Preservation of the cluster core upon formation of $Ti_3O(OPr^i)_8(benzoate)_2$ from $Ti_3O(OR)_{10}$

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L e t t e r

The cluster $Ti_3O(OPr^i)_8(benzoate)_2$ is obtained upon reaction of $Ti_3O(OPr^i)_{10}$ or $Ti_3O(OPr^i)_9(OMe)$ with benzoic acid. The remarkable feature of this substitution reaction is that the cluster structure is approximately preserved. $Ti_3O(OPr^i)_8(benzoate)_2$ undergoes a dynamic exchange processes of the propoxy groups in solution.

Organically modified transition-metal oxide clusters (OMTOCs) are interesting building blocks for the synthesis of inorganic–organic hybrid materials.[1] The most general approach is to use complexing multidentate ligands, such as carboxylates, sulfonates, phosphonates, β-diketonates, *etc.*, to bind the organic groups, which may carry functional groups, directly to the metal atoms at the surface of the cluster.

OMTOCs with multidentate organic ligands can be prepared by two strategies. The multidentate groups can either be grafted to a pre-formed cluster ("surface modification" method) or introduced during the cluster synthesis ("*in-situ*" method). The latter method has been successfully used for the preparation of a variety of carboxylate- or β-diketonate-substituted metal oxide clusters by reaction of metal alkoxides with carboxylic acids or β-diketones,[1] where concomitant ester formation results in the formation of oxo and hydroxo ligands.

The surface modification method is less general. The reason is that the post-synthesis modification of the cluster surface by organic groups requires (i) reactive surface groups, such as OH, Cl or OR, and (ii) the simultaneous balancing of charges and co-ordination numbers upon substitution of these groups. Substitution can therefore only be expected to proceed without major difficulties, if both the number of the occupied co-ordination sites and the charges of the entering ligands are the same as those of the leaving groups. For example, when $Ti_{16}O_{16}(OEt)_{32}$ was reacted with small proportions of carboxylic acids, a fraction of the bridging OEt groups was replaced by bridging carboxylate groups; the resulting cluster has not been structurally characterized. For higher carboxylate:Ti proportions, the cluster was degraded.[2] However, the presence of bridging alkoxo ligands does not guarantee that substitution by bidentate ligands will take place. Reaction of $Ti_7O_4(OEt)_{20}$ with benzoic acid resulted in the formation of the new cluster $Ti_6O_4(OEt)_{14}(OOCPh)_2$ with concomitant major rearrangement of the cluster core, despite the presence of bridging OR groups in the starting cluster.[3] Even complete degradation may occur, as observed for the reaction of $Zr_4O_2(OMc)_{12}$ with acetylacetone.[4]

We now report a rare example where the general structure of a titanium oxo alkoxo cluster was preserved upon substitution of alkoxo ligands by carboxylates. When a toluene solution of the cluster $Ti_3O(OPr^i)_{10}$ (**1a**) or $Ti_3O(OPr^i)_9(OMe)$ (**1b**)[5] was reacted with 1.5 equivalents of benzoic acid, the new cluster $Ti_3O(OPr^i)_8(OOCPh)_2$ (**2**) was obtained in high yield (eqn. 1). A higher portion of benzoic acid (such as 2 equivalents as required by eqn. 1) leads to a degradation of **2** and to lower yields.

$$Ti_3O(OR)_{10} + 2\,PhCOOH \rightarrow$$
$$\underset{\mathbf{1}}{}$$
$$\underset{\mathbf{2}}{Ti_3O(OPr^i)_8(OOCPh)_2} + 2\,ROH \quad (1)$$
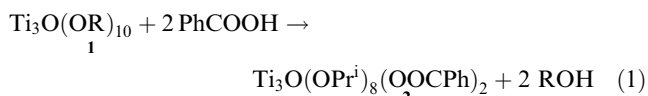
The molecular structure of **2** was determined by an X-ray structure analysis. Fig. 1 shows the comparison with the structure of the starting cluster **1b** (**1a** is isostructural[5]). The three titanium atoms in **1** are capped by one oxygen atom and one alkoxy group. Three propoxy groups bridge the edges of the
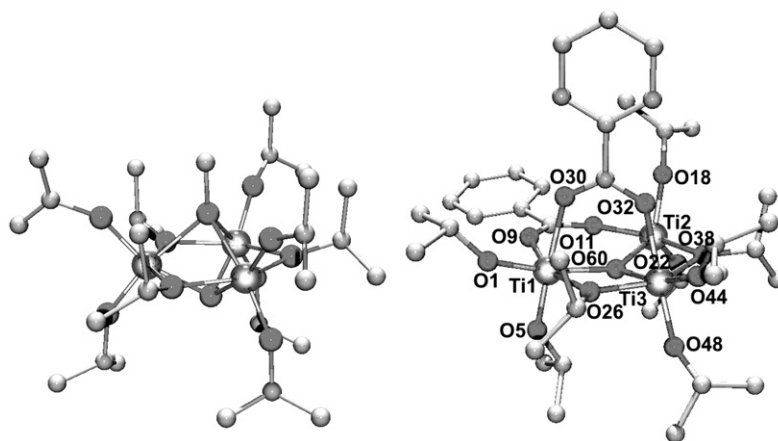

Fig. 1 A comparison of the structures of $Ti_3O(OPr^i)_9(OMe)$ (**1b**) (left) and $Ti_3O(OPr^i)_8(OOCPh)_2$ (**2**) (right).

Ti₃ triangle, and the remaining propoxy groups are terminally bonded to the titanium atoms. In **2**, one of the benzoate ligands (O9/O11) replaces a bridging alkoxy group. According to the general considerations made above, this is an expected reaction because both the co-ordination numbers and charges are preserved. However, the group substituted by the second benzoate ligand (O30/O32) is the μ_3 alkoxy group capping the Ti₃ triangle. Because a tridentate ligand is replaced by a bidentate ligand with the same charge, one of the co-ordination sites at one of the titanium atoms must be left empty. One titanium atom (Ti2) does indeed change its co-ordination number from 6 to 5.

Clusters of this structural type were already obtained, and structurally characterized, upon reaction of $Ti(ONp)_4$ (Np = CH_2CMe_3) with acetic acid or *tert*-butylacetic acid;[6] the acetate derivative was postulated as an intermediate in the formation of $Ti_6O_4(OPr^i)_{12}(acetate)_4$ from $Ti(OPr^i)_4$ and acetic acid.[7]

The dynamic behavior of compound **2** in CD_2Cl_2 solution was studied at different temperatures by 1D and 2D NMR spectroscopy. The proton spectrum at 298 K showed resonances in three distinct regions, *i.e.* 8.3–7.1 ppm (C_6H_5), 5.3–4.3 ppm (very broad and unstructured, CH) and 1.6–0.9 ppm (CH_3). In the HSQC and HMBC spectra six resolved O^iPr signals were observed, five assigned to O^iPr groups from the cluster and one from free isopropanol.[8] In the EXSY spectrum at room temperature (Fig. 2), exchange signals were observed between all the different O^iPr groups.

By cooling the solution to 233 K, a sharpening of the broad proton signals of the CH groups of the O^iPr groups was observed. When the solution was further cooled to 193 K, the CH signals of the O^iPr groups showed again a broadening and a further splitting. In contrast, the aromatic region remained nearly unchanged. The HSQC (Fig. 3) and HMBC spectra at this temperature showed now signals of eight distinct isopropanolate groups, seven from the cluster and one of the free isopropanol. At this temperature, exchange of the O^iPr groups was no longer observed.

Titanium oxo alkoxo clusters (with only oxo and alkoxo substituents) range in size from $Ti_3O(OR)_{10}$ to $Ti_{17}O_{24}(O^iPr)_{20}$.[9] A general reactivity pattern emerges. While some of the alkoxo ligands in the bigger clusters (starting with $Ti_{11}O_{13}(O^iPr)_{18}$[10]) can be replaced by other alkoxo groups, the opposite is true for the exchange of alkoxo groups against
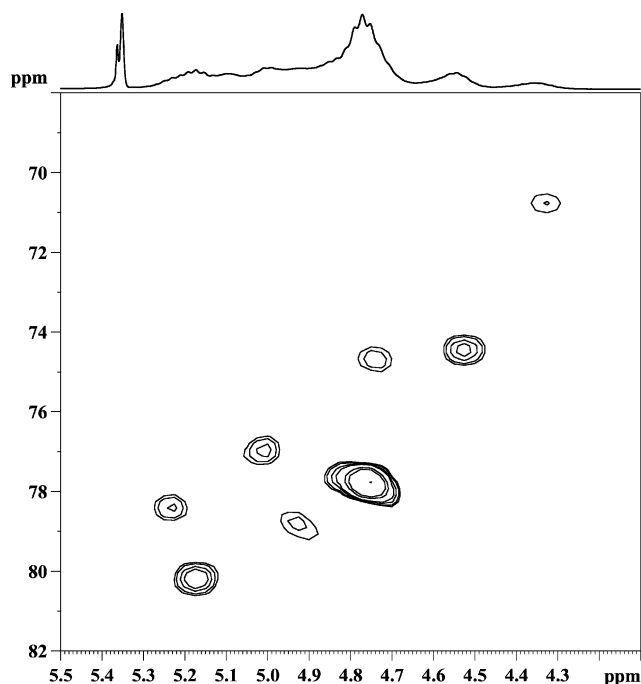

Fig. 3 HSQC spectrum of **2** (CD_2Cl_2) at 193 K (CH region).

carboxylate ligands. We found that only $Ti_3O(OR)_{10}$ undergoes substitution with concomitant preservation of the general cluster structure (this work). $Ti_7O_4(OEt)_{20}$ also reacts with benzoic acid, but the cluster structure is completely re-organized.[3] When $Ti_{11}O_{13}(O^iPr)_{18}$ is reacted with benzoic acid, complete degradation is observed. The same was observed for $Ti_{12}O_{16}(O^iPr)_{16}$.[2]

Experimental

Synthesis of 2 from 1

The solution of 0.41 g (3.37 mmol) of benzoic acid in 5 ml toluene was added dropwise to a stirred solution of 1.73 g (2.25 mmol) of **1a** in 15 ml of toluene. Stirring was continued at room temperature for 14 h, then all volatile compounds were removed *in vacuo*. The solid residue was dissolved in 4 ml of toluene, and 20 ml of acetonitrile were added. Storage of the solution at −30 °C resulted in the crystallization of **2** within two weeks (1.20 g, 61% yield relative to the employed amount of **1a**).

The same cluster was obtained from 0.73 g (1.00 mmol) of **1b** and 0.18 g (1.51 mmol) of benzoic acid by the same procedure (0.60 g, 69% yield relative to the employed amount of **1b**).

Compound 2. NMR (CD_2Cl_2, 193 K, ¹H/¹³C; δ/ppm): benzoate (12 signals from 14 possible ¹³C signals resolved):
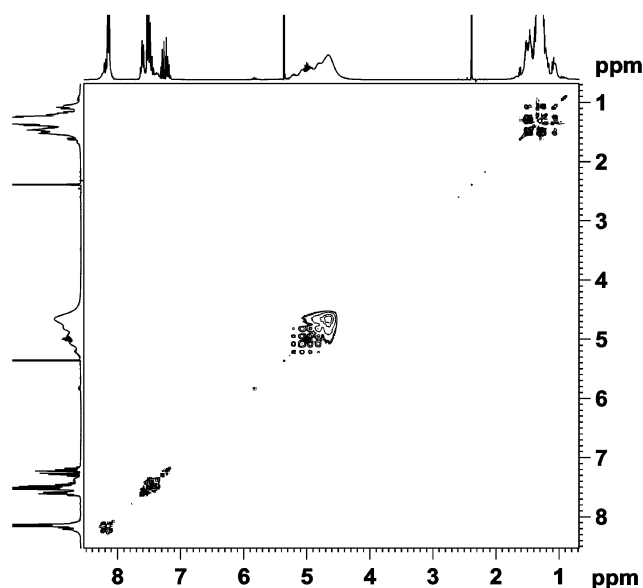

Fig. 2 EXSY spectrum of **2** (CD_2Cl_2) at room temperature.

8.12/130.2, 8.00/129.5, 7.52/132.5, 7.44/128.4, 7.31/129.0, 7.23/128.4, 7.17/129.1, 7.15/125.4, 134.8, 138.7, 170.2, 171.6; CH of O^{i}Pr (8 signals from 9 possible resolved): 5.22/78.3, 5.16/80.0, 5.00/76.8, 4.92/78.7, 4.76/77.6 (free ^{i}PrOH), 4.75/74.6, 4.53/74.3, 4.35/70.7; CH$_3$ of O^{i}Pr (9 signals): 1.42/24.4, 1.40/23.2, 1.29/25.7, 1.25/23.6, 1.18/26.4 (free ^{i}PrOH), 1.17/25.3, 1.11/25.1, 1.09/23.4, 0.96/25.1. Anal. calc. for C$_{38}$H$_{66}$O$_{13}$Ti$_3$: C 52.2, H 7.6, Ti 16.4. Found: C 50.3, H 7.6, Ti 16.4%.

X-Ray crystallography

Single crystal data were collected on a Siemens SMART diffractometer with a CCD area detector (Mo-K$_\alpha$ radiation, $\lambda = 71.073$ pm). The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structure was solved by direct methods (SHELXS86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom.

CCDC reference number 188068. See http://www.rsc.org/suppdata/nj/b2/b208255a/ for crystallographic data in CIF or other electronic format.

Crystallographic data for **2**: C$_{38}$H$_{66}$O$_{13}$Ti$_3$: $M = 874.6$, monoclinic, space group $P2_1/c$, $a = 1191.42(7)$, $b = 3793.0(2)$, $c = 1140.83(7)$ pm, $\beta = 115.129(1)$, $V = 4667.6(6) \times 10^6$ pm^3, $Z = 4$, $T = 294$ K, $\mu = 0.555$ mm^{-1}, 11 463 independent reflections, $R_{int} = 0.0253$, $R_1 = 0.0517$, w$R_2 = 0.1178$.

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8　The sample used for NMR spectroscopy still contained some isopropanol from the preparation procedure. Residual isopropanol is difficult to remove by drying, even in high vacuum, possibly due to hydrogen bonding. Only crystallization yields isopropanol-free samples of **2**.

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