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Ti^{IV} and Mo^{V} complexes with diesters. The crystal structure of [o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$], [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] and [$o$-$C_6H_4(CO_2Et)_2Cl_3MoO$] · C_6H_6

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Abstract

The crystal structures of [o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$] (I), in the presence of activators a good catalyst for olefin polymerization, [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] (II) and [$o$-$C_6H_4(CO_2Et)_2Cl_3MoO$] (III), have been determined by X-ray diffraction methods and refined by a full-matrix least-squares technique to $R = 0.036$, 0.041 and 0.055 for 2775, 2437 and 2776 independent non-zero reflections for I, II and III, respectively. The crystals of I are triclinic, space group $P\bar{1}$ with two molecules in a unit cell of dimensions $a = 10.475(8)$, $b = 10.078(9)$, $c = 13.683(9)$ Å, $\alpha = 88.75(7)$, $\beta = 72.65(6)$, $\gamma = 66.95(7)°$. The crystals of II are monoclinic, space group $P2_1/c$, with four molecules in a cell with $a = 10.045(8)$, $b = 21.032(22)$, $c = 13.193(9)$ Å, $\beta = 128.91(6)°$. The titanium atoms in I and II are octahedrally coordinated by four chlorine and two carbonyl oxygen atoms of coordinated o-diester molecules in the *cis* position. The crystals of III are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions $a = 9.722(12)$, $b = 8.073(12)$, $c = 15.683(21)$ Å, $\alpha = 83.46(9)$, $\beta = 75.81(9)$, $\gamma = 67.74(9)°$. Three Cl atoms, one oxo oxygen and two O atoms of the carbonyl groups form a distorted octahedron around the molybdenum atom. The chelate ligand atoms and the titanium atom in I or molybdenum atom in III form a seven-membered ring which is five-membered in II.

Introduction

In previous papers we have described the synthesis, properties and structure of various titanium(IV) aromatic diester complexes [1–3]. We have found that *ortho*-diesters form with $TiCl_4$ monomeric complexes of the formula [o-$C_6H_4(CO_2R)_2TiCl_4$] [1,3] and *meta*-diesters form dimeric compounds of the formula [$Ti_2\{\mu$-m-$C_6H_4(CO_2R)_2\}_2Cl_8$] [2]. In contrast, *para*-diesters react with $TiCl_4$ to produce complexes which exist in the solid state as linear polymers [3]. It is also known that the o-$C_6H_4(CO_2R)_2$ esters with bulky R groups as internal and external donors have a great influence on the stereospecifity of the polymerization process and on the isotacticity of polypropylene [4]. A deeper understanding of conformational preferences of coordinated o-diester molecules depends upon elucidation as to whether the replacement of a Ti atom by another transition metal could influence the M–O–C bond angles and M–O–C–C torsion angles in such complexes. As a continuation of our study on this subject we describe here the crystal structures of: [o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$] I, [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] II, and [$o$-$C_6H_4(CO_2Et)_2Cl_3MoO$]$\cdot C_6H_6$ III.

Experimental

All reactions were carried out under dinitrogen in dried solvents by a Schlenk-tube technique. Anhydrous $TiCl_4$, $MoCl_5$ and diethyl phthalate were obtained commercially. Bis(2-phenylethyl) o-phthalate and bis(2-phenylethyl) oxalate were obtained in our laboratory by a standard procedure, namely reaction of o-phthalic or oxalic acid with 2-phenylethyl alcohol [5]. IR spectra were recorded on a Perkin–Elmer 180 spectrometer.

[o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$]

3 cm^3 of $TiCl_4$ (5.18 g; 27 mmol) was added dropwise to a solution of 10.52 g (28.1 mmol) of o-$C_6H_4(CO_2CH_2CH_2Ph)_2$ in 80 cm^3 of n-hexane and stirred under N_2. After 0.5 h the yellow precipitate was filtered off and washed with n-hexane (3 × 10 cm^3). Crystals suitable for analysis of structure were grown by slow diffusion of n-hexane into a solution of the complex in CH_2Cl_2.

[$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$]

3 cm^3 of $TiCl_4$ (27.3 mmol) was added dropwise to a solution of 8.15 g (27.3 mmol) $(CO_2CH_2CH_2Ph)_2$ in 100 cm^3 of n-hexane. The mixture was stirred for 2 h and then the yellow precipitate was filtered off and washed with n-hexane (3 × 10 cm^3). To obtain crystals suitable for X-ray analysis 1 g of [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] was dissolved in 20 cm^3 of CH_2Cl_2 at room temperature. This solution was next cooled in a refrigerator to 253 K. The yellow crystals were formed overnight.

[o-$C_6H_4(CO_2Et)_2Cl_3MoO$]$\cdot C_6H_6$

4.0 cm^3 (20 mmol) of o-$C_6H_4(CO_2Et)_2$ was added dropwise to a solution of $MoCl_5$ (2.73 g; 10 mmol) in 80 cm^3 of C_6H_6. The deep brown mixture was stirred for 2 h and then warmed for 1 h. After slow cooling a deep-brown precipitate settled, which was filtered off. The filtrate was next evaporated under vacuum to 50 cm^3. After two months the green crystals were filtered off and washed with 10 cm^3 of n-hexane. Further condensation of the solution to 20 cm^3 caused the precipitation of o-phthalic acid anhydride (m.p. 130.5–131.0 °C).

X-ray crystal structure determination

Crystal data. $C_{24}H_{22}Cl_4O_4Ti$ (I) $M = 564.15$, $a = 10.475(8)$, $b = 10.078(9)$, $c = 13.683(9)$ Å, $\alpha = 88.75(7)$, $\beta = 72.65(6)$, $\gamma = 66.95(7)$, $U = 1261(2)$ Å^3, $D_m = 1.481$ g cm^{-3}, $Z = 2$, $D_c = 1.485(3)$ g cm^{-3}, $F(000) = 576$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.71069$ Å, $\mu = 8.03$ cm^{-1}, $T = 302(1)$ K. $C_{18}H_{18}Cl_4O_4Ti$ (II) $M = 488.05$, $a = 10.045(8)$ Å, $b = 21.032(22)$ Å, $c = 13.193(9)$ Å, $\beta = 128.91(6)°$, $U = 2169(10)$ Å^3, $D_m = 1.495$ g cm^{-3}, $Z = 4$, $D_x = 1.495(10)$ g cm^{-3} $F(000) = 992$, space group $P2_1/c$, Mo-K_α radiation, $\mu = 9.20$ cm^{-1}, $T = 296(1)$ K. $C_{12}H_{14}Cl_3MoO_5 \cdot C_6H_6$ (III) $M = 518.66$, $a = 9.722(12)$, $b = 8.073(12)$, $c = 15.683(21)$ Å, $\alpha = 83.46(9)$, $\beta = 75.81(9)$, $\gamma = 67.74(9)°$, $U = 1104(3)$ Å^3, $D_m = 1.604$ g cm^{-3}, $Z = 2$, $D_x = 1.560(5)$ g cm^{-3}, $F(000) = 522$, space group $P\bar{1}$, Mo-K_α radiation, $\mu = 9.70$ cm^{-1}, $T = 300(2)$ K.

Preliminary data for all crystals were obtained from Weissenberg photographs. Suitable portions of dimensions $0.1 \times 0.5 \times 0.5$ mm for I, $0.5 \times 0.5 \times 0.5$ mm for II and $0.6 \times 0.7 \times 0.45$ mm for III were cut from large crystals and sealed in capillaries. The intensity data for all crystals were recorded on a Syntex $P2_1$ automated diffractometer with graphite-monochromatized Mo-K_α radiation. The intensities of two standard reflections, monitored after every 50 scans, showed ±4%, ±6% and ±6% variation for I, II and III, respectively. 3625 reflections up to $2\theta = 46°$ for I, 3287 up to $2\theta = 52°$ for II, and 4163 up to $2\theta = 50°$ for III were measured by the $2\theta/\theta$ scan technique from which 2775 for I, 2447 for II, and 2776 for III with $I > 3\sigma(I)$ were used for structure determination. Neutral atom scattering factors were calculated from ref. 6; real and imaginary components of anomalous dispersion were included for all non-H atoms. All three structures were solved by the heavy atom method and refined by the full-matrix least-squares technique [7]. The H-atoms from methyl groups were located from difference maps and refined under the constraint that $d(\text{C–H}) = 1.08$ Å. All other H-atoms were included in geometrically calculated positions. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Minimum and maximum absorption corrections were (DIFABS [8]): 0.925 and 1.130 for I, 0.923 and 1.099 for II, and 0.902 and 1.103 for III, respectively. The final R and R_w were (0.0358 and 0.0377), (0.0402 and 0.0445) and (0.0544 and 0.0539) for I, II and III, respectively. For the last cycle of the refinement the maximal Δ/σ ratio was 0.06 for I, 0.06 for II and 0.10 for III, and the final difference maps showed a general background within -0.26 and 0.30, -0.22 and 0.22, and -0.50 and 1.04 e Å^{-3} for I, II and III, respectively. In the case of II an isotropic extinction correction of the form $1 - xF_c^2/\sin\theta$ was applied; refinement of x gave the value $6.22(16) \times 10^{-7}$. The final atom parameters for I are listed in Table 1, for II in Table 2 and for III in Table 3.

Results and discussion

Synthesis and structure of [o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$]

The addition of bis(2-phenylethyl) *o*-phthalate to $TiCl_4$ in n-hexane, in a 1:1 molar ratio, leads to a diamagnetic, air-sensitive, yellow compound of the above stoichiometry, that is soluble in and crystallizes from dichloromethane. The compound is insoluble in aliphatic and aromatic hydrocarbons. The IR spectrum of this compound shows bands at 1645vs,br cm^{-1} due to ν(C=O), and 1320s and 375vs cm^{-1}, which can be assigned to ν(C–O) and ν(Ti–Cl), respectively.

$$TiCl_4 + o\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2 \xrightarrow{\text{n-hexane}} \underset{\text{(I)}}{[o\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti]} \qquad (1)$$

The structure of the tetrachloro[bis(2-phenylethyl) *o*-phthalate]titanium(IV) molecule is depicted in Fig. 1. Selected bond lengths, bond angles and torsion angles are listed in Table 4. Four Cl atoms and two O atoms of the ligand carbonyl groups form a distorted octahedron around the titanium atom. The molecule of

Table 1

Final atom parameters for tetrachloro[bis(2-phenylethyl) *o*-phthalate]titanium(IV)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.02803(7)	0.29617(7)	0.16420(5)	0.0275(4)	0.0304(4)	0.0324(4)	0.0019(3)	−0.0056(3)	−0.0068(3)
Cl(1)	0.21957(11)	0.15566(12)	0.21975(8)	0.0427(6)	0.0487(7)	0.0401(6)	0.0096(5)	−0.0171(5)	−0.0074(5)
Cl(2)	−0.13603(11)	0.44850(11)	0.09105(9)	0.0388(6)	0.0414(6)	0.0620(7)	0.0157(5)	−0.0231(6)	−0.0126(5)
Cl(3)	−0.03065(12)	0.11082(11)	0.14028(9)	0.0415(6)	0.0349(6)	0.0776(8)	0.0075(6)	−0.0158(6)	−0.0158(5)
Cl(4)	−0.11693(14)	0.38791(15)	0.32305(9)	0.0529(8)	0.0756(9)	0.0411(7)	−0.0087(6)	0.0073(6)	−0.0096(7)
O(1)	0.10567(28)	0.45840(27)	0.15466(20)	0.0313(16)	0.0322(16)	0.0436(16)	−0.0038(12)	−0.0107(13)	−0.0115(13)
O(2)	0.17944(27)	0.23848(26)	0.01228(18)	0.0306(16)	0.0341(16)	0.0298(14)	−0.0005(12)	−0.0070(12)	−0.0129(13)
O(3)	0.21924(29)	0.60622(29)	0.13820(21)	0.0358(16)	0.0347(17)	0.0540(18)	−0.0045(14)	−0.0142(14)	−0.0105(14)
O(4)	0.36845(28)	0.17342(30)	−0.13033(19)	0.0371(16)	0.0547(19)	0.0311(16)	−0.0089(13)	−0.0058(13)	−0.0177(15)
C(1)	0.2187(5)	0.4785(5)	0.1262(3)	0.0383(24)	0.0345(24)	0.0305(21)	−0.0020(18)	−0.0172(19)	−0.0122(20)
C(2)	0.3059(5)	0.2223(4)	−0.0332(3)	0.0330(23)	0.0249(21)	0.0282(21)	−0.0016(17)	−0.0054(18)	−0.0063(18)
C(3)	0.0854(5)	0.7240(5)	0.2047(4)	0.0348(26)	0.0298(25)	0.0904(37)	−0.0129(25)	−0.0229(26)	0.0014(21)
C(4)	0.1340(6)	0.8003(5)	0.2701(4)	0.0564(31)	0.0323(26)	0.0702(33)	−0.0097(24)	−0.0179(27)	−0.0117(24)
C(5)	0.2840(5)	0.1455(5)	−0.1890(4)	0.0425(25)	0.0601(30)	0.0351(23)	−0.0082(21)	−0.0161(20)	−0.0193(24)
C(6)	0.3966(6)	0.0593(6)	−0.2888(4)	0.0533(30)	0.0865(41)	0.0336(25)	−0.0173(25)	−0.0067(23)	−0.0208(30)
C(11)	0.3691(4)	0.3662(4)	0.0818(3)	0.0303(21)	0.0323(22)	0.0334(21)	0.0021(18)	−0.0103(18)	−0.0114(18)
C(12)	0.4755(5)	0.3794(5)	0.1170(4)	0.0364(25)	0.0470(28)	0.0521(27)	−0.0102(22)	−0.0133(21)	−0.0144(22)
C(13)	0.6178(5)	0.2762(5)	0.0865(4)	0.0373(26)	0.0537(30)	0.0640(31)	−0.0006(24)	−0.0234(24)	−0.0169(23)
C(14)	0.6564(5)	0.1604(5)	0.0154(4)	0.0291(23)	0.0466(28)	0.0554(28)	0.0019(22)	−0.0079(21)	−0.0095(21)
C(15)	0.5530(5)	0.1482(5)	−0.0234(4)	0.0352(24)	0.0365(24)	0.0396(23)	−0.0035(20)	−0.0037(19)	−0.0127(20)
C(16)	0.4079(4)	0.2480(4)	0.0109(3)	0.0287(21)	0.0343(23)	0.0262(20)	0.0013(17)	−0.0069(17)	−0.0114(18)

C(21)	0.2423(6)	0.6964(5)	0.3170(4)	0.0620(33)	0.0384(27)	0.0355(24)	−0.0085(21)	−0.0096(23)	−0.0086(24)
C(22)	0.3809(6)	0.6948(6)	0.2927(5)	0.0588(34)	0.0605(34)	0.0655(34)	−0.0136(28)	−0.0228(28)	−0.0144(29)
C(23)	0.4873(8)	0.5956(8)	0.3264(6)	0.0854(51)	0.0781(47)	0.0963(50)	−0.0305(39)	−0.0489(42)	0.0017(39)
C(24)	0.4524(11)	0.4954(9)	0.3866(6)	0.159(8)	0.0717(50)	0.0699(49)	−0.0149(39)	−0.0677(56)	0.0090(56)
C(25)	0.3172(11)	0.4951(9)	0.4133(5)	0.159(8)	0.0876(55)	0.0536(39)	0.0162(36)	−0.0163(49)	−0.0378(61)
C(26)	0.2093(8)	0.5975(7)	0.3783(5)	0.0912(49)	0.0688(41)	0.0583(36)	0.0034(31)	−0.0014(34)	−0.0212(36)
C(31)	0.3233(5)	0.0456(6)	−0.3665(4)	0.0486(28)	0.0630(32)	0.0277(22)	−0.0096(22)	−0.0033(20)	−0.0206(25)
C(32)	0.2855(7)	0.1548(6)	−0.4288(4)	0.1155(50)	0.0746(40)	0.0510(31)	0.0066(28)	−0.0324(33)	−0.0543(37)
C(33)	0.2241(7)	0.1401(7)	−0.5031(4)	0.1185(54)	0.0856(44)	0.0453(31)	0.0114(31)	−0.0292(33)	−0.0436(41)
C(34)	0.1995(7)	0.0205(7)	−0.5138(4)	0.0845(42)	0.0968(47)	0.0457(31)	−0.0132(32)	−0.0190(30)	−0.0434(37)
C(35)	0.2345(7)	−0.0879(6)	−0.4513(4)	0.0926(44)	0.0654(37)	0.0600(34)	−0.0142(29)	−0.0182(31)	−0.0405(34)
C(36)	0.2946(6)	−0.0732(6)	−0.3771(4)	0.0741(36)	0.0488(31)	0.0488(29)	−0.0033(24)	−0.0160(27)	−0.0199(27)

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(3)	0.030	0.799	0.158	0.081(17)	H(15)	0.586	0.060	−0.081	0.105(19)
H(31)	0.013	0.680	0.253	0.074(16)	H(22)	0.406	0.774	0.246	0.120(24)
H(4)	0.184	0.865	0.223	0.069(15)	H(23)	0.595	0.596	0.306	0.196(39)
H(41)	0.039	0.870	0.331	0.084(17)	H(24)	0.535	0.415	0.413	0.135(25)
H(5)	0.225	0.083	−0.148	0.057(13)	H(25)	0.293	0.416	0.461	0.179(33)
H(51)	0.208	0.246	−0.204	0.081(17)	H(26)	0.101	0.599	0.399	0.098(21)
H(6)	0.468	0.114	−0.321	0.067(15)	H(32)	0.304	0.252	−0.420	0.105(20)
H(61)	0.460	−0.048	−0.273	0.096(20)	H(33)	0.196	0.225	−0.552	0.115(22)
H(12)	0.446	0.473	0.170	0.063(14)	H(34)	0.152	0.010	−0.572	0.099(19)
H(13)	0.698	0.286	0.118	0.102(19)	H(35)	0.215	−0.184	−0.460	0.082(16)
H(14)	0.767	0.079	−0.010	0.037(11)	H(36)	0.319	−0.157	−0.327	0.080(16)

Table 2

Final atomic parameters with esd's in parentheses for $C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.40348(10)	0.75676(4)	0.47711(8)	0.0475(5)	0.0395(5)	0.0501(5)	0.0061(4)	0.0315(5)	0.0044(4)
Cl(1)	0.60704(19)	0.69212(7)	0.52113(15)	0.084(2)	0.086(2)	0.087(2)	0.0160(9)	0.0601(9)	0.0363(9)
Cl(2)	0.46071(16)	0.84617(6)	0.42583(13)	0.0574(8)	0.0633(9)	0.076(2)	0.0154(7)	0.0411(8)	−0.0089(7)
Cl(3)	0.53605(17)	0.78287(6)	0.68682(12)	0.0700(9)	0.0575(8)	0.0520(8)	−0.0038(6)	0.0347(7)	0.0002(7)
Cl(4)	0.20521(19)	0.72142(7)	0.26849(12)	0.082(2)	0.0650(9)	0.0512(8)	−0.0033(7)	0.0378(8)	−0.0166(8)
O(1)	0.1813(4)	0.80483(14)	0.4384(3)	0.050(2)	0.035(2)	0.071(3)	0.013(2)	0.041(2)	0.005(2)
O(2)	0.2744(4)	0.68772(13)	0.5162(3)	0.057(3)	0.033(2)	0.061(3)	0.008(2)	0.042(2)	0.007(2)
O(3)	−0.0467(4)	0.79273(13)	0.4306(3)	0.047(2)	0.036(2)	0.065(3)	0.012(2)	0.037(2)	0.005(2)
O(4)	0.0566(4)	0.67515(13)	0.5207(3)	0.062(3)	0.031(2)	0.055(2)	0.005(2)	0.041(2)	0.001(2)
C(1)	0.0905(6)	0.77394(20)	0.4518(4)	0.042(3)	0.033(3)	0.043(3)	0.002(2)	0.024(3)	0.000(3)
C(2)	0.1480(6)	0.70591(19)	0.5005(4)	0.051(3)	0.030(3)	0.038(3)	−0.001(2)	0.028(3)	−0.003(3)
C(3)	−0.1010(6)	0.85898(21)	0.3841(6)	0.049(3)	0.043(3)	0.077(4)	0.021(3)	0.039(3)	0.012(3)
C(4)	−0.2553(7)	0.87091(22)	0.3727(6)	0.074(4)	0.043(3)	0.095(5)	0.010(3)	0.066(4)	0.011(3)
C(5)	0.1136(7)	0.61062(19)	0.5772(5)	0.073(4)	0.031(3)	0.052(3)	0.009(3)	0.044(3)	0.005(3)
C(6)	0.0276(7)	0.59609(21)	0.6343(5)	0.061(4)	0.045(3)	0.075(4)	0.012(3)	0.050(3)	0.005(3)
C(11)	−0.3186(6)	0.9380(3)	0.3273(5)	0.044(3)	0.044(3)	0.063(4)	−0.000(3)	0.038(3)	0.001(3)
C(12)	−0.4238(7)	0.9524(3)	0.1970(6)	0.050(4)	0.071(4)	0.059(4)	−0.015(3)	0.033(3)	0.001(3)
C(13)	−0.4790(8)	1.0144(3)	0.1556(6)	0.074(5)	0.096(5)	0.062(4)	0.022(4)	0.043(4)	0.037(4)
C(14)	−0.4334(8)	1.0615(3)	0.2422(7)	0.075(5)	0.056(4)	0.096(5)	0.022(4)	0.062(4)	0.023(3)
C(15)	−0.3331(7)	1.0472(3)	0.3718(6)	0.067(4)	0.044(4)	0.081(5)	−0.011(3)	0.041(4)	−0.002(3)
C(16)	−0.2749(7)	0.9862(3)	0.4135(5)	0.066(4)	0.057(4)	0.049(4)	0.002(3)	0.025(3)	0.012(3)
C(21)	0.0540(6)	0.5288(2)	0.6821(5)	0.045(3)	0.041(3)	0.046(3)	0.003(3)	0.030(3)	0.001(3)
C(22)	0.1994(7)	0.4942(3)	0.7281(6)	0.054(4)	0.051(3)	0.089(4)	0.018(3)	0.050(4)	0.006(3)
C(23)	0.2169(7)	0.4317(3)	0.7694(5)	0.057(4)	0.055(4)	0.077(4)	0.027(3)	0.043(4)	0.015(3)
C(24)	0.0925(7)	0.4042(3)	0.7662(5)	0.070(4)	0.042(3)	0.047(3)	0.007(3)	0.033(3)	−0.005(3)
C(25)	−0.0505(7)	0.4376(3)	0.7234(5)	0.062(4)	0.054(4)	0.052(3)	−0.004(3)	0.039(3)	−0.016(3)
C(26)	−0.0690(6)	0.4995(3)	0.6820(5)	0.045(3)	0.048(3)	0.046(3)	−0.001(3)	0.030(3)	−0.005(3)

Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(3)	−0.000	0.892	0.453	0.07	H(6)	0.078	0.628	0.715	0.07	H(16)	−0.193	0.976	0.516	0.07
H(31)	−0.131	0.865	0.290	0.07	H(61)	−0.108	0.604	0.561	0.07	H(22)	0.300	0.516	0.732	0.07
H(4)	−0.355	0.838	0.303	0.07	H(12)	−0.464	0.915	0.126	0.07	H(23)	0.330	0.405	0.804	0.07
H(41)	−0.224	0.864	0.467	0.07	H(13)	−0.559	1.025	0.053	0.07	H(24)	0.107	0.356	0.798	0.07
H(5)	0.076	0.576	0.502	0.07	H(14)	−0.476	1.110	0.209	0.07	H(25)	−0.149	0.416	0.722	0.07
H(51)	0.251	0.610	0.652	0.07	H(15)	−0.299	1.084	0.442	0.07	H(26)	−0.182	0.526	0.649	0.07

Table 3

Final atomic parameters with esd's in parentheses for $[o\text{-}C_6H_4(CO_2Et)_2Cl_3MoO]\cdot C_6H_6$

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo	0.21295(7)	0.22575(9)	0.23518(4)	0.0618(4)	0.0706(5)	0.0610(4)	0.0127(3)	−0.0104(3)	−0.0109(3)
Cl(1)	0.4332(3)	0.2127(4)	0.1392(2)	0.074(2)	0.130(3)	0.125(3)	0.032(2)	0.006(2)	−0.025(2)
Cl(2)	0.1239(3)	0.1660(4)	0.1194(2)	0.138(2)	0.105(2)	0.071(2)	−0.010(2)	−0.017(2)	−0.048(2)
Cl(3)	0.2618(3)	0.3738(4)	0.3380(2)	0.088(2)	0.117(2)	0.097(2)	0.008(2)	−0.046(2)	−0.026(2)
O(1)	0.0243(6)	0.7040(8)	0.0895(4)	0.083(4)	0.100(4)	0.080(4)	0.045(4)	−0.034(3)	−0.050(3)
O(2)	−0.2469(5)	0.4009(7)	0.3900(3)	0.064(3)	0.085(4)	0.044(3)	0.011(3)	−0.009(3)	−0.023(3)
O(3)	0.0961(5)	0.5068(6)	0.1935(4)	0.067(3)	0.070(4)	0.075(4)	0.024(3)	−0.028(3)	−0.024(3)
O(4)	−0.0132(5)	0.3035(7)	0.3104(3)	0.062(3)	0.081(4)	0.057(3)	0.021(3)	−0.011(3)	−0.015(3)
O(5)	0.2667(6)	0.0151(7)	0.2799(4)	0.095(4)	0.070(4)	0.100(5)	0.041(4)	−0.017(4)	−0.019(3)
C(1)	0.1827(10)	0.6984(13)	0.0616(6)	0.095(6)	0.124(8)	0.110(8)	0.067(7)	−0.046(6)	−0.067(6)
C(2)	0.2015(10)	0.7819(14)	−0.0230(6)	0.098(7)	0.179(12)	0.093(8)	−0.001(8)	−0.001(6)	−0.063(7)
C(3)	−0.1896(8)	0.2908(13)	0.4646(5)	0.080(5)	0.117(8)	0.050(5)	0.027(5)	−0.018(4)	−0.031(5)
C(4)	−0.3206(9)	0.2957(13)	0.5322(5)	0.111(7)	0.156(10)	0.063(6)	0.034(6)	−0.014(5)	−0.060(7)
C(5)	−0.2531(8)	0.6952(10)	0.1141(5)	0.072(5)	0.080(6)	0.065(5)	0.023(4)	−0.029(4)	−0.025(4)
C(6)	−0.4027(9)	0.7048(12)	0.1259(6)	0.081(6)	0.111(7)	0.084(6)	0.031(6)	−0.041(5)	−0.033(5)
C(7)	−0.4633(8)	0.6147(11)	0.1941(6)	0.059(4)	0.103(7)	0.081(6)	0.009(5)	−0.027(4)	−0.025(4)
C(8)	−0.3746(7)	0.5151(10)	0.2538(5)	0.062(5)	0.082(6)	0.059(5)	0.003(4)	−0.013(4)	−0.022(4)
C(9)	−0.2249(7)	0.5036(9)	0.2442(4)	0.057(4)	0.061(5)	0.046(4)	0.001(3)	−0.015(3)	−0.015(3)

Table 3 (continued)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(10)	−0.1595(7)	0.5941(9)	0.1720(5)	0.060(4)	0.064(5)	0.050(4)	0.005(4)	−0.017(3)	−0.020(4)
C(11)	−0.0046(8)	0.5961(9)	0.1547(5)	0.073(5)	0.059(5)	0.053(5)	0.007(4)	−0.018(4)	−0.024(4)
C(12)	−0.1483(7)	0.3944(9)	0.3163(5)	0.058(4)	0.059(5)	0.050(4)	0.005(4)	−0.010(4)	−0.023(4)
C(13)	−0.2944(13)	0.8315(14)	0.4245(7)	0.131(9)	0.107(8)	0.102(8)	0.019(7)	−0.032(7)	−0.057(7)
C(14)	−0.3738(11)	0.9481(13)	0.3676(8)	0.075(6)	0.097(8)	0.151(11)	−0.001(7)	−0.035(7)	−0.016(5)
C(15)	−0.2970(15)	1.0099(13)	0.2960(8)	0.150(10)	0.084(7)	0.105(9)	0.017(6)	−0.060(8)	−0.033(7)
C(16)	−0.1395(16)	0.9598(16)	0.2803(8)	0.159(11)	0.104(9)	0.108(9)	−0.027(7)	0.016(8)	−0.078(9)
C(17)	−0.0608(12)	0.8408(17)	0.3380(11)	0.078(7)	0.108(10)	0.195(15)	−0.045(9)	−0.020(8)	−0.034(7)
C(18)	−0.1413(14)	0.7791(14)	0.4087(9)	0.126(9)	0.084(7)	0.171(13)	0.011(8)	−0.088(9)	−0.029(7)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(1)	0.261	0.561	0.059	0.10(3)	H(5)	−0.208	0.767	0.059	0.08(3)
H(11)	0.205	0.769	0.108	0.11(3)	H(6)	−0.471	0.784	0.081	0.12(3)
H(2)	0.321(2)	0.753(9)	−0.051(3)	0.20	H(7)	−0.579	0.620	0.202	0.07(2)
H(21)	0.143(7)	0.925(2)	−0.018(2)	0.20	H(8)	−0.423	0.446	0.308	0.08(3)
H(22)	0.155(8)	0.732(8)	−0.066(2)	0.20	H(13)	−0.355	0.781	0.482	0.17(5)
H(3)	−0.120	0.345	0.488	0.11(3)	H(14)	−0.496	0.990	0.380	0.10(3)
H(31)	−0.123	0.155	0.445	0.17(5)	H(15)	−0.358	1.100	0.250	0.20
H(4)	−0.286(3)	0.204(8)	0.585(3)	0.20	H(16)	−0.079	1.013	0.224	0.19(5)
H(41)	−0.397(5)	0.258(10)	0.506(2)	0.20	H(17)	0.062	0.798	0.327	0.15(4)
H(42)	−0.380(6)	0.430(3)	0.557(4)	0.20	H(18)	−0.081	0.685	0.454	0.16(4)

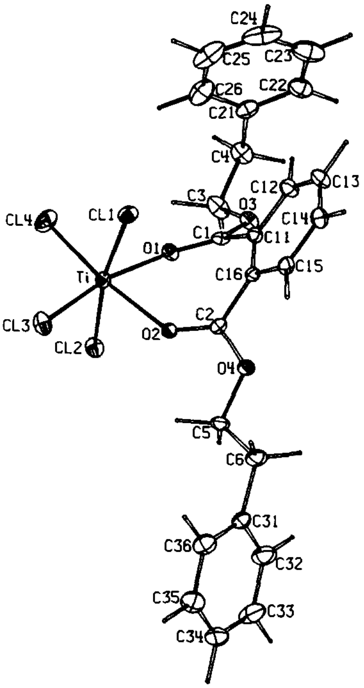

Fig. 1. Structure and numbering scheme of the [o-$C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti$] molecule.

bis(2-phenylethyl) o-phthalate is coordinated to the titanium atom via two carbonyl oxygen atoms. The chelate ligand and the titanium atom form a seven-membered ring. The general geometry around the titanium atom is similar to that observed earlier in [o-$C_6H_4(CO_2{}^iBu)_2Cl_4Ti$] [3]. The titanium atom is placed 2.078(3) Å from carbonyl oxygen O(1) and 2.130(3) Å from carbonyl oxygen O(2). The Ti–O–C bond angles are typical for $TiCl_4$ o-phthalate diester complexes. The differentiations of the C(1)–O(3)–C(3)–C(4) and C(2)–O(4)–C(5)–C(6) as well as of the O(3)–C(3)–C(4)–C(21) and O(4)–C(5)–C(6)–C(31) torsion angles (see Table 4) show the different orientation of the phenyl rings of the 2-phenylethyl alcohol residues towards the benzene ring of the o-phthalate moiety. The carbonyl groups C(1)–O(1) and C(2)–O(2) remain in the preferred conformation, synperiplanar to the O(3)–C(3) and O(4)–C(5) bonds, respectively. The plane through O(1), C(1), O(3), C(11) and the plane through O(2), C(2), O(4), C(16) form an angle of about 40° with the o-phthalate diester phenyl ring.

In the crystal two types of short inter- and intramolecular contacts are observed. The chlorine atom Cl(1) is 3.299(4) Å from carbon atom C(16) and the chlorine atom Cl(2) is 3.327(4) Å and 3.302(4) Å from carbon atom [$C(1^{-x,1-y,-z})$ and $C(2^{-x,1-y,-z})$] of the adjacent molecule, respectively.

Synthesis and structure of [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$]

In order to elucidate whether the number of atoms in the ring formed by the chelate ester ligand with the titanium atom has an influence on the geometry around the titanium atom, the complex compound formulated as [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] was investigated.

Table 4

Selected bond lengths (Å), bond angles (°) and torsion angles (°) for tetrachloro[bis(2-phenylethyl) *o*-phthalate]titanium(IV)

Ti–Cl(1)	2.290(2)	Ti–Cl(3)	2.241(2)
Ti–Cl(2)	2.281(2)	Ti–Cl(4)	2.215(2)
Ti–O(1)	2.078(3)	Ti–O(2)	2.130(3)
O(1)–C(1)	1.227(6)	O(2)–C(2)	1.230(5)
C(1)–C(11)	1.481(6)	C(2)–C(16)	1.476(6)
C(1)–O(3)	1.303(5)	C(2)–O(4)	1.301(4)
O(3)–C(3)	1.479(6)	O(4)–C(5)	1.462(6)
C(3)–C(4)	1.504(7)	C(5)–C(6)	1.516(6)
C(4)–C(21)	1.506(7)	C(6)–C(31)	1.522(7)
Cl(3)–Ti–Cl(1)	93.6(1)	Cl(2)–Ti–Cl(1)	170.6(1)
Cl(3)–Ti–Cl(4)	101.2(1)	Cl(2)–Ti–Cl(4)	93.3(1)
Cl(3)–Ti–Cl(2)	92.4(1)	Cl(1)–Ti–Cl(4)	92.6(1)
O(1)–Ti–Cl(1)	87.7(1)	O(2)–Ti–Cl(1)	86.9(1)
O(1)–Ti–Cl(2)	85.0(1)	O(2)–Ti–Cl(2)	86.0(1)
O(1)–Ti–Cl(3)	168.4(1)	O(2)–Ti–Cl(3)	89.0(1)
O(1)–Ti–Cl(4)	90.3(1)	O(2)–Ti–Cl(4)	169.8(1)
O(1)–Ti–O(2)	79.6(2)		
Ti–O(1)–C(1)	142.1(3)	Ti–O(2)–C(2)	139.3(3)
O(1)–C(1)–C(11)	126.6(4)	O(2)–C(2)–C(16)	127.2(4)
O(1)–C(1)–O(3)	122.0(4)	O(2)–C(2)–O(4)	121.8(4)
O(3)–C(1)–C(11)	111.3(4)	O(4)–C(2)–C(16)	111.0(4)
C(1)–C(11)–C(16)	124.4(4)	C(2)–C(16)–C(11)	124.6(4)
C(1)–O(3)–C(3)	118.8(4)	C(2)–O(4)–C(5)	119.5(4)
O(3)–C(3)–C(4)	106.4(4)	O(4)–C(5)–C(6)	104.9(4)
C(3)–C(4)–C(21)	112.6(5)	C(5)–C(6)–C(31)	111.0(5)
Ti–O(1)–C(1)–C(11)	−1.8(11)	Ti–O(2)–C(2)–C(16)	−3.1(8)
Ti–O(1)–C(1)–O(3)	−177.5(8)	Ti–O(2)–C(2)–O(4)	174.6(7)
O(1)–C(1)–C(11)–C(16)	40.4(11)	O(2)–C(2)–C(16)–C(11)	−41.6(9)
O(1)–C(1)–O(3)–C(3)	11.6(10)	O(2)–C(2)–O(4)–C(5)	4.0(8)
C(1)–O(3)–C(3)–C(4)	136.0(9)	C(2)–O(4)–C(5)–C(6)	−167.4(7)
O(3)–C(3)–C(4)–C(21)	−46.6(9)	O(4)–C(5)–C(6)–C(31)	−169.5(7)

The compound was readily obtained in high yield by the reaction of $TiCl_4$ with bis(2-phenylethyl) oxalate in n-hexane. The compound is soluble in CH_2Cl_2 but insoluble in aliphatic and aromatic hydrocarbons.

$$TiCl_4 + C_2O_4(CH_2CH_2Ph)_2 \xrightarrow{\text{n-hexane}} \underset{\text{(II)}}{[C_2O_4(CH_2CH_2Ph)_2Cl_4Ti]} \qquad (2)$$

The structure of the $[C_2O_4(CH_2CH_2Ph)_2Cl_4Ti]$ molecules and the numbering scheme are depicted in Fig. 2. Selected bond lengths, bond angles and torsion angles are listed in Table 5. The molecule of bis(2-phenylethyl) oxalate is coordinated to the titanium atom via carbonyl oxygen atoms. The Ti atom and the chelate ligand form a five-membered ring. In the complex molecule four chlorine atoms and two oxygen atoms form a distorted octahedron around the titanium atom. The titanium atom is placed 2.198(4) and 2.212(4) Å from the O(1) and O(2) atoms along the direction of sp^2-hybridized oxygen lone pairs (Ti–O(1)–C(2) and Ti–O(2)–C(2) bond angles of 117.6(4) and 117.2(4)° are similar) in the plane of

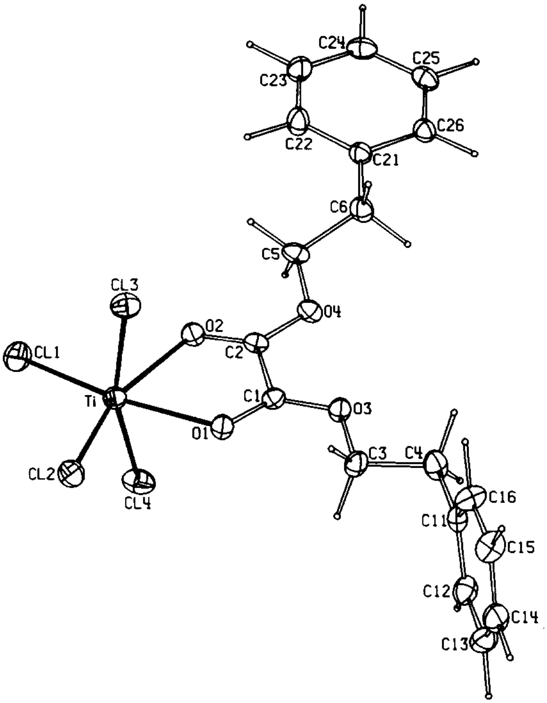

Fig. 2. Structure and numbering scheme of the [$C_2O_4(CH_2CH_2Ph)_2Cl_4Ti$] molecule.

the carbonyl groups. The average Ti–Cl bond length is a little shorter (Table 5) than the average Ti–Cl bond distance in complex I. Hence, electrostatic repulsion among the co-ordinated Cl atoms could explain the Cl(3)–Ti–Cl(4) bond angle being 162.4(1)° compared with the 170.6(1)° of the analogous Cl(1)–Ti–Cl(2) bond angle in compound I. According to this, the extensive overlap of orbitals of titanium and oxygen atoms as well as the short Ti–O bond distances might be expected. In reality, the Ti–O bond lengths in II are the longest that have been observed for $TiCl_4$ diester compounds [1–3].

The coordinated chelate molecule contains four planar parts: two aromatic rings and two COO groups. These last two planar fragments form an angle of 3.0(8)°. The two aromatic rings are almost perpendicular, tilted by 92.1(8)°. The C(1)–O(3)–C(3)–C(4) and C(2)–O(4)–C(5)–C(6) torsion angles, −177.3(13) and 159.7(8)°, are different, contrary to what is observed in I. The O(1)–C(1)–C(2)–O(2) torsion angle of −3.1(13)° is similar to the corresponding angles in free oxalate diester molecules [8,9]. Both carbonyl groups C(1)–O(1) and C(2)–O(2) are in the preferred conformation, *syn*-periplanar to O(3)–C(3) and O(4)–C(5) bonds, respectively [10].

The IR spectrum has a very strong broad band at 1687 cm^{-1} [ν(C=O)], a strong band at 1308 cm^{-1} [ν(C–O)] and a very strong band at 390 cm^{-1} due to ν(Ti–Cl).

Synthesis and structure of [o-$C_6H_4(CO_2Et)_2Cl_3MoO$] · C_6H_6

In order to understand more thoroughly whether a change of Lewis acid could exercise an effect on conformational preferences of *o*-phthalate diester chelate ligands, the interaction of Mo_2Cl_{10} and diethyl *o*-phthalate was studied.

Table 5

Principal interatomic distances (Å), bond angles (°) and torsion angles (°) for $[C_2O_4(CH_2CH_2Ph)_2Cl_4Ti]$

Ti–Cl(1)	2.208(2)	Ti–Cl(2)	2.194(2)
Ti–Cl(3)	2.259(2)	Ti–Cl(4)	2.282(2)
Ti–O(1)	2.198(4)	Ti–O(2)	2.212(4)
O(1)–C(1)	1.220(7)	O(2)–C(2)	1.213(8)
C(1)–O(3)	1.285(5)	O(4)–C(2)	1.280(7)
O(3)–C(3)	1.482(5)	O(4)–C(5)	1.479(5)
C(3)–C(4)	1.482(11)	C(5)–C(6)	1.492(10)
C(4)–C(11)	1.508(7)	C(6)–C(21)	1.504(6)
C(1)–C(2)	1.526(6)		
Cl(1)–Ti–Cl(2)	103.3(1)	Cl(1)–Ti–Cl(3)	95.2(1)
Cl(1)–Ti–Cl(4)	94.5(1)	Cl(2)–Ti–Cl(3)	95.9(1)
Cl(2)–Ti–Cl(4)	96.1(1)	Cl(3)–Ti–Cl(4)	162.4(1)
O(1)–Ti–Cl(1)	169.0(2)	O(2)–Ti–Cl(1)	96.7(2)
O(1)–Ti–Cl(2)	87.6(2)	O(2)–Ti–Cl(2)	160.0(2)
O(1)–Ti–Cl(3)	84.5(2)	O(2)–Ti–Cl(3)	81.7(2)
O(1)–Ti–Cl(4)	83.1(2)	O(2)–Ti–Cl(4)	82.6(2)
O(1)–Ti–O(2)	72.4(2)		
Ti–O(1)–C(1)	117.6(4)	Ti–O(2)–C(2)	117.2(4)
C(1)–O(3)–C(3)	116.4(4)	C(2)–O(4)–C(5)	117.9(4)
O(1)–C(1)–O(3)	127.0(5)	O(2)–C(2)–O(4)	128.0(5)
O(1)–C(1)–C(2)	116.1(5)	O(2)–C(2)–C(1)	116.5(5)
O(3)–C(1)–C(2)	116.8(5)	O(4)–C(2)–C(1)	115.5(5)
O(3)–C(3)–C(4)	106.9(5)	O(4)–C(5)–C(6)	106.2(5)
C(3)–C(4)–C(11)	110.6(5)	C(5)–C(6)–C(21)	113.5(5)
Ti–O(1)–C(1)–C(2)	2.8(10)	Ti–O(2)–C(2)–C(1)	1.7(9)
Ti–O(1)–C(1)–O(3)	−177.9(13)	Ti–O(2)–C(2)–O(4)	−177.8(13)
O(1)–C(1)–O(3)–C(3)	0.4(12)	O(2)–C(2)–O(4)–C(5)	3.9(12)
C(1)–O(3)–C(3)–C(4)	−177.3(13)	C(2)–O(4)–C(5)–C(6)	159.7(11)
O(3)–C(3)–C(4)–C(11)	179.3(9)	O(4)–C(5)–C(6)–C(21)	172.9(8)

Attempts at preparation of the molybdenum $MoCl_5$ complex with diethyl *o*-phthalate were unsuccessful; a brown product was obtained which probably was the starting Mo_2Cl_{10}. When the product was filtered off and the solution was left in the refrigerator, after two months, green crystals appeared. The further condensation of the solution caused the precipitation of *o*-phthalic acid anhydride. EtCl was detected chromatographically in the solution.

$$Mo_2Cl_{10} + 2\ o\text{-}C_6H_4(CO_2Et)_2 \xrightarrow{C_6H_6} \underset{\text{(III)}}{[o\text{-}C_6H_4(CO_2Et)_2Cl_3MoO]} + EtCl + C_6H_4(CO)_2O \qquad (3)$$

The IR spectrum of **III** presents the stretching ν(Mo=O) mode at 995s cm^{-1}, the band at 1650vs,br cm^{-1} due to ν(C=O) and the band at 340 cm^{-1} assigned to ν(Mo–Cl). The compound is paramagnetic. Its magnetic moment is 1.69 μ_B. The structure of the (diethyl *o*-phthalate)trichlorooxomolybdenum(V) molecule is presented in Fig. 3. Principal interatomic distances, bond angles and torsion angles are summarized in Table 6. Three Cl atoms, one oxo-oxygen and two O atoms of the carbonyl groups form the distorted octahedron around the molybdenum atom.

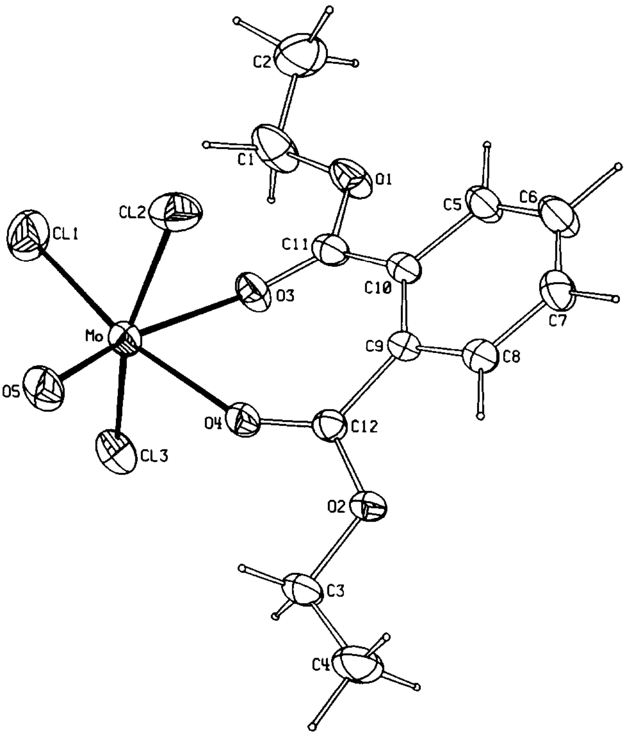

Fig. 3. Structure and numbering scheme of the [o-$C_6H_4(CO_2Et)_2Cl_3MoO$] molecule.

The O(3), C(11), C(10), C(9), C(12) and O(4) atoms of the chelate ligand and Mo atom form a seven-membered ring. The multiply bonded oxo O(5) atom (1.701(5) Å from the Mo atom) is trans to the carbonyl oxygen O(3). The Mo–O(3) bond length (2.222(5) Å) is longer than the Mo–O(4) bond length (2.115(5) Å). This disparity between the two Mo–O(carbonyl) bonds reflects the *trans*-weakening influence of the multiply bonded oxygen atom [11]. The three Cl atoms are in a meridional arrangement, with Mo–Cl(1), *trans* to O(4), shorter [2.268(3) Å] than the Mo–Cl(2) and Mo–Cl(3) [2.359(3) Å; 2.345(3) Å] mutually *trans* Mo–Cl bonds. With O(4), the three Cl atoms form a virtually square equatorial plane. Typically, the Mo atom is displaced 0.31(1) Å out of this plane towards the oxo ligand O(5) [12]. Thus, overall, the bond lengths and bond angles in the coordination sphere of the molybdenum atom show no significant differences from those in [$O\{P(NMe)_3O\}_2Cl_3MoO$] and [$(PPh_3O)_2Cl_3MoO$] [13,14]. The coordinated diethyl o-phthalate molecule contains two planar carboxylic groups, which are tilted by 6.1(8)° and 30.6(8)° with respect to the aromatic ring. The molybdenum atom is not coplanar with the planes through O(4), C(12), O(2), C(3) and O(3), C(11), O(1), C(1) atom, being displaced by −0.13(1) and 1.07(1) Å.

The non-bonded benzene molecules are so located in the crystal, that they separate the complex molecules of compound III (Fig. 4).

In the crystal of [o-$C_6H_4(CO_2Et)_2Cl_3MoO$] · C_6H_6 there are short inter- and intramolecular contacts. The chlorine atom Cl(2) is 3.276(7) Å from carbon atom

Table 6

Principal interatomic distances (Å), bond angles (°) and torsion angles (°) for the [o-$C_6H_4(CO_2Et)_2$-Cl_3MoO]·C_6H_6 crystal

Mo-Cl(1)	2.268(3)	Mo-Cl(2)	2.359(3)
Mo-Cl(3)	2.345(3)	Mo-O(3)	2.222(5)
Mo-O(4)	2.115(5)	Mo-O(5)	1.701(5)
O(1)-C(1)	1.478(11)	O(2)-C(3)	1.476(9)
C(1)-C(2)	1.421(12)	C(3)-C(4)	1.434(11)
O(1)-C(11)	1.313(8)	O(2)-C(12)	1.300(8)
O(3)-C(11)	1.227(9)	O(4)-C(12)	1.224(9)
C(11)-C(10)	1.469(11)	C(12)-C(9)	1.516(9)
C(10)-C(5)	1.410(10)	C(9)-C(8)	1.395(10)
C(5)-C(6)	1.393(12)	C(8)-C(7)	1.402(11)
C(9)-C(10)	1.425(9)	C(6)-C(7)	1.364(12)
Cl(1)-Mo-Cl(2)	89.5(1)	Cl(1)-Mo-Cl(3)	91.5(1)
Cl(2)-Mo-Cl(3)	162.8(1)	O(5)-Mo-Cl(1)	100.4(2)
O(5)-Mo-Cl(2)	97.3(2)	O(5)-Mo-Cl(3)	99.4(2)
O(5)-Mo-O(3)	168.3(3)	O(5)-Mo-O(4)	94.0(3)
O(3)-Mo-Cl(1)	91.2(2)	O(4)-Mo-Cl(1)	165.5(2)
O(3)-Mo-Cl(2)	81.7(2)	O(4)-Mo-Cl(2)	87.9(2)
O(3)-Mo-Cl(3)	81.0(2)	O(4)-Mo-Cl(3)	87.9(2)
O(3)-Mo-O(4)	74.3(2)		
Mo-O(3)-C(11)	140.7(5)	Mo-O(4)-C(12)	148.6(5)
O(3)-C(11)-C(10)	126.6(7)	O(4)-C(12)-C(9)	129.8(6)
O(3)-C(11)-O(1)	119.2(7)	O(4)-C(12)-O(2)	120.8(6)
O(1)-C(11)-C(10)	114.1(6)	O(2)-C(12)-C(9)	111.4(6)
C(11)-O(1)-C(1)	117.3(7)	C(12)-O(2)-C(3)	117.3(6)
O(1)-C(1)-C(2)	108.7(8)	O(2)-C(3)-C(4)	106.7(7)
C(11)-C(10)-C(5)	117.4(7)	C(12)-C(9)-C(8)	114.1(6)
C(11)-C(10)-C(9)	125.3(6)	C(12)-C(9)-C(10)	126.4(6)
C(5)-C(10)-C(9)	117.3(7)	C(8)-C(9)-C(10)	119.5(6)
C(10)-C(5)-C(6)	121.7(7)	C(9)-C(8)-C(7)	121.5(7)
C(5)-C(6)-C(7)	120.6(8)	C(8)-C(7)-C(6)	119.3(8)
C(2)-C(1)-O(1)-C(11)	163.4(15)	C(4)-C(3)-O(2)-C(12)	-170.2(11)
C(1)-O(1)-C(11)-O(3)	5.5(12)	C(3)-O(2)-C(12)-O(4)	-1.6(12)
O(1)-C(11)-O(3)-Mo	-128.3(15)	O(2)-C(12)-O(4)-Mo	-172.8(13)

C(11), which is in turn 3.370(13) Å from the C(16) carbon atom of the solvating benzene molecules.

The mechanism of o-phthalic acid anhydride and EtCl formation during reaction 3 is unknown and is the subject of further investigations.

Conclusions

These results show the significant influence of the number of atoms in the ring formed by the titanium atom and the chelate ligand upon M-O-C bond angles and M-O(ester) bond lengths.

In [o-$C_6H_4(CO_2R)_2Cl_4Ti$] [1], where R = Et the titanium atom is almost coplanar with the ester groups. This complex could be considered as an "idealized" structure because the diethyl o-phthalate chelate ligand is so coordinated to $TiCl_4$, that the complex molecule has crystallographic $m(C_s)$ point symmetry.

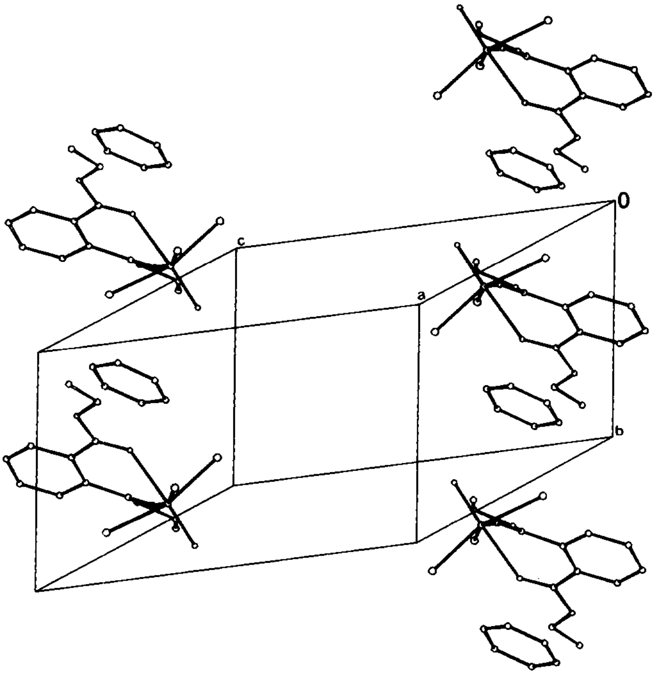

Fig. 4. The packing arrangement in the $[o\text{-}C_6H_4(CO_2Et)_2Cl_3MoO]\cdot C_6H_6$ crystal.

Instead, when the substituents are bulky, the general geometry around Ti atom in $[o\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2Cl_4Ti]$ and $[o\text{-}C_6H_4(CO_2{}^iBu)_2Cl_4Ti]$ is similar but a little different from that in $[o\text{-}C_6H_4(CO_2Et)_2Cl_4Ti]$. The complex molecules, when $R = {}^iBu$ or $R = CH_2CH_2Ph$, are asymmetric. This is demonstrated by the fact that the dihedral angles Ti–O–C–C as well as Ti–O–C bond angles and Ti–O distances differ for the carbonyl groups. The values of two Ti–O–C (117.6(4) and 117.2(4)°) bond angles in $[C_2O_4(CH_2CH_2Ph)_2Cl_4Ti]$ are smaller than observed for titanium *o*-diester compounds [15]. This probably results from the fact that the Ti atom is bound by two carbonyls of conjugated ester groups in a five-membered ring chelate. Elucidation of the dependence of the number of atoms in a ring formed by chelate ligand and Ti atom on Ti–O–C and Ti–O–C–C angles needs further crystallographic studies.

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