

Synthesis and X-ray Crystal Structure of the $\text{TiMgCl}_5\text{OH}(\text{CH}_3\text{COOC}_2\text{H}_5)_4$ Adduct

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(Received October 26, 1987)

Abstract

The reaction between MgClOH and TiCl_4 in ethylacetate solution affords an unusual binuclear Mg-Ti complex arising from a OH ligand exchange between Mg and Ti atoms. The molecular and crystal structure of the title adduct has been determined by X-ray diffraction. The structure was solved by direct and Fourier methods and refined by blocked full-matrix least-squares to $R = 0.078$ using 4031 observed reflections. The crystal system is triclinic, space group $P\bar{1}$, with two molecules per cell. The unit cell constants are $a = 9.623(3)$, $b = 9.783(3)$, $c = 17.015(5)$ Å, $\alpha = 99.82(2)^\circ$, $\beta = 96.49(2)^\circ$ and $\gamma = 111.15(2)^\circ$. The structure is built up from binuclear molecules, Mg and Ti atoms are placed within two slightly deformed octahedra sharing an edge by a double chlorine bridge. The structure undergoes a high degree of positional disorder, which obviously limits the accuracy of the results.

Introduction

Binary halide complexes of Group IV(B) and V(B) transition metals have been prepared by the reaction of tetra and trivalent halides with chloride ion donors either as molten salts or in amphoteric aprotic solvents [1–4]. Depending on reaction conditions penta- and hexa-halocomplexes are usually obtained, although binuclear compounds have also been reported [5].

However, defined mixed chlorides are formed very often only in the presence of electron donor molecules [6]. Actually chloride-ion transfer from divalent metal chlorides occurs more easily in the presence of suitable Lewis bases which can stabilize the resulting cation.

Extensive work by Driessen and Groeneveld [7–11] on the existence of complexes of divalent metals

with weakly coordinating ligands pointed out that relatively large anions are needed to stabilize metal ions with weakly coordinating ligands. In the last ten years great attention has been drawn to magnesium halide supported catalysts for ethylene and propylene polymerizations. In spite of the enormous number of different claims, the most successful catalyst systems are based on a surprisingly limited number of basic ingredients. They comprise MgCl_2 , TiCl_4 , and a Lewis base. Accordingly, the chemistry and properties of binuclear Mg-Ti halocomplexes should be taken into account.

In this connection, in the last few years extensive work has been undertaken in our laboratories on the existence of complexes between MgCl_2 and TiCl_4 . Previous papers were devoted to both their syntheses and X-ray structure [12–14]. This class of compounds, in conjunction with organoaluminium compounds, is able to polymerize ethylene with fairly high productivity [15].

In this paper we now report the synthesis and X-ray structure of a unique Ti(IV) compound arising from the reaction between MgClOH and TiCl_4 in ethylacetate. The main surprising feature of this compound is due to an unexpected shift from Mg to Ti of the hydroxyl ligand leading to a non-polymeric hydroxy-chloro titanium complex.

Experimental

Synthesis of the $\text{TiMgCl}_5(\text{OH}) \cdot 4(\text{CH}_3\text{COOC}_2\text{H}_5)$ adduct

In a three-necked Schlenk tube, equipped with a magnetic stirrer, reflux condenser, and a nitrogen inlet, were placed 24.4 mmol $\text{Mg}(\text{OH})\text{Cl}$ and 160 ml anhydrous $\text{CH}_3\text{COOC}_2\text{H}_5$. The suspension was heated to 60°C and TiCl_4 (24.4 mmol) was slowly added under vigorous stirring. A yellow colour developed quite soon. The resulting hot solution was filtered and concentrated under vacuum to small volume. On standing overnight 13.3 g of yellow crystals were obtained.

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Elemental analyses were performed by the Analytical Department of the Donegani Institute as already reported [16]. Ethyl acetate was determined by G.C. The analytical data agree with the formula $\text{TiMgCl}_5(\text{OH})\cdot 4(\text{CH}_3\text{COOC}_2\text{H}_5)$. Found: C, 29.65; H, 4.98; Mg, 3.70; Ti, 7.80; Cl, 31.78, ethyl acetate, 53.17. Calc. for $\text{C}_{16}\text{H}_{33}\text{O}_9\text{MgTiCl}_5$: C, 31.05; H, 5.37; Mg, 3.93; Ti, 7.74; Cl, 28.64; ethyl acetate, 56.94%.

The IR spectrum shows the hydroxyl stretching band at 3360 cm^{-1} and the characteristic absorptions of the carbonyl group of the complexed $\text{CH}_3\text{COOC}_2\text{H}_5$ (1685 and 1730 cm^{-1}).

X-ray Analysis

A single yellow crystal of approximate size $0.3 \times 0.4 \times 0.5$ mm placed in a glass capillary tube, sealed under dry nitrogen, was mounted on a ENRAF-NONIUS CAD-4 diffractometer at room temperature. Intensity data were collected by the use of graphite monochromated $\text{Mo K}\alpha$ radiation, using $\theta/2\theta$ scan technique. The unit cell dimensions were obtained by a least-squares fit of 18 reflections. 7116 independent reflections ($h \pm 12, k \pm 12, l \pm 22$) were collected in the range $3^\circ \leq \theta \leq 30^\circ$, of which 4031 were considered observed having $I > 3\sigma(I)$. Three standard reflections, periodically monitored, ascertained crystal stability. All intensities were corrected for Lorentz and polarization effects, while no adsorption correction was deemed necessary.

The structure was solved by direct methods using MULTAN 80 program [17], followed by successive difference Fourier maps. Further refinement in the space group $P\bar{1}$ gave the remainder of the structure, but two collections of peaks bonded to Ti and Mg atoms respectively, both in the equatorial position, indicated two sites of disorder. The hydroxyl oxygen bonded to Ti was found to be equatorial (equatorial plane being defined as the plane containing the two bridging Cl atoms) and involved in statistical substitution with one of the terminal Cl atoms. To locate these atoms, each of the two equatorial positions bonded to Ti was splitted and the O and Cl atoms were refined as four separate entities each of them with a site occupation factor fixed at 0.5.

A more precise location was unsuccessful therefore no other attempt was made to locate the H hydroxyl atom. During the refinement the two distances Ti—O and Ti—Cl were constrained in all but the last least-squares cycle. Owing to this constraint, the coordinates of the Cl and O atoms were found to be very strongly correlated. Disorder of the atoms over two positions affects also one of the two ethylacetate residues equatorially bonded to Mg atoms (that one in position 3 in Fig. 1). Accordingly the atoms of this residue, splitted in two positions, were refined with s.o.f. equal to 0.5 be-

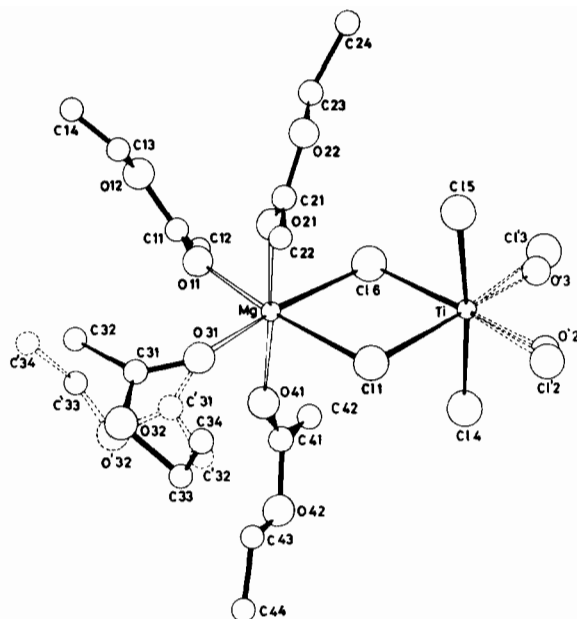


Fig. 1. A perspective view of the $\text{TiMgCl}_5\text{OH}(\text{CH}_3\text{COOC}_2\text{H}_5)_4$ adduct with the atom numbering scheme.

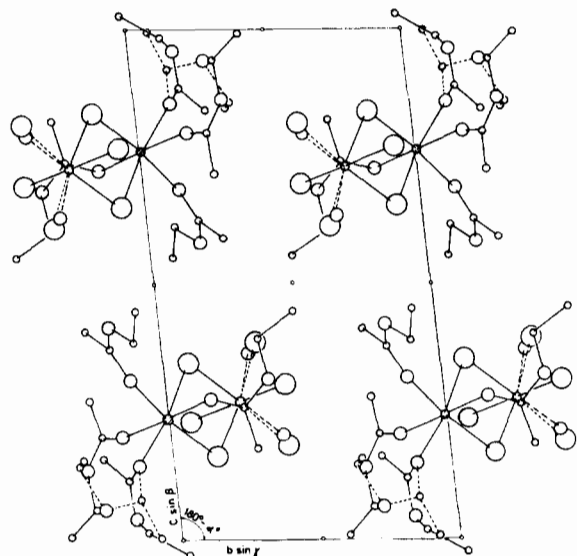


Fig. 2. Packing arrangement of the $\text{TiMgCl}_5\text{OH}(\text{CH}_3\text{COOC}_2\text{H}_5)_4$ adduct as viewed down the a axis.

cause any attempt to refine the accuracy factors failed.

Difficulties were also found in locating the ethyl group of the residue named 4 whose high thermal parameters suggest some degree of rotational disorder. The blocked full-matrix least-squares refinement was carried out with anisotropic temperature factors for all non-H atoms with the exception of the splitted atoms of the disordered ethylacetate group. Hydrogen atoms were located in fixed positions on the basis of F map or on stereochemical grounds.

The final discrepancy factors, based on the observed reflections and calculated with a weighting function of the form $1/w = \sigma(F_o) + 0.0018|F_o|$, were $R = 0.078$ and $R_w = 0.088$.

The final atomic coordinates for non-H atoms with the equivalent isotropic temperature factors are listed in Table I. An arbitrary view of the molecule showing the atom numbering scheme is given in Fig. 1, while some selected geometrical parameters are reported in Table II. The packing arrangement of the adduct is shown in Fig. 2. See also 'Supplementary Material'.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) for Non-H Atoms and Equivalent Isotropic Temperature Factors B (\AA^2)^a

Atom	x	y	z	B
Ti	212(1)	2582(1)	2717(1)	4.3(1)
Cl(1)	1019(2)	857(2)	3473(1)	4.4(1)
Cl'(2)	-457(5)	4119(5)	1835(2)	4.5(2)
O'(2)	-408(11)	3999(10)	2035(5)	2.4(2)
O'(3)	-701(9)	3084(8)	3658(4)	2.8(2)
Cl'(3)	-508(4)	3354(4)	3880(2)	4.2(2)
Cl(4)	-2097(2)	694(2)	2337(1)	6.6(1)
Cl(5)	2604(2)	4333(2)	3047(1)	5.6(1)
Cl(6)	1135(2)	1554(2)	1617(1)	4.5(1)
Mg	2107(2)	-119(2)	2408(1)	3.8(1)
O(11)	2883(5)	-1313(5)	3151(3)	5.8(2)
C(11)	2902(7)	-1913(6)	3755(4)	4.8(2)
O(12)	4142(5)	-1869(5)	4176(2)	5.4(2)
C(12)	1539(8)	-2732(8)	4121(5)	7.3(2)
C(13)	5577(8)	-1013(9)	3878(5)	8.3(2)
C(14)	6812(9)	-843(9)	4460(5)	7.9(2)
O(21)	4124(4)	1530(4)	2767(3)	5.2(2)
C(21)	5058(6)	2677(6)	2607(4)	4.8(2)
O(22)	5939(4)	3693(4)	3163(2)	4.9(2)
C(22)	5317(7)	3039(8)	1795(4)	6.5(2)
C(23)	5730(7)	3431(7)	3967(4)	5.9(2)
C(24)	6645(8)	4881(8)	4470(5)	7.4(2)
O(31)	2858(5)	-777(5)	1454(3)	6.0(2)
C(31)	3356(11)	-1698(11)	1156(7)	4.9(1)
O(32)	3248(10)	-1896(10)	375(6)	6.9(1)
C(32)	4062(13)	-2593(12)	1591(8)	6.2(1)
C(33)	2166(15)	-1293(14)	-151(10)	7.8(1)
C(34)	3284(16)	197(16)	-297(11)	10.7(2)
C'(31)	2715(15)	-1342(15)	782(11)	8.8(1)
O'(32)	2616(12)	-2687(12)	618(8)	9.3(1)
C'(32)	2401(15)	-698(14)	-37(11)	8.1(1)
C'(33)	2972(16)	-3432(16)	1465(12)	11.1(2)
C'(34)	4390(17)	-3343(17)	1535(14)	14.1(2)
O(41)	139(4)	-1829(4)	2006(3)	5.8(2)
C(41)	-1161(7)	-2564(6)	2035(4)	5.7(2)
O(42)	-2112(5)	-3236(5)	1382(3)	6.9(2)
C(42)	-1868(8)	-2820(8)	2766(5)	7.2(2)
C(43)	-1449(10)	-3029(10)	629(6)	10.1(2)
C(44)	-2634(14)	-4106(13)	55(7)	14.7(2)

^ae.s.d.s. given in parentheses.

TABLE II. Molecular Dimensions

Bond lengths (\AA)	
Ti-Cl(1)	2.458(2)
Ti-Cl'(2)	2.373(6)
Ti-O'(2)	2.054(8)
Ti-O'(3)	2.032(8)
Ti-Cl'(3)	2.347(4)
Ti-Cl(4)	2.316(2)
Ti-Cl(5)	2.306(2)
Ti-Cl(6)	2.477(2)
Cl(1)-Mg	2.504(3)
Cl(6)-Mg	2.531(3)
Mg-O(11)	2.020(5)
Mg-O(21)	2.029(4)
Mg-O(31)	2.017(6)
Mg-O(41)	2.040(4)
O(11)-C(11)	1.209(8)
C(11)-O(12)	1.306(8)
C(11)-C(12)	1.491(10)
O(12)-C(13)	1.492(9)
C(13)-C(14)	1.414(11)
O(21)-C(21)	1.224(6)
C(21)-O(22)	1.311(6)
C(21)-C(22)	1.470(10)
O(22)-C(23)	1.427(8)
C(23)-C(24)	1.526(9)
O(31)-C(31)	1.273(14)
O(31)-C'(31)	1.216(18)
C(31)-O(32)	1.321(16)
C(31)-C(32)	1.468(19)
O(32)-C(33)	1.587(19)
C(33)-C(34)	1.519(18)
C'(31)-O'(32)	1.299(20)
C'(31)-C'(32)	1.600(25)
O'(32)-C'(33)	1.702(23)
C'(33)-C'(34)	1.327(24)
O(41)-C(41)	1.205(7)
C(41)-O(42)	1.329(8)
C(41)-C(42)	1.474(11)
O(42)-C(43)	1.486(11)
C(43)-C(44)	1.464(13)
Bond angles ($^\circ$)	
Cl(5)-Ti-Cl(6)	88.3(1)
Cl(4)-Ti-Cl(6)	87.3(1)
Cl(4)-Ti-Cl(5)	175.1(1)
Cl'(3)-Ti-Cl(6)	171.4(1)
Cl'(3)-Ti-Cl(5)	90.5(1)
Cl'(3)-Ti-Cl(4)	93.6(1)
O'(3)-Ti-Cl(6)	170.8(2)
O'(3)-Ti-Cl(5)	98.0(2)
O'(3)-Ti-Cl(4)	86.1(2)
O'(2)-Ti-Cl(6)	94.0(2)
O'(2)-Ti-Cl(5)	90.4(3)
O'(2)-Ti-Cl(4)	92.0(3)
O'(2)-Ti-Cl'(3)	94.5(3)
O'(2)-Ti-O'(3)	92.7(3)
Cl'(2)-Ti-Cl(6)	89.2(1)
Cl'(2)-Ti-Cl(5)	90.9(1)
Cl'(2)-Ti-Cl(4)	91.2(1)
Cl'(2)-Ti-Cl'(3)	99.3(2)
Cl'(2)-Ti-O'(3)	97.5(3)

(continued)

TABLE II. (continued)

Bond angles (°)	
Cl(1)–Ti–Cl(6)	83.0(1)
Cl(1)–Ti–Cl(5)	89.0(1)
Cl(1)–Ti–Cl(4)	88.3(1)
Cl(1)–Ti–Cl'(3)	88.5(1)
Cl(1)–Ti–O'(3)	90.3(2)
Cl(1)–Ti–O'(2)	176.9(3)
Cl(1)–Ti–Cl'(2)	172.2(1)
Ti–Cl(1)–Mg	98.5(1)
Ti–Cl(6)–Mg	97.3(1)
Cl(1)–Mg–Cl(6)	80.9(1)
Cl(6)–Mg–O(41)	89.0(2)
Cl(6)–Mg–O(31)	91.8(2)
Cl(6)–Mg–O(21)	92.0(1)
Cl(6)–Mg–O(11)	173.5(2)
Cl(1)–Mg–O(41)	93.9(2)
Cl(1)–Mg–O(31)	172.7(2)
Cl(1)–Mg–O(21)	89.4(2)
Cl(1)–Mg–O(11)	93.0(2)
O(31)–Mg–O(41)	84.9(2)
O(21)–Mg–O(41)	176.7(2)
O(21)–Mg–O(31)	92.0(2)
O(11)–Mg–O(41)	93.9(2)
O(11)–Mg–O(31)	94.2(2)
O(11)–Mg–O(21)	85.5(2)
Mg–O(11)–C(11)	152.5(5)
O(11)–C(11)–C(12)	124.5(7)
O(11)–C(11)–O(12)	123.0(6)
O(12)–C(11)–C(12)	112.3(6)
C(11)–O(12)–C(13)	116.4(5)
O(12)–C(13)–C(14)	109.7(7)
Mg–O(21)–C(21)	146.3(4)
O(21)–C(21)–C(22)	124.1(6)
O(21)–C(21)–O(22)	121.9(6)
O(22)–C(21)–C(22)	114.0(5)
C(21)–O(22)–C(23)	117.1(5)
O(22)–C(23)–C(24)	106.3(5)
Mg–O(31)–C'(31)	154.4(8)
Mg–O(31)–C(31)	146.2(6)
O(31)–C(31)–C(32)	126.9(10)
O(31)–C(31)–O(32)	118.4(10)
O(32)–C(31)–C(32)	114.7(10)
C(31)–O(32)–C(33)	118.4(10)
O(32)–C(33)–C(34)	100.3(11)
O(31)–C'(31)–C'(32)	127.9(12)
O(31)–C'(31)–O'(32)	123.7(15)
O'(32)–C'(31)–C'(32)	107.9(13)
C'(31)–O(32)–C'(33)	110.4(13)
O'(32)–C'(33)–C'(34)	107.8(14)
Mg–O(41)–C(41)	152.7(5)
O(41)–C(41)–C(42)	125.3(6)
O(41)–C(41)–O(42)	121.6(6)
O(42)–C(41)–C(42)	113.1(6)
C(41)–O(42)–C(43)	115.2(6)
O(42)–C(43)–C(44)	102.9(8)
Selected torsion angles (°)	
Cl(5)–Ti–Cl(6)–Mg	86.2(1)
Cl(4)–Ti–Cl(6)–Mg	–91.7(1)
O'(2)–Ti–Cl(6)–Mg	176.5(3)

(continued)

TABLE II. (continued)

Selected torsion angles (°)	
Cl'(2)–Ti–Cl(6)–Mg	177.1(3)
Cl(1)–Ti–Cl(6)–Mg	–3.1(1)
O'(3)–Ti–Cl(1)–Mg	176.7(2)
Cl'(3)–Ti–Cl(1)–Mg	–175.7(1)
Cl(4)–Ti–Cl(1)–Mg	90.6(1)
Cl(5)–Ti–Cl(1)–Mg	–85.3(1)
Cl(6)–Ti–Cl(1)–Mg	3.2(1)
Ti–Cl(1)–Mg–O(11)	174.5(2)
Ti–Cl(1)–Mg–O(21)	89.0(2)
Ti–Cl(1)–Mg–O(41)	–91.4(2)
Ti–Cl(1)–Mg–Cl(6)	–3.1(1)
Ti–Cl(6)–Mg–Cl(1)	3.0(1)
Ti–Cl(6)–Mg–O(21)	–86.0(2)
Ti–Cl(6)–Mg–O(31)	–178.0(2)
Ti–Cl(6)–Mg–O(41)	97.1(2)
Cl(6)–Mg–O(41)–C(41)	–84.3(10)
Cl(1)–Mg–O(41)–C(41)	–3.4(10)
Cl(6)–Mg–O(31)–C(31)	–167.4(11)
Cl(6)–Mg–O(21)–C(21)	–29.0(8)
Cl(1)–Mg–O(21)–C(21)	–110.0(8)
Cl(1)–Mg–O(11)–C(11)	18.9(10)
O(31)–Mg–O(41)–C(41)	–176.2(11)
O(11)–Mg–O(41)–C(41)	89.9(10)
O(21)–Mg–O(31)–C(31)	100.5(11)
O(11)–Mg–O(31)–C(31)	14.9(11)
O(11)–Mg–O(21)–C(21)	157.0(8)
O(21)–Mg–O(11)–C(11)	108.0(11)
O(31)–Mg–O(11)–C(11)	–160.4(10)
O(41)–Mg–O(11)–C(11)	–75.2(10)
O(31)–Mg–O(21)–C(21)	62.9(8)
O(41)–Mg–O(31)–C(31)	–78.6(11)
Mg–O(11)–C(11)–O(12)	–138.8(8)
Mg–O(11)–C(11)–C(12)	38.8(14)
O(11)–C(11)–O(12)–C(13)	0.6(9)
C(12)–C(11)–O(12)–C(13)	–177.3(6)
C(11)–O(12)–C(13)–C(14)	169.5(6)
Mg–O(21)–C(21)–O(22)	151.2(5)
Mg–O(21)–C(21)–C(22)	–29.8(11)
O(21)–C(21)–O(22)–C(23)	–2.2(9)
C(22)–C(21)–O(22)–C(23)	178.7(5)
C(21)–O(22)–C(23)–C(24)	–168.7(5)
Mg–O(31)–C(31)–O(32)	158.6(8)
Mg–O(31)–C(31)–C(32)	–21.5(19)
O(31)–C(31)–O(32)–C(33)	–14.8(16)
C(32)–C(31)–O(32)–C(33)	165.4(10)
C(31)–O(32)–C(33)–C(34)	94.9(13)
Mg–O(41)–C(41)–O(42)	149.0(7)
Mg–O(41)–C(41)–C(42)	–31.1(15)
O(41)–C(41)–O(42)–C(43)	0.7(10)
C(42)–C(41)–O(42)–C(43)	–179.2(6)
C(41)–O(42)–C(43)–C(44)	168.8(7)

Results and Discussion

The structure consists of two slightly distorted octahedral arrangements one around Ti and the other around the Mg atom. Ti(IV) is octahedrally coordinated by five chlorine atoms and by one

hydroxyl ligand. The Mg atom is similarly coordinated by the carbonyl oxygens of four ethylacetate molecules and by two bridging Cl atoms. The two octahedra share an edge by the double chlorine bridge between Ti and Mg. The four carbonyl oxygens of the ethylacetate ligands act as a donor towards the Mg atom. The hydroxyl oxygen, equatorially bonded to the Ti atom, undergoes statistical substitution with a chlorine atom. Each of the two atoms are splitted in two separate positions with s.o.f. 0.5. Analogously the ethylacetate moiety in position 3 appears distorted over two positions with site occupancy 0.5. The geometry of the title compound is to be compared with those of the strictly related $\text{TiMgCl}_6(\text{CH}_3\text{COOC}_2\text{H}_5)_4$ (hereafter **II**) and $\text{TiMgCl}_5(\text{OOCCH}_2\text{Cl})\cdot(\text{ClCH}_2\text{COOC}_2\text{H}_5)_3$ (hereafter **III**) adducts [14], the last one having an additional carboxylic ligand bridging the Ti and Mg atoms. The mean Ti–Cl (non-bridging) distance of 2.335(4) Å is considerably longer than the corresponding mean distances observed in **II** and **III** and in many other TiCl_4 adducts [18, 19]. In fact the average Ti–Cl (non-bridging) bond length, involving Ti(IV) in an octahedral arrangement, is expected to be in the range 2.20–2.25 Å [14, 20, 21]. Taking into account only the Ti(IV) octahedrally coordinated adducts, a longer Ti–Cl distance was found in one Ti–Cl bond of the TiCl_6 moiety of complex **III** [22, 23] and in the $[\text{Ti(IV)Cl}_5(\text{THF})]$ anion [24].

The mean Ti–Cl (bridging) length of 2.468(2) Å agrees well with that of **II** but is longer than the average distance found in **III**, where the Mg and Ti interatomic distance is closer owing to the further carboxyl bridge. Accordingly, the non-bonded Ti–Mg distance of 3.761(3) Å found in the title structure is longer than in the more constrained moiety in **III** (3.61 Å).

The Mg–Cl distances are close to the values found in **II** and **III**. The average Mg–O length of 2.027(4) Å is in agreement with the expected value [24]. The mean values of the Cl–Ti–Cl and Cl–Ti–O bond angles are 89.83(2)° and 173.57(2)° and the mean values of Cl–Mg–O and Cl–Mg–Cl bond angles are 90.04(2)° and 174.31(2)°, showing a quite slight deviation from the ideal octahedral coordination around the Ti and Mg atoms.

The ethylacetate ligands 1, 2 and 4 display the same conformation, while some differences have been found for residue 3 owing to disorder. Disorder may account for some highly distorted bond lengths which can otherwise hardly be explained. The Mg–O(1)–C(1)–C(2) torsion angle is nearly 30° for residues 1, 2 and 3, while a value close to gauche conformation was found in 4. The Mg–O(1)–C(1)–O(2) torsion angle is nearly 150° in 1, 2 and 4 and about 100° in 3. The coordination of carbonyl carbon is planar in molecule 2, 3 and 4 and only slightly

TABLE III. Some Non-bonded Intra and Intermolecular Contacts

Atoms	O...C (Å)	Symmetry operation for C
O(11)...C(31)	3.49(1)	x, y, z
O(11)...C(32)	3.35(1)	x, y, z
O(41)...C'(31)	3.33(2)	x, y, z
O(22)...C(42)	3.45(1)	$x + 1, y + 1, z$
O(32)...C(34)	3.16(1)	$-x + 1, -y, -z$
O'(32)...C(44)	3.29(2)	$-y, -y - 1, -z$
O(42)...C'(34)	3.37(2)	$x - 1, y, z$

distorted in 1 and 3. In residue 1, 2 and 4 the O(1)–C(1) and O(2)–C(3) bonds are in *cis* positions across the C(1)–O(2) bond while the C(1)–O(2) bond is *trans* with respect to the C(3)–C(4) bond across O(2)–C(3).

A similar succession of torsion angles has been found in **II** and **III**, in $(\text{TiCl}_4\cdot\text{O}_3\text{C}_{10}\text{H}_{12})_2$ [19] and $(\text{TiCl}_4\cdot\text{CH}_3\text{COOC}_2\text{H}_5)_2$ [18]. The different conformation adopted by the residue 3 and 3' is to be related with the positional disorder found in this part of the molecule. The crystal packing is governed by some short non-bonded contacts of the O...C type. The shortest (less than 3.5 Å) intermolecular distances are reported in Table III.

As a final remark, it should be pointed out that the existence of a Ti(IV) compound having either an OH or a Cl ligand is rather unexpected. It is well known that transition metal compounds of group IV(B) are strongly oxophilic in nature so that they display a great reactivity towards hydroxilic molecules. Moreover, the tendency of the metal to expand its coordination number goes hand in hand with the high bridging properties of oxygen atoms. These two features dominate the chemical and physical properties of Ti–O compounds leading to a class of complex, highly bridging molecules [25]. Accordingly, by reaction under appropriate conditions of MgClOH and TiCl_4 , one should expect HCl evolution with the consequent formation of an oxo-bridged moiety. In our knowledge, the OH/Cl ligand exchange from MgClOH to TiCl_4 reported in this paper has never been observed for IV(B) transition metals, constituting an unique example in the chemistry of Ti–O compound [26].

Supplementary Material

Lists of the observed and calculated structure factors, of the anisotropic thermal parameters and of the fractional atomic coordinates for H atoms are available from the authors on request.

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