Syntheses and single-crystal structures of novel soluble phosphonato- and phosphinato-bridged titanium oxo alkoxides

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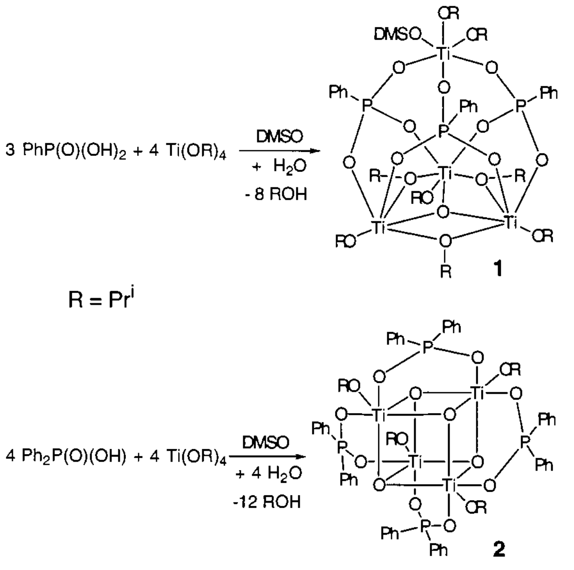
The reactions of $PhP(O)(OH)_2$ or $Ph_2P(O)OH$ with $Ti(OPr^i)_4$ in DMSO give the soluble tetranuclear complexes $[Ti_4(\mu_3\text{-}O)(OPr^i)_5(\mu\text{-}OPr^i)_3(PhPO_3)_3]\cdot DMSO$ 1 or $[Ti(\mu_3\text{-}O)(OPr^i)(Ph_2PO_2)]_4\cdot 0.5DMSO$ 2, the first examples of phosphonato- and phosphinato-bridged titanium oxo alkoxides, which have been characterised by single-crystal X-ray diffraction.

Metal oxo alkoxides are not only models of the molecular species present at the initial stages of the sol–gel processing of metal alkoxides, but they also serve as molecular building blocks for the design of oxide materials by sol–gel processing and metal–organic chemical vapour deposition (MOCVD).[1–3] The reactivity towards hydrolysis and condensation of metal oxo alkoxides is lower than in the parent alkoxides, and may be further decreased *via* replacement of some of the alkoxide ligands by carboxylate, β-diketonate or sulfonate ligands. Furthermore, the use of such ligands allows the introduction of organic functionalities for organic–inorganic hybrid materials applications.[4,5]

Recently, we proposed the use of organophosphorus acids as coupling molecules to prepare organic–inorganic hybrids by a sol–gel route, as the P–C bond is stable towards hydrolysis and P–OH groups readily condense with M–OR groups. A two-step synthesis was used, involving first the condensation between the organophosphorus acid and a metal alkoxide, followed by hydrolysis–condensation of the remaining alkoxy groups.[6] When titanium isopropoxide and phenylphosphonic acid were used as precursors ^{31}P NMR investigations pointed to the formation of a soluble intermediate. In the present work, we report the structural characterization of this intermediate and of another compound obtained starting from titanium isopropoxide and diphenylphosphinic acid (Scheme 1).

To our knowledge, compounds **1** and **2** are the first examples of titanium oxo alkoxides modified by tridentate phosphonate (RPO_3^{2-}) or bidentate phosphinate ($R_2PO_2^-$) ligands, whereas modification by bidentate carboxylate groups has been extensively studied.[7,8] Layered titanium phosphates and phosphonates are well known,[9] and polymeric titanium alkoxo-phosphinates have been reported;[10] however, very few molecular structures of titanium complexes with phosphato,[11,12] phosphonato[13,14] or phosphinato[15] ligands have been reported to date, whereas these ligands have been widely used to synthesise hybrid polynuclear oxo anions such as vanadates[16] and molybdates.[17]

The Ti–O–P bonds in **1** and **2** result from the condensation of P–OH and Ti–OPr^i groups.[11] Most likely, the Ti–O–Ti bonds are formed by partial hydrolysis of Ti–OPr^i groups as non-hydrolytic condensation with elimination of an ether would require temperatures above 150 °C. In the case of **1**, the sources of water could be DMSO and/or phenylphosphonic acid even after careful drying,[15] although condensation of P–OH groups in the presence of $Ti(OPr^i)_4$ cannot be completely ruled out. Nevertheless, in order to obtain **2** in a good yield, water had to be added to the reaction mixture.†



Scheme 1

The molecular structures of **1** and **2** and selected bond distances and angles are given in Figs. 1 and 2.‡ Compound **1** is made up of discrete clusters that consist of four titanium atoms, three tridentate phosphonato groups, three μ-isopropxy groups and one μ_3-oxygen atom. The Ti–O–P core is best described as being based on a six-membered $Ti_3(\mu\text{-}OPr^i)_3$ ring adopting a chair conformation with alternating isopropoxy groups and six-coordinated Ti atoms; these Ti atoms are linked *via* a μ_3-O atom [Ti–μ_3-O–Ti 104.49(8)–106.08(8)°] leading to a Ti_3O_4 fragment. The markedly distorted octahedral geometry at Ti(1), Ti(2), and Ti(3) is built up by two bridging μ-OPr^i groups [Ti–O 2.014(2)–2.044(2) Å], one terminal OPr^i group [Ti–O 1.770(2)–1.781(2) Å], two phosphonato-oxygen atoms [Ti–O 1.947(2)–1.984(2) Å] and the μ_3-oxygen atom which is *trans* to the terminal OPr^i groups [Ti–O 1.949(2)–1.976(2) Å]. The *trans* O–Ti–O angles are in the range 162.27(8)–175.49(8)°. Each phosphonato group bridges two Ti atoms of the six membered ring and Ti(4) [Ti(4)–O 1.955(2)–2.095(2) Å]. In addition to these three phosphonato-oxygen atoms, the distorted octahedral geometry at Ti(4) [O–Ti–O *trans* angles 171.24(8)–172.56(8)°] involves two terminal OPr^i groups [Ti(4)–O(18)/O(19) 1.833(2)/1.786(2) Å] and a coordinated DMSO molecule [Ti(4)–O(4) 2.059(2) Å].

The molecular structure of **2** is best described as a distorted cube consisting of a Ti_4O_4 core with the titanium and oxygen atoms occupying alternating corners. The Ti atoms show a distorted octahedral geometry [*trans* O–Ti–O angles 161.61(7)–177.29(7)°] built up by one terminal OPr^i group [Ti–O 1.759(2)–1.790(2) Å], two phosphinato oxygen atoms [Ti–O 2.002(2)–2.040(2) Å] and three unsymmetrically bonded μ_3-oxygen atoms. The Ti–μ_3-O bonds *trans* to the isopropxy groups are

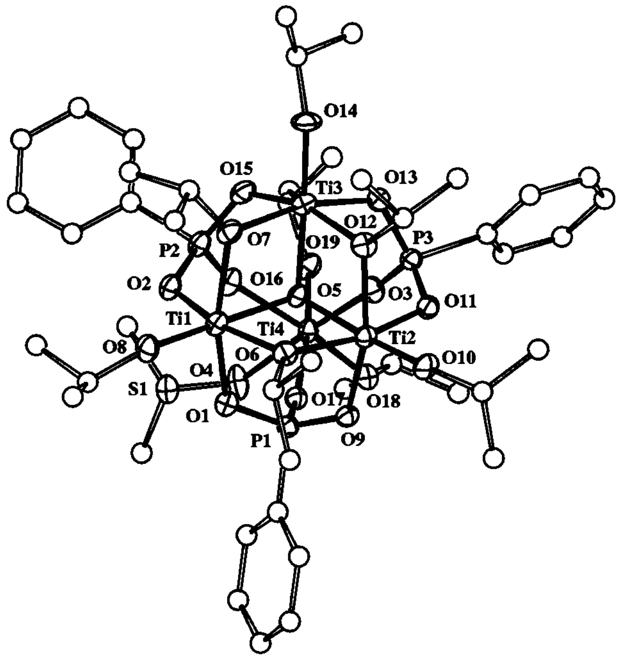


Fig. 1 Molecular structure of **1**. Thermal ellipsoids are shown at 60% probability. For clarity, hydrogens atoms are omitted and carbon atoms are represented by open circles. Selected interatomic distances (Å) and bond angles (°) are: Ti(1)–O(1) 1.953(2), Ti(1)–O(5) 1.976(2), Ti(1)–O(6) 2.014(2), Ti(1)–O(8) 1.781(2), Ti(4)–O(3) 1.955(2), Ti(4)–O(16) 2.095(2), Ti(4)–O(17) 2.040(2); O(1)–Ti(1)–O(7) 162.33(8), O(2)–Ti(1)–O(6) 165.22(8), O(5)–Ti(1)–O(8) 175.37(8), O(3)–Ti(4)–O(4) 172.56(8), O(16)–Ti(4)–O(18) 171.24(8), O(17)–Ti(4)–O(19) 171.83(8).

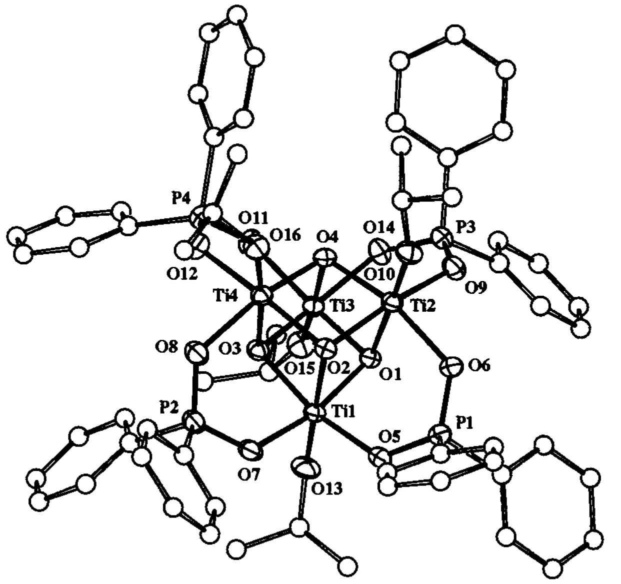


Fig. 2 Molecular structure of **2**. Thermal ellipsoids are shown at 60% probability. For clarity, hydrogens atoms are omitted and carbon atoms are represented by open circles. Selected interatomic distances (Å) and bond angles (°) are: Ti(1)–O(1) 1.903(2), Ti(1)–O(2) 2.160(2), Ti(1)–O(3) 1.938(2), Ti(1)–O(5) 2.004(2), Ti(1)–O(7) 2.014(2), Ti(1)–O(13) 1.765(2); O(1)–Ti(1)–O(7) 164.32(7), O(2)–Ti(1)–O(13) 177.29(7), O(3)–Ti(1)–O(5) 162.03(7).

slighlty longer [Ti–μ_3-O 2.107(2)–2.163(2) Å] than those *trans* to the phosphinato oxygen atoms [Ti–μ_3-O 1.888(2)–1.938(2) Å]. Four sides of the Ti_4O_4 cube are capped by four phosphinato groups, each bridging two Ti atoms. This type of structure has been proposed for oxotitanium compounds modified by phosphonato[12] or carboxylato ligands.[18]

The basic structural arrangement of **1** and **2** is retained in solution, as demonstrated by the ^{31}P NMR data in solution and in the solid-state.† In the field of organic–inorganic hybrids, these clusters present two main interests: first, as intermediates in the sol–gel route to hybrids that we are developing, secondly, as novel building blocks for the preparation of nanostructured hybrid materials.

Notes and references

† *Syntheses*: $[Ti_4(\mu_3\text{-}O)(OPr^i)_5(\mu\text{-}OPr^i)_3(PhPO_3)_3]\cdot DMSO$ **1**. $Ti(OPr^i)_4$ (3.56 g, 12.52 mmol) was added to a solution of $PhP(O)(OH)_2$ (1.00 g, 6.33 mmol) in 5 mL of dried DMSO, resulting in a cloudy mixture. After several hours a clear solution was obtained. Colourless crystals of **1** were obtained from this solution after several days. These crystals were filtered off, washed with two 5 mL portions of Et_2O and dried *in vacuo* giving 1.02 g [40% yield based on $PhP(O)(OH)_2$]. Colourless needles suitable for single-crystal X-Ray diffraction were recrystallised from a concentrated DMSO solution and mounted in inert oil. Calc. for $C_{44}H_{77}O_{19}P_3STi_4$: C, 43.08; H, 6.78; P, 7.57; S, 2.61; Ti, 15.61. Found: C, 48.85; H, 6.52; P, 8.20; S, 3.22; Ti, 15.80. ^{31}P NMR: δ 8.45, 8.65 (CH_2Cl_2, 200 MHz), 8.0, 7.0 (solid-state, 400 MHz). $[Ti(\mu_3\text{-}O)(OPr^i)\text{-}(Ph_2PO_2)]_4\cdot 0.5DMSO$ **2**. To a solution of $Ti(OPr^i)_4$ (1.00 g, 3.52 mmol) in 15 mL of dried DMSO was added dropwise a solution of $Ph_2P(O)OH$ (767 mg, 3.52 mmol) and H_2O (34 µL, 1.88 mmol) in 15 mL of DMSO. After stirring at room temperature for 12 h, the resulting cloudy mixture was heated to 80 °C until a clear solution was obtained, which was then allowed to cool slowly to ambient temperature. The crystallised colourless needles were filtered off, washed with 3 mL dried DMSO and dried *in vacuo* giving 720 mg (58% yield) of **2**. X-Ray quality crystals were obtained from a dilute DMSO solution and mounted in inert oil. Calc. for $C_{61}H_{71}O_{16.5}P_4S_{0.5}Ti_4$: C, 52.35; H, 5.48; P, 8.85; S, 1.15; Ti, 13.68. Found: C, 51.98; H, 6.30; P, 10.10; S, 1.37; Ti, 15.10. ^{31}P NMR: δ 33.0 (CH_2Cl_2, 200 MHz), 33.3 (solid-state, 400 MHz).

‡ Data for both structures were collected on a STOE-IPDS with Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystal data for **1** : $C_{44}H_{77}O_{19}P_3STi_4$ at 160 K, $M = 1226.63$, monoclinic, $P2_1/n$ (no. 14), $a = 11.6668(13)$, $b = 13.9198(12)$, $c = 35.885(3)$ Å, $\beta = 90.533(15)°$, $V = 5827.5(10)$ Å^3, $D_c = 1.398$ g cm^{-3}, $Z = 4$, $\mu = 0.712$ mm^{-1}. Of the 27893 reflections, 5980 unique reflections were used in the final least-squares refinement on F_o^2 for 640 variable parameters to yield $wR(\text{all}) = 0.0549$ and $R(\text{obs}) = 0.0249$ for 4478 observed reflections $>4\sigma(F_o)$. For **2** $C_{61}H_{71}O_{16.5}P_4S_{0.5}Ti_4$ at 180 K, $M = 1399.69$, monoclinic, $P2_1/c$ (no. 14), $a = 12.4983(10)$, $b = 16.1317(14)$, $c = 33.706(3)$ Å, $\beta = 97.141(10)°$, $V =$ 6743.1(10) Å^3, $D_c = 1.379$ g cm^{-3}, $Z = 4$, $\mu = 0.630$ mm^{-1}. Of the 52425 reflections, 10165 unique reflections were used in the final least-squares refinement on F_o^2 for 793 variable parameters to yield $wR(\text{all}) = 0.0607$ and $R(\text{obs}) = 0.0240$ for 6923 observed reflections $>4\sigma(F_o)$. CCDC reference number 186/1420. See http://www.rsc.org/suppdata/dt/1999/1537/ for crystallographic files in .cif format.

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