

Structure of the 4,4'-Bipyridyl Clathrate of Octaaquagadolinium(III) Chloride

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Abstract. $[\text{Gd}(\text{H}_2\text{O})_8]\text{Cl}_3 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2$, $M_r = 720$, $F(000) = 718$, tetragonal, $P4c2$, $a = b = 8.901$ (2), $c = 19.319$ (4) Å, $V = 1530.6$ Å³, $Z = 2$, $D_m = 1.53$ (1), $D_x = 1.561$ Mg m⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 17.886$ mm⁻¹. The structure was solved by heavy-atom techniques and refined by least squares to $R = 0.068$ for 1350 structure amplitudes including both $F(hkl)$ and $F(khl)$. The $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ coordination polyhedron is in the form of an S_4 (4) dodecahedron with two different Gd–O bond lengths: Gd–O(1) = 2.451 (10) and Gd–O(2) = 2.354 (10) Å. Chloride ions and 4,4'-bipyridyl (4,4'-bpy) molecules are in bridging positions between complex cations, forming O–H...N and O–H...Cl hydrogen bonds involving all the water H atoms. Deformation of the 4,4'-bpy molecular geometry occurs.

Introduction. The structure determination of the title compound forms part of our investigations of mixed lanthanide(III) complexes with high coordination numbers (Bukowska-Strzyżewska & Tosik, 1977, 1978). The title compound was first prepared by Czakis-Sulikowska & Radwańska-Dozczekalska (1976). Colorless, air-stable crystals were kindly provided by Professor Czakis-Sulikowska. They 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 tetragonal symmetry. Systematic absences $0kl$ and $h0l$ with l odd correspond to space group $Pccm$ or $Pcc2$. The structure was solved in $Pcc2$, but after the refinement and determination of the absolute polarity of the crystals, the structure was found to be tetragonal, space group $P4c2$. The large differences observed in the intensities $I(hkl)$ and $I(khl)$ were caused only by the anomalous scattering of the Gd and Cl atoms. A crystal was ground into a sphere of radius 0.15 mm. 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 CAD-4 diffractometer. The crystal density measured by flotation in CH_3I /benzene indicated two formula units per unit cell. Intensities were measured in the θ - 2θ scan mode. 1350 independent reflections $|I| \geq 1.96\sigma(I)$ were used for

the structure determination. Refinement led to convergence (all shift/e.s.d. values less than 0.3 and final $R = 0.068$). The resulting atomic coordinates indicated tetragonal symmetry, space group $P4c2$.

All differences between atomic parameters related by the symmetry of this space group were $< 1.96\sigma$ (80% of the differences were $< 1\sigma$). This allowed us to treat $F(hkl)$ and $F(khl)$ as Bijvoet's $F(\mathbf{h})$ and $F(-\mathbf{h})$ pairs and confirm the absolute polarity of the crystal by comparing the 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 65 most significant pairs, for which $|\Delta F_o| \geq 100\sigma(\Delta F_o)$ and $|\Delta F_c| \geq |F_c(\mathbf{h})| + |F_c(-\mathbf{h})|/20$, Bijvoet's coefficient defined as $B = \sum \Delta F_c \Delta F_o / \sum |\Delta F_c \Delta F_o|$ was +1.00, which unequivocally indicated the correct polarity of the crystal. The final atomic parameters are given in Table 1.* Atomic scattering factors and dispersion corrections for Gd and Cl were taken from *International Tables for X-ray Crystallography* (1974). Maximum and minimum values of anisotropic thermal parameters are U_{11} for C(2), 0.105 (14) Å² and U_{23} for C(3).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36271 (16 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 Gd, $\times 10^3$ for the other atoms)

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Gd	0	0	10000	230 (4)
Cl(1)	0	0	7500	59 (3)
Cl(2)	5000	0	9200 (4)	48 (3)
O(1)	1534 (11)	69 (18)	8947 (5)	46 (6)
O(2)	2545 (11)	319 (13)	10298 (5)	39 (6)
N(1)	1688 (18)	5942 (19)	8680 (8)	55 (9)
C(1)	1437 (28)	6099 (28)	8009 (14)	79 (16)
C(2)	2161 (26)	5267 (23)	7512 (19)	68 (15)
C(3)	3129 (19)	4057 (19)	7747 (8)	40 (9)
C(4)	3240 (27)	3824 (26)	8451 (11)	64 (11)
C(5)	2519 (28)	4818 (34)	8905 (11)	75 (18)

−0.0167 (7) Å², respectively. The H atoms of the pyridine rings are in calculated positions, those of the water molecules were located from a difference map. All calculations were carried out with the XRAY system (Stewart, Kundell & Baldwin, 1970) on a Riad-32 computer.

Discussion. A view of the unit-cell contents projected along [110] is shown in Fig. 1. The crystals consist of [Gd(H₂O)₈]³⁺ ions, Cl[−] ions and 4,4'-bpy molecules. Around Gd the eight H₂O molecules form an S₄ (4̄) dodecahedron with five different edges and two different bond lengths. A view of the coordination polyhedron is shown in Fig. 2. Adjacent complex ions are linked along z by Cl(1)⋯H−O(1) hydrogen bonds with Cl(1)⋯O(1) 3.112 (10) Å, and along x and y by Cl(2)⋯H−O(1) and Cl(2)⋯H−O(2) hydrogen bonds with Cl(2)⋯O(1) and Cl(2)⋯O(2) 3.124 (10) and 3.059 (9) Å. Adjacent [Gd(H₂O)₈]³⁺ ions are also connected along z by 4,4'-bpy molecules forming N⋯H−O(2) hydrogen bonds with N⋯O(2) 2.683 (18) Å. All Gd and Cl atoms and nearly all H₂O molecules lie in the xOz and Oyz planes and only the 4,4'-bpy molecules are inside the unit cell. They have twofold symmetry [twofold axis perpendicular to the inter-ring C(3)−C(3') bond]. The almost planar 4,4'-bpy molecules are nearly parallel to the (110) and (1̄10) planes. The pyridine rings are planar within experimental errors, but the 4,4'-bpy molecule is not planar (Table 2). The dihedral angle between the two pyridine

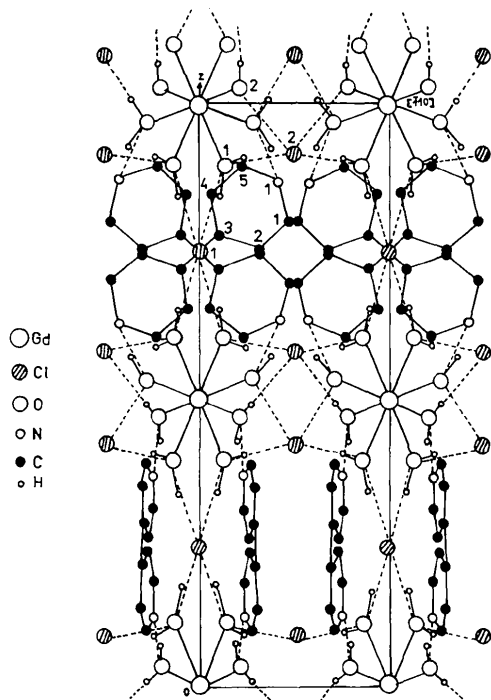


Fig. 1. View of the unit-cell contents along [110]. Dashed lines indicate hydrogen bonds.

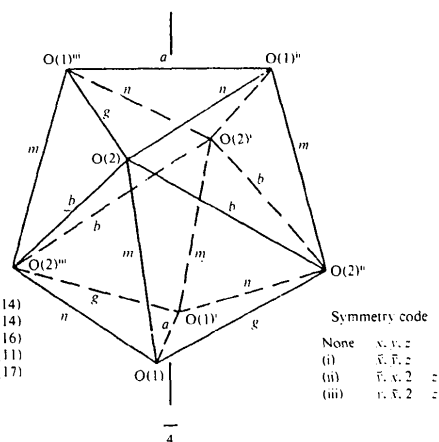


Fig. 2. The [Gd(H₂O)₈]³⁺ coordination polyhedron and lengths of edges (Å).

Table 2. *Least-squares planes and atom deviations* (Å)

The equations of the planes are expressed in direct space as $PX + QY + RZ = S$. The atoms listed are those included in the plane calculation. E.s.d.'s are in the range 0.015–0.023 Å.

Plane (1): $6.29819X + 6.28971Y + 0.02042Z = 4.64985$

N(1)	0.17	N(1')	0.17
C(1)	0.11	C(1')	0.11
C(2)	0.04	C(2')	0.04
C(3)	−0.11	C(3')	−0.11
C(4)	−0.19	C(4')	−0.19
C(5)	−0.02	C(5')	−0.02

Plane (2): $6.99842X + 5.47058Y - 0.10942Z = 4.40869$

$$\chi^2 = 10.5; 0.025 \leq p \leq 0.01$$

N(1)	0.038	C(3)	0.025
C(1)	−0.045	C(4)	−0.033
C(2)	0.012	C(5)	0.002

The acute angle between the two pyridine rings is 14 (1)°. The acute angle between lines C(3)−N(1) and C(3')−N(1') is 12 (1)°. Symmetry code: none: x, y, z; (') y, x, 1.5 - z.

Table 3. *Bond lengths* (Å) *and angles* (°)

[Gd(H₂O)₈]³⁺ coordination polyhedron

[Gd(H ₂ O) ₈] ³⁺ coordination polyhedron		Symmetry code	
Gd−O(1)	2.451 (10)	None	x, y, z
Gd−O(2)	2.354 (10)	(i)	x̄, y, z
O(1)−Gd−O(1')	67.8 (3)	(ii)	ȳ, x, 2 - z
O(1)−Gd−O(2)	70.4 (3)	(iii)	y, x̄, 2 - z
O(1)−Gd−O(2) ⁱ	80.8 (5)	(')	y, x, 1.5 - z
O(1)−Gd−O(2) ⁱⁱ	75.8 (5)		
O(2)−Gd−O(2) ⁱⁱ	93.4 (4)		

4,4'-Bpy molecule

C(1)−C(2)	1.37 (4)	N(1)−C(1)−C(2)	123 (2)
C(2)−C(3)	1.45 (3)	C(1)−C(2)−C(3)	117 (3)
C(3)−C(4)	1.38 (3)	C(2)−C(3)−C(4)	118 (2)
C(4)−C(5)	1.40 (3)	C(3)−C(4)−C(5)	119 (2)
C(5)−N(1)	1.32 (3)	C(4)−C(5)−N(1)	122 (2)
C(3)−C(3')	1.51 (2)	C(1)−N(1)−C(5)	120 (2)
C(1)−N(1)	1.32 (3)	C(2)−C(3)−C(3')	122 (2)
		C(4)−C(3)−C(3')	120 (2)

planes is 14 (1)°. The angle between the N(1)–C(3) and N(1')–C(3') lines is 12 (1)°, indicating a distinct bending of the C(3)–C(3') bond. This seems to be caused by N···H–O hydrogen bonds and packing forces. The shortest C···C non-bonded contact, between C(1) atoms related by the twofold axis, is 3.22 (4) Å. Bond lengths are given in Table 3. In spite of the high symmetry of the coordination polyhedron and the small size of the identical ligands, two distinctly different bond lengths Gd–O(1) = 2.451 (10) and Gd–O(2) = 2.354 (10) Å occur. There are many examples of crystal structure investigations of mixed aqua complexes of lanthanide(III) ions (Habenschuss & Spedding, 1980; Rohrbaugh & Jacobson, 1974; Fuller & Jacobson, 1976; Miliński, Ribár & Satavić, 1980; Eriksson, Larsson & Niinistö, 1978). The complexes of [LX_x(H₂O)_y]^{3-x}, where L = Gd³⁺, Sm³⁺, Nd³⁺, Pr³⁺, La³⁺, Lu³⁺, Ho³⁺, Ce³⁺, X = NO₃⁻, Cl⁻, HCO₃⁻ and 1 ≤ x ≤ 3 and 4 ≤ y ≤ 7, have different coordination numbers (CN) (8 ≤ CN ≤ 11) and different coordination polyhedra. The most common coordination polyhedron for CN = 8 is the square antiprism, for CN = 9 the monocapped square antiprism and for CN = 10 the bicapped square antiprism. The differences between L–O_w bond lengths within the same coordination polyhedron in the mixed complexes range from 0.022 (6) to 0.058 (6) Å – distinctly less than in the dodecahedral S₄ polyhedron of the [Gd(H₂O)₈]³⁺ ion.

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Structure du Pentacarbonyl(isocyanure de benzoyle)chrome*

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Abstract. [Cr(CO)₅(CNCOC₆H₅)], monoclinic, *P*2₁/*c*, *C*_{2h}⁵, *a* = 6.059 (2), *b* = 7.217 (1), *c* = 32.138 (8) Å, β = 93.30 (1)°, *V* = 1402.9 Å³, *d*_x = 1.53 Mg m⁻³, *Z* = 4. The structure was refined to *R* = 0.034 and *R*_w = 0.039 for 1503 diffractometer data (Mo *K*α radiation). The Cr–C(isocyanide) and mean Cr–C(carbonyl) distances are 1.928 (3) and 1.900 (4) Å respectively

and the coordination shell of the Cr atom is an almost perfect octahedron. The angle around the N atom between the isocyanide ligand and the organometallic moiety has a value of 173.9 (3)°. All the atoms of the isocyanide group lie close to the benzene-ring mean plane, the maximum departure being 0.13 Å. Intermolecular interactions are weak.

Introduction. L'intérêt des isocyanures –CNR réside principalement dans le fait qu'ils ont des effets σ
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* Le Ligande Isocyanure de Benzoyle –CNCOPh. I.