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# Preparation and crystal structure of a new ion-pair complex with anionic tetramethylethylene-bridged dicyclopentadienyl ytterbium chloride

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## Abstract

The ion-pair $(Me_4C_2Cp_2YbCl_2)^-(Mg_2Cl_3 \cdot 6THF)^+ \cdot THF$ (Cp = cyclopentadienyl and THF = tetrahydrofuran) was prepared by the reaction of $Me_4C_2Cp_2Mg_2Cl_2 \cdot 4THF$ with anhydrous ytterbium chloride in THF. X-Ray diffraction intensities were collected with a four-circle diffractometer at −80 °C. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a$ 16.911(5), $b$ 13.268(5), $c$ 13.772(4) Å, $\alpha$ 116.52(2), $\beta$ 111.30 (2), $\gamma$ 87.61 (3)°, and $D_{calc}$ 1.45 g $cm^{-3}$ for $Z = 2$. Final $R$ value is 0.051 for 6566 independent observed reflections. The structure of the cation shows that the two magnesium atoms, each attached to three THF molecules, are bridged by three chlorines, thus forming two distorted octahedra joined along three common edges. In the anion, the ytterbium atom is coordinated in a pseudo-tetrahedral geometry by two chlorines and two Cp rings which are bridged by the tetramethylethylene. Both the bridged angles at the ethylene carbon atoms are greater than those in a normal tetrahedron, viz. 114.6(9)°, which indicates that the ligand is strained.

## Introduction

It has been shown by several authors [1–4] that it is possible to stabilize dicyclopentadienyl metal halides and prevent the disproportionation of dicyclopentadienyl lanthanide chlorides when the bridged dicyclopentadienyl is used as a ligand because the ligand framework is stabilized by an interannular chelate ring. Secaur et al. [1] have reported the synthesis of a series of bridged dicyclopentadienyluranium chlorides and have determined the crystal structure of one such derivative. Subsequent reports on various dicyclopentadienyl lanthanide chlorides having bridged ligands and crystal structures involving silicon-bridged ligands have appeared [3–5]. In 1983, Schwemlein and Brintzinger [2] prepared titanocene and zirconocene derivatives with tetramethylethylene-bridged dicyclopentadienyl under

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the reductive coupling of 6,6-dimethylfulvene and subsequent reaction of the anionic product with $TiCl_3$ or $ZrCl_4$ in tetrahydrofuran (THF). However, there have been no reports on the ethylene-bridged ligand lanthanide chlorides and their X-ray studies, mainly because of crystal instability.

We have prepared the extremely air-sensitive crystal of the tetramethylethylene-bridged dicyclopentadienyl ytterbium chloride as a salt of the magnesium complex cation and determined its crystal structure at low temperature. This is the first crystal structure of a carbon-bridged dicyclopentadienyl lanthanide chloride complex to be reported.

## Experimental

*Preparation of the crystal.* Solid anhydrous ytterbium chloride (1.0 g, 3.6 mmol) in a Schlenk flask was heated under reduced pressure for several minutes until gas evolution had ceased, then the flask was cooled, and filled with nitrogen. THF (40 ml) was added and the solution was left to stand overnight. $(CH_3)_4C_2(C_5H_4)_2$-$Mg_2Cl_2 \cdot 4THF$ (2.2 g, 3.6 mmol) [2] was added to the anhydrous ytterbium chloride solution at room temperature. After the mixture had been stirred for about 6 h the solution was concentrated to about 20 ml. Then the flask was centrifuged and the precipitates were removed from the solution. The solution was evaporated under reduced pressure to give an orange-yellow powder.

The solid was dissolved in a mixture of toluene (6 ml) and THF (15 ml), and petroleum ether was added to the solution until it became slightly turbid. The solution was then placed in a refrigerator for crystallization and orange-yellow crystals separated after several days.

*Determination of the crystal structure.* Since the crystals are unstable at room temperature and in air, a crystal of dimensions $0.4 \times 0.3 \times 0.3$ mm$^3$ was selected in a cool stream of nitrogen for measurement.

The intensity data were collected on a Nicolet R3m/E four-circle diffractometer equipped with a LT-1 low-temperature device at about $-80\,^{\circ}$C, by use of graphite-

Table 1

Crystallographic data for $(Me_4C_2Cp_2YbCl_2)^-(Mg_2Cl_3 \cdot 6THF)^+ \cdot THF$

| | |
|---|---|
| Formula | $C_{44}H_{76}Cl_5Mg_2O_7Yb$ |
| Formula weight | 1116.1 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 16.911(5) |
| $b$, Å | 13.268(5) |
| $c$, Å | 13.772(4) |
| $\alpha$, ° | 116.52(2) |
| $\beta$, ° | 111.30(2) |
| $\gamma$, ° | 87.61(3) |
| $V$, Å$^3$ | 2549(1) |
| $Z$ | 2 |
| $D_{calc}$, g cm$^{-3}$ | 1.45 |
| $\mu$, cm$^{-1}$ | 22.6 |
| Radiation | Mo-$K_\alpha$ ($\lambda = 0.71069$ Å) |

monochromated Mo-$K_\alpha$ radiation, scan speed of 6°/min and scan range of 1.0°. One check reflection was measured after every 68 reflections. A total of 8270 reflections were collected within the range $3° < 2\theta < 55°$, of which 6566 reflections with $I > 2.5\sigma(I)$ were considered observed. No significant change was observed in the intensity of the check reflection, which shows that the crystal is stable during data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption. The crystallographic data are listed in Table 1.

The structure was solved by heavy-atom method and refined by block-diagonal least-squares method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced at theoretical positions. Further refinements led to final convergence at $R = 0.051$ and $R_w = 0.053$.

All calculations were performed with an Eclipse S/140 computer by a SHELXTL program system.

## Results and discussion

The coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 2, and main bond distances and angles are given in Tables 3 and 4.

The crystal structure study shows that the compound with component $(CH_3)_4C_2(C_5H_4)_2YbCl_2 \cdot Mg_2Cl_3 \cdot 7THF$ is mainly an ion-pair, which consists of the complex anion $[(CH_3)_4C_2(C_5H_4)_2YbCl_2]^-$ and complex cation $[Mg_2Cl_3 \cdot 6THF]^+$; a free THF is present in the lattice. Figures 1 and 2 depict the structures of the anion and the cation with atomic numbering schemes, respectively.

In the complex anion, the ytterbium atom is pseudotetrahedrally surrounded by the two chlorines and the two bridged cyclopentadienyl (Cp) rings. The cen(1)–Yb–cen(2) angle (cen = centroid of the Cp ring) 121.0° is smaller than the 135–140° in the $Cp'_2LnX_2ML_2$ complexes [6] ($Cp' = \eta^5$-$C_5Me_5$, Ln = lanthanide element and M = Li, Al), but similar to those observed in $(Me_2SiCp''_2NdCl)_2ClLi(THF)_2$ (121.3°) and $Me_2SiCp''_2$ $NdCH(SiMe_3)_2$ (121.6°) [5] ($Cp'' = \eta^5$-$C_5Me_4$), which have silicon-bridged ligands. In addition, the Cl(1)–Yb–Cl(2) angle of 96.7(1)° is comparable with Cl–Ln–Cl angle of 97.1(1)° in $(Me_2SiCp''_2NdCl)_2ClLi(THF)_2$ but larger than those of the complexes with non-bridged ligands, such as 85.95(2)° in $Cp'_2YbCl_2Li(ether)_2$, 87.14(3)° in $[CpSi(C_6H_5)_2Me]_2YbCl_2Li(ether)_2$ and 73.36(3)° in $Cp'_2YbCl_2AlCl_2$ [6]. These facts show that the steric effects for the various bridged ligands are similar. The steric effects of Cp or Cp′ rings which are not bridged are much greater than those of the corresponding bridged ligands, so that the chlorines are repelled to make the Cl–Ln–Cl angle smaller. The carbon atoms of each Cp ring are coplanar with the maximum deviation from the least-squares plane being 0.011 Å. The average Yb–C($\eta^5$) distance of 2.602(6) Å * is similar to those of the related ytterbium complexes [6,7].

The conformation of the bridged ligand that coordinates to a metal is of interest. The complex anion may be regarded as having an annular structure, that is, the two cen's, two carbons [C(11) and C(12)] and $Yb^{3+}$ form a 'five-membered ring'. The Cp

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* The average value is calculated as $\bar{x} = (\Sigma x_i)/n$ and the standard deviation as $\sigma(\bar{x}) = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$.

Table 2

Coordinates ($\times 10^5$ for Yb and $\times 10^4$ for others) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) for the non-hydrogen atoms

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Yb | 37443(2) | 19400(2) | 11134(3) | 32(0.2) |
| Cl(1) | 4285(2) | 2541(2) | −64(2) | 60(1) |
| Cl(2) | 2693(2) | 3385(2) | 1433(2) | 55(1) |
| C(1) | 3196(5) | −58(6) | 751(6) | 36(4) |
| C(2) | 2471(5) | 419(6) | 369(6) | 40(4) |
| C(3) | 2428(5) | 494(6) | −632(6) | 45(4) |
| C(4) | 3132(6) | 64(6) | −890(6) | 49(4) |
| C(5) | 3600(6) | −276(6) | −49(7) | 45(4) |
| C(6) | 4550(5) | 1492(6) | 2846(6) | 34(3) |
| C(7) | 5177(6) | 1725(9) | 2472(8) | 69(6) |
| C(8) | 5244(7) | 2900(10) | 2786(9) | 84(7) |
| C(9) | 4665(8) | 3379(8) | 3308(8) | 81(6) |
| C(10) | 4277(6) | 2525(6) | 3347(6) | 51(4) |
| C(11) | 3463(6) | −315(7) | 1788(7) | 55(5) |
| C(12) | 4302(7) | 377(7) | 2794(7) | 67(5) |
| C(13) | 2772(7) | 194(11) | 2437(10) | 95(8) |
| C(14) | 3290(10) | −1507(8) | 1382(9) | 136(9) |
| C(15) | 4492(8) | 485(10) | 3949(8) | 102(7) |
| C(16) | 5037(8) | −408(11) | 2441(13) | 127(10) |
| Mg(1) | 9517(2) | 7179(2) | 2773(2) | 26(1) |
| Mg(2) | 11117(2) | 6437(2) | 4272(2) | 28(1) |
| Cl(3) | 10657(1) | 8391(1) | 4816(1) | 34(1) |
| Cl(4) | 9536(1) | 5815(1) | 3568(1) | 32(1) |
| Cl(5) | 10773(1) | 6343(1) | 2313(1) | 31(1) |
| O(2) | 9578(3) | 8300(4) | 2102(4) | 33(2) |
| C(21) | 9580(5) | 7873(6) | 919(6) | 38(4) |
| C(22) | 10063(7) | 8848(8) | 993(8) | 74(6) |
| C(23) | 10389(10) | 9691(10) | 2206(10) | 134(9) |
| C(24) | 10043(7) | 9430(7) | 2811(7) | 67(5) |
| O(3) | 8568(3) | 7991(4) | 3329(4) | 31(2) |
| C(31) | 8382(5) | 8016(6) | 4288(6) | 39(4) |
| C(32) | 7746(5) | 8850(7) | 4501(6) | 46(4) |
| C(33) | 7284(5) | 8751(7) | 3277(7) | 45(4) |
| C(34) | 7994(5) | 8632(5) | 2826(6) | 32(3) |
| O(4) | 8592(3) | 6059(4) | 1152(4) | 29(2) |
| C(41) | 7736(6) | 5748(6) | 1014(7) | 43(4) |
| C(42) | 7429(6) | 4571(7) | 23(8) | 58(5) |
| C(43) | 8205(7) | 4132(7) | −199(9) | 67(6) |
| C(44) | 8763(5) | 5152(6) | 183(6) | 46(4) |
| O(5) | 11298(3) | 4730(4) | 3698(4) | 36(2) |
| C(51) | 11709(6) | 4208(6) | 4438(7) | 52(5) |
| C(52) | 11785(8) | 3057(7) | 3636(7) | 80(6) |
| C(53) | 11083(6) | 2739(6) | 2505(7) | 60(5) |
| C(54) | 10916(5) | 3849(5) | 2476(6) | 38(4) |
| O(6) | 12407(3) | 6869(4) | 4652(4) | 36(2) |
| C(61) | 12755(6) | 8011(7) | 5003(10) | 75(7) |
| C(62) | 13078(8) | 7834(17) | 4083(14) | 149(14) |
| C(63) | 13490(8) | 6799(13) | 3928(11) | 113(9) |
| C(64) | 12910(6) | 6102(8) | 4071(9) | 69(6) |
| O(7) | 11456(3) | 6707(4) | 5970(4) | 35(2) |
| C(71) | 12320(5) | 7034(8) | 6868(6) | 54(4) |
| C(72) | 12229(6) | 6937(8) | 7860(7) | 71(5) |
| C(73) | 11387(7) | 7363(8) | 7845(7) | 64(5) |

Table 2 (continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(74) | 10850(5) | 6936(6) | 6544(6) | 41(4) |
| O(8) | 6476(6) | 5499(9) | 2845(9) | 140(7) |
| C(81) | 6136(9) | 6251(13) | 3660(9) | 124(9) |
| C(82) | 5414(9) | 6593(15) | 3077(14) | 131(12) |
| C(83) | 5124(9) | 5840(12) | 1865(12) | 107(9) |
| C(84) | 5871(8) | 5287(12) | 1729(10) | 105(8) |

rings as shown in Fig. 1b have an almost eclipsed conformation viewed perpendicularly to the YbCl$_2$ plane. If the tetramethylethylene group was also eclipsed, the complex anion would be unstable because of the methyl steric interference. In fact, the tetramethylethylene adopts a distorted staggered conformation with the torsion angles: C(1)–C(11)–C(12)–C(6) = 23.3(5)°, C(13)–C(11)–C(12)–C(15) = 47.1(8)°, and C(14)–C(11)–C(12)–C(16) = 46.4(8)°. It can be seen from Table 4 that some bond angles about C(11) and C(12) deviate from the normal values owing to the crowding imposed by an imperfectly staggered conformation. This results in two kinds of C–CH$_3$ bonds, the axial bonds involving C(13) and C(16) with an average distance of 1.662(5) Å and the equatorial bonds involving C(14) and C(15) with an average distance 1.435(9) Å. It is noteworthy that both the bond angles C(1)–C(11)–C(12) and C(11)–C(12)–C(6) are 114.6(9)°, larger than the usual angles of a tetrahedron, which indicates that the 'five-membered ring' is strained. We conjecture that for Me$_4$C$_2$Cp$_2$LnCl$_2$ · Mg$_2$Cl$_3$ · $n$THF compounds, the C(1)–C(11)–C(12)

Table 3

Main bond distances (Å)

| | | | |
|---|---|---|---|
| Yb–Cl(1) | 2.528(3) | C(7)–C(8) | 1.416(18) |
| Yb–Cl(2) | 2.562(2) | C(8)–C(9) | 1.389(18) |
| Yb–C(1) | 2.612(8) | C(9)–C(10) | 1.364(17) |
| Yb–C(2) | 2.582(8) | C(11)–C(12) | 1.523(10) |
| Yb–C(3) | 2.601(6) | C(11)–C(13) | 1.666(17) |
| Yb–C(4) | 2.624(6) | C(11)–C(14) | 1.426(14) |
| Yb–C(5) | 2.615(7) | C(12)–C(15) | 1.443(16) |
| Yb–C(6) | 2.596(8) | C(12)–C(16) | 1.657(17) |
| Yb–C(7) | 2.564(9) | Mg(1)–Cl(3) | 2.549(2) |
| Yb–C(8) | 2.601(9) | Mg(1)–Cl(4) | 2.493(3) |
| Yb–C(9) | 2.624(8) | Mg(1)–Cl(5) | 2.509(3) |
| Yb–C(10) | 2.605(8) | Mg(1)–O(2) | 2.094(6) |
| C(1)–C(2) | 1.395(11) | Mg(1)–O(3) | 2.081(6) |
| C(1)–C(5) | 1.417(15) | Mg(1)–O(4) | 2.081(4) |
| C(1)–C(11) | 1.521(14) | Mg(2)–Cl(3) | 2.532(3) |
| C(2)–C(3) | 1.399(13) | Mg(2)–Cl(4) | 2.520(3) |
| C(3)–C(4) | 1.393(13) | Mg(2)–Cl(5) | 2.490(3) |
| C(4)–C(5) | 1.393(13) | Mg(2)–O(5) | 2.089(5) |
| C(6)–C(7) | 1.433(16) | Mg(2)–O(6) | 2.091(6) |
| C(6)–C(10) | 1.378(11) | Mg(2)–O(7) | 2.055(6) |
| C(6)–C(12) | 1.518(14) | | |

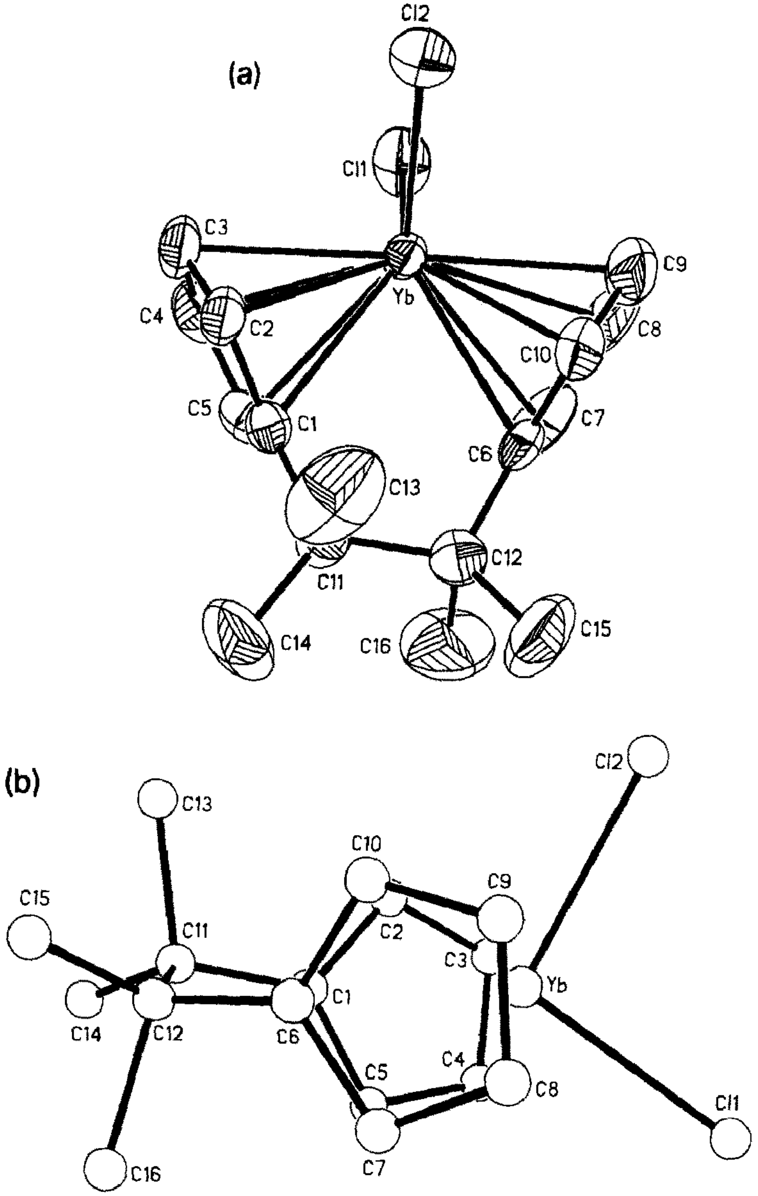

Fig. 1. (a) A perspective drawing of the complex anion $(Me_4C_2Cp_2YbCl_2)^-$. (b) A view perpendicular to the $YbCl_2$ plane, showing the conformations of the Cp rings and the tetramethylethylene group.

and C(11)–C(12)–C(6) angles will increase and the stability of the compounds will decrease with an increase in the ion radius of lanthanide. The assumption has been confirmed by the fact that $Me_4C_2Cp_2Mg_2Cl_2 \cdot 4THF$ treated with anhydrous $LnCl_3$ in a 1 : 2 molar ratio, if Ln = Yb, to give $Me_4C_2Cp_2LnCl_2Mg_2Cl_3 \cdot n$THF in 10-15% yield, and $Me_4C_2Cp_2Ln_2Mg_2\ Cl_8 \cdot n$THF, a reddish chain complex [8] in 85–90% yield. If Ln = Pr or Nd, the reddish chain complex is the sole product (yield 100%).

In the complex cation $(Mg_2Cl_3 \cdot 6THF)^+$, the two $Mg^{2+}$ ions, each of which is attached to three THF molecules, are bridged by three chlorines to form two

Table 4

Main bond angles ( ° )

| | | | |
|---|---|---|---|
| Cl(1)-Yb-Cl(2) | 96.7(1) | Cl(3)-Mg(1)-O(3) | 90.3(1) |
| C(2)-C(1)-C(5) | 105.4(8) | Cl(3)-Mg(1)-O(4) | 174.3(2) |
| C(2)-C(1)-C(11) | 126.2(8) | Cl(4)-Mg(1)-Cl(5) | 86.2(1) |
| C(5)-C(1)-C(11) | 128.4(7) | Cl(4)-Mg(1)-O(2) | 176.3(2) |
| C(1)-C(2)-C(3) | 109.6(8) | Cl(4)-Mg(1)-O(3) | 93.6(2) |
| C(2)-C(3)-C(4) | 108.0(7) | Cl(4)-Mg(1)-O(4) | 91.3(2) |
| C(3)-C(4)-C(5) | 107.1(9) | Cl(5)-Mg(1)-O(2) | 90.2(2) |
| C(4)-C(5)-C(1) | 109.8(8) | Cl(5)-Mg(1)-O(3) | 174.0(1) |
| C(7)-C(6)-C(10) | 104.6(8) | Cl(5)-Mg(1)-O(4) | 95.3(2) |
| C(7)-C(6)-C(12) | 127.3(8) | O(2)-Mg(1)-O(3) | 89.9(2) |
| C(10)-C(6)-C(12) | 128.0(9) | O(2)-Mg(1)-O(4) | 89.8(2) |
| C(6)-C(7)-C(8) | 107.3(9) | O(3)-Mg(1)-O(4) | 90.8(2) |
| C(7)-C(8)-C(9) | 108.7(12) | Cl(3)-Mg(2)-Cl(4) | 82.8(1) |
| C(8)-C(9)-C(10) | 106.2(10) | Cl(3)-Mg(2)-Cl(5) | 84.4(1) |
| C(9)-C(10)-C(6) | 113.2(10) | Cl(3)-Mg(2)-O(5) | 171.3(2) |
| C(1)-C(11)-C(12) | 114.6(9) | Cl(3)-Mg(2)-O(6) | 99.2(2) |
| C(1)-C(11)-C(13) | 106.4(8) | Cl(3)-Mg(2)-O(7) | 90.4(2) |
| C(1)-C(11)-C(14) | 110.3(7) | Cl(4)-Mg(2)-Cl(5) | 86.1(1) |
| C(12)-C(11)-C(13) | 100.5(7) | Cl(4)-Mg(2)-O(5) | 88.6(2) |
| C(12)-C(11)-C(14) | 120.5(9) | Cl(4)-Mg(2)-O(6) | 173.4(2) |
| C(13)-C(11)-C(14) | 102.1(11) | Cl(4)-Mg(2)-O(7) | 97.4(2) |
| C(6)-C(12)-C(11) | 114.6(8) | Cl(5)-Mg(2)-O(5) | 93.9(2) |
| C(6)-C(12)-C(15) | 112.0(7) | Cl(5)-Mg(2)-O(6) | 87.9(2) |
| C(6)-C(12)-C(16) | 103.8(10) | Cl(5)-Mg(2)-O(7) | 173.4(2) |
| C(11)-C(12)-C(15) | 119.8(11) | O(5)-Mg(2)-O(6) | 89.2(2) |
| C(11)-C(12)-C(16) | 103.5(6) | O(5)-Mg(2)-O(7) | 91.9(2) |
| C(15)-C(12)-C(16) | 100.1(10) | O(6)-Mg(2)-O(7) | 88.9(2) |
| Cl(3)-Mg(1)-Cl(4) | 83.0(1) | Mg(1)-Cl(3)-Mg(2) | 77.4(1) |
| Cl(3)-Mg(1)-Cl(5) | 83.7(1) | Mg(1)-Cl(4)-Mg(2) | 78.6(1) |
| Cl(3)-Mg(1)-O(2) | 95.9(1) | Mg(1)-Cl(5)-Mg(2) | 78.9(1) |

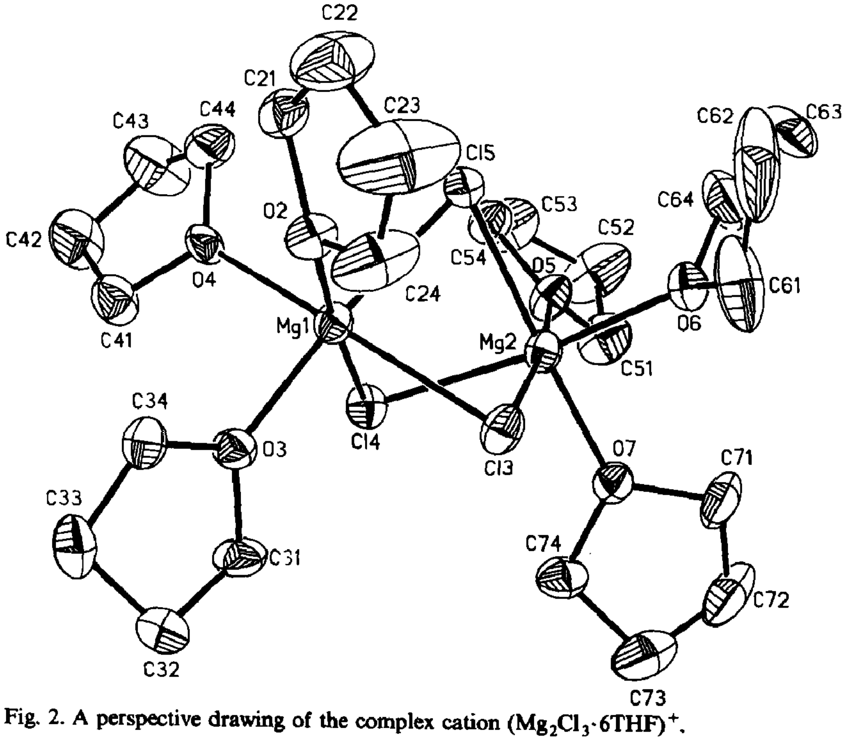

Fig. 2. A perspective drawing of the complex cation $(Mg_2Cl_3 \cdot 6THF)^+$.

distorted octahedra linked together through three common edges. The intersect angles of the three Mg–Cl–Mg planes in the $Mg_2Cl_3$ unit are 63.3, 60.8 and 55.9°, showing a trigonal bipyramid. That the average Mg–Cl distance of 2.516(9) Å is in accord with the sum of ion radii for $Mg^{2+}$ and $Cl^-$ (2.53 Å) [9] suggests that the Mg–Cl–Mg bridging bonds are ionic.

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