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A Convenient High-yield Synthesis of Some Titanium(IV) Oxo Cluster Compounds: Crystal Structure of $[Ti_3Cl_3(\mu\text{-}O_2CC_6H_4Me\text{-}p)_5(\mu\text{-}O)(\mu_3\text{-}O)]$

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The reaction of $TiCl_4$ with a series of *para*-substituted benzoic acids ($p\text{-}XC_6H_4CO_2H$; X = Me, Et, F or I) yields the new trinuclear oxo clusters $[Ti_3Cl_3(\mu\text{-}O_2CC_6H_4X\text{-}p)_5(\mu\text{-}O)(\mu_3\text{-}O)]$ in good yield; $p\text{-}Bu^tC_6H_4CO_2H$ gives $[\{[TiCl(O_2CR)_2]_2O\}_n]$ but $p\text{-}MeOC_6H_4CO_2H$ yields only a black intractable tar.

The general properties and useful chemical reactions of oxo derivatives of the early transition metals has made such derivatives the target for many studies.[1] However, as has been emphasised recently, there are relatively few high-yield routes to such compounds.[2] Of the routes which have been established, including the oxidation of organometallic precursors and the addition of an organic group to a metal oxo compound, the most important is still the controlled hydrolysis of suitable metal derivatives.[3a,b] For the Group 4 (Ti, Zr, Hf) elements in particular the overwhelming number of starting materials used to date for the hydrolysis reactions contain a metal–halogen bond(s) and a cyclopentadienyl (C_5H_5 or C_5Me_5) group. Several di-, tri- and tetra-nuclear oxo clusters have been obtained as exemplified by $[\{Ti(C_5H_5)Cl_2\}_2O]$,[4] $[\{Ti(C_5Me_5)Cl\}_3(\mu\text{-}O)_3]$,[2] $[\{Ti(C_5Me_5)Br(\mu\text{-}O)\}]$ [5a] and $[\{Ti(C_5Me_5)\}_4(\mu\text{-}O)_6]$ [5b] respectively. There are a few examples of other titanium compounds which do not contain any cyclopentadienyl group, and these include $[\{TiCl(L)(\mu\text{-}O_2CPh)_2\}_2(\mu\text{-}O)]$ (L = ethyl acetate or tetrahydrofuran),[6a] $[Ti_4(C_6H_{15}N_3)(\mu\text{-}O)_6]Br_4{\cdot}4H_2O$ ($C_6H_{15}N_3$ = 1,4,7-triazacyclononane),[6b] $Cs_4[Ti(nta)(\mu\text{-}O)]_4{\cdot}6H_2O$ (nta = nitrilotriacetate),[6c] $[Ti_6(OBu^n)_8(O_2CMe)_8(\mu\text{-}O)_2(\mu_3\text{-}O)_2]$ [6d] and $[Ti_{16}O_{16}(OEt)_{32}]$.[6e] We present here an alternative route, to a range of titanium oxo cluster compounds, which neither involves hydrolysis reactions nor requires the presence of any stabilising cyclopentadienyl group.

We have recently reported a high-yield synthesis of a tetranuclear oxo cluster $[Ti_4Cl_6(\mu\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$ obtained by heating $TiCl_4$ with benzoic acid to moderate temperatures (100–150 °C).[7] While attempting to extend this reaction using other acids we have found that the reaction is dependent to a surprising extent on peripheral substituents attached to the aryl ring of benzoic acid. Thus a new family of trinuclear oxo derivatives with the general formula $[Ti_3Cl_3(O_2CR)_5O_2]$ **1** are obtained in quantitative, or reasonable, yield from a range of *para*-substituted acids $p\text{-}XC_6H_4CO_2H$ [X = Me **1a** (yield of purified oxo derivative 99%), Et (31%), F (81%) or I (44%)]. The reaction conditions are simple, namely heating $TiCl_4$ (1 mol) with the acid (2–2.5 mol) either in refluxing light petroleum (b.p. 100–120 °C) or in the absence of solvent at temperatures up to 150 °C. After the evolution of HCl the products precipitate as pale yellow or yellow-orange solids typical of titanium(IV) derivatives. All the new compounds gave satisfactory analytical and spectroscopic data† and they are soluble in halogenated and aromatic solvents, but insoluble in aliphatic hydrocarbons.

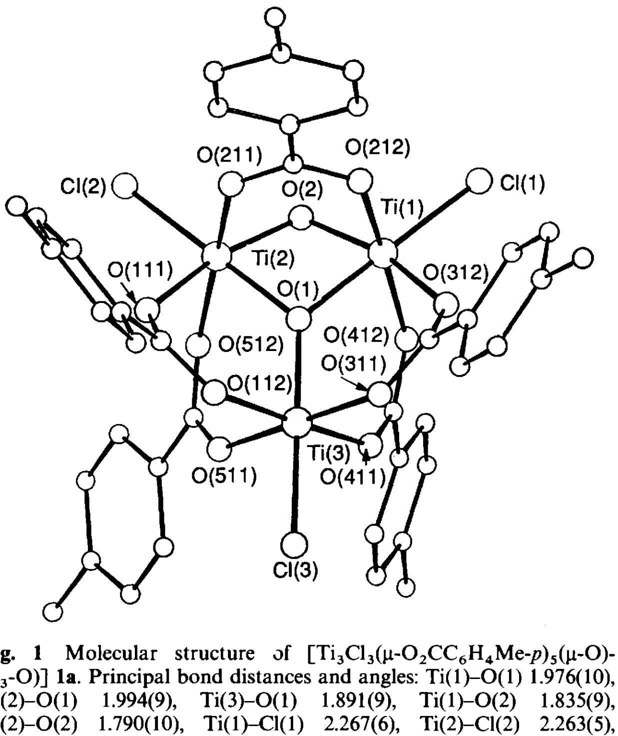

Fig. 1 Molecular structure of $[Ti_3Cl_3(\mu\text{-}O_2CC_6H_4Me\text{-}p)_5(\mu\text{-}O)(\mu_3\text{-}O)]$ **1a**. Principal bond distances and angles: Ti(1)–O(1) 1.976(10), Ti(2)–O(1) 1.994(9), Ti(3)–O(1) 1.891(9), Ti(1)–O(2) 1.835(9), Ti(2)–O(2) 1.790(10), Ti(1)–Cl(1) 2.267(6), Ti(2)–Cl(2) 2.263(5), Ti(3)–Cl(3) 2.261(5), Ti–O(carboxylate) 1.943(9)–2.035(9) Å; Ti(2)–O(1)–Ti(1) 93.4(4), Ti(2)–O(2)–Ti(1) 105.6(5), Ti(3)–O(1)–Ti(2) 130.8(5), Ti(3)–O(1)–Ti(1) 131.6(5), O(1)–Ti(1)–Cl(1) 178.7(3), O(1)–Ti(2)–Cl(2) 178.3(3) and O(1)–Ti(3)–Cl(3) 177.8(3)

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† Typical analytical and spectroscopic data: **1a** (Found: C, 50.1; H, 3.85; Cl, 11.20; Ti, 15.0. Calc. for $C_{40}H_{35}Cl_3O_{12}Ti_3$: C, 50.3; H, 3.70; Cl, 11.15; Ti, 15.0%); major IR bands (Nujol mull) 1610, 1585, 1535, 1510, 1410, 1180, 770, 620, 520, 480, 400 and 360 cm^{-1}; ^1H NMR [220 MHz, $CDCl_3$, reference $SiMe_4$ (δ 0)] δ 8.40 (relative intensity 2), 8.25 (2), 8.0 (1) and overlapping multiplet centred at 7.20 (5) (Ph), overall integrated ratio of two sets of δ 7.20 and 8.0–8.4 is 10:10, δ 2.38(6), 2.30(6) and 2.28(3) (*p*-Me); $[Ti_3Cl_3(O_2CC_6H_4F\text{-}p)_5O_2]$ (Found: C, 42.9; H, 2.10; Ti, 14.0. Calc. for $C_{35}H_{20}Cl_3F_5O_{12}Ti$: C, 43.0; H, 2.05; Ti, 14.7%); major IR bands (Nujol mull) 1600, 1550, 1510, 1420, 1150, 780, 630, 500, 380 and 350 cm^{-1}; ^1H NMR δ 8.40 (2), 8.25 (2), 8.0 (1) and δ 7.25 (m, 2), 7.10 (m, 3) (Ph), overall intensity 10:10.

While they do show some air reactivity associated with the presence of the Ti–Cl bonds, nevertheless the overall stability of these oxo derivatives is demonstrated by the lack of further reaction when they are heated to 100–120 °C in the presence of excess of acid. Using $TiCl_4:RCO_2H$ molar ratios up to 1:4 yields only the oxo derivative with free unco-ordinated acid remaining as indicated by a ν(C=O) band at 1690 cm^{-1}. As the mole ratio of acid is reduced this band becomes weaker until at a 1:2.5 ratio only the oxo species is obtained.

The presence of bridging carboxylate groups is indicated by the $\nu(CO_2^-)$ asymmetric and symmetric stretches near 1540 and 1410 cm^{-1} respectively,[8] while ν(Ti–O) and ν(Ti–Cl) appear as strong bands near 770 and 400 cm^{-1} respectively. The ^1H NMR data provide extra structural information in that for the p-$MeC_6H_4CO_2H$ derivative in particular the five carboxylate groups in the product appear to be in three different environments. Thus the resonances from the *p*-Me substituent consist of three signals at δ 2.28 (relative intensity 1), 2.30 (2) and 2.38 (2).

The X-ray crystal structure* of $[Ti_3Cl_3(O_2CC_6H_4Me\text{-}p)_5O_2]$ **1a** (Fig. 1) bears out the above data, and confirms that the molecule consists of a central $Ti_3(\mu\text{-}O)(\mu_3\text{-}O)$ unit with one unique carboxylate group bridging Ti(1) and Ti(2), and the other four carboxylates forming two sets of bridging groups between Ti(2) and Ti(3) and Ti(1) and Ti(3). The inequivalence between these two sets, as indicated by the NMR data, arises from the overall configuration of the molecule. All the titanium atoms are in distorted-octahedral environments, and each is co-ordinated by five oxygen and one chlorine atom. The only other titanium oxo carboxylate structure for comparison is $[Ti_3(C_5H_5)_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(\mu\text{-}O_2CH)_3]^+[O_2CH]^-\cdot 2HCO_2H$ which, although containing a central Ti_3O unit,[3b] is significantly different from the compound reported here, and contains both bridging hydroxy and carboxylate groups. A better model for comparison is the series of trinuclear oxo-centred basic carboxylates of general formula $[M_3L_3(\mu_3\text{-}O)(\mu\text{-}O_2CR)_6]^+$, which are common for metals although not titanium in the trivalent state, with ligands attached to the metal.[12] Clearly the change to the IV oxidation state in the present compounds introduces the chloride, and formally the cationic charge and one carboxylate group are replaced by the μ-O group.

The solid-state structure offers little assistance in the understanding of the reaction pathways involved in the product formation when the *para*-substituted acids are used. The presence of the corresponding acid chloride (*e.g.* p-MeC_6H_4COCl) in the original mother-liquor from the reaction together with the stoichiometry, the evolution of HCl, and the quantitative yield at least for the *p*-Me derivative suggests an overall reaction (1) ($R = p\text{-}XC_6H_4$; X = Me, Et, F or I).

$$3TiCl_4 + 7RCO_2H \longrightarrow [Ti_3Cl_3(O_2CR)_5O_2] + 2RCOCl + 7HCl \quad (1)$$

The acid appears to have a triple role in that it provides (*i*) a proton for the HCl formation, (*ii*) an acyl group which removes further chlorines as RCOCl, and (*iii*) a remaining oxygen atom which contributes to the metal oxo cluster. However, the reaction products can vary since we have also found in other preliminary experiments that the use of p-$Bu^tC_6H_4CO_2H$ leads to a less soluble product formulated empirically as $[\{TiCl(O_2CR)_2\}_2O]$ ($R = p\text{-}Bu^tC_6H_4$), while with p-$MeOC_6H_4CO_2H$ only a black intractable tar was obtained. Clearly then, although a new class of titanium oxo compounds can be obtained easily with many *para*-substituted benzoic acids, subtle effects must influence the type of product obtained, since as mentioned above the use of benzoic acid itself leads to the different type of cluster $[Ti_4Cl_6(\mu\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$. We are currently attempting to define these effects further in order to utilise the potential of these reactions more fully.

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* Crystal data for $C_{40}H_{35}Cl_3O_{12}Ti_3$ **1a**: monoclinic, space group $P2_1/c$, $a = 13.745(3)$, $b = 17.029(4)$, $c = 19.645(4)$ Å, $\beta = 108.06(3)°$, $M = 957.76$, $U = 4374.52$ Å^3, $Z = 4$, $D_c = 1.454$ g cm^{-3}, $F(000) = 1952$, $R = 0.0699$ for 2136 reflections with $I/\sigma(I) > 3.0$ corrected for absorption [μ(Mo-Kα) = 7.11 cm^{-1}]. Yellow crystal 0.26 × 0.23 × 0.12 mm mounted in a sealed Lindemann tube. Data collected in the range θ 3–25° using a θ–2θ scan with a scan width of 0.90° as described previously.[9] Eequivalent reflections merged to give 2136 reflections with $I/\sigma(I) > 3.0$. Empirical absorption corrections applied after initial refinement with isotropic thermal parameters.[10] A solution revealing the positions of all the non-hydrogen atoms was obtained using the direct-methods module of SHELXS 86.[11] Phenyl groups were treated as rigid groups with idealised geometry (C–C 1.395 Å). The hydrogen atoms were included at calculated positions (C–H 1.08 Å) assuming idealised sp^3 or sp^2 hybridisation as appropriate, the position of the best located hydrogen atom being used to define the orientation of the methyl groups. Their thermal parameters were tied to free variables in the refinement resulting in final values of 0.11 (sp^2) and 0.16 (methyl) Å^2. The Ti, Cl and O atoms were assigned anisotropic thermal parameters in the final cycles of full-matrix refinement[11] which converged at $R = 0.0699$ and $R' = 0.0630$ with weights of $w = 1/\sigma^2(F_o)$ assigned to the individual reflections. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

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