Titanium Oxo Carboxylate Compounds. Crystal and Molecular Structures of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[Ti_3Cl_3O_2(O_2CEt)_5]$ and an Unusual Quantitative Conversion of a Ti_2O to a Ti_3O_2 Oxo Derivative†

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Reaction of $TiCl_4$ with alkyl carboxylic acids RCO_2H (R = Me, Et or Bu^t) using a 1:1 (Ti:acid) molar ratio at 0 °C yielded the dinuclear chloro carboxylates $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R = Et or Bu^t). When a 1:2.5 ratio is used at 25 °C oxygen abstraction occurs to yield $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R = Me, Et or Bu^t). When R = Et another product, $[Ti_2Cl_3O(O_2CEt)_3(EtCO_2H)]$, was also obtained. At 40–70 °C the oxo compounds (R = Et or Bu^t) decompose quantitatively to form the trinuclear species $[Ti_3Cl_3O_2(O_2CR)_5]$, but the compound with R = Me remains unchanged up to 110 °C. The co-ordinated acid in $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ is displaced by tetrahydrofuran (thf) to yield $[\{TiCl_2(O_2CR)(thf)\}_2O]$ (R = Me, Et or Bu^t), and in contrast to the former, these species are stable up to 110 °C. The crystal structures of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[Ti_3Cl_3O_2(O_2CEt)_5]$ have been determined, and show $[Ti(\mu\text{-}O)(\mu\text{-}O_2CR)_2Ti]$ and $[Ti_3(\mu\text{-}O)(\mu_3\text{-}O)]$ cores respectively. The comparative reactivity of alkyl and aryl acids towards $TiCl_4$ is discussed.

Compounds containing metal–oxo–carboxylate fragments exhibit a wide range of structural features and diverse chemical reactions, and they are attracting attention as versatile intermediates.[1–3] For the early transition metals various oxo–carboxylate derivatives containing the cyclopentadienyl (cp) group are known,[4,5] but in an attempt to expand the chemistry of oxo compounds we have chosen species which do not contain the cp group. Thus for titanium(IV) in particular various workers have found that $TiCl_4$ reacts with both aryl and alkyl carboxylic acids at 25–50 °C to yield the trichloro carboxylates $[TiCl_3(O_2CR)]$.[6–9] At higher temperatures (> 100 °C) using molar ratios of $TiCl_4$: acid beyond 1:1, and up to 1:2.5, the reactions with the aryl acids afford polynuclear oxo species such as $[Ti_4Cl_6O_2(O_2CR)_6]$ (R = Ph)[10] and $[Ti_3Cl_3O_2(O_2CR)_5]$ (R = $p\text{-}MeC_6H_4$, *etc.*).[11] In contrast at intermediate temperatures (≈ 50–70 °C) the alkyl (but not the aryl) acids (R = Me or Bu^t) with a 1:2.5 mol ratio afford high yields of dinuclear oxo compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ which contain a $[Ti(\mu\text{-}O)(\mu\text{-}O_2CR)_2Ti]$ core.[12] We have been able to isolate the two closely related aryl compounds $[\{TiCl_2(O_2CPh)L\}_2O]$ (L = EtO_2CMe or tetrahydrofuran), but these have originated from partial hydrolysis of $[TiCl_3(O_2CPh)]$ using the respective ligand as solvent.[13] Additionally, in a preliminary study, we have noted another possible link between the alkyl and aryl acids, in that the dinuclear compound $[\{TiCl_2(\mu\text{-}O_2CBu^t)(Bu^tCO_2H)\}_2O]$ decomposed thermally to another oxo species which was not identified completely, but was tentatively suggested to be of the type $[Ti_3Cl_3O_2(O_2CBu^t)_5]$.[12] In order to clarify the precise nature of the overall reactions occurring between $TiCl_4$ and the alkyl acids we have examined in more detail the series RCO_2H (R = Me, Et or Bu^t), with particular reference to the initial reaction, and the thermal stability of the products. This paper reports the results of this study.

Results and Discussion

Reaction of $TiCl_4$ with the alkyl acids RCO_2H (R = Me, Et or Bu^t) has been studied under various conditions. The use of a 1:1 molar ratio of $TiCl_4$:alkyl acid in light petroleum (b.p. 60–80 °C) at 0 °C leads to the evolution of one mole of hydrogen chloride and formation of the yellow air-sensitive dinuclear species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ **1** (R = Et or Bu^t). The IR and ^1H NMR spectra of **1** show close similarities with the three previously reported compounds of this type for R = $p\text{-}ClC_6H_4$, $p\text{-}FC_6H_4$ or CH=CHMe,[6] indicating that they all possess closely related structures with an acid molecule co-ordinated to one of the two titanium atoms, which are in turn linked by a bridging carboxylate and two chlorine atoms. Warming these compounds to 50 °C leads to the loss of a second mole of HCl and formation of the trichlorocarboxylates $[TiCl_3(O_2CR)]$ **2** (R = Et or Bu^t) (see Scheme 1).

A major change in the reaction occurs when a 1:2.5 (Ti:acid) molar ratio is used, since even at 25 °C pale yellow or colourless air-sensitive precipitates are obtained. We have previously identified two of the products as being the dinuclear oxo species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R = Me **3a** or Bu^t **3b**),[12] and we have now shown that the propanoate analogue (R = Et **3c**) has a similar composition. All the reactions proceed in high yield by an oxo-abstraction process with the concomitant formation of HCl and the acid chloride, indicating that the acid not only provides a carboxylate group but also splits cleanly into three fragments *viz.* RCO, O and H, with the oxygen atom forming the metal-oxo fragment [equation (1); R = Me, Et or Bu^t]·

$$2TiCl_4 + 5RCO_2H \xrightarrow{25\,^{\circ}C} [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 2RCOCl + 3HCl \quad (1)$$

Differences exist between these oxo derivatives in that the propanoate yields two products. When the reaction is carried out in carbon tetrachloride the major product **3c** precipitates in ≈ 70% yield over a period of 4–5 h. A minor product

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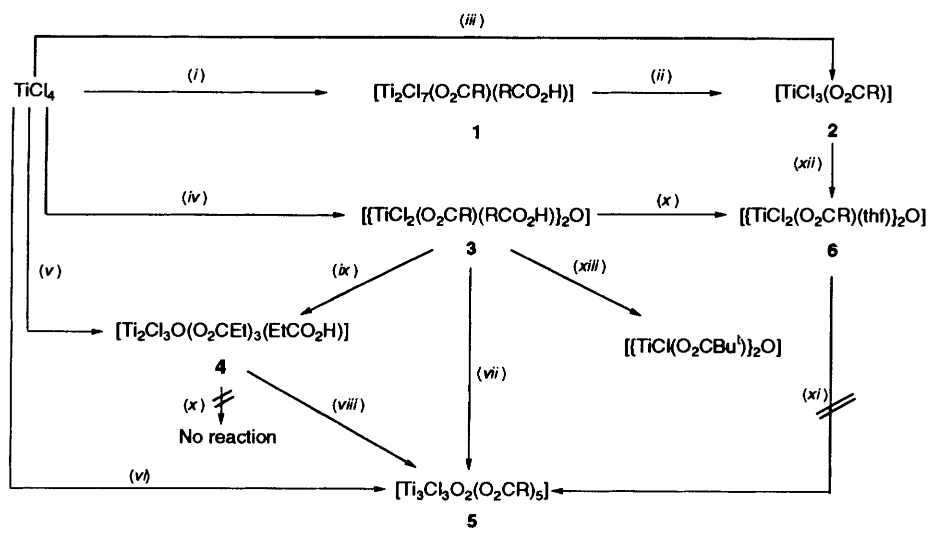
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 R = Me, Et, Bu^t (see text). (*i*) 1 : 1 (Ti : acid) mole ratio, ratio only quoted hereafter, 0–25 °C; (*ii*) warm to 50 °C; (*iii*) 1 : 1 at 50 °C; (*iv*) 1 : 2.5 at 25 °C; (*v*) 1 : 2.5 at 25 °C, minor product; (*vi*) 1 : 2.5 at 80 °C; (*vii*) heat to 70 °C, 0.5 h; (*viii*) heat to 70 °C, 0.5 h; (*ix*) stir 25 °C, 4 d; (*x*) 2 moles thf, 25 °C; (*xi*) no reaction at 110 °C, 12 h; (*xii*) 1 mole H_2O added to 2 moles of **2** in thf solution, 25 °C; (*xiii*) 1 : 2.5 at 120 °C, same product obtained using $(Bu^tCO_2)_2O$

$[Ti_2Cl_3O(O_2CEt)_3(EtCO_2H)]$ **4** (≈ 15%) remains in solution and since this is formed later in the reaction it probably arises by the loss of a further mole of HCl from **3c**. When the reaction is carried out in hexane a similar proportion of each product occurs early in the reaction, but over 4 d the quantity of the minor product steadily increases, and the final precipitate consists entirely of this material. The crystal structure of the major product **3c** confirms that it is the oxo derivative $[Ti_2Cl_4(\mu\text{-}O)(\mu\text{-}O_2CEt)_2(EtCO_2H)_2]$. We have been unable to obtain crystals of compound **4** suitable for a crystallographic study, but the spectroscopic properties (IR, NMR; see Experimental section) of the two products indicate structural similarities. However the two solids show significant differences in that the co-ordinated acid molecules in the major, but not the minor, product can be displaced by tetrahydrofuran (thf) (see below), and the major product is readily soluble in $CHCl_3$, CH_2Cl_2 and $C_{65}Me$, while the minor product is only slightly soluble. An earlier report has also noted that two solids are formed in this reaction when a 1 : 2 molar ratio (Ti : acid) is used.[14] It was suggested that the products consisted of two forms (α, β) of the bis-(carboxylate) $[TiCl_2(O_2CEt)_2]$. Since the IR spectra of our major **3c** and minor **4** products correspond with the limited data published previously it would appear that these α- and β-forms are in fact **3c** and **4**.

The crystal structure of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ **3c** is similar to, but more precisely defined than, the trimethylacetate derivative **3b**.[12] It contains the characteristic $[M(\mu\text{-}O)(\mu\text{-}O_2CR)_2M]$ fragment, found for a number of metals,[15] with each titanium atom showing a slightly distorted octahedral co-ordination (Fig. 1). The three non-bridging positions on each metal are occupied by two chlorine atoms, and an acid molecule which is *trans* to the bridging μ-O group, as found in **3b**, and co-ordinated through the carbonyl oxygen atom. The constraints imposed by the two bridging carboxylate ligands cause the Ti–O–Ti angle to be bent (137.6°), but the Ti–Ti separation of 3.340 Å indicates the absence of any significant Ti–Ti bonding. The Ti–Ti distance is however about 0.2 Å less than those typically found in cyclopentadienyl oxo compounds, *e.g.* $[\{Ti(C_5H_4Me)Cl(\mu\text{-}O)\}_4]$ (Ti–O–Ti 157°, Ti–Ti 3.53–3.58 Å), where the metal atoms are linked only by a μ-O bridge.[16] The Ti–μ-O distance is the shortest of the Ti–O bonds which are in the order Ti–O (acid ligand) 2.095 Å > Ti–O (carboxylate anion) 2.061 Å > Ti–μ-O (bridge) 1.794 Å. Although the protonic hydrogen of the co-ordinated acid was not detected from the diffraction data, hydrogen-bonding interactions are indicated between this atom and the adjoining oxygen of the bridging carboxylate group by the short O(21)–O(24) and O(12)–O(14) distances of 2.689(4) and 2.701(4) Å respectively. The sum of the van der Waals radii for oxygen is 3.04 Å.[17] These interactions are also reflected in an increase in the hydrogen-bonded oxygen to titanium distances [*e.g.* Ti(2)–O(21) 2.131(2) compared with Ti(1)–O(11) 1.992(2) Å, where O(21) is the hydrogen-bonded oxygen], and a small decrease in Ti–O(hydrogen-bonded)–C(carboxylate) angles. Selected bond lengths and angles are shown in Table 1.

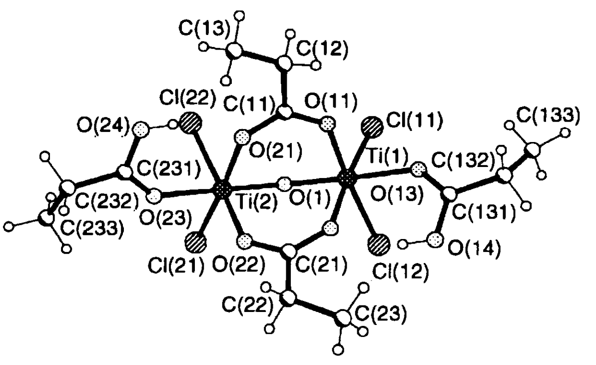


Fig. 1 Molecular structure of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ **3c** showing the crystallographic numbering scheme

When the oxo-propanoate **3c** is refluxed in light petroleum (b.p. 60–80 °C) for 0.5 h some HCl and acid chloride are evolved, and colourless crystalline $[Ti_3Cl_3(\mu\text{-}O)(\mu_3\text{-}O)(\mu\text{-}O_2CEt)_5]$ **5a** remains. The recrystallised product **5a** can be isolated in yields of at least 85% based on Ti. The overall reaction can be represented by equation (2). It is relevant that

$$3[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow 2[Ti_3Cl_3O_2(O_2CEt)_5] + EtCOCl + EtCO_2H + 5HCl \qquad (2)$$

the other propanoate compound **4** can also be converted to **5a** by refluxing in chloroform, suggesting that the conversion of **3c** may be a stepwise process proceeding *via* **4** to the eventual product [equations (3) and (4)]. The carbonyl absorption bands

$$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow [Ti_2Cl_3O(O_2CEt)_3(EtCO_2H)] + HCl \qquad (3)$$

Table 1 Selected bond lengths (Å) and angles (°) for $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ **3c**

Ti(1)–Ti(2)	3.339(2)	Ti(1)–O(1)	1.791(2)
Ti(1)–O(11)	1.992(2)	Ti(1)–O(13)	2.113(2)
Ti(1)–O(12)	2.127(2)	Ti(1)–Cl(11)	2.2370(13)
Ti(1)–Cl(12)	2.2754(11)	Ti(2)–O(1)	1.791(2)
Ti(2)–O(22)	1.988(2)	Ti(2)–O(23)	2.078(2)
Ti(2)–O(21)	2.131(2)	Ti(2)–Cl(21)	2.2374(12)
Ti(2)–Cl(22)	2.2814(13)	O(12)–C(21)	1.262(4)
O(13)–C(131)	1.224(4)	O(22)–C(21)	1.261(4)
O(1)–Ti(1)–O(11)	90.61(10)	O(1)–Ti(1)–O(13)	167.67(9)
O(11)–Ti(1)–O(13)	79.96(9)	O(1)–Ti(1)–O(12)	88.86(9)
O(11)–Ti(1)–O(12)	83.65(10)	O(13)–Ti(1)–O(12)	82.26(9)
O(1)–Ti(1)–Cl(11)	98.25(8)	O(11)–Ti(1)–Cl(11)	94.02(8)
O(13)–Ti(1)–Cl(11)	90.38(7)	O(12)–Ti(1)–Cl(11)	172.56(7)
O(1)–Ti(1)–Cl(12)	99.06(8)	O(11)–Ti(1)–Cl(12)	164.46(8)
O(13)–Ti(1)–Cl(12)	88.62(7)	O(12)–Ti(1)–Cl(12)	84.41(7)
Cl(11)–Ti(1)–Cl(12)	96.57(5)	O(1)–Ti(2)–O(22)	90.43(10)
O(1)–Ti(2)–O(23)	168.28(10)	O(22)–Ti(2)–O(23)	80.85(10)
O(1)–Ti(2)–O(21)	88.65(9)	O(22)–Ti(2)–O(21)	82.75(10)
O(23)–Ti(2)–O(21)	82.53(9)	O(1)–Ti(2)–Cl(21)	97.87(8)
O(22)–Ti(2)–Cl(21)	94.45(8)	O(23)–Ti(2)–Cl(21)	90.65(7)
O(21)–Ti(2)–Cl(21)	172.95(7)	O(1)–Ti(2)–Cl(22)	98.87(8)
O(22)–Ti(2)–Cl(22)	163.55(8)	O(23)–Ti(2)–Cl(22)	87.90(8)
O(21)–Ti(2)–Cl(22)	83.93(7)	Cl(21)–Ti(2)–Cl(22)	97.65(5)
Ti(2)–O(1)–Ti(1)	137.61(12)	C(11)–O(11)–Ti(1)	133.5(2)
C(21)–O(12)–Ti(1)	132.6(2)	C(131)–O(13)–Ti(1)	138.6(2)
C(11)–O(21)–Ti(2)	132.2(2)	C(21)–O(22)–Ti(2)	134.2(2)
C(231)–O(23)–Ti(2)	141.5(3)	O(21)–C(11)–O(11)	123.7(3)
O(22)–C(21)–O(12)	123.5(3)	O(13)–C(131)–O(14)	121.6(3)

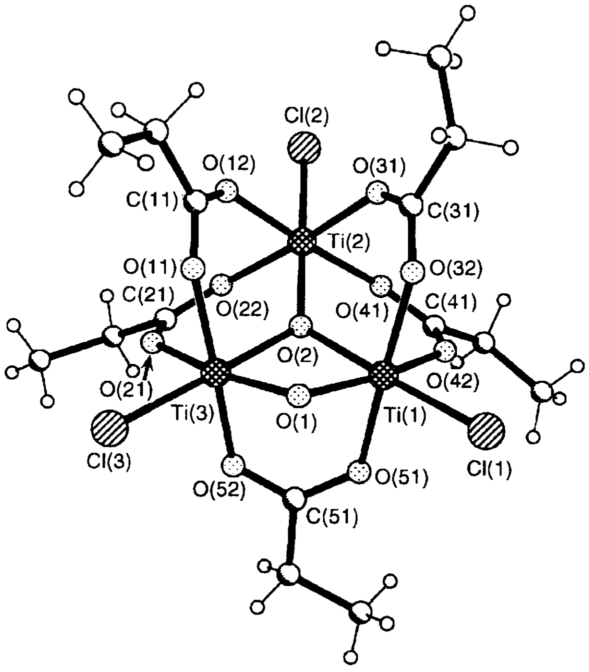


Fig. 2 Molecular structure of $[Ti_3Cl_3O_2(O_2CEt)_5]$ **5a** showing the crystallographic numbering scheme

$$3[Ti_2Cl_3O(O_2CEt)_3(EtCO_2H)] \longrightarrow 2[Ti_3Cl_3O_2(O_2CEt)_5] + EtCOCl + EtCO_2H + 2HCl \quad (4)$$

of the acid chloride and the free carboxylic acid can clearly be seen in the IR of the filtrate liquor, consistent with the above equations. The facile and quantitative conversion of a Ti_2O to a Ti_3O_2 species appears to be unique, but at present the pathway of the reaction remains obscure.

Table 2 Selected bond lengths (Å) and angles (°) for $[Ti_3Cl_3O_2(O_2CEt)_5]$ **5a**

Ti(1)–Ti(3)	2.872(2)	Ti(1)–Cl(1)	2.269(2)
Ti(1)–O(1)	1.827(4)	Ti(1)–O(2)	1.969(4)
Ti(1)–O(32)	1.984(5)	Ti(1)–O(42)	2.020(4)
Ti(1)–O(51)	2.017(4)	Ti(2)–Cl(2)	2.287(2)
Ti(2)–O(2)	1.891(4)	Ti(2)–O(12)	2.013(5)
Ti(2)–O(22)	1.952(5)	Ti(2)–O(31)	1.995(5)
Ti(2)–O(41)	1.931(5)	Ti(3)–Cl(3)	2.271(2)
Ti(3)–O(1)	1.808(4)	Ti(3)–O(2)	1.977(4)
Ti(3)–O(11)	1.982(5)	Ti(3)–O(21)	2.035(4)
Ti(3)–O(52)	1.970(5)	O(11)–C(11)	1.268(8)
O(12)–C(11)	1.264(9)	O(21)–C(21)	1.261(7)
O(22)–C(21)	1.261(8)	O(31)–C(31)	1.249(8)
O(32)–C(31)	1.270(8)	O(41)–C(41)	1.283(8)
O(42)–C(41)	1.249(8)	O(51)–C(51)	1.267(8)
O(52)–C(51)	1.263(8)		
Cl(1)–Ti(1)–O(1)	100.5(1)	Cl(1)–Ti(1)–O(2)	177.6(1)
O(1)–Ti(1)–O(2)	79.5(2)	Cl(1)–Ti(1)–O(32)	89.6(1)
O(1)–Ti(1)–O(32)	97.2(2)	O(2)–Ti(1)–O(32)	88.1(2)
Cl(1)–Ti(1)–O(42)	95.8(1)	O(1)–Ti(1)–O(42)	162.6(2)
O(2)–Ti(1)–O(42)	84.5(2)	O(32)–Ti(1)–O(42)	88.9(2)
Cl(1)–Ti(1)–O(51)	92.8(1)	O(1)–Ti(1)–O(51)	88.3(2)
O(2)–Ti(1)–O(51)	89.6(2)	O(32)–Ti(1)–O(51)	173.5(2)
O(42)–Ti(1)–O(51)	84.9(2)	Cl(2)–Ti(2)–O(2)	177.6(1)
Cl(2)–Ti(2)–O(12)	92.8(1)	O(2)–Ti(2)–O(12)	89.1(2)
Cl(2)–Ti(2)–O(22)	91.5(1)	O(2)–Ti(2)–O(22)	87.1(2)
O(12)–Ti(2)–O(22)	88.1(2)	Cl(2)–Ti(2)–O(31)	92.5(1)
O(2)–Ti(2)–O(31)	89.2(2)	O(12)–Ti(2)–O(31)	82.7(2)
O(22)–Ti(2)–O(31)	170.1(2)	Cl(2)–Ti(2)–O(41)	90.8(1)
O(2)–Ti(2)–O(41)	87.5(2)	O(12)–Ti(2)–O(41)	171.3(2)
O(22)–Ti(2)–O(41)	99.7(2)	O(31)–Ti(2)–O(41)	89.3(2)
Cl(3)–Ti(3)–O(1)	101.6(1)	Cl(3)–Ti(3)–O(2)	178.7(1)
O(1)–Ti(3)–O(2)	79.7(2)	Cl(3)–Ti(3)–O(11)	91.9(2)
O(1)–Ti(3)–O(11)	96.4(2)	O(2)–Ti(3)–O(11)	87.7(2)
Cl(3)–Ti(3)–O(21)	94.1(1)	O(1)–Ti(3)–O(21)	163.9(2)
O(2)–Ti(3)–O(21)	84.7(2)	O(11)–Ti(3)–O(21)	87.0(2)
Cl(3)–Ti(3)–O(52)	91.5(1)	O(1)–Ti(3)–O(52)	90.4(2)
O(2)–Ti(3)–O(52)	88.7(2)	O(11)–Ti(3)–O(52)	171.6(2)
O(21)–Ti(3)–O(52)	85.1(2)	Ti(1)–O(1)–Ti(3)	104.4(2)
Ti(1)–O(2)–Ti(2)	131.0(2)	Ti(1)–O(2)–Ti(3)	93.4(2)
Ti(2)–O(2)–Ti(3)	131.1(2)	Ti(3)–O(11)–C(11)	133.2(4)
Ti(2)–O(12)–C(11)	136.7(4)	O(11)–C(11)–O(12)	123.0(6)
Ti(3)–O(21)–C(21)	137.4(4)	Ti(2)–O(22)–C(21)	132.3(4)
O(21)–C(21)–O(22)	123.1(6)	Ti(2)–O(31)–C(31)	137.6(4)
Ti(1)–O(32)–C(31)	132.4(4)	O(31)–C(31)–O(32)	124.4(6)
Ti(2)–O(41)–C(41)	133.4(4)	Ti(1)–O(42)–C(41)	138.6(4)
O(41)–C(41)–O(42)	122.5(6)	Ti(1)–O(51)–C(51)	127.5(4)
Ti(3)–O(52)–C(51)	128.6(4)	O(51)–C(51)–O(52)	122.4(6)

In contrast the acetate **3a** remains unchanged up to 110 °C, and retains the co-ordinated acid ligands, but conversion of the pivalate **3b** to a similar trinuclear species $[Ti_3Cl_3O_2(O_2CBu^t)_5]$ **5b**, occurs at 40 °C. It is clear therefore that the thermal stability of the oxo species **3** increases as R = Bu^t (**3b**) < Et (**3c**) ≪ Me (**3a**).

The crystal structure of complex **5a** shows a core of three titanium atoms which are linked by μ_3-O and μ-O bridges, and additionally joined by the five propanoate ligands. The metal atoms are in distorted octahedral environments and each is attached to five oxygen and one chlorine atoms (Fig. 2). This is the first crystal structure for a Ti_3–oxo derivative of an alkyl acid, but the average Ti–μ_3-O distance of 1.946 Å is close to that of 1.953 Å found in the analogous *p*-methylbenzoate derivative $[Ti_3Cl_3O_2(O_2CC_6H_4Me\text{-}p)_5]$,[11] and 1.961 Å in the tetranuclear species $[Ti_4Cl_6(O_2CPh)_6]$.[6] There is a slight inequivalence in the three Ti–μ_3-O distances due to the presence of an additional Ti–μ-O bridge on two of the titanium centres. The angles around the μ_3-O total 355.5° indicating that the Ti_3–μ_3-O core is not quite planar, and the oxygen is raised slightly out of the plane. Selected bond lengths and angles are given in Table 2.

The ^1H NMR spectrum of **5a** shows three quartets at δ 2.62–2.45 and three triplets at δ 1.33–1.11 from the ethyl groups

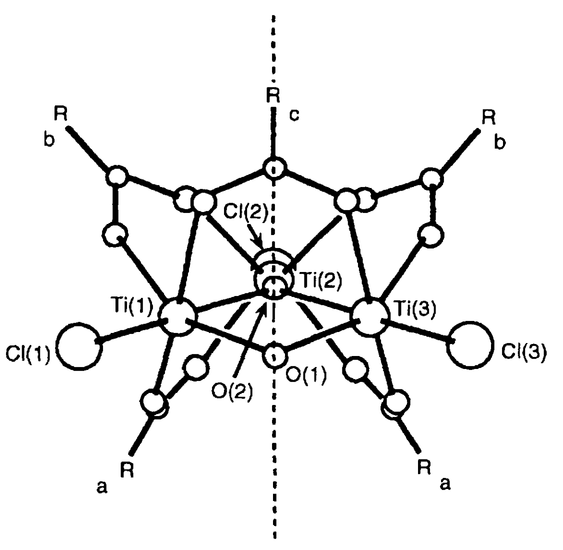


Fig. 3 The approximate mirror place (dashed line) in $[Ti_3Cl_3O_2(O_2CEt)_5]$ **5a** showing the three spatially different types of carboxylate ligand (R = Et) labelled a, b and c giving a ratio of 2:2:1

of the carboxylate ligands. Both of these groups of multiplets exhibit a 2:2:1 intensity pattern due to inequivalence of the five carboxylate groups. No hydroxyl proton resonance is observed as expected. It is now clear that the 2:2:1 arrangement is common to all species of the type $[Ti_3Cl_3O_2(O_2CR)_5]$ (R = alkyl or aryl), and provides a useful aid for the identification of these compounds. Although not perfectly symmetrical the propanoate **5a**, has an approximate mirror plane (Fig. 3), leading to three types (2:2:1) of carboxylate groups. We have also re-examined the product obtained from heating the dinuclear pivalate derivative **3b**,[12] and confirm it to be the trinuclear compound $[Ti_3Cl_3O_2(O_2CBu^t)_5]$.

The reaction of $TiCl_4$ with RCO_2H can also proceed directly to form products of the type **5**. Thus when a 1:2.5 mole ratio of reactants for R = Et, Bu^t are heated at 80 °C in light petroleum (b.p. 60–80 °C) for 1 h the solid products consist only of **5a** and **5b** respectively. In preliminary studies using R = Bu^t we have found that a further variation occurs at even higher temperatures, since under similar conditions except at 120 °C a colourless solid slowly precipitates over 3 h. The air-sensitive solid is very sparingly soluble in a range of organic solvents and an identical solid may also be obtained by heating a mixture of $TiCl_4$ with the anhydride $(Bu^tCO_2)_2O$ under similar conditions. In this case no HCl is evolved, and Bu^tCOCl can be detected in the mother-liquor from its IR spectrum. The elemental analyses of both solids correspond to $[\{TiCl(O_2CBu^t)_2\}_2O]$, consistent with equation (5). When other acids (R = Et or Pr^n) are used

$$2TiCl_4 + 5(Bu^tCO_2)_2O \longrightarrow [\{TiCl(O_2CBu^t)_2\}_2O] + 6Bu^tCOCl \quad (5)$$

only black intractable masses are produced under the above conditions, and we have not therefore pursued these reactions further.

Although the co-ordinated acid molecules in **3** are stabilised by some hydrogen bonding, they are nevertheless easily and quantitatively displaced by thf to yield the corresponding $[\{TiCl_2(O_2CR)(thf)\}_2O]$ (R = Me **6a**, Et **6b** or Bu^t **6c**). The spectroscopic properties of **6** reflect the change in composition, and indicate that a simple ligand displacement has occurred without any change to the central $[M(\mu\text{-}O_2CR)_2(\mu\text{-}O)M]$ core. Thus in the IR and NMR spectra of **6** the ν(OH) of the acid is no longer present, while the bands from the carboxylate groups are very similar to those in **3**, and new absorptions appear from the co-ordinated thf molecules. In contrast the minor product in the propanoate reaction **4** undergoes no reaction when thf is added.

In the absence of the co-ordinated acid it is not surprising that compounds **6** are more thermally robust than those of type **3**, and they remain unchanged even after refluxing in toluene for extended periods. It should also be noted that compounds **6a** and **6c** have been previously prepared, albeit in moderate yields of 55 and 30% respectively, by the controlled hydrolysis of $[TiCl_3(O_2CR)]$ (R = Me or Bu^t) in the presence of thf.[6,13] The cleaner, non-hydrolytic, route reported here raises the yields to 86 (**6a**), 79 (**6b**) and 90% (**6c**).

In summary the above reactions offer simple, high yielding and non-hydrolytic routes to a series of functional titanium oxo compounds as well as indicating some unusual structural transformations. They also provide a more comprehensive understanding of the conditions required and the specific products obtained. Although several of the reactions appear to be general for a range of alkyl and aryl carboxylic acids, we are currently extending the range of acids even more widely to determine whether, and the extent to which, anomalous reactions occur.

Experimental

Experiments were carried out using Schlenk-type apparatus, or in a glove-box, under an atmosphere of dry nitrogen. All solvents were dried and distilled from calcium hydride or sodium diphenylketyl, titanium tetrachloride was of reagent grade and used as received (Aldrich), and the carboxylic acids were recrystallised from CH_2Cl_2 or distilled from P_2O_5 or the acid anhydride prior to use.

Infrared spectra were obtained using either a Perkin-Elmer 1720X FT-IR or 580B spectrophotometer with Nujol mulls between CsI plates. The NMR spectra were run on a Bruker Associates ACF 250 spectrometer using $CDCl_3$ solutions with shifts referenced to $SiMe_4$ (δ 0). Microanalyses were carried out by Butterworth Laboratories, Teddington, or Medac Ltd., Brunel University, while titanium was determined using a Pye-Unicam SP6-250 spectrometer with a titanium(IV) peroxo compound absorbing at 410 nm, and chloride was estimated by the Volhard method. Compounds **3a** and **3b** were prepared as previously described.[12]

Preparations.—$[Ti_2Cl_7(O_2CR)(RCO_2H)]$ **1** (R = Et or Bu^t). A typical procedure is as follows. Titanium tetrachloride (1.9 g, 10 mmol) was added dropwise to a stirred solution of trimethylacetic acid (1 g, 9.8 mmol) in light petroleum (40 cm^3) at 20 °C. The resulting yellow solution was stirred for 2 h, within which time a lemon-yellow precipitate was produced. The solid was isolated from the reaction liquor by filtration, washed with light petroleum (3 × 20 cm^3) and dried by pumping under vacuum for 6 h. Yield 2.2 g (86%) (Found: C, 22.20; H, 3.65; Ti, 17.80. $C_{10}H_{19}Cl_7O_4Ti_2$ requires C, 22.0; H, 3.50; Ti, 17.50%). ^1H NMR ($CDCl_3$) δ 10.30 (1 H, br) and 1.49–1.13 (18 H, m). IR bands (cm^{-1}) 3285 (w, br) [ν(OH)], 1603s [$\nu(C{=}O)_{coord.acid}$], 1500s [$\nu(CO_2)_{asym}$], 1485 (sh), 1461s, 1445(sh), 1410s, 1375s, 1365s [$\nu(CO_2)_{sym}$], 1354m, 1225s, 1180m, 1038m, 872m, 783m, 656m, 615m, 598m, 576m, 560m, 470m, 430s, 410s, 370s [ν(Ti–Cl)], 272m [ν(Ti–Cl–Ti)].

R = Et. Yield 89% (Found: C, 14.80; H, 2.30; Ti, 19.40. $C_6H_{11}Cl_7O_4Ti_2$ requires C, 14.70; H, 2.25; Ti, 19.50%). ^1H NMR ($CDCl_3$) δ 9.81 (1 H, br), 2.88–2.68 (4 H, q) and 1.40–1.27 (6 H, t). IR bands (cm^{-1}) 3276w (br) [ν(OH)], 1601s [$\nu(C{=}O)_{coord.acid}$], 1496 δ [$\nu(CO_2)_{asym}$], 1463s, 1419s, 1374s, 1365 (sh) [$\nu(CO_2)_{sym}$], 1303m, 1180m, 1084m, 1020m, 803m, 673m, 579m, 515w, 432s, 415 (sh), 369m [ν(Ti–Cl)], 273m [ν(Ti–Cl–Ti)].

$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ **3c**. Titanium tetrachloride (1.9 g, 10 mmol) was added dropwise to a stirred solution of propanoic acid (1.9 cm^3, 25 mmol) in carbon tetrachloride (40 cm^3) at room temperature. The resulting yellow solution was stirred for 4 h, within which time a colourless precipitate was produced. The solid was isolated from the reaction liquor by filtration and recrystallised from dichloromethane layered with light petroleum. The colourless crystalline product was filtered off and washed with light petroleum (2 × 20 cm^3) and dried by pumping under vacuum for 5 h. Yield (recrystallised product) 2.31 g (84%) (Found: C, 26.50; H, 4.20; Ti, 17.50. $C_{12}H_{22}Cl_4O_9Ti_2$ requires C, 26.30; H, 4.05; Ti, 17.50%). ^1H NMR ($CDCl_3$) δ 11.3 (1 H, br), 2.65–2.47 (4 H, q) 1.36–1.20 (6 H, t). IR bands (cm^{-1}) 3200m (br) [ν(OH)], 1650s [$\nu(C{=}O)_{coord.acid}$], 1520s [$\nu(CO_2)_{asym}$], 1466s, 1435 (sh), 1405s [$\nu(CO_2)_{sym}$], 1380s, 1305s, 1269s, 1243m, 1082m, 1021m, 811m, 736s (br) [ν(TiOTi)], 659m, 580m, 488m, 430 (sh), 415s, 370s [ν(Ti–Cl)].

[$Ti_2Cl_3O(O_2CEt)_3(EtCO_2H)$] **4**. Titanium tetrachloride (1.9 g, 10 mmol) was added dropwise to a stirred solution of propanoic acid (1.9 cm^3, 25 mmol) in light petroleum (b.p. 60–80 °C) and the resulting yellow solution and precipitate were stirred for 2 d at 25 °C. The solid was isolated from the reaction liquor by filtration, washed with light petroleum (3 × 30 cm^3) and dried by pumping under vacuum for 4 h. Yield 2.11 g (83%) (Found: C, 28.0; H, 4.10; Ti, 18.50. $C_{12}H_{21}Cl_3O_9Ti_2$ requires C, 28.20; H, 4.10; Ti, 18.70%). ^1H NMR ($CDCl_3$) δ 8.45 (1 H, br), 2.70–2.45 (8 H, q) 1.35–1.10 (12 H, t). IR bands (cm^{-1}) 1608s [$\nu(C{=}O)_{coord.acid}$], 1520s [$\nu(CO_2)_{asym}$], 1456s, 1397s [$\nu(CO_2)_{sym}$], 1370s, 1270s, 1083m, 1021w, 903m, 807m, 720w, 700 (sh), 684m [ν(TiOTi)], 557m, 552s, 446s, 400s, 350s, [ν(Ti–Cl)], 330 (sh), 270w.

[$Ti_3Cl_3O_2(O_2CEt)_5$] **5a**. Compound [{$TiCl_2(O_2CEt)(EtCO_2H)$}$_2$O] **3c** (1 g, 1.8 mmol) was suspended in light petroleum (b.p. 60–80 °C, 30 cm^3) and refluxed for 0.5 h to give a colourless precipitate. After cooling, the precipitate was isolated from the reaction liquor by filtration and recrystallised from a dichloromethane solution (30 cm^3) layered with light petroleum (70 cm^3). The colourless crystals were filtered off, washed with cold petroleum (3 × 20 cm^3) and dried by pumping under vacuum for 4 h. Yield (recrystallised product) 0.66 g (85%). (Found: C, 27.50; H, 3.95; Ti, 22.10. $C_{15}H_{25}Cl_3O_{12}Ti_3$ requires C, 27.80; H, 3.90; Ti, 22.20%). ^1H NMR ($CDCl_3$) δ 2.62–2.45 (6 H, q) and 1.33–1.11 (9 H, t). IR bands (cm^{-1}) 1561s [$\nu(CO_2)_{asym}$], 1530s [$\nu(CO_2)_{asym}$], 1466s, 1440s [$\nu(CO_2)_{sym}$], 1407s [$\nu(CO_2)_{sym}$], 1378s, 1280s, 1086m, 1081m, 901w, 812m, 715m, 680m, 645s, 597m, 570m, 450m, 420m, 365m (sh), 340s [ν(Ti–Cl)].

[$Ti_3Cl_3O_2(O_2CBu^t)_5$] **5b**. Compound [{$TiCl_2(O_2CBu^t)(Bu^tCO_2H)$}$_2$O] **3b** (1.5 g, 2.3 mmol) was suspended in light petroleum (b.p. 60–80 °C, 40 cm^3) and heated to 40 °C for 0.5 h within which time the precipitate dissolved. Some solvent was then removed to precipitate the product and the colourless powder was isolated by filtration, washed with cold, light petroleum (3 × 20 cm^3) and dried by pumping under vacuum for 4 h. Yield 1.1 g (92%) (Found: C, 39.60; H, 6.00; Ti, 18.75. $C_{25}H_{45}Cl_3O_{12}Ti_3$ requires C, 38.10; H, 5.70; Ti, 18.25%). ^1H NMR ($CDCl_3$) δ 1.28 (18 H, s), 1.25 (18 H, s) and 1.20 (9 H, s). IR bands (cm^{-1}) 1558s [$\nu(CO_2)_{asym}$], 1522s [$\nu(CO_2)_{asym}$], 1462s, 1427s [$\nu(CO_2)_{sym}$], 1410s [$\nu(CO_2)_{sym}$], 1380s, 1224s, 1034w, 785m, 716m, 665s [ν(TiOTi)], 611s, 558m, 475s, 408m, 375 (sh), 355s [ν(Ti–Cl)].

[{$TiCl_2(O_2CR)(thf)$}$_2$O] **6** (R = Me, Et or Bu^t). All the compounds were prepared using the same method. A typical procedure for R = Bu^t is as follows. Compound [{$TiCl_2(O_2CBu^t)(Bu^tCO_2H)$}$_2$O] **3b** (1 g, 1.5 mmol) was dissolved in toluene (30 cm^3) at room temperature, to which thf (0.24 cm^3, 3 mmol) was added with stirring. After 15 min, light petroleum (70 cm^3) was added to precipitate the product. The solid was isolated by filtration, washed with light petroleum (3 × 25 cm^3) and dried by pumping under vacuum for 4 h. Yield 0.81 g (90%) (Found: C, 35.90; H, 5.65; Ti, 15.90. $C_{18}H_{34}Cl_4O_7Ti_2$ requires C, 36.0; H, 5.70; Ti, 15.95%). ^1H NMR ($CDCl_3$) δ 4.8 (4 H, br), 2.20 (4 H, br), 1.34–1.25 (9 H, m). IR bands (cm^{-1}) 1525s [$\nu(CO_2)_{asym}$], 1480 (sh), 1457s, 1420s [$\nu(CO_2)_{sym}$], 1378s, 1365 (sh), 1226s, 1030w, 1009m [$\nu(COC)_{asym}$], 924m, 858m [$\nu(COC)_{sym}$], 780 (sh), 724s (br) [ν(TiOTi)], 675m, 599m, 550w, 453s, 390s, 350s [ν(Ti–Cl)].

R = Et. Yield 0.68 g (80%) (Found: C, 30.55; H, 4.80; Ti, 17.60. $C_{14}H_{26}Cl_4O_7Ti_2$ requires C, 30.90; H, 4.80; Ti, 17.60%). ^1H NMR ($CDCl_3$) δ 4.90 (4 H, br) 2.63–2.47 (2 H, q), 2.22 (4 H, br) and 1.27–1.15 (3 H, t). IR bands (cm^{-1}) 1531s [$\nu(CO_2)_{asym}$], 1463s, 1430s (sh) [$\nu(CO_2)_{sym}$], 1378s, 1302m, 1082w, 1012m [$\nu(COC)_{asym}$], 958w, 923w, 855w–m, 821m [$\nu(COC)_{sym}$], 725m–s [ν(TiOTi)], 672m, 660m, 565w, 511w, 430 (sh), 420s, 400 (sh), 350s [ν(Ti–Cl)].

R = Me. Yield 0.66 g (86%) (Found: C, 27.50; H, 4.20; Ti, 18.65. $C_{12}H_{22}Cl_4O_7Ti_2$ requires C, 27.95; H, 4.30; Ti, 18.60%). ^1H NMR ($CDCl_3$) δ 4.80 (4 H, br), 2.23 (4 H, br) and 2.23–1.85 (3 H, m). IR bands (cm^{-1}) 1547s [$\nu(CO_2)_{asym}$], 1457m, 1447s [$\nu(CO_2)_{sym}$], 1410 (sh), 1379m, 1253m, 1177w, 1041m, 1010s [$\nu(COC)_{asym}$], 960m, 922m, 857s [$\nu(COC)_{sym}$], 750 (sh), 723s [ν(TiOTi)], 715 (sh), 681m, 633w, 553w, 421s, 380s, 355s [ν(Ti–Cl)].

Reaction of $TiCl_4$ *with* Bu^tCO_2H *and* $(Bu^tCO_2)_2O$ *at Higher Temperatures*.—Both reactions were carried out using the same conditions. Thus $TiCl_4$ (1.1 cm^3, 10 mmol) was added dropwise to a stirred solution of $(Bu^tCO_2)_2O$ (6.5 cm^3, 25 mmol) in light petroleum at 25 °C, and the mixture heated to 120 °C for 3 h over which time a colourless solid precipitated. After filtering the solid was washed with light petroleum (3 × 25 cm^3), and dried by pumping under vacuum for 5 h. Yield 2.62 g (88%). The solids from both reactions showed identical IR spectra with bands at 1590s, 1550s, 1510s, 1413s, 1225s, 720s, 603s, 560s, 461s, 410m and 390m cm^{-1}. The solids were not sufficiently soluble for NMR measurements (Found: C, 41.10; H, 6.20; Cl, 12.00; Ti, 16.00. $C_{20}H_{36}Cl_2O_9Ti_2$ requires C, 40.90; H, 6.20; Cl, 12.10; Ti, 16.30%).

Crystal-structure Determinations.—Crystals of compounds **3c** and **5a** were mounted in sealed Lindemann capillaries under an argon atmosphere.

Crystal data for **3c**. $C_{12}H_{22}Cl_4O_9Ti_2$, M = 547.90, monoclinic, a = 34.128(11), b = 8.291(3), c = 16.503(6) Å, β = 104.61(3), U = 4519(3) $Å^3$ (by least-squares refinement on diffractometer angles for 30 automatically centred reflections), T = 220(2) K, λ = 0.710 73 Å, space group $C2/c$, Z = 8, D_c = 1.611 Mg m^{-3}, $F(000)$ = 2224. Colourless irregular block. Crystal dimensions 0.66 × 0.34 × 0.20 mm, μ(Mo-Kα) = 1.217 mm^{-1}.

Crystal data for **5a**. $C_{15}H_{25}Cl_3O_{12}Ti_3$, M = 647.4, monoclinic, a = 13.193(4), b = 11.780(5), c = 17.384(6) Å, β = 95.67(3)°, U = 2688 $Å^3$ (by least-squares refinement on diffractometer angles for 15 automatically centred reflections) T = 290 K, λ = 0.710 73 Å, space group $P2_1/n$, Z = 4, D_c = 1.60 g cm^{-3}, $F(000)$ = 1312. Colourless air-sensitive block. Crystal dimensions: 0.77 × 0.34 × 0.25 mm, μ(Mo-Kα) = 1.22 mm^{-1}.

Data collection and processing. Data were collected with a Siemans P3R3 four-circle diffractometer, ω–2θ mode. The crystals were held at 220(2) K with the Oxford Cryostream Cooler (version 2.4). Details and processing are as follows. For $C_{12}H_{22}Cl_4O_9Ti_2$: ω scan speed 3–29° min^{-1}, depending upon the intensity of the 2 s pre-scan, backgrounds were measured at each end of the scan for 0.25 of the scan time. 4039 Reflections measured (1.5 ⩽ θ ⩽ 25°, *hkl* ranges 0–40, 0–9, −19 to 19), 3977 unique (R_{int} = 0.0246), analytical absorption correction (max. and min. transmission factors = 0.82, 0.66).

For $C_{15}H_{25}Cl_3O_{12}Ti_3$: ω scan speed 2.5–15° min^{-1}, 5209 reflections measured (1.5 ⩽ θ ⩽ 25°, *hkl* ranges: 0–15; 0–14; −20 to 20), 4743 unique (R_{int} = 0.025), Gaussian absorption correction (max., min. transmission factors = 0.91, 0.66), 2881 reflections with $I \geqslant 2\sigma(I)$, crystal decay 6%, corrected during processing.

Table 3 Atomic coordinates (× 10^4) for **3c**

Atom	x	y	z
Ti(1)	1440(1)	4555(1)	172(1)
Ti(2)	1092(1)	2094(1)	1432(1)
Cl(11)	1136(1)	4257(1)	−1189(1)
Cl(12)	2064(1)	3714(1)	95(1)
Cl(21)	1399(1)	−310(1)	1623(1)
Cl(22)	462(1)	1210(1)	746(1)
O(1)	1266(1)	2731(2)	547(1)
O(11)	980(1)	5772(3)	417(2)
O(12)	1738(1)	5159(3)	1429(1)
O(13)	1609(1)	6933(3)	−51(1)
O(14)	2147(1)	7616(4)	947(2)
O(21)	797(1)	4365(3)	1409(2)
O(22)	1548(1)	3254(3)	2197(1)
O(23)	918(1)	1833(3)	2545(1)
O(24)	435(1)	3531(4)	2618(2)
C(11)	760(1)	5550(4)	916(2)
C(12)	441(1)	6781(5)	907(4)
C(13)	222(3)	6745(15)	1577(6)
C(13A)	75(2)	6200(13)	1157(7)
C(21)	1761(1)	4456(4)	2118(2)
C(22)	2054(1)	5033(5)	2906(2)
C(23)	2345(2)	6306(7)	2822(3)
C(131)	1882(1)	7887(4)	237(2)
C(132)	1920(1)	9484(4)	−138(2)
C(133)	1850(2)	9494(6)	−1060(3)
C(231)	664(1)	2283(5)	2892(2)
C(232)	599(1)	1506(6)	3653(3)
C(233)	719(4)	−274(9)	3713(7)
C(233A)	512(11)	−282(14)	3490(16)

Table 4 Atomic coordinates (× 10^4) for **5a**

Atom	x	y	z
Ti(1)	2776.3(8)	1501.8(9)	5596.4(6)
Ti(2)	4589.4(9)	3493.8(9)	6354.9(7)
Ti(3)	3611.6(9)	1025.3(9)	7151.7(7)
Cl(1)	1833.5(14)	569.2(17)	4632.6(11)
Cl(2)	5679.7(14)	4995.0(15)	6300.5(11)
Cl(3)	3593.8(17)	−410.2(16)	8021.9(13)
O(1)	3086(3)	335(3)	6272(3)
O(2)	3646(3)	2295(3)	6412(2)
O(11)	5062(3)	745(4)	7007(3)
O(12)	5708(3)	2446(4)	6790(3)
C(11)	5808(5)	1395(6)	6921(4)
C(12)	6859(6)	917(8)	7006(6)
C(13)	6974(8)	−317(9)	7197(7)
O(21)	4116(3)	2199(4)	7959(3)
O(22)	4346(3)	3870(3)	7415(3)
C(21)	4220(5)	3262(5)	7995(4)
C(22)	4158(6)	3831(5)	8752(4)
C(23)	4284(7)	3057(7)	9444(4)
O(31)	4950(3)	2868(4)	5351(3)
O(32)	3989(3)	1360(4)	5013(3)
C(31)	4737(5)	2017(6)	4939(4)
C(32)	5401(6)	1731(7)	4320(5)
C(33)	6365(6)	2368(8)	4329(5)
O(41)	3503(4)	4352(3)	5802(3)
O(42)	2537(3)	3069(4)	5143(3)
C(41)	2743(6)	4076(6)	5320(4)
C(42)	2111(6)	5013(6)	4964(5)
C(43)	1205(10)	4657(10)	4455(9)
O(51)	1550(3)	1835(3)	6166(2)
O(52)	2240(3)	1520(3)	7362(3)
C(51)	1483(5)	1756(5)	6886(4)
C(52)	477(5)	1898(6)	7201(4)
C(53)	−412(6)	2112(8)	6610(5)

Structure analysis and refinement. The structures were solved by direct methods using SHELXTL-PLUS. For $C_{12}H_{22}Cl_4O_9Ti_2$: full-matrix least-squares refinement on F^2 for all data using SHELXL 93.[18] Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms (see below for exceptions); H atoms were given isotropic thermal parameters equal to 1.2 (or 1.5 for methyl hydrogens) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached. The carbon atoms C(13) and C(233) were fitted to an isotropic disordered model. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 9.6877P]$ where $P = (F_o + 2F_c^2)/3$. Goodness-of-fit on F^2 was 1.044, $R1$ [for $I > 2\sigma(I)$] = 0.0388, $wR2$ = 0.1103. Data/restraints/parameters 3974/4/251. Largest difference peak and hole 0.774 and −0.451 e Å^{-3}.

For $C_{15}H_{25}Cl_3O_{12}Ti_3$: Full-matrix least-squares refinement on F with non-hydrogen atoms anisotropic and hydrogen atoms given fixed isotropic thermal parameters, $U = 0.08$ Å^2. Hydrogen atoms were inserted at calculated position; methyl groups were treated as rigid CH_3 units, with their initial orientation based on a staggered configuration. The weighting scheme $w = 1/[\sigma^2(F_o) + 0.002F_o^2]$ was shown to be satisfactory by a weight analysis. Final $R = 0.048$, $R' = 0.075$, $S = 0.71$; 313 parameters refined. Largest positive and negative peaks on a final difference Fourier synthesis were ±0.25 e Å^{-3}.

Programs and computers used and sources of scattering factor data are given in ref. 12. Atomic coordinates are given in Tables 3 and 4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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