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# An Octameric Titanium Oxo Metallacycle with Host–Guest Interactions

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Treatment of $TiCl_4$ with carboxylic acids $RCO_2H$ (R = $C_6F_5$, $CH_2C_6F_5$, $CH_2OC_6F_5$) yields a series of titanium oxo compounds; the X-ray molecular structure of $[TiO(O_2CC_6F_5)_2]$ reveals an octameric unit and a unique 16-membered $Ti_8O_8$ ring, with two toluene molecules encapsulated above and below the ring in the molecular cavity.

While there is continuing interest in metal oxo species, and their extensive applications as inorganic materials, the pathways and intermediates involved in converting simple precursors, such as metal alkoxides/halides/carboxylates, to higher molecular mass metal oxo aggregates are complex and not well understood.[1] Controlled hydrolysis combined with condensation reactions have resulted in the identification of species such as $[Ti_6O_4(OBu^n)_8(O_2CMe)_8]$,[2] $[Ti_{12}O_{16}(OPr^i)_{16}]$,[3] and $[W_2O_5(OMe)_4]^{2-}$.[4] We have reported that compounds of the type $[Ti_4O_2Cl_6(O_2CPh)_6]$, and $[\{TaOCl_2(O_2CC_6H_4M\text{-}p)\}_4]$ can be obtained directly, and in high yield, from reaction of the metal halide with a carboxylic acid, by using the carboxylate group as the source of the oxygen atoms in the metal–oxo framework.[5] We now report the controlled preparation of some new titanium oxo species, and the single crystal X-ray structure of a unique octameric oxometametallacycle, which also shows the unusual feature of the inclusion of two toluene molecules within the molecular cavity.

Reaction of $TiCl_4$ with the fluoroaryl acids $RCO_2H$ (R = $C_6F_5$, $CH_2C_6F_5$) in toluene at 25 °C using mole ratios varying from 1 : 1 to 1 : 2.5 (Ti : acid) yields the yellow air-sensitive dinuclear oxo derivatives $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ **1**† in high yields (80–85%), eqn. (1).

$$2TiCl_4 + 5RCO_2H \rightarrow [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + RCOCl + 3\,HCl \quad (1)$$

Products of type **1** have also been obtained with the normal alkyl and aryl acids.[6] However, in contrast to these systems a notable change in the above reaction occurs when the mixture is heated in refluxing toluene for 4 h; the initial orange solution becomes lighter in colour, acyl chloride can again be detected in the supernatant liquid, and golden yellow air-stable crystals of $[TiO(O_2CR)_2]_n$ **2**† (R = $C_6F_5$, **2a**; $CH_2C_6F_5$, **2b**) deposit on cooling, with **2a** forming well-defined crystals. Optimum yields of 80–90% are obtained when a 1 : 3 (Ti : acid) molar ratio is used, eqn. (2).

$$nTiCl_4 + 3nRCO_2H \rightarrow [TiO(O_2CR)_2]_n + nRCOCl + 3nHCl \quad (2)$$

Both products **2** can also be obtained, albeit in lower yields of 20–30%, from the dinuclear species **1** by refluxing in toluene, indicating that **1** is a likely intermediate in the reaction pathway leading to **2**. Formation of **2** could occur by the elimination of HCl from the reaction of the coordinated acid in **1** with a Ti–Cl bond on an adjacent molecule. The extra $RCO_2H$ required to give high yields of **2** provides precisely the extra oxygen in the Ti–O–Ti system, with the concomitant formation of HCl and RCOCl from the remaining Ti–Cl bonds on the adjacent molecules.

An X-ray study of **2a** shows the presence of an octameric structure with $[Ti(\mu\text{-}O)(\mu\text{-}O_2CC_6F_5)_2]$ repeating units, forming an overall 16-membered $Ti_8O_8$ ring (Fig. 1).‡ The titanium atoms are in a distorted octahedral environment, and form a nearly regular planar octagon with an average Ti–Ti separation of 3.232 Å, precluding any metal–metal interaction. The bridging oxygen atoms are also nearly in this plane lying alternately above and below it, the largest deviation being 0.60 Å. One of the two bridging carboxylate groups in each unit lies in the equatorial $Ti_8$ plane, while the other is essentially perpendicular to it, alternating above and below it around the ring. The overall structure includes several solvent toluene molecules, some disordered and in partially occupied sites; of particular interest are the two toluene molecules that lie within the cavities formed by the two axial sets of four pentafluorophenyl groups (Fig. 2). They are held within the cavities by van der Waals contacts to the two parallel pentafluorophenyl groups and C–H···O hydrogen bonds to the bridging oxygens. The head-to-head methyl–methyl distance is also quite short (C···C 3.32 Å). π–π Contacts appear to cause the aryl groups to incline inwards towards the included toluene molecules (ring centres to aryl plane distances 3.53, 3.74 and 3.60, 3.65 Å, respectively). We have not yet determined whether these toluene molecules can be displaced by other species, but we have found that while the reaction does proceed in other hydrocarbon solvents that allow a temperature of over 100 °C to be attained we have so far only obtained suitable crystals for an X-ray study from a toluene solution. In the crystal the number of toluene molecules in each asymmetric unit is approximately six, and on prolonged pumping under vacuum a non-crystalline cream-coloured solid of composition $\mathbf{2a}\cdot 3C_6H_5Me$ remains. It is also of interest to note that we have been unable to obtain crystals of **2b** from any of a variety of solvents, and the solid recovered from a toluene solution after pumping analyses as pure non-solvated **2b**. Compounds similar to **2** have been reported as $[3TiO(O_2CR)_2\cdot 2RCO_2H]$, and these on heating to 70 °C yield $[TiO(O_2CR)_2]$ (R = $CF_3$, $C_2F_5$, $C_3F_7$) based on analytical data.[7] Other compounds with the latter formulation have also been claimed for the lower alkyl acids,[8] although we have not yet been able to prepare such species, and have obtained instead derivatives such as $[Ti_3O_2Cl_3(O_2CR)_5]$ (R = Et, $CMe_3$) at 100 °C.[6,9]

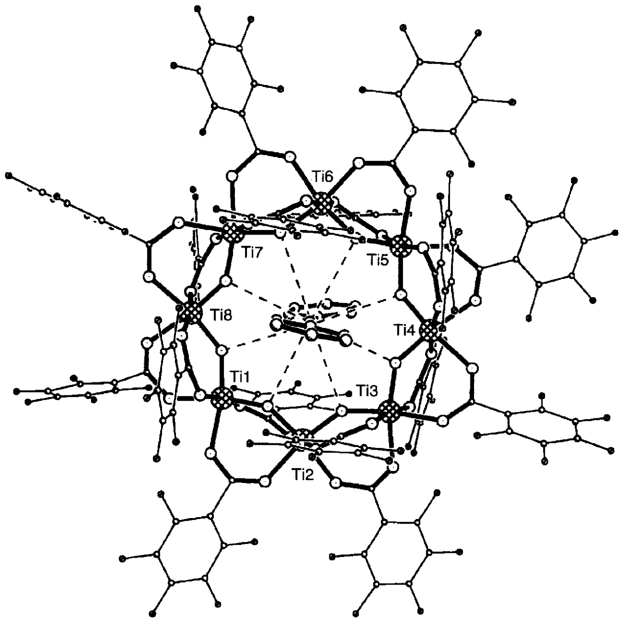

**Fig. 1** Axial view of octamer **2a** showing encapsulated toluene molecules. Selected bond lengths and angles: Ti–μ-O 1.76–1.83 Å, Ti–O (carboxylate) 1.94–2.09 Å, Ti–μ-O–Ti 133.2–136.6°.

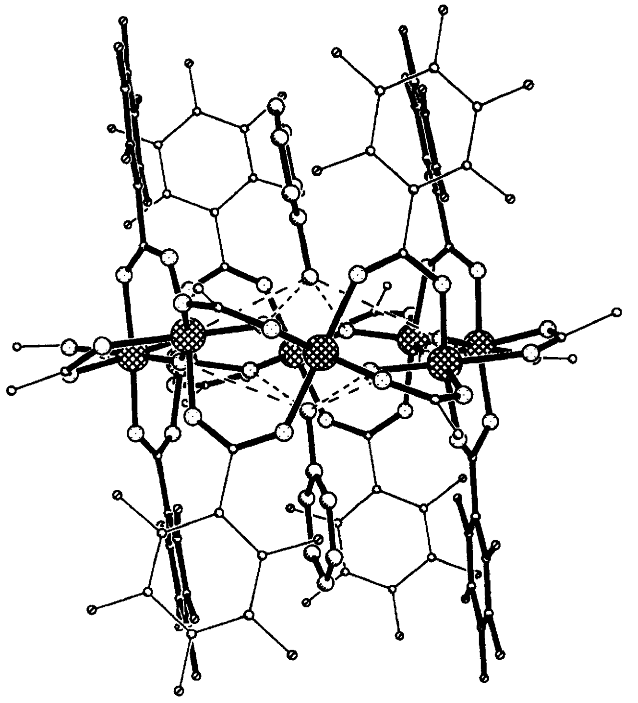

**Fig. 2** Equatorial view of octamer **2a** showing encapsulated solvent toluene molecules [all but 4 atoms removed from equatorial pentafluorobenzoates]. Distance between centroids of toluenes and planes of parallel aryl rings, 3.53–3.74 Å.

In contrast, the reaction of $TiCl_4$ with $C_6F_5OCH_2CO_2H$ (mole ratio Ti : acid = 2 : 3) in benzene at 25 °C yields the yellow solid $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ **3** in 70% yield. In this case, unlike **1** there is no coordinated neutral acid ligand present, presumably due to the ethereal oxygen of the $C_6F_5OCH_2$ group occupying the sixth coordination site. However, the addition of thf results in a near quantitative conversion to $[\{TiCl_2(O_2CCH_2OC_6F_5)(thf)\}_2O]$, similar to the products obtained with the alkyl acids (R = Me, Et, $CMe_3$).[9] In refluxing benzene, using a Ti : acid ratio of 1 : 2.5, further reaction occurs to yield $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4]$ **4**.† While we have not yet been able to obtain crystals suitable for an X-ray study it is interesting to note that this also forms a solvate, $0.75C_6H_6.0.25C_6H_{14}$, when it is precipitated by the addition of *n*-hexane, and the solvent cannot be removed even after prolonged pumping under high vacuum. We are currently extending the range of reaction conditions of this type of reaction in an attempt to clarify the overall reaction pathways, and to widen further the types of oxo derivatives obtained.

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## Footnotes

† *Selected data* (**1**, **2**, **3** and **4** gave analytical data fully consistent with their formulation): for **1** R = $C_6F_5$, IR ν/cm$^{-1}$ 1613, 1543 ($O_2C$), 752 (Ti–O–Ti); R = $CH_2C_6F_5$, IR ν/cm$^{-1}$ 1632, 1545, 787; $^1H$ NMR ($CDCl_3$ δ 3.98–3.80 ($CH_2$, 8H), 9.02 ($CO_2H$, br, 2H). For **2a**, IR ν/cm$^{-1}$ 1576, 1400, 769. For **2b**, IR ν/cm$^{-1}$ 1572, 1398, 782; $^1H$ NMR ($CDCl_3$) δ 3.81 (s, 2H), 3.40 (s, 2H, rel. intens. 1 : 1). For **3**, IR ν/cm$^{-1}$ 1584, 1560, 1450, 1410, 718; $^1H$ NMR ($CDCl_3$) δ 4.30 ($CH_2$, 8H), 7.2 ($C_6H_6$, 4H), 1.28 and 0.94 ($C_6H_{14}$, 3.5H).

‡ *Crystal data* for **2a**·$[\{TiO(O_2CC_6F_5)_2\}_8]nC_7H_8$ (*n* approx. 6): $C_{112}F_{80}O_{40}Ti_8$, $M = 3888.3 + 552.8$ (= 4441.1), triclinic, space group $P\bar{1}$, $a = 18.271(10)$, $b = 18.592(10)$, $c = 29.790(10)$ Å, $\alpha = 102.85(4)$, $\beta = 98.31(4)$, $\gamma = 106.62(4)°$, $U = 9216$ Å$^3$, $Z = 2$, $D_c = 1.60$ g cm$^{-3}$, Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 0.48 mm$^{-1}$; $T = 290$ K, $R = 0.140$ for 6944 unique observed $[I/\sigma(I) > 2.0]$ reflections. A poorly diffracting colourless block crystal was mounted in a Lindemann capillary. Data were collected with a Siemens R3m four circle diffractometer in ω–2θ mode. Maximum 2θ was 45°. Reflections were processed using profile analysis to give 24128 reflections (all unique), of which 6944 were considered observed $[I/\sigma(I) > 2.0]$. These were corrected for Lorentz and polarization effects, but not for absorption effects. Crystal dimensions were 0.20 × 0.45 × 0.32 mm. Space group $P\bar{1}$ was assumed and shown to be correct by the successful refinement. The structure was solved with considerable difficulty (probably because of the weak diffraction) by direct methods, using MITHRIL[10] running with TEXAN[11] with a group of eight titanium atoms which could be picked out from the initial E-maps as a randomly oriented group. This was followed by DIRDIF[12] repetitively to build up the fragment of the central ring and most of the bridging atoms. The light atoms were then readily found by E-map expansion and successive Fourier syntheses in SHELXTL PLUS.[13] As well as the $(TiO)_8$ unit, the asymmetric unit contains at least five full toluene molecules (one with two alternative methyl positions) and three molecules disordered about centres of inversion (one of these part-occupied). Residual electron density indicated the possible presence of additional solvent, and also the likelihood of more complex disorder than that described by the modelling used. The toluene solvent molecules were all treated as symmetrical hexagons. Anisotropic temperature factors were used for Ti, most O and F atoms. Hydrogen atoms were not included. Final refinement was on *F* by least squares methods refining 1119 parameters in two blocks. Largest positive and negative peaks on a final difference Fourier synthesis were of height ±0.9 eÅ$^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0005$ was used and shown to be satisfactory by a weight analysis. Final $R = 0.140$, $R_w = 0.152$, $S = 3.2$. The exceptionally high final *R*-value is not unexpected in view of the poor diffraction (and low ratio of observed to total reflections), and the high degree of disorder in the structure. Computing was with SHELXTL PLUS. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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