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Crystal Structure of a Dysprosium Trichloride Complex with Oxygen Donor Ligands*

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Lanthanide ions are typical hard acids complexing with hard bases, e.g., chloride and oxygen donor ligands. The extraction, chemistry and optical properties of lanthanide trichlorides are closely related to the coordination geometries of $[\mathrm{LnCl}_n\mathrm{O}_m]^{3-n}$ derivatives.

Recently the 'Packing Saturation Rule', applied to lanthanide (Ln) coordination compounds [1], showed that the solid angle factors sums (SAFs) of the coordinating ligands are in a stable region, SAF = 0.78 ± 0.10. According to this rule most of the possible coordination polyhedra for $\mathrm{LnCl}_n\mathrm{O}_m$ derivatives should lie in the stable region. The lanthanide trihalides form with hexamethylphosphoramide (HMPA) 1:3 complexes of the type $\mathrm{LnCl_3L_3}$ [2, 3], whereas with $\mathrm{LnBr_3}$ they form 1:4 complexes of the type $\mathrm{LnBr_3L_4(H_2O)_3}$ [3].

In order to establish the coordination number in these trichloro complexes, as polymeric forms involving halogen bridges could be present, the crystal structure of the dysprosium derivative has been undertaken.

Results and Discussion

Crystal Data

$\mathrm{DyCl_3(HMPA)_3}$: $M_r = 806.47$, monoclinic, space group $P2_1/n$, $a = 14.804(2)$, $b = 22.976(3)$, $c = 11.585(2)$ Å, $\beta = 109.02(3)°$, $U = 3725(1)$ Å^3, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $R = 0.045$ for 4260 observations $[I \geqslant 3\sigma(I)]$.

The crystal structure consists of discrete $\mathrm{DyCl_3(HMPA)_3}$ molecules. A view of the molecule down the *a* axis is shown in Fig. 1. Dysprosium has a coordination number of six, involving three oxygen atoms from the three HMPA groups and three chlorine atoms arranged in an octahedral polyhedron.

There are two possible isomers: one with the three chlorines and the three oxygen *cis* to each other; and

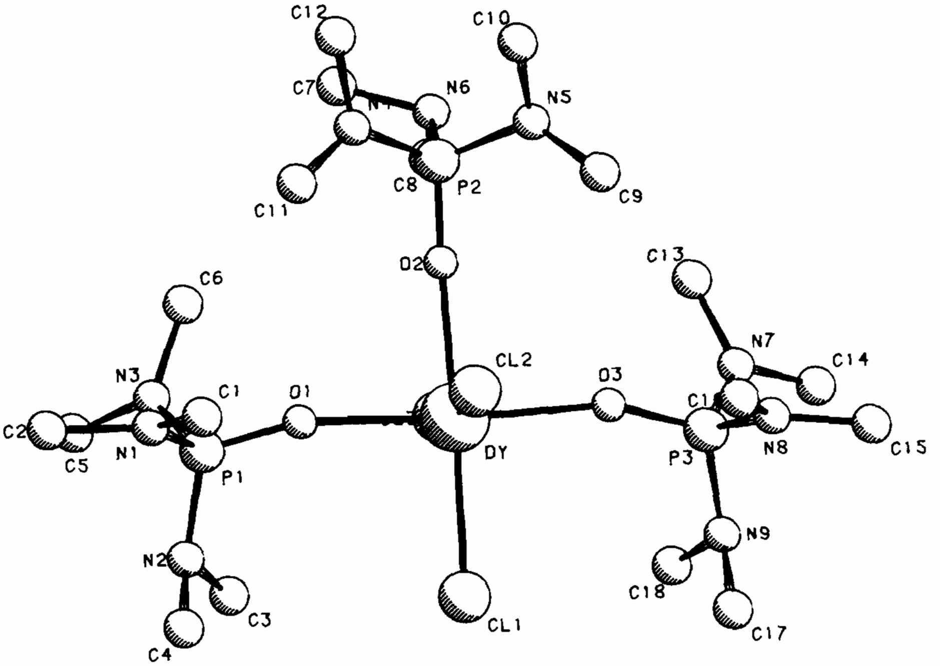

Fig. 1. The $\mathrm{DyCl_3(HMPA)_3}$ molecule viewed down the *a* axis.

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the other with two chlorines in the *trans* position and also the two oxygens in the *trans* position. The second isomer is preferred in the crystals owing to the steric demands of the ligands.

The best mean plane calculated through the O(1), O(2) and O(3) atoms and Cl(1) shows no significant deviations of the atoms from planarity, while the Dy atom is 0.027(1) Å out of this plane in the direction of Cl(3). An examination of the bond distances and angles in the first-coordination sphere shows that the Dy–Cl bond distances are equal in the limit of their e.s.d.s (Dy–Cl range 2.626(4)–2.637(2) Å). Some significant distances and angles with e.s.d.s in parentheses are reported in Table I.

Some *trans* effect seems to be present in the Dy–O(2) bond distances *trans* to Cl(1); the value of 2.269(7) Å is slightly longer when compared with Dy–O(1) = 2.244(6) and Dy–O(3) = 2.245(6) Å.

However, it should be noted that the angle Cl(2)–Dy–Cl(3) is 171.0(1)°, Cl(2)–Dy–O(2) is 84.8(2)° and Cl(3)–Dy–O(2) is 86.4(2)°, indicating a bending in the direction of the O(2) atom *trans* to Cl(1). This could be due to the large fan angle of chloride (45°) compared to that of the oxygen (38°) (see Table II), which is also responsible for the bending in the angles Dy–O(1)–P(1) = 161.0(4)° and Dy–O(3)–P(3) = 158.9°. The three phosphorus atoms are out of the Cl(1) O(3) O(2) O(1) plane: P(1) by 0.302(3), P(2) by −0.141(3) and P(3) by 0.256(3) Å. The three bulky ligands tend to distribute themselves more uniformly by bending P(1) and P(3) in the Cl(1) direction, while P(2) is in the Cl(2) direction. (The chlorine ion is more space demanding than HMPA in the first-order coordination sphere but exerts no secondary effect.) The solid angle factors sum of the donor atoms is 0.730 and the vector sum of the SAFs of the donor atoms is 0.006, in agreement with the 'Packing Saturation Rule' and 'Packing Centre Rule' [4].

TABLE I. Some Significant Bond Distances and Angles[a]

Distances (Å)		Angles (°)	
Dy–Cl(1)	2.626(4)	O(3)–Dy–O(2)	89.8(2)
Dy–Cl(2)	2.637(2)	O(1)–Dy–O(2)	86.9(2)
Dy–Cl(3)	2.634(3)	O(1)–Dy–O(3)	176.4(2)
Dy–O(1)	2.244(6)	Cl(3)–Dy–O(2)	86.4(2)
Dy–O(3)	2.245(6)	Cl(3)–Dy–O(3)	89.3(2)
Dy–O(2)	2.269(7)	Cl(3)–Dy–O(1)	91.8(2)
O(1)–P(1)	1.483(6)	Cl(2)–Dy–O(2)	84.8(2)
P(1)–N(1)	1.624(8)	Cl(2)–Dy–O(3)	88.6(2)
P(1)–N(2)	1.634(8)	Cl(2)–Dy–O(1)	89.8(2)
P(1)–N(3)	1.635(10)	Cl(2)–Dy–Cl(3)	171.0(1)
O(3)–P(3)	1.496(6)	Cl(1)–Dy–O(2)	177.6(2)
P(3)–N(7)	1.631(11)	Cl(1)–Dy–O(3)	92.2(2)
P(3)–N(8)	1.619(8)	Cl(1)–Dy–O(1)	91.1(2)
P(3)–N(9)	1.636(9)	Cl(1)–Dy–Cl(3)	95.0(1)
O(2)–P(2)	1.472(7)	Cl(1)–Dy–Cl(2)	93.9(1)
P(2)–N(4)	1.60(1)	Dy–O(1)–P(1)	161.0(4)
P(2)–N(5)	1.60(1)	Dy–O(2)–P(2)	174.9(4)
P(2)–N(6)	1.62(2)	Dy–O(3)–P(3)	158.8(4)

[a] e.s.d.s are in parentheses.

TABLE II. Steric Parameters of some Selected Ligands in Coordination Compounds

Ligands[a]	FA (°)	SAF	
Cl^-	45	0.14	
Oxygen donor ligands	33	0.085	(OR_2)
	37	0.10	(OH^-)
	38	0.105	amides sulfoxide phosphine oxide

[a] As an approximation all oxygen donor ligands have SAF = 0.1 for estimation.

An interesting comparison can be made between the bond lengths found here and those of $GdCl_3(C_7H_8O_2)_3$ [5], where the ligands are in the *cis* configuration. The difference in ionic radii between Gd and Dy is 0.026 Å (using the Shannon values [6]), but this difference is not confirmed by the results of the two structure determinations. The Gd–Cl bond distances (average 2.634(3) Å) and Dy–Cl distance (2.632(3)) are equal, while Gd–O (2.337(5) Å) and Dy–O (2.253(6) Å) are significantly different; this could be related either to the different geometric isomers in which the two compounds crystallize or to the different donor capacity of the neutral ligands.

From the view point of magnetic and spectral studies, it is worth noting that Cl(1)–Dy–O(2) (177.6(2)°) is approximately coincident with the *c* crystallographic axis. The structure of the analogous Pr derivative is also known, but the two compounds are not isomorphous [7] although they are practically isostructural.

Supplementary Material

Details of data collection, lists of atomic coordinates and structure factors F_o and F_c are available from the authors on request.

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