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Reactions of TiCl_4 with diesters. Crystal structures of $[\text{CH}_2(\text{CO}_2\text{Et})_2\text{Cl}_4\text{Ti}]$ and $[\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2\text{Cl}_4\text{Ti}]$ *

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Abstract

Direct reactions of TiCl_4 with diethyl malonate in n-hexane or with bis(2-phenoxoethyl) succinate in toluene yield the crystalline compounds $[\text{CH}_2(\text{CO}_2\text{Et})_2\text{Cl}_4\text{Ti}]$ (1) and $[\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2\text{Cl}_4\text{Ti}]$ (2), respectively. The crystal structures of both complexes have been determined by a single crystal X-ray diffraction study, and refined by full-matrix least-squares techniques to an R of 0.034 and 0.038 for 1575 and 1490 independent non-zero reflections for 1 and 2, respectively. Crystals of 1 are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 7.716(10)$, $b = 18.21(2)$, $c = 12.384(10)$ Å, $\beta = 127.29(8)^\circ$. Crystals of 2 are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.680(12)$, $b = 10.178(11)$, $c = 14.398(15)$ Å, $\alpha = 78.45(9)^\circ$, $\beta = 74.16(9)^\circ$, $\gamma = 88.45(9)^\circ$. The titanium atoms in 1 and 2 are octahedrally-coordinated by four chlorine atoms and two carbonyl oxygen atoms of coordinated diester molecules. The titanium atoms and the chelate ligand atoms form the six-membered ring in 1 and the seven-membered ring in 2.

1. Introduction

Monomeric complexes of the general formula $[\text{o-C}_6\text{H}_4(\text{CO}_2\text{R})_2\text{Cl}_4\text{Ti}]$ have been investigated [1–3] in order to explain the influence of aromatic diesters as internal and external donors on the stereospecificity of the polymerization and isotacticity of polypropylene. The chelate $\text{o-C}_6\text{H}_4(\text{CO}_2\text{R})_2$ ligand molecules are coordinated to the titanium atom *via* carbonyl oxygen atoms, forming seven-membered rings with the Ti atom. A deeper understanding of conformational preferences of these complexes is necessary, to answer such questions as whether the number of atoms in the ring formed by chelate ligands and the titanium atom could influence the dihedral Ti–O–C–C angles as well as the Ti–O–C bond angles and Ti–O distances. Here we describe the crystal structures and properties of the title compounds as a continuation of our studies on this subject.

2. Experimental details

All reactions were carried out under nitrogen in dried solvents by Schlenk techniques. Anhydrous TiCl_4 was obtained commercially. Bis(2-phenoxoethyl) succinate was obtained by reaction of succinic acid with 2-phenoxoethyl alcohol in benzene. Diethyl malonate was obtained by a standard procedure *viz.*, reaction of malonic acid with ethyl alcohol, in the presence of *p*-toluenesulfonic acid [4]. IR spectra were recorded on a Perkin-Elmer 180 spectrometer.

2.1. Synthesis of tetrachloro(diethyl malonate-*O,O'*)-titanium(IV) (1)

3 cm³ (19.8 mmol) of diethyl malonate was added dropwise to a mixture of 3 cm³ (27.3 mmol) of TiCl_4 in 100 cm³ of n-hexane and stirred under nitrogen. After 2 h the light-yellow precipitate was filtered off, washed with 20 cm³ of n-hexane and dried *in vacuo*. Yield 6.37 g; 92%. 6.25 g (17.9 mmol) of the precipitate was dissolved in 30 cm³ of CH_2Cl_2 and cooled to 253 K. After one week multi-faced, light-yellow crystals suitable for X-ray examination were formed. (Found: Cl, 39.27, Ti, 12.83. $\text{C}_7\text{H}_{12}\text{Cl}_4\text{O}_4\text{Ti}$ calc.: Cl, 40.53, Ti, 13.69%.) IR (Nujol): $\nu(\text{C=O})$ 1666, $\nu(\text{Ti-Cl})$ 390 cm⁻¹.

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* Tetrachloro(diethyl malonate-*O,O'*)titanium(IV); Tetrachloro[bis(2-phenoxoethyl)succinate-*O,O'*]titanium(IV).

2.2. Synthesis of tetrachloro[bis(2-phenoxoethyl) succinate-O,O']titanium(IV) (2)

To the stirred mixture of 9.13 g (25.5 mmol) of $\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2$ in 100 cm^3 of toluene 3 cm^3 (27.3 mmol) of TiCl_4 was added dropwise. After a few minutes an orange precipitate was obtained which was filtered off, washed with n-hexane ($3 \times 5 \text{ cm}^3$) and dried *in vacuo*. Yield 12.44 g; 89%. 25 cm^3 of CH_2Cl_2 was then added to 12.5 g of the complex and the mixture heated under reflux. After 0.5 h the solution was filtered off for crystallization overnight. The orange, needle-shaped crystalline compound was filtered off and washed with n-hexane ($3 \times 5 \text{ cm}^3$). The crystals were always twinned. For X-ray examination, crystals were cut along the plane of twinning and mounted in a glass capillary. (Found: Cl, 25.12; Ti, 8.32 $\text{C}_{20}\text{H}_{22}\text{Cl}_4\text{O}_6\text{Ti}$ calc.: Cl, 25.87; Ti, 8.74%). IR (Nujol): $\nu(\text{C}=\text{O})$ 1648, $\nu(\text{Ti}-\text{Cl})$ 375 cm^{-1} .

2.3. Crystallography

Crystal data for 1. $\text{C}_7\text{H}_{12}\text{Cl}_4\text{O}_4\text{Ti}$, $M = 349.88$, $a = 7.716(10)$, $b = 18.21(2)$, $c = 12.384(10)$ Å, $\beta = 127.29(8)^\circ$, $U = 1384(3)$ Å³, $D_m = 1.65 \text{ g cm}^{-3}$, $Z = 4$, $D_c = 1.679(5) \text{ g cm}^{-3}$, $F(000) = 704$, monoclinic, space group $P2_1/c$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu = 13.9 \text{ cm}^{-1}$, $T = 296(1)$ K.

Crystal data for 2. $\text{C}_{20}\text{H}_{22}\text{Cl}_4\text{O}_6\text{Ti}$, $M = 548.11$, $a = 8.680(12)$, $b = 10.178(11)$, $c = 14.398(15)$ Å, $\alpha = 78.45(9)$, $\beta = 74.16(9)$, $\gamma = 88.45(9)^\circ$, $U = 1198(3)$ Å³, $D_m = 1.49 \text{ g cm}^{-3}$, $Z = 2$, $D_c = 1.519(4) \text{ g cm}^{-3}$, $F(000) = 560$, triclinic, space group $P\bar{1}$, Mo $K\alpha$ radiation, $\mu = 8.3 \text{ cm}^{-1}$, $T = 298(1)$ K.

2.4. Data collection and processing

Preliminary data for all crystals were obtained from Weissenberg photographs. Portions of dimensions $0.8 \times 0.7 \times 0.8 \text{ mm}$ (1) and $0.2 \times 0.6 \times 0.1 \text{ mm}$ (2) were cut and sealed in capillaries. The intensity data for both crystals were recorded on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. 1674 reflections up to $2\theta = 56^\circ$ for 1 and 2420 reflections up to $2\theta = 42^\circ$ for 2 were measured by $2\theta/\theta$ scan technique from which 1575 for 1 and 1490 for 2 with $I > 3\sigma(I)$ were used for structure determination. Neutral atom scattering factors were from ref. 5; real and imaginary components of anomalous dispersion were included for all non-H atoms. The structures were solved by the heavy atom method and refined by full-matrix least-squares [6]. The H-atoms from methyl groups were located from difference maps and refined under the constraint $d(\text{C}-\text{H}) = 1.08$ Å. All other H atoms were included in geometrically calculated posi-

TABLE 1. Final atomic parameters with esd's in parentheses for complex 1

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.24840(15)	0.66530(5)	0.34831(9)	0.0341(5)	0.0340(6)	0.0295(5)	0.0032(5)	0.0250(5)	0.0050(5)
Cl(1)	0.4236(3)	0.56315(9)	0.36958(18)	0.0841(12)	0.0489(10)	0.0818(12)	0.0213(9)	0.0656(11)	0.0329(10)
Cl(2)	0.2941(3)	0.72525(8)	0.20992(14)	0.0507(8)	0.0502(9)	0.0390(8)	0.0112(7)	0.0351(7)	0.0062(8)
Cl(3)	0.5380(3)	0.71885(10)	0.53865(14)	0.0356(8)	0.0967(13)	0.0363(8)	-0.0129(9)	0.0236(7)	-0.0080(9)
Cl(4)	-0.0888(3)	0.61962(8)	0.17810(15)	0.0503(9)	0.0550(10)	0.0458(9)	-0.0146(8)	0.0303(8)	-0.0121(8)
O(1)	0.1798(6)	0.62421(19)	0.4782(4)	0.0449(22)	0.0394(22)	0.0447(22)	0.0100(18)	0.0381(20)	0.0107(19)
O(2)	0.0767(6)	0.75483(18)	0.3486(4)	0.0340(20)	0.0354(20)	0.0388(21)	0.0024(17)	0.0302(18)	0.0061(16)
O(3)	0.0271(6)	0.60601(20)	0.5802(4)	0.0482(23)	0.0390(22)	0.0480(23)	0.0056(18)	0.0401(21)	-0.0012(18)
O(4)	-0.1338(6)	0.82349(20)	0.3733(4)	0.0477(23)	0.0409(23)	0.0514(24)	0.0128(19)	0.0401(21)	0.0166(20)
C(1)	0.0420(9)	0.6404(3)	0.4938(6)	0.0355(29)	0.0312(29)	0.0326(28)	-0.0053(23)	0.0252(26)	-0.0062(23)
C(2)	-0.0500(8)	0.7611(3)	0.3768(5)	0.0276(27)	0.0374(32)	0.0244(26)	0.0014(23)	0.0145(24)	0.0034(24)
C(3)	0.1851(10)	0.5465(4)	0.6636(6)	0.0707(43)	0.0315(32)	0.0625(40)	0.0169(30)	0.0503(37)	0.0135(32)
C(4)	0.3898(11)	0.5769(4)	0.7841(7)	0.0609(44)	0.0689(50)	0.0579(44)	0.0149(37)	0.0328(38)	0.0149(38)
C(5)	-0.0685(11)	0.8901(4)	0.3372(7)	0.0728(45)	0.0386(37)	0.0687(44)	0.0215(33)	0.0546(41)	0.0160(33)
C(6)	0.1326(15)	0.9215(4)	0.4582(8)	0.131(8)	0.0548(47)	0.0778(55)	-0.0101(40)	0.0790(58)	-0.0259(48)
C(7)	-0.1268(8)	0.6982(3)	0.4166(6)	0.0291(28)	0.0449(33)	0.0404(31)	0.0063(27)	0.0258(26)	0.0022(26)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(31)	0.219	0.517	0.603	0.07	H(52)	-0.041	0.876	0.264	0.08
H(32)	0.115	0.510	0.696	0.07	H(61)	0.291(5)	0.896(3)	0.519(5)	0.10
H(41)	0.484(7)	0.528(2)	0.838(5)	0.09	H(62)	0.136(9)	0.967(2)	0.404(5)	0.10
H(42)	0.467(7)	0.606(3)	0.748(5)	0.09	H(63)	0.095(8)	0.942(3)	0.524(4)	0.10
H(43)	0.384(8)	0.612(2)	0.853(4)	0.09	H(71)	-0.269	0.674	0.326	0.06
H(51)	-0.197	0.930	0.294	0.08	H(72)	-0.170	0.7191	0.479	0.06

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

tions. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Absorption corrections [7] were applied for both crystals. The minimum and maximum absorption corrections were 0.885 and 1.145 and 0.904 and 1.107, for **1** and **2**, respectively. Final R and R_w were (0.0339 and 0.0405) and (0.0374 and 0.0335) for **1** and **2**, respectively. For the last cycle of refinement the maximal Δ/σ ratio was 0.04 for **1** and 0.03 for **2**. Final atomic parameters, selected bond lengths, bond angles and torsion angles are in Tables 1–4.

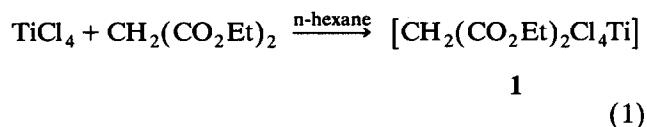
Additional material, deposited at the Cambridge Crystallographic Data Centre, comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

3. Results and discussion

3.1. Synthesis and structure of $[\text{CH}_2(\text{CO}_2\text{Et})_2\text{Cl}_4\text{Ti}]$ (**1**)

Complex **1** was investigated in order to elucidate whether the number of atoms in the ring formed by the chelate ester ligand with the Ti atom influences the geometry around the latter. The reaction of diethyl malonate with TiCl_4 at 1 : 1 molar ratio gave a yellow, diamagnetic and air-sensitive compound of the above stoichiometry. The compound is soluble in CH_2Cl_2 or

1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ but insoluble in aliphatic and aromatic hydrocarbons. The IR spectrum has a very strong broad band at 1666 cm^{-1} [$\nu(\text{C}=\text{O})$] and a very strong band at 390 cm^{-1} , due to $\nu(\text{Ti}-\text{Cl})$.



The molecular structure of tetrachloro(diethyl malonate)titanium(IV) and the numbering scheme are depicted in Fig. 1. The titanium atom is octahedrally-coordinated by four chlorine atoms and two oxygen atoms of the carbonyl groups. The chelate ligand and the Ti atom form a six-membered ring, which in the complex has a boat conformation. There are four molecules in the unit cell. The Ti–Cl bonds *trans* to the carbonyl oxygens as well as those mutually *trans* (see Table 2), are similar to those found in **2**. The molecule has a pseudo-mirror plane of symmetry going through Cl(3), Cl(4), Ti and C(7) atoms. The Cl(3)–Ti–Cl(4) bond angle of $165.6(1)^\circ$ is slightly greater than the corresponding one ($162.4(1)^\circ$) in $[\text{C}_2\text{O}_4(\text{CH}_2\text{CH}_2\text{Ph})_2\text{Cl}_4\text{Ti}]$ [3]. The titanium atom is placed 2.112(4) and 2.102(4) Å from carbonyl oxygens O(1) and O(2), respectively.

TABLE 2. Selected bond lengths (Å) and angles ($^\circ$) for **1**

Ti–Cl(1)	2.219(2)	Ti–Cl(2)	2.233(2)
Ti–Cl(3)	2.262(2)	Ti–Cl(4)	2.293(2)
Ti–O(1)	2.112(4)	Ti–O(2)	2.102(4)
C(1)–O(1)	1.226(9)	C(2)–O(2)	1.226(8)
C(1)–O(3)	1.305(7)	C(2)–O(4)	1.295(7)
C(3)–O(3)	1.484(7)	C(5)–O(4)	1.483(8)
C(1)–C(7)	1.486(8)	C(2)–C(7)	1.503(8)
C(3)–C(4)	1.474(10)	C(5)–C(6)	1.471(11)
Cl(1)–Ti–Cl(2)	97.6(1)	Cl(1)–Ti–Cl(3)	95.3(1)
Cl(1)–Ti–Cl(4)	94.3(1)	Cl(2)–Ti–Cl(3)	94.2(1)
Cl(2)–Ti–Cl(4)	95.2(1)	Cl(3)–Ti–Cl(4)	165.6(1)
O(1)–Ti–Cl(1)	91.6(2)	O(2)–Ti–Cl(1)	171.5(2)
O(1)–Ti–Cl(2)	170.7(2)	O(2)–Ti–Cl(2)	90.9(2)
O(1)–Ti–Cl(3)	84.5(2)	O(2)–Ti–Cl(3)	83.6(2)
O(1)–Ti–Cl(4)	84.4(2)	O(2)–Ti–Cl(4)	85.3(2)
O(1)–Ti–O(2)	79.9(2)	C(1)–C(7)–C(2)	112.6(5)
Ti–O(1)–C(1)	132.5(4)	Ti–O(2)–C(2)	133.2(4)
C(1)–O(3)–C(3)	118.6(5)	C(2)–O(4)–C(5)	118.3(5)
O(1)–C(1)–O(3)	121.9(6)	O(2)–C(2)–O(4)	122.7(6)
O(1)–C(1)–C(7)	125.2(6)	O(2)–C(2)–C(7)	124.3(6)
O(3)–C(1)–C(7)	112.9(5)	O(4)–C(2)–C(7)	113.0(5)
O(3)–C(3)–C(4)	110.8(6)	O(4)–C(5)–C(6)	110.7(7)
Ti–O(1)–C(1)–C(7)	0.5(15)	Ti–O(2)–C(2)–C(7)	–2.9(11)
O(1)–C(1)–O(3)–C(3)	1.2(13)	O(2)–C(2)–O(4)–C(5)	–1.7(11)
C(1)–O(3)–C(3)–C(4)	83.5(11)	C(2)–O(4)–C(5)–C(6)	–86.0(14)
C(7)–C(1)–O(3)–C(3)	179.6(12)	C(7)–C(2)–O(4)–C(5)	179.1(9)
O(1)–Ti–O(2)–C(2)	–20.0(11)	O(2)–Ti–O(1)–C(1)	21.3(10)
O(1)–C(1)–C(7)–C(2)	–32.0(12)	O(2)–C(2)–C(7)–C(1)	33.2(12)

The Ti–O(1)–C(1) and Ti–O(2)–C(2) bond angles of $132.5(4)^\circ$ and $133.2(4)^\circ$, are smaller than similar bond angles in **2** (Table 4), but larger than the Ti–O–C angles [117.4°] in the $[\text{C}_2\text{O}_4(\text{CH}_2\text{CH}_2\text{Ph})_2\text{Cl}_4\text{Ti}]$ complex [3]. The titanium atom is coplanar with the O(1)–C(1)–O(3) and O(2)–C(2)–O(4) groups (the torsion angles Ti–O(1)–C(1)–O(3) and Ti–O(2)–C(2)–O(4) are

$178.7(10)^\circ$ and $178.0(10)^\circ$, respectively). All the bond lengths and angles and the torsion angles in the close environment of the Ti atom are similar to those found elsewhere, for example in the six-membered ring complex of TiCl_4 with acetic anhydride [8].

In the complex molecule the planes through O(1), C(1), O(3) and O(2), C(2), O(4) atoms are tilted by

TABLE 3. Final atomic parameters with esd's in parentheses for complex **2**

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.26748(14)	0.24971(13)	−0.01624(8)	0.0362(9)	0.0422(9)	0.0369(8)	−0.0032(7)	−0.0074(7)	0.0019(7)
Cl(1)	0.46593(22)	0.37840(20)	−0.12184(14)	0.0497(14)	0.0714(15)	0.0768(15)	0.0147(12)	−0.0100(12)	−0.0164(12)
Cl(2)	0.40960(21)	0.12110(20)	0.06875(13)	0.0535(14)	0.0670(15)	0.0640(13)	0.0042(11)	−0.0226(11)	0.0165(11)
Cl(3)	0.26155(22)	0.10582(18)	−0.11912(13)	0.0662(15)	0.0610(14)	0.0514(13)	−0.0220(11)	−0.0077(11)	0.0058(11)
Cl(4)	0.19864(24)	0.39289(20)	0.09103(14)	0.0910(17)	0.0675(15)	0.0673(14)	−0.0332(12)	−0.0341(13)	0.0192(13)
O(1)	0.0549(6)	0.1438(5)	0.0723(3)	0.0400(33)	0.0577(34)	0.0353(29)	−0.0011(24)	0.0022(26)	0.0053(27)
O(2)	0.1060(6)	0.3593(5)	−0.0832(4)	0.0396(34)	0.0449(32)	0.0457(30)	0.0036(23)	−0.0188(27)	0.0014(25)
O(3)	−0.1444(5)	0.1409(5)	0.2067(4)	0.0509(34)	0.0681(36)	0.0263(30)	−0.0088(26)	0.0017(26)	0.0088(27)
O(4)	−0.0104(6)	0.3824(5)	−0.2042(4)	0.0683(38)	0.0786(39)	0.0248(29)	−0.0135(28)	−0.0189(28)	0.0042(31)
O(5)	−0.1324(6)	0.1436(6)	0.4067(4)	0.0718(37)	0.0836(42)	0.0255(31)	−0.0047(28)	0.0017(27)	−0.0021(32)
O(6)	0.1691(6)	0.3902(6)	−0.4140(4)	0.0540(35)	0.1192(48)	0.0417(33)	−0.0278(32)	−0.0117(30)	0.0115(33)
C(1)	−0.0814(10)	0.1754(7)	0.1116(6)	0.0476(57)	0.0433(49)	0.0421(54)	−0.0140(40)	−0.0069(48)	−0.0007(43)
C(2)	−0.0064(9)	0.3331(7)	−0.1138(5)	0.0427(59)	0.0423(49)	0.0374(51)	−0.0170(39)	−0.0150(45)	0.0154(42)
C(3)	−0.1887(8)	0.2557(8)	0.0575(5)	0.0229(42)	0.0688(53)	0.0374(45)	−0.0097(39)	−0.0001(36)	0.0113(39)
C(4)	−0.1482(8)	0.2483(7)	−0.0522(5)	0.0334(46)	0.0607(51)	0.0408(47)	−0.0071(38)	−0.0126(38)	−0.0014(39)
C(5)	−0.0430(9)	0.0579(8)	0.2596(5)	0.0741(59)	0.0851(62)	0.0276(45)	0.0017(42)	−0.0101(43)	0.0274(50)
C(6)	−0.1358(10)	0.0246(8)	0.3670(5)	0.0816(62)	0.0745(62)	0.0338(49)	−0.0080(44)	−0.0081(44)	0.0169(49)
C(7)	0.1250(10)	0.4718(8)	−0.2666(5)	0.0869(66)	0.0654(58)	0.0294(45)	−0.0002(43)	0.0010(46)	−0.0157(52)
C(8)	0.2406(9)	0.3992(8)	−0.3363(5)	0.0626(56)	0.0837(62)	0.0274(43)	−0.0017(42)	−0.0119(43)	−0.0043(48)
C(11)	−0.2014(9)	0.1301(9)	0.5062(6)	0.0503(54)	0.0778(65)	0.0330(52)	−0.0092(49)	−0.0112(43)	0.0004(48)
C(12)	−0.2735(10)	0.0172(9)	0.5685(6)	0.125(8)	0.0586(60)	0.0334(51)	−0.0042(45)	0.0045(50)	−0.0154(55)
C(13)	−0.3388(11)	0.0199(10)	0.6671(6)	0.141(9)	0.0793(71)	0.0371(58)	−0.0018(50)	0.0019(55)	−0.0308(65)
C(14)	−0.3290(10)	0.1308(10)	0.7039(6)	0.0998(72)	0.0769(70)	0.0351(51)	−0.0082(52)	−0.0058(48)	−0.0065(59)
C(15)	−0.2540(10)	0.2435(9)	0.6419(6)	0.116(8)	0.0589(62)	0.0461(55)	−0.0148(49)	−0.0067(52)	−0.0099(56)
C(16)	−0.1906(10)	0.2439(9)	0.5416(6)	0.0880(65)	0.0768(67)	0.0442(57)	−0.0072(49)	−0.0067(48)	−0.0279(53)
C(21)	0.2684(10)	0.3637(8)	−0.5010(6)	0.0511(60)	0.0541(54)	0.0419(53)	−0.0101(41)	−0.0044(48)	−0.0079(44)
C(22)	0.2083(9)	0.3980(8)	−0.5809(6)	0.0488(57)	0.110(8)	0.0413(51)	−0.0189(50)	−0.0148(48)	−0.0045(49)
C(23)	0.2973(12)	0.3749(9)	−0.6712(6)	0.0904(77)	0.103(8)	0.0392(58)	−0.0186(49)	−0.0143(55)	−0.0184(63)
C(24)	0.4466(12)	0.3219(8)	−0.6809(7)	0.0800(76)	0.0672(63)	0.0477(59)	−0.0126(47)	−0.0013(55)	−0.0008(54)
C(25)	0.5052(10)	0.2916(8)	−0.6020(7)	0.0604(62)	0.0796(66)	0.0680(65)	−0.0073(54)	−0.0005(57)	0.0180(51)
C(26)	0.4187(10)	0.3107(8)	−0.5088(6)	0.0610(62)	0.0711(60)	0.0531(57)	−0.0122(45)	−0.0084(49)	0.0099(50)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(3)	−0.310	0.219	0.092	0.08	H(81)	0.354	0.455	−0.366	0.10
H(31)	−0.179	0.359	0.063	0.08	H(12)	−0.280	−0.074	0.541	0.12
H(4)	−0.250	0.281	−0.079	0.08	H(13)	−0.399	−0.069	0.716	0.12
H(41)	−0.125	0.145	−0.059	0.08	H(14)	−0.380	0.130	0.781	0.12
H(5)	−0.015	−0.033	0.231	0.10	H(15)	−0.244	0.333	0.670	0.12
H(51)	0.067	0.112	0.251	0.10	H(16)	−0.133	0.334	0.492	0.12
H(6)	−0.081	−0.057	0.406	0.10	H(22)	0.092	0.443	−0.573	0.12
H(61)	−0.258	−0.004	0.374	0.10	H(23)	0.249	0.399	−0.734	0.12
H(7)	0.080	0.556	−0.309	0.10	H(24)	0.517	0.305	−0.752	0.12
H(71)	0.187	0.507	−0.220	0.10	H(25)	0.623	0.251	−0.611	0.12
H(8)	0.260	0.300	−0.298	0.10	H(26)	0.467	0.285	−0.446	0.12

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

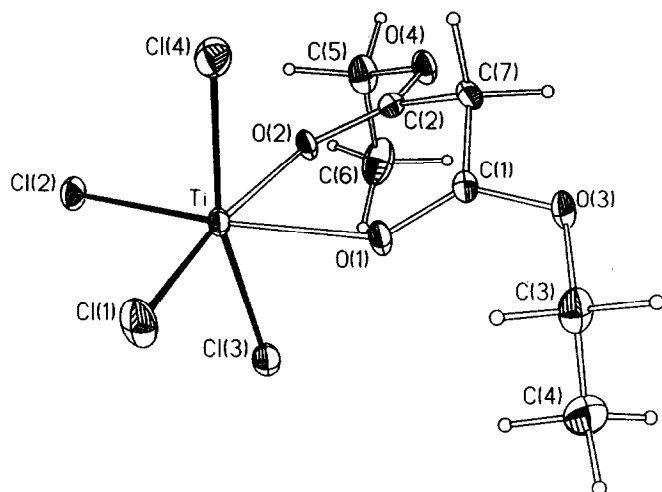


Fig. 1. Structure and numbering scheme of the $[\text{CH}_2(\text{CO}_2\text{Et})_2\text{Cl}_4\text{Ti}]$ molecule.

$32.1(8)^\circ$. The carbonyl groups $\text{C}(1)\text{--O}(1)$ and $\text{C}(2)\text{--O}(2)$ remain in the preferred *synperiplanar* conformation to the $\text{O}(3)\text{--C}(3)$ and $\text{O}(4)\text{--C}(5)$ bonds.

In this complex, too, short intramolecular contacts are observed. The chlorine atom $\text{Cl}(3)$ is $2.943(5)$ and $2.913(4)$ Å from carbonyl oxygen atoms $\text{O}(1)$ and $\text{O}(2)$, respectively. On the contrary, the chlorine atom $\text{Cl}(4)$ is closer ($2.964(4)$ Å) to $\text{O}(1)$ than to $\text{O}(2)$ ($2.981(4)$ Å).

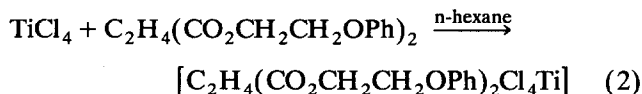
3.2. Synthesis and structure of $[\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2\text{Cl}_4\text{Ti}]$ (2)

The addition of $\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2$ to TiCl_4 in toluene, in a 1:1 molar ratio, leads to the orange, air-sensitive compound **2** formulated as $[\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2\text{Cl}_4\text{Ti}]$. This complex is soluble in CH_2Cl_2 and 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ but insoluble in n-hexane.

TABLE 4. Selected bond lengths (Å) and angles ($^\circ$) for **2**

Ti–Cl(1)	2.211(2)	Ti–Cl(2)	2.197(2)
Ti–Cl(3)	2.293(2)	Ti–Cl(4)	2.284(2)
Ti–O(1)	2.113(5)	Ti–O(2)	2.088(5)
C(1)–O(1)	1.229(9)	C(2)–O(2)	1.230(9)
C(1)–O(3)	1.307(9)	C(2)–O(4)	1.308(8)
C(1)–C(3)	1.497(10)	C(2)–C(4)	1.484(10)
C(3)–C(4)	1.540(9)		
C(5)–O(3)	1.461(9)	C(7)–O(4)	1.473(9)
C(5)–C(6)	1.510(9)	C(7)–C(8)	1.507(10)
C(6)–O(5)	1.443(9)	C(8)–O(6)	1.438(8)
Cl(1)–Ti–Cl(2)	98.1(1)	Cl(1)–Ti–Cl(3)	95.0(1)
Cl(1)–Ti–Cl(4)	95.5(1)	Cl(2)–Ti–Cl(3)	95.6(1)
Cl(2)–Ti–Cl(4)	94.7(1)	Cl(3)–Ti–Cl(4)	164.1(1)
O(1)–Ti–Cl(1)	171.1(2)	O(2)–Ti–Cl(1)	89.4(2)
O(1)–Ti–Cl(2)	90.8(2)	O(2)–Ti–Cl(2)	172.5(2)
O(1)–Ti–Cl(3)	83.7(2)	O(2)–Ti–Cl(3)	84.6(2)
O(1)–Ti–Cl(4)	84.1(2)	O(2)–Ti–Cl(4)	83.6(2)
O(1)–Ti–O(2)	81.8(2)		
Ti–O(1)–C(1)	135.1(5)	Ti–O(2)–C(2)	136.2(5)
O(1)–C(1)–C(3)	124.4(7)	O(2)–C(2)–C(4)	123.7(7)
C(1)–C(3)–C(4)	113.8(6)	C(2)–C(4)–C(3)	113.2(6)
O(3)–C(5)–C(6)	107.3(6)	O(4)–C(7)–C(8)	110.9(6)
O(1)–C(1)–O(3)	121.4(7)	O(2)–C(2)–O(4)	121.4(7)
C(1)–O(3)–C(5)	114.5(6)	C(2)–O(4)–C(7)	116.6(6)
C(3)–C(1)–O(3)	114.1(7)	C(4)–C(2)–O(4)	114.9(6)
C(5)–C(6)–O(5)	107.2(6)	C(7)–C(8)–O(6)	106.8(6)
C(6)–O(5)–C(11)	115.9(6)	C(8)–O(6)–C(21)	117.7(6)
Ti–O(1)–C(1)–C(3)	57.5(10)	Ti–O(2)–C(2)–C(4)	56.4(10)
Ti–O(1)–C(1)–O(3)	–122.0(10)	Ti–O(2)–C(2)–O(4)	–125.5(10)
O(1)–C(1)–O(3)–C(5)	–2.8(9)	O(2)–C(2)–O(4)–C(7)	–0.7(10)
O(1)–C(1)–C(3)–C(4)	23.7(10)	O(2)–C(2)–C(4)–C(3)	29.8(10)
C(1)–C(3)–C(4)–C(2)	–77.2(10)		
C(1)–O(3)–C(5)–C(6)	–178.4(7)	C(2)–O(4)–C(7)–C(8)	102.1(10)
C(3)–C(1)–O(3)–C(5)	177.6(9)	C(4)–C(2)–O(4)–C(7)	177.5(10)
O(3)–C(5)–C(6)–O(5)	–75.3(8)	O(4)–C(7)–C(8)–O(6)	76.6(9)
O(1)–Ti–O(2)–C(2)	–47.3(9)	O(2)–Ti–O(1)–C(1)	–42.5(8)
C(5)–C(6)–O(5)–C(11)	–175.5(7)	C(7)–C(8)–O(6)–C(21)	161.6(10)

Its IR spectrum shows bands at 1648 cm^{-1} (vs, br) due to $\nu(\text{C}=\text{O})$, and 375 (vs) cm^{-1} , assigned to $\nu(\text{Ti}-\text{Cl})$.



2

The structure of complex **2** and its numbering scheme are presented in Fig. 2. In the complex, four chlorine atoms and two carbonyl oxygen atoms form a distorted octahedron around the titanium atom. The chelate ligand and the titanium atom form a seven-membered ring. There are two molecules in the unit cell. The complex molecule has a pseudo 2-fold axis of symmetry. At first glance the main features of this complex (monomeric, octahedrally coordinated titanium, *etc.*) are very similar to those of **1**, but the out-of-plane bonding of the Ti atom to carbonyl groups and the Ti–O–C–C torsion angles clearly distinguish the two structures. In **2**, the torsion angles Ti–O(1)–C(1)–C(3) and Ti–O(2)–C(2)–C(4) being $57.5(10)^\circ$ and $56.4(10)^\circ$, are much larger than the corresponding ones in the previously reported complexes of TiCl_4 with *o*-diesters [1–3]. These values indicate that the Ti atom remains out of the plane through O(1), C(1), O(3), C(3) atoms and through O(2), C(2), O(4), C(4) atoms, similar to what is seen in the complex of TiCl_4 and acryloylmethyl lactate [9], where the Ti atom is bonded extremely out-of-plane (Ti–O(1)–C–C and Ti–O(2)–C–C are 64° and -132°). Such an out-of-plane bonding shows considerable bending of Ti atom towards the π cloud of the carbonyl groups [10]. This indicates that in addition to σ bonding between titanium atom and carbonyl ligand, π bonding can also exist, which might be responsible for the orange colour of compound **2**. The orange colour was also that of the complex formed in reaction of TiCl_4 with *p*-ethylanisate $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_6(\text{CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{Et})_2]$ [11], in which the Ti–O–C–C torsion angle is 45.7° . The complex **1** and those where the Ti atom is coplanar with the carbonyl ligands are yellow [1–3].

The Ti–Cl(1) and Ti–Cl(2) bond lengths in **2** are $2.211(2)$ and $2.197(2)\text{ \AA}$ respectively. The Cl(3)–Ti–Cl(4) bond angle is $164.1(1)^\circ$. The Ti–O(1) and Ti–O(2) bond lengths as well as the Ti–O(1)–C(1) and Ti–O(2)–C(2) bond angles (see Table 4) agree well with the average Ti–O bond lengths and Ti–O–C bond angles found in [(diester) Cl_4Ti] [1–3].

The coordinated chelated molecule contains four planar parts: O(1), C(1), O(3), C(3); O(2), C(2), O(4), C(4) and two aromatic rings. The first two form the angle of $49.4(8)^\circ$. The two aromatic rings are almost perpendicular (tilted by $95.4(8)^\circ$). The alcohol residues form extended chains in the complex. The O(3)–C(5)–C(6)–O(5) and O(4)–C(7)–C(8)–O(6) torsion angles ($-75.3(8)^\circ$ and $76.6(9)^\circ$) are similar but the C(5)–C(6)–O(5)–C(11) and C(7)–C(8)–O(6)–C(21) dihedral angles ($-175.5(7)^\circ$ and $161.6(10)^\circ$) are different. The carbonyl groups O(1)–C(1) and O(2)–C(2) are in *synperiplanar* conformation to the O(3)–C(5) and O(4)–C(7) bonds, respectively. Both Cl(3) and Cl(4) chlorine atoms in **2** are involved in rather short intramolecular contacts. The chlorine atom Cl(3) is placed $3.267(8)$ and $3.232(7)\text{ \AA}$ from the carbon C(1) and C(2) atoms respectively. In turn, the chlorine atom Cl(4) (*trans* to Cl(3)) remains $3.245(8)$ and $3.239(7)\text{ \AA}$ from the same carbon atoms. These distances are shorter than the sum of the van der Waals radii.

We have also obtained other compounds of the formula $[\text{C}_2\text{H}_4(\text{CO}_2\text{R})_2\text{Cl}_4\text{Ti}]$ (where R = Et, Pr, Bu), but only when R = $\text{CH}_2\text{CH}_2\text{OPh}$ were crystals suitable for X-ray analysis obtained.

It is interesting, that considering other known seven-membered ring compounds with aromatic *o*-diesters [*o*- $\text{C}_6\text{H}_4(\text{CO}_2\text{R})_2\text{Cl}_4\text{Ti}$] [1–3] only in the complex with bulky ^iBu group is the titanium atom bound out-of-plane (Ti–O–C–C torsion angles are $27.0(16)$ and $21.8(15)^\circ$). This fact probably plays an important role in the propylene polymerization process, because when $\text{C}_6\text{H}_4(\text{CO}_2-^i\text{Bu})_2$ is used as internal and external donor the isotacticity of polypropylene is very high [12–14].

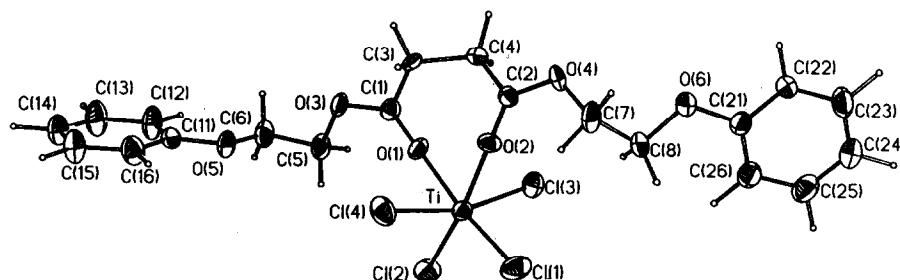


Fig. 2. Structure and numbering scheme of the $[\text{C}_2\text{H}_4(\text{CO}_2\text{CH}_2\text{CH}_2\text{OPh})_2\text{Cl}_4\text{Ti}]$ molecule.

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References

- 1 J. Utko, P. Sobota and T. Lis, *J. Organomet. Chem.*, **334** (1987) 341.
- 2 P. Sobota, J. Utko and T. Lis, *J. Organomet. Chem.*, **393** (1990) 349.
- 3 P. Sobota, S. Szafert, J. Utko and T. Lis, *J. Organomet. Chem.*, **423** (1992) 195.
- 4 G. Brauer, *Handbook of Preparative Inorganic Chemistry*, New York, 1963, p. 729.
- 5 *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, 1974.
- 6 G. M. Sheldrick, *SHELX-76, Program for Crystal Structure Solution*, University of Cambridge, 1976.
- 7 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.
- 8 B. Viard, M. Poulain, D. Grandjean and J. Anandrut, *J. Chem. Res.*, (1983) 850.
- 9 T. Poll, J. O. Metter and G. Helmchen, *Angew. Chem., Int. Ed. Engl.*, **24** (1985) 112.
- 10 S. Shambayati, W. E. Crowe and S. L. Schreiber, *Angew. Chem., Int. Ed. Engl.*, **29** (1990) 256.
- 11 I. W. Basi, M. Calcaterra and R. Intrito, *J. Organomet. Chem.*, **127** (1977) 305.
- 12 T. Keii and K. Soga, in *Catalytic Polymerization of Olefins*, Elsevier, New York, 1986.
- 13 R. Mulhaupt, U. Klabude and S. D. Ittle, *J. Chem. Soc., Chem. Commun.*, (1985) 1745.
- 14 P. Sobota, *Polym.-Plast. Technol. Eng.*, **26** (1989) 493.