# The crystal structure and properties of $\left[\mathrm{TiCl}_{4}\left\langle\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}\right\}\right]$ and $\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}\left\{\mu-\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right\}\right]$ 

Piotr Sobota *, Sławomir Szafert, Tadeusz Głowiak<br>Faculty of Chemistry, University of Wroclaw, 14 F. Joliot-Curie, 50-383 Wroctan, Poland

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#### Abstract

The reactions of $\mathrm{TiCl}_{4}$ with $\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}_{3}\right.$ and $\mathrm{AlCl}_{3}$ with $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}_{2}\right.$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ gave $\left[\mathrm{TiCl}_{4}\left\{\mathrm{CH}^{2}\left(\mathrm{CO}_{2} \mathrm{Et}_{3}\right]\right](1)\right.$ and $\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}(\mu\right.$ $\left.\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right]$ (2) respectively. The crystal structures of 1 and 2 have been determined by a single crystal X -ray diffraction studies and refined by full-matrix least squares techniques to $R_{1}=0.0272$ and 0.0282 (for 2654 and 1274 unique non-zero reflections) for 1 and 2 respectively. The crystals of 1 belong to the space group $C 2 / c$ with $Z=8$ and $a=17.131(8), b=10.715(3), c=18.512(5) \AA$ and $\beta=92.97(3)^{\circ}$. The titanium atom in 1 is octahedrally coordinated by four terminal chlorine atoms and two oxygen atoms in cis position from the coordinated triester molecule. Crystals of 2 are monoclinic, space group $P 2_{1} / c, Z=4, a=14.109(2), b=10.049(2)$, $c=15.644(3) \AA$ and $\beta=116.65(2)^{\circ}$. In the molecular dimeric compound, each aluminium atom is tetrahedrally coordinated by three terminal chlorine atoms and one oxygen utom from the bridging diethyl succinate molecule.


Keywords: Olefin polymerization; Crystal structure; Titanium; Aluminium; Ester compounds

## 1. Introduction

Polymerization studies have revealed that the incorporation of Ziegler-Natta catalysts supported on $\mathrm{MgCl}_{2}$ with organic diesters results in higher stereospecific performance of the polymerization process [I]. The enhancement of isospecific activity is strongly dependent on the nature of the esters. The initial activity of the catalysts with $o$-, $m$ - or $p$-diesters is different. Hence, the studies on the interaction between ester molecules and each of the catalyst components are of great importance. It has been shown that in the reaction of $\mathrm{TiCl}_{4}$ with diester the monomeric $\left[\mathrm{TiCl}_{4}\right.$ (diester)] (where diester $=o . \mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ [2], o- $\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2}-\mathrm{i}-\right.$ $\mathrm{Bu})_{2}$ [3], o- $\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right)_{2}$ [4], $\mathrm{C}_{2} \mathrm{O}_{4}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Ph}\right)_{2}$ [4], $\mathrm{CH}_{2}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ [5] or $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{OPh}\right)_{2}$ [5]), the dimeric $\left[\mathrm{Ti}_{2} \mathrm{Cl}_{8}(\mu \text {-diester })_{2}\right.$ ] (diester $=m-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}[6]$ or $m-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{Fh}\right)_{2}$ [7]) or the polymeric $\left[\mathrm{TiCl}_{4}\right.$ - diester] (diester $=p-\mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Me}\right)_{2}$ [3]) compounds are formed depending on the structure of the diester molecule. The reactions of $\mathrm{TiCl}_{4}$ with the aromatic

[^0]triester 1,3,5-benzenetricarboxylate in $1: 3$ and $1: 1$ ratios gave polymeric $\left[3 \mathrm{TiCl}_{4} \cdot 1,3,5=\mathrm{C}_{6} \mathrm{H}_{3}\left(\mathrm{CO}_{2} \mathrm{Me}\right)_{3}\right]$ and dimeric $\left[\mathrm{Ti}_{2} \mathrm{Cl}_{\mathrm{g}}\left\{\mu-1,3,5-\mathrm{C}_{6} \mathrm{H}_{3}\left(\mathrm{CO}_{2} \mathrm{Me}\right)_{3}\right\}_{2}\right]$ compounds respectively [8].

To elucidate the different behaviour of esters during the catalytic propylene polymerization process, the reaction of the aliphatic diester $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ and triester $\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}$ with $\mathrm{AlCl}_{3}$ and $\mathrm{TiCl}_{4}$ respectively were studied. In this paper, the syntheses, properties and crystal structures of $\left[\mathrm{TiCl}_{4}\left\{\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}\right\}\right]$ and $\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}\left(\mu-\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right)\right]$ are described.

## 2. Experimental details

All manipulations were carried out under dinitrogen in dry solvents by use of Schlenk system and vacuum line. Anhydrous $\mathrm{TiCl}_{4}, \mathrm{AlCl}_{3}$ and triethyl methanetricarboxylate were commercial materials. Diethyl succinate was obtained by standard procedure, i.e. reaction of succinic acid with ethyl alcohol in the presence of $p$-toluenesulphonic acid [9]. Solvents were dried and purified by standard techniques. Infrared spectra were obtained using a Perkin-Elmer 180 spectrometer.

### 2.1. Sywthesis of tetrachloro(triethyl methanetricarbox-ylate- $0,0^{\prime}$ )titanium( $/ V$ ) (1)

To $1 \mathrm{~cm}^{3}$ of $\mathrm{TiCl}_{4}(1.7 \mathrm{~g}, 9.1 \mathrm{mmol})$ in $60 \mathrm{~cm}^{3}$ of $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 2.0 \mathrm{~cm}^{3}(9.4 \mathrm{mmol})$ of triethyl methanetricarboxylate was added dropwise and the yellow solution was stirred for 1 h at room temperature. Next the solution was filtered and the volume was reduced under vacuum to $30 \mathrm{~cm}^{3}$. After $\mathbf{2 4 h}$, the orange needle-shaped crystals were filtered off and washed with $n$-hexane ( $3 \times 5 \mathrm{~cm}^{3}$ ). Yield 3.5 g ( $91.2 \%$ ). Anal. Found: $\mathrm{Cl}, 35.7$; Ti, $10.3 . \mathrm{C}_{10} \mathrm{H}_{16} \mathrm{Cl}_{4} \mathrm{O}_{6} \mathrm{Ti}$. Calc.: $\mathrm{Cl}, 33.6$; Ti, $11.4 \%$. IR (Nujol, $\mathrm{cm}^{-1}$ ): 1752 (vs, br), 1636 (vs, br), 1380 (s), 1360 (m), 1348 (s), 1310 (s), 1212 (s), 1126 (m), 984 (s), 852(s), 376(s), 328 (m).

### 2.2. Synthesis of $\mu$-(diethyl succinate-

 O, O') kexachlorodialuminium(III) (2)To a suspension of 2.1 g ( 15.7 mmol ) of $\mathrm{AlCl}_{3}$ in $100 \mathrm{~cm}^{3}$ of dichloromethane $1.4 \mathrm{~cm}^{3}(8.4 \mathrm{mmol})$ of $\mathrm{di}-$ ethyl succinate was added. The mixture was stirred at room temperature until the complete dissolution of $\mathrm{AlCl}_{3}$ and the volume was reduced under vacuum to $50 \mathrm{~cm}^{3}$. After 4 weeks, the colourless crystals were filtered off and washed with $n$-hexane ( $3 \times 5 \mathrm{~cm}^{3}$ ). Yield 2.2 g (59.4\%). Anal. Found: $\mathrm{Cl}, 46.9$; $\mathrm{Al}, 12.5$. $\mathrm{C}_{8} \mathrm{H}_{14} \mathrm{Al}_{2} \mathrm{Cl}_{6} \mathrm{O}_{4}$, Calc: $\mathrm{Cl}, 48.3 ; \mathrm{Al}, \quad 12.2 \%$. IR (Nujol, $\mathrm{cm}^{-1}$ ); 1604 (vs, br), 1520 (s), 1414 (s), 1382 (s), 1250 (m), 1186 (m), 1156 (m), $492(\mathrm{~s}), 438(\mathrm{~m})$, 428 (m), 408 (m), 392 ( s ).

### 2.3. X-ray crystal structure determination

Crystal data for (1). $\mathrm{S}_{10} \mathrm{H}_{16} \mathrm{Cl}_{4} \mathrm{O}_{6}{ }^{\prime} \mathrm{Ti}, \mathrm{M}=421.93$, $a=17.131(8), \quad b=10.715(3), c=18.512(5) \AA, \quad \beta=$ $92.97(3)^{\circ}, V=3393(3) A^{3}, \quad D_{m}=1.666, \quad D_{c}=$ $1.652(1) \mathrm{g} \mathrm{cm}^{-3}, Z=8, F(000)=1712$, space group $C 2 / c, ~ M o K \alpha$ radjation $\lambda=0.71069 \AA, \mu=$ $1.15 \mathrm{~mm}^{-1}$.

Crystal data for (2). $\mathrm{C}_{8} \mathrm{H}_{14} \mathrm{Cl}_{6} \mathrm{O}_{4} \mathrm{Al}_{2}, M=440.85$. $a=14.109(2), b=10,049(2), c$ (25.644(3) A, $\beta=$ $116.65(2)^{\mathrm{a}}, V=1982(8) A^{3}, \quad D_{\mathrm{m}}=1.459, \quad D_{\mathrm{c}}=$ $1.477(1) \mathrm{g} \mathrm{cm}^{-3}, Z a 4, F(000)=888$, space group $P 2, / c$, Mo $K \alpha$ radiation $\lambda=0.71069 \AA, \mu=$ $0.96 \mathrm{~mm}^{-1}$.

Preliminary data for both crystals were obtained from Weissenberg photographs. Intensities were collected using a Kuma KM4 four circle diffrictometer in the $\omega \mathrm{m} 2 \theta$ mode (with crystals of dimensions $0.4 \times 0.3 \times 0.4 \mathrm{~mm}^{3}$ for 1 and $0.5 \times 0.6 \times 0.5 \mathrm{~mm}^{3}$ for 2 ) and MoK $\alpha$ radiation. The crystals were cut from large crystals. Cell parameters were ubtained ficma least squares fit of the setting angles of 40 reflections in the range $20<2 \theta<$ $27^{\circ}$ for 1 and 2. The data collection was performed in $T=120.0(5) \mathrm{K}$ for 1 using the Oxford System

Cryostream Cooler, and $T=298(1) \mathrm{K}$ for 2. For both crystals the intensities of three standard reflections, monitored every 100 intensity scans showed no evidence of crystal decay. $4480\left(4<2 \theta<56^{\circ}\right)$ and 3718 ( $4<2 \theta<50^{\circ}$ ) reflections were measured for 1 and 2 respectively, from which 2654 and 1274 unique reflections with $I>3.0 \sigma(I)$ were used for calculations ( $R_{\text {int }}$ $=0.0195$ and 0.0127 for 1 and 2 respectively). The structures were solved by the Patterson method and refined by full matrix least squares calculations using shelxl93 [10]. The number of refined parameters was 190 for 1 and 181 for 2 . Neutral atom scattering factors and anomalous dispersion terms used in the refinement were taken from Ref. [11]; real and imaginary components of anomalous dispersion were included for all non-H atoms. The hydrogen atoms were put in calculated positions with $d(C-H)=1.08 \AA$ and introduced as fixed contributors in the final stage of refinement. The absorption corrections following the difabs [12] procedure were applied for 2: minimum and maximum absorption corrections were 0.884 and 1.054 for 1 and 0.810 and 1.042 for 2 . The final $R_{1}$ and $\omega R_{2}$ were 0.0272 and 0.0653 for 1 and 0.0282 and 0.0694 for 2 . The final weighting scheme of the form $w=1 / \sigma^{2}\left(F_{0}^{2}\right)$ $+(0.0256 P)^{2}+7.32 P$ and $w=1 / \sigma^{2}\left(F_{0}^{2}\right)+$ $(0.0352 P)^{2}+1.96 P$ (where $P$ is defined as $\left(F_{0}^{2}+\right.$ $\left.2 F_{c}^{2}\right) / 3$ ) were applied for 1 and 2 respectively. For the last cycle of the refinement the maximum value of the ratio $\Delta / \sigma$ was below $0.005 \AA$ for 1 and 2 . The final difference map showed a general background within $=0.28$ and $0.38 \mathrm{e}^{-3}$ for 1 and -0.22 and $0.16 \mathrm{e} \AA^{-3}$ for 2.

## 3. Results and discussion

### 3.1. Synthesis and structure of $\left[\mathrm{TiCl}_{4}\left\{\mathrm{CH}_{\left.\left(\mathrm{CO}_{2} \mathrm{Et}_{3}\right\}\right]}\right\}\right.$

 (1)The addition of triethyl methanetricarboxylate to $\mathrm{TiCl}_{4}$ in a $1: 1$ molar ratio leads to a diamagnetic, air-sensitive, orange compound with $\mathrm{TiCl}_{4}$. $\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}$ stoichiometry. The compound is well soluble and crystallizes from $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and should be stored under $\mathrm{N}_{2}$. The IR spectrum of 1 shows stretching $\nu(\mathrm{C}=0)$ modes at $1752(\mathrm{vs}, \mathrm{br}) \mathrm{cm}^{-1}$ and $1636(\mathrm{vs}, \mathrm{br}) \mathrm{cm}^{-1}$ characteristic for uncoordinated and coordinated carbonyl group, respectively, as well as bands at 376 (s) and $328(\mathrm{~m}) \mathrm{cm}^{-1}$ due to $\nu(\mathrm{Ti}-\mathrm{Cl})$ vibrations.
$\mathrm{TiCl}_{4}+\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}{ }^{\mathrm{CH}_{2} \mathrm{Cl}_{2}}\left[\mathrm{TiCl}_{4}\left(\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}_{3}\right)\right]\right.$


Fig. 1. Structure and the numbering scheme of the $\left[\mathrm{TiCl}_{4}\left(\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}\right)\right]$ molecule.

The structure of 1 is depicted in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 1. Crystals of 1 consist of the discrete $\left[\mathrm{TiCl}_{4}\left\{\mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}\right\}\right]$ molecules. The titanium atom is octahedrally coordinated by four terminal chlorine atoms and two mutually cis carbonyl oxygen atoms from triester molecules. The third $\mathrm{C}=\mathrm{O}$ group remains uncoordinated. Each triester molecule is coordinated to a Ti atom by two carbonyl oxygen atoms. The chelate ligand and the Ti atom form a six-membered ring. The $\mathrm{Ti}-\mathrm{Cl}(1)$ and $\mathrm{Ti}-\mathrm{Cl}(2)$ bond lengths cis to carbonyl oxygen $\mathrm{O}(1)$ and $O(2)$ atoms are $2.260(1) \AA$ and $2.271(1) \AA$ respec-
tively, and are similar to those found in $\left[\mathrm{TiCl}_{4}\right.$ (diester)] compounds where they range from $2.259(2)$ to $2.293(2) \AA[4,5]$. The $\mathrm{Ti}-\mathrm{Cl}(3)$ and $\mathrm{Ti}-\mathrm{Cl}(4)$ bond lengths of $2.208(1) \AA$ and $2.214(1) \AA$ as well as the $\mathrm{Ti}-\mathrm{O}(1)$ and $\mathrm{Ti}-\mathrm{O}(2)$ distances of $2.144(2) \AA$ and $2.122(2) \AA$ are typical for complexes of [TiCl ${ }_{4}$ (diester)] [2-5]. The $\mathrm{Cl}-\mathrm{Ti}-\mathrm{Cl}$ and $\mathrm{Cl}-\mathrm{Ti}-\mathrm{O}$ bond angles (see Table 1) show the octahedron around the Ti atom to be distorted. The $\mathrm{Ti}-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(4)$ and $\mathrm{Ti}-\mathrm{O}(2)-\mathrm{C}(2)-$ $\mathrm{C}(4)$ torsion angles of $5.3(9)^{\circ}$ and $-6.6(8)^{\circ}$ show that the titanium atom is coordinated nearly in the planes of both $\mathrm{O}(1)-\mathrm{C}(1)$ and $\mathrm{O}(2)-\mathrm{C}(2)$ carbonyl groups ( $0.14 \AA$ below the first plane and $0.13 \AA$ above the second one). The carbonyl groups $O(1)-C(1), O(2)-C(2)$ and $O(3)-$ $C(3)$ remain in the preferred conformation, synperiplanar to $O(4)-C(5), O(5)-C(7)$ and $O(6)-C(9)$ bonds respectively [13]. The plane through $O(1), C(1), O(4)$, $C(4)$ atoms and the plane through $O(2), C(2), O(5)$, $\mathrm{C}(4)$ atoms form the angle of $34.9^{\circ}$. In the crystal no short inter- and intramolecular contacts are observed.
3.2. Synthesis and structure of $\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}\{\mu\right.$ $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ \}] (2)

A suspension of $\mathrm{AlCl}_{3}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ under $\mathrm{N}_{2}$ reacts with diethyl succinate in $2: 1$ molar ratio. The resulting colouriess compound is diamagnetic, air-sensitive and should be stored under dinitrogen. It is insoluble in aliphatic hydrocarbons but well soluble in halogenated hydrocarbons. The IR spectrum of the $\left\langle\mathrm{Al}_{2} \mathrm{Cl}_{6} \backslash \mu\right.$ -

Table 1
Selected bond lengths ( $A$ ), bond angles (deg) and torsion angles (deg) for complex 1

| Tiuclin | $2.260(1)$ | $0(1)=C(1)$ | $1.209(3)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{T}=\mathrm{Cl(2)}$ | $2.271(1)$ | $O(2)=C(2)$ | 1.223 (3) |
| $\mathrm{Ti}=\mathrm{Cl}(3)$ | $2.208(1)$ | $O(3)-C(3)$ | $1.196(3)$ |
| T ${ }^{\text {c }}$ CK(4) | $2.214(1)$ | C(1) $=0(4)$ | 1.305(3) |
| $\mathrm{Ti}=0(1)$ | $2.144(2)$ | $C(2) 0(5)$ | 1.286 (3) |
| Timo ${ }^{(2)}$ | 2.122(2) | $C(3)-0(6)$ | $1.316(3)$ |
| $\mathrm{CK}(1)=\mathrm{T}-\mathrm{Cl}(2)$ | 166.9(1) | $\mathrm{Cl}(3)-\mathrm{Ti}-\mathrm{Cl}(4)$ | 101.4(1) |
| CK(1)-Ti-Cl(3) | 94.7(1) | $\mathrm{Cl}(3)-\mathrm{Ti}-\mathrm{O}(1)$ | 168.1(1) |
| CK(1)-TI--Cl(4) | 92.9(1) | $\mathrm{Cl}(3)-\mathrm{Ti}-\mathrm{O}(2)$ | 89.4(1) |
| $\mathrm{Cl}(1)-\mathrm{Ti}-\mathrm{O}(1)$ | 83.4(1) | $\mathrm{Cl}(4)-\mathrm{Ti}-\mathrm{O}(1)$ | 90.5(1) |
| $\mathrm{Cl}(1)-\mathrm{Ti}-\mathrm{O}(2)$ | 86.4(1) | $\mathrm{Cl}(4)-\mathrm{Ti}-\mathrm{O}(2)$ | 169.2 (1) |
| $\mathrm{Cl}(2)-\mathrm{Ti}-\mathrm{Cl} 3$ ) | 94.9(1) | $\mathrm{O}(1) \mathrm{TTi} \mathrm{O}(2)$ | 78.7(1) |
| $\mathrm{Cl}(2)=\mathrm{Ti}-\mathrm{Cl}(4)$ | 93.8(1) | $\mathrm{Ti}-\mathrm{O}(1)-\mathrm{C}(1)$ | 132.5(2) |
| $\mathrm{Cl}(2)-\mathrm{Ti}-\mathrm{O}(1)$ | 85.4(1) | Ti-O(2)-C(2) | 133.6(2) |
| C(2)-Ti-O(2) | 84.9(1) |  |  |
| Ti-O(1)-C(1)-C(4) | -5.3(9) | $\mathrm{Ti}-\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(4)$ | -6.6(8) |
| $O(1)-C(1)-O(4)-C(5)$ | 0.17 ) | $O(2)-C(2)-O(5)-C(7)$ | 1.9(8) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(4)-\mathrm{C}(2)$ | -30.3(8) | $O(2)-C(2)-C(4)-C(1)$ | 36.2(6) |
| $\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(4)-\mathrm{C}(3)$ | 91.1(6) | $\mathrm{O}(2)-\mathrm{C}(2)-\mathrm{C}(4)-\mathrm{C}(3)$ | -89.1(6) |
| $C(1)-0(4)-C(5)-C(6)$ | 85.3(5) | C(2)-0(5)-C(7)-C(8) | -122.5(6) |
| $C(1)-C(4)-C(3)-O(3)$ | - 153.616 ) | $C(2)-C(4)-C(3)-0(3)$ | -29.. ${ }^{(6)}$ |
| $\mathrm{C}(1)-\mathrm{C}(4)-\mathrm{C}(3)-0(6)$ | 28.7(6) | $C(2)-C(4)-C(3)-O(6)$ | $153.1(6)$ |
| $C(4)-C(3)-O(6)-C(9)$ | -177.4(5) | $O(3)-C(3)-O(6)-C(9)$ | $5.1(6)$ |
| $C(3)-O(6)-C(9)-C(10)$ | 169.1(6) |  |  |



Fig. 2. Structure and the numbering scheme of the $\left(\mathrm{Al}_{2} \mathrm{Cl}_{6} f \mu\right.$ $\left.\left.\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right)\right]$ molecule.
$\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ )] compound shows the characteristic band of a coordinated carbonyl group at 1604(vs, br) $\mathrm{cm}^{-1}$.

$$
\begin{align*}
& 2 \mathrm{AlCl}_{3}+\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2} \\
& \stackrel{\mathrm{CH}_{2} \mathrm{Cl}_{2}}{ }\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}\left\{\mu-\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right)\right] \tag{2}
\end{align*}
$$

Compound 2 was shown by X-ray diffraction studies to have a dimeric structure. The overall view of the $\left[\mathrm{Al}_{2} \mathrm{Cl}_{6}\left(\mu-\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right)\right]$ molecule and the numbering scheme are shown in Fig. 2. Principal bond distances and angles, as well as torsion angles, are given in Table 2. In the dimer, each aluminium atom is tetrahedrally coordinated by three terminal chloride atoms and one carbonyl oxygen atom from the coordinated diester molecule. The $\mathrm{Al}=\mathrm{Cl}$ bond distances vary from $2.088(2)$ to $2,104(2) \AA$ and are similar to those found in $\left[\mathrm{AlCl}_{3}\left(\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{CO}_{3} \mathrm{Et}\right)\right](2.110(2)$ and $2.102(2) \mathcal{A})[14]$ and are still shorter than the $\mathrm{Al}=\mathrm{Cl}$ bond distances in the $\left[\mathrm{AlCl}_{2}(\mathrm{THF})_{4}\right]^{\dagger}$ cation [15]. The $\mathrm{Al}(1)=\mathrm{O}(1)$ and $\mathrm{Al}(2)=\mathrm{O}(2)$ bond lengths are $1.794(4) \AA$ and $1.803(4) \AA$
respectively. The carbonyl $O(1)-C(1)$ and $O(2)-C(2)$ bond distances of $1.246(6)$ and $1.244(7) \AA$ are shorter compared with the carbonyl $\mathrm{C}-\mathrm{O}$ bond distance in the free ester ethyl benzoate, which is $1.36(1) \AA$ [16]. The $\mathrm{Al}(1)-\mathrm{O}(1)-\mathrm{C}(1)$ and $\mathrm{Al}(2)-\mathrm{O}(2)-\mathrm{C}(4)$ bond angles of $141.4(4)^{\circ}$ and $135.2(4)^{\circ}$ are much lower than the corresponding one in $\left[\mathrm{AlCl}_{3}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{Et}\right)\right]\left(168.4(3)^{\circ}\right)$ which is now much closer to the ideal angle of $120^{\circ}$. This indicates that the $\mathrm{Al}-\mathrm{O}$ bond is more covalent in 2 than in the $\mathrm{Al}-\mathrm{O}$ bond in $\left[\mathrm{AlCl}_{3}\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CO}_{2} \mathrm{Et}\right)\right.$ ]. The values of both $\mathrm{Al}-\mathrm{O}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ and $\mathrm{Al}(2)-\mathrm{O}(2) \mathrm{C}(4)-\mathrm{C}(3)$ torsion angles ( $0.9(9)$ and $\left.-6.4(8)^{\circ}\right)$ indicate that both aluminium atoms are bound in the plane of $\mathrm{O}(1)-\mathrm{C}(1)$ and $O(2)-C(4)$ carbonyl groups respectively. The $O(1)-$ $C(1)$ and $O(2)-C(4)$ carbonyl bonds are in the preferred synperiplanar conformation to $\mathrm{O}(3)-\mathrm{C}(5)$ and $\mathrm{O}(4)-$ C(7) bond respectively [14].

## 4. Conclusion

Complexes 1 and 2 were investigated in order to elucidate whether the structure of ester molecules can affect the structure of its compound with one of the Ziegler-Natta-type catalyst component. It was found that in the $\left.\left[\mathrm{TiCl}_{4} / \mathrm{CH}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{3}\right)\right]$ complex the titanium atom is octahedrally coordinated b; four chlorine atoms and two carbonyl oxygen atoms of ine triester molecule. The third $\mathbf{C = O}$ group remains uncoordinated. In this complex the chelate ester ligand and titanium atom form a six-membered ring, similar to the complex [ $\left.\mathrm{TiCl}_{4}\left(\mathrm{CH}_{2}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right)\right]$. In contrast to this behaviour. three or two titanium atoms are coordinated via carbonyl groups to the $1,3,5-\mathrm{C}_{6} \mathrm{H}_{3}\left(\mathrm{CO}_{2} \mathrm{Me}\right)$, ligand and the polymeric [ $3 \mathrm{TiCl}_{4} \cdot 1,3,5-\mathrm{C}_{6} \mathrm{H}_{3}\left(\mathrm{CO}_{2} \text { Me }\right)_{3}$ ] or the dimeric $\left[\mathrm{Ti}_{2} \mathrm{Cl}_{8}\left(\mu-1,3,5-\mathrm{C}_{6} \mathrm{H}_{3}\left(\mathrm{CO}_{2} \mathrm{Me}_{3}\right]_{2}\right]\right.$ compounds are formed [8].

Table 2
Selected bond lengths ( $\AA$ ), bond angles (deg) and torsion angles (deg) for complex 2

| $A K 1)=C K(1)$ | 2.10.(2) | AK2)-CK(4) | $2.102(3)$ |
| :---: | :---: | :---: | :---: |
| $A \mathrm{Al}(1) \mathrm{Cr}(2)$ | $2.092(2)$ | AK2)-CK( 5 | 2.102(3) |
| Alf $=$ CH(3) | $2.090(2)$ | $A{ }^{(2)}$-CK(6) | 2.088(3) |
| $A(1)=0(1)$ | 1,794(4) | Ar 2 ) $=\mathrm{C}(2)$ | 1.803(4) |
| O(1)-C(1) | 1.246(6) | $O(2)=C(4)$ | 1.244(7) |
| $\mathrm{Cr}(1)=A(1)=\mathrm{CH}(2)$ | 112.4(1) | $C((4)=A K(1)-C(4)$ | 111.8(2) |
| $C(1)=A(1)-C(3)$ | 112.1(1) | C(4)-AI(1)-Cl(5) | 114.0.2) |
| C(1)-A(1)-0(1) | 107.9(2) | $C(4)-A M(1)-O(2)$ | 106.2(2) |
| $\mathrm{Cl}(2)-\mathrm{Al}(1)-\mathrm{Cl}(3)$ | 114.0(1) | $\mathrm{C}(5)=\mathrm{AK}(1)=\mathrm{C}(5)$ | 113.9(2) |
| $C(3)=A(1)-0(1)$ | 104.4(2) | $C(5)-A(1)-O(2)$ | 103.7(2) |
| $C 1(3)=A(1)-O(1)$ | 105.4(2) | CK(6)-Al( ${ }^{\text {( }}$-O(2) | 106.4(2) |
| $A K(1)=O(1)=C(1)$ | 141.4(4) | $A^{(2)}-\mathrm{O}(2) \cdot \mathrm{C}(4)$ | 135.2(4) |
| $A K(1)=0(1)=C(1)-0(3)$ | - $178.3(7)$ | $A(2)-O(2)-C(4)-O(4)$ | 173.9(5) |
| $A K(1)-O(1)-C(1)-C(2)$ | 0.99) | $A(2)-O(2)-C(4)-C(3)$ | -6.4(8) |
| O(1)-C(1)-O(3)-C( 5 | 1.48) | $O(2)-C(4)-O(4)-C(7)$ | 2.9 (8) |
| $0(1)-C(1)-C(2)=C(3)$ | 151.6(7) | $O(2)-C(4)-C(3)-C(2)$ | -172.2(7) |
| C(1)-O(3)-C(5)-C(6) | 163.8(7) | $\mathrm{C}(4)-0(4)-\mathrm{C}(7)-\mathrm{C}(8)$ | -161.1(7) |
| $C(1)=C(2)=C(3)-C(4)$ | -65.3(7) |  |  |

Diethyl succinate and $\mathrm{AlCl}_{3}$ give the dimeric compound 2. In the dimer, two $\mathrm{AICl}_{3}$ molecules are linked together by the $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ ligand. Similar reaction of $\mathrm{MgCl}_{2}$ with diethyl succinate gives the ionic compound $\left.\left[\mathrm{Mg}_{2} \mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}_{2}\right)_{3}\right] \mathrm{MgCl}_{4}\right]$ [17]. The crystal structure of the $\left.\left[\mathrm{MgIC}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right\}_{3}\right]^{2+}$ cation consists of $\left.\left[\mathrm{Mg}_{2} \mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right]_{2}\right]^{2+}$ units linked by other diethyl succinate molecules to generate a linear polymer. However, $\mathrm{TiCl}_{4}$ and $\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}$ form the monomeric [ $\mathrm{TiCl}_{4}\left\{\mathrm{C}_{2} \mathrm{H}_{4}\left(\mathrm{CO}_{2} \mathrm{Et}\right)_{2}\right.$ ]] complex [5]. In this complex the chelate ester ligand and the titanium atom form a seven-membered ring. It becomes obvious that each of the catalyst components can react with esters in various manners.

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[^0]:    ${ }^{*}$ Corresponding author.

