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Synthesis and structure of polymeric [1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ · 3TiCl$_4$] and dimeric [[μ-1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$]$_2$Cl$_8$Ti$_2$] · 2CH$_2$Cl$_2$ compounds *

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Abstract

The reaction of TiCl$_4$ with trimethyl 1,3,5-benzenetricarboxylate in 1 : 3.5 and 1 : 1 ratios in 1,2-dichloroethane and dichloromethane gave [1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ · 3TiCl$_4$]$_n$ (1) and [[μ-1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$]$_2$Cl$_8$Ti$_2$] · 2CH$_2$Cl$_2$ (2), respectively. In the crystalline state compound 1 is a two-dimensional polymer. Each of the 1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ molecules behaves as a bridging ligand, bridging three Ti atoms. The titanium atoms are coordinated to the trimethyl 1,3,5-benzenetricarboxylate ester molecule via carbonyl oxygen atoms and to two bridging and three terminal chlorine atoms. The crystal of 2 consists of dimeric complex molecules with a crystallographic symmetry centre and with dichloromethane molecules located between them. The titanium atoms are octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of two trimethyl 1,3,5-benzenetricarboxylate ligands in the *cis* position. One of the –CO$_2$Me ligand groups remains uncoordinated. The phenyl rings are not strictly planar and the average separation between them in complex molecules is 3.44(1) Å.

1. Introduction

In order to understand the high stereoselectivities of the processes of diene addition [1,2] and propylene polymerization [3–8], the reactions of TiCl$_4$ with trimethyl 1,3,5-benzenetricarboxylate were studied. Here we describe the crystal structure of the title compounds.

2. Experimental details

All manipulations were carried out under an inert atmosphere using a standard Schlenk system and vacuum line. Anhydrous TiCl$_4$ and 1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ were of commercial grade (Aldrich). Solvents were dried and purified by standard techniques. IR spectra were recorded on a Perkin–Elmer 180 spectrophotometer. Microanalyses were performed at the University of Wrocław.

2.1. Syntheses

2.1.1. Polymer of [{tris(di-μ-chloro)-μ$_3$-(trimethyl 1,3,5-benzenetricarboxylate-O,O'O")}nonachlorotrititanium(IV)]

1.92 cm^3 of TiCl$_4$ (17.5 mmol) was added dropwise to a solution of 1.26 g (5 mmol) of 1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ in 80 cm^3 1,2-dichloroethane. The mixture was stirred for 0.5 h and then heated under reflux until complete dissolution of the yellow precipitate. After 24 h at 327 K the yellow crystalline compound was filtered off and washed with 1,2-C$_2$H$_4$Cl$_2$ (3 × 5 cm^3). Yield 3.34 g (81.4%). Anal. Found: Cl, 51.79; Ti, 17.53. C$_{12}$H$_{12}$Cl$_{12}$O$_6$Ti$_3$ calc.: Cl, 51.80; Ti, 17.49%. IR (Nujol): ν(Ti–Cl) 375s, 390sh, 412vs, 425sh, 432sh, and 445sh; ν(C=O) 1635vs, br and 1650sh; other 497w, 520w, 720m, 731s, 902w, 992m, 1158w and 1598 cm^{-1}.

2.1.2. Di-μ-[trimethyl 1,3,5-benzenetricarboxylate-O,O']octachlorodititanium(IV) dichloromethane (1/2)

To 4.5 g of trimethyl 1,3,5-benzenetricarboxylate (1.8 mmol) in 100 cm^3 dichloromethane was added dropwise 2 cm^3 (3.45 g; 1.8 mmol) of TiCl$_4$ with stirring. After 1 h the yellow precipitate was filtered off and washed with n-hexane (3 × 5 cm^3). Yield 4.6 g

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* Polymer: [{tris(di-μ-chloro)-μ$_3$-(trimethyl 1,3,5-benzenetricarboxy-late-O,O',O")}nonachlorotrititanium(IV)]. Dimer: di-μ-[trimethyl 1,3,5-benzenetricarboxylate-O,O']octachlorodititanium-(IV) di-chloromethane (1/2).

(47.6%). A portion of the compound (3 g) was heated in 80 cm^3 CH$_2$Cl$_2$ under reflux and left to crystallize. After 24 h yellow needles of X-ray quality of **2** were formed. They were filtered off, washed with n-hexane (3 × 5 cm^3) and vacuum dried. Anal. Found: Cl, 26.89; Ti, 9.13. C$_{24}$H$_{24}$Cl$_8$O$_{12}$Ti$_2$ · 2CH$_2$Cl$_2$ calc.: Cl, 26.92; Ti, 9.11%. IR (Nujol): ν(C=O) 1640vs, 1652vs, 1660sh; ν(Ti–Cl) 386vs; other 794w, 812w, 892w, 912w, 948w, 968m, 994s, 1154w, 1172w, 1274vs, 1294vs cm^{-1}.

2.2. Crystallography

2.2.1. Crystal data for 1

Yellow crystals, C$_{12}$H$_{12}$Cl$_{12}$O$_6$Ti$_3$, $M = 821.4$. Monoclinic, space group $P2_1/c$, $a = 9.042(5)$, $b = 14.178(13)$, $c = 22.32(2)$ Å, $\beta = 92.04(7)°$, $U = 2860(4)$ Å^3, $Z = 4$, $D_c = 1.908(4)$ g cm^{-3}, $D_m = 1.88$ g cm^{-3}, $F(000) = 1608$, $T = 298(1)$ K, μ(Mo Kα) = 19.7 cm^{-1}, λ(Mo Kα) = 0.71069 Å.

2.2.2. Crystal data for 2

Yellow crystals, C$_{24}$H$_{24}$Cl$_8$O$_{12}$Ti$_2$ · 2CH$_2$Cl$_2$, $M = 1053.7$. Triclinic, space group $P\bar{1}$, $a = 9.620(7)$, $b = 10.360(9)$, $c = 11.517(9)$ Å, $\alpha = 67.09(7)$, $\beta = 81.89(7)$, $\gamma = 84.94(7)°$, $U = 1046(2)$ Å^3. $Z = 1$, $D_c = 1.673(3)$ g cm^{-3}, $D_m = 1.67$ g cm^{-3}, $F(000) = 528$, $T = 295(2)$ K, μ(Mo Kα) = 12.0 cm^{-1}.

2.3. Data collection and processing

Both crystals were sealed in glass capillaries. Preliminary data were recorded by photographic methods. Intensities were collected with a Syntex P2$_1$ four-circle diffractometer in the ω-2θ mode (with crystals of dimensions 0.6 × 0.5 × 0.4 mm for **1** and 0.8 × 0.8 × 0.6 mm for **2**) and Mo Kα radiation; 5442 (4 < 2θ < 52°) and 5337 (4 < 2θ < 52°) reflections were measured for **1** and **2**, respectively, of which 3418 (**1**) and 2746 (**2**) with $I > 3.0$ $\sigma(I)$ were used for calculations. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELX76 [9]. Atomic scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 10. The hydrogen atoms of methyl groups were deduced from difference maps and refined with the constraint d(C–H) = 1.08 Å. All other hydrogen atoms were included in geometrically calculated positions. The CH$_2$Cl$_2$ molecule in **2** was partially disordered. The absorption corrections following the DIFABS [11] procedure were applied; minimum and maximum absorption corrections were 0.863 and 1.092 (for **1**) and 0.934 and 1.051 (for **2**). An isotropic extinction correction of the form $1 - xF_c^2 \sin \theta$ was applied. The parameter x converged to $1.38(5) \times 10^{-7}$ for **1** and to $6.5(3) \times 10^{-7}$ for **2**. A weighting scheme of the form $w = 1/\sigma^2(F_o)$

was applied for both structures. Final R (= $\Sigma \parallel F_o \mid - \mid F_c \parallel /\Sigma \mid F_o \mid$) and R' (= $[\Sigma w(\mid F_o \mid - \mid F_c \mid)^2/\Sigma wF_o^2]^{1/2}$) values were 0.0354 and 0.0395 for **1** and 0.0370 and 0.0386 for **2**, respectively. For the last cycle of the refinement the maximum value of the ratio Δ/σ was 0.11 for **1** and 0.07 for **2**, and the final difference maps showed a general background within the ranges −0.36 and 0.42 and −0.27 and 0.023 e Å^{-3} for **1** and **2**, respectively. The final positional and thermal parameters for the non-hydrogen atoms are given in Tables 1–4.

3. Results and discussion

3.1. Synthesis and structure of [1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ · 3TiCl$_4$], (1)
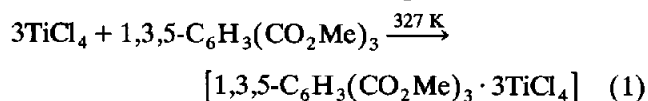
Addition of trimethyl 1,3,5-benzenetricarboxylate to TiCl$_4$ in 1,2-dichloroethane, in a molar ratio of 1 : 3.5, leads to diamagnetic, air-sensitive, yellow crystals of composition 1,3,5-C$_6$H$_3$(CO$_2$Me)$_3$ · 3TiCl$_4$, which can

TABLE 1. Fractional atomic coordinates for compound **1**

Atom	x	y	z
Ti(1)	0.57643(10)	0.43294(7)	0.13109(4)
Ti(2)	0.20274(10)	0.50224(7)	0.19538(4)
Ti(3)	0.69075(9)	0.48044(7)	0.53936(4)
Cl(1)	0.42844(14)	0.40879(9)	0.22173(6)
Cl(2)	0.35212(14)	0.53115(10)	0.10630(6)
Cl(11)	0.67827(16)	0.48687(13)	0.04899(6)
Cl(12)	0.76445(16)	0.35747(11)	0.17470(8)
Cl(13)	0.47181(17)	0.31010(12)	0.08677(8)
Cl(21)	0.01590(15)	0.57942(10)	0.14833(7)
Cl(22)	0.08786(16)	0.44438(11)	0.27291(6)
Cl(23)	0.30026(19)	0.62682(11)	0.24073(7)
Cl(3)	0.46723(13)	0.39116(9)	0.50559(6)
Cl(31)	0.87865(15)	0.58194(11)	0.55125(6)
Cl(32)	0.80158(17)	0.34798(11)	0.56546(8)
Cl(33)	0.59311(15)	0.50961(12)	0.62667(6)
O(1)	0.6425(4)	0.55519(23)	0.17544(15)
O(2)	0.8587(4)	0.88062(23)	0.35297(15)
O(3)	0.7516(4)	0.46234(23)	0.45099(15)
O(11)	0.7017(5)	0.70812(25)	0.17509(16)
O(21)	0.9159(4)	0.79778(23)	0.43594(15)
O(31)	0.7698(5)	0.38365(24)	0.36570(16)
C(1)	0.7417(6)	0.6265(4)	0.26499(22)
C(2)	0.7876(6)	0.7113(4)	0.29125(22)
C(3)	0.8260(5)	0.7130(4)	0.35216(22)
C(4)	0.8181(6)	0.6316(4)	0.38655(21)
C(5)	0.7732(6)	0.5479(4)	0.35984(22)
C(6)	0.7345(6)	0.5447(4)	0.29810(22)
C(11)	0.6897(6)	0.6256(4)	0.20079(22)
C(12)	0.6572(10)	0.7156(6)	0.11194(28)
C(21)	0.8682(6)	0.8050(4)	0.37929(23)
C(22)	0.9602(8)	0.8829(5)	0.46726(27)
C(31)	0.7630(6)	0.4612(4)	0.39646(23)
C(32)	0.7667(9)	0.2938(4)	0.39789(31)

be stored under nitrogen. The compound is insoluble in aliphatic and aromatic hydrocarbons.

The IR spectrum of this compound shows bands at 1635vs, br cm^{-1} due to ν(C=O), and 375s, 390sh and 412vs, br cm^{-1}, which can be assigned to ν(Ti–Cl).

$$3TiCl_4 + 1,3,5\text{-}C_6H_3(CO_2Me)_3 \xrightarrow{327\ K}$$

$$[1,3,5\text{-}C_6H_3(CO_2Me)_3 \cdot 3TiCl_4] \quad (1)$$

1

Compound **1** in the crystalline state is a two-dimensional polymer (Fig. 1). Selected bond lengths, bond angles and torsion angles are listed in Table 5. The asymmetric unit consists of three Ti atoms, twelve Cl atoms and one ester molecule. All titanium atoms are coordinated to two bridging and three terminal chlorine atoms giving $Cl_3Ti(\mu\text{-}Cl)_2TiCl_3$ moieties. (Such "dimers" are formed by Ti(1)···Ti(2) and Ti(3)···

Ti(3^i) atoms, where Ti(3^i) atoms are related to Ti(3) atoms by centres of symmetry). Furthermore the titanium atoms are coordinated to the ester molecules via carbonyl oxygen atoms so that the coordination spheres of three crystallographically independent titanium atoms are similar. The ester molecule itself is bonded to three crystallographically different Ti atoms: Ti(1), Ti(2^{iii}) and Ti(3), where the Ti(3^{iii}) atom is related to the Ti(3) atom by a two-fold axis of rotation (see Fig. 1 and Table 5).

The titanium atoms Ti(1), Ti(2) and Ti(3) are located 2.073(3), 2.099(3) and 2.082(3) Å from the O(1), O(2) and O(3) carbonyl oxygens, respectively. The Ti–Cl(terminal) bond lengths range from 2.197(2) to 2.242(2) Å, whereas the average Ti–Cl(bridge) distance is 2.49(2) Å. The Ti–Cl and Ti–O bond lengths and Cl–Ti–Cl and Cl–Ti–O bond angles (see Table 5) are comparable to those found in other Ti^{4+} chloro-com-

TABLE 2. Final anisotropic thermal parameters for compound **1**

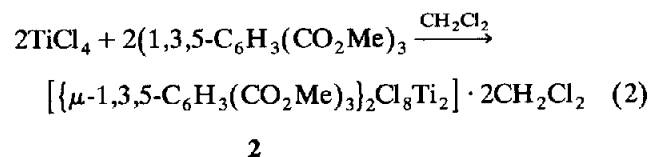| Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti(1)	0.0298(6)	0.0373(6)	0.0317(6)	−0.0103(5)	0.0011(5)	−0.0050(5)
Ti(2)	0.0315(6)	0.0273(6)	0.0300(5)	−0.0013(5)	0.0003(4)	0.0029(5)
Ti(3)	0.0252(5)	0.0356(6)	0.0241(5)	0.0040(5)	−0.0042(4)	0.0029(5)
Cl(1)	0.0322(7)	0.0346(8)	0.0305(7)	0.0037(6)	−0.0017(6)	0.0004(6)
Cl(2)	0.0349(8)	0.0447(8)	0.0280(7)	0.0047(7)	−0.0020(6)	−0.0018(7)
Cl(11)	0.0482(9)	0.089(2)	0.0324(8)	−0.0042(9)	0.0076(7)	−0.0067(9)
Cl(12)	0.0417(9)	0.0490(9)	0.067(2)	−0.0023(9)	−0.0042(8)	0.0069(8)
Cl(13)	0.0454(9)	0.059(2)	0.083(2)	−0.0439(9)	0.0085(9)	−0.0122(9)
Cl(21)	0.0401(8)	0.0395(9)	0.0600(9)	0.0061(8)	−0.0053(7)	0.0111(7)
Cl(22)	0.0469(9)	0.061(2)	0.0371(9)	0.0038(8)	0.0105(7)	0.0005(8)
Cl(23)	0.071(2)	0.0374(9)	0.0502(9)	−0.0120(8)	−0.0066(9)	−0.0035(8)
Cl(3)	0.0310(8)	0.0239(7)	0.0376(8)	0.0033(6)	−0.0056(6)	0.0008(6)
Cl(31)	0.0343(8)	0.0562(9)	0.0446(9)	−0.0056(8)	−0.0050(7)	−0.0109(8)
Cl(32)	0.0466(9)	0.0518(9)	0.066(2)	0.0234(9)	−0.0073(8)	0.0161(8)
Cl(33)	0.0404(8)	0.082(2)	0.0246(7)	−0.0005(8)	−0.0006(6)	−0.0033(9)
O(1)	0.038(3)	0.030(3)	0.028(2)	−0.004(2)	−0.003(2)	−0.005(2)
O(2)	0.031(2)	0.024(2)	0.036(3)	0.002(2)	−0.006(2)	−0.001(2)
O(3)	0.032(2)	0.031(2)	0.031(3)	0.002(2)	0.002(2)	0.000(2)
O(11)	0.064(3)	0.030(3)	0.034(3)	0.004(2)	−0.012(2)	−0.004(2)
O(21)	0.045(3)	0.029(2)	0.028(3)	−0.003(2)	−0.012(2)	0.001(2)
O(31)	0.061(3)	0.024(3)	0.037(3)	−0.004(2)	0.002(2)	−0.001(2)
C(1)	0.029(3)	0.029(3)	0.025(3)	−0.002(3)	−0.002(3)	0.001(3)
C(2)	0.031(3)	0.023(3)	0.030(3)	0.001(3)	−0.002(3)	−0.000(3)
C(3)	0.022(3)	0.026(3)	0.031(3)	−0.005(3)	−0.002(3)	0.002(3)
C(4)	0.024(3)	0.027(3)	0.026(3)	−0.005(3)	0.000(3)	0.003(3)
C(5)	0.029(3)	0.023(3)	0.029(3)	−0.001(3)	0.003(3)	0.004(3)
C(6)	0.027(3)	0.024(3)	0.029(3)	−0.005(3)	0.001(3)	0.000(3)
C(11)	0.030(3)	0.028(3)	0.032(4)	0.002(3)	0.004(3)	−0.002(3)
C(12)	0.099(6)	0.058(5)	0.035(4)	0.020(4)	−0.025(4)	−0.007(5)
C(21)	0.025(3)	0.030(4)	0.033(4)	−0.002(3)	−0.000(3)	0.001(3)
C(22)	0.068(5)	0.044(4)	0.039(4)	−0.016(3)	−0.015(4)	−0.008(4)
C(31)	0.021(3)	0.032(3)	0.031(4)	−0.003(3)	0.000(3)	0.004(3)
C(32)	0.085(6)	0.021(4)	0.062(5)	0.004(4)	0.001(4)	−0.005(4)

The anisotropic temperature factors are expressed as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.

plexes containing organic esters [12–14]. The carbon atoms of the methyl groups C(12), C(22) and C(32) are *syn* to O(1), O(2) and O(3), respectively.

It is interesting, that not only the 1,3,5-C_6H_3-$(CO_2Me)_3$ but also the p-$C_6H_4(CO_2Me)_2$ diester yields with $TiCl_4$ polymeric [p-$C_6H_4(CO_2Me)_2 \cdot TiCl_4$] compound [12]. The last-named compound consists of the dimeric $Cl_3Ti(\mu$-$Cl)_2TiCl_3$ moieties connected by two carbonyl oxygen atoms of the ligands. However, only the linear polymers could be distinguished in its crystal structure [12]. It follows that the third –CO_2Me group present in 1,3,5-$C_6H_3(CO_2Me)_3$ allows the formation of the two-dimensional polymer in the solid, but only when $TiCl_4$ is present in excess during crystallization. It should be remembered that other non-polymeric ester compounds [15–17] [(L)$Cl_3M(\mu$-$Cl)_2MCl_3$(L)] with the moiety, where M = Ti, Zr and L = CH_3CO_2Et or p-$CH_3OC_6H_4CO_2Et$, are also known.

3.2. Synthesis and structure of [{μ-1,3,5-$C_6H_3(CO_2$-$Me)_3$}$_2Cl_8Ti_2$] · $2CH_2Cl_2$ (2)

Further studies aimed to elucidate whether at the other $TiCl_4 : 1,3,5$-$C_6H_3(CO_2Me)_3$ ratios other compounds could be formed. The addition in dichloromethane of 1,3,5-$C_6H_3(CO_2Me)_3$ to $TiCl_4$, in ratios of 1:1 and 1:2 leads to good yields of the yellow air-sensitive compound 2. The compound is insoluble in aliphatic and aromatic hydrocarbons and can be stored under nitrogen.

$$2TiCl_4 + 2(1,3,5\text{-}C_6H_3(CO_2Me)_3 \xrightarrow{CH_2Cl_2}$$

$$[\{\mu\text{-}1,3,5\text{-}C_6H_3(CO_2Me)_3\}_2Cl_8Ti_2] \cdot 2CH_2Cl_2 \quad (2)$$

2

The IR spectrum in Nujol shows the expected bands at 1640vs cm^{-1}, 1652vs cm^{-1}, 1660sh cm^{-1} and 1730s cm^{-1} due to ν(C=O) of coordinated and non-coordinated carbonyl groups, respectively. The peak at 386vs cm^{-1} was attributed to ν(Ti–Cl).
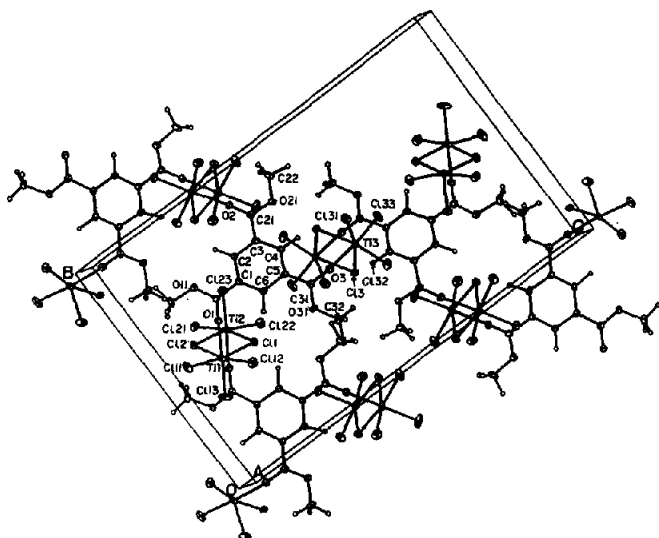
Compound 2 in the crystalline state exists as centrosymmetric dimers. The structure of one molecule viewed perpendicularly to the ring plane is depicted in Fig. 2 and principal interatomic distances, bond angles and torsion angles are listed in Table 6. In the complex molecule four chlorine atoms and two carbonyl oxygen atoms, from two trimethyl 1,3,5-benzenetricarboxylate ligands (in the *cis* position), form a distorted octahedron around the Ti atom. Each ester molecule is coordinated to two titanium atoms via two carbonyl oxygen atoms. In such a way one of the CO_2Me group of each ligand remains non-coordinated. The phenyl rings in the molecules are parallel (because the molecules are centrosymmetric) with separation of

3.44(1) Å and are only slightly mutually shifted, so the C(1), C(2), C(3), C(4), C(5), and C(6) carbon atoms of the one ring are close to the C(4′), C(5′), C(6′), C(1′), C(2′) and C(3′) atoms of the second ring, respectively (see Fig. 2). The centres of these two rings are shifted mutually by *ca.* 0.4 Å. This shifting is much smaller than those observed earlier [13,18–21]. Note also that the distance of 3.44(1) Å between the parallel carbon rings in the molecule of 2, is greater than that of 3.36(1) Å observed in compounds with stacks. This expansion is most likely to be due to the repulsion between the electrons of the two parallel rings. It was observed earlier that at the similar location of the phenyl rings (as in 2) electronic repulsion of the mutual ring leads to deformation of the phenyl rings [22]. The rings in 2 are not strictly planar. The C(2) and C(5) atoms are located over the plane formed by C(1), C(6), C(4) and C(3) atoms, so the angle between two planes formed by the C(2), C(1), C(6), C(5) atoms, and C(2) C(3), C(4), C(5) atoms is 178.2(4)°. A similar effect was

TABLE 3. Fractional atomic coordinates for compound 2

Atom	x	y	z
Ti	0.24665(7)	0.82079(7)	0.69996(6)
Cl(1)	0.26732(10)	0.99351(10)	0.50180(10)
Cl(2)	0.26169(11)	0.61416(11)	0.87367(10)
Cl(3)	0.30000(13)	0.95438(13)	0.79590(11)
Cl(4)	0.01483(10)	0.84845(12)	0.73717(11)
C(1)	0.6044(4)	0.6705(4)	0.5376(4)
C(2)	0.6975(4)	0.5570(4)	0.5450(4)
C(3)	0.7163(4)	0.5111(4)	0.4457(4)
C(4)	0.6468(4)	0.5792(4)	0.3389(4)
C(5)	0.5585(4)	0.6946(4)	0.3304(4)
C(6)	0.5358(4)	0.7390(4)	0.4307(4)
C(11)	0.5703(4)	0.7135(4)	0.6466(4)
C(12)	0.6383(5)	0.7151(6)	0.8347(4)
C(31)	0.8032(4)	0.3824(4)	0.4553(4)
C(32)	0.9870(5)	0.2273(5)	0.5511(6)
C(51)	0.4866(5)	0.7637(5)	0.2139(4)
C(52)	0.3016(6)	0.9211(7)	0.1258(5)
O(11)	0.4611(3)	0.7777(3)	0.6607(3)
O(12)	0.6647(3)	0.6781(3)	0.7246(3)
O(31)	0.7837(3)	0.3113(3)	0.3963(3)
O(32)	0.8979(3)	0.3529(3)	0.5328(3)
O(51)	0.5201(4)	0.7463(5)	0.1173(4)
O(52)	0.3804(3)	0.8483(4)	0.2309(3)
C(10)	1.0234(7)	0.3256(7)	0.9222(5)
Cl(5) [a]	0.9483(2)	0.4501(2)	0.7957(2)
Cl(51) [a]	0.885(4)	0.398(4)	0.828(4)
Cl(6) [a]	1.0926(3)	0.1830(3)	0.8907(3)
Cl(61) [a]	1.153(2)	0.231(3)	0.927(2)
Cl(62) [a]	1.038(2)	0.151(2)	0.937(2)

[a] The occupancy factors for Cl(5), Cl(51), Cl(6), Cl(61) and Cl(62) are 0.95, 0.05, 0.81, 0.06 and 0.13, respectively.

Fig.1. View of the $[1,3,5\text{-}C_6H_3(CO_2Me)_3 \cdot 3TiCl_4]_n$ crystal structure.

observed in the compound $[\{\mu\text{-}m\text{-}C_6H_4(CO_2Et)_2\}_2\text{-}Cl_8Ti_2]$ [13]. On the contrary, when the titanium atoms in **1** are coordinated to all three carbonyl oxygens of the $1,3,5\text{-}C_6H_3(CO_2Me)_3$ ligand (see Fig. 1) and the distance between phenyl rings is much larger the phenyl rings are strictly planar. It is important to note, that in a similar manner, in the complex $[\{\mu_3\text{-}C_6H_3(CO_2\text{-}Me)_3\}(AlCl_3)_3]$ where the three Al atoms are also coordinated to all carbonyl oxygen atoms of the ester molecule, the phenyl ring is not strictly planar [23].

In $[\{\mu\text{-}1,3,5\text{-}C_6H_3(CO_2Me)_3\}_2Cl_8Ti_2] \cdot 2CH_2Cl_2$ (**2**) crystals, short intermolecular contacts are observed. The Cl(1) atom is 3.259(4) Å from $C(11^{1-x,2-y,1-z})$ atoms of the adjacent complex molecule. The solvated CH_2Cl_2 molecules are located between dimeric complex molecules of $[\{\mu\text{-}1,3,5\text{-}C_6H_3(CO_2Me)_3\}_2Cl_8Ti_2]$ (Fig. 3).

TABLE 4. Final heavy-atom thermal parameters for compound **2**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.0441(4)	0.0382(4)	0.0388(4)	−0.0179(4)	−0.0032(3)	0.0109(3)
Cl(1)	0.0619(7)	0.0418(6)	0.0480(6)	−0.0109(5)	−0.0068(5)	0.0047(5)
Cl(2)	0.0703(7)	0.0503(7)	0.0444(6)	−0.0093(5)	−0.0057(5)	0.0113(5)
Cl(3)	0.0928(9)	0.0665(8)	0.0658(8)	−0.0454(7)	−0.0108(6)	0.0066(6)
Cl(4)	0.0462(6)	0.0701(8)	0.0634(7)	−0.0216(6)	0.0012(5)	0.0177(5)
Cl(5) [a]	0.090(2)	0.093(2)	0.086(2)	0.0011(9)	−0.0224(9)	0.0107(9)
Cl(6) [a]	0.099(2)	0.085(2)	0.104(2)	−0.035(2)	−0.004(2)	0.027(2)
C(10)	0.124(5)	0.093(5)	0.057(4)	−0.026(4)	−0.020(3)	0.028(4)
C(1)	0.036(2)	0.038(3)	0.038(2)	−0.014(2)	−0.002(2)	0.000(2)
C(2)	0.039(2)	0.037(3)	0.040(3)	−0.014(2)	−0.006(2)	0.001(2)
C(3)	0.040(2)	0.033(2)	0.044(3)	−0.015(2)	−0.003(2)	−0.001(2)
C(4)	0.044(3)	0.039(3)	0.039(3)	−0.017(2)	−0.002(2)	0.000(2)
C(5)	0.044(3)	0.037(3)	0.037(2)	−0.011(2)	−0.005(2)	0.001(2)
C(6)	0.039(2)	0.039(3)	0.037(2)	−0.013(2)	−0.004(2)	0.005(2)
C(11)	0.039(3)	0.039(3)	0.040(3)	−0.014(2)	−0.007(2)	0.005(2)
C(12)	0.075(4)	0.091(4)	0.056(3)	−0.044(3)	−0.025(3)	0.020(3)
C(31)	0.043(3)	0.037(3)	0.045(3)	−0.015(2)	−0.005(2)	0.002(2)
C(32)	0.073(4)	0.053(3)	0.094(4)	−0.036(3)	−0.042(3)	0.030(3)
C(51)	0.062(3)	0.058(3)	0.046(3)	−0.020(3)	−0.015(2)	0.010(2)
C(52)	0.093(4)	0.097(5)	0.070(4)	−0.026(4)	−0.045(3)	0.037(4)
O(11)	0.041(2)	0.062(2)	0.047(2)	−0.027(2)	−0.004(2)	0.011(2)
O(12)	0.052(2)	0.064(2)	0.047(2)	−0.029(2)	−0.020(2)	0.018(2)
O(31)	0.057(2)	0.039(2)	0.053(2)	−0.022(2)	−0.014(2)	0.009(2)
O(32)	0.056(2)	0.052(2)	0.068(2)	−0.033(2)	−0.025(2)	0.017(2)
O(51)	0.135(4)	0.116(4)	0.056(3)	−0.051(3)	−0.041(3)	0.060(3)
O(52)	0.068(2)	0.081(3)	0.057(2)	−0.031(2)	−0.028(2)	0.029(2)
	U_{iso}					
Cl(51) [a]	0.079(9)					
Cl(61) [a]	0.054(5)					
Cl(62) [a]	0.081(5)					

The anisotropic temperature factors are expressed as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)]$.
[a] The occupancy factors for Cl(5), Cl(51), Cl(6), Cl(61) and Cl(62) are 0.95, 0.05, 0.81, 0.06 and 0.13, respectively.

TABLE 6. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for compound 2 [a]

Ti–Cl(1)	2.282(2)
Ti–Cl(3)	2.208(2)
Ti–O(11)	2.095(3)
O(11)–C(11)	1.218(5)
O(51)–C(51)	1.191(6)
O(32)–C(32)	1.454(6)
C(1)–C(2)	1.397(5)
C(3)–C(4)	1.390(5)
C(5)–C(6)	1.385(5)
C(1)–C(11)	1.476(5)
C(5)–C(51)	1.490(5)
C(31)–O(32)	1.299(5)
Ti–Cl(2)	2.302(2)
Ti–Cl(4)	2.225(2)
Ti–O(31')	2.129(3)
O(31)–C(31)	1.220(5)
O(12)–C(12)	1.446(6)
O(52)–C(52)	1.434(6)
C(2)–C(3)	1.383(5)
C(4)–C(5)	1.383(5)
C(6)–C(1)	1.386(5)
C(3)–C(31)	1.484(6)
C(11)–O(12)	1.297(4)
C(51)–O(52)	1.330(6)
Cl(1)–Ti–Cl(2)	165.2(1)
Cl(1)–Ti–Cl(4)	95.4(1)
Cl(2)–Ti–Cl(4)	94.6(1)
Cl(1)–Ti–O(11)	85.6(1)
Cl(2)–Ti–O(11)	83.4(1)
Cl(3)–Ti–O(11)	89.7(1)
Cl(4)–Ti–O(11)	174.3(1)
O(11)–Ti–O(31')	84.8(2)
C(2)–C(1)–C(11)	120.6(4)
C(1)–C(2)–C(3)	118.9(4)
C(2)–C(3)–C(31)	120.5(4)
C(3)–C(4)–C(5)	120.2(4)
C(4)–C(5)–C(51)	118.0(4)
C(1)–C(6)–C(5)	120.1(4)
C(1)–C(11)–O(12)	115.0(4)
C(3)–C(31)–O(31)	121.8(4)
O(31)–C(31)–O(32)	124.2(4)
C(5)–C(51)–O(52)	111.4(4)
Ti–O(11)–C(11)	160.4(3)
C(11)–O(12)–C(12)	118.3(4)
C(51)–O(52)–C(52)	117.1(4)
Cl(1)–Ti–Cl(3)	94.9(1)
Cl(2)–Ti–Cl(3)	94.9(1)
Cl(3)–Ti–Cl(4)	95.8(1)
Cl(1)–Ti–O(31')	84.6(1)
Cl(2)–Ti–O(31')	84.6(1)
Cl(3)–Ti–O(31')	174.5(1)
Cl(4)–Ti–O(31')	89.7(1)
C(2)–C(1)–C(6)	120.5(4)
C(6)–C(1)–C(11)	118.8(4)
C(2)–C(3)–C(4)	120.6(4)
C(4)–C(3)–C(31)	118.7(4)
C(4)–C(5)–C(6)	119.7(4)
C(6)–C(5)–C(51)	122.3(4)
C(1)–C(11)–O(11)	121.7(4)
O(11)–C(11)–O(12)	123.4(4)

TABLE 6 (continued)

C(3)–C(31)–O(32)	113.9(4)
C(5)–C(51)–O(51)	124.5(5)
O(51)–C(51)–O(52)	124.1(5)
Ti'–O(31)–C(31)	177.4(3)
C(31)–O(32)–C(32)	118.4(4)
Ti–O(11)–C(11)–C(1)	72.2(30)
C(32)–O(32)–C(31)–O(31)	0.0(20)
C(12)–O(12)–C(11)–O(11)	0.8(16)
C(52)–O(52)–C(51)–O(51)	0.7(14)

[a] Primed atoms are related to unprimed by $1 - x$, $1 - y$, $1 - z$.

The Ti–Cl, Ti–O bond lengths, Cl–Ti–Cl, Cl–Ti–O bond angles and torsion angles (see Table 6) are comparable to those in the previously known dimeric [{(μ-m-$C_6H_4(CO_2R)_2$}$_2Cl_8Ti_2$] complexes [13,14].

At the substrate molar ratio 1:1 (reaction 2), the 1,3,5-$C_6H_3(CO_2Me)_3$ ester behaves like the m-$C_6H_4(CO_2R)_2$ diesters [13,14] to produce compound 2 of dimeric structure. In those compounds the octahedral titanium atom and the four Cl and two O atoms that are coordinated form cis-$TiCl_4O_2$ units, as in the monomeric compounds [o-$C_6H_4(CO_2R)_2TiCl_4$] [14,24]. Instead, in 1 and in compounds with monoesters $e.g.$ [($CH_3CO_2Et)Cl_3Ti(\mu$-$Cl)_2TiCl_3(CH_3$-$CO_2Et)$] [15–17] or in the polymeric [p-$C_6H_4(CO_2$-$Me)_2 \cdot TiCl_4$] compound [12] the $Cl_3Ti(\mu$-$Cl)_2TiCl_3$ moiety is present. Hence, it follows that small changes in entropy combined with chelating effect and reaction conditions primarily decide the geometry around the titanium
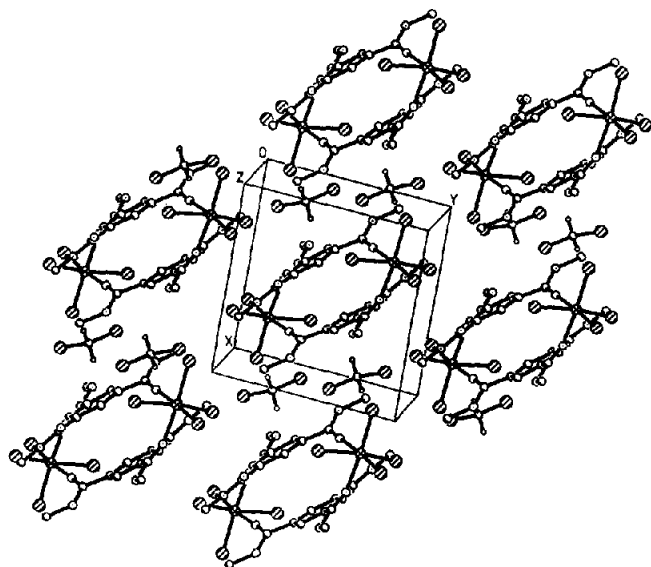

Fig. 3. The packing arrangement in the [{(μ-1,3,5-$C_6H_3(CO_2$-Me)$_3$}$_2Cl_8Ti_2$]·2CH_2Cl_2 crystal.

atom followed by the stereospecifity of reactions process.

Supplementary material available: Tables of observed and calculated structure factors, and hydrogen atom parameters for 1 and 2 compounds are available from the authors.

Acknowledgment

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