*Hydrogen bonding*.* There is no intramolecular hydrogen bonding. The phosphate groups are involved in extensive hydrogen bonding with water molecules and exocyclic hydroxyls as shown in Fig. 2. The ring oxygen O(5) and phosphate ester oxygen O(1) are not involved in hydrogen bonding. The phosphate ester oxygen O(6) accepts a hydrogen bond from water molecule O*W*(7). Each of the three furanose hydroxyl groups has two close contacts – to a $Na^+$ ion and a phosphate oxygen. The symmetry-related molecules are linked by O(3)···O(10) and O(4)···O(11) hydrogen bonds.

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* See deposition footnote.

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# Structure of the Hydrated Complex between Lanthanum Chloride and 1,5,12,16,23,26,29,32-Octaoxa$[10^{3,14}][5\cdot5]$orthocyclophane, $C_{24}H_{30}O_8.LaCl_x(OH)_{3-x}.yH_2O$

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**Abstract.** $M_r = 763\cdot6$ for $x = 2\cdot5$ (1), $y = 4\cdot5$ (2), triclinic, $P\bar{1}$, $a = 11\cdot325$ (2), $b = 12\cdot934$ (3), $c = 11\cdot551$ (4) Å, $\alpha = 104\cdot80$ (2), $\beta = 100\cdot62$ (2), $\gamma = 101\cdot15$ (2)°, $U = 1555$ Å$^3$, $Z = 2$, $D_m = 1\cdot637$, $D_x = 1\cdot631$ g cm$^{-3}$, $\lambda(\text{Mo } K\bar{\alpha}) = 0\cdot71069$ Å, $\mu(\text{Mo } K\bar{\alpha}) = 16\cdot5$ cm$^{-1}$, $F(000) = 744$, $T = 295$ K, $R = 0\cdot032$ for 4038 observations (all data with $3° < \theta \le 22\cdot5°$). Each unit cell contains a pseudocentrosymmetric 'dimer' $[Cl(C_{24}H_{30}O_8)LaX]_2$ where $X$ is the site occupied by $Cl^-$ in one half and $OH^-$ in the other half, with an O—H···Cl hydrogen bond across the centre of symmetry. The La atom is ten-coordinated by the eight O atoms of the ligand in an end-capped trigonal prism with Cl and $X$ on two faces. Another $Cl^-$ anion and water molecules occupy disordered sites in channels through the crystal.

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**Introduction.** The synthetic macrobicyclic polyether $L$ (Fig. 1), named in the title, gives, with alkali metals, complexes having high formation constants in water and in methanol (Parsons, 1978; Hanson, Parsons & Truter, 1979). The crystal structures of the uncomplexed molecule (Owen, 1981*a*) and of its complex with ammonium iodide (Bandy, Kennard, Parsons & Truter, 1984) have been determined. Recently we have made a series of complexes of $L$ and related compounds, *e.g.* $L'$ (Fig. 1) with lanthanoid chlorides; elemental analyses correspond approximately to 1:1 stoichiometry $L$:$LnCl_3$ but crystalline products were obtained only in the presence of water. Crystal structure analysis of the complex formed between $L$ and $LaCl_3.7H_2O$ (BDH AR) showed that partial hydrolysis had taken place, as reported in the preliminary communication (Benetollo, Bombieri, de Paoli, Hughes, Parsons & Truter, 1984).

**Experimental.** Crystals are sensitive in air to warmth so were manipulated in an unheated room; clear, colourless, diamond-shaped plate 0·3 × 0·3 × 0·36 mm mounted on a fibre and coated with epoxy resin; $D_m$ by flotation in $CCl_4$–60/80 petroleum; preliminary photographic examination; Enraf–Nonius CAD-4 diffractometer with monochromated Mo radiation; 25 reflections with $9{\cdot}4 < \theta < 10{\cdot}7°$ used for cell-dimensions' refinement; absorption correction (from $\psi$-scan measurements) applied, max. transmission 0·994, min. 0·967; index ranges measured $h$ 0 to 12, $k$ −13 to 13, $l$ −12 to 12; two reflections ($\bar{1}15$ and $51\bar{2}$), measured after every 10 000 s of X-ray exposure time, showed steady reduction in intensities over period of measurement, overall deterioration 5·0%; total number of reflections measured 4300, giving 4049 unique reflections with $\theta_{\max} = 22{\cdot}5°$; $R_{\rm int} = 0{\cdot}040$ for 251 merged equivalent measurements; 3592 reflections have $I > 2\sigma(I)$; data corrected by Bayesian methods to ensure no negative intensity values.

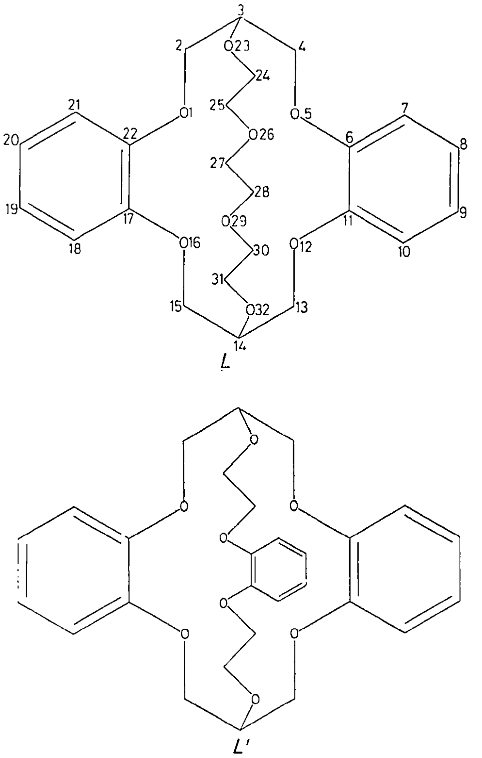

Fig. 1. The ligand, $L$, showing the atom-numbering scheme. H atoms have the same number as the bonded C atom, those in methylene groups being distinguished additionally by *a* and *b*. The structural formula of a related compound, $L'$, is also shown.

Structure solved by Patterson methods (for La-atom coordinates), electron density maps (for remaining non-hydrogen atoms of complex molecule) and difference maps (for solvent atoms); coordinates of H atoms in the complex molecule calculated in idealized geometries and set to 'ride' on their bonded C atoms; La, Cl, O and C atoms in the complex molecule refined anisotropically; $U_{\rm iso}$'s of H atoms refined individually and freely; atoms, treated as O, in the solvent region refined laboriously, often with damping factors, varying the temperature factors (anisotropic for some atoms, isotropic for others) and site-occupancy factors in alternate cycles; refinement was by large-block least-squares methods (La + ligand molecule in one block, La + $Cl^-$ ions + solvent molecules in second block), minimizing $\sum w(\Delta F)^2$; final $R = 0{\cdot}032$, $R_w = 0{\cdot}036$ for 4038 reflections, omitting 11 with $\theta < 3°$, weighted from counting statistics, $w = \sigma(F)^{-2}$; improved reliability shown by greater consistency in the lengths of chemically similar bonds; final $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0·6 (in solvent atoms), and 0·04 (in ligand molecule); max. and min. $\rho$ 0·49 and −0·37 e Å$^{-3}$ in final difference synthesis; scattering factors were calculated using an analytical approximation (*International Tables for X-ray Crystallography,* 1974). Computer programs included CAD-4 processing program (from Hursthouse, 1976), *EMPABS* for absorption corrections (Sheldrick, 1978), *BAYES* for negative intensity corrections (Owen, 1983; based on French & Wilson, 1978), *SHELX*76 for structure determination and refinement (Sheldrick, 1976), *GEOM* for molecular-geometry calculations and preparation of tables (Owen, 1981*b*) and *ORTEP*II for the diagrams (Johnson, 1971).

**Discussion.** Final atomic parameters are in Table 1.[*] The ligand in this structure (Fig. 2) has an approximate twofold axis of symmetry through the C(27)–C(28)

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39750 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond. Table 2 showing details of molecular geometry is laid out to demonstrate this. The angles between the normals to the mean plane through O(23), O(26), O(29), O(32) and La (maximum deviation 0·17 Å) and the benzene rings C(6)–C(11) and C(17)–C(22) are 61·0 (2) and 54·3 (1)°. The O atoms form an end-capped trigonal prism around La. The triangular faces are formed by O(1), O(5), O(26) and O(16), O(12), O(29), with La—O distances to the aliphatic O atoms averaging 2·64 (1) Å and to the aromatic ones 2·70 (1) Å; the end-capping atoms O(23) and O(32) are at 2·56 (2) Å, *i.e.* significantly closer, as predicted for this geometry (Burdett, Hoffmann & Fay, 1978). Ten coordination is completed by two anions on the less-hindered rectangular faces. Although site *X* is occupied equally by OH and by Cl the maximum electron density is at the same distance as for Cl(1).

The most nearly comparable lanthanoid structure is that of lanthanum nitrate–222 cryptate (4,7,13,16,-21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) (Hart, Hursthouse, Malik & Moorhouse, 1978) in which the six La—O distances are comparable with those found here but the end-capping atoms are N at 2·83 (2) Å and, as the two-coordinated nitrate ions are both bidentate, the coordination number is twelve.

Table 1. *Atomic parameters: fractional coordinates* ($\times 10^4$); *isotropic temperature factors* $U_{iso}$ ($Å^2 \times 10^3$) *or, if marked with an asterisk,* $U_{eq}$ ($Å^2 \times 10^3$); *site-occupancy factors* (*s.o.f.*) (1·0 *if not shown*); *e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

| | $x$ | $y$ | $z$ | $U_{iso}/U_{eq}$ | S.o.f. |
|---|---|---|---|---|---|
| La | 3027·6 (2) | 998·2 (2) | 2500·8 (2) | 38·3 (1)* | |
| O(1) | 1537 (3) | 1864 (3) | 3807 (3) | 57 (1)* | |
| C(2) | 1563 (5) | 1755 (5) | 5020 (4) | 75 (3)* | |
| C(3) | 2797 (5) | 1531 (5) | 5480 (4) | 70 (3)* | |
| C(4) | 3909 (5) | 2478 (5) | 5769 (4) | 75 (3)* | |
| O(5) | 4093 (3) | 2652 (3) | 4617 (2) | 58 (1)* | |
| C(6) | 5159 (4) | 3452 (4) | 4701 (5) | 64 (2)* | |
| C(7) | 6044 (5) | 4039 (5) | 5781 (5) | 83 (3)* | |
| C(8) | 7053 (6) | 4790 (6) | 5708 (8) | 108 (4)* | |
| C(9) | 7185 (6) | 4965 (5) | 4646 (8) | 99 (3)* | |
| C(10) | 6298 (4) | 4394 (4) | 3560 (6) | 73 (3)* | |
| C(11) | 5280 (4) | 3626 (4) | 3585 (5) | 57 (2)* | |
| O(12) | 4332 (2) | 2987 (2) | 2575 (3) | 53 (1)* | |
| C(13) | 4317 (5) | 3241 (4) | 1432 (4) | 64 (2)* | |
| C(14) | 3120 (4) | 2548 (4) | 540 (4) | 56 (2)* | |
| C(15) | 1968 (4) | 2822 (4) | 845 (4) | 55 (2)* | |
| O(16) | 1801 (2) | 2490 (2) | 1911 (2) | 46 (1)* | |
| C(17) | 776 (3) | 2685 (3) | 2347 (4) | 43 (2)* | |
| C(18) | −36 (4) | 3221 (3) | 1869 (4) | 55 (2)* | |
| C(19) | −1021 (5) | 3378 (4) | 2404 (5) | 70 (2)* | |
| C(20) | −1189 (5) | 3006 (4) | 3366 (5) | 75 (3)* | |
| C(21) | −372 (4) | 2477 (4) | 3844 (5) | 66 (2)* | |
| C(22) | 621 (4) | 2335 (3) | 3338 (4) | 50 (2)* | |
| O(23) | 2992 (3) | 642 (3) | 4589 (3) | 60 (1)* | |
| C(24) | 2411 (5) | −438 (4) | 4614 (5) | 73 (3)* | |
| C(25) | 3005 (5) | −1190 (4) | 3849 (5) | 72 (3)* | |
| O(26) | 2811 (3) | −1020 (2) | 2665 (3) | 60 (1)* | |
| C(27) | 3319 (5) | −1741 (4) | 1833 (4) | 71 (3)* | |
| C(28) | 2835 (5) | −1681 (4) | 566 (5) | 70 (2)* | |
| O(29) | 3211 (3) | −553 (2) | 578 (2) | 53 (1)* | |
| C(30) | 2860 (5) | −433 (4) | −618 (4) | 61 (2)* | |
| C(31) | 3425 (5) | 737 (4) | −510 (4) | 62 (2)* | |
| O(32) | 3008 (3) | 1406 (2) | 463 (2) | 54 (1)* | |
| Cl(1) | 5469·0 (9) | 909 (1) | 3027 (1) | 59·4 (5)* | |
| *X* | 633 (2) | −150 (2) | 1198 (2) | 78·9 (8)* | † |
| Solvent region | | | | | |
| Cl(3) | −814 (9) | −831 (7) | 2708 (12) | 72 (3)* | 0·35 (2) |
| Cl(4) | −2896 (4) | −5127 (4) | 516 (6) | 151 (3)* | 0·50 (2) |
| O*w*(1) | −5282 (8) | −6464 (6) | −1347 (6) | 151 (4)* | 0·83 (2) |
| O*w*(2) | −702 (13) | −5724 (11) | −739 (13) | 183 (5) | 0·53 (2) |
| O*w*(3) | −317 (12) | −3226 (10) | 2394 (11) | 185 (4) | 0·58 (2) |
| O*w*(4) | −2863 (14) | −4310 (12) | 1505 (13) | 188 (5) | 0·57 (2) |
| O*w*(51) | −2042 (16) | −5483 (13) | −639 (16) | 118 (5) | 0·30 (2) |
| O*w*(52) | −1531 (20) | −5598 (15) | −1145 (18) | 129 (6) | 0·30 (2) |
| O*w*(6) | −1885 (19) | −3470 (16) | 2150 (17) | 177 (6) | 0·37 (2) |
| O*w*(7) | −4451 (14) | −6075 (13) | −977 (14) | 154 (6) | 0·47 (2) |
| O*w*(8) | −768 (35) | −6396 (29) | −2952 (33) | 142 (12) | 0·15 (2) |
| O*w*(9) | −937 (14) | −1258 (9) | 2553 (14) | 93 (6)* | 0·65 (2) |

† The atom *X* was treated in the X-ray analysis as a $Cl^-$ ion with a site-occupancy factor of 0·75 (1). In the crystal, this site is believed to be fully occupied, by either a $Cl^-$ or a hydroxide ion with equal probability.

Table 2. *Interatomic distances* (Å) *and torsion angles* (°)

(*a*) Environment of the $La^{3+}$ ion

Distances to donor atoms

| | | | |
|---|---|---|---|
| O(1) | 2·681 (3) | O(12) | 2·679 (3) |
| O(5) | 2·693 (2) | O(16) | 2·734 (3) |
| O(26) | 2·633 (3) | O(29) | 2·656 (3) |
| O(23) | 2·575 (3) | O(32) | 2·537 (3) |
| Cl(1) | 2·751 (1) | *X* | 2·760 (2) |

(*b*) Dimensions in the ligand

| Type of bond | Range | Weighted mean distance [with σ(mean distance)] |
|---|---|---|
| $C_{(sp^2)}$—O | 1·379–1·399 | 1·389 (4) |
| $C_{(sp^3)}$—O | 1·417–1·450 | 1·435 (3) |
| $C_{(sp^2)}$—$C_{(sp^2)}$ | 1·332–1·395 | 1·375 (4) |
| $C_{(sp^3)}$—$C_{(sp^3)}$ | 1·487–1·510 | 1·495 (3) |

Torsion angles, e.s.d. 0·4–0·6°

| | | | |
|---|---|---|---|
| C(17)–C(22)–O(1)–C(2) | 165 | C(6)–C(11)–O(12)–C(13) | 171 |
| C(22)–O(1)–C(2)–C(3) | −165 | C(11)–O(12)–C(13)–C(14) | −172 |
| O(1)–C(2)–C(3)–C(4) | 69 | O(12)–C(13)–C(14)–C(15) | 67 |
| C(2)–C(3)–C(4)–O(5) | −70 | C(13)–C(14)–C(15)–O(16) | −70 |
| C(3)–C(4)–O(5)–C(6) | −175 | C(14)–C(15)–O(16)–C(17) | 180 |
| C(4)–O(5)–C(6)–C(11) | −178 | C(15)–O(16)–C(17)–C(22) | 178 |
| O(5)–C(16)–C(11)–O(12) | 0 | O(16)–C(17)–C(22)–O(1) | 2 |
| O(1)–C(2)–C(3)–O(23) | −52 | O(12)–C(13)–C(14)–O(32) | −54 |
| O(5)–C(4)–C(3)–O(23) | 52 | O(16)–C(15)–C(14)–O(32) | 52 |
| C(2)–C(3)–O(23)–C(24) | −83 | C(13)–C(14)–O(32)–C(31) | −94 |
| C(4)–C(3)–O(23)–C(24) | 151 | C(15)–C(14)–O(32)–C(31) | 140 |
| C(3)–O(23)–C(24)–C(25) | −166 | C(14)–O(32)–C(31)–C(30) | −163 |
| O(23)–C(24)–C(25)–O(26) | −57 | O(32)–C(31)–C(30)–O(29) | −55 |
| C(24)–C(25)–O(26)–C(27) | −178 | C(31)–C(30)–O(29)–C(28) | −174 |
| C(25)–O(26)–C(27)–C(28) | 168 | C(30)–O(29)–C(28)–C(27) | 176 |
| O(26)–C(27)–C(28)–O(29) | 59 | | |

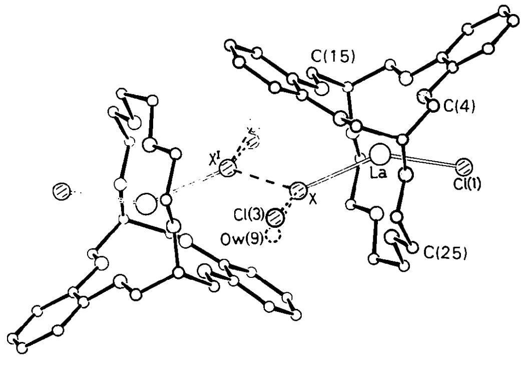

Fig. 2. Two complexes related by a centre of symmetry with an indication of the contacts from *X* (OH, Cl) to Cl(3) or a water molecule O*w*(9). For clarity the La—O bonds are not drawn.

The geometry found for the ligand here contrasts with that in the ammonium complex (Bandy *et al.*, 1984) for which the O atoms O(1), O(23), O(26), O(29), O(32) and O(16) are equidistant from the ammonium N atom so forming a pseudo benzo-18-crown-6 ring; the angle between the normal to the six-O plane and that to C(17)–C(22) is 30·8 (2)°, whereas the corresponding angle to the normal to the C(6)–C(11) plane is 87·9 (2)°; O(5) and O(12) are not coordinated.

The average bond lengths in our complex, Table 2, are not significantly different from those in the ammonium complex or the uncomplexed molecule (Owen, 1981*a*). Torsion angles follow the general rule: approximately *gauche* for O—C—C—O, and O—C—C—C, or *trans* for C—O—C—C with the necessary exception of *cis* O—C—C—O at the benzene rings. With the pseudo benzo-18-crown-6 structure in the ammonium complex, one angle in the ring, *viz* C(24)—C(25)—O(26)—C(27), violates the rule, being 107 (1)°. In the lanthanum complex, that angle is −178·1 (4)° and the exceptional angles are found at the bridgehead C atoms about C(3)–O(23) and C(14)–O(32). Detailed examination of the 'fingerprint' region, 900–1200 cm$^{-1}$, of the infrared spectra showed that the ammonium and lanthanum complexes, while similar, were distinguishable (and both very different from the uncomplexed ligand) and, further, that the ligand in the hydrated sodium iodide complex probably has the same conformation as in the lanthanum, not the ammonium, complex.

An essential feature of obtaining crystals appeared to be the presence of moisture and the water has had two effects. Firstly, in hydrolysis so that there are equal numbers of $LaCl_2(L)^+$ and $LaCl(OH)(L)^+$ cations in the unit cell; these are held by O—H···Cl hydrogen bonds, 3·028 (4) Å, Fig. 2, to form 'dimers'. Secondly, there are water molecules in channels through the crystal parallel to **a** (Fig. 3). These water molecules and the equivalent of one Cl$^-$ ion per La occupy sites with disorder; the arrangement found in the hydrophobic channels, however, differs from that in the potassium chloride complex of the macrobicyclic ligand *L*′ (Fig. 1) which contains $[KL']^+$ cations with only van der Waals interactions to the channels of disordered water and Cl$^-$ ions (Hanson & Truter, 1982). In our complex, the *X* entity is 2·79 (1) Å from the site of Cl(3) with an estimated 0·35 occupancy, *i.e.* less than the 0·5 occupation of *X* by OH. When Cl(3) is not occupied, a hydroxide ion or a water molecule may occupy the neighbouring site, O*w*(9). In turn, Cl(3) or O*w*(9) may each be hydrogen bonded to water molecules O*w*(3) or O*w*(6); O*w*(3) may be hydrogen bonded to Cl(4) which has 0·5 occupation. The water/anion channels are thus connected by hydrogen bonds to the $[LaLClX]_2$ dimer cations and, through the cations, to neighbouring water/anion channels. Apart from the possibility of a

O*w*(1″)
centrosymmetrical Cl(4) Cl(4″) entity, the
O*w*(1)

contents of the channels cannot be centrosymmetrically arranged.

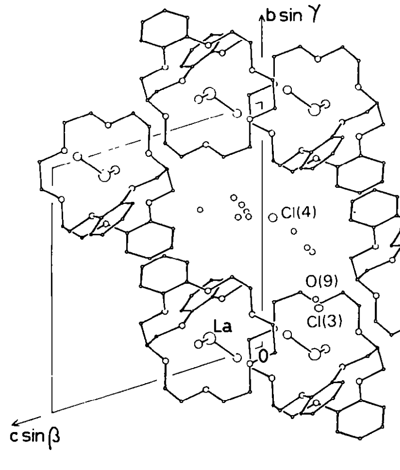

Fig. 3. The structure projected along **a**. Only half the solvent molecules in the channel are shown, *i.e.* without application of the centre of symmetry at (0,½,0); the larger circle represents Cl(4). Cl(3) and O*w*(9) are just hidden by the ligand, as indicated in one instance.

The total occupation, as refined, corresponds to one La$^{3+}$ ion, one *L* ligand, 4·75 water molecules, 0·5 hydroxide and 2·35 Cl$^-$ ions. For neutrality, a further 0·15 OH$^-$ or Cl$^-$ is required, the corresponding electron density being in any of the peaks assigned to water molecules. From the ratio of C:Cl in the elemental analysis there were 24:2·47 atoms, so the missing density is probably Cl$^-$. The adjusted number of water molecules is 4·45, close to the value calculated from the volume and density, but more than the value 2·5–3·0 obtained by direct measurement with the Karl Fischer method (see *e.g.* Mitchell & Smith, 1980).

For comparison, the starting material, $LaCl_3.7H_2O$ (Habenschuss & Spedding, 1979), consists of doubly bridged centrosymmetrical dimeric cations $[(H_2O)_7LaCl_2La(H_2O)_7]^{4+}$ with La—Cl distances 2·924 and 2·958 (2) Å, nine coordination being completed by the water molecules with La—O 2·520–2·587 (6) Å. In our complex the single bridge gives a much greater La···La separation [7·6159 (5) *cf.* 4·720 (2) Å] and replacement of the water molecules, which engage in intensive hydrogen bonding, by a neutral ligand, has resulted in additional ion pairing to reduce the charge density.

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# Structure of Dichlorobis[*P,P,P′,P′*-tetramethyl-*o*-phenylenebis(phosphine)]nickel(III) Hexafluorophosphate Dihydrate, $[NiCl_2\{P_2(CH_3)_4(C_6H_4)\}_2]PF_6.2H_2O$

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**Abstract.** $M_r = 706{\cdot}9$, monoclinic, $C2/m$, $a = 12{\cdot}467\ (6)$, $b = 10{\cdot}497\ (4)$, $c = 11{\cdot}241\ (7)$ Å, $\beta = 100{\cdot}79\ (4)°$, $V = 1445$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}625$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}108$ mm$^{-1}$, $F(000) = 726$, room temperature, final $R = 0{\cdot}087$ for 1365 unique reflections. The Ni atom has a tetragonally distorted octahedral configuration with chlorine atoms in the axial positions and the anionic P atom has a regular octahedral configuration. The Ni—Cl and Ni—P bond lengths are 2·424 (4) and 2·255 (3) Å. The anion and cation are held together by van der Waals forces.

**Introduction.** Phosphines act as $\pi$-bond acceptors and $\sigma$-bond donors. The vacant $3d$ orbitals of the P atoms are capable of interaction with filled non-bonding $d$ orbitals of a transition metal. Chelating diphosphine ligands are commonly used in the stabilization of a large number of oxidation states for many transition metals. With the lower oxidation states of the metals, the reducing properties of the ligands are an advantage, but in higher oxidation states any tendency towards dissociation will result in decomposition, since such complexes contain both an oxidizing and a reducing agent.

$Ni^{III}$ complexes of Group V*b* donors offer a wealth of data over VI*b* donors that is of considerable importance in the elucidation of their electronic structures. EPR studies of dihalo complexes reveal a highly delocalized molecular wave function for the unpaired electron as evidenced by the very well resolved superhyperfine structure from all the immediately bonded nuclei of the ligands (Manoharan & Rogers, 1970; Bernstein & Gray, 1972). Sethulakshmi, Subramanian, Bennett & Manoharan (1979) have carried out EPR investigations on $[Ni(dp)_2Cl_2]ClO_4$ and $[Ni(dp)_2Br_2]PF_6$ without complete X-ray crystal structure data.

In the present compound, both dipolar interaction and hyperfine local field contribute to the broadening of the EPR peak (Ramakrishna, 1982). But the estimation of their relative contributions leading to the simulation of the line width can be made only with the availability of the detailed crystal structure. This prompted us to carry out the present work.

We report here the structure of the title compound, hereafter represented as $[Ni(dp)_2Cl_2]^+.[PF_6]^-.2H_2O$.

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