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An open chain trinuclear titanium(IV) isopropoxide species formed with the tridentate ligand *cis*,*cis*–cyclohexane–1,3,5-trialkoxide $[C_6H_9O_3]^{3-}$. Crystal structure of $[\{Ti(OPr^i)_3\}_2\{\mu\text{-}Ti(C_6H_9O_3\text{-}O^1,O^5)_2\}]$

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Reaction of titanium(IV) tetraisopropoxide with *cis*,*cis*-cyclohexane-1,3,5-triol $[C_6H_9(OH)_3, H_3L]$ affords the novel trinuclear titanium(IV) alkoxide species $[\{Ti(OPr^i)_3\}_2\{\mu\text{-}Ti(C_6H_9O_3\text{-}O^1,O^5)_2\}]$ $\{L = [C_6H_9O_3]^{3-}\}$ which possesses a unique open-chain V-shaped arrangement of three titanium atoms, with the central 6-co-ordinate Ti atom bonded to two tridentate L groups, and with each of the two terminal Ti atoms 5-co-ordinate, forming bonds to three non-bridging isopropoxide groups, and to two bridging oxygen atoms, one from each of the two ligands L.

Alkoxides of the Group 4 elements, and especially those of titanium, continue to be a subject of interest with respect to their structure and diverse chemistry.[1] They also find many applications; for example, they act as catalysts in the manufacture of esters and polyolefins,[2] as well as in asymmetric synthesis using the Katsuki–Sharpless epoxidation procedure,[3] and they are important precursors in sol–gel technology leading to species such as mesoporous titanium(IV) oxides and more recently titania–silica catalysts.[4]

However, the high susceptibility of $[Ti(OR)_4]$ (R = alkyl, aryl) species to hydrolysis remains a problem in relation both to their handling and reactivity, since any hydrolysis can result in some loss of catalytic activity and the formation of Ti–O–Ti bonds, with the eventual precipitation of insoluble oxo species.[5] We are currently investigating the potential of compatible supporting ligands which could modify, but not seriously impair, the reactivity of the $[Ti(OR)_4]$ alkoxides. The use of multidentate alkoxide ligands in this role is one possibility, since such ligands usually possess a high charge that is compatible with the higher oxidation states of the early transition metals. This together with the presence of a rigid chelating framework could offer an increase in the stability of the overall alkoxide species.

In our initial studies we have used the potentially tridentate *cis*,*cis*-cyclohexane-1,3,5-trialkoxide ligand L^{3-}, which is derived from the corresponding and easily accessible triol (H_3L), and we now report the results of the reaction of H_3L with $[Ti(OPr^i)_4]$. The addition of $[Ti(OPr^i)_4]$ to a stirred suspension of H_3L (1 : 1 molar ratio) in toluene at 25 °C yields a clear solution from which the colourless solid product $[Ti_3(OPr^i)_6L_2]$ **1** may be obtained by removal of the solvent [eqn. (1)].

$$3[Ti(OPr^i)_4] + 2H_3L \longrightarrow [Ti_3(OPr^i)_6L_2] + 6\,Pr^iOH \quad (1)$$

It is interesting to note that **1** is apparently the only Ti(IV) species formed since the use of other molar ratios (H_3L : Ti = 1 : 2, 1 : excess) always yields the same solid.† The product is readily soluble in a range of aromatic, and even to a small extent in aliphatic, solvents. It is slowly hydrolysed by moist air, but it is noticeably less reactive to moisture than the parent $[Ti(OPr^i)_4]$.

The crystal structure of **1** ‡ shows the novel feature of two cyclohexane trialkoxide ligands bonded to the central titanium of an open V-shaped trinuclear metal unit, with a central 6-co-ordinate titanium flanked by two 5-co-ordinate metal centres (Fig. 1). In the open metal framework the two terminal titanium atoms Ti(1) and Ti(3) make an angle of 120.94(5)° at the central Ti(2) atom. The two trialkoxides are both bonded to the central metal atom in a tridentate mode, with the added feature that in each ligand two of the oxygen donor centres are also bridging to each of the terminal titanium atoms. The third oxygen of the two trialkoxide ligands is uniquely bonded to the central Ti(2) atom. The six isopropoxide groups are distributed evenly between the two terminal titanium atoms, and this is a rare example of a complex in which the isopropoxides do not occupy any of the bridging positions.

Not unexpectedly the co–ordination around both the central and terminal metal atoms shows a considerable distortion from octahedral and trigonal bipyramidal geometries respectively. For example, the O(6)–Ti(2)–O(3) angle is 72.86(17)° and O(3)–Ti(1)–O(7) is 166.0(2)°. The terminal Ti–O(isopropoxide) and the unique Ti(2)–O(2) distances are all near 1.80 Å, but there is a distinct asymmetry in the Ti_2O_2 bridge system where the Ti(1)–O(6) and Ti(2)–O(6) distances are 1.978(4) and 2.084(4) Å respectively. These distances are similar to those observed in the dimeric titanium(IV) neopentoxide $[Ti(\mu\text{-}OCH_2CMe_3)(OCH_2CMe_3)_3]_2$ where the terminal Ti–O distances are all near 1.80 Å, while the Ti_2O_2 bridge bond lengths vary from 1.965(4) to 2.104(4) Å.[6] Other trinuclear Ti(IV) alkoxide species that have been reported are very different to **1**. They include the (μ_3-oxo)alkoxides, $[Ti_3(\mu_3\text{-}O)(OPr^i)_{10}]$ and $[Ti_3(\mu_3\text{-}O)(\mu_3\text{-}OMe)(\mu\text{-}OPr^i)_3(OPr^i)_6]$ that contain three 6-co-ordinate Ti(IV) centres,[7] and the trinuclear Ti(III) species, $[Ti_3(OPh)_9(TMEDA)_2]$ (TMEDA = $Me_2NCH_2CH_2NMe_2$). The structure of the latter shows that the two terminal Ti atoms are identical and 6-co-ordinate, being bonded to one bidentate TMEDA, and four phenoxide groups. Two of these four phenoxides are also bridged to the central 5-co–ordinate Ti, and the latter is also bonded to a single non–bridging phenoxide.[8] The angle between the three Ti atoms is 151.92(6)°, in contrast to the angle of 120.94(5)° found in **1**.

The structure of **1** in the solid state is in accord with the solution ^1H and ^{13}C NMR spectra in toluene-d_8. In the ^1H NMR the integrals of the resonances from L^{3-} are in a 2 : 1 ratio, consistent with the asymmetric bonding of the ligands. Thus the equatorial and axial CH_2 protons are centred at δ 2.60 and 2.36 and 1.63 and 1.46 [area ratio 2 : 1; from those attached to {C8(C4) and C10(C6)}, and C12(C2)] respectively, and the equatorial CHO protons are at δ 5.08 and 4.41. The

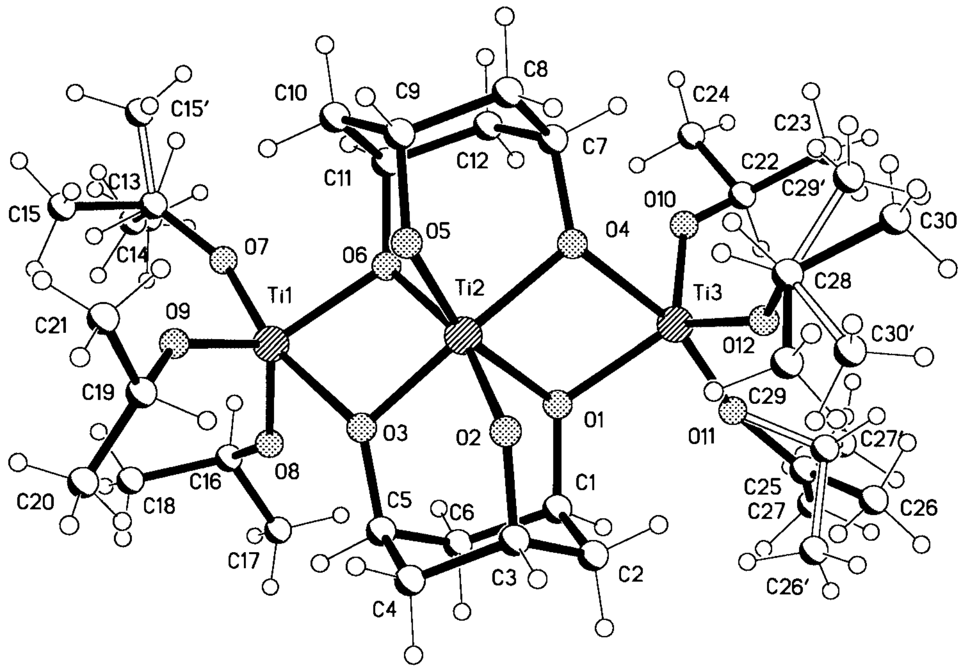

Fig. 1 Molecular structure of **1**. Selected bond lengths (Å) and angles (°): Ti(1)–O(3) 2.087(4), Ti(1)–O(6) 1.978(4), Ti(2)–O(6) 2.084(4), Ti(2)–O(3) 1.973(4), Ti(2)–O(2) 1.829(4), Ti(2)–O(1) 2.104(4), Ti(2)–O(4) 1.964(4), Ti(3)–O(1) 1.975(4), Ti(3)–O(4) 2.089(4), Ti(1)–O(7) 1.803(5); O(3)–Ti(1)–O(6) 72.72(17), O(3)–Ti(1)–O(7) 166.0(2), O(3)–Ti(2)–O(6) 72.86(17), O(2)–Ti(2)–O(4) 109.71(19), O(2)–Ti(2)–O(6) 162.55(19), O(1)–Ti(3)–O(4) 72.68(16).

six isopropoxide groups are equivalent indicating either fluxionality of the 5-coordinate Ti(IV) centres, or rapid exchange of the isopropoxide groups. They show resonances at δ 4.83 (septet, 6H; ^3J 6 Hz) and 1.29 (doublet, 36H). The proton decoupled ^{13}C spectrum shows the expected six resonances.† Indications are that the same structure is retained in the gas phase, since in the E.I. mass spectrum although the parent ion was not found (RMM = 759, based on ^{49}Ti), ions were observed at m/z values of 700, 641 and 582 corresponding to the loss of one, two and three isopropoxide groups respectively.

It is relevant to compare the present results with those from earlier work. While there are previous reports of this trialkoxide ligand bonding in a tridentate fashion to a single metal centre,[9] there are no structurally characterised examples of the asymmetric bonding as observed here. However, for the closely related ligand, 1,3,5-(trifluoromethyl)cyclohexane-1,3,5-trialkoxide, there is one example where the three oxygen atoms are bridge-bonded to Cu(II) and Cd(II) centres, and the more distantly related inositolate(3−) ligand is known to bridge between iron atoms.[10]

In general there have been surprisingly few reports of the use of trialkoxide ligands in combination with the early transition metals, and with the Group 4 elements in particular the only well characterised derivatives with L are a series of substituted cyclopentadienyl compounds of the type [Cp′Ti(L)] [Cp′ = C_5H_5, C_5Me_5, $C_5H_3(SiMe_3)_2$, *etc.*].[11] A report of the reaction of other trialkoxide species, namely 1,1,1-tris(hydroxymethyl)ethane (H_3THME) and 1,1,1-tris(hydroxymethyl)propane (H_3THMP) with [M(OPr^i)$_4$] (M = Ti, Zr) has shown the existence of the tetranuclear cage systems [L′$_2$M$_4$(OPr^i)$_{10}$] (L′ = THME, THMP; M = Ti, Zr), which act as precursors to ceramic thin films.[12] An earlier preliminary report by the same workers claimed that a product with the same composition was formed with L, but this has not been subsequently confirmed.[13] Some related cluster metal oxo trialkoxide complexes are also known for the elements of Groups 5 and 6, for example $[NH_4]_4[V_{10}O_{16}(THMP)_4]\cdot 4H_2O$ and $[Bu^n{}_4N]_2[Mo_3O_7(THME)_2]$.[14]

Therefore, the present results illustrate that for the first time, and in contrast to earlier studies, it is now possible to stabilise a unique open chain titanium alkoxide system by the use of an appropriate alkoxide ligand. It is also noteworthy that the complex contains two terminal titanium centres that are co-ordinatively unsaturated, and hence potentially useful as catalytic sites. We are currently investigating further reactions involving other chelating O-donor ligands in order to determine whether such ligands are able in general to stabilise unusual metal alkoxide species.

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Notes and references

† Compound **1** was prepared by adding [Ti(OPr^i)$_4$] (1.37 cm^3, 4.53 mmol) to a stirred suspension of dehydrated H_3L (0.3 g, 2.26 mmol) in dry toluene (25 cm^3) at room temperature. The resulting suspension was stirred further until a clear solution was obtained. The solvent was then removed *in vacuo*, and the resultant colourless solid was washed thoroughly with hexane, filtered off and dried by pumping *in vacuo*. Yield 40% [Found (required for $C_{30}H_{60}O_{12}Ti_3$): C, 46.8 (47.6); H, 7.9 (8.0%)]. ^{1}H NMR ($C_6D_5CD_3$, 300 MHz, 295 K): δ 5.08 (mult, cyclo-CH, 4H$_{eq}$), 4.83 (sept, isoprop-CH, 6H), 4.41 (mult, cyclo-CH, 2H$_{eq}$), 2.62, 2.57 (d/mult, cyclo-CH$_2$, 2H$_{eq}$) and 2.38, 2.33 (d/mult, cyclo-CH$_2$, 4H$_{eq}$) [area ratio 1:2; doublets of multiplets ($^2J_{av}$ 14 Hz) from equatorial protons attached to C12(C2) and from those attached to {C8(C4) and C10(C6)} respectively], 1.65, 1.61 (d/mult, cyclo-CH$_2$, 4H$_{ax}$) and 1.48, 1.43 (d/mult, cyclo-CH$_2$, 2H$_{ax}$) [area ratio 2:1; from those attached to {C8(C4) and C10(C6)}, and C12(C2) respectively], 1.30, 1.28 (d, isoprop-CH$_3$, 36H). ^{13}C NMR (75.48 MHz DEPT spectrum): δ 77.7 (6 CH, Me$_2$CH-O), 74.4 (2 CH, C5, C9), 73.3, {4 CH, C7(C3) and C11(C1)}, 38.5 {4 CH$_2$, C8(C4) and C10(C6)}, 38.1 (2 CH$_2$, C12,C2), and 26.6 [12 CH$_3$, (CH$_3$)$_2$CHO].

‡ Data were collected using a Siemens SMART CCD area-detector diffractometer. An absorption correction was applied using SADABS.[15] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 for all data using SHELXL 97.[16] All the isopropoxide groups are disordered. Crystal data: $C_{30}H_{60}O_{12}Ti_3$, M = 756.48, monoclinic, a = 19.1305(6), b = 9.8798(2), c = 20.7186(6) Å,

$\beta = 91.66(3)$, $U = 3914.29(18)$ Å^3, $T = 180(2)$ K, space group $P2_1/n$, $Z = 4$, μ(Mo-Kα) = 0.649 mm^{-1}, 18697 reflections measured, 6856 unique ($R_{\mathrm{int}} = 0.097$). The final values of $R1$ [$I > 2\sigma(I)$] and $wR2$ are 0.089 and 0.1812 respectively. CCDC reference number 186/1502. See http://www.rsc.org/suppdata/dt/1999/2647/ for crystallographic files in .cif format.

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