Rearrangement of a Titanium Alkoxide Cluster upon Substitution of the Alkoxide Groups by Carboxylate Ligands − Synthesis of $[Ti_6O_4(OEt)_{14}(OOCPh)_2]$ from $[Ti_7O_4(OEt)_{20}]$

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Reaction of $[Ti_7O_4(OEt)_{20}]$ with benzoic acid results in the formation of the new cluster $[Ti_6O_4(OEt)_{14}(OOCPh)_2]$ with concomitant rearrangement of the cluster structure. The molecular structure of the new cluster was determined by single-crystal X-ray diffraction and can be represented by the extended formula $[Ti_6(\mu_4\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_6(\mu_2\text{-benzoate})_2(\mu_1\text{-}OEt)_8]$.

Introduction

Metal oxide clusters capped by reactive organic groups are interesting building blocks for the synthesis of inorganic-organic hybrid materials due to their well-defined shape and their size in the lower nanometer range.[1] A key issue for the preparation of organically modified transition metal oxide clusters (OMTOCs) is the attachment of suitable organic groups to the metal atoms at the cluster surface. The introduction of organic groups can often be achieved with bi- (or multi)dentate (chelating or bridging) groups, such as carboxylates, sulfonates, phosphonates, β-diketonates, etc. These groups may also carry organic functionalities, such as polymerizable double bonds.

OMTOCs 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 used successfully for the preparation of carboxylate- or β-diketonate-substituted metal oxide clusters by reaction of metal alkoxides with carboxylic acids or β-diketones,[1,2] where concomitant ester formation results in the formation of oxo and hydroxo ligands. There are also well-established routes for the preparation of a variety of neutral or (mostly) charged metal oxide clusters. The subsequent modification of their surface by organic groups requires: (i) reactive groups, such as OH, Cl or OR, bonded to the surface metal atoms, and (ii) the simultaneous balancing of charges and coordination numbers upon substitution of these groups. The latter is only possible without major difficulties if both the number of the occupied coordination 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 amounts of carboxylic acids, a few of the bridging OEt groups were replaced by bridging carboxylate groups (for higher carboxylate:Ti proportions, the cluster core was cleaved).[3]

The substitution of mono-anionic, *mono*dentate groups (OR, OH, Cl etc.) by mono-anionic, *bi*dentate ligands (carboxylates, β-diketonates, etc.) requires either rearrangement of the cluster or a change of the coordination modes of the bridging groups (e.g., bridging OR or OH to terminal, or μ_3 oxygens to μ_2 oxygens) to make additional coordination sites available. Reaction of the clusters with bidentate ligands may even lead to the complete degradation to monomeric compounds; for example, $[Zr(acac)_2(OMc)_2]$ (OMc = methacrylate, acac = acetylacetonate) was obtained from the reaction of $[Zr_4O_2(OMc)_{12}]$ with acetylacetone.[4]

Results and Discussion

In this paper we describe the rearrangement of a titanium oxoalkoxide cluster upon partial substitution of alkoxide groups by carboxylate groups. Among the many structurally characterised titanium polyoxoalkoxides with compositions ranging from $[Ti_3O(OR)_{10}]$ to $[Ti_{18}O_{27}(OR)_{18}]$[5] we have selected $[Ti_7O_4(OEt)_{20}]$ (**1**) as a model compound.[6,7] When **1** was reacted with a 1.5-molar excess of benzoic acid in benzene solution at ambient temperature [Equation (1); monitored by ^{13}C NMR spectroscopy], both starting compounds were completely consumed (more than 1.5 equivalents of benzoic acid results in the formation of increasing amounts of a poorly soluble precipitate). The NMR spectra of the reaction solution indicated the presence of a single cluster. When the volatile compounds were removed and the resulting residue was dissolved in heptane, the ^{13}C NMR spectrum was still that of the initially formed cluster. From this solution, crystals of $[Ti_6O_4(OEt)_{14}(OOCPh)_2]$ (**2**) precipitated at −20 °C. The ^{13}C NMR spectra of the initially formed cluster (the composition and structure of which is still unknown) and **2** are very similar, but can be clearly distinguished. The main difference is that **2** shows more signals in the CH_2 and CH_3 region than the initially formed cluster. The formation of **2** from the initial cluster is reversible, i.e. if the crystals are redissolved in the mother

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liquid, the spectrum of the initial cluster is again observed. This indicates that **2** is in equilibrium with the initial cluster. Once **2** was isolated analytically pure and dissolved in heptane, it did not reconvert into the initial cluster. We can exclude that the formation of both the initial cluster and **2** is due to the presence of water — which might be produced by ester formation between benzoic acid and the cleaved ethanol — because both the initial cluster and **2** (precipitating from its solution) were observed when **1** was reacted with acetic benzoic anhydride instead of benzoic acid. In the latter reaction, ethyl acetate was formed as a by-product.

$$[\mathrm{Ti_7O_4(OEt)_{20}}]\ (\mathbf{1}) + 1.5\ \mathrm{PhCOOH} \rightarrow [\mathrm{Ti_6O_4(OEt)_{14}(OOCPh)_2}]\ (\mathbf{2}) + \ldots \qquad (1)$$

The structure of **2** was determined by a single crystal X-ray structure analysis (Figure 1). The composition of **2** formally differs from that of **1** by a $\mathrm{Ti(OEt)_4}$ unit and the substitution of two of the remaining ethoxide ligands by benzoate ligands. An inspection of the molecular structures shows, however, that this is accompanied by an extensive structural rearrangement. The titanium atoms are octahedrally coordinated in both clusters. The total 42 coordination sites in **1** (general formula $\mathrm{Ti_7O_4X_{20}}$, X = mono-anionic ligand) are occupied by two μ_4-O, two μ_3-O, eight bridging OEt and twelve terminal OEt {i.e., $[\mathrm{Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_8(\mu_1\text{-}OEt)_{12}}]$}.[7,8] In the resulting $\mathrm{Ti_6}$ cluster **2**, only 36 coordination sites are available for the ligands. Thus, when two bridging OEt ligands are formally replaced by two bridging benzoate ligands, other ligands must change their coordination mode in order to adjust for the smaller number of available coordination sites. As a matter of fact, two of the bridging oxygen atoms in **2** are μ_2 coordinated, rather than μ_3 in **1**, i.e. the extended formula of **2** is $[\mathrm{Ti_6(\mu_4\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_6(\mu_2\text{-}benzoate)_2(\mu_1\text{-}OEt)_8}]$. The changing of the two oxygen atoms from a μ_3 coordination mode to μ_2 necessarily implies that the titanium octahedra in **1** and **2** are connected in a different way (Figure 2).

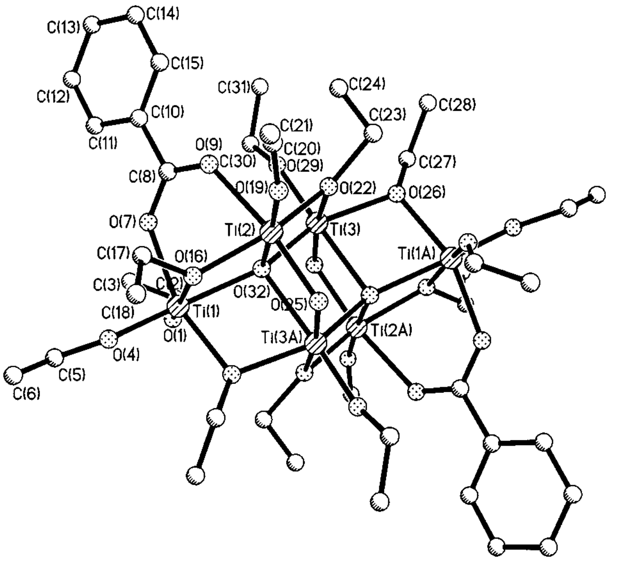

Figure 1. Molecular structure of $[\mathrm{Ti_6O_4(OEt)_{14}(OOCPh)_2}]$ (**2**); selected distances (in pm) and bond angles (in °): Ti(1)−O(1) 177.3(4), Ti(1)−O(4) 177.4(4), Ti(1)−O(7) 204.3(4), Ti(1)−O(16) 208.9(4), Ti(1)−O(26) 201.1(4), Ti(1)−O(32) 208.2(3), Ti(2)−O(9) 216.6(4), Ti(2)−O(19) 177.0(4), Ti(2)−O(16) 196.2(4), Ti(2)−O(22) 193.9(4), Ti(2)−O(25) 183.2(4), Ti(2)−O(32) 208.6(3), Ti(3)−O(22) 208.5(4), Ti(3)−O(26) 201.5(4), Ti(3)−O(25) 183.9(3), Ti(2)−O(29) 176.9(4), Ti(3)−O(32) 196.6(3), Ti(3)−O(32)* 214.2(3). Ti(1)−O(16)−Ti(2) 102.0(2), Ti(2)−O(22)−Ti(3) 103.6(2), Ti(2)−O(25)−Ti(3)* 109.9(2), Ti(1)−O(32)−Ti(2) 98.2(1), Ti(1)−O(32)−Ti(3) 150.6(1), Ti(2)−O(32)−Ti(3) 102.7(2), Ti(3)−O(32)−Ti(3)* 100.6(2), Ti(1)−O(32)−Ti(3)* 99.6(1), Ti(2)−O(32)−Ti(3)* 90.6(1); *symmetry-equivalent atoms

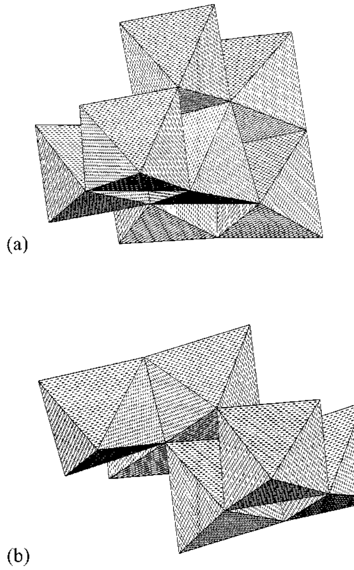

Figure 2. Arrangement of the Ti octahedra in **1** (a)[6,7] and **2** (b)

Several types of carboxylate-substituted titanium polyoxoalkoxides have been obtained by reaction of $\mathrm{Ti(OR)_4}$ with carboxylic acids,[9−11] with the degree of substitution by carboxylate groups (r = carboxylate/Ti ratio) ranging from 1.78 in $[\mathrm{Ti_9O_8(OR)_4(OOCR')_{16}}]$ to 0.5 in $[\mathrm{Ti_4O_2(OR)_{10}(OOCR')_2}]$. Compared with the known clusters, **2** is exceptional in two respects: (i) it is the only cluster prepared by substitution of a pre-formed polyoxoalkoxide (with concomitant rearrangement of the cluster core), and (ii) it has the lowest degree of substitution (r = 0.33). Interestingly, only the two clusters with the lowest degree of substitution, $[\mathrm{Ti_4O_2(OR)_{10}(OOCH)_2}]$[10] and **2**, contain μ_4-oxygens, while the other clusters are less condensed with only μ_2- and μ_3-oxygens. For example, in the other known cluster with the general composition $\mathrm{Ti_6O_4X_{16}}$, $[\mathrm{Ti_6O_4(O\mathit{i}Pr)_{12}(OOCMe)_4}]$,[11] the two additional carboxylate groups (compared to **2**) do not replace two μ_2-OR groups; instead, the coordination mode of both the μ_4-oxygens in **2** is changed to μ_3 in order to accommodate the two bridging ligands {i.e., the extended formula is $[\mathrm{Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}O\mathit{i}Pr)_6(\mu_2\text{-}acetate)_4(\mu_1\text{-}O\mathit{i}Pr)_6}]$}.

Experimental Section

All operations were carried out in Schlenk tubes under an argon atmosphere.

$\mathrm{Ti_6O_4(OEt)_{14}(OOCPh)_2}$ (2): A solution of benzoic acid (64 mg, 0.52 mmol) in 5 mL of benzene was added dropwise at room temperature to a solution of $\mathrm{Ti_7O_4(OEt)_{20}}$ [**1**: ^{13}C NMR δ = 18.5, 18.8, 19.0, 19.2, 19.6, 19.67, 19.74 ($\mathrm{CH_3}$), 66.0, 70.4, 70.8, 70.9, 71.4, 71.5, 71.6, 71.8 ($\mathrm{CH_2}$)] (450 mg, 0.35 mmol) in 5 mL of benzene. The solution was stirred for 12 h at 25 °C. After removal of all volatiles and addition of heptane (5 mL) the following ^{13}C NMR spectrum was observed: δ = 18.4, 18.9, 19.3 ($\mathrm{CH_3}$), 69.1, 71.0, 71.5, 72.6, 72.8 ($\mathrm{CH_2}$), 128.2, 130.2, 131.9, 135.0 (Ph), 172.2 (COO). From this solution, cluster **2** crystallized at −20 °C during 12 h. Yield 304 mg (0.25 mmol; yield: 61% relative to Ti, 93% relative to benzoic acid). Selected spectroscopic and analytic data of **2**: $\mathrm{C_{42}H_{80}O_{22}Ti_6}$ calcd. C 41.2, H 6.6, Ti 23.5; found C 41.0, H 6.2, Ti 23.6. − ^{13}C NMR δ = 17.8, 17.9, 18.2, 18.4, 18.9, 19.3, 19.4 ($\mathrm{CH_3}$), 69.1, 69.6, 71.1, 71.6, 73.0, 73.3, 74.3 ($\mathrm{CH_2}$), 128.3, 130.4, 132.0, 135.2 (Ph), 172.3 (COO). − IR (KBr): $\tilde{\nu}$ = 841 (w), 890 (s), 924 (s), 1069 (vs), 1124 (vs), 1352 (s), 1375 (s), 1401 (s, COO sym), 1447 (vs), 1469 (m), 1493 (m), 1552 (s), 1595 (s, COO asym), 1821 (w), 1934 (w), 2697 (w), 2858 (vs), 2924 (vs), 2968 (vs), 3065 (w).

X-ray Structure Analysis of 2. A selected crystal (0.54 × 0.32 × 0.22 mm) was mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated Mo-K_α radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 4.40 cm. A hemisphere of data was collected by a combination of three sets of exposures at 294 K. Each set had a different φ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. 12010 reflections were collected. 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. Crystal data: M = 1224.29, monoclinic, Z = 2, a = 1245.8(2), b = 1780.9(3), c = 1417.7(3) pm, β = 108.351(4), U = 2985.4(9)·10^6 pm^3, space group $P2_1/n$, D_{calc} = 1.362 gcm^{-3}, μ(Mo-K_α) = 8.31 cm^{-1} The structure was solved by direct methods (SHELXS-86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms using 3631 unique reflections. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. R_1 = 0.042 [$I > 2\sigma(I)$], R_2 = 0.121, GOF = 1.013.

Crystallographic data (excluding structure factors) for the structure of **2** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 157 873. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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