Crystal and Molecular Structure of Hexakisantipyrineyttrium Tri-iodide

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The structure of the title compound has been determined by single-crystal *X*-ray diffraction. Crystals are rhombohedral with $Z = 3$ in a unit cell (based on hexagonal axes) of dimensions: $a = 13{\cdot}896(3)$, $c = 31{\cdot}986(6)$ Å, $\gamma = 120°$, space group $R\bar{3}$. The structure was solved by Patterson and Fourier methods and refined by least-squares using 825 observed three-dimensional photographic data to R 0·073. The Y^{3+} ion is co-ordinated to six antipyrine molecules through the carbonyl oxygen and the molecular symmetry is $\bar{3}$, S_6. The angle between the normals to the phenyl ring and the pyrazole ring is 58°.

It is well known that antipyrine ‡ forms complexes with transition, alkaline-earth, and rare-earth metals. Up to 1966 the only one whose structure had been reported was hexakisantipyrineterbium tri-iodide. This was a preliminary report [1] and further details have not appeared.[2]

Interest in the antipyrine complexes arose in connection with the fluorescence studies of rare-earth compounds [1,3,4] and in connection with the geometry of the antipyrine molecule and the metal oxygen bonding in these complexes.[5,6] It has also been reported [1] that *X*-ray powder photographs of mixed rare-earth–hexakis(antipyrine) iodide complexes suggest that the compounds are isostructural. In order to complement the preliminary work on the terbium complex the structural investigation of the yttrium complex[7] was therefore undertaken.

EXPERIMENTAL

Crystals are colourless, well formed, and show the following forms; basal pinacoid {0001}, two rhombohedra {01$\bar{1}$2} and {10$\bar{1}$1}. The principal refractive indices [8] are ε 1·74, ω 1·61.

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‡ Antipyrine = 2,3-dimethyl-1-phenyl-Δ^3-pyrazoline-5-one.

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Crystal Data (Based on Hexagonal Axes).—$C_{66}H_{72}I_3N_{12}O_6Y$, $M = 1599$, Rhombohedral, $a = 13{\cdot}896(3)$, $c = 31{\cdot}986(6)$ Å, $c/a = 2{\cdot}30$, $U = 5351$ Å^3, $D_m = 1{\cdot}488$ (by flotation), $Z = 3$, $D_c = 1{\cdot}488$ g cm^{-3}. Systematic absences for $-h + k + l \neq 3n$, space group $R\bar{3}$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$; μ(Cu-K_α) = 128 cm^{-1}. Crystal radius 100·9 microns $\sigma(r)$ −1·6%. Laue symmetry $\bar{3}$. Point group $\bar{3}$.

Cell dimensions were determined by use of a modified Farquhar and Lipson method,[9] with spherical crystals.[10]

Intensity Measurements.—Three-dimensional X-ray diffraction data from a spherical crystal were collected by the integrating method and film photometry [11–13] for layers h 0—11. The exposure time for integrating films was 12 days and for non-integrating films 4 days. Over 2000 intensities were measured and data reduction gave 825 symmetry-independent structure amplitudes $|F_o|^2$ out of a possible 1842 reflections (ignoring systematic absences) in the range $2\sin\theta$ 0·14—1·76. Data were corrected for Lorentz, polarisation, and absorption effects and correlated by a least-squares method.[12,14] The distribution probability [15] was 0·591 and the space group was determined to be centrosymmetric, in keeping with a negative result obtained in the piezoelectric test.[16]

During the exposures the crystal turned brown. However the intensity pattern did not alter over 1440 h and i.r. spectra of exposed and unexposed crystals were identical.

Structure Solution and Refinement.—The positions of the yttrium and two iodine atoms in the asymmetric unit were found from an unsharpened Patterson synthesis and were almost identical to those in ref. 1. The data were phased [17] using the heavy atoms with normal scattering factors for Y^{3+} and I^-.[18] Fourier summations [19] of the phased data produced a satisfactory trial structure. Successive cycles of full-matrix least-squares of positional and thermal motion parameters were carried out until all parameter shifts were $< 0{\cdot}1\sigma$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1$ for all data. Atomic scattering factors for neutral carbon, nitrogen, and oxygen were taken from ref. 18 and anomalous scattering factors for Y and I from ref. 20. The final R was 0·073. Positional and thermal parameters are listed in Table 1, and molecular geometry in Table 2, and Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20866 (21 pp., 1 microfiche).* All computational work was carried out on the University of London ATLAS computer.

TABLE 1

Fractional co-ordinates and thermal motion parameters (all × 10⁴) * derived from least-squares refinement

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y	0	0	0	418(22)	418(22)	570(21)	209(11)	0	0
I(1)	0	0	5000	1915(51)	1915(51)	829(52)	957(26)	0	0
I(2)	0	0	2100(01)	1343(29)	1343(29)	829(26)	671(15)	0	0
N(1)	3069(15)	2658(14)	519(05)	785(125)	741(117)	674(104)	484(114)	−234(107)	−59(98)
N(2)	3679(17)	3264(17)	877(06)	1020(161)	1137(176)	881(155)	481(143)	−400(127)	−273(127)
C(3)	3001(25)	2768(25)	1213(07)	1277(235)	1460(249)	674(155)	807(213)	−117(176)	−117(176)
C(4)	1994(20)	1883(18)	1100(06)	1056(191)	822(191)	622(155)	382(147)	−283(127)	−215(117)
C(5)	2031(19)	1769(18)	664(06)	748(161)	616(139)	829(155)	418(136)	39(137)	98(127)
O(5)	1398(10)	1104(10)	401(04)	646(88)	624(88)	726(104)	95(73)	−156(68)	−254(68)
C(21)	4653(20)	4407(20)	817(10)	814(176)	704(176)	2125(311)	−213(154)	−546(185)	−341(176)
C(31)	3403(27)	3317(26)	1642(07)	2216(330)	1790(286)	829(155)	833(260)	−653(195)	−770(185)
C(11)	3597(16)	2675(14)	130(07)	521(132)	470(125)	1088(155)	202(106)	59(127)	−78(117)
C(12)	3087(19)	2719(20)	−245(08)	580(176)	1401(155)	933(155)	87(169)	−215(156)	−556(176)
C(13)	3621(31)	2649(33)	−624(08)	587(367)	2179(367)	777(155)	312(215)	−302(330)	215(215)
C(14)	4537(35)	2520(38)	−614(08)	916(345)	1783(404)	2177(415)	660(233)	507(371)	1199(322)
C(15)	4998(27)	2536(34)	−222(14)	1233(382)	2032(249)	2281(415)	1218(257)	127(361)	751(273)
C(16)	4546(17)	2587(18)	152(08)	448(147)	902(176)	1607(259)	301(132)	429(146)	273(156)

* The Debye–Waller factor is defined as $T = \exp[-2\pi^2 \sum_i \sum_j a_i^* a_j^* h_i h_j U_{ij}]$.

TABLE 2

Interatomic bond distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Distances

Y–O(5)	2·190(13)	N(2)–C(21)	1·498(33)
O(5)–C(5)	1·234(25)	N(1)–C(11)	1·441(29)
C(5)–C(4)	1·406(28)	C(11)–C(16)	1·387(37)
C(5)–N(1)	1·427(30)	C(11)–C(12)	1·410(36)
C(4)–C(3)	1·371(41)	C(12)–C(13)	1·449(40)
C(3)–N(2)	1·367(35)	C(13)–C(14)	1·373(64)
C(3)–C(31)	1·533(35)	C(14)–C(15)	1·401(61)
N(2)–N(1)	1·422(27)	C(15)–C(16)	1·369(52)

(*b*) Angles

O(5)–Y–O(5′)	89·2(0·5)	N(2)–N(1)–C(5)	107·3(1·9)
Y–O(5)–C(5)	167·0(1·6)	N(2)–N(1)–C(11)	122·5(1·7)
O(5)–C(5)–C(4)	135·0(2·7)	C(11)–N(1)–C(5)	125·5(1·7)
O(5)–C(5)–N(1)	117·4(2·4)	N(1)–C(11)–C(16)	117·0(2·1)
N(1)–C(5)–C(4)	107·6(2·2)	N(1)–C(11)–C(12)	118·3(1·9)
C(5)–C(4)–C(3)	106·5(2·2)	C(12)–C(11)–C(16)	124·6(2·1)
C(4)–C(3)–N(2)	112·5(2·9)	C(11)–C(12)–C(13)	115·0(3·0)
C(4)–C(3)–C(31)	129·6(3·3)	C(12)–C(13)–C(14)	121·9(4·4)
N(2)–C(3)–C(31)	117·7(3·0)	C(13)–C(14)–C(15)	117·8(4·5)
C(3)–N(2)–N(1)	106·0(2·4)	C(14)–C(15)–C(16)	124·3(3·5)
C(3)–N(2)–C(21)	131·7(2·5)	C(15)–C(16)–C(11)	116·2(2·9)
C(21)–N(2)–N(1)	118·7(2·3)		

* Symmetry operator for O(5) to produce O(5′) is $-y$, $x - y$, z.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

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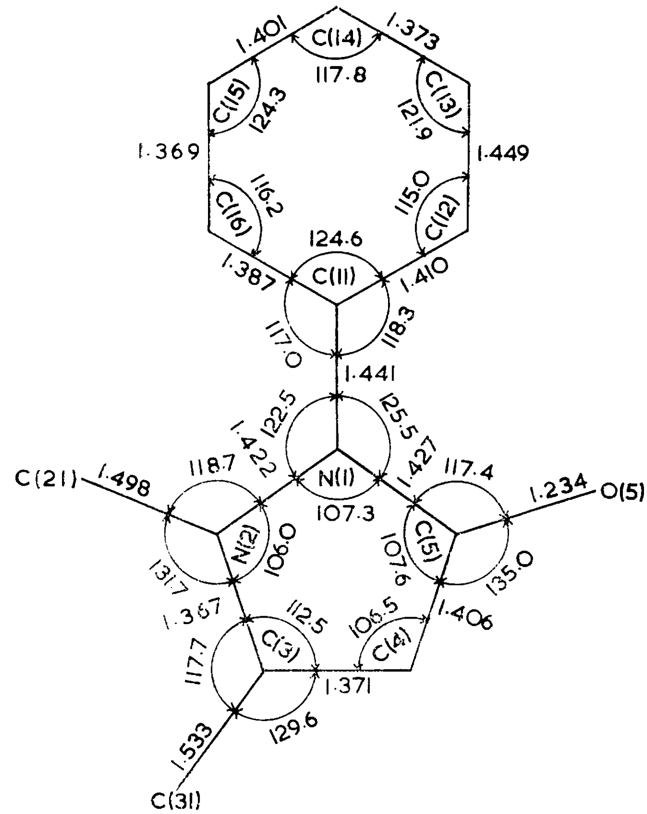

FIGURE 1 Bond distances and angles of the antipyrine group

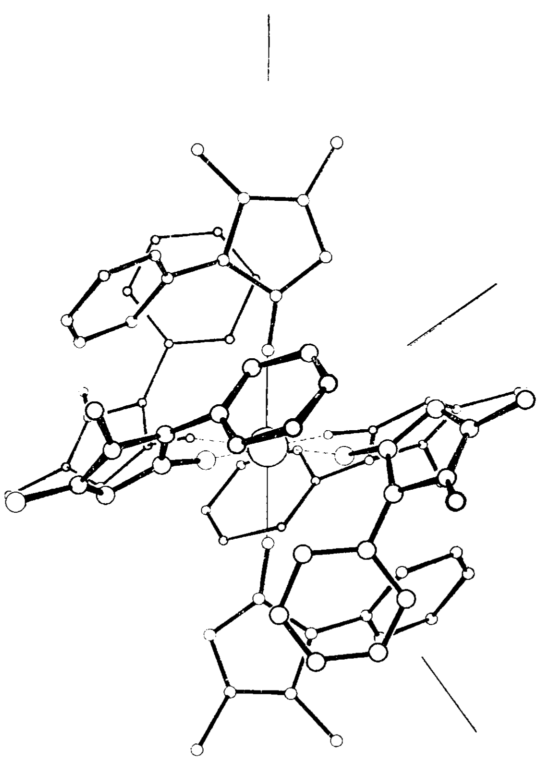

FIGURE 2 Molecular co-ordination viewed down *a*

DISCUSSION

Description of the Molecular Structure.—The atom numbering system used for the antipyrine group is given in Figure 1.

Co-ordination Around the Y^{3+} *Ion.*—The Y^{3+} ion in the structure occupies a symmetry centre at the origin of the unit cell. Six antipyrine molecules are octahedrally disposed about the Y^{3+} ion which is entirely in keeping with the stereochemical arrangement predicted by the valence-bond and ligand-field theories. The Y–O bond length is 2·19(1) Å which is somewhat shorter than those in Y_2BeO_4.[21] The O–Y–O– bond angles of 89·20(50) and 90·80(50)° are in good agreement with the theoretical value of 90°. The oxygen packing around the Y^{3+} ion leads to O · · · O contacts of 3·073 and 3·119 Å. The distance between two oxygens related by the centre of symmetry on which the Y atom is positioned is 4·378 Å. Figure 2 shows the molecular co-ordination about Y^{3+}.

Geometry of the Antipyrine Molecule.—The geometry of the antipyrine molecule is shown in Figure 1 and torsion angles in Table 3. The benzene ring and pyrazole ring are both planar within experimental error (Table 4). Equations of the mean planes and displacements of the atoms from them are given in Table 4. The interplanar angle is 58°. Distances and angles appear to be in good agreement with those reported.[5,6]

TABLE 3

Torsion angles (°)

N(1)–N(2)–C(3)–C(4)	0
N(1)–N(2)–C(3)–C(31)	–174
N(1)–C(5)–C(4)–C(3)	–3
N(1)–C(11)–C(12)–C(13)	–176
N(1)–C(11)–C(16)–C(15)	176
N(2)–N(1)–C(5)–C(4)	3
N(2)–N(1)–C(5)–O(5)	–176
N(2)–N(1)–C(11)–C(12)	–140
N(2)–N(1)–C(11)–C(16)	43
N(2)–C(3)–C(4)–C(5)	2
C(3)–N(2)–N(1)–C(5)	–2
C(3)–N(2)–N(1)–C(11)	–159
C(3)–C(4)–C(5)–O(5)	176
C(4)–C(3)–N(2)–C(21)	158
C(4)–C(5)–N(1)–C(11)	159
C(5)–N(1)–N(2)–C(21)	–164
C(5)–N(1)–C(11)–C(12)	68
C(5)–N(1)–C(11)–C(16)	–109
C(5)–C(4)–C(3)–C(31)	176
O(5)–C(5)–N(1)–C(11)	–20
C(21)–N(2)–N(1)–C(11)	40
C(21)–N(2)–C(3)–C(31)	–17
C(11)–C(12)–C(13)–C(14)	2
C(11)–C(16)–C(15)–C(14)	–3
C(12)–C(11)–C(16)–C(15)	0
C(12)–C(13)–C(14)–C(15)	–4
C(13)–C(12)–C(11)–C(16)	1
C(13)–C(14)–C(15)–C(16)	5

Molecular Packing.—The molecular packing within the unit cell is shown in Figure 3. The crystal structure can be considered as a rhombohedrally packed structure of dimpled spheres, the dimples are at the N and S poles of the sphere with the crystallographic *c* axis passing through N–S. The sphere is formed by six

[21] L. A. Harris and H. L. Yakel, *Acta Cryst.*, 1967, **22**, 354.

antipyrine molecules co-ordinated to Y through oxygen. The three iodide ions associated with Y sphere are

TABLE 4

Equations * of mean planes, with atom displacements (Å) in square brackets

Plane (1): N(1), N(2), C(3)—(5) $\quad 0{\cdot}793X - 0{\cdot}600Y + 0{\cdot}107Z = 4{\cdot}595$

[N(1) −0·02, N(2) 0·01, C(3) 0·01, C(4) −0·02, C(5) 0·02, O(5) 0·08, C(21) −0·39, C(31) −0·10, C(11) 0·41]

Plane (2): C(11)—(16) $\quad 0{\cdot}085X + 0{\cdot}996Y - 0{\cdot}022Z = 5{\cdot}015$

[C(11) −0·01, C(12) 0·00, C(13) 0·01, C(14) −0·03, C(15) 0·02, C(16) 0·00]

* In the form $AX + BY + CZ = D$ where X is parallel to the crystallographic a axis, Y is perpendicular to X and in the plane ab, and Z is perpendicular to X and Y and completes a right-handed set of axes XYZ.

located in the elongated space along the three-fold axis between two Y spheres. The closest approach of two iodide ions is *ca.* 9 Å. The nearest atoms to the iodide ions are listed in Table 5. The 2-methyl attached

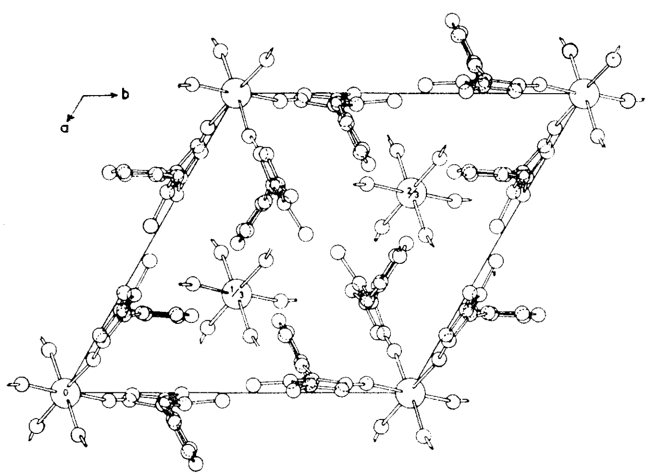

FIGURE 3 Molecular packing in the lower third of the unit cell

through N of the pyrazolone group is *ca.* 4 Å from the iodide ion at $z = 0{\cdot}21$ and 5·1 Å from that at $z = 0{\cdot}5$. The 3-methyl attached through C is *ca.* 4·7 Å from both iodides. The temperature factors of all atoms in the structure are high. This fact is not so surprising when it is noted that the intensities of the reflections recorded fall off rapidly with sin θ. High temperature factors for iodine, carbon, and nitrogen are not unknown. In the structure determination [22] of NMe_4Ag_2 isotropic temperature factors after refinement were given as I 6·7—8·5 and C and N both 9 Å^2.

Molecular contacts of the antipyrine group which are <3·6 Å are given in Table 6 and the contacts of the iodide ions with the antipyrine groups are given in Table 5.

TABLE 5

Molecular contacts <5 Å involving the iodide ions

Atom (1)	Atom (2)	Distance Å	Symmetry operators for atom (2) *
I(1)	··· C(31)	4·71	(1)—(6)
I(1)	··· C(14)	4·25	(7)—(9), (13)—(15)
I(2)	··· N(2)	4·26	(7)—(9)
I(2)	··· C(3)	4·92	(10)—(12)
I(2)	··· C(3)	4·75	(7)—(9)
I(2)	··· C(4)	4·18	(10)—(12)
I(2)	··· C(21)	4·00	(7)—(9)
I(2)	··· C(31)	4·90	(10)—(12)
I(2)	··· C(31)	4·71	(7)—(9)
I(2)	··· C(16)	4·32	(7)—(9)

* Operators

(1) $-\frac{1}{3} + x, -\frac{2}{3} + y, \frac{1}{3} + z$
(2) $\frac{1}{3} - x, \frac{2}{3} - y, \frac{2}{3} - z$
(3) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$
(4) $-\frac{2}{3} + y, -\frac{1}{3} - x + y, \frac{1}{3} - z$
(5) $-\frac{1}{3} - x + y, \frac{1}{3} - x, \frac{1}{3} + z$
(6) $\frac{1}{3} + x - y, -\frac{1}{3} + x, \frac{2}{3} - z$
(7) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$
(8) $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$
(9) $-\frac{1}{3} + x - y, -\frac{2}{3} + x, \frac{1}{3} - z$
(10) x, y, z
(11) $-y, x - y, z$
(12) $-x + y, -x, z$
(13) $-\frac{2}{3} + x, -\frac{1}{3} + y, \frac{2}{3} + z$
(14) $\frac{1}{3} - y, -\frac{1}{3} + x - y, \frac{2}{3} + z$
(15) $\frac{1}{3} - x + y, \frac{2}{3} - x, \frac{2}{3} + z$

TABLE 6

Intermolecular contacts <3·6 Å for the antipyrine group

N(1) ··· C(14^{I})	3·59	O(5) ··· O(5^{I})	3·12
C(5) ··· C(13^{I})	3·55	O(5) ··· C(12^{IV})	3·40
O(5) ··· O(5^{II})	3·07	C(15) ··· C(15^{V})	3·48
O(5) ··· O(5^{III})	3·07	C(15) ··· C(15^{VI})	3·48
O(5) ··· O(5^{IV})	3·12		

Roman numeral superscripts refer to the following transformations relative to the reference molecule at x, y, z:

I	$x - y, x, -z$	IV	$y, -x + y, -z$
II	$-y, x - y, z$	V	$1 - y, x - y, z$
III	$-x + y, -x, z$	VI	$1 - x + y, 1 - x, z$

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