(9)–C(52)	118.7 (5)	C(47)–C(46)–C(45)	118.7 (10)
		C(48)–C(49)–C(50)	118.2 (9)
O(2)–Eu(1)–O(3)	71.7 (1)	C(49)–C(50)–C(51)	119.2 (9)
O(2)–Eu(1)–O(6)	81.6 (1)	C(52)–C(51)–C(50)	119.7 (9)
O(2)–Eu(1)–O(7)	85.2 (1)		
O(2)–Eu(1)–N(9)	71.9 (1)	C(14)–C(13)–C(10)	108.7 (5)
O(3)–Eu(1)–O(4)	75.0 (1)	C(14)–C(13)–C(11)	114.0 (6)
O(3)–Eu(1)–O(7)	80.8 (1)	C(14)–C(13)–C(12)	106.9 (5)
O(3)–Eu(1)–N(8)	79.7 (1)	C(16)–C(17)–C(18)	111.2 (6)
O(4)–Eu(1)–O(5)	71.7 (1)	C(16)–C(17)–C(19)	108.7 (8)
O(4)–Eu(1)–N(8)	77.4 (1)	C(16)–C(17)–C(20)	110.2 (7)
O(4)–Eu(1)–N(9)	72.3 (1)	C(25)–C(24)–C(21)	106.7 (8)
O(5)–Eu(1)–O(6)	76.2 (1)	C(25)–C(24)–C(22)	108.7 (7)
O(5)–Eu(1)–N(8)	70.8 (1)	C(25)–C(24)–C(23)	113.5 (6)
O(5)–Eu(1)–N(9)	75.7 (1)	C(27)–C(28)–C(29)	108.8 (9)
O(6)–Eu(1)–O(7)	71.2 (1)	C(27)–C(28)–C(30)	113.0 (9)
O(6)–Eu(1)–N(9)	78.8 (1)	C(27)–C(28)–C(31)	106.4 (10)
O(7)–Eu(1)–N(8)	70.9 (1)	C(36)–C(35)–C(32)	110.8 (8)
N(8)–Eu(1)–N(9)	140.3 (1)	C(36)–C(35)–C(33)	114.0 (7)
		C(36)–C(35)–C(34)	106.0 (6)
O(2)–C(14)–C(13)	115.0 (4)	C(38)–C(39)–C(40)	107.0 (6)
O(3)–C(16)–C(17)	116.3 (4)	C(38)–C(39)–C(41)	114.3 (5)
O(4)–C(25)–C(24)	114.3 (4)	C(38)–C(39)–C(42)	106.7 (6)
O(5)–C(27)–C(28)	114.8 (4)		
O(6)–C(36)–C(35)	116.2 (4)	C(10)–C(13)–C(11)	107.2 (6)
O(7)–C(38)–C(39)	114.6 (4)	C(10)–C(13)–C(12)	110.8 (5)
		C(11)–C(13)–C(12)	109.3 (6)
O(2)–C(14)–C(15)	123.3 (4)	C(18)–C(17)–C(19)	109.0 (9)
O(3)–C(16)–C(15)	124.4 (4)	C(18)–C(17)–C(20)	112.7 (9)
O(4)–C(25)–C(26)	124.5 (4)	C(19)–C(17)–C(20)	104.8 (6)
O(5)–C(27)–C(26)	124.1 (5)	C(21)–C(24)–C(22)	108.5 (7)
O(6)–C(36)–C(37)	123.9 (4)	C(21)–C(24)–C(23)	110.2 (8)
O(7)–C(38)–C(37)	123.0 (4)	C(22)–C(24)–C(23)	109.0 (7)
		C(29)–C(28)–C(30)	120.8 (13)
C(14)–C(15)–C(16)	124.7 (4)	C(29)–C(28)–C(31)	104.0 (12)
C(25)–C(26)–C(27)	125.2 (5)	C(30)–C(28)–C(31)	102.3 (12)
C(36)–C(37)–C(38)	124.8 (4)	C(32)–C(35)–C(33)	110.8 (8)
		C(32)–C(35)–C(34)	111.3 (9)
C(13)–C(14)–C(15)	121.6 (4)	C(33)–C(35)–C(34)	103.5 (6)
C(17)–C(16)–C(15)	119.3 (4)	C(40)–C(39)–C(41)	108.4 (7)
C(24)–C(25)–C(26)	121.1 (4)	C(40)–C(39)–C(42)	112.1 (6)
C(28)–C(27)–C(26)	121.1 (5)	C(41)–C(39)–C(42)	108.4 (7)
C(35)–C(36)–C(37)	119.9 (4)		
C(39)–C(38)–C(37)	122.3 (4)		

Table 6. *Edge lengths in the coordination polyhedron*

<i>s</i> Edges		<i>l</i> Edges	
N(9)–O(2)	2.926 Å	N(9)–O(6)	3.187 Å
N(9)–O(4)	2.973	N(9)–O(5)	3.095
O(2)–O(3)	2.738	O(2)–O(6)	3.055
O(3)–O(4)	2.867	O(2)–O(7)	3.145
N(8)–O(5)	2.913	O(3)–O(7)	3.030
N(8)–O(7)	2.888	O(3)–N(8)	3.215
O(5)–O(6)	2.916	O(4)–N(8)	3.133
O(6)–O(7)	2.730	O(4)–O(5)	2.767

Eu(III) ion does not lie in either of the pyridine planes (Table 7). This distortion, as measured by the Eu–N–*para* C angles amounts to about 8° [the Eu(1)–N(8)–C(45) angle is 171.2 (3)^o and the Eu(1)–N(9)–C(50) angle is 172.5 (3)^o]; it results from a close (3.13 Å) contact (see Fig. 5) between an oxygen atom [O(2) or O(7)] and an *ortho* pyridine carbon atom [C(52) or C(43) respectively] which displaces the pyridine rings toward the O(4)–O(5) chelate.

Table 7. Deviations of atoms from least-squares planes ($\text{\AA} \times 10^3$)

Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 3 lies between that plane and the origin. The direction cosines ($\times 10^4$), q , are with respect to orthogonal axes. The r.m.s. deviation ($\text{\AA} \times 10^3$) of the boldface atoms from the plane is δ . D is the distance (in \AA) from the plane to the origin.

	Plane	Plane	Plane	Plane	Plane				
Atoms	1	Atoms 2	Atoms 3	Atoms 4	Atoms 5				
Eu(1)	-326	Eu(1)	33	Eu(1)	324	Eu(1)	-380	Eu(1)	335
O(2)	6	O(4)	9	O(6)	-5	N(8)	-4	N(9)	2
O(3)	-5	O(5)	-9	O(7)	6	C(43)	1	C(48)	-5
C(13)	-114	C(24)	-76	C(35)	78	C(44)	16	C(49)	4
C(14)	-10	C(25)	-25	C(36)	10	C(45)	-22	C(50)	2
C(15)	-3	C(26)	2	C(37)	0	C(46)	-2	C(51)	0
C(16)	12	C(27)	23	C(38)	-11	C(47)	11	C(52)	-2
C(17)	27	C(28)	87	C(39)	-36				
$q_b \times (a \times b)$	9945	-6339	3665	-6357	3507				
q_b	314	-3826	9293	6031	-7518				
$q_a \times b$	995	6721	460	4818	5584				
D	3.41	-1.82	4.23	1.85	-0.99				
δ	8	16	8	12	3				

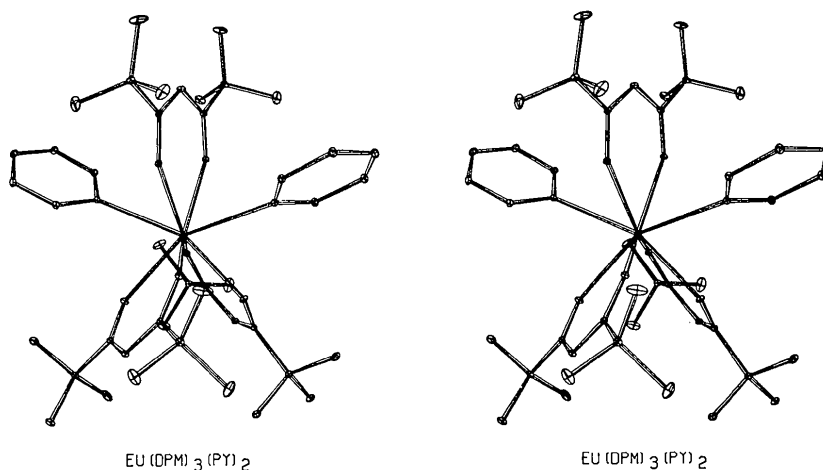


Fig. 2. Stereoview of the nonhydrogen atoms in one molecule. The view point for the right eye is the same as that used in Fig 1.

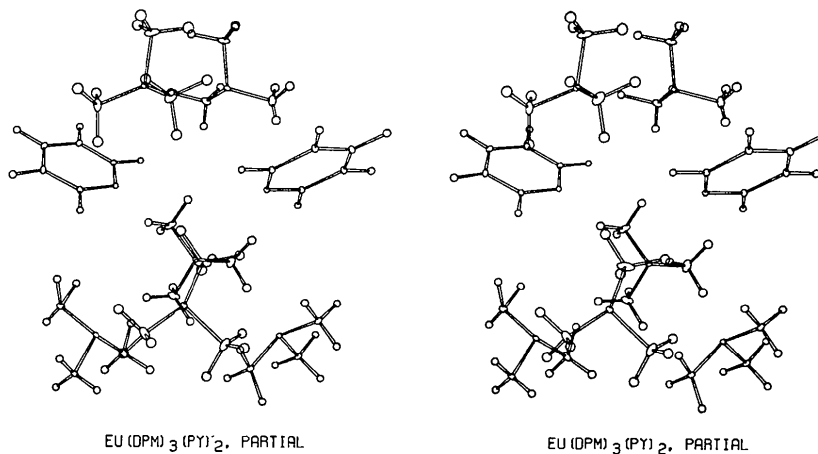


Fig. 3. Stereoview from the same point as the one shown in Fig. 2. The complete t-butyl groups and pyridine rings with 64 of the 67 hydrogen atoms [all but the methine hydrogen atoms: H(15), H(26), and H(37)] are shown.

The average Eu–O bond length is 2.347 Å, while the average Eu–N distance, 2.649 Å, is much longer. These values compare with the Ho–O and Ho–N distances of 2.27 and 2.53 Å in the structure of $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$ (4-pic is 4-picoline or 4-methylpyridine) (Horrocks, Sipe & Luber, 1971). The decrease in the bond length to oxygen by about 0.08 Å can be attributed to the lanthanide contraction (Shannon & Prewitt, 1969). The greater difference observed for the Eu–N bonds, 0.12 (1) Å, is in agreement with the observation that the Eu(III) complex is less stable with respect to loss of

pyridine than are similar complexes of the other lanthanides (Hinckley, 1971).

The molecular structure of this complex closely resembles that of $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$ (Horrocks, Sipe & Luber, 1971), but the crystal structure is quite different. $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$ crystallizes in the orthorhombic space group $Pbcn$ with the crystallographic C_2 axis passing through the Ho(III) ion. In the structure reported here the $\text{Eu}(\text{dpm})_3(\text{py})_2$ molecule lies at a site of no crystallographic symmetry. This molecule has an approximate twofold axis, *i.e.* rotation about a line which passes through the Eu(III) ion and bisects the O(4)–O(5) chelate ring carries one pyridine ring into the other and carries the O(2)–O(3) chelate into the O(6)–O(7) chelate. Examination of bond angles and distances in Table 5 reveals that a number of parameters which would be equal if the C_2 axis were exact, differ by several standard deviations from their average: for example, the angles O(4)–Eu(1)–N(8) and O(5)–Eu(1)–N(9) differ from their average by 8σ . Furthermore, a twofold axis would be required to lie in the N(8)Eu(1)N(9) plane and to pass through C(26), but C(26) is displaced from this plane by 0.28 Å. Still, the deviations from twofold symmetry are not great and appear to result from crystal packing (see Table 8 and Fig. 6). The results of n.m.r. experiments are probably best interpreted by considering the molecule to have twofold symmetry since these experiments are carried out in solution where solid phase distortions are absent. The fact that this molecular structure is similar to that of $\text{Ho}(\text{dpm})_3(4\text{-pic})_2$, regardless of the different arrangement of the molecules within the crystal, increases the probability that this structure is maintained in solution.

Fig. 5 illustrates how a pyridine moiety fits into the molecule. The pyridine ring is severely constrained by many short intramolecular contacts, and has little free-

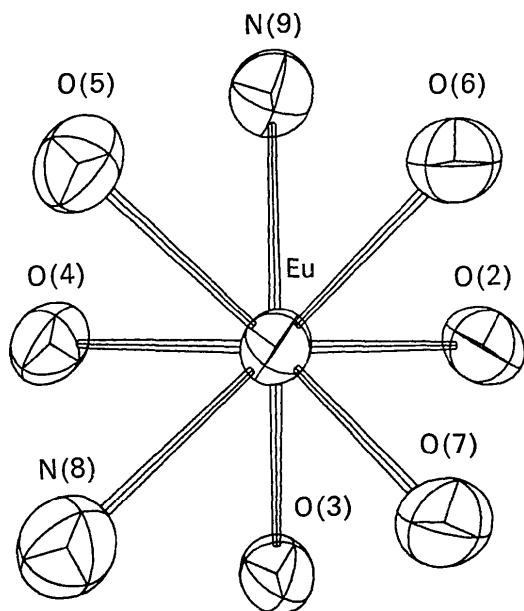


Fig. 4. The Eu(III) coordination sphere viewed along a line approximately normal to the square faces of the antiprism. Ellipsoids of 50% probability are shown.

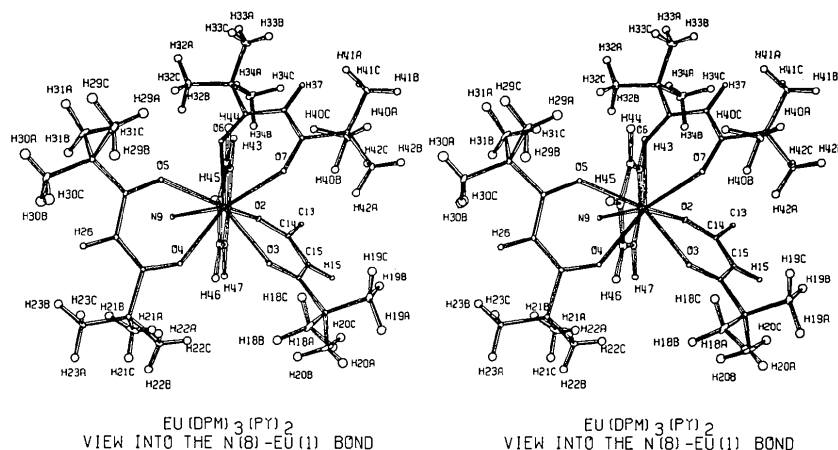


Fig. 5. Stereoview illustrating the intramolecular environment of a complexed pyridine molecule viewed along the Eu(III)–N(8) bond. The methyl groups attached to C(13), and the pyridine ring of N(9), are omitted since these are far from the pyridine ring which is shown. Ellipsoids of 1% probability are used.

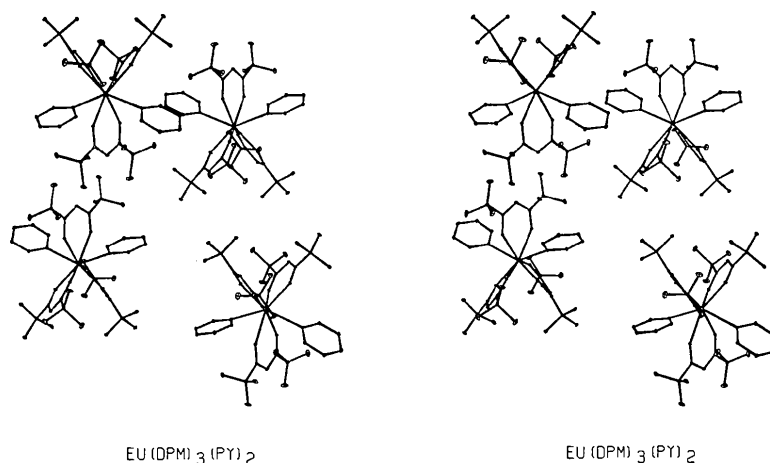


Fig. 6. Stereoview illustrating the packing of $\text{Eu}(\text{dpm})_3(\text{py})_2$ molecules in the crystal. Ellipsoids of 1% probability are used.

dom in its choice of position. It exhibits intramolecular distances which are comparable to the sum of van der Waals radii with four chelate ring atoms: O(7)–C(43), 3.12; O(4)–C(47), 3.20; O(5)–C(43), 3.25 and C(25)–C(47), 3.56 Å. In addition, there are two such contacts

Table 8. *Some non-bonded interatomic distances*

All intermolecular distances less than 4.0 Å are given, except for those involving hydrogen atoms.

The first atom of each pair has coordinates as given in Table 1. The second atom is related to the first by the symmetry operation given in the subheading.

($x, y, -1+z$)	C(32)···C(45)	3.74 Å
	C(32)···C(46)	3.68
($-1+x, y, z$)	C(41)···C(51)	3.80
($1-x, -y, -z$)	C(30)···C(49)	3.75
	C(30)···C(50)	3.85
($-x, 1-y, -z$)	C(12)···C(12)	3.57
($x, y, 1+z$)	C(18)···C(49)	3.67
	C(18)···C(50)	3.70
($-x, -y, 1-z$)	C(44)···C(45)	3.97
($1-x, -y, 1-z$)	C(23)···C(46)	3.81
($-x, 1-y, 1-z$)	C(19)···C(42)	3.96
($1-x, 1-y, 1-z$)	C(20)···C(52)	3.78

with methyl groups: C(29)–C(43), 3.72; and C(40)–C(43), 3.77 Å. Furthermore, five other intramolecular contacts are within 0.25 Å of the sum of the van der Waals radii. The pyridine ring is thus relatively fixed in its position, and its thermal parameters are correspondingly small. Even in solution, free rotation on the n.m.r. time scale about the Eu–N bond is not expected.

Since the position occupied by the pyridine molecule is so crowded, it is unlikely that substrates with larger steric requirements can adopt this molecular structure. We would expect that donor groups such as primary and secondary alcohols and amines, as well as aldehydes, ketones, carboxylic acids and amides with primary or secondary alpha carbons might be accommodated in a structure of the type described here. However, we would not expect tertiary amines and alcohols,

nor aldehydes, ketones, carboxylic acids and amides with tertiary alpha carbon atoms, to adopt this structure. Further structural work is in progress to test this hypothesis.

The low symmetry of $\text{Eu}(\text{dpm})_3(\text{py})_2$ found in this study does not support the various attempts to correlate observed dipolar shifts with molecular structure through the use of only the $G(\theta, r)$ geometric factor. The appropriate equation, for molecules of this symmetry, requires two geometric factors and is similar to the equation quoted originally by Hinckley (1969). However, a recent treatment of dipolar shifts (Kurland & McGarvey, 1970; McGarvey, 1970) suggests that for a metal ion such as Eu(III), which has multiple populated electronic states (Weissman, 1971), the equation quoted by Hinckley should be modified to yield $\Delta\nu/\nu_0 = D_1(3 \cos^2 \theta - 1)/r^3 + D_2 \sin^2 \theta \cos 2\Omega/r^3$. Accordingly, for molecules with less than threefold symmetry, such as $\text{Eu}(\text{dpm})_3(\text{py})_2$, two geometric factors $G(\theta, r)$ and $G(\theta, r, \Omega)$, are needed.

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References

- COTTON, F. A. & WOOD, J. S. (1964). *Inorg. Chem.* **3**, 245.
- CRAMER, R. E. & SEFF, K. (1972). *Chem. Commun.* p. 400 and to be published.
- CUNNINGHAM, J. A., SANDS, D. E. & WAGNER, W. F. (1967). *Inorg. Chem.* **6**, 499.
- ERASMUS, C. S. & BOEYENS, J. C. A. (1971). *J. Cryst. Mol. Struct.* **1**, 83.
- HINCKLEY, C. C. (1969). *J. Amer. Chem. Soc.* **91**, 5160.
- HINCKLEY, C. C. (1971). Private communication.
- HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235.
- HORROCKS, W. DEW. JR & SIPE, J. P., III (1971). *J. Amer. Chem. Soc.* **93**, 6800.

- HORROCKS, W. DEW. JR., SIPE, J. P., III & LUBER, J. R. (1971). *J. Amer. Chem. Soc.* **93**, 5256.
- HUBBARD, C. R., QUICKSALL, C. O. & JACOBSON, R. A. (1971). Ames Laboratory Fast Fourier, Iowa State Univ. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- KURLAND, R. J. & MCGARVEY, B. R. (1970). *J. Magn. Resonance*, **2**, 286.
- LIPPARD, S. J. & RUSS, B. J. (1968). *Inorg. Chem.* **7**, 1686.
- MCGARVEY, B. R. (1970). *J. Chem. Phys.* **53**, 86.
- PHILLIPS, T., II, SANDS, D. E. & WAGNER, W. F. (1968). *Inorg. Chem.* **7**, 2295.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925.
- SIEVERS, R. E. (1972). To be published.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3178.
- WEISSMAN, S. I. (1971). *J. Amer. Chem. Soc.* **93**, 4928.

Acta Cryst. (1972). **B28**, 3293

Structure Cristalline et Moléculaire de la Testostérone Hydratée – Etude de l'Interaction Stéroïde–Eau pour Certains Dérivés 17 β -ol.

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The crystal structure of hydrated testosterone ($P2_1$, $Z=2$; $C_{19}O_2H_{28} \cdot H_2O$) ($a=9.622$, $b=8.099$, $c=11.148$ Å, $\beta=97^\circ 49'$) was solved by simultaneous use of symbolic addition and multisolution methods. The final residual is $R=0.045$. The molecular conformation of testosterone agrees with those previously described for androstanolone and androstendione. The molecular arrangement looks like that in androstanolone. The particular localization of the water molecule in the 17 β ol steroid derivatives is discussed.

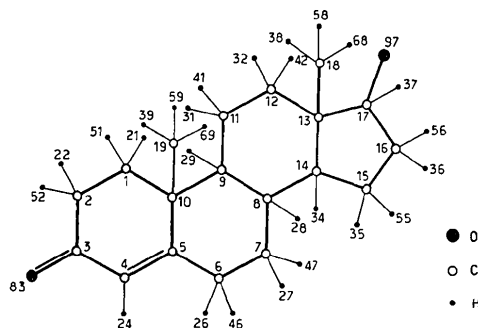
Parallèlement à l'étude des composés à action oestrogène (Busetta & Hospital, 1972; Busetta, Courseille, Geoffre & Hospital, 1972) nous avons entrepris un travail analogue sur les stéroïdes à action androgène. Nous présentons ici une structure hydratée de la testostérone. Nous avons remarqué une localisation particulière de la molécule d'eau dans les structures de l'oestradiol hémihydratée et de l'androstanolone (Busetta, Courseille, Fornies Marquina & Hospital, 1972); attribuant cette localisation à la présence du groupement 17 β -ol dans ces molécules, nous avons cherché à obtenir également pour la testostérone une forme hydratée. Une forme orthorhombique avait déjà été cristallisée par Thakkar & Jones (1970) à partir d'une solution aqueuse; par évaporation d'une solution de testostérone dans l'éthanol (alcool 95°), nous avons obtenu une forme hydratée différente, appartenant au système monoclinique $P2_1$ relativement voisine de celle de l'androstanolone hydratée.

Les paramètres cristallins mesurés sur un diffractomètre Siemens avec la radiation Cu $K\alpha$ sont représentés ci-dessous:

Groupe spatial monoclinique $P2_1$ $Z=2$

$$\begin{aligned} a &= 9,622 \text{ \AA} \\ b &= 8,099 \pm 0,005 \\ c &= 11,149 \\ \beta &= 97,81^\circ \pm 0,15^\circ \\ V &= 859,3 \text{ \AA}^3 \end{aligned}$$

Composition chimique, $C_{19}O_2H_{28} \cdot H_2O$



I. Détermination de la structure

La structure a été déterminée par méthodes directes en utilisant simultanément l'addition symbolique et la multisolution (Germain, Main & Woolfson, 1970). L'origine a été déterminée par le processus de convergence:

$$\begin{aligned} 409 & E=4,32 & \phi=0^\circ \\ \bar{3}01 & E=2,70 & \phi=0 \\ 718 & E=2,28 & \phi=0 \end{aligned}$$

Nous avons utilisé 3 symboles pour amorcer la génération de phases:

$$\begin{aligned} 608 & E=3,05 & m (0 \text{ ou } \pi) \\ 237 & E=2,91 & a \\ \bar{3}16 & E=2,46 & b \end{aligned}$$