Synthesis and X-ray crystal structure of the $[Ti_2(OC_2H_5)_8Cl]_2Mg_2(\mu\text{-}Cl)_2$ complex

L. Malpezzi*
Dipartimento di Chimica del Politecnico, P.zza L. da Vinci 32, 20133 Milan (Italy)

U. Zucchini and **T. Dall'Occo**
Centro Ricerche G. Natta, HIMONT ITALIA, P. le Donegani 12, 44100 Ferrara (Italy)

(Received May 17, 1990; revised September 24, 1990)

Abstract

The reaction between $Ti(OC_2H_5)_4$ and $MgCl_2$ in the 2:1 stoichiometric ratio yields the title bimetallic complex from which single crystals were obtained after recrystallization from n-heptane solution. The molecular structure was determined by X-ray diffraction. The molecule crystallizes in the monoclinic, space group $P2_1/n$ system, with two molecules per unit cell and $a=13.900(9)$, $b=14.624(8)$, $c=13.982(8)$ Å and $\beta=95.05(4)°$, $V=2831(3)$ Å^3, $D_{calc}=1.292$ g/cm^3. A high degree of position disorder affecting some ethyl groups limits the accuracy of the refinement and causes a rather high final discrepancy factor R of 0.076. The molecule is centrosymmetric and lies on a crystallographic centre of symmetry. The asymmetric unit in the cell, i.e. half molecule, is built up by three face-shared pseudooctahedra centered on the two Ti and Mg atoms and is surrounded by the eight terminal ethyl groups. The two asymmetric parts of the molecule are bonded to each other by a double chlorine bridge between the two Mg atoms. Some speculations on a possible way to form the complex are presented.

Introduction

The discovery, in the late sixties, of the so called 'high activity' Ziegler–Natta catalysts for the polymerization of ethylene and, in the early seventies, of alpha-olefins, has allowed enormous industrial development in the field and has also stimulated many scientific studies worldwide. These modern catalysts are mainly composed by magnesium chloride and a titanium halide with, or without, an electron donor and are effective together with an aluminum alkyl. Aiming to clarify the origins of this 'high activity', several researchers from different laboratories studied bimetallic halide complexes of magnesium and titanium prepared in electron donor solvents, such as ethylacetate [1], ethylchloroacetate [2], tetrahydrofurane [3] and phosphorous oxychloride [4]. These complexes show well-defined stoichiometry, ionic character only in some cases [3, 4] and crystalline structure that has been investigated by single crystal X-ray diffraction [1–3].

In this connection, due to our interest in studying the behaviour in the ethylene polymerization [5] of catalysts from $MgCl_2$ and titanium tetra-alkoxides, instead of titanium halides, a work was undertaken on complexes between $Ti(OR)_4$, where R is an alkyl, and $MgCl_2$. From the patent literature [6, 7], it was known that $MgCl_2$ easily dissolves in some titanium tetra-alkoxides. However, in only one case had the reaction product been isolated [8] showing, by powder X-ray diffraction, an essentially crystalline structure. Nevertheless no information either on the nature or on the type of the formed complex had been given.

This paper deals with the synthesis and the X-ray structure of the complex arising from the 1:2 stoichiometric reaction between $MgCl_2$ and $Ti(OC_2H_5)_4$.

Experimental

The synthesis and all other manipulations were carried out under a dry nitrogen atmosphere [9]. Solvents were purified and dried by known methods [10]. $MgCl_2$ was an anhydrous powder product (water content less than 0.3 wt.%). $Ti(OC_2H_5)_4$ was prepared from $TiCl_4$ and anhydrous ethyl alcohol according to the literature method [11] and then distilled under vacuum (116 °C, 0.03 mm Hg).

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

Synthesis of the [$Ti_2(OC_2H_5)_8Cl]_2Mg_2(\mu$-$Cl)_2$ complex

$MgCl_2$ (72 mmol) and $Ti(OC_2H_5)_4$ (30 ml) were introduced into a three necked round bottom flask equipped with magnetic stirrer, reflux condenser and nitrogen inlet. The suspension was warmed up to 80 °C, dry n-heptane (150 ml) was added and finally it was refluxed until complete dissolution of the salt was obtained (3 h). The obtained colorless solution was filtered at 80 °C and then slowly cooled to room temperature. After 4 h residence time at r.t. and one night at 0 °C, the solid product obtained was filtered off and then recrystallized from dry n-heptane (200 ml). A total of 20.1 g of transparent colorless crystals was obtained. An additional 7.4 g of crystalline product were recovered from the mother liquid (69 wt.% total yield based on the $MgCl_2$).

The elemental analyses agree with the molecular formula $Ti_2(OC_2H_5)_8Cl]_2Mg_2(\mu$-$Cl)_2$. *Anal.* Found: Mg, 4.65; Ti, 18.05; Cl, 12.75; C, 34.46; H, 7.35. Calc. for $C_{32}H_{80}O_{16}Mg_2Ti_4Cl_4$: Mg, 4.41; Ti, 17.38; Cl, 12.86; C, 34.86; H, 7.25%. Melting point: 213–215 °C.

Molecular weight, determined by the cryoscopic method [12] in dry benzene solution at a concentration from 30 to 50 mmol/l, gave an average value of 1038 g/mol.

The IR spectrum showed the typical absorption bands of $Ti(OC_2H_5)_4$ with only minor shifts in the region 850–1200 cm^{-1}. The ^1H NMR in d-8 toluene solution at 363 K showed a sharp quartet and a sharp triplet at 4.39 and 1.39 ppm, respectively, from TMS as internal standard. At lower temperature (223 K) a splitting of the two signals into sharp quartets, at 4.13, 4.24, 4.40 + 4.35, 4.54 + 4.50, 4.70 ppm for CH_2 and into sharp triplets at 1.08, 1.25 + 1.27, 1.74, 1.91 ppm for CH_3 was observed.

TABLE 1. Fractional atomic coordinates ($\times 10^4$) for non-H atoms and equivalent isotropic temperature factors

Atom	x	y	z	B (Å^2)
Ti(1)	2496(1)	2806(1)	5468(1)	6.2
Ti(2)	2419(1)	3627(1)	3474(1)	6.2
Mg	4017(1)	4248(1)	4838(1)	5.3
Cl(1)	5735(1)	4146(1)	4730(1)	6.4
Cl(2)	3900(1)	3362(1)	6497(1)	7.5
O(1)	2531(2)	4148(2)	4938(2)	5.6
O(2)	3492(2)	2941(2)	4427(2)	5.2
O(3)	3504(3)	4417(3)	3437(3)	6.3
O(4)	1625(3)	2791(3)	4274(3)	6.9
O(5)	2636(3)	1619(3)	5586(3)	8.4
O(6)	1669(3)	2991(3)	6330(3)	8.5
O(7)	1487(3)	4374(4)	3019(4)	8.0
O(8)	2509(3)	2900(4)	2482(3)	8.5
C(11)	1884(4)	4853(4)	5189(5)	8.2
C(12)	2172(12)	5123(12)	6314(12)	8.7
C(12′)	1930(14)	5294(13)	5994(15)	9.2
C(21)	4035(4)	2214(4)	4024(5)	7.2
C(22)	4803(4)	1828(4)	4754(5)	8.3
C(31)	3772(4)	4993(4)	2685(4)	7.4
C(32)	4519(5)	4556(5)	2128(5)	9.6
C(41)	917(4)	2124(5)	3895(5)	9.4
C(42)	62(5)	2138(6)	4403(8)	14.3
C(51)	2514(11)	845(11)	6118(12)	9.6
C(52)	2378(22)	12(21)	5427(22)	14.1
C(51′)	2693(16)	593(17)	5408(18)	12.8
C(52′)	1931(18)	203(16)	5907(17)	13.5
C(61)	1254(15)	2505(16)	7115(15)	11.4
C(62)	1853(16)	2839(16)	8105(17)	9.7
C(61′)	1264(13)	3051(15)	7232(15)	11.0
C(62′)	1821(16)	2450(15)	7881(16)	11.7
C(71)	651(15)	5041(14)	2763(15)	12.2
C(72)	87(20)	4743(19)	2024(19)	14.0
C(71′)	928(21)	4759(21)	2212(22)	16.5
C(72′)	250(27)	4256(22)	2321(26)	17.8
C(81)	2377(12)	2236(11)	1681(12)	8.6
C(82)	2578(15)	2723(15)	755(15)	10.9
C(81′)	2059(12)	2602(12)	1599(12)	9.2
C(82′)	2908(15)	2405(14)	922(15)	11.1

X-ray analysis

To prevent decomposition particular care was taken to avoid contact of the product with moisture. Several crystals, approximately of 0.3 × 0.3 × 0.5 mm were selected and each of them was placed in a glass capillary tube sealed under dry nitrogen, to find a specimen suitable for X-ray analysis. Intensity data were collected on an Enraf-NONIUS CAD4 diffractometer at room temperature with a graphite monochromated Mo Kα radiation. The unit cell dimensions were obtained by least-squares fit of 18 reflections. A data set of 5391 independent reflections ($h \pm 16$; $k + 17$; $l + 16$) was recorded in the range $3° \leq \theta \leq 28°$; 3553 of these, with $I > 3.5\sigma(I)$, were used for the structure refinement. During data collection, the intensities of three periodically monitored stan-

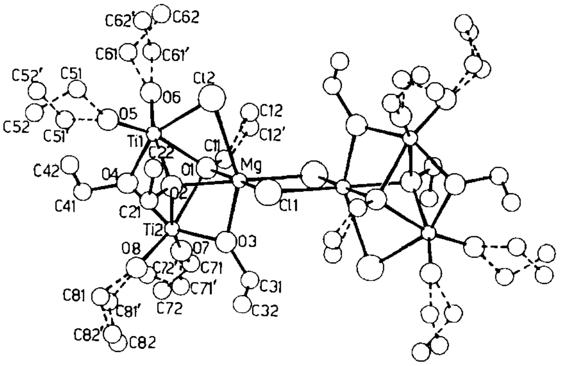


Fig. 1. A perspective view of the complex with the atom numbering scheme of the crystallographic independent unit.

dard reflections decreased continuously by up to 7.5% over the whole period of data collection.

All intensities were corrected for Lorentz and polarization effects, as well as for background attenuation, but absorption correction was deemed unnecessary.

The structure was solved by the direct method using the MULTAN80 program [13] followed by subsequent difference Fourier maps with the SHELX76 program [14]. Difficulties were found in locating some ethyl groups indicating sites of disorder in these parts of the molecule. Any attempt to assign a unique position to each of these atoms also failed because of their very high and unrealistic temperature factors as well as the presence of many additional peaks in the ΔF maps. It was therefore decided to split each of the disorder carbon atoms into two positions and their population parameters were estimated taking into account the derived temperature factors.

The blocked full-matrix least-squares refinement was carried out with anisotropic temperature factors for all non-H and non-disordered C atoms. The final discrepancy factors, based on the observed reflections and calculated with a unit weight, were $R=0.079$ and $R_w=0.078$.

The final fractional atomic coordinates for all non-H atoms with the equivalent isotropic temperature factors are listed in Table 1. A view of the complex showing the atomic numbering scheme of the asymmetric unit is given in Fig. 1. Selected geometrical parameters are reported in Table 2. See also 'Supplementary material'.

TABLE 2. Molecular dimensions

Selected bond lengths (Å)	
Ti(1)–Cl(2)	2.458(2)
Ti(1)–O(1)	2.100(4)
Ti(1)–O(2)	2.103(3)
Ti(1)–O(4)	1.974(4)
Ti(1)–O(5)	1.753(4)
Ti(1)–O(6)	1.758(5)
Ti(2)–O(1)	2.177(4)
Ti(2)–O(2)	2.158(3)
Ti(2)–O(3)	1.904(4)
Ti(2)–O(4)	2.044(4)
Ti(2)–O(7)	1.770(5)
Ti(2)–O(8)	1.761(5)
Mg–Cl(1)	2.411(2)
Mg–Cl(1′)	2.441(2)
Mg–Cl(2)	2.674(2)
Mg–O(1)	2.088(3)
Mg–O(2)	2.109(4)
Mg–O(3)	2.041(4)
Selected bond angles (°)	
O(5)–Ti(1)–O(6)	99.3(2)
O(4)–Ti(1)–O(6)	101.1(2)
O(4)–Ti(1)–O(5)	97.1(2)
O(2)–Ti(1)–O(6)	165.8(2)
O(2)–Ti(1)–O(5)	94.8(2)
O(2)–Ti(1)–O(4)	78.9(2)
O(1)–Ti(1)–O(6)	97.7(2)
O(1)–Ti(1)–O(5)	162.4(2)
O(1)–Ti(1)–O(4)	75.2(2)
O(1)–Ti(1)–O(2)	68.4(1)
Cl(2)–Ti(1)–O(6)	94.6(2)
Cl(2)–Ti(1)–O(5)	101.4(2)
Cl(2)–Ti(1)–O(4)	153.5(1)
Cl(2)–Ti(1)–O(2)	80.6(1)
Cl(2)–Ti(1)–O(1)	81.7(1)
O(7)–Ti(2)–O(8)	101.0(2)
O(4)–Ti(2)–O(8)	98.6(2)
O(4)–Ti(2)–O(7)	98.8(2)
O(3)–Ti(2)–O(8)	103.5(2)
O(3)–Ti(2)–O(7)	99.9(2)
O(3)–Ti(2)–O(4)	147.6(2)
O(2)–Ti(2)–O(8)	96.4(2)
O(2)–Ti(2)–O(7)	162.5(2)
O(2)–Ti(2)–O(4)	76.1(2)
O(2)–Ti(2)–O(3)	78.1(1)
O(1)–Ti(2)–O(8)	161.4(2)
O(1)–Ti(2)–O(7)	96.4(2)
O(1)–Ti(2)–O(4)	72.1(2)
O(1)–Ti(2)–O(3)	79.8(1)
O(1)–Ti(2)–O(2)	66.0(1)
O(2)–Mg–O(3)	76.4(1)
O(1)–Mg–O(3)	79.0(2)

Results and discussion

The molecule is centrosymmetric and lies on a crystallographic centre of symmetry, so that the asymmetric unit in the cell is only half of the molecule. Each symmetric part of the molecule consists of three distorted face-shared octahedral arrangements (hereinafter Oc1, Oc2, Oc3) around the two titanium and the magnesium atoms and is surrounded by the terminal ethyl groups. Ti(1) is hexacoordinated by five oxygen and one chlorine atoms, Ti(2) by six oxygen atoms and Mg by three oxygen and three chlorine atoms. Each of the three octahedral environments shares, with the other two, a face delimited by three oxygen atoms so that two oxygen atoms (O(1) and O(2)) belong to all three octahedra.

The titanium–oxygen distances vary in a considerable range depending on the number of metal atoms coordinated to the oxygen [15]: O(1) and O(2), bonded to three metal atoms, have a mean Ti–O distance of 2.135(4) Å; O(3) and O(4), bonded to two metal atoms, of 1.974(3) Å; the other five, bonded to one metal atom, of 1.761(5) Å. The Cl(2) atom is a common vertex to Oc1 and Oc3 with the Ti(1)–Cl(2) distance (2.458(2) Å) only a little shorter than the average value found for a $\text{TiCl}_{(\text{bridging})}$ length [2, 16]. A very surprisingly long Mg–Cl(2) distance

(2.673(2) Å) was found, suggesting a very weak link probably due to the strong distortion of the octahedral arrangement. The pseudooctahedral geometry in the molecule (Fig. 2) is also confirmed by the bond angles around the hexacoordinated Ti(1), Ti(2) and Mg atoms, the deviation from the theoretical value being up to 21°.

The Ti(1)...Ti(2) non-bonded distance is 3.028(2) Å, remarkably shorter than the distance of about 3.35 Å resulting in the tetrametric molecule of $Ti(OCH_3)_4$, where the titanium atoms display a similar face-shared octahedral arrangement [17].

The Ti(1)...Mg and Ti(2)...Mg non-bonded distances are 3.166(2) and 2.942(2) Å, respectively.

The ethyl groups are strongly affected by disorder and, accordingly, the groups named 1, 5, 7 and 8 were split into two positions in Fig. 1. The mean O–C bond length is 1.44(1) Å. Owing to the disorder, a detailed description of the geometry of the ethyl groups would be meaningless.

The two symmetric parts of the complex are bound together through the double chlorine bridge between the two magnesium atoms. The planar Mg_2Cl_2 core is a slightly asymmetric rhombus with the two unequivalent Mg–Cl bond distances of 2.411(2) and 2.441(2) Å and the two Cl–Mg–Cl and Mg–Cl–Mg valence angles of 87.5(1) and 92.5(1)°, respectively. The non-bonded Mg...Mg distance is 3.504(3) Å, understandably longer than the distance of 3.169(4) Å found by Sobota *et al.* [3] between two magnesium atoms bridged by three chlorine atoms.

Now some speculations on a possible mechanism of complex formation can be put forward, taking also into account cryoscopic and conductivity measurements in benzene solution (complex proved not to have ionic character). If one considers that $Ti(OC_2H_5)_4$ exists in some degrees of association [18] in dependence on physical state [15], temperature and solution concentration [11, 12, 19], the reaction Scheme 1 could be suggested.

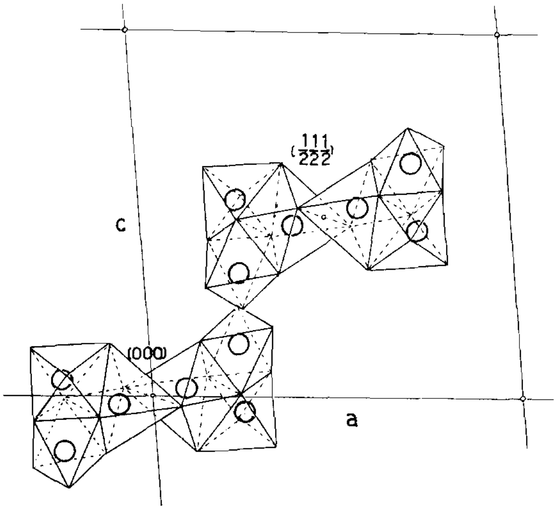
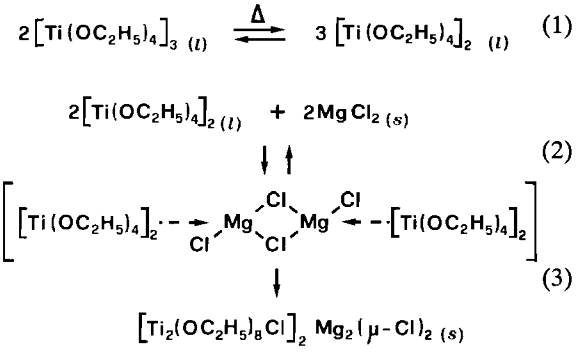


Fig. 2. A partial projection of the distorted octahedra viewed along the *b* axis. The hexacoordinated metal atoms are symbolized by open circles. Carbon atoms are omitted for clarity.



Scheme 1.

Step (1) yields a dimer titanium species characterized both by a coordination vacancy of one of the two titanium atoms and by an increased ability of the alkoxide groups to form coordination bonds. Accordingly, nucleophilic attack by the alkoxide groups on the (110) face of the $MgCl_2$ crystal – that is supposed to be the most Lewis acidic one [20] – could take place (step (2)), while the closest chlorine atom of the $MgCl_2$ completes titanium coordination. A concerted or consecutive reaction of two dimeric titanium species will cause breaking of the $MgCl_2$ crystalline lattice and formation of the complex. To the best of our knowledge this is the first well characterized Ti–Mg complex without coordinated electron donor molecules.

Supplementary material

Lists of anisotropic temperature factors for non-H atoms and observed and calculated structure factors are available on request from the Cambridge Crystallographic Data Centre.

Acknowledgement

Dr G. Giunchi of Keramont Italia is gratefully acknowledged for some helpful advice on the discussion of the structure.

References

1 J. C. J. Bart, I. W. Bassi, M. Calcaterra, E. Albizzati, U. Giannini and S. Parodi, *Z. Anorg. Allg. Chem.*, *482* (1981) 121.

2 J. C. J. Bart, I. W. Bassi, M. Calcaterra, E. Albizzati, U. Giannini and S. Parodi, *Z. Anorg. Allg. Chem., 496* (1983) 205.

3 P. Sobota, J. Utko and T. Lis, *J. Chem. Soc., Dalton Trans.,* (1984) 2077.

4 A. Greco, G. Bertolini and S. Cesca, *J. Appl. Polym. Sci., 25* (1980) 2045.

5 U. Zucchini and T. Dall'Occo, in S. Sivaram (ed.), *Polymer Science, Contemporary Themes,* Vol. 1, McGraw-Hill, New Delhi, 1991, p. 221.

6 E. Berger, Solvay & Cie, *Ger. Offen, 2324766* (1974).

7 U. Zucchini and I. Cuffiani, Montedison S.p.A., *Ger. Offen. 2822809* (1978).

8 C. E. Capshew, Phillips Petroleum Co., *Eur. Patent Applic. 7425* (1980).

9 D. F. Shriver, *The Manipulations of Air-Sensitive Compounds,* McGraw-Hill, New York, 1969.

10 A. I. Vogel, *Practical Organic Chemistry,* Longmans Green and Co., London, 1959.

11 W. R. Russo and W. H. Nelson, *J. Am. Chem. Soc., 92* (1970) 1521.

12 R. L. Martin and G. Winter, *J. Chem. Soc.,* (1961) 2947.

13 P. Main, S. F. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, *MULTAN 80,* a crystal system of computer programs for the automatic solution of crystal structure from X-ray diffraction data, Universities of York, U.K. and Louvain, Belgium, 1980.

14 G. M. Sheldrick, *SHELX76*, program for crystal structure determination, University of Cambridge, U.K., 1976.

15 J. A. Ibers, *Nature (London), 197* (1963) 686.

16 G. Giunchi, E. Albizzati, L. Malpezzi and E. Giannetti, *Inorg. Chim. Acta, 147* (1988) 159.

17 D. A. Wright and D. A. Williams, *Acta Crystallogr., Sect. B, 24* (1968) 1107.

18 D. C. Bradley, R. C. Mehrotra and D. P. Geur, *Metal Alkoxides,* Academic Press, London, 1978.

19 R. L. Martin and G. Winter, *Nature (London), 197* (1963) 687.

20 U. Giannini, G. Giunchi, E. Albizzati and P. C. Barbè, in M. Fontanille and A. Guyot (eds.), *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization,* NATO ASI Series C: Mathematical and Physical Sciences, Vol. 215, 1987, p. 473.