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The compound $[Ti_4O_4\{OCH_2CH_2N(CH_3)_2\}_8]$ containing the new Ti_4O_4 cluster core

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Received 6th March 2001, Accepted 10th April 2001
First published as an Advance Article on the web 26th April 2001

Reaction of $[Ti(OPr^i)_4]$ with the bidentate ligand $(CH_3)_2NCH_2CH_2O^-$ (DMEA) followed by controlled hydrolysis yields the new tetranuclear compound $[Ti_4O_4(DMEA)_8]$ involving a novel Ti_4O_4 central core and three different bonding modes of the DMEA ligand.

Within the past decade, studies of the controlled hydrolysis of titanium compounds have produced a wide range of Ti–O clusters. These range from those with simple Ti_2O_2,[1] and Ti_3O cores,[2] to trimeric Ti_3O_3 ring compounds,[3] and compounds based on Ti_6O_{8-n} ($n = 4$, 2, 0),[4] Ti_7O_4,[5] Ti_8O_6,[5] and $Ti_{10}O_8$,[5] $Ti_{11}O_{13}$,[6] $Ti_{12}O_{16}$,[4c,7] $Ti_{16}O_{16}$,[8] $Ti_{18}O_{22}$,[9] $Ti_{18}O_{27}$,[10] and $Ti_{17}O_{24}$[11] central units. Various Ti_4 based compounds have also been reported.[12–18] In this communication, we wish to report the synthesis and full characterisation by single crystal X-ray analysis of the compound $[Ti_4O_4(DMEA)_8]$ which contains a hitherto unknown tetranuclear Ti_4O_4 central core.

Reaction of $[Ti(OPr^i)_4]$ with excess DMEAH in toluene gives a clear yellow solution, which, after removal of solvent, yields a viscous yellow oil, soluble in toluene and known to be $[Ti(DMEA)_4]$ **1**. In contrast, we find that if the reaction is carried out with a 1 : 2 mixture of $[Ti(OPr^i)_4]$ and DMEAH, the product is the mixed ligand complex $[Ti(OPr^i)_2(DMEA)_2]$ **2**. Controlled exposure of compound **1** to water yields colourless prisms of the compound $[Ti_4O_4(DMEA)_8]$, **3**,† which has been fully characterised on the basis of single crystal analysis (see Scheme 1). Crystals obtained directly by the procedure outlined above were found to be suitable for single crystal X-ray diffraction.‡ The established molecular structure shown in Fig. 1 consists of four edge-sharing octahedra, with each of the four titanium atoms co-ordinated to five O, and one N atom.

$$[Ti(OPr^i)_4] + 4\,Me_2NCH_2CH_2OH \longrightarrow \underset{\mathbf{1}}{[Ti(OCH_2CH_2NMe_2)_4]}$$

$$[Ti(OPr^i)_4] + 2\,Me_2NCH_2CH_2OH \longrightarrow \underset{\mathbf{2}}{[Ti(OPr^i)_2(OCH_2CH_2NMe_2)_2]}$$

$$4\,[Ti(OCH_2CH_2NMe_2)_4] + 4\,H_2O \longrightarrow \underset{\mathbf{3}}{[Ti_4O_4(OCH_2CH_2NMe_2)_8]}$$

$$4\,[Ti(OPr^i)_4] + 8\,Me_2NCH_2CH_2OH + 4\,H_2O \longrightarrow \underset{\mathbf{3}}{[Ti_4O_4(OCH_2CH_2NMe_2)_8]}$$

Scheme 1

Within the central core of **3** are the four titanium atoms, two μ- and two μ_3-oxide bridges, and two μ-alkoxide bridges provided by bidentate DMEA ligands. Of the eight DMEA ligands, four chelate through both their O and N donor atoms, and four are terminally bonded through the oxygen. Two Ti(IV) ions are co-ordinated to two μ_3-oxide bridges, and the two others to one μ_3-oxide bridge. There is a significant *trans* influence, with each short Ti–O bond *trans* to a long Ti–O, or Ti–N, bond. The bond angles around each Ti(IV) are not exactly 90°, and there is slight distortion of the octahedra.

It is clear that the structural motif adopted by the central Ti_4O_4 core in compound **3** is governed by the nature of the ligand employed. In this work the versatile nature of the DMEA ligand, which is able to adopt terminal (through the O-atom), chelating and bridging modes, provides an ideal template for the construction of the new Ti_4O_4 unit. The inherent flexibility of the NCCO backbone means that DMEA is able to act both as a five-ring chelating ligand, and as a four-atom bridging ligand, since it is free from the π-bond constraints imposed upon other bidentate ligands with similar numbers of atoms (such as oxalate). The ability of the ligand to readily interchange its bonding capabilities is supported by NMR spectroscopic analysis, which exhibits a simple, ligand-dominated, spectrum compatible with the anticipated ligand interconversion on the NMR timescale.

The cluster core in $[Ti_4O_4(DMEA)_8]$ has four oxo- and two alkoxo-bridges compared to the six alkoxide bridges in the methoxide and ethoxide structures. The structure combines two μ_3-oxo bridges, two μ-oxo bridges and two μ-alkoxo bridges around the four Ti(IV) atoms in a manner that has not been seen previously. Like the cluster core in $[Ti(OEt)_4]_4$[12a] and $[Ti(OMe)_4]_4$,[12b] the structure is based on four edge sharing octahedra around each Ti.

From an examination of previously established structures, it would appear that the new compound **3** prepared in this work falls within the series of tetranuclear titanium compounds with Ti_4O_0, Ti_4O_2, Ti_4O_4 (this work) and Ti_4O_6 environments. This differs from others with an apparently similar Ti_4O_4 core in that they are not cyclic. The cluster cores of the most similar tetranuclear titanium structures are shown and classified in Fig. 2.

There are various ways of discussing the relationship between the different structural forms shown in Fig. 2; all based on Ti_4O_n units. The simplest is probably to consider the systematic change in the connectivities observed. As we progress from **D** to **G** to **E** to **F**, or from **D** to **B** to **H** to **C**, the number of Ti–O connections systematically increases from 8 to 10 to 12 to 14, corresponding to increasing cluster formation from the original ring compound.

Across the range of compounds, the bridging or chelating nature of the ligands seems to be highly important in determining the cluster structure adopted by the tetranuclear titanium compounds. If we consider the two highly similar cluster cores **A** and **F**, **A** has alkoxide ligands providing the bridging O atoms, yet there are four bridging oxide ligands in **F**. This is due to the bidentate nature of the DMEA ligand, which directs each Ti(IV) centre to have a co-ordination sphere containing five O and one donor N ligand. So to maintain charge neutrality in the overall complex, four of the bridging O atoms are now provided by oxide ligands in **3**, as against none in the compounds $[Ti(OEt)_4]_4$ and $[Ti(OMe)_4]_4$.

DOI: 10.1039/b102099o

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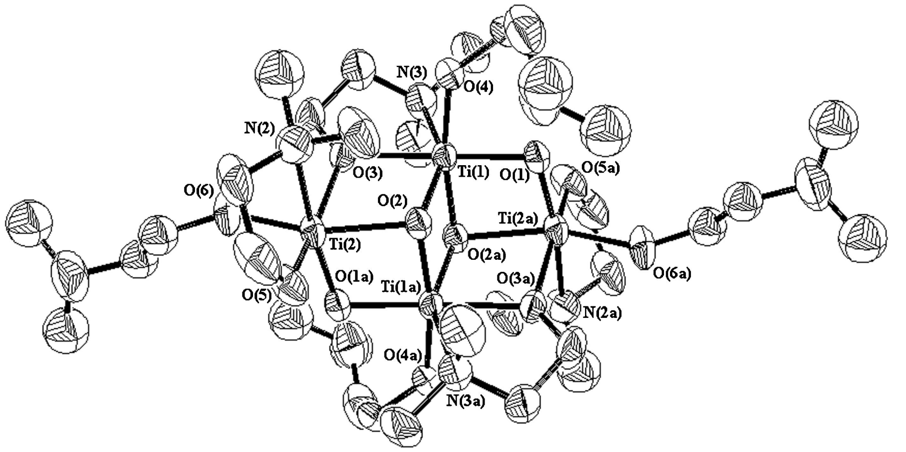

Fig. 1 The molecular structure of [Ti$_4$O$_4$(DMEA)$_8$], **3**. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.869(3), Ti(1)–O(3) 2.035(3), Ti(1)–O(4) 1.856(3), Ti(1)–O(2a) 2.060(3), Ti(1)–O(2) 1.869(3), Ti(1)–N(3) 2.304(4), Ti(2)–O(6) 1.845(3), Ti(2)–O(2) 2.064(3), Ti(2)–O(5) 1.876(4), Ti(2)–O(3) 2.047(3), Ti(2)–O(1a) 1.811(3), Ti(2)–N(2) 2.351(4); Ti(2)–O(1a)–Ti(1a) 107.33(14), Ti(1)–O(2)–Ti(1a) 98.29(13), Ti(1)–O(2)–Ti(2) 107.59(13), Ti(1a)–O(2)–Ti(2) 91.93(11), O(2)–Ti(1)–O(1) 109.39(13), O(1)–Ti(1)–O(2a) 79.63(11), O(2)–Ti(1)–O(3) 77.29(12), O(3)–Ti(1)–O(2a) 95.33(12), O(2)–Ti(1)–O(2a) 81.71(13), O(1)–Ti(1)–O(3) 170.72(14), O(1a)–Ti(2)–O(3) 101.99(14), O(1a)–Ti(2)–O(2) 80.85(11), O(3)–Ti(2)–O(2) 72.85(11).

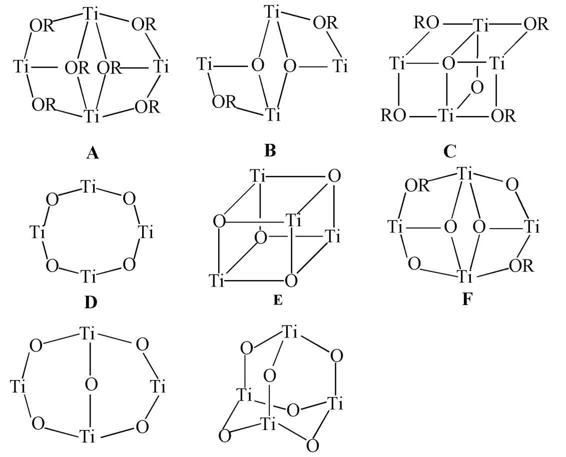

Fig. 2 Different Ti$_4$ – oxo cores. **A** Ti$_4$O$_0$;[12] **B** Ti$_4$O$_2$;[13] **C** Ti$_4$O$_2$;[14] **D** Ti$_4$(μ-O)$_4$;[15] **E** Ti$_4$(μ$_3$-O)$_4$;[16] **F** unique Ti$_4$O$_4$ core of compound **3**; **G** Ti$_4$(μ-O)$_5$;[17] **H** Ti$_4$(μ-O)$_6$.[18]

We found that both compound **1** and compound **3** are catalysts for the second esterification of phthalic anhydride, using 2-ethylhexan-1-ol.[19]§ It would appear that whilst compound **3** is clearly a product of hydrolysis of the original monomeric species, the extent of Ti-oxo clustering is insufficient to remove all catalytic activity. It would seem reasonable to propose compound **3** to be an intermediate in the decomposition pathway for homogeneous Ti(IV) catalysts to large, insoluble and unreactive Ti-oxo aggregates.

In conclusion, this work emphasises the wide and diverse chemistry of Ti–O clusters available, which would appear to be sensitive to the nature of the bonded ligands. In this work, the ligand DMEA clearly plays a significant role in the stabilisation of the new Ti$_4$O$_4$ core.

We wish to thank ICI SYNETIX for financial support (T. O.) and the EPSRC for a research grant (M. C. K.). We wish to thank Dr J. E. Davies for determining the X-ray structure of **3**.

Notes and references

† DMEAH (3.5 ml, 33.9 mmol) was added to titanium isopropoxide (1 ml, 3.4 mmol) in toluene (10 ml). The mixture was stirred under nitrogen at 50–60 °C for 19 hours. Volatiles were removed *in vacuo* leaving **1** (1.1 g, 82%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.25 (s, 6.0H, N(CH$_3$)$_2$), 2.45 (s, 2.0H, NCH$_2$), 3.58 (s, 2.0H, OCH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$): δ 45.1 (N(CH$_3$)$_2$), 58.6 (NCH$_2$), 60.6 (OCH$_2$). MS (EI) *m/z* 312.2 (M$^+$ − Me$_2$NCH$_2$CH$_2$O), 243.1, 224.1 (M$^+$ − 2Me$_2$NCH$_2$CH$_2$O), 89.1 (Me$_2$NCH$_2$CH$_2$OH). MS (FAB) *m/z* 423.2 (MNa$^+$), 401.3 (MH$^+$), 328.1 (M$^+$ − Me$_2$NCH$_2$CH$_2$), 291.1 (MNa$^+$ − Me$_2$NCH$_2$CH$_2$O − Me$_2$N), 189.1.

DMEAH (1.4 ml, 13.6 mmol) was added to titanium isopropoxide (2 ml, 6.8 mmol) in toluene (10 ml). The mixture was stirred under nitrogen at 50–60 °C for 19 hours. Volatiles were removed *in vacuo* leaving **2** (2.0 g, 87%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.19 (d, 6H, $^{3}J_{\text{H–H}} = 6.0$ Hz, CH(CH$_3$)$_2$), 2.25 (s, 6.0H, N(CH$_3$)$_2$), 2.45 (t, 2.0H, $^{3}J_{\text{H–H}} = 5.4$ Hz, NCH$_2$), 3.58 (t, 2.0H, $^{3}J_{\text{H–H}} = 5.4$ Hz, OCH$_2$), 4.01 (septet, 1H, $^{3}J_{\text{H–H}} = 6.0$ Hz, OCH). ^{13}C NMR (400 MHz, CDCl$_3$): δ 25.4 (CH(CH$_3$)$_2$), 45.2 (N(CH$_3$)$_2$), 58.6 (NCH$_2$), 60.6 (OCH$_2$), 64.4 (OCH). MS (EI) *m/z* 254.1 (M$^+$ − Me$_2$NCH$_2$CH$_2$O), 218.0, 172.0, 143.0, 86.1 (Me$_2$NCH$_2$CH$_2$O − 2H), 71.1 (Me$_2$NCH$_2$CH$_2$ − H).

Controlled exposure of **1** to atmospheric water induced formation of individual crystals of **3** (141 mg, 21%). Compound **3** has also been made by the reaction between a mixture of 0.5 molar equivalents of water and 3 molar equivalents of DMEAH to 1 molar equivalent of [Ti(OPr^{i})$_4$]. The volatiles were removed *in vacuo*. A further 4 molar equivalents of DMEAH were added, and after further reaction, the volatiles were removed *in vacuo* to generate crystalline **3** in 62% yield. X-Ray quality crystals were found to have the same unit cell as those produced by the method reported above. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.26 (s, 6.0H, N(CH$_3$)$_2$), 2.45 (s, 2.0H, NCH$_2$), 3.59 (s, 2.0H, OCH$_2$). ^{13}C NMR (400 MHz, CDCl$_3$): δ 45.2 (N(CH$_3$)$_2$), 58.6 (NCH$_2$), 60.6 (OCH$_2$). Found C, 38.1; H, 8.1; N, 11.1. Calc. for C$_{32}$H$_{80}$N$_8$O$_{12}$Ti$_4$: C, 40.0; H, 8.4; N, 11.7%. ESI MS showed a range of decomposition products retaining the Ti$_4$O$_4$ core.

‡ Crystal data for **3**: C$_{32}$H$_{80}$N$_8$O$_{12}$Ti$_4$, $M_r = 960.64$, crystal dimensions 0.18 × 0.18 × 0.15, space group $P2_1/c$ (no. 14), $a = 10.4440(9)$, $b = 11.4790(9)$, $c = 20.085(5)$ Å, $\beta = 90.24(5)°$, $V = 2408(3)$ Å^3, $Z = 2$, $\mu = 0.698$ mm^{-1}, $T = 180(2)$ K, 7716 reflections collected for $3.5 < \theta < 25.2°$, 4182 independent reflections, $R1 = 0.063$ for reflections with $I > 2\sigma(I)$, $wR2 = 0.167$ (for all data). Data collection Rigaku RAXIS-IIC image plate detector, full matrix least-squares refinement on F^2, SHELXTL-97.[20] CCDC reference number 159819. See http://www.rsc.org/suppdata/dt/b1/b102099o/ for crystallographic data in CIF or other electronic format.

§ In a typical procedure, phthalic anhydride (1.3 g, 8.6 mmol) was reacted with 2-ethylhexan-1-ol (2.7 cm^3, 17.3 mmol) in the presence of Ti(IV) (1 mol%) at 150 °C for 12 hours. Synthesis of dioctyl phthalate was observed by ^{13}C NMR, according to acceptable industry standards.

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