Preparation and X-ray crystallographic characterisation of the trititanate [Ti$_3$O(μ-OPr^i)$_3$(OPr^i)$_4${Me$_2$C(O)CH=C(O)CH$_2$C(O)Me$_2$}], a reaction product of [Ti(OPr^i)$_4$] and propan-2-one

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Reaction of Ti(OPr^i)$_4$ with propan-2-one, under initially anhydrous conditions, yields a colourless moisture-sensitive crystalline product which is structurally identified as the trinuclear oxoalkoxide [Ti$_3$O{μ-OPr^i}$_3$(OPr^i)$_4${Me$_2$C(O)CH=C(O)CH$_2$C(O)Me$_2$}] containing a coordinated C$_9$ ligand derived from the condensation of propan-2-one.

There is considerable current interest in the identification and structural characterisation of titanium(IV) polyoxoalkoxides of the general formula [Ti$_x$O$_y$(OR)$_{4x-2y}$] (where the value of y/x is defined as the degree of condensation) which comprise intermediates in the condensation process between molecular Ti(OR)$_4$ entities and bulk TiO$_2$.[1] At present several structurally characterised titanium(IV) polyoxoalkoxides are known, with y/x values in the range 0.57–1.33, as exemplified by [Ti$_{16}$O$_{16}$(OEt)$_{32}$] and [Ti$_7$O$_4$(OEt)$_{20}$]. The lowest degree of polycondensation ($y/x = 0.33$) to be found in these types of complexes is represented by a single example of a recently structurally characterised trinuclear oxoalkoxide [Ti$_3$O(O-Me)(OPr^i)$_9$], obtained from the reaction of [Ti(OPr^i)$_4$] with water and methanol in isopropyl alcohol solution.[1] Titanium alkoxides are themselves widely used as catalysts for esterification, transesterification, and condensation reactions, and cross-linking of ester-containing resins and epoxides.[2] The reaction mechanisms involved in many of these transformations remain somewhat obscure although they are commonly interpreted in terms of the intermediacy of simple mononuclear titanium alkoxide complexes.[3,4]

Since the production of condensed titanium(IV) poly-oxoalkoxides generally involves the controlled hydrolysis of the parent alkoxides, we reasoned that the ready ability of aldehydes and ketones to undergo condensation reactions of the aldol type,[4] with the co-production of water, might (*i*) facilitate such hydrolyses with a high degree of control and (*ii*) lead to the possible isolation and detection of coordinated intermediate fragments of aldol coupling. Consistent with this idea we have found that mixing [Ti(OPr^i)$_4$] with freshly distilled dry propan-2-one and allowing to stand at room temp. under an atmosphere of dry dinitrogen leads to the deposition of a highly moisture-sensitive colourless crystalline product from a yellow solution.† X-Ray crystallographic analysis has shown this to represent the second example of a presumed family of low-nuclearity titanium polyoxoalkoxides based on a Ti$_3$O$_{11}$ core, which is formulated as

[Ti$_3$O(μ-OPr^i)$_3$(OPr^i)$_4${Me$_2$C(O)CH=C(O)CH$_2$C(O)Me$_2$}] **1**

The molecular structure of **1**‡ (Fig. 1) contains a trinuclear Ti$_3$O core supported by three doubly bridging [O(4), O(4a), O(4b)] and four monodentate isopropoxide groups. Three of the latter [O(5), O(5a), O(5b)] are located on one side of the Ti$_3$-triangular face within which the μ_3-oxygen atom O(3) is situated, and the fourth OPr^i group O(2″) is on the other side together with the tridentate C$_9$ ligand, which is the enolate form of a trimeric condensation product of propan-2-one, 2,6-dimethylhept-3-en-2,4,6-triol. The 2,6-oxygen atoms [O(2), O(2′)]

of the enolate ligand are each coordinated in a monodentate manner to separate titanium atoms, while the central four-coordinate oxygen atom O(1) occupies a triply bridging position within interaction distance of all three titanium atoms, yielding a central Ti$_3$O$_{11}$ core which corresponds to the central arrangement of three distorted face sharing octahedra found in [Ti$_3$O(OMe)(OPr^i)$_9$] (where a methoxide ligand provides the second μ_3-O unit).

The space group symmetry $R\bar{3}$ m in the crystal structure of **1** implies a molecular C_{3v} symmetry. Fig. 2 illustrates the resulting disorder at the C$_9$-ligand face to the Ti$_3$ triangle, which is generated by a crystallographic threefold axis and three associated mirror planes. Therefore both terminally arranged Me$_2$CO units [O(2), C(3), C(4), C(5) and O(2)′, C(3′), C(4′), C(5′)] of the enolate ligand and the monodentate isopropoxide ligand [O(2″), C(3″), C(4″), C(5″)] occupy crystallographically identical positions. Beyond it the methyl groups are split over two positions. In the central ligand unit [–CH=C(O)–CH$_2$–] the oxygen atom O(1) is located on a fully occupied site (3 m), while C(1) in α position is symmetrically distributed over three and C(2) in β position over six sites, resulting in crystallographically identical positions for the sp^2 hybridised alkenic centre C(2) and the sp^3 hybridised methylene centre C(2′). However owing to the crystal symmetry, both central ligand bonds C(1)=C(2) [1.320(9) Å] and C(1)–C(2′) [1.620(9) Å] are

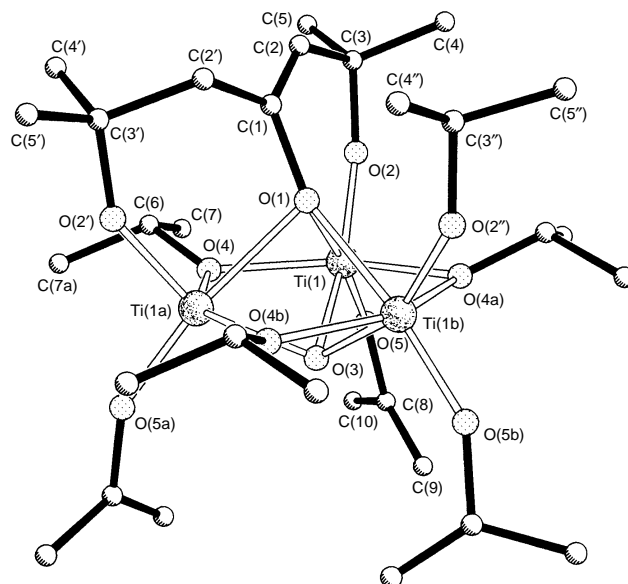**Fig. 1** Molecular structure of **1**. Selected interatomic distances (Å) and angles (°): Ti(1)···Ti(1a) 2.962(2), Ti(1)–O(1) 2.205(4), Ti(1)–O(2) 1.803(3), Ti(1)–O(3) 1.969(4), Ti(1)–O(4) 2.024(3), Ti(1)–O(5) 1.780(4), O(1)–C(1) 1.47(2), C(1)–C(2) 1.32(2), C(1)–C(2′) 1.62(2), C(2)–C(3) 1.56(2), O(2)–C(3) 1.43(2); C(2)–C(1)–C(2′) 125(1), C(1)–C(2)–C(3) 111(1), C(1)–C(2′)–C(3′) 131(1).
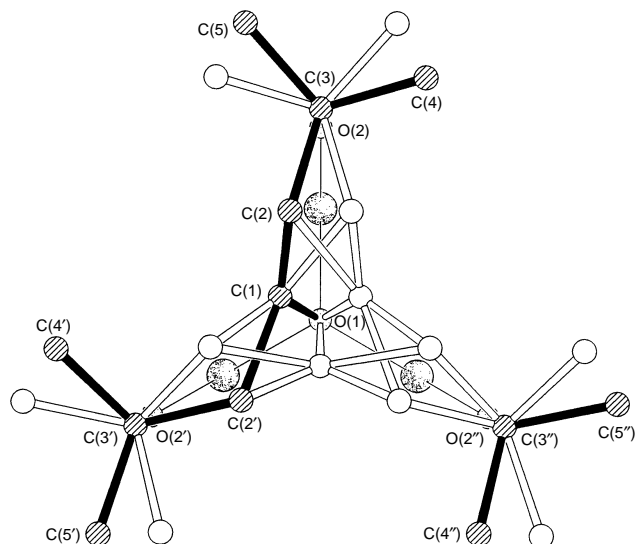
Fig. 2 C_9-ligand face of Ti_3 unit illustrating the disorder along the crystallographic threefold axis. The six remaining OPr^i ligands have been omitted for clarity.

chemically as well as crystallographically non-equivalent, because each one is generated by a different symmetry operation [relative to C(1)].

The very closely related structures of **1** and [$Ti_3O(OMe)(O-Pr^i)_9$], where formally the tridentate C_9-ligand is substituted by one methoxide and two isopropoxide ligands illustrates a highly flexible ligand behaviour on a more or less rigid Ti_3O_{11} core, which then can act as a template in the formation of the C_9-triolate ligand by a co-condensation reaction of three enolate moieties derived from propan-2-one.

Consistent with the structural observations relating to the identification and characterisation of the coordinated C_9 triolate ligand, GC–MS analysis of the mother-liquors from which the crystals were isolated confirms the presence of the common aldol condensation products of propan-2-one, namely, 4-methylpent-3-en-2-one (mesityl oxide) and 2,6-dimethylhepta-2,5-dien-4-one (phorone), together with propan-2-one and isopropyl alcohol. In addition, ^{1}H NMR spectra of the reaction solutions show the appearance of new resonances at δ 1.87 and 6.09 which may be attributed to the presence of phorone and/or mesityl oxide and δ 3.56 which is consistent with the presence of hydroxyl protons present in, for example, diacetone alcohol. In view of the mild reaction conditions used in the preparative work, it is not unlikely that initially formed hydroxylated
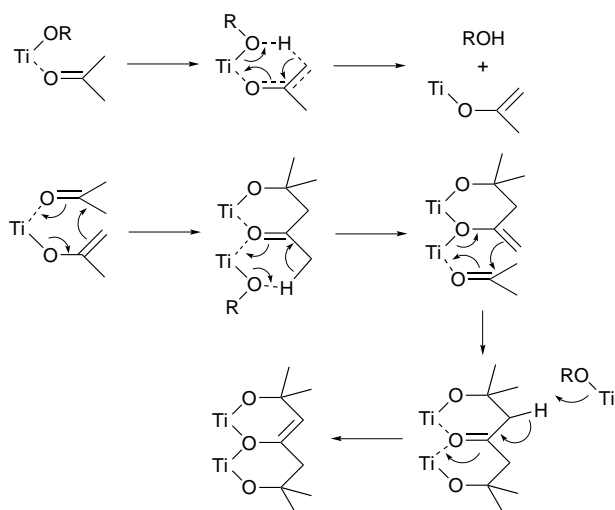
products of condensation are also present in the reacting solution but are dehydrated to, for example, mesityl oxide, within the injection ports of the gas chromatograph.

The mechanism by which this unprecedented reaction product is formed is at present unclear. Notwithstanding an equilibrium constant (in water) of 2.5×10^{-6} for the enolisation of propan-2-one[5] it seems most likely that the initial step in the reaction the involvement of coordination of propanone in the enolate form to the titanium centre, followed by the titanium alkoxide promoted oligomerisation reaction, as indicated in Scheme 1.§ Such reactions may prove, contrary to conventional wisdom,[3,4] the involvement of polynuclear rather than mononuclear reaction intermediates. Finally, it should be noted that the isolation and characterisation of **1** may also be of relevance to processes occurring during the initial stages of formation of polyketones.

Scheme 1

Footnotes and References

1 V. W. Day, T. A. Eberspacher, Y. Chen, J. Hao and W. Klemperer, *Inorg. Chim. Acta*, 1995, **229**, 391 and references therein.
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