An Unusual Ring Structure of an Oligomeric Oxotitanium Alkoxide Carboxylate

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$Ti_9O_8(OPr)_4$(methacrylate)$_{16}$ was obtained by the reaction of $Ti(OPr)_4$ with an excess of methacrylic acid and analyzed by X-ray diffraction. The compound consists of a ring of nine [TiO_6] octahedra linked by six μ_2- and only two μ_3-oxide bridges.

When metal alkoxides are treated with carboxylic acids, β-diketones, or related compounds, the alkoxide groups are replaced to some extent by the corresponding bidentate anionic ligands (BL^-).[1] There are three main objectives in using compounds of the type $E(OR)_y(BL)_x$ as precursors in sol-gel chemistry: (i) they have a lower reactivity than the parent alkoxides, (ii) organic functions can be introduced in the derived materials,[2] and (iii) the size of the primarily formed oxo particles can be controlled.[1] The primary hydrolysis products are the building blocks for organically modified non-silicate sol-gel materials. Chemical "nanoengineering" of sol-gel materials is only possible when several fundamental structural issues concerning the oxo clusters are understood and eventually controlled: (i) the coordination number of the central atom, (ii) the kind of linkage of the coordination polyhedra (vertex-, edge-, face-sharing), (iii) the number of shared vertices, edges, or faces, and (iv) the coordination mode of the organic ligands.

Carboxylates are often used as the bidentate ligands. One particular advantage of such compounds is that they allow the easy introduction of functional substituents. We recently succeeded in characterizing a coherent series of oxozirconium carboxylate clusters derived from the corresponding alkoxides.[3] The structures of $Zr_6(OH)_4O_4(OMc)_{12}$ (OMc = methacrylate), [$Zr_6(OH)_4O_4$(acrylate)$_{12}$]$_2$ and $Zr_6(OH)_4O_4(OOCR)_{12}(PrOH)$ [R = $C(Me){=}CH_2$, C_6H_5] are highly condensed, with a $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4$ cluster core and octacoordinate zirconium atoms. When the Zr/bidentate ligand ratio is increased from 1:2 to 1:3, the structures open up, as in $Zr_4O_2(OMc)_{12}$ with a distorted butterfly structure (hepta- and octacoordinate Zr atoms)[3] or polymeric $[Zr(OnPr)(O_3SMe)_3]_\infty$ (heptacoordinate Zr atoms).[4] A high degree of substitution by bidentate ligands is possible because of the high coordination numbers of the zirconium atoms.

In contrast to the compounds discussed above, the maximum coordination number of titanium is 6. This restricts the maximum carboxylate/titanium ratio (x) of oxotitanium carboxylates to 2, i.e. to the composition $TiO(OOCR)_2$ (provided that all carboxylate ligands are bidentate). In oxotitanium carboxylate *alkoxide* derivatives x must be < 2 to accommodate the OR ligands. The maximum value of x found in structurally characterized oxotitanium carboxylate alkoxides to date is 1.33 in $Ti_6O_4(OR)_8(OOCR')_8$ [R′ = Me: R = Et, *n*Bu, *i*Pr;[5] R′ = $C(Me){=}CH_2$: R = Et[6]]. Smaller degrees of substitution were found in $Ti_6O_4(OR)_{12}(OOCR')_4$ [R′ = Me: R = *i*Pr; R′ = $\mu_3\text{-}CCo_3(CO)_9$: R = Et] and $Ti_4O_4(OR)_4[OOC{-}CCo_3(CO)_9]_4$ (R = *i*Pr, Ph).[7] The titanium atoms are octahedrally coordinated in all derivatives, and the carboxylate ligands are bridging. The linkage of the octahedra shows variations with the main difference between the cluster types being the ratio between shared vertices and edges.

Results

We have isolated a crystalline derivative of composition $Ti_9O_8(OPr)_4(OMc)_{16}$ (**1**) with $x = 1.78$. This compound was obtained by treating $Ti(OPr)_4$ with a 4-fold excess of methacrylic acid. The water for the hydrolysis of the OPr groups was generated in situ by esterification of methacrylic acid with the cleaved alcohol. We do not currently have any information regarding the sequence of the substitution and hydrolysis reactions necessary to convert $Ti(OPr)_4$ to **1**. We would like to emphasize that we did not intend to identify all products formed in this particular reaction. Instead, our goal was to gather additional structural information on carboxylate-substituted oxotitanium compounds as potential building blocks in titania-based inorganic-organic hybrid materials. The unusual structure of **1** is shown in Figure 1.

The compound consists of a ring of nine [TiO_6] octahedra linked by six μ_2- and only two μ_3-oxide bridges. All titanium atoms are octahedrally coordinated and all methacrylate groups are bridging, as in the known oxotitanium carboxylates. However, the higher degree of substitution by

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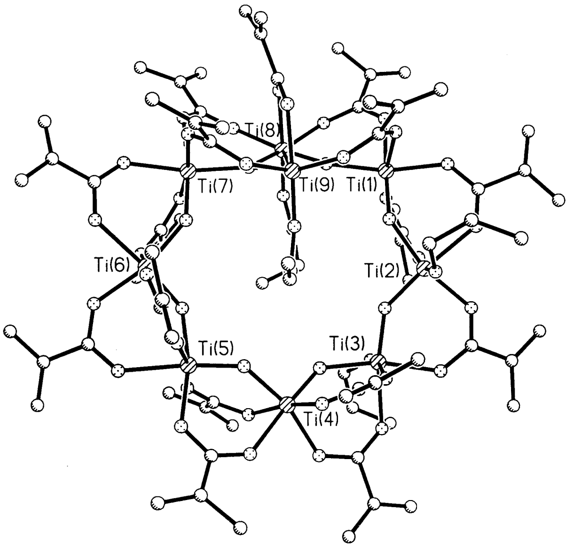
Figure 1. The structure of $Ti_9O_8(OPr)_4(methacrylate)_{16}$ (**1**)[a]

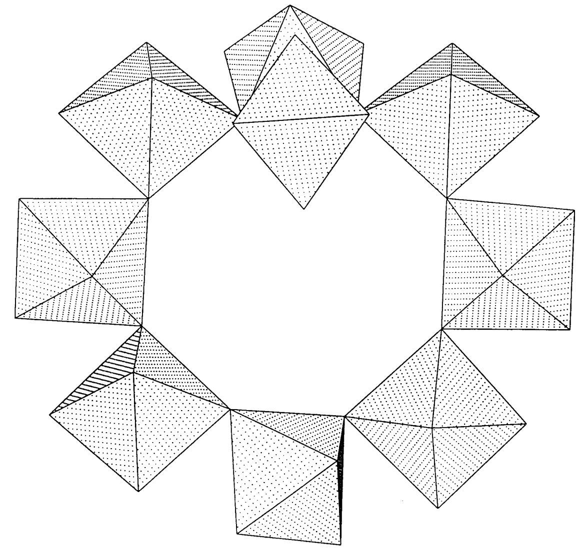


[a] Selected bond lengths [pm] and angles [°]: Ti(1)−O(215) 193.4(11), Ti(1)−O(212) 173.7(10), Ti(2)−O(212) 192.2(11), Ti(2)−O(210) 181.1(12), Ti(3)−O(210) 179.3(11), Ti(3)−O(213) 191.6(11), Ti(4)−O(213) 171.5(11), Ti(4)−O(211) 191.1(12), Ti(5)−O(211) 171.5(11), Ti(5)−O(214) 190.2(11), Ti(6)−O(214) 173.4(11), Ti(6)−O(216) 190.1(12), Ti(7)−O(216) 174.2(11), Ti(7)−O(217) 193.3(12), Ti(8)−O(217) 195.3(11), Ti(8)−O(215) 195.5(11), Ti(9)−O(215) 194.0(10), Ti(9)−O(217) 194.5(11); O(212)−Ti(1)−O(215) 96.6(5), O(210)−Ti(2)−O(212) 100.5(5), O(210)−Ti(3)−O(213) 99.0(5), O(213)−Ti(4)−O(211) 99.6(5), O(211)−Ti(5)−O(214) 97.9(5), O(214)−Ti(6)−O(216) 100.0(5), O(216)−Ti(7)−O(217) 97.6(5), O(215)−Ti(8)−O(217) 78.4(4), O(215)−Ti(9)−O(217) 78.9(5), Ti(3)−O(210)−Ti(2) 142.8(6), Ti(5)−O(211)−Ti(4) 135.4(6), Ti(1)−O(212)−Ti(2) 136.0(6), Ti(4)−O(213)−Ti(3) 136.0(6), Ti(6)−O(214)−Ti(5) 134.8(6), Ti(1)−O(215)−Ti(9) 125.3(6), Ti(1)−O(215)−Ti(8) 134.1(6), Ti(9)−O(215)−Ti(8) 100.5(5), Ti(7)−O(216)−Ti(6) 133.5(6), Ti(7)−O(217)−Ti(9) 126.6(5), Ti(7)−O(217)−Ti(8) 132.2(5), Ti(9)−O(217)−Ti(8) 100.4(5).

the bidentate carboxylate ligands forces the structure to become less condensed, since a coordination number larger than 6 (as in the Zr structures) is not possible. Unlike the less substituted derivatives, which are known, only two of the octahedra [Ti(8) and Ti(9)] share an edge, while the other octahedra [Ti(1)−Ti(7)] share *cis* vertices (Figure 2), i.e. only two oxygen atoms [O(215) and O(217)] are μ_3, while the remaining six oxygen atoms are μ_2.

All but two pairs of neighboring Ti octahedra are bridged by two methacrylate ligands. Ti(8)/Ti(9) and Ti(2)/Ti(3) are connected by only one methacrylate bridge, the second bridge is replaced by two OPr ligands (one at each Ti atom). This makes the macrocycle asymmetric with regard to the OPr substitution. There is a remarkable alternation in the bond distances of the μ_2-O bridges. With the exception of O(210), which bridges the OPr-substituted metal atoms Ti(2) and Ti(3), each μ_2-O bridge exhibits a long (190.1−193.4 pm) and a short (171.5−173.7 pm) Ti−O distance, although the *trans* substituent is the same (carboxylate bridge). The asymmetric Ti−O−Ti distances are compensated for by asymmetric carboxylate bridges, i.e. the Ti−O(carboxylate) distance *trans* to a short Ti−O(bridge) distance is lengthened [208.8−215.5 pm vs. 197.1−210.8 pm for the other Ti−O(carboxylate) distances].

Figure 2. Linkage of the coordination octahedra in $Ti_9O_8(OPr)_4(methacrylate)_{16}$ (**1**)



The overall structure is a balance between the sum of all coordination numbers and charges (c.n. 6 and charge +4 per titanium atom). The structural features in **1** can be understood by first considering a hypothetical structure of $[TiO_{2/2}(OOC{-}R)_2]_n$ with two bridging carboxylate ligands and one μ_2-oxide per formula unit. If two bridging carboxylate ligands are replaced by four monodentate OR groups, the sum of all c.n. is maintained, but there are two additional negative charges. These must be compensated for by the loss of one oxide. This, on the other hand, creates two empty coordination sites, which is compensated for by two other μ_2-oxygen atoms becoming μ_3. $[Ti(\mu_2\text{-}O)(OOCR')_2]_n$ is thus converted into $Ti_n(\mu_2\text{-}O)_{n-3}(\mu_3\text{-}O)_2(OR)_4(OOCR')_{2n-2}$. In all known oxotitanium alkoxide structures,[8] including the carboxylate-substituted derivatives mentioned above,[5][6][7] most $[TiO_6]$ octahedra share edges, and there is a substantial number of μ_3-oxygen atoms, characteristic of the rutile structure. In the structure of **1**, only one pair of octahedra shares an edge and, as a consequence, there are only two μ_3-oxygen atoms. This is an alternative way of expressing the above statement that a high value of x results in more open (= less condensed) structures.

The consequence for sol-gel processing is that for the first-row transition elements the bidentate ligand:metal ratio (x) should not be forced to high values if sufficiently condensed oxo structures are desired. A "natural" limit appears to be $x = 1.33$, as has been found in the structures of the $Ti_6O_4(OR)_8(OOCR')_8$ derivatives. Higher values of x result in polymeric rather than condensed structures. Only if the metal center can increase its coordination number beyond 6 do higher values of x still give condensed oxo clusters.

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Experimental Section

Preparation of **1**: 2.5 g (29 mmol) of methacrylic acid (Aldrich, as received) was mixed under Ar with 2.07 g (7.3 mmol) of $Ti(OPr)_4$ (Aldrich, as received) and stored in a closed Schlenk tube at ambient temperature. An orange solid (2.98 g) precipitated during 7 d, consisting of an approximate 1:1 mixture of an amorphous powder and colorless crystals. A suitable crystal was selected for X-ray structure analysis.

X-ray Structure Analysis for **1**: Monoclinic, space group *Ia*, a = 2357.24(5), b = 1855.37(1), c = 2610.62(6) pm, β = 112.933(1)°, V = 10515.2(3)$\cdot 10^6$ pm^3, $d_{calcd.}$ = 1.362 g cm^{-3} for Z = 4. $F(000)$ = 4456, $\mu(Mo\text{-}K_{\alpha})$ = 0.727 mm^{-1}, λ = 71.073 pm, T = 203 K, crystal size = 0.14 × 0.10 × 0.08 mm. A crystal was sealed in a glass capillary and mounted on a Siemens SMART diffractometer with a CCD area detector. A hemisphere of data was collected by a combination of three sets of exposures (24943 reflections). Each set had a different ϕ angle for the crystal, and each exposure took 15 s and covered 0.3° in ω ($2.8° \le 2\Theta \le 46.0°$). The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied (10712 unique reflections). The structure was solved by direct methods (SHELS86). 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. Refinement converged at R_1 = 0.069 [for 7062 reflections with $I > 2\sigma(I)$], wR_2 = 0.150 $\{w = [\sigma^2(F_o)^2 + (0.0887 P)^2 + 17.77P]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3\}$; final GOF = 1.064. The final difference map showed no peak larger than +0.942 e^{-3} and no hole larger than −0.359 e Å^{-3}.[9]

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[1] U. Schubert, N. Hüsing, N. Lorenz, *Chem. Mater.* **1995**, *7*, 2010.

[2] C. Sanchez, M. In, *J. Non-Cryst. Solids* **1992**, *147/148*, 1.

[3] G. Kickelbick, U. Schubert, *Chem. Ber.* **1997**, *130*, 473. − G. Kickelbick, P. Wiede, U. Schubert, *Inorg. Chem.*, submitted.

[4] A. Lorenz, G. Kickelbick, U. Schubert, *Chem. Mater.*, in press.

[5] S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, *Inorg. Chem.* **1989**, *28*, 4439. − I. Gautier-Luneau, A. Mosset, J. Galy, *Z. Kristallogr.* **1987**, *180*, 83. − I. Laaziz, A. Larbot, C. Guizard, J. Durand, L. Cot, *Acta Crystallogr.* **1990**, *C46*, 2332.

[6] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, *Chem. Mater.* **1992**, *4*, 291.

[7] S. Doeuff, Y. Dromzee, C. Sanchez, *C. R. Acad. Sci., Sect. 2* **1989**, *308*, 1409. − X. Lei, M. Shang, T. P. Fehlner, *Organometallics* **1996**, *15*, 3779.

[8] R. Schmid, A. Mosset, J. Galy, *J. Chem. Soc., Dalton Trans.* **1991**, 1999. − V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park, F. S. Rosenberg, *J. Am. Chem. Soc.* **1991**, *113*, 8190. − V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park, *J. Am. Chem. Soc.* **1993**, *115*, 8469. − V. W. Day, T. A. Eberspacher, Y. Chen., J. Hoa, W. G. Klemperer, *Inorg. Chim. Acta* **1995**, *229*, 391. − N. Stenou, F. Robert, C. Sanchez, *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 487. − C. F. Campana, Y. Chen., V. W. Day, W. G. Klemperer, R. A. Sparks, *J. Chem. Soc., Dalton Trans.* **1996**, 691.

[9] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge C82 1EZ, UK [fax int. code +44(0)1223/336-033, e-mail: deposit@ccdc.cam.ac.uk] quoting the depository number CCDC-100716.

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