

Metal-assisted Activation of the C–O Bond of 2-Hydroxyethylmethacrylate. Synthesis and Molecular Structure of $\text{Ti}_5(\text{OPr}^i)_9(\mu\text{-OPr}^i)(\mu, \eta^2\text{-OC}_2\text{H}_4\text{O})(\mu_3, \eta^2\text{-OC}_2\text{H}_4\text{O})_3(\mu_4, \eta^2\text{-OC}_2\text{H}_4\text{O})$

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$\text{Ti}_5(\text{OPr}^i)_9(\mu\text{-OPr}^i)(\text{OC}_2\text{H}_4\text{O})_5$ is formed by the reaction between $\text{Ti}(\text{OPr}^i)_4$ and 2-hydroxyethylmethacrylate in toluene at room temperature; the pentanuclear aggregate is asymmetric with the titanium atoms displaying coordination numbers of five, six and seven.

Polymerizable ligands have been used in the sol–gel process as a means to develop synchronous polymerization routes to hybrid materials¹ and/or to control particle size and morphology.² 2-Hydroxyethylmethacrylate (HEMA) allows access to non-shrinking sol–gel composites based on silica.¹ It appeared a good candidate for the development of metal alkoxides possessing polymerizable OR ligands, its organic cross-linking functionality being *a priori* more accessible in a metal coordination sphere than that of a methacrylate ligand.³ We report the reaction between titanium alkoxides and HEMA affording the polynuclear glycolate complex $\text{Ti}_5(\text{OPr}^i)_{10}(\text{OC}_2\text{H}_4\text{O})_5$ as a result of C–O bond cleavage reactions mediated by the transition metal.

Titanium isopropoxide in toluene was treated with 2-hydroxy-ethylmethacrylate (1:1 stoichiometry) at room temp. Monitoring of the reaction indicates evolution of the polymerizable ligand with progressive loss of the double bond as evidenced by the disappearance of the $\nu_{\text{C}=\text{C}}$ absorption band at 1637 cm^{-1} in the FTIR and of the multiplets characteristic of the CH_2 groups at δ 6 and 5.5 in the ^1H NMR spectra. FTIR data also support the loss of the carbonyl group. The ^1H NMR pattern is complex suggesting several types of environments for the $\text{OC}_2\text{H}_4\text{O}$ groups; these results were puzzling.[†]

Crystals suitable for X-ray investigation[‡] were obtained by recrystallization from hexane of the crude, pasty product obtained after a reaction time of 20 h. Compound **1** corresponds to a pentanuclear aggregate of formula $\text{Ti}_5(\text{OPr}^i)_9(\mu\text{-OPr}^i)(\mu, \eta^2\text{-OC}_2\text{H}_4\text{O})(\mu_3, \eta^2\text{-OC}_2\text{H}_4\text{O})_3(\mu_4, \eta^2\text{-OC}_2\text{H}_4\text{O})$ (Fig. 1). The most salient feature is the presence of the $\text{OC}_2\text{H}_4\text{O}$ ligands. The

molecular structure is quite asymmetric with three types of surroundings for the metals, Ti(1), Ti(2) and Ti(3) are six coordinate, Ti(4) is seven coordinate and Ti(5) is five coordinate. Variable numbers of terminal isopropoxide ligands, from one for Ti(1) to three for Ti(5), are observed for the different titanium atoms. The ethyleneglycolate ligands derived from HEMA are all chelating-bridging but they display four types of coordination behaviour. One of them is chelating doubly bridging [O(2), O(1)], there are two types of μ_3, η^2 ligands, two of them assemble the three metals by two doubly bridging alkoxy donors [O(5), O(6) and O(8), O(7), respectively], the other is chelating triply bridging [O(9)–O(10)] and finally, the last one O(3)–C(3)–C(4)–O(4) assembles four metals in a fly-over manner (μ_4, η^2). This coordination mode imposes notable strain in the assembly of the various polyhedra, resulting in the sharing of a face between the polyhedra based on Ti(3) and Ti(4). The overall structure is a rather compact Ti_5O_{20} core, it can be considered as corresponding to a distorted rhombus {reminiscent of that of $[\text{Ti}(\text{OR})_4]_4$ albeit the arrangement of the polyhedra is different}⁴ with an additional polyhedron, corresponding to Ti(5) connected along an edge to the polyhedron of Ti(4) (Fig. 2).

The Ti–O bond distances range from 1.72(2) to 2.26(1) Å, the order of variation being $\text{Ti-OPr}^i < \text{Ti-}\eta^2\text{-OC}_2\text{H}_4\text{O} < \text{Ti-}\mu\text{-OPr}^i \sim \text{Ti-}\mu\text{-OC}_2\text{H}_4\text{O} \sim \text{Ti-}\mu_3\text{-OC}_2\text{H}_4\text{O} < \text{Ti-}\mu_4\text{-OC}_2\text{H}_4\text{O}$. Most Ti bridges, even that involving the OPr^i group are asymmetrical, with Ti–O–Ti angles ranging from $140.2(6)$ to $96.3(5)^\circ$. The Ti– OC_2H_4 bond lengths are spread over a large range [1.83(1)–2.26(1) Å], the terminal η^2 -ones [Ti(1)–O(9)

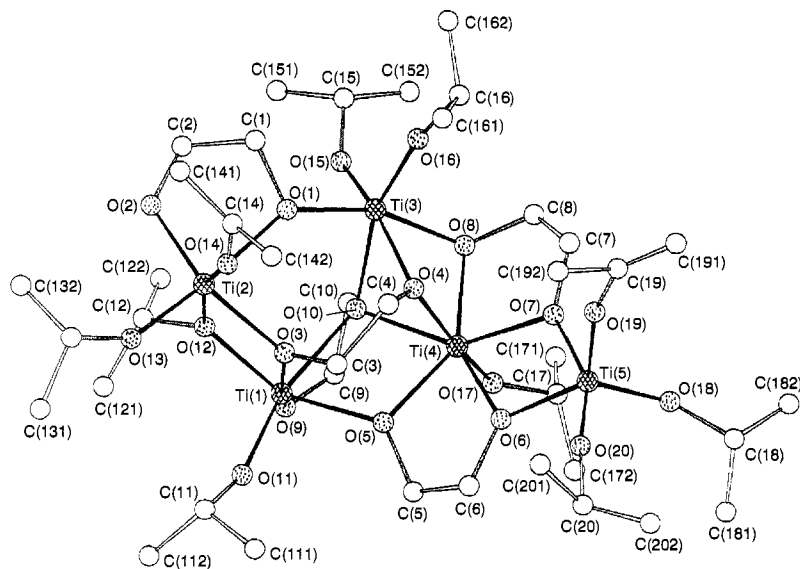


Fig. 1 Molecular structure of compound **1** showing the atom-labelling scheme. Selected distances (Å) and angles ($^\circ$): Ti– OPr^i 1.77(1) av., Ti– $\mu\text{-OPr}^i$ 1.93(1), 2.11(1), Ti– $\eta^2\text{-OC}_2\text{H}_4$ 1.85(1) av., Ti– $\mu\text{-OC}_2\text{H}_4$, 2.00(1)–2.26(1); Ti–O–C 152.8(6) av. (terminal OPr^i)

and Ti(2)–O(2)] being the shortest. The values of the terminal Ti–OPrⁱ bonds lengths (1.72–1.81 Å) are in agreement with those reported in the literature,⁵ while the Ti–OC₂H₄ bond lengths are significantly longer than the values observed for [Ti(OC₂H₄O)₃]²⁻ in which the glycolate ligands are all chelating.⁶ The terminal alkoxo groups have large Ti–O–C angles [mean value 152.81(6)°], as commonly observed for early transition metals. Ti(1), Ti(2) and Ti(3) have severely distorted octahedral surroundings, while the stereochemistry around Ti(5) is that of a capped tetrahedron and that of Ti(4) corresponds to a distorted pentagonal bipyramid. The non-bonding Ti...Ti distances range from 3.021(5) [for Ti(3)...Ti(4)] to 3.952(7) Å [for Ti(1)...Ti(3)], they are typical of other polynuclear titanium compounds.⁵

A surprising feature is the coexistence of adjacent seven- and five-coordinate titanium centres, Ti(4) and Ti(5), respectively. Whereas five-coordinate titanium is quite common for titanium isopropoxide derivatives and has been observed for instance for Sm₄TiO(OPrⁱ)₁₄,⁷ seven-coordinate titanium is to the best of our knowledge unknown for titanium alkoxide chemistry.⁸ The high coordination number is probably favoured by the narrow bite angle of the ethyleneglycolate ligands [79.2(7)° av.]. Oxo and non-oxo titanium alkoxide aggregates of various nuclearity have been reported.^{4,9} Compound **1** represents, to the best of our knowledge, the first example of a pentanuclear titanium alkoxide aggregate. It is also the largest non-oxo alkoxide aggregate reported so far for titanium presumably, as a result of the tendency of the diolate ligands to act as bridging, and thus assembling ligands. Although a number of pentanuclear aggregates, in which the metals are generally assembled around a Xⁿ⁻ ligand (X = oxo, hydroxo, nitrido or carbido), have been reported recently for large metals,¹⁰ M₅ clusters remain scarce.¹¹ The formation of the disymmetric, pentanuclear Ti₅O₂₀ cluster, and the number of terminal isopropoxide ligands borne by the various metallic centres, reflect probably the presence of mono- and di-substituted ethyleneglycolate titanium derivatives together with unconverted Ti(OPrⁱ)₄ in the reaction medium corresponding to a 1 : 1 stoichiometry. The diversity of the bridging–chelating coordination modes might be another important factor in directing the overall assembly.

The striking observation is the formation of the ethyleneglycolate ligands. They can only result from cleavage of the C–O bond of the HOC₂H₄OC(O)CMe=CH₂ ligand. The reaction is selective and compound **1** is obtained in reproducible and high yields (ca. 60% crystalline material), independently of the purity of HEMA (stabilized or distilled). Its formation is likely to be mediated by the electrophilic metal centre and by the generation of five-membered rings. Although the mechanism of

the reaction has not been extensively investigated, one can observe the formation of alkoxide–alcohol intermediates in which the carbonyl moiety interacts with the metal (νCO₂ at 1564 and νOH at 3420 cm⁻¹ in the IR by comparison to 1720 and 3428 cm⁻¹ for free HEMA). Similar complexes have been considered to be involved in the early steps of the synthesis of hydroxyethylmethacrylate–aluminium alkoxides used as catalysts for the ring-opening polymerization of lactides or lactones.¹² When the metal is less coordinatively unsaturated, a slow down of the process is observed and thus also supports assistance by the metal. Moreover, when the reaction with Ti(OPrⁱ)₄ is carried out in isopropyl alcohol or by using the titanium ethoxide oligomer, [Ti(OEt)₄]₄, in toluene, longer reaction times are required for completion of the formation of ethyleneglycolate ligands. Use of larger amounts of the polymerizable alcohol, (e.g. Ti(OPrⁱ)₄; HEMA 1 : 2 stoichiometry) led to a mixture and no complete modification of HEMA was observed after 20 h. On the other hand, alcohol exchange reactions between Si(OEt)₄ and HEMA (1 : 1 stoichiometry) were unsuccessful even under reflux (3 h) in toluene and no evolution of the polymerizable alcohol was observed.

The reactions between titanium or other metal alkoxides and ethylene glycol have been reported to give insoluble derivatives.⁴ Their polymeric nature is probably favoured by hydrogen bonding owing to remaining hydroxy functionalities and complete deprotonation of ethylene glycol usually requires assistance of a base as a general feature.¹³ The synthetic route of **1** offers an easy access to the OC₂H₄O²⁻ ligand. Compound **1** is soluble in common organic solvents (hexane, toluene, THF, less so in alcohols) and can thus be used as a precursor for other titanium based materials. Controlled hydrolysis of **1** in THF indicates differential hydrolysis, the isopropoxide ligands being the most susceptible.

Finally, depending on the reaction conditions (time, solvent, stoichiometry, nature of the metals, nature of the initial OR and thus of the nuclearity), the organic cross-linking sites of precursors to hybrid materials based on metal alkoxides and HEMA can be the expected polymerizable alkoxide at the metal coordination sphere but also non-coordinated moieties resulting from the heterolytic cleavage of the C–O acyl bond. Similar observations—cleavage of the C–O bond—have been observed for HEMA in the presence of other electrophilic metal alkoxides.¹⁴

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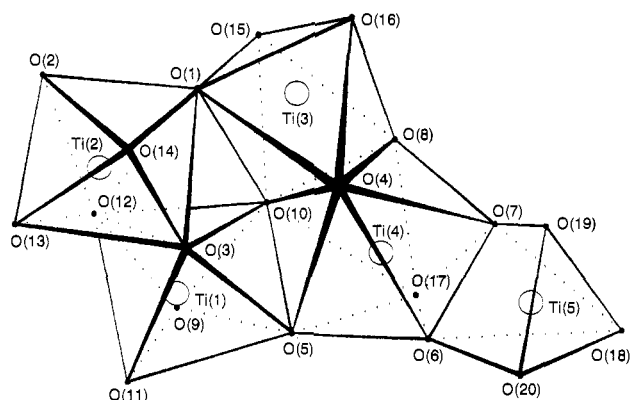


Fig. 2 Polyhedral representation of **1**: octahedra based on Ti(1) and Ti(2) have a common edge, Ti(2) and Ti(3) share an apex, the pentagonal bipyramid based on Ti(4) is connected to the Ti(3) octahedron along a face, to the Ti(1) one by an edge and shares also an edge with the Ti(5) polyhedron

Footnotes

† Spectroscopic data for Ti₅(OPrⁱ)₁₀(OC₂H₄O)₅: IR (Nujol) ν/cm⁻¹ 1164s, 1126s, 1085s, 1033s (νC–OR); 617s, 610s, 550m, 515m, 430m νTi–OR; ¹H NMR (CDCl₃) δ 1.2–1.44 (overlapping doublets, J 6 Hz, 60 H, CH₃), 3.90–5.04 (overlapping multiplets, 30 H, OC₂H₄O and CH).

‡ Crystal data for C₄₀H₉₀O₂₀Ti₅ **1**: M = 1430.6, triclinic, space group P $\bar{1}$; a = 11.513(5), b = 16.096(9), c = 16.148(8) Å, α = 78.70(4), β = 79.49(4), γ = 87.67(4)°, U = 2856(2) Å³, D_c = 1.33 g cm⁻³, for Z = 2, μ(Mo–Kα) = 7.31 cm⁻¹.

The selected crystal, protected with paratone-N (Exxon) was transferred onto a Nonius CAD-4 diffractometer at –100 °C. Intensity data were collected at low temperature using graphite monochromated Mo–Kα radiation (λ = 0.71073 Å). Accurate cell dimensions and orientation matrix were obtained from least-squares refinement of the setting angles of 25 well-defined reflections. No decay in the intensities of two standard reflections was observed during the course of data collection. The usual corrections for Lorentz and polarization effects were applied. Computations were performed using the PC version of CRYSTALS.¹⁵ Scattering factors and corrections for anomalous dispersion were taken from ref. 16. The structure was resolved by direct methods (SHELXS-86)¹⁷ and refined by least-squares analysis with anisotropic thermal parameters for titanium atoms and isotropic thermal parameters for all other non-hydrogen atoms. Hydrogen atoms were introduced as fixed contributors in theoretical

positions and their coordinates were recalculated after each cycle of refinement. The structure was refined to $R = 0.0749$ ($R_w = 0.086$) with the use of 2263 reflections for 286 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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