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Di- μ -chloro-tetrachlorobis(diethyl *o*-phthalate)ditanium(III), a new intermediate for the synthesis of titanium(III) compounds: crystal structure and properties

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Abstract

Di- μ -chloro-tetrachlorobis(diethyl *o*-phthalate)ditanium(III) tetra(dichloromethane) was obtained by direct reaction of TiCl_4 , diethyl *o*-phthalate and metallic aluminum in CH_2Cl_2 . The crystal structure was determined by X-ray diffraction methods and refined by a full-matrix least-squares technique to $R = 0.0495$ for 2026 independent non-zero reflections. Crystals are triclinic, space group $P\bar{1}$, with one complex molecule in the unit cell of dimensions: $a = 10.475(8)$, $b = 10.843(9)$, $c = 11.190(12)$ Å, $\alpha = 76.91(8)$, $\beta = 73.39(7)$, $\gamma = 81.10(7)^\circ$. The crystals contain dimeric molecules possessing crystallographic symmetry centres. The titanium(III) ions are octahedrally coordinated by two terminal and two bridging chlorine atoms and two carbonyl oxygen atoms of diethyl *o*-phthalate. The magnetic susceptibility and ESR measurements revealed an antiferromagnetic exchange interaction between titanium atoms in the dimer.

Introduction

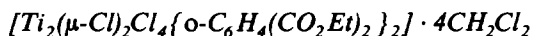
Polymerization studies have revealed that the interaction of aromatic esters with Ziegler–Natta catalyst supported on MgCl_2 results in high isotacticity [1]. Hence, studies on the interaction between ester molecules and each of the catalyst components are very important. It was found that in the reaction between TiCl_4 and ester the dimeric [2–4] $[\text{LCl}_3\text{Ti}(\mu\text{-Cl})_2\text{TiCl}_3\text{L}]$ ($\text{L} = \text{CH}_3\text{CO}_2\text{Et}$ or $\text{CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{Et}$) and $[\text{Ti}_2\{\mu\text{-}m\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2\text{Cl}_8]$ and monomeric [5,6] *cis*- $[\text{TiCl}_4(\text{C}_6\text{H}_5\text{CO}_2\text{Et})_2]$ or $[\text{TiCl}_4\{\textit{o}\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}]$ compounds are formed. The active catalyst centre is widely believed to be Ti^{3+} but compounds of Ti^{3+} with ester molecules were unknown [7].

In this paper the crystal structure and properties of $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_4\{\textit{o}\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2] \cdot 4\text{CH}_2\text{Cl}_2$ are described.

Experimental section

General procedures and materials

All manipulations were carried out under N_2 using standard Schlenk-tube techniques. Commercial anhydrous $TiCl_4$ and diethyl *o*-phthalate were used. ESR spectra were obtained on an SE type X-band spectrometer, while solid-state magnetic moments were determined by the Faraday method. The ESR spectral intensity of Ti^{3+} species was measured quantitatively by comparing the double integrated spectra of the title compound and that of a standard heptane solution of 2,2,6,6-tetramethylpiperidin-1-oxyl. IR spectra were obtained using a Perkin-Elmer 180 spectrometer. 1H NMR spectra were recorded on a BS-567 A Tesla 100 MHz spectrometer.



To 1 cm^3 (9.1 mmol) $TiCl_4$ and an excess of aluminum turnings (0.5 g) in 50 cm^3 CH_2Cl_2 was added dropwise 3.6 cm^3 (18.2 mmol) of diethyl *o*-phthalate, after which the mixture was stirred under N_2 for 20 h. The reaction proceeded slowly as indicated by a progressive colour change from yellow to brown. After 20 h the aluminum turnings were filtered off and the solution was left at 277 K for crystallization. After 48 h the brown crystalline compound precipitated. It was filtered off and washed with n-hexane (3×5 cm^3) (yield 3.8 g, 76%). Further standing of the filtrate at 277 K (60 h) led to precipitation of the white compound, which was filtered off and washed with n-hexane (3×5 cm^3). Yield 0.58 g, 54%. Anal. Found: C, 30.6; H, 3.4; Cl, 45.5; Ti, 8.8. Calc. for $C_{28}H_{36}Cl_{14}O_8Ti_2$: C, 30.8; H, 3.3; Cl, 45.4; Ti, 8.8%. Anal. Found: C, 40.4; H, 3.8; Cl, 30.0; Al, 8.3. Calc. for $C_{12}H_{14}Cl_3O_4Al$: C, 40.5; H, 3.9; Cl, 29.9; Al, 7.6%.

The crystalline brown titanium compound is sensitive to air and undergoes decomposition when stored in light in a closed flask under N_2 . Crystals are stable when stored in the post-reaction mixture and under saturated vapour of CH_2Cl_2 for one month, but decompose after drying under vacuum. Multi-faced crystals for X-ray examination were taken directly from the post-reaction solution. The crystals are dark brown in reflected light and bright brown in transmitted light.

Crystallography

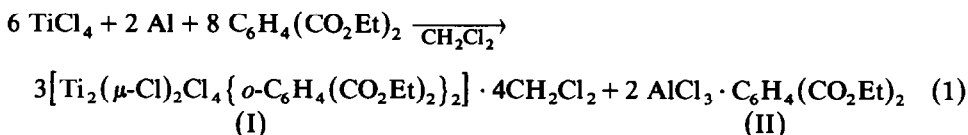
Crystal data: $C_{24}H_{28}Cl_6O_8Ti_2 \cdot 4CH_2Cl_2$, $M = 1092.7$, $a = 10.475(8)$, $b = 10.843(9)$, $c = 11.190(12)$ Å, $\alpha = 76.91(8)$, $\beta = 73.39(7)$, $\gamma = 81.10(7)^\circ$, $U = 1181(2)$ Å³, $D_m = 1.524$ g cm^{-3} , $D_c = 1.537(3)$ g cm^{-3} , $F(000) = 550$, space group $P\bar{1}$, $Z = 1$, Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 11.8$ cm^{-1} , $T = 299(1)$ K.

Preliminary Weissenberg photographs showed the crystals to be triclinic. A crystal fragment was cut from the bulk species and mounted in a capillary. A Syntex P2₁ four-circle diffractometer was used. Cell parameters were obtained from a least-squares fit of the setting angles of 15 reflections in the range $20 < 2\theta < 27^\circ$. The diffraction data were collected by the $\theta/2\theta$ scan technique with graphite monochromatized Mo- K_α radiation. The full Ewald sphere up to $2\theta = 42^\circ$ was collected. The intensities of two standard reflections, which were monitored after each 50 intensity scans, decreased by approximately 10% over the period of data collection. No corrections for crystal decomposition were applied. Of the 4480 reflections collected, 2026 with $I > 3\sigma(I)$ were used for the structure analysis;

$R_{\text{merg}} = 0.0224$. The structure was solved by direct methods and refined by full-matrix least squares [8]. The H atoms from the methyl groups were located from a difference-Fourier synthesis and refined with the constraint that $d(\text{C-H}) = 1.08 \text{ \AA}$. All other H-atoms were included in geometrically calculated positions. Neutral atom scattering factors were utilized and were corrected for real and imaginary components [9]. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. An absorption correction following the DIFABS [10] procedure was applied; minimum and maximum absorption corrections were 0.878 and 1.179, respectively. The final R and R_w values were 0.0495 and 0.0516 for the observed reflections. For the last cycle of the refinement the maximal value of the Δ/σ ratio was 0.16 and the final difference map showed a general background within $\pm 0.38 \text{ e \AA}^3$. The final atom parameters are given in Table 1.

Results and discussion

The addition of metallic aluminum turnings to the mixture of TiCl_4 and diethyl *o*-phthalate in CH_2Cl_2 give a brown air-sensitive crystalline compound formulated as I and the white aluminum compound II.



Compound I was shown by X-ray diffraction studies to have a dimeric structure. The overall view of the $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_4\{\text{o-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2]$ molecule and the numbering scheme are shown in Fig. 1. The packing of the crystal is shown in Fig. 2. Principal bond distances and angles are given in Table 2. The titanium atoms surrounded by two bridging chlorine atoms and by two terminal chlorine atoms and two carbonyl oxygen atoms of diethyl *o*-phthalate molecules form a slightly distorted edge-sharing di-octahedron. The Cl(3) atom is situated *trans* to the O(1) atom while O(1) is *cis* to bridging chlorine atoms [11*]. The $\text{Ti}-\text{Cl}_{\text{bridge}}$ bond lengths are 2.430(3) and 2.502(3) and the $\text{Ti} \cdots \text{Ti}$ distance is 3.629(4) Å. These values are similar to those reported for $[\text{Ti}_2(\mu\text{-Cl})_2(\pi\text{-C}_{10}\text{H}_8)(\pi\text{-C}_5\text{H}_5)]$ [12]. The $\text{Ti}-\text{Cl}_{\text{bridge}}$ bond lengths are also similar to those in $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_6(\text{L})_2]$ [3] [2.509(2) Å] where $\text{L} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{Et}$. The terminal $[\text{Ti}-\text{Cl}(2)$ and $\text{Ti}-\text{Cl}(3)]$ distances [2.343(3) and 2.308(3) Å] are longer than the $\text{Ti}-\text{Cl}_{\text{terminal}}$ distances [2.234(2), 2.233(2), 2.255(2) Å] found in $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_6(\text{L})_2]$ [3]. The observed difference approximately matches the difference between the Ti^{3+} and Ti^{4+} ionic radii of 0.76 and 0.68 Å [13], respectively. The diethyl *o*-phthalate molecules are coordinated to the titanium atoms via the carbonyl oxygen atoms. The chelate ligands and titanium atoms form a seven-membered ring. The benzene ring is planar and almost coplanar with the plane formed by the C(12), C(10), C(9) and C(11) atoms. The benzene ring forms angles of 36.9(5) and 41.1(5)° with the planes of the ester groups [C(9), C(11), O(1), O(3)] and [C(10), C(12), O(2), O(4)], respectively. Structural data for the coordinated diethyl *o*-phthalate molecules are, for example, similar to those

* Reference number with asterisk indicates a note in the list of references.

Table 1

Final atom parameters for the di- μ -chloro-tetrachlorobis(diethyl *o*-phthalate)dittitanium(III) tetra(dichloromethane) crystal

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	0.51941(11)	0.38655(12)	0.39772(13)	0.0196(7)	0.0393(8)	0.0551(10)	-0.0070(7)	-0.0072(6)	-0.0041(6)
Cl(1)	0.37685(16)	0.57997(17)	0.43792(18)	0.0292(10)	0.0467(12)	0.0608(14)	-0.0130(10)	-0.0150(9)	0.0039(8)
Cl(2)	0.43512(18)	0.36878(20)	0.23025(20)	0.0391(12)	0.0747(15)	0.0653(15)	-0.0228(12)	-0.0155(11)	-0.0045(10)
Cl(3)	0.38465(19)	0.24467(19)	0.54773(21)	0.0444(12)	0.0546(14)	0.0743(16)	0.0043(11)	-0.0129(11)	-0.0193(10)
Cl(4)	0.76378(29)	0.02491(30)	-0.36251(32)	0.0944(22)	0.1195(26)	0.1318(29)	-0.0270(22)	-0.0203(20)	0.0011(18)
Cl(5)	0.50942(29)	-0.00535(30)	-0.17212(31)	0.0911(21)	0.1217(26)	0.1225(27)	-0.0378(21)	-0.0271(19)	0.0079(18)
Cl(6)	0.84704(29)	0.34208(34)	0.00920(28)	0.0912(21)	0.1797(34)	0.0816(22)	-0.0275(21)	-0.0112(17)	-0.0303(21)
Cl(7)	0.72605(43)	0.22022(42)	-0.12285(44)	0.1832(41)	0.1750(41)	0.1999(45)	-0.0843(35)	-0.0500(35)	-0.0410(32)
Ox(1)	0.65313(43)	0.50344(43)	0.26857(46)	0.0200(28)	0.0479(31)	0.0624(37)	-0.0032(26)	-0.0047(25)	-0.0074(22)
Ox(2)	0.68004(44)	0.25219(42)	0.34883(49)	0.0237(31)	0.0425(32)	0.0803(41)	-0.0171(28)	-0.0113(27)	-0.0004(23)
Ox(3)	0.80969(46)	0.62265(48)	0.14335(51)	0.0388(31)	0.0562(36)	0.0685(40)	0.0119(32)	-0.0139(28)	-0.0130(27)
Ox(4)	0.87078(44)	0.13379(46)	0.29259(52)	0.0306(29)	0.0440(34)	0.0945(46)	-0.0241(32)	-0.0074(28)	0.0024(26)
C(1)	0.7100(9)	0.6967(9)	0.0765(10)	0.0567(59)	0.0682(66)	0.1079(85)	0.0353(63)	-0.0315(62)	-0.0034(54)
C(2)	0.7867(13)	0.7751(16)	-0.0408(13)	0.1111(11)	0.149(14)	0.114(12)	0.061(11)	-0.0328(87)	-0.0032(96)
C(3)	0.7963(8)	0.0352(8)	0.2800(10)	0.0449(51)	0.0502(55)	0.1185(85)	-0.0350(56)	-0.0108(57)	-0.0098(43)
C(4)	0.8973(12)	-0.0639(11)	0.2309(16)	0.0820(80)	0.0694(80)	0.207(16)	-0.0755(95)	0.0112(97)	-0.0127(64)
C(5)	0.9738(7)	0.5317(8)	0.3020(8)	0.0303(45)	0.0586(56)	0.0581(55)	-0.0132(43)	-0.0079(40)	-0.0124(39)

C(6)	1.0764(8)	0.4748(9)	0.3545(8)	0.0311(48)	0.0814(69)	0.0742(64)	-0.0214(54)	-0.0125(45)	-0.0163(45)
C(7)	1.0897(8)	0.3471(9)	0.3987(8)	0.0300(48)	0.0844(72)	0.0722(65)	-0.0172(55)	-0.0177(43)	-0.0020(46)
C(8)	0.9988(7)	0.2721(8)	0.3870(8)	0.0322(46)	0.0532(55)	0.0722(62)	-0.0096(45)	-0.0174(43)	0.0027(39)
C(9)	0.8786(6)	0.4596(7)	0.2940(7)	0.0205(40)	0.0510(52)	0.0444(49)	-0.0055(39)	-0.0061(35)	-0.0037(35)
C(10)	0.8932(7)	0.3275(7)	0.3363(7)	0.0215(41)	0.0484(51)	0.0569(53)	-0.0133(41)	-0.0083(37)	0.0021(34)
C(11)	0.7701(7)	0.5282(7)	0.2372(7)	0.0402(51)	0.0370(47)	0.0460(52)	-0.0111(40)	-0.0040(40)	-0.0037(37)
C(12)	0.8015(8)	0.2372(7)	0.3263(7)	0.0327(49)	0.0367(49)	0.0529(53)	-0.0055(39)	-0.0092(38)	-0.0010(37)
C(13)	0.5979(10)	-0.0180(12)	-0.3254(11)	0.0920(81)	0.1088(98)	0.0991(89)	-0.0330(73)	0.0375(70)	0.0119(66)
C(14)	0.7050(10)	0.3384(12)	-0.0410(11)	0.0734(76)	0.128(11)	0.0939(88)	-0.0308(82)	-0.0004(68)	0.0293(66)
Atom	x	y	z	U_{iso}	Atom	x	y	z	U_{iso}
H(2)	0.841(11)	0.695(8)	-0.082(11)	0.159(58)	H(4)	0.947(8)	-0.019(7)	0.136(3)	0.095(35)
H(21)	0.857(11)	0.839(8)	-0.044(13)	0.68(11)	H(41)	0.860(10)	-0.150(6)	0.227(7)	0.168(48)
H(22)	0.719(3)	0.825(11)	-0.097(7)	0.55(11)	H(42)	0.967(9)	-0.086(10)	0.289(8)	0.32(11)
H(1)	0.641	0.757	0.136	0.106(56)	H(3)	0.735	0.075	0.215	0.086(29)
H(11)	0.655	0.633	0.053	0.094(31)	H(31)	0.733	-0.004	0.371	0.079(27)
H(5)	0.967	0.633	0.267	0.073(25)	H(7)	1.170	0.304	0.442	0.068(23)
H(6)	1.148	0.533	0.361	0.114(33)	H(8)	1.011	0.170	0.418	0.064(23)
H(13)	0.602	-0.115	-0.336	0.187(58)	H(14)	0.686	0.428	-0.102	0.196(62)
H(23)	0.546	0.044	-0.391	0.135(42)	H(24)	0.621	0.323	0.041	0.142(43)

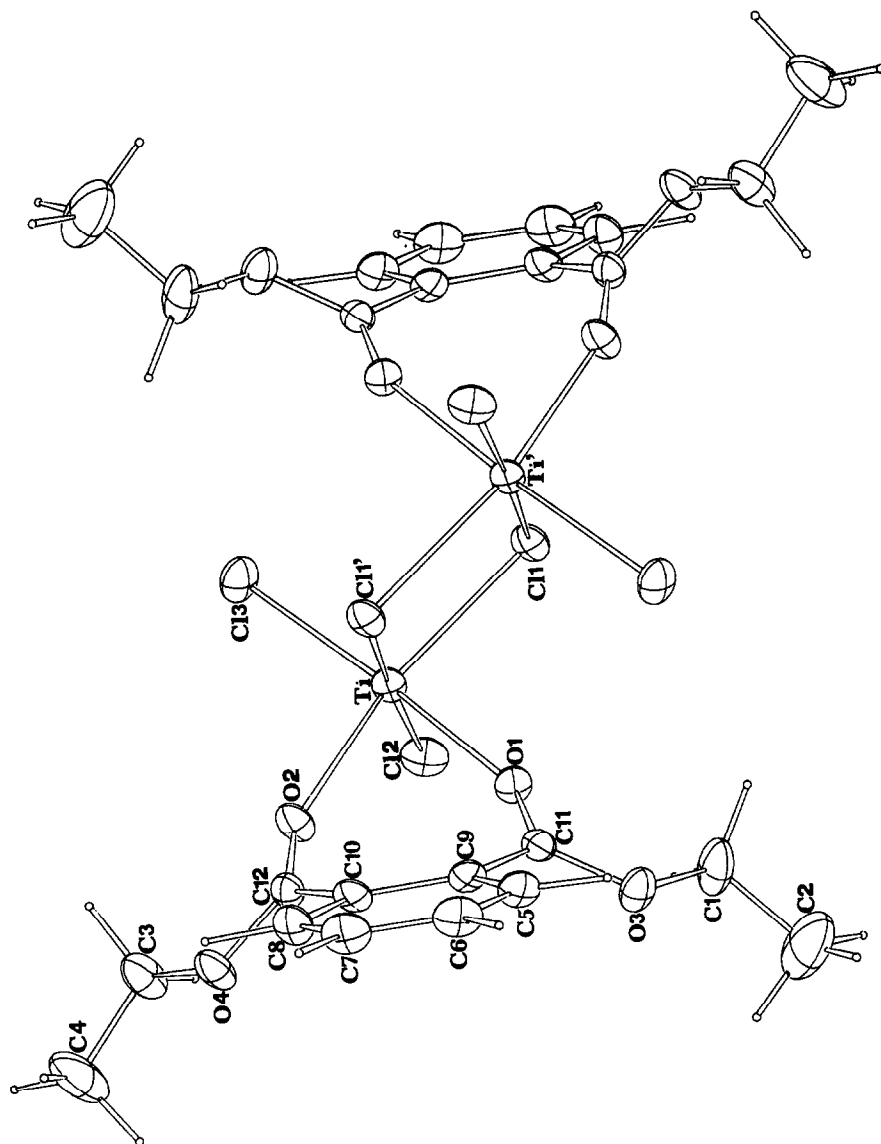


Fig. 1. View of $[\text{Ti}_2(\mu\text{-Cl})\text{Cl}_4(\sigma\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2)_2]$ molecule.

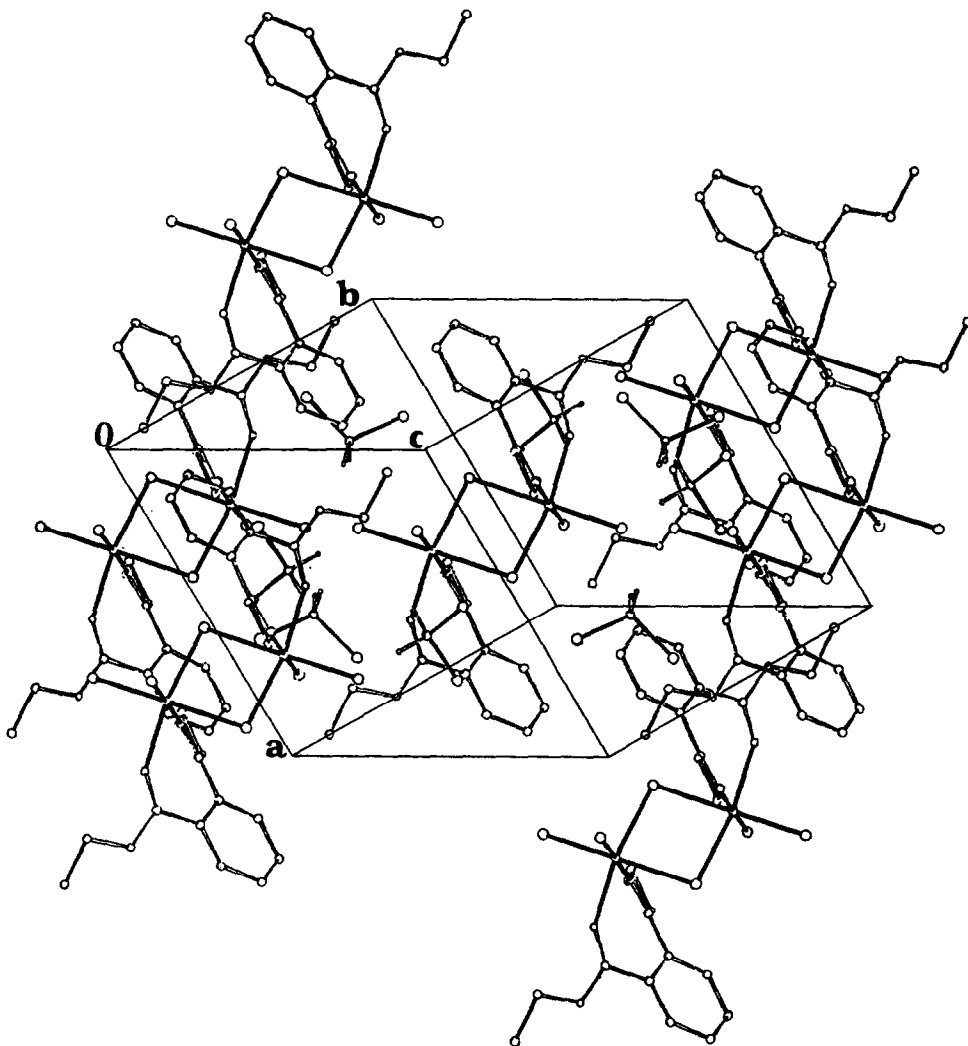


Fig. 2. View of the crystal packing of $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_4\{\text{C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2]\cdot 4\text{CH}_2\text{Cl}_2$. (The H-atoms of complex molecules are omitted for clarity).

found in $[\text{o-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\text{TiCl}_4]$ [6]. The Ti–O(1) distance of 2.054(5) Å [which is *trans* to Cl(3)] is slightly shorter than the Ti–O(2) distance of 2.081(5) Å [which is *trans* to Cl(1)]. In the $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_4\{\text{o-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2]$ molecule short intramolecular contacts between chlorine atoms and the carbon atoms of the phenyl groups occur. The contacts between Cl(1) ... C(10^{1-x,1-y,1-z}) and Cl(1) ... C(9^{1-x,1-y,1-z}) are 3.402(8) and 3.395(7) Å and are probably responsible for arrangement of the molecules in the solid state (see Fig. 2). A similar type of C ... Cl interaction was observed earlier, for example in $[\text{Ti}_2\{\mu\text{-}m\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2\text{Cl}_8]$ [4].

Magnetic susceptibilities of $[\text{Ti}_2\{\mu\text{-Cl}\}_2\text{Cl}_4\{\text{o-C}_6\text{H}_4(\text{CO}_2\text{Et})_2\}_2]\cdot 4\text{CH}_2\text{Cl}_2$ were determined between 4.2 and 293 K. The temperature dependence of molecular susceptibility is typical for an antiferromagnetic $d^1\text{-}d^1$ coupling, with μ_{eff} per

Table 2

Principal interatomic distances (Å), bond angles (°), and torsion angles (°) for $[\text{Ti}_2(\mu\text{-Cl})_2\text{Cl}_4\{\text{C}_6\text{H}_4(\text{COOEt})_2\}_2]\cdot 4\text{CH}_2\text{Cl}_2^a$

Ti...Ti	3.629(4)	Ti-Cl(1')	2.502(3)
Ti-Cl(1)	2.430(3)	Ti-Cl(2)	2.343(3)
Ti-Cl(3)	2.308(3)	Ti-O(1)	2.054(5)
Ti-O(2)	2.081(5)		
O(1)-C(11)	1.228(9)	O(2)-C(12)	1.217(9)
O(3)-C(11)	1.311(9)	O(4)-C(12)	1.307(9)
O(3)-C(1)	1.486(11)	O(4)-C(3)	1.470(10)
C(1)-C(2)	1.482(17)	C(3)-C(4)	1.469(15)
C(11)-C(9)	1.479(10)	C(12)-C(10)	1.515(10)
C(9)-C(5)	1.393(10)	C(10)-C(8)	1.381(10)
C(5)-C(6)	1.368(11)	C(8)-C(7)	1.395(11)
C(10)-C(9)	1.402(10)	C(6)-C(7)	1.360(13)
Cl(1)-Ti-Cl(1')	85.3(1)	Cl(1)-Ti-Cl(2)	94.0(1)
Cl(1)-Ti-Cl(3)	97.4(8)	Cl(1)-Ti-O(1)	86.3(2)
Cl(1)-Ti-O(2)	165.3(2)	Cl(1')-Ti-Cl(2)	174.7(1)
Cl(1')-Ti-Cl(3)	90.7(2)	Cl(1')-Ti-O(1)	86.5(2)
Cl(1')-Ti-O(2)	87.7(2)	Cl(2)-Ti-Cl(3)	94.6(1)
Cl(2)-Ti-O(1)	88.2(2)	Cl(2)-Ti-O(2)	91.8(2)
Cl(3)-Ti-O(1)	175.1(2)	Cl(3)-Ti-O(2)	95.6(2)
O(1)-Ti-O(2)	80.3(3)	Ti-Cl(1)-Ti'	94.7(1)
Ti-O(1)-C(11)	143.4(5)	Ti-O(2)-C(12)	141.1(5)
Ti-O(2)-C(12)-C(10)	5.0(19)	Ti-O(2)-C(12)-O(4)	-177.3(18)
C(12)-O(4)-C(3)-C(4)	175.1(16)	C(11)-O(3)-C(1)-C(2)	-167.1(19)
Ti-O(1)-C(11)-O(3)	-176.9(20)	Ti-O(1)-C(11)-C(9)	4.1(20)

^a Atoms marked with a prime are related to those at x, y, z by a centre of symmetry at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

titanium atom 0.43 and 1.43 B.M. at 4.2 and 293 K, respectively. The spin-spin interaction model based on the exchange Hamiltonian $-2S_1S_2$ where $S_1 = S_2 = 1/2$ was used. The best fit was obtained for $J = -42 \text{ cm}^{-1}$ and $g = 2.27$ (paramagnetic impurity 2.5%). For the solid compound I ESR spectra give the g parameters: $g_1 = 1.94$, $g_2 = 1.98$, $g_3 = 1.99$. The spin concentration of the investigated compound is only about 1% of total Ti^{3+} . Therefore 99% of Ti^{3+} is ESR-silent. The ESR spectra at 77 and 293 K are almost identical except for a fivefold increase in intensity (Curie law dependence) at reduced temperature. Therefore we conclude that the ESR silence of Ti^{3+} ions in I is not due to rapid spin lattice relaxations; thus the Cl-bridged Ti^{3+} ions are expected to interact by superexchange which would result in antiferromagnetism [14,15]. This observation could be of great importance in the explanation of the structure of the active metal centre because the real catalyst has 80% of Ti^{3+} ESR-silent [16].

The IR spectrum in Nujol shows the expected bands due to coordinated diethyl *o*-phthalate molecules ($\nu(\text{CO})$ at 1675 (vs) and 1636 (s) cm^{-1}) and at 320 (sh) and 364 (vs) cm^{-1} attributed to $\nu(\text{Ti}-\text{Cl})$. The ^1H NMR spectra (297 K, CD_2Cl_2) shows broad signals at δ 0.7, 3.8 and 6.9 ppm (ratio 6:4:4) which can be assigned to CH_3 , CH_2 and phenyl ring hydrogens, respectively. The structural type of the title compound has been hitherto unknown in Ti^{III} chemistry, because titanium dimers obtained by other procedures usually contain cyclopentadienyl ligands [17-19].

During preparation of the title compound a white air-sensitive crystalline compound II is formed. The IR spectra for the aluminium compound show the stretching $\nu(\text{Al}-\text{Cl})$ mode at 375 (vs), 430 (s), 480(s) cm^{-1} , and a $\nu(\text{CO})$ at 1665 (s), 1635 (vs) cm^{-1} . In the ^1H NMR spectra recorded in CD_2Cl_2 solution signals at δ 1.6, 4.8 and 8.0 ppm (ratio 6 : 4 : 4) are attributed to CH_3 , CH_2 and the phenyl ring, respectively. Further work is now in progress to elucidate the structure and properties of the aluminum compound.

Supplementary material available: Tables of observed and calculated structure factors for compound I (12 pages) are available from the authors.

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References and notes

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