

Reaction of Lanthanoid Chlorides and Macrobicyclic Polyethers; Crystal Structure of the Hydrated Complex between Lanthanum Chloride and 1,5,12,16,23,26,29,32-octaoxa[10^{3,14}][5.5]orthocyclophane

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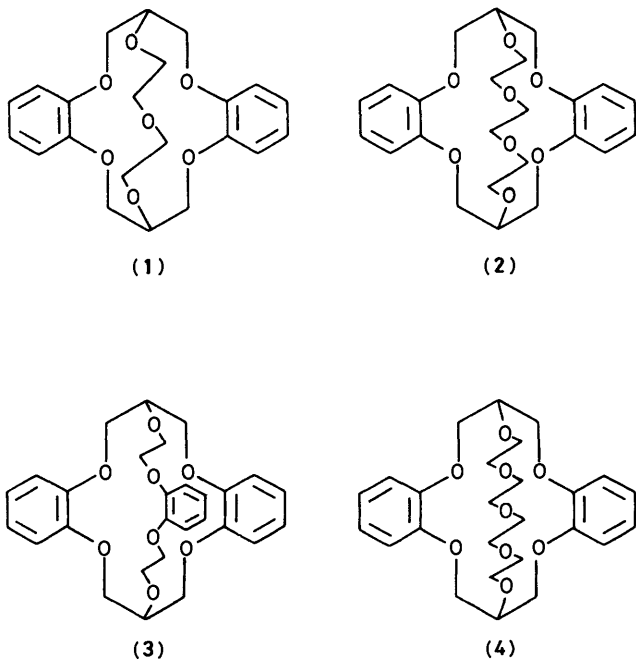
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The crystal structure of the title compound shows that partial hydrolysis has occurred to give complex dimer cations containing an O—H ··· Cl bond $[\text{Cl}(\text{C}_{24}\text{H}_{30}\text{O}_8)\text{La}(\text{OH})\text{ClLa}(\text{C}_{24}\text{H}_{30}\text{O}_8)\text{Cl}]^{2+}$ connected through further hydrogen bonds with chloride ions and water molecules disordered in channels; the lanthanum is ten-co-ordinated, by the eight oxygen atoms of the ligand in a bis-end-capped trigonal prism with anions on two faces.

To investigate the effects of small differences in cation radius on the structure and bonding by macrobicyclic polyethers, we have made a series of complexes of lanthanoid (Ln) chlorides with the ligands (1)–(4) which have been shown^{1,2} to form strong complexes with alkali metals. In carefully controlled anhydrous conditions with pure LnCl_3 , only amorphous products were obtained. The presence of moisture appears necessary for crystallisation; this was shown by the hydroxy stretching bands in the i.r. spectra, which were independent of the solvent used. These spectra were similar in the 'fingerprint' region to those of the complexes between the corresponding ligands and alkali metal cations.

For $\text{Ln} = \text{La}, \text{Nd}, \text{Sm},$ or Gd elemental analyses indicated a ratio of LnCl_3 :ligand of approximately 1:1, but because the solvent is labile and samples change weight on the balance, the analytical figures are not definitive. Crystals of most samples became opaque on exposure to the atmosphere, and we have so far been able to determine the crystal structure of only one example. This showed some interesting features and is reported here.



Use of BDH A.R. $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ with ligand (2) dissolved in 1:1 mol ratio in methanol gave a crystalline sample for which the elemental analysis was found: C, 37.21; H, 4.32; Cl, 11.30%. $\text{C}_{24}\text{H}_{30}\text{O}_8 \cdot \text{LaCl}_3$ requires C, 41.6; H, 4.37; Cl, 15.37%.

Similar difficulty in analysis had been encountered with the potassium chloride complex of (3)² and shown to result from the chloride anion and water (not methanol) molecules occupying disordered positions in columns through the crystal.^{3,4}

If, in the present complex, the carbon found corresponds to 24 atoms (*i.e.* no methanol of solvation), there are 33.2 atoms of hydrogen and 2.5 of chlorine. Crystal structure determination has established the constitution apart from the exact number of molecules of water of hydration.

Crystal data: $\text{C}_{24}\text{H}_{30}\text{O}_8 \cdot \text{LaCl}_x(\text{OH})_{3-y} \cdot y\text{H}_2\text{O}$. For $x = 2.5$, $y = 4.5$, $M = 763.6$. Triclinic, $a = 11.325(2)$, $b = 12.934(3)$, $c = 11.551(4)$ Å, $\alpha = 104.80(2)$, $\beta = 100.62(2)$, $\gamma = 101.15(2)^\circ$, $U = 1555$ Å³, space group $P\bar{1}$, $D_m = 1.637$ g cm⁻³ (by flotation), $D_c = 1.631$ g cm⁻³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 16.5$ cm⁻¹.

Crystals are colourless, clear, diamond-shaped plates, and sensitive in air to warmth; a sample with edges $0.3 \times 0.3 \times 0.36$ mm was mounted on a fibre and coated with epoxy resin in an unheated room.

Intensities, measured on an automated four-circle diffractometer with monochromated radiation, were corrected for absorption, for slight deterioration, and by Bayesian statistical methods to ensure no negative net values. 4049 Unique reflections, with $1.2 < \theta < 22.5^\circ$ were used in the structure analysis. The La atom, two 'chloride ions,' and the macrobicyclic ligand were identified readily from Patterson and electron density maps. Peaks in subsequent difference maps have been labelled either as oxygen atoms (of water molecules or hydroxide ions) or as chloride ions, and their positions with site-occupancy-factors (s.o.f.s) or thermal parameters have been allowed to refine. R is now 0.032 (R_w 0.30) for 4038 reflections (omitting the lowest angle planes).[‡]

As Figure 1 shows, the lanthanum ion is surrounded by all eight oxygen atoms of the ligand and it makes two additional contacts, one to a chloride ion Cl(1), and the other to an entity which, when treated as chloride, had an improbably high vibration parameter and which is only 3.028(4) Å from a centrosymmetrically related entity. This is now identified as a

[‡] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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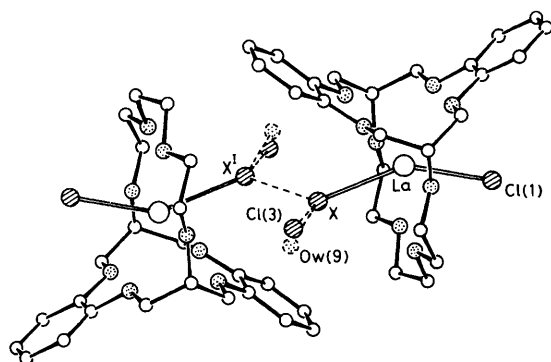


Figure 1. A view of the hydrogen-bonded dimer, in which two $[\text{La}(\mathbf{2})\text{ClX}]^+$ complex cations [$\mathbf{2}$] is the bicyclic polyether molecule, and X is either a chloride or a hydroxide ion] are connected through the $\text{X} \cdots \text{X}^1$ hydrogen bond across a centre of symmetry.

site, X, with equal occupation by a chloride ion or a hydroxide ion, so that the average across the centre of symmetry is an $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bond. The $[\text{Cl} \cdot (\mathbf{2}) \cdot \text{LaOH} \cdot \text{Cl} \cdot \text{La} \cdot (\mathbf{2}) \cdot \text{Cl}]^{2+}$ cations pack to form channels, parallel to the crystallographic a axis, in which there are disordered water molecules and chloride ions, none of which appears to have full site occupation. One of these chloride ions, Cl(3), however, is at 2.79(1) Å from the X site and can only be present when the OH group is present at X, *i.e.* with a maximum occupancy of 0.5. Another site, 0.52(1) Å from Cl(3), and 2.98(1) Å from X, is partially occupied by a hydroxide ion or water molecule, Ow(9). Cl(3) and Ow(9) are also at acceptable hydrogen bonding distances from two water molecules in the solvent region. These contacts between the channel atoms and the complex cation contrasts with the complete separation found in $[\text{K} \cdot (\mathbf{3})]^+ \text{Cl} \cdot x\text{H}_2\text{O}^3$ and in $[\text{NH}_4 \cdot (\mathbf{2})]^{2+} 2\text{I} \cdot x\text{H}_2\text{O}$,⁵ and we believe this structure to be the first having such complex-solvent channel interactions.

Despite the low R value, the accuracy of this structure is limited by the impossibility of fitting the disordered electron

density. The sums of refined s.o.f.s. of the atoms identified from peaks in the solvent region account, approximately, for the chloride ion required by elemental analysis and for 4.7 molecules of water. This is close to the value 4.3–4.7 calculated from the volume and density (or from the sums of the volumes of ligand,⁶ lanthanum trichloride,⁷ and water molecules at 24.5 Å³ per water⁸), but rather more than 2.5–3.0 from direct measurement of the water content by the Karl Fischer method.

The lanthanum ion is ten-co-ordinate. Six of the ligand oxygen atoms form an approximate trigonal prism [$\text{La}-\text{O}$ 2.633(3)–2.734(3) Å], end-capped by the oxygen atoms attached to the bridgehead carbon atoms, [$\text{La}-\text{O}$ 2.575(3) and 2.537(3) Å]; two of the prism faces are occupied by Cl(1) and X, [$\text{La}-\text{Cl}/\text{X}$ 2.751(1) and 2.760(2) Å]. The six $\text{La}-\text{O}$ distances of the trigonal prism are comparable with those in $[\text{La}(\text{crypt-and } 222)(\text{NO}_3)_2]^+$, the lanthanum nitrate complex with 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane;⁹ however, here, the end-capping nitrogen atoms are further away, $\text{La}-\text{N}$ 2.813–2.848 Å, and the two co-ordinated anions are bidentate nitrate ions giving twelve co-ordination.

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