

The crystal structure and properties of [TiCl₄(CH(CO₂Et)₃)] and [Al₂Cl₆(μ -C₂H₄(CO₂Et)₂)]

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Abstract

The reactions of TiCl₄ with CH(CO₂Et)₃ and AlCl₃ with C₂H₄(CO₂Et)₂ in CH₂Cl₂ gave [TiCl₄CH(CO₂Et)₃] (1) and [Al₂Cl₆(μ -C₂H₄(CO₂Et)₂]) (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 C2/c with Z=8 and a=17.131(8), b=10.715(3), c=18.512(5)Å 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 $P2_1/c$, Z=4, a=14.109(2), b=10.049(2), c=15.644(3)Å 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 MgCl, with organic diesters results in higher stereospecific performance of the polymerization process [1]. 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 TiCl₄ with diester the monomeric [TiCl₄(diester)] (where diester = $o \cdot C_6 H_4(CO_2 Et)_2$ [2], $o \cdot C_6 H_4(CO_2 - i - i)_2$ Bu)₂ [3], $o-C_6H_4(CO_2CH_2CH_2Ph)_2$ [4], $C_2O_4(CH_2CH_2Ph)_2$ [4], $CH_2(CO_2Et)_2$ [5] or $C_2H_4(CO_2CH_2CH_2OPh)_2$ [5]), the dimeric $[Ti_2Cl_8(\mu\text{-diester})_2]$ (diester = m-C₆H₄(CO, Et), [6] or m-C₆H₄(CO₂CH₂CH₂Ph)₂ [7]) or the polymeric [TiCl₄ · diester] (diester = p-C₆H₄(CO₂Me)₂ [3]) compounds are formed depending on the structure of the diester molecule. The reactions of TiCl₄ with the aromatic

To elucidate the different behaviour of esters during the catalytic propylene polymerization process, the reaction of the aliphatic diester $C_2H_4(CO_2Et)_2$ and triester $CH(CO_2Et)_3$ with $AlCl_3$ and $TiCl_4$ respectively were studied. In this paper, the syntheses, properties and crystal structures of $[TiCl_4(CH(CO_2Et)_3)]$ and $[Al_2Cl_6\{\mu-C_2H_4(CO_2Et)_2\}]$ are described.

2. Experimental details

All manipulations were carried out under dinitrogen in dry solvents by use of Schlenk system and vacuum line. Anhydrous TiCl₄, AlCl₃ 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.

triester 1,3,5-benzenetricarboxylate in 1:3 and 1:1 ratios gave polymeric [3TiCl₄·1,3,5-C₆H₃(CO₂Me)₃] and dimeric [Ti₂Cl₈{ μ -1,3,5-C₆H₃(CO₂Me)₃}₂] compounds respectively [8].

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2.1. Synthesis of tetrachloro(triethyl methanetricarboxylate-0,0')titanium(IV) (1)

To 1 cm^3 of TiCl₄ (1.7 g, 9.1 mmol) in 60 cm^3 of CH₂Cl₂, 2.0 cm³ (9.4 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 cm^3 . After 24h, the orange needle-shaped crystals were filtered off and washed with *n*-hexane (3 × 5 cm³). Yield 3.5 g (91.2%). Anal. Found: Cl, 35.7; Ti, 10.3. C₁₀H₁₆Cl₄O₆Ti. Calc.: Cl, 33.6; Ti, 11.4%. IR (Nujol, 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 μ-(diethyl succinate-O,O')hexachlorodialuminium(III) (2)

To a suspension of $2.1 \,\mathrm{g}$ (15.7 mmol) of AlCl₃ in $100 \,\mathrm{cm}^3$ of dichloromethane $1.4 \,\mathrm{cm}^3$ (8.4 mmol) of diethyl succinate was added. The mixture was stirred at room temperature until the complete dissolution of AlCl₃ 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 (3×5 cm³). Yield 2.2 g (59.4%). Anal. Found: Cl, 46.9; Al, 12.5. C₈H₁₄Al₂Cl₆O₄. Calc.: Cl, 48.3; Al, 12.2%. IR (Nujol, cm⁻¹): 1604 (vs, br), 1520 (s), 1414 (s), 1382 (s), 1250 (m), 1186 (m), 1156 (m), 492 (s), 438 (m), 428 (m), 408 (m), 392 (s).

2.3. X-ray crystal structure determination

Crystal data for (1). $C_{10}H_{16}Cl_4O_6Ti$, M=421.93, a=17.131(8), b=10.715(3), c=18.512(5)Å, $\beta=92.97(3)^\circ$, V=3393(3)Å³, $D_m=1.666$, $D_c=1.652(1)$ g cm⁻³, Z=8, F(000)=1712, space group C2/c, Mo K α radiation $\lambda=0.71069$ Å, $\mu=1.15$ mm⁻¹.

Crystal data for (2). $C_8H_{14}Cl_6O_4Al_2$, M=440.85, a=14.109(2), b=10.049(2), c=15.644(3) Å, $\beta=116.65(2)^\circ$, V=1982(8) Å³, $D_m=1.459$, $D_c=1.477(1)$ g cm⁻³, Z=4, F(000)=888, space group $P2_1/c$, Mo K α radiation $\lambda=0.71069$ Å, $\mu=0.96$ mm⁻¹.

Preliminary data for both crystals were obtained from Weissenberg photographs. Intensities were collected using a Kuma KM4 four circle diffractometer in the ω -2 θ 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 Mo K α radiation. The crystals were cut from large crystals. Cell parameters were obtained from a 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) K for 1 using the Oxford System

Cryostream Cooler, and T = 298(1)K for 2. For both crystals the intensities of three standard reflections, monitored every 100 intensity scans showed no evidence of crystal decay. 4480 ($4 < 2\theta < 56^{\circ}$) 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_{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 Å 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 wR_2 were 0.0272 and 0.0653 for 1 and 0.0282 and 0.0694 for 2. The final weighting scheme of the form $w = 1/\sigma^2(F_0^2)$ $+ (0.0256P)^2 + 7.32P$ and $w = 1/\sigma^2(F_0^2) +$ $(0.0352P)^2 + 1.96P$ (where P is defined as $(F_0^2 +$ $2F_c^2$)/3) were applied for 1 and 2 respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was below 0.005 Å for 1 and 2. The final difference map showed a general background within -0.28 and $0.38e \text{ Å}^{-3}$ for 1 and -0.22 and $0.16e \text{ Å}^{-3}$ for **2**.

3. Results and discussion

3.1. Synthesis and structure of $[TiCl_4\{CH(CO_2Et)_3\}]$ (1)

The addition of triethyl methanetricarboxylate to $TiCl_4$ in a 1:1 molar ratio leads to a diamagnetic, air-sensitive, orange compound with $TiCl_4$. $CH(CO_2Et)_3$ stoichiometry. The compound is well soluble and crystallizes from CH_2Cl_2 and should be stored under N_2 . The IR spectrum of 1 shows stretching $\nu(C=O)$ modes at 1752 (vs, br) cm⁻¹ and 1636(vs, br) cm⁻¹ characteristic for uncoordinated and coordinated carbonyl group, respectively, as well as bands at 376 (s) and 328(m) cm⁻¹ due to $\nu(Ti-Cl)$ vibrations.

$$TiCl_4 + CH(CO_2Et)_3 \xrightarrow{CH_2Cl_2} \left[TiCl_4 \left\{ CH(CO_2Et)_3 \right\} \right]$$
(1)

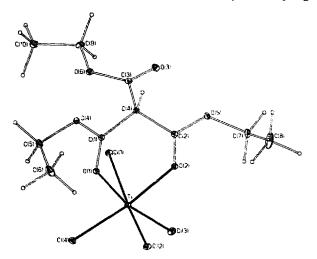


Fig. 1. Structure and the numbering scheme of the [TiCl₄(CH(CO₂Et)₃)] molecule.

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 [TiCl₄(CH(CO₂Et)₃)] molecules. The titanium atom is octahedrally coordinated by four terminal chlorine atoms and two mutually cis carbonyl oxygen atoms from triester molecules. The third C=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 Ti-Cl(1) and Ti-Cl(2) bond lengths cis to carbonyl oxygen O(1) and O(2) atoms are 2.260(1) Å and 2.271(1) Å respec-

tively, and are similar to those found in [TiCl₄(diester)] compounds where they range from 2.259(2) to 2.293(2) Å [4,5]. The Ti-Cl(3) and Ti-Cl(4) bond lengths of 2.208(1) A and 2.214(1) A as well as the Ti-O(1) and Ti-O(2) distances of 2.144(2) Å and 2.122(2) Å are typical for complexes of [TiCl₄(diester)] [2-5]. The Cl-Ti-Cl and Cl-Ti-O bond angles (see Table 1) show the octahedron around the Ti atom to be distorted. The Ti-O(1)-C(1)-C(4) and Ti-O(2)-C(2)-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 O(1)-C(1) and O(2)-C(2) carbonyl groups (0.14 Å)below the first plane and 0.13 Å 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), C(4) atoms form the angle of 34.9°. In the crystal no short inter- and intramolecular contacts are observed.

3.2. Synthesis and structure of $[Al_2Cl_6\{\mu-C_2H_4(CO_2Et)_2\}]$ (2)

A suspension of AlCl₃ in CH₂Cl₂ under N₂ reacts with diethyl succinate in 2:1 molar ratio. The resulting colourless 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 [Al₂Cl₆ \(\mu\)-

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

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Ti-Cl(1)	2.260(1)	O(1)-C(1)	1.209(3)	
Ti=C!(2)	2.271(1)	Q(2)-C(2)	1.223(3)	
Ti_C(3)	2.208(1)	O(3)-C(3)	1.196(3)	
Ti-CI(4)	2.214(1)	C(1)=O(4)	1.305(3)	
Ti-O(1)	2.144(2)	C(2)-O(5)	1.286(3)	
Ti-O(2)	2.122(2)	C(3)-O(6)	1.316(3)	
CI(1)-TI-CI(2)	166.9(1)	Cl(3)-Ti-Cl(4)	101.4(1)	
CK(1)-Ti-Cl(3)	94.7(1)	Cl(3)-Ti-O(1)	168.1(1)	
Cl(1)-TiCl(4)	92.9(1)	Cl(3)-Ti-O(2)	89.4(1)	
Cl(1)-Ti-O(1)	83.4(1)	Cl(4)-Ti-O(1)	90.5(1)	
Cl(1)-Ti-O(2)	86.4(1)	Cl(4)-Ti-O(2)	169.2(1)	
Cl(2)-Ti-Cl(3)	94.9(1)	O(1)-Ti-O(2)	78.7(1)	
Cl(2)-Ti-Cl(4)	93.8(1)	Ti=O(1)-C(1)	132.5(2)	
Cl(2)-Ti-O(1)	85.4(1)	Ti-O(2)-C(2)	133.6(2)	
Cl(2)-Ti-O(2)	84.9(1)			
Ti-O(1)-C(1)-C(4)	-5.3(9)	Ti-O(2)-C(2)-C(4)	-6.6(8)	
O(1)-C(1)-O(4)-C(5)	0.1(7)	O(2)-C(2)-O(5)-C(7)	1.9(8)	
O(1)-C(1)-C(4)-C(2)	- 30.3(8)	O(2)-C(2)-C(4)-C(1)	36.2(6)	
Q(1)-C(1)-C(4)-C(3)	91.1(6)	O(2)C(2)C(4)C(3)	-89.1(6)	
C(1)-O(4)-C(5)-C(6)	85.3(5)	C(2)-U(5)-C(7)-C(8)	- 122.5(6)	
C(1)-C(4)-C(3)-O(3)	153.6(6)	C(2)-C(4)-C(3)-O(3)	-29.0(6)	
C(1)-C(4)-C(3)-O(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)			

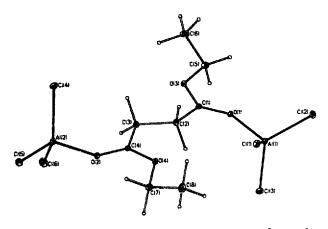


Fig. 2. Structure and the numbering scheme of the $[Al_2Cl_6(\mu-C_2H_4(CO_2Et)_2)]$ molecule.

C₂H₄(CO₂Et)₂]] compound shows the characteristic band of a coordinated carbonyl group at 1604(vs, br)cm⁻¹.

$$2AICl_{3} + C_{2}H_{4}(CO_{2}Et)_{2}$$

$$\xrightarrow{CH_{2}Cl_{2}} [Al_{2}Cl_{6} \{ \mu - C_{2}H_{4}(CO_{2}Et)_{2} \}]$$
(2)

Compound 2 was shown by X-ray diffraction studies to have a dimeric structure. The overall view of the $[Al_2Cl_6\{\mu-C_2H_4(CO_2Et)_2\}]$ 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 Al-Cl bond distances vary from 2.088(2) to 2.104(2) Å and are similar to those found in $[AlCl_3(C_6H_5CO_2Et)](2.110(2)$ and 2.102(2) Å) [14] and are still shorter than the Al-Cl bond distances in the $[AlCl_2(THF)_4]^+$ cation [15]. The Al(1)-O(1) and Al(2)-O(2) bond lengths are 1.794(4) Å and 1.803(4) Å

respectively. The carbonyl O(1)-C(1) and O(2)-C(2)bond distances of 1.246(6) and 1.244(7) Å are shorter compared with the carbonyl C-O bond distance in the free ester ethyl benzoate, which is 1.36(1) Å [16]. The A(1)-O(1)-C(1) and A(2)-O(2)-C(4) bond angles of 141.4(4)° and 135.2(4)° are much lower than the corresponding one in $[AlCl_3(C_6H_5CO_2Et)]$ (168.4(3)°) which is now much closer to the ideal angle of 120°. This indicates that the Al-O bond is more covalent in 2 than in the Al-O bond in $[AlCl_3(C_6H_5CO_7Et)]$. The values of both AI-O(1)-C(1)-C(2) and AI(2)-O(2)C(4)-C(3)torsion angles (0.9(9)) and (0.9(9)) indicate that both aluminium atoms are bound in the plane of O(1)-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 O(3)-C(5) and 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 [TiCl₄(CH(CO₂Et)₃)] complex the titanium atom is octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of the triester molecule. The third C=O group remains uncoordinated. In this complex the chelate ester ligand and titanium atom form a six-membered ring, similar to the complex [TiCl₄(CH₂(CO₂Et)₂)]. In contrast to this behaviour, three or two titanium atoms are coordinated via carbonyl groups to the 1,3,5-C₆H₃(CO₂Me), ligand and the polymeric $[3TiCl_4 \cdot 1,3,5-C_6H_3(CO_2Me)_3]$ or the dimeric $[Ti_2Cl_8(\mu-1,3,5-C_6H_3(CO_2Me)_3]_2$ compounds are formed [8].

Table 2
Selected bond lengths (Å), bond angles (deg) and torsion angles (deg) for complex 2

A(1)-C(1)	2.104(2)	AK2)-CK4)	2.102(3)
AK(1)=CK(2)	2.092(2)	AK2)-CK5)	2.102(3)
AK!)=CK3)	2.090(2)	AK2)-CK6)	2.088(3)
Al(1)=O(1)	1,794(4)	A(2)-O(2)	1.803(4)
O(1)-C(1)	1.246(6)	O(2)-C(4)	1.244(7)
CI(1)=AI(1)=CI(2)	112.4(1)	CI(4)-AK1)-CK4)	111.8(2)
CK(1)-AK(1)-CK(3)	112.1(1)	Cl(4)-Al(1)-Cl(5)	114.0(2)
CK(1)-AK(1)-O(1)	107.9(2)	CK4)-AK1)-O(2)	106,2(2)
CK2)-AK1)-CK3)	114.0(1)	CK5)-AK1)-CK5)	113.9(2)
Cl(2)-Al(1)-O(1)	104.4(2)	CK(5)-AK(1)-O(2)	103.7(2)
CK(3)=AK(1)=Q(1)	105.4(2)	CK(6)-AK(1)-O(2)	106.4(2)
AK(1)=O(1)=C(1)	141.4(4)	Al(2)-O(2) -C(4)	135.2(4)
AKI)=O(1)=C(1)=O(3)	- 178.3(7)	A(2)-O(2)-C(4)-O(4)	173.9(5)
AK(1)-O(1)-C(1)-C(2)	0.9(9)	Al(2)-O(2)-C(4)-C(3)	-6.4(8)
D(1)-C(1)-O(3)-C(5)	1.4(8)	O(2)-C(4)-O(4)-C(7)	2.9(8)
O(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)	C(4)-O(4)-C(7)-C(8)	- 161.1(7)
C(1)-C(2)-C(3)-C(4)	-65.3(7)		

Diethyl succinate and AlCl₃ give the dimeric compound 2. In the dimer, two AlCl₃ molecules are linked together by the $C_2H_4(CO_2Et)_2$ ligand. Similar reaction of MgCl₂ with diethyl succinate gives the ionic compound [Mg{ $C_2H_4(CO_2Et)_2$ }₃ [MgCl₄] [17]. The crystal structure of the [Mg{ $C_2H_4(CO_2Et)_2$ }₃]²⁺ cation consists of [Mg{ $C_2H_4(CO_2Et)_2$ }₂]²⁺ units linked by other diethyl succinate molecules to generate a linear polymer. However, TiCl₄ and $C_2H_4(CO_2Et)_2$ form the monomeric [TiCl₄{ $C_2H_4(CO_2Et)_2$ }] 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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