Acta Cryst. (1982). B**38**, 950–951

Structure of the 4,4′-Bipyridyl Clathrate of Octaaquayttrium(III) Chloride

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(*Received* 30 *June* 1981; *accepted* 23 *October* 1981)

Abstract. $[Y(H_2O)_8]Cl_3.2C_{10}H_8N_2$, $M_r = 651{\cdot}27$, $F(000) = 668$, orthorhombic, $Pcc2$, $a = b = 8{\cdot}883\,(2)$, $c = 19{\cdot}231\,(4)$ Å, $V = 1517{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}44\,(1)$, $D_x = 1{\cdot}434$ g cm^{-3}, Mo $K\alpha$ radiation, $\mu = 27{\cdot}55$ cm^{-1}. The compound is isostructural with $[Gd(H_2O)_8]Cl_3.2C_{10}H_8N_2$ [Bukowska-Strzyżewska & Tosik (1982). *Acta Cryst.* B**38**, 265–267]. The structure was refined to $R = 0{\cdot}068$ for 1111 diffractometer data. It contains separate $[Y(H_2O)_8]^{3+}$ ions with Y coordinated to eight H_2O molecules with two different Y—O bond lengths [2·425 (6) and 2·327 (6) Å]. The coordination polyhedron forms a C_2 dodecahedron (approximate to S_4) connected with the Cl^- ions by twelve O—H···Cl hydrogen bonds and with the 4,4′-bipyridyl (4,4′-bpy) molecules by four O—H···N bonds.

Introduction. The determination of the crystal structure of $[Y(H_2O)_8]Cl_3.(4,4'\text{-bpy})_2$ is a part of a study in which we intended to investigate the structural effect of change of the central ion of the lanthanide complex ion. The structure was assumed to be similar to $[Gd(H_2O)_8]Cl_3.(4,4'\text{-bpy})_2$ which has space group $P\bar{4}c2$ and similar lattice constants: $a = b = 8{\cdot}901\,(2)$ and $c = 19{\cdot}319\,(4)$ Å (Bukowska-Strzyżewska & Tosik, 1982). The title compound was first prepared by Czakis-Sulikowska & Radwańska-Doczekalska (1976). The colorless, air-stable crystals showed a strong piezoelectric effect. Preliminary oscillation and Weissenberg photographs showed orthorhombic symmetry, although the values of the cell parameters ($a = b$) and the intensities of the majority of the reflections indicated an approximation to tetragonal symmetry. Systematic extinctions were observed for $0kl$ and $h0l$ with l odd which corresponds to the space group D^3_{2h} ($Pccm$) or C^3_{2v} ($Pcc2$). The structure was solved in the non-centrosymmetric $Pcc2$ group, but after the refinement and determination of the absolute polarity of the crystal, the distribution of Y, Cl and O atoms appeared to be tetragonal in the space group D^6_{2d} ($P\bar{4}c2$). In order to collect intensity data the crystal was ground into a sphere of radius 0·015 cm. Unit-cell dimensions and their standard deviations were derived from a least-squares fit to the setting angles of 15 carefully centered reflections on a Syntex $P2_1$ single-crystal automatic diffractometer. The crystal density was measured by flotation in CH_3I/benzene. The intensity data were collected by the ω–2θ scanning technique. A set of 1111 independent intensities with $I \geq 1{\cdot}96\sigma(I)$ was used for the structure determination. Least-squares refinement of positional and anisotropic temperature parameters of the non-H atoms resulted in $R = \sum (||F_o| - |F_c||)/\sum |F_o| = 0{\cdot}068$. Atomic scattering factors corrected for anomalous dispersion were taken from Cromer & Waber (1974). Final refinement gave the atomic parameters listed in Table 1.* The maximal value of U_{ii} was U_{22}[Cl(2)] = 0·0178 Å^2. The average shift in the final cycle of refinement was 20% of the

* Lists of structure factors, anisotropic thermal parameters and deviations from least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36498 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\times 10^4$ *for* Y, $\times 10^3$ *for the other atoms*)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq} (Å^2)
Y	0	0	10000	252 (6)
Cl(1)	0	0	7485 (4)	54 (3)
Cl(2)	5000	0	9174 (4)	85 (5)
Cl(3)	0	5000	10816 (3)	81 (5)
O(1)	1531 (10)	75 (21)	8954 (4)	44 (5)
O(2)	2514 (10)	339 (10)	10306 (5)	34 (6)
O(3)	−17 (20)	1543 (10)	11039 (4)	42 (4)
O(4)	−323 (12)	2511 (10)	9692 (5)	41 (7)
N(1)	1672 (19)	5993 (19)	8656 (9)	70 (11)
C(1)	1453 (25)	6185 (25)	7949 (10)	71 (14)
C(2)	2102 (26)	5272 (18)	7446 (14)	73 (14)
C(3)	3115 (18)	4076 (17)	7716 (8)	42 (8)
C(4)	3281 (22)	3800 (20)	8465 (10)	55 (11)
C(5)	2567 (22)	4916 (39)	8929 (10)	87 (15)
N(11)	5996 (14)	1636 (16)	6316 (8)	51 (8)
C(11)	6235 (30)	1489 (25)	6975 (10)	79 (15)
C(12)	5247 (26)	2087 (28)	7434 (13)	81 (15)
C(13)	4039 (19)	3099 (18)	7236 (9)	41 (9)
C(14)	3815 (19)	3225 (20)	6562 (10)	51 (10)
C(15)	4890 (35)	2544 (21)	6100 (9)	67 (11)

0567-7408/82/030950-02$01.00

Table 2. *Bond distances* (Å) *and angles* (°) *with their standard deviations*

(*a*) Coordination polyhedron

		Average values			Average values
Y–O(1)	2·428 (8)	2·425 (6)	Y–O(2)	2·329 (9)	2·327 (6)
Y–O(3)	2·423 (8)		Y–O(4)	2·325 (9)	
O(1)–Y–O(1^{i})	68·2 (3)	68·6 (2)	O(1)–Y–O(2)	70·7 (3)	70·6 (2)
O(3)–Y–O(3^{i})	68·9 (3)		O(3)–Y–O(4)	70·5 (3)	
O(2)–Y–O(4)	93·4 (3)	93·7 (2)	O(1)–Y–O(4^{i})	75·3 (5)	74·7 (4)
O(2)–Y–O(4^{i})	94·0 (3)		O(2)–Y–O(3)	74·0 (5)	
O(1)–Y–O(4)	80·3 (5)	81·1 (4)			
O(2)–Y–O(3^{i})	81·9 (5)				

(*b*) 4,4′-Bpy molecule

C(1)–N(1)	1·38 (3)	C(11)–N(11)	1·29 (3)
C(1)–C(2)	1·39 (3)	C(11)–C(12)	1·35 (3)
C(2)–C(3)	1·49 (3)	C(12)–C(13)	1·45 (3)
C(3)–C(4)	1·47 (3)	C(13)–C(14)	1·32 (3)
C(4)–C(5)	1·48 (3)	C(14)–C(15)	1·44 (3)
C(5)–N(1)	1·35 (3)	C(15)–N(11)	1·34 (3)
C(3)–C(13)	1·51 (2)		
C(1)–N(1)–C(5)	123 (2)	C(11)–N(11)–C(15)	119 (2)
N(1)–C(1)–C(2)	124 (2)	N(11)–C(11)–C(12)	120 (2)
C(1)–C(2)–C(3)	115 (2)	C(11)–C(12)–C(13)	123 (2)
C(2)–C(3)–C(4)	122 (2)	C(12)–C(13)–C(14)	115 (2)
C(3)–C(4)–C(5)	116 (2)	C(13)–C(14)–C(15)	118 (2)
C(4)–C(5)–N(1)	120 (2)	C(14)–C(15)–N(11)	123 (2)
C(2)–C(3)–C(13)	122 (2)	C(12)–C(13)–C(3)	127 (2)
C(4)–C(3)–C(13)	117 (1)	C(14)–C(13)–C(3)	118 (2)

Symmetry code: none x,y,z; (i) $-x,-y,z$.

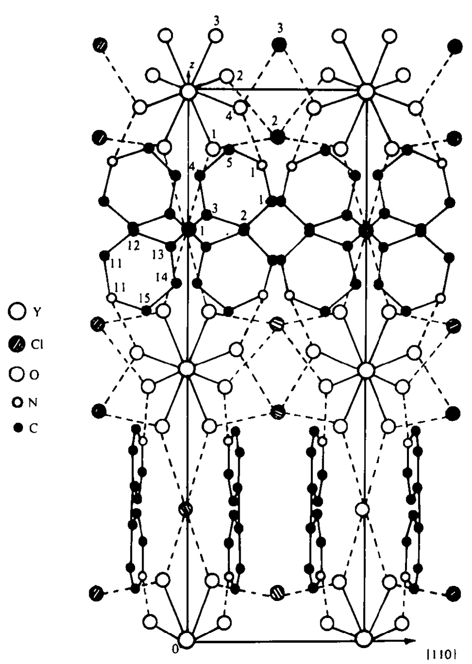

Fig. 1. View of the unit-cell contents along [110] showing atom numbering.

standard error. The absolute polarity of the crystal was confirmed by comparing the Bijvoet differences $\Delta F_o = F_o(\mathbf{h}) - F_o(-\mathbf{h})$ with $\Delta F_c = F_c(\mathbf{h}) - F_c(-\mathbf{h})$ for the 56 most significant Bijvoet pairs, for which $|\Delta F_o| > 2\sigma(\Delta F_o)$ and $|\Delta F_c| > [|F_c(\mathbf{h})| + |F_c(-\mathbf{h})|]/50$. Bijvoet's coefficient defined as $B = \sum \Delta F_c . \Delta F_o / \sum |\Delta F_c \Delta F_o|$ was

Table 3. *Intermolecular distances less than* 3·6 Å

(*a*) Shortened by hydrogen bonds

Cl(1)–O(1)	3·136 (10)	Cl(2)–O(2)	3·116 (10)
Cl(1)–O(3^{i})	3·101 (10)	Cl(3)–O(4)	3·107 (10)
Cl(2)–O(1)	3·111 (9)	N(1)–O(4)	2·677 (20)
Cl(3)–O(3)	3·101 (8)	N(11)–O(2)	2·618 (17)

(*b*) Shortened by packing forces

C(1)–C(1^{ii})	3·33 (3)	C(2)–C(11^{iii})	3·36 (3)
C(11)–C(11^{iv})	3·44 (3)	C(12)–C(1^{iii})	3·46 (3)
C(1)–C(2^{ii})	3·55 (3)	C(1)–C(11^{iii})	3·46 (3)
C(11)–C(12^{iv})	3·55 (3)	C(2)–C(12^{iii})	3·32 (3)

Symmetry code: (i) $x, -y, z - \frac{1}{2}$; (ii) $-x, 1 - y, z$; (iii) $1 - x, 1 - y, z$; (iv) $1 - x, -y, z$.

0·996, which unequivocally indicated the correct polarity of the crystal. All calculations were carried out with the programs of the XRAY system (Stewart, Kundell & Baldwin, 1970) on a Riad-32 computer.

Discussion. Bond lengths and angles are listed in Table 2. The structure is illustrated in Fig. 1. It is quite similar to the structure of the Gd compound. The difference in space groups is the result of the lack in the Y crystals of the twofold symmetry axis which relates the two pyridine rings of the bpy molecules in the Gd crystals. The coordination polyhedron of $[Y(H_2O)_8]^{3+}$ is a C_2 dodecahedron very close to S_4. As in the $[Gd(H_2O)_8]^{3+}$ complex, two distinctly different Y–O bonds are observed: Y–$[O(1),O(3)]_{av}$ = 2·425 (8) and Y–$[O(2),O(4)]_{av}$ = 2·327 (9) Å [these bonds in the Gd complex are 2·451 (10) and 2·354 (10) Å]. This indicates almost identical deformation of the coordination polyhedra in both complexes and a constant difference [0·026 (6) Å] in the Y–O and Gd–O bond lengths. Fig. 1 shows the interatomic contacts shortened by hydrogen bonds. All twelve O–Cl distances of these bonds are identical within 3σ, $(O\cdots Cl)_{av}$ = 3·110 (5) Å (Table 3). The pyridine rings (planar within experimental error) form a dihedral angle of 16·3 (10)°. The angle between the N(1)–C(3) and C(13)–N(11) lines is 12·5 (10)°, identical to that in the Gd structure.

This work was supported by Project MR-I-9 from the Polish Academy of Sciences.

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