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## The crystal structure and properties of di- $\mu$ -*m*-diethylphthalateoctachlorodititanium(IV)

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### Abstract

The crystal structure of dimeric  $\{\text{Ti}_2[\mu\text{-}m\text{-C}_6\text{H}_4(\text{COOEt})_2]_2\text{Cl}_8\}$ , which in the presence of activators is a good catalyst for olefin polymerization, has been determined by X-ray diffraction and refined by full-matrix least squares to  $R = 0.0333$  for 1990 independent non-zero reflexions. Crystals are triclinic, space group  $P\bar{1}$ ,  $Z = 1$ , in a cell of dimensions:  $a = 8.940(5)$ ,  $b = 10.466(8)$ ,  $c = 10.427(8)$  Å,  $\alpha = 97.28(6)$ ,  $\beta = 107.61(4)$ ,  $\gamma = 108.13(4)^\circ$ . The crystal consists of dimeric molecules possessing crystallographic symmetry centre. The titanium atoms are octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of the two *m*-diethylphthalate in the *cis* position. The two ester ligands and the two Ti atoms form a sixteen-membered ring. The phenyl rings are not quite planar; the average separation between them is 3.36(1) Å.

### Introduction

Polymerization studies reveal that the interaction of esters with the Ziegler–Natta catalyst supported on  $\text{MgCl}_2$  ensured high isotacticity [1].

It was found that reaction between  $\text{TiCl}_4$  and the esters, the dimeric [2,3]  $[(\text{L})\text{Cl}_3\text{Ti}(\mu\text{-Cl})_2\text{TiCl}_3(\text{L})]$  ( $\text{L} = \text{CH}_3\text{COOEt}$  or  $\text{CH}_3\text{OC}_6\text{H}_4\text{COOEt}$ ) and monomeric [4] *cis*- $[(\text{C}_6\text{H}_5\text{COOEt})_2\text{TiCl}_4]$  or  $[o\text{-C}_6\text{H}_4(\text{COOEt})_2\text{TiCl}_4]$  compounds [5] are formed. In the last complex the Ti atoms are octahedrally coordinated by four chlorine atoms and two carbonyl oxygen atoms of the *o*-diethylphthalate. The chelating ligand atoms together with the titanium atom form a seven-membered ring with Cl and Ti atoms located above the phenyl ring.

The enhancement of isospecific activity is very dependent on the nature of the ester [6]. To elucidate the different behaviour of aromatic esters in the polymerization the reaction of *m*-diethylphthalate with  $\text{TiCl}_4$  was studied. Here we describe the crystal structure of the  $\{\text{Ti}_2[\mu\text{-}m\text{-C}_6\text{H}_4(\text{COOEt})_2]_2\text{Cl}_8\}$  complex.

## Experimental

All reactions were carried out under  $N_2$  in dried solvents by Schlenk-tube techniques. Anhydrous  $TiCl_4$  was obtained commercially. *m*-Diethylphthalate was made in our laboratory by a standard procedure viz., reaction of isophthalic acid with ethanol in the presence of *p*-toluenesulfonic acid [7]. IR spectra were recorded on a Perkin-Elmer 180 spectrometer.

### *Di-μ-m-diethylphthalateoctachlorodititanium(IV)*

To 2 cm<sup>3</sup> of  $TiCl_4$  (3.45 g; 18.2 mmol) was added dropwise 4.40 g (18.2 mmol) of  $m-C_6H_4(COOEt)_2$  and stirred into 150 cm<sup>3</sup> n-hexane under  $N_2$ . After 1 h the yellow precipitate was filtered off and washed with n-hexane ( $3 \times 15$  cm<sup>3</sup>). Yield 7.2 g; 96%. A portion of the compound (2 g) was heated in 60 cm<sup>3</sup>  $CH_2Cl_2$  under reflux and left to crystallize. The crystals usually form as needles. Crystals suitable for the X-ray data were grown by slow diffusion of n-hexane into a solution of the title compound in  $CH_2Cl_2$ .

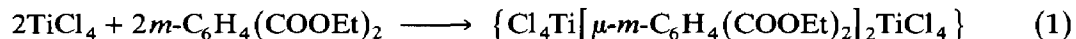
### Crystal structure determination

*Crystal data.*  $C_{24}H_{28}Cl_8O_8Ti_2$ ,  $M = 823.9$ ,  $a = 8.940(5)$ ,  $b = 10.466(8)$ ,  $c = 10.427(8)$  Å,  $\alpha = 97.28(6)$ ,  $\beta = 107.61(4)$ ,  $\gamma = 108.13(4)^\circ$ ,  $U = 857(2)$  Å<sup>3</sup>,  $D_m = 1.603$  gcm<sup>-3</sup>,  $D_c = 1.596(2)$  gcm<sup>-3</sup>,  $F(000) = 416$ , space group  $P\bar{1}$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu = 11.45$  cm<sup>-1</sup>,  $T = 299 \pm 2$  K.

Preliminary Weissenberg photographs showed the crystals to be triclinic. A sample of dimensions  $0.6 \times 0.25 \times 0.5$  mm was cut from a large crystal and sealed in a capillary. A Syntex  $P2_1$  four-circle diffractometer was used. Cell parameters were obtained from a least-squares fit of the setting angles of 15 reflections in the range  $20 < 2\theta < 30^\circ$ . The diffraction data were collected by a  $\theta/2\theta$  scan technique with graphite-monochromatized Mo- $K_\alpha$  radiation. Half an Ewald sphere up to  $2\theta = 50^\circ$  was collected. Two check reflections measured after each 50 reflections showed  $\pm 3\%$  variation. Of the 2441 reflections collected, 1990 with  $I > 3\sigma(I)$  were used for the structure analysis. The structure was solved by direct methods and refined by full-matrix least squares [8]. The H atoms were located from difference-Fourier synthesis. The positional parameters of the H atoms were refined with the constraint that  $d(C-H) = 1.08$  Å. Neutral atom scattering factors were taken from ref. 9. The Ti, Cl, O and C scattering factors were corrected for real and imaginary components. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(F_o)$ . The final  $R$  and  $R_w$  values were 0.0333 and 0.0351 for the observed reflections. For the last cycle of the refinement the maximal value of the  $\Delta/\sigma$  ratio was 0.05 and the final difference map showed a general background within  $-0.28$  and  $0.30$  eÅ<sup>-3</sup>. The final atoms parameters are given in Table 1.

## Results and discussion

The addition of *m*-diethylphthalate to  $TiCl_4$ , in a 1:1 ratio, in n-hexane gave a yellow air-sensitive compound formulated as  $\{Ti_2[\mu-m-C_6H_4(COOEt)_2]_2Cl_8\}$ .



The new species is diamagnetic. The IR spectrum shows a stretching  $\nu(C=O)$  mode

Table 1

Final positional and thermal parameters with e.s.d.s in parentheses for  $(C_{12}H_{14}O_4)_2Cl_8Ti_2$ 

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Ti	0.36872(9)	0.74927(7)	0.71474(7)	0.0294(5)	0.0351(4)	0.0340(4)	0.0108(3)	0.0122(4)	0.0161(4)
Cl(1)	0.14303(15)	0.58525(11)	0.73518(13)	0.0457(8)	0.0391(6)	0.0646(8)	0.0119(6)	0.0264(7)	0.0088(6)
Cl(2)	0.52221(15)	0.92807(12)	0.66312(13)	0.0467(8)	0.0482(7)	0.0636(8)	0.0230(6)	0.0335(7)	0.0203(6)
Cl(3)	0.52107(15)	0.81538(13)	0.94052(11)	0.0413(8)	0.0741(9)	0.0351(6)	0.0126(6)	0.0079(6)	0.0188(7)
Cl(4)	0.48003(15)	0.59677(12)	0.65895(13)	0.0537(8)	0.0531(7)	0.0626(8)	0.0177(6)	0.0251(7)	0.0362(7)
O(1)	0.21278(37)	0.70416(31)	0.50770(29)	0.043(2)	0.061(2)	0.033(2)	0.010(2)	0.009(2)	0.030(2)
O(2)	-0.24976(36)	1.10776(28)	0.25416(28)	0.042(2)	0.040(2)	0.045(2)	0.014(2)	0.022(2)	0.025(2)
O(3)	0.16574(35)	0.70915(29)	0.28753(28)	0.038(2)	0.049(2)	0.041(2)	0.017(2)	0.021(2)	0.026(2)
O(4)	-0.09628(38)	1.04203(31)	0.14287(30)	0.049(2)	0.055(2)	0.046(2)	0.024(2)	0.027(2)	0.033(2)
C(1)	0.3164(9)	0.6440(8)	0.1535(7)	0.088(5)	0.114(6)	0.067(4)	0.041(4)	0.052(4)	0.071(5)
C(2)	0.2992(7)	0.6535(6)	0.2922(5)	0.052(4)	0.068(4)	0.053(3)	0.022(3)	0.031(3)	0.041(3)
C(3)	0.0609(8)	1.2341(7)	0.0750(7)	0.059(4)	0.066(4)	0.081(5)	0.026(4)	0.033(4)	0.019(4)
C(4)	-0.1096(7)	1.1366(5)	0.0504(5)	0.055(4)	0.056(3)	0.043(3)	0.023(3)	0.024(3)	0.028(3)
C(5)	-0.0288(6)	0.8725(4)	0.3099(4)	0.030(3)	0.035(3)	0.032(3)	0.006(2)	0.010(2)	0.015(2)
C(6)	-0.0035(5)	0.7800(4)	0.3919(4)	0.027(3)	0.033(3)	0.033(3)	0.004(2)	0.010(2)	0.014(2)
C(7)	-0.1024(6)	0.7397(4)	0.4703(5)	0.034(3)	0.033(3)	0.041(3)	0.010(2)	0.012(3)	0.013(3)
C(8)	-0.2264(6)	0.7934(5)	0.4689(5)	0.032(3)	0.041(3)	0.048(3)	0.014(2)	0.020(3)	0.015(3)
C(9)	-0.2482(6)	0.8905(5)	0.3925(5)	0.029(3)	0.038(3)	0.045(3)	0.010(2)	0.015(3)	0.016(2)
C(10)	-0.1493(5)	0.9287(4)	0.3127(4)	0.029(3)	0.032(2)	0.033(3)	0.005(2)	0.008(2)	0.013(2)
C(11)	0.1334(6)	0.7290(4)	0.4022(5)	0.030(3)	0.032(3)	0.036(3)	0.007(2)	0.010(2)	0.011(2)
C(12)	-0.1704(5)	1.0359(4)	0.2343(4)	0.027(3)	0.034(3)	0.032(3)	0.004(2)	0.007(2)	0.012(2)
Atom	x	y	z	$U_{iso}$	Atom	x	y	z	$U_{iso}$
H(2)	0.261(6)	0.557(3)	0.321(5)	0.065(15)	H(9)	-0.334(4)	0.940(4)	0.401(4)	0.040(12)
H(21)	0.406(4)	0.732(4)	0.375(4)	0.066(16)	H(11)	0.198(4)	0.573(4)	0.078(4)	0.068(17)
H(4)	-0.193(5)	1.189(5)	0.060(5)	0.069(16)	H(12)	0.343(8)	0.747(3)	0.137(7)	0.110(24)
H(41)	-0.161(6)	1.062(4)	-0.047(3)	0.068(16)	H(13)	0.402(6)	0.594(5)	0.141(6)	0.097(20)
H(5)	0.044(5)	0.898(4)	0.246(4)	0.043(12)	H(31)	0.097(7)	1.298(5)	0.177(3)	0.086(19)
H(7)	-0.086(5)	0.661(3)	0.524(4)	0.045(12)	H(32)	0.177(6)	1.216(8)	0.096(8)	0.177(36)
H(8)	-0.304(5)	0.748(4)	0.524(4)	0.042(12)	H(33)	0.068(9)	1.320(5)	0.026(7)	0.160(32)

at  $1635\text{cm}^{-1}$  (vs) and  $1650\text{cm}^{-1}$  (vs), a  $\nu(\text{C}-\text{O})$  at  $1335\text{cm}^{-1}$  (vs), a  $\nu(\text{Ti}-\text{Cl})$  at  $365\text{cm}^{-1}$  (vs) and  $385\text{cm}^{-1}$  (s), and phenyl ring at  $1585\text{cm}^{-1}$  (w) and  $1600\text{cm}^{-1}$  (m).

The complex in the crystal is dimeric. The structure of  $\{\text{Cl}_4\text{Ti}[\mu\text{-}m\text{-}\text{C}_6\text{H}_4(\text{COOEt})_2]_2\text{TiCl}_4\}$  and the numbering scheme are depicted in Fig. 1. Selected bond lengths and angles are listed in Table 2. In the molecule four Cl atoms and two O atoms from the two *m*-diethylphthalate ligands (in the *cis* position) form a distorted octahedron around the titanium atoms. Each of the *m*-diethylphthalate molecules is coordinated to two titanium atoms via two carbonyl oxygen atoms. The atoms of the two chelate ligands and the two titanium atoms form a sixteen-membered ring.

The phenyl rings are not strictly planar. The C(5) and C(8) atoms are located over the plane formed by C(6), C(7), C(9) and C(10) atoms, so the angle between

Table 2

Principal interatomic distances (Å), bond angles ( $^\circ$ ), and torsion angles ( $^\circ$ ) for di- $\mu$ -*m*-diethylphthalateoctachlorodititanium(IV)<sup>a</sup>

Ti-Cl(1)	2.294(3)	Ti-Cl(2)	2.315(3)
Ti-Cl(3)	2.222(3)	Ti-Cl(4)	2.231(3)
Ti-O(1)	2.083(3)	Ti-O(2 <sup>1</sup> )	2.133(4)
C(1)-C(2)	1.494(8)	C(3)-C(4)	1.470(9)
C(2)-O(3)	1.473(7)	C(4)-O(4)	1.473(6)
C(11)-O(3)	1.319(5)	C(12)-O(4)	1.313(5)
C(11)-O(1)	1.223(5)	C(12)-O(2)	1.222(6)
C(11)-C(6)	1.461(7)	C(12)-C(10)	1.494(6)
C(5)-C(6)	1.396(6)	C(5)-C(10)	1.384(7)
C(6)-C(7)	1.386(6)	C(10)-C(9)	1.394(6)
C(7)-C(8)	1.387(7)	C(9)-C(8)	1.393(6)
C(1)-C(2)-O(3)	107.2(5)	C(3)-C(4)-O(4)	108.8(5)
C(2)-O(3)-C(11)	116.8(4)	C(4)-O(4)-C(12)	120.7(4)
O(3)-C(11)-O(1)	121.2(4)	O(4)-C(12)-O(2)	124.9(4)
O(3)-C(11)-C(6)	115.1(4)	O(4)-C(12)-C(10)	112.5(4)
O(1)-C(11)-C(6)	123.6(4)	O(2)-C(12)-C(10)	122.6(4)
C(11)-C(6)-C(5)	120.6(4)	C(12)-C(10)-C(9)	120.2(4)
C(11)-C(6)-C(7)	118.6(4)	C(12)-C(10)-C(9)	118.9(4)
C(5)-C(6)-C(7)	120.8(4)	C(5)-C(10)-C(9)	120.8(4)
C(6)-C(7)-C(8)	119.7(4)	C(10)-C(9)-C(8)	119.4(4)
C(7)-C(8)-C(9)	120.3(4)	C(6)-C(5)-C(10)	119.0(4)
Ti-O(1)-C(11)	156.0(4)	Ti <sup>1</sup> -O(2)-C(12)	173.9(4)
Cl(1)-Ti-Cl(2)	167.6(1)	Cl(1)-Ti-Cl(3)	94.8(1)
Cl(2)-Ti-Cl(3)	93.8(1)	Cl(2)-Ti-Cl(4)	93.6(1)
Cl(1)-Ti-Cl(4)	94.1(1)	Cl(3)-Ti-Cl(4)	96.9(1)
Cl(1)-Ti-O(1)	84.8(1)	Cl(1)-Ti-O(2 <sup>1</sup> )	86.3(1)
Cl(2)-Ti-O(1)	85.6(1)	Cl(2)-Ti-O(2 <sup>1</sup> )	85.0(1)
Cl(3)-Ti-O(1)	173.2(1)	Cl(3)-Ti-O(2 <sup>1</sup> )	88.9(1)
Cl(4)-Ti-O(1)	89.9(1)	Cl(4)-Ti-O(2 <sup>1</sup> )	174.1(1)
O(1)-Ti-O(2 <sup>1</sup> )	84.3(2)		
C(1)-C(2)-O(3)-C(11)	-178.4(7)	C(3)-C(4)-O(4)-C(12)	119.9(11)
C(2)-O(3)-C(11)-O(1)	1.1(9)	C(4)-O(4)-C(12)-O(2)	-2.3(12)
Ti-O(1)-C(11)-C(6)	-60.5(16)	C(10)-C(12)-O(2)-Ti <sup>1</sup>	143.2(14)

<sup>a</sup> Symmetry code: (i)  $-x, 2-y, 1-z$ .

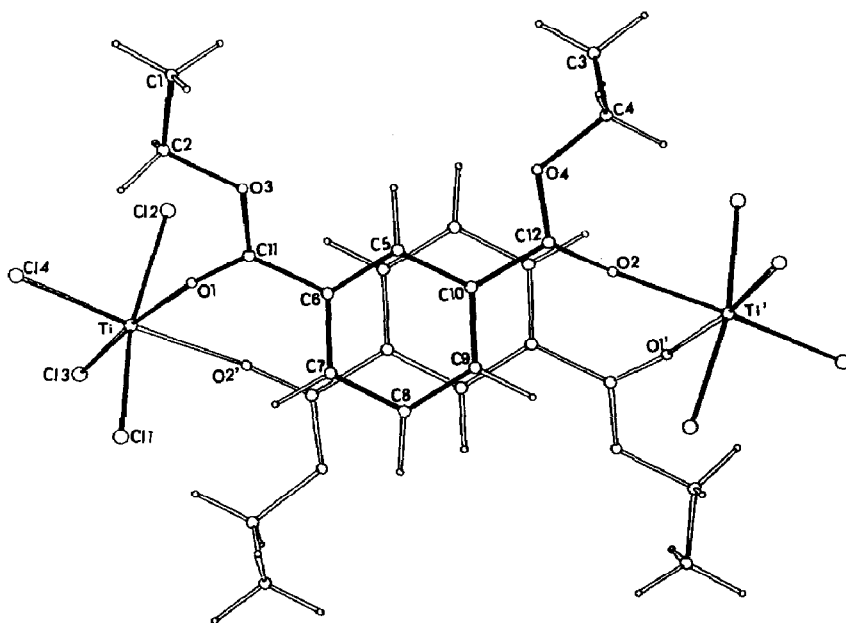


Fig. 1. View of  $\{\text{TiCl}_4[\mu\text{-}m\text{-C}_6\text{H}_4(\text{COOEt})_2]\}_2\text{TiCl}_4$  perpendicular to the benzene ring. Primed and unlabelled atoms are related to labelled atoms by the inversion centre.

two planes formed by the C(5), C(6), C(7) C(8) atoms, and the C(5), C(10), C(9), C(8) atoms is  $177.6(8)^\circ$ . The perturbations in the  $\pi$ -electron ring system caused by electron withdrawal by the ester groups are responsible for the angular distortion in the part of the ring opposite the substituent. Such an effect has been observed [10] in many benzene substituent derivatives.

The methyl group C(1) is *trans* to the C(11) atom and C(3) is in an anticlinal position to C(12) atom (see torsion angles in Table 2).

The C=O bond lengths in the coordinated carbonyl groups C(11)–O(1) [1.223(7) Å] and C(12)–O(2) [1.222(6) Å] are close to the the C=O bond length of 1.23(1) Å for the free carbonyl group [11]. The Ti–Cl distances vary somewhat but are similar to those in *cis*-[(C<sub>6</sub>H<sub>5</sub>COOEt)<sub>2</sub>TiCl<sub>4</sub>] [4] and [*o*-C<sub>6</sub>H<sub>4</sub>(COOEt)<sub>2</sub>TiCl<sub>4</sub>] [5]. The Ti–O(1) distance 2.083(3) Å is a little shorter than the Ti–O(2) bond length 2.133(4) Å. The angles Ti–O(1)–C(11) [ $156.0(4)^\circ$ ] and Ti–O(2)–C(12) [ $173.9(4)^\circ$ ] are different. The difference between the Ti–O bond lengths is most probably attributable to the intramolecular interaction between the phenyl rings.

The planes of the phenyl rings in  $\{\text{Cl}_4\text{Ti}[\mu\text{-}m\text{-C}_6\text{H}_4(\text{COOEt})_2]\}_2\text{TiCl}_4$  molecules are parallel and are separated by an average of 3.36(1) Å, a typical distance observed in other complexes with stacked aromatic molecules [12,13]. The two phenyl rings are shifted mutually, so the C(5) and C(9) carbon atoms of the one ring are close to the C(9') and C(5') atoms of the second ring, respectively. The packing of the crystal is shown in Fig. 2. There are two types of rather short intermolecular contacts. The chlorine atoms Cl(1) and Cl(3) are 3.253(4) Å and 3.384(4) Å from carbon atoms of the adjacent C(11<sup>-x,1-y,1-z</sup>) and C(12<sup>x+1,y,2+1</sup>) molecules, respectively. These distances are shorter than the sum of the van der Waals radii.

<sup>1</sup>H NMR spectrum in *d*-chloroform shows the signals typical for *m*-diethyl-

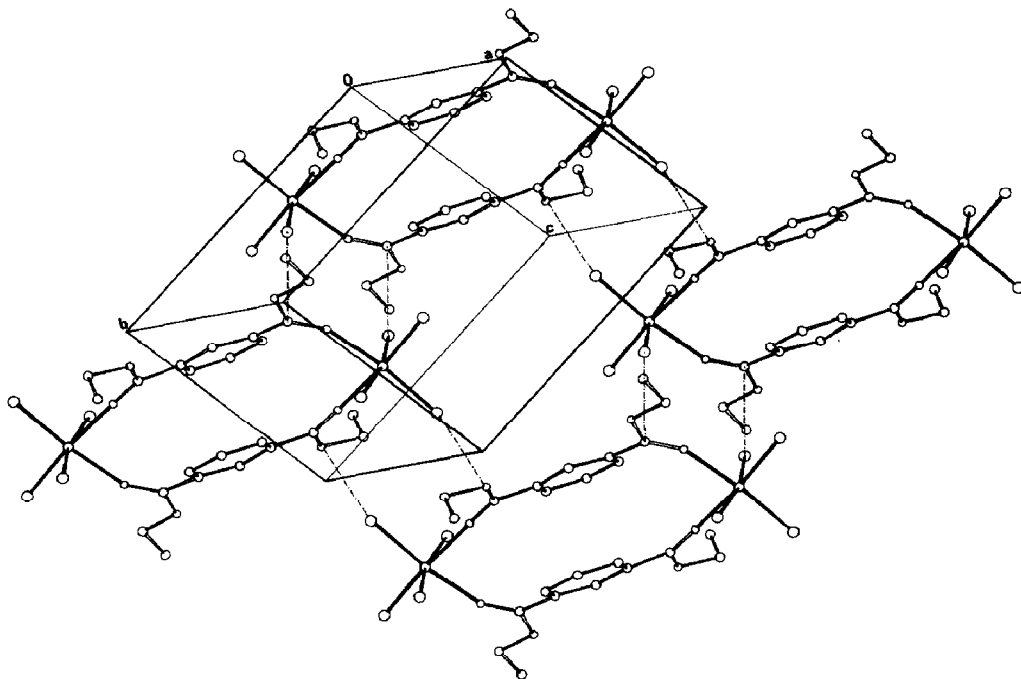
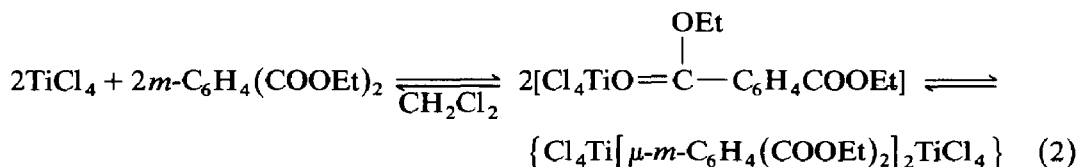


Fig. 2. The packing arrangement in the  $\{\text{TiCl}_4[\mu\text{-}m\text{-C}_6\text{H}_4(\text{COOEt})_2]_2\text{TiCl}_4\}$  crystal. The shortest intermolecular distances  $\text{Cl}(1)\cdots\text{C}(11)$  and  $\text{Cl}(3)\cdots\text{C}(12)$  between adjacent molecules are denoted as broken lines. The H atoms are omitted for clarity.

phthalate and no changes in the splitting of the phenyl ring proton signals were observed. The NMR data allow us to postulate the formation of the  $[\text{Cl}_4\text{Ti}(\text{EtOOC})\text{C}_6\text{H}_4(\text{COOEt})]$  monomer in reaction between  $\text{TiCl}_4$  and *m*-diethylphthalate in  $\text{CH}_2\text{Cl}_2$ .



In that compound only one carbonyl group oxygen atom forms the coordinate  $\text{Ti}-\text{O}(1)$  bond, because of this the titanium atom probably has the coordination number five. During crystallization two monomer molecules undergo head-to-tail dimerization to give the longer  $\text{Ti}-\text{O}(2)$  and stacked phenyl bondings. The elucidation of intramolecular and intermolecular interactions in the solid state should help to explain the effect of the aromatic ester on polymer isotacticity.

*Supplementary material available:* A list of  $F_o/F_c$  values have been deposited at the Cambridge Crystallographic Data Centre.

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