Synthesis of New Titanium–Oxo Cluster Compounds: X-Ray Structure of the Tetranuclear Oxide $[Ti_4Cl_6(\mu_2\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$

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Titanium–oxo cluster compounds can be obtained in high yields by the action of carboxylic acids on titanium tetrachloride; X-ray structure analysis of the benzoate derivative $[Ti_4Cl_6(\mu_2\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$ reveals the presence of a previously unknown Ti_4O_2 core structure.

Oxo cluster compounds of the early transition elements are of continuing interest due in part to their role in mixed valence systems and as models for heterogeneous catalysts.[1] For titanium most known species are associated with the presence of a $(C_5H_5)Ti$ [or $(C_5Me_5)Ti$] group, *e.g.* $[Ti(C_5Me_5)Br(\mu\text{-}O)]_4\cdot CHCl_3$ which contains a Ti_4O_4 ring.[2,3] A similar titanium oxo unit is found in one of the rarer cluster derivatives which do not contain the C_5H_5 or C_5Me_5 group, namely $Cs_4[Ti(nta)(\mu\text{-}O)]_4\cdot 6H_2O$ (nta = nitrilotriacetate)[4] with other known compounds being typified by $[Ti_4(C_6H_{15}N_3)(\mu\text{-}O)_6]Br\cdot 4H_2O$ with an adamantane-like Ti_4O_6 core,[5] and the hexanuclear $[Ti_6(OBu^n)_8(O_2CMe)_8(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2]$ obtained from a sol–gel process.[6]

We now report an unexpected and facile route to a range of titanium–oxo cluster compounds, together with X-ray data which demonstrate the existence of a new Ti_4O_2 core arrangement. Previous studies have shown that titanium tetrachloride and carboxylic acids react easily and cleanly at

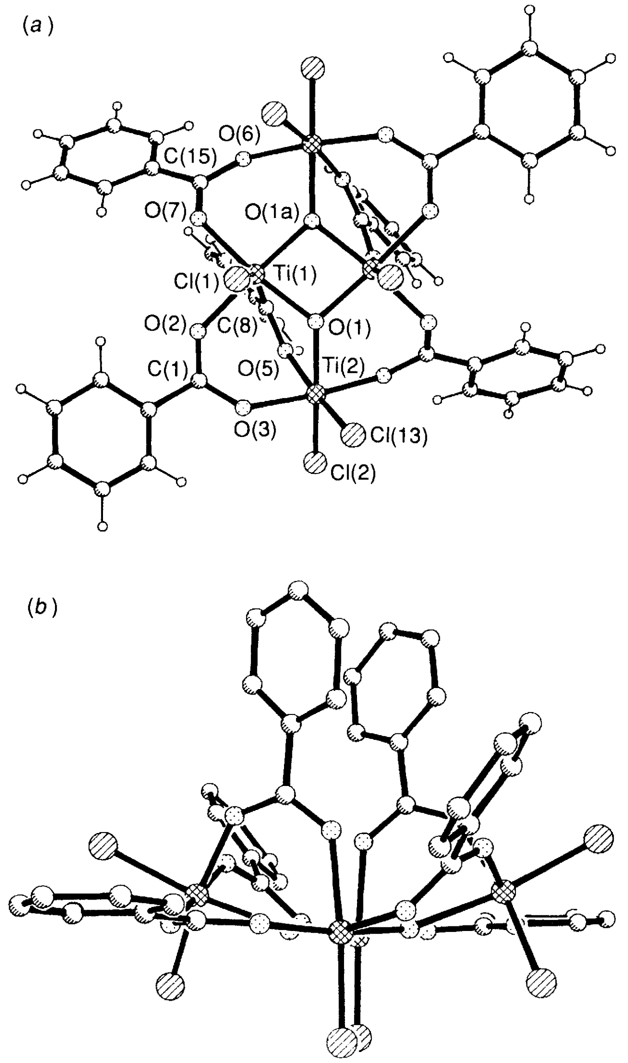

Fig. 1 Molecular structure of $[Ti_4Cl_6(\mu_2\text{-}O_2CC_6H_5)_6(\mu_3\text{-}O)_2]$ **1** (*a*) View perpendicular to the (Ti_4O_2 plane. Selected bond lengths (Å) and angles (°) are: Ti(1)–O(1) 1.898(5), Ti(2)–O(1) 2.065(5), Ti(1)–Cl(1) 2.227(3), Ti(2)–Cl(2) 2.239(3), Ti(2)–Cl(3) 2.218(3), Ti(1)–O(2) 2.013(5), Ti(2)–O(3) 1.926(6), Ti(1)–O(4) 2.075(6), Ti(2)–O(5) 2.021(6); O(1)–Ti(1)–O(1a) 81.1(2), O(5)–Ti(2)–O(1) 82.4(2), Cl(2)–Ti(2)–Cl(3) 97.9(1), O(6)–C(15)–O(7) 121.9(7), O(2)–C(1)–O(3) 122.0(7), O(4)–C(8)–O(5) 124.0(8). (*b*) From the direction of the (Ti_4O_2) plane, showing the different character of the two sides of the molecule. H atoms omitted for clarity.

room temperature, and using a 1 : 1 molar ratio the monocarboxylate derivatives, $[TiCl_3(O_2CR)]$ (R = alkyl, aryl), are obtained.[7,8] While attempting to extend this reaction to obtain the bis-carboxylates $[TiCl_2(O_2CR)_2]$, by using higher temperatures, we have observed that a quite different reaction occurs producing titanium–oxo cluster compounds in remarkably high yield.

When $TiCl_4$ is mixed with a range of acids RCO_2H (R = alkyl, aryl) at room temperature using molar ratios ranging from 1 : 2 to 1 : 4 the monocarboxylate $[TiCl_3(O_2CR)]$ is still the major product with an excess of acid remaining. However, on heating to 100–150 °C, either in light petroleum or even in the absence of solvent, distinct oxo species are obtained as the only isolable products. The course of the reaction is not clear at the moment. While it might be inferred that $[TiCl_3(O_2CR)]$ is a key intermediate, because of the reaction ratios of $TiCl_4 : RCO_2H$ required as outlined below, the monocarboxylate clearly requires the presence of further acid to form the oxo species in the high yields obtained. As an example, when $TiCl_4$ and benzoic acid (1 : 2 molar ratio) are heated in refluxing light petroleum (100–120 °C) HCl is evolved and the oxo species $[Ti_4Cl_6(O_2CPh)_6O_2]$ **1** is obtained in quantitative (99%) yield. We have found that other acids yield compounds of different stoichiometry. Thus, using similar conditions 2-$MeC_6H_4CO_2H$ yields $[Ti_4Cl_5(O_2CC_6H_4Me\text{-}2)_7O_2]$ (99%), 2-(and 3-)$ClC_6H_4CO_2H$ and Bu^tCO_2H yield $[Ti_3Cl_4(O_2CC_6H_4Cl)_4O_2]$ (50%) and $[Ti_2Cl_2(O_2CBu^t)_4O]$ (73%) respectively, while 4-$Bu^tC_6H_4CO_2H$ also gives $[Ti_2Cl_2(O_2CC_6H_4Bu^t\text{-}4)_4O]$ but only in 10% yield after recrystallisation to separate it from other, as yet unidentified, oxo compounds.† All the products are yellow or yellow–orange solids, typical of Ti^{IV} derivatives, and are soluble in halogenated hydrocarbons, moderately soluble in aromatic hydrocarbons, slightly soluble in Et_2O and MeCN, but insoluble in aliphatic hydrocarbons. The slight air reactivity of the species indicates that the Ti–Cl bonds remain as reactive centres and we are currently exploring this reactivity further.

The corresponding acid chloride, RCOCl, is also obtained as a by-product in the reactions. In view of the high yields of the products it is probable therefore that the reactions proceed simply, as shown in eqn. (1) for benzoic acid, with the carboxylate anion providing both the oxo and acyl groups.

$$4TiCl_4 + 8PhCO_2H \rightarrow [Ti_4Cl_6(\mu_2\text{-}O_2CPh)_6(\mu_3\text{-}O)_2] + 8HCl + 2PhCOCl \tag{1}$$

As further confirmation of this stoichiometry, if a slight excess of $TiCl_4$ is used then a small quantity of the known solid adduct $[TiCl_4\cdot PhCOCl]$ can be isolated by sublimation. Clearly some slight variations in the stoichiometry are required for the other oxo species, but overall optimum yields are obtained when a molar ratio near 1 : 2.5 ($TiCl_4 : RCO_2H$) is used, the addition of further acid simply resulting in unreacted acid remaining after heating.

The compound **1** has been characterised by X-ray crystallography and exhibits both oxo and carboxylate bridges. It has a Ti_4O_2 oxo–metal core consisting of four Ti atoms bound by two triply bridging oxo ligands. The existence of the related $[\{Ph_2Sn(O_2CCCl_3)\}_2O]_2$ emphasises that the M_4O_2 unit has particular stability.[9] There are two different metal environ-

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† *Crystal data* for $[C_{42}H_{30}Cl_6O_{14}Ti_4]$ **1**: orthorhombic, space group *Pnna*, a = 13.457(5), b = 19.159(6), c = 19.023(7) Å, M = 1163.0, U = 4905(3) Å^3, Z = 4, D_c = 1.57 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 10.1 cm^{-1}, T = 290 K, R = 0.066 for 2030 unique observed $[I/\sigma(I) \geq 2.0]$ reflections. Crystal character: orange–yellow blocks. Data were collected with a Nicolet-P2$_1$ diffractometer using graphite monochromated Mo-Kα radiation. 4344 Unique reflections were collected. A Gaussian absorption correction was applied (T 0.60–0.84). The heavy atoms were found from a Patterson synthesis and the light atoms from successive Fourier syntheses. Anisotropic refinement was used for all non-H atoms; hydrogen atoms were in fixed postions (U = 0.07 Å^2). 299 Parameters were refined (on F). The maximum difference Fourier peaks were ±0.5 e Å^{-3}. A weighting scheme of the form $W = 1/[\sigma^2(F) + 0.0006F^2]$ was used. Max. shift/error = 0.5. Computing was with SHELXTL on a Data General DG30. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

All the compounds isolated exhibited satisfactory analytical and spectroscopic data. Analytical and selected spectroscopic data as follows. For compound (**1**): Found C, 43.6; H, 2.9; Cl, 18.3; Ti, 15.1. Calc. C, 43.4; H, 2.6; Cl, 18.3; Ti, 16.5%; yellow crystals; IR ν_{max}/cm^{-1} 1590s, 1540s, 1490s, 1170s, 1065m, 1020s, 715s, 650s, 520s, 435m and 350s. For $[Ti_4Cl_5(O_2CC_6H_4CH_3)_7O_2]$: Found C, 49.3; H, 3.6; Cl, 13.3; Ti, 14.2. Calc. C, 49.9; H, 3.7; Cl, 13.2; Ti, 14.2%; IR ν_{max}/cm^{-1} 1600s, 1580m, 1520s, 1160m, 740s, 630s, 500s, 445m and 360s. For $[Ti_3Cl_4(O_2CC_6H_4Cl)_4O_2]$: Found C, 35.4; H, 1.8; Ti, 15.3. Calc. C, 35.8; H, 1.7; Ti, 15.3%; IR ν_{max}/cm^{-1} 1590s, 1570sh, 1420msh, 1160m, 1060m, 740s, 640m, 520s, 450m and 380s cm^{-1}. In spite of repeated attempts using EI and FAB mass spectrometric techniques useful mass spectra could not be obtained for the various compounds reported here.

ments in **1**, such that two of the titanium atoms are each bonded to two terminal chlorine atoms, while the other two titanium atoms are each bonded only to a single terminal chlorine. The overall coordination of all the metal atoms is distorted octahedral. The complex shows a notable feature in that the carboxylate bridges lie principally on one side of the molecule, giving this side a strongly hydrophobic character, while the halogen substituents lie on the other side and remain accessible for further reaction (Fig. 1*b*).

Finally, it it is interesting to note that with the lower alkyl acids RCO_2H (*e.g.* R = Et, Pr^n, CCl_3) both the simple bis-carboxylates, $[Cl_2Ti(O_2CR)_2]$, and the oxo species, $[TiO(O_2CR)_2]$, have been reported as possible products, although neither type has been fully characterised.[8] Further studies on these compounds are now clearly desirable to define these reactions more closely.

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