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Mechanistic aspects of the hydrolysis and condensation of titanium alkoxides complexed by tripodal ligands†

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Titanium alkoxides $Ti(OR)_4$ (R = Et, Pr^i and Bu^n) react with tris(hydroxymethyl)nitromethane (THMNM-H_3) with retention of their basic tetrameric structural unit even after hydrolysis and condensation. The chemical reactivity of these molecular precursors are analyzed using a model based on a point charge approximation of density functional equations. Based on these theoretical results plausible reaction pathways can be anticipated, providing a deep insight into the mechanism of formation of these new molecular structures. Consequences for the sol–gel processing of titania-based material and for the rational design of novel solid-state materials are also briefly addressed.

Introduction

Transition metal alkoxides $M(OR)_n$ are widely used as molecular precursors of metal oxides $MO_{n/2}$ in sol–gel chemistry.[1] Among them titanium(IV) alkoxides have been attracting much attention owing to their widespread occurrence in conventional (*e.g.* paints, inks, plastics, cosmetics, ceramics) as well as high-tech materials (*e.g.* coatings, membranes, photoanodes, capacitors). Moreover, the non-toxicity of titania, TiO_2, appears to be rather appealing for biological applications requiring either inert supports such as for enzyme immobilization or hybrid organic–inorganic networks for biomineralization. Titanium alkoxides are easily hydrolyzed affording oligomeric oxo-alkoxide species displaying a wide range of nuclearity: trimers,[2] heptamers,[3] decamers,[4] undecamers,[5] dodecamers[5] and hexadecamers.[3] In all cases mentioned above, the basic tetrameric unit of these compounds[6,7] is either lost (R = Pr^i) or is deeply engaged in compact edge-sharing assemblies (R = Et). From a mechanistic point of view, the formation of a $[Ti(OR)_4]_4$ oligomer from tetrahedral $Ti(OR)_4$ monomers may be rationalized by noticing that direct addition of two $Ti(OR)_4$ tetrahedra leads to a dimer $[(RO)_4Ti(OR)_2Ti(OR)_4]$ displaying edge-sharing between a $Ti(OR)_6$ octahedron and a $Ti(OR)_4$ tetrahedron (Fig. 1).

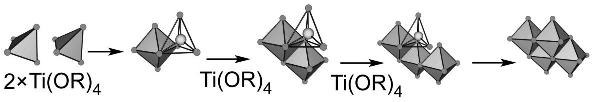

Fig. 1 Formation of a planar $[Ti_4(OR)_{16}]$ tetramer through successive addition of $Ti(OR)_4$ tetrahedra.

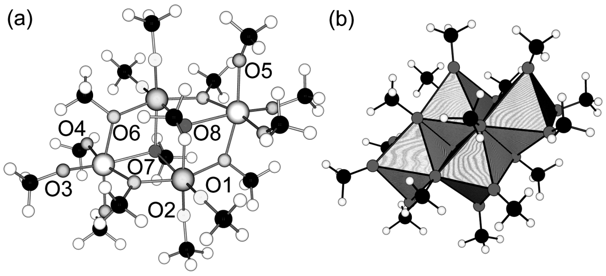

Fig. 2 (a) Molecular structure of $Ti(OMe)_4$ according to Wright and Williams.[6] Partial charges on oxygen atoms are −0.740 (O8), −0.665 (O6), −0.663 (O7), −0.581 (O1), −0.580 (O2), −0.527 (O3), −0.497 (O4) and −0.484 (O5). (b) Polyhedral view of the $[Ti_4(OMe)_{16}]$ tetramer.

Repetition of this process may lead either to a tetramer $Ti_4(OR)_{16}$ (smallest cyclic species containing only sixfold-coordinated titanium atoms) or to an infinite edge-sharing octahedral chain $[(RO)_2Ti(OR)_{4\times 1/2}] \equiv Ti(OR)_4$. Although for R = Me, both structures have been characterized in the solid state,[8] only in the case of the tetrameric unit was its structure elucidated by a single-crystal X-ray diffraction study.[6] As shown in Fig. 2, the existence of three kinds of OR groups (ten terminal OR positions, four μ_2-OR bridges and two μ_3-OR bridges) in this tetrameric structure raises the question of their relative reactivity towards hydrolysis or substitution upon reaction with X–OH molecules. Another interesting point concerns the possibility of molecular control of the oxolation process by using such oligomers as building blocks for a rational design of novel solid-state materials[9] or of porous metal–organic frameworks.[10] This paper is an attempt to provide some experimental and theoretical answers to these fundamental questions which appears to be relevant both to supramolecular and sol–gel chemistry.

Theory

Within the frame of the partial charge model,[11] any chemical compound can be characterized by four global mean values, symbolized hereafter as ⟨EN⟩, ⟨GH⟩, ⟨EB⟩ and ⟨GI⟩. ⟨EN⟩ corresponds to the mean electronegativity of the system and may be identified to the energy situated halfway between the HOMO and the LUMO. $e^2\langle GH\rangle$ measures the global hardness which should scale like the HOMO–LUMO gap. ⟨EB⟩ reflects the energetic balance between all attractive ($\delta^+ \cdots \delta^-$) and repulsive ($\delta^+ \cdots \delta^+$ or $\delta^- \cdots \delta^-$) interactions between atomic pairs. Finally, ⟨GI⟩ is a global ionicity index ranging from 0 to 100% which helps to decide whether a given compound should be considered as ionic (⟨GI⟩ >50%) or covalent (⟨GI⟩ <50%). Partial charges δ have been evaluated using the Allen electronegativity

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† Electronic supplementary information (ESI) available: Partial charge calculations and spectroscopic data of reagents. See http://www.rsc.org/suppdata/dt/b1/b103398k/

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scale[12,13] and atomic orbital radii[14] for approximating the chemical hardness. Detailed reports of all partial charge calculations made for this paper (charge distribution, frontier and retrosynthetic indexes for each atom in the asymmetric unit cell) are available as ESI. †

Applying this partial charge model to the $Ti(OMe)_4$ molecular network leads to $\langle EN \rangle = 12.37$ V, $e^2\langle GH \rangle = 5.7$ eV and $\langle GI \rangle = 31.3\%$. A comparison between the electrostatic balances (EB) of the network ($\langle EB \rangle_{net} = -139.3$ eV for $Z = 1$) and of the isolated tetramer ($\langle EB \rangle_{mol} = -139.2$ eV) shows that crystal packing forces are rather weak (-4.1 kJ mol^{-1}). Retrosynthetic indexes[11] reveal that these van der Waals interactions are mainly concentrated on bridging groups (μ_3-OR and μ_2-OR). However, NMR studies on these oligomeric titanium alkoxides at room temperature reveal that bridging and terminal OR groups are indistinguishable on the NMR time-scale. Since the proton transfer from an incoming water molecule is considerably faster than the OR exchange process, this particular geometry raises the problem of the relative reactivity of bridging and terminal OR groups. Fig. 2 shows the charge distribution derived from our partial charge model. It may be convenient to convert the negative charges found on oxygen atoms into approximate pK_a values[15] (±1 unit) using the following relationship adapted to the Allen scale: $-pK_a = 17.3 + 39.5 \times q(O)$. The result obtained clearly demonstrates a significantly higher basicity for bridging groups (pK_a: O8 = 11.9, O6 = 9.0 and O7 = 8.9) than for terminal groups (pK_a: O1 = 5.7, O2 = 5.6, O3 = 3.5, O4 = 2.3 and O5 = 1.8). These results indicate that bridging groups should be hydrolyzed first, thus explaining the rather compact structures found for the resulting oxo-alkoxides, and the localization of the oxo groups at the core of the architecture.

Based on these results, we have investigated the possibility of substituting all reactive bridging OR groups by a suitable multidentate ligand. The planar geometry of the tetramer and the triangular disposition of the bridging OR groups suggested the use of a tripodal ligand of the type $XC(CH_2OH)_3$. A survey of the Cambridge Structural Database showed that tris(hydroxymethyl)ethane or tris(hydroxymethyl)propane react with titanium isopropoxide to yield a tetrameric complex in the expected way,[14] despite the fact that titanium isopropoxide is known to be monomeric in the liquid state.[16] In order to elucidate the influence of the OR group, we have undertaken a structural investigation on products formed by reacting $Ti(OR)_4$ (R = Et, Pr^i and Bu^n) with tris(hydroxymethyl)nitromethane (THMNM-H_3). It is worth noting that the presence of the nitro group allows on one hand ^{17}O- and ^{14}N-NMR studies and, on the other hand, further functionalization of the ligand.

Experimental

All reagents were commercial products bought in their purest form and used without further purification. ^1H and ^{13}C NMR spectra were recorded at 200 MHz on a BRUKER WP200 SY spectrometer. ^{17}O and ^{14}N NMR spectra were recorded at 400 MHz in 10 mm tubes on a BRUKER spectrometer. References for ^{17}O and ^{14}N NMR chemical shifts were tap water and aqueous nitrate ion, respectively. FT-IR spectra were recorded between 400 and 4000 cm^{-1} on a BRUKER IF25 spectrometer. Spectroscopic data of reagents are provided as ESI. †

Reaction of $Ti(OEt)_4$ with THMNM-H_3 1

Translucid platelet-like crystals with hexagonal morphology were formed after few hours from a clear yellow solution obtained by injecting 20 ml of a 0.33 M solution of THMNM-H_3 in ethanol into 14 ml of pure titanium ethoxide (67 mmol) under vigorous stirring.

IR (KBr, cm^{-1}): 1534s (ν_{as}N–O), 1375s, 1446m, 1375s (ν_s-N–O), 1343s. ^1H NMR ($CDCl_3$): δ 1.15 (overlapping multiplets, 15 H, CH_3), 1.64 (singlet, large, OH), 3.71 (quadruplet, 2 H, CH_2), 4.32–4.97 (overlapping multiplets, 14 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 18.4 (CH_3), 19.3 (CH_3), 19.6 (CH_3), 58.4 (μ_3-OCH_2), 72.1 (μ_2-OCH_2), 73.1 (OCH_2), 74.2 (OCH_2), 78.4 (OCH_2), 84.6 (CNO_2). ^{17}O NMR ($CDCl_3$): δ −184.9 (μ_3-OCH_2), 116.8 (μ_2-OCH_2), 423.8 (OCH_2), 840.7 (NO_2). ^{14}N NMR ($CDCl_3$): δ 250.3 (NO_2).

Reaction of $Ti(OPr^i)_4$ with THMNM-H_3 2

Translucid platelet-like crystals with square morphology were formed within a few days from a clear colorless solution obtained by injecting 3 ml of a 0.33 M solution of THMNM-H_3 in isopropanol into 40 ml of pure titanium isopropoxide (134 mmol) under vigorous stirring.

IR (KBr, cm^{-1}): 1542s (ν_{as}N–O), 1453m, 1347s (ν_sN–O). ^1H and ^{13}C NMR ($CDCl_3$): hydrolyzed species. ^{17}O NMR ($CDCl_3$): δ 296 (μ_3-OTi), 42 (μ_4-OTi), 532 (NO_2). ^{14}N NMR ($CDCl_3$): δ 261.7 (NO_2).

Reaction of $Ti(OBu^n)_4$ with THMNM-H_3 3

Translucid rod-like crystals suitable for X-ray diffraction were deposited after a week from a clear yellowish solution obtained by injecting 45 ml of a 0.33 M solution of THMNM-H_3 in *n*-butanol into 22.5 ml of pure titanium *n*-butoxide (132 mmol) under vigorous stirring.

IR (KBr, cm^{-1}): 1540s (ν_{as}N–O), 1462m, 1373m, 1342s (ν_sN–O). ^1H, ^{13}C, ^{17}O and ^{14}N NMR ($CDCl_3$): hydrolyzed species.

Crystal structure determination

X-Ray single crystal diffraction measurements were made using a Philips PW1100/16 diffractometer using graphite monochromated Cu-Kα radiation.

It is worth noting that in contrast to **2**, crystal data for **1** and **3** show some fairly large thermal displacement parameters. Despite the fact that the data were recorded at low temperature (173 K), this shows that some terminal ethoxy, butoxy and nitro groups are still vibrating. This is well in line with NMR data showing that these compounds are indeed very labile species and highly susceptible to hydrolysis. Consequently, if the titanium oxygen cores are correct, further data recording at lower temperature under an inert atmosphere is needed to confirm the position of some of these terminal groups.

Crystal data. $C_{28}H_{62}N_2O_{20}Ti_4$, $M = 938.4$, monoclinic, space group $P2_1/n$ (no. 14), $a = 13.970(4)$, $b = 11.088(3)$, $c = 17.488(5)$ Å, $\beta = 96.19(2)°$, $U = 2693.1$ Å^3, $T = 173$ K, $Z = 2$, μ(Cu-Kα) = 54.840 cm^{-1}, 3552 reflections measured, 2622 unique ($R_{int} = 0.043$). The final $wR(F^2)$ was 0.070.

Crystal data. $C_{38}H_{82}N_2O_{20}Ti_4$, $M = 1078.7$, monoclinic, space group $C2/c$ (no. 15), $a = 18.351(5)$, $b = 13.158(4)$, $c = 18.182(5)$ Å, $\beta = 102.44(2)°$, $U = 4287.2$ Å^3, $T = 173$ K, $Z = 4$, μ(Cu-Kα) = 68.101 cm^{-1}, 2634 reflections measured, 1723 unique ($R_{int} = 0.048$). The final $wR(F^2)$ was 0.063.

Crystal data. $C_{80}H_{168}N_4O_{38}Ti_8$, $M = 2177.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.057(3)$, $b = 14.115(4)$, $c = 18.362(5)$ Å, $\alpha = 70.45(2)$, $\beta = 81.54(2)$, $\gamma = 86.30(2)°$, $U = 2670.8$ Å^3, $T = 173$ K, $Z = 1$, μ(Mo-Kα) = 6.358 cm^{-1}, 11 266 reflections measured, 5089 unique ($R_{int} = 0.078$). The final $wR(F^2)$ was 0.093.

CCDC reference numbers 158128–158130.

See http://www.rsc.org/suppdata/dt/bl/b103398k/ for crystallographic data in CIF or other electronic format.

Results

Compound **1** displays the same basic structural unit as $Ti(OEt)_4$[7] with, as expected, all six bridging OR groups substituted

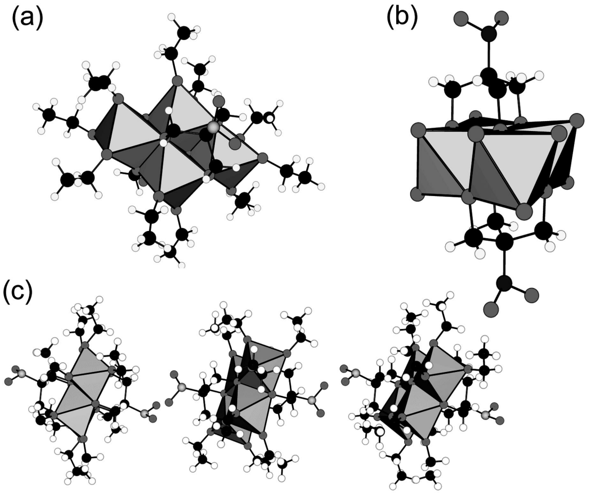

Fig. 3 (a) Molecular structure of compound **1**. (b) Sandwich structure of **1**. (c) van der Waals chain through nitro groups based on **1**. Selected distances (Å) and angles (°): Ti–OEt 1.761(3)–1.800(3), Ti–(μ_2-OH$_2$) 1.960(3)–2.140(3), Ti–(μ_3-OCH$_2$) 2.170(3)–2.243(3); Ti–(μ_3-O)–Ti 97.6(1)–106.7(1), Ti–(μ_2-O)–Ti 109.0(1), Ti–O–Et 130.5(1)–164.2(1).

by two tripodal ligands. The two tripods are situated above and below the plane defined by the four titanium atoms (Fig. 3).

The tetrameric unit of **1** may be described as $[Ti_4(OEt)_{10}\text{-}\{(\mu_2\text{-}OCH_2)_2(\mu_3\text{-}OCH_2)C(NO_2)\}_2]$. In the solid state, these units are strongly associated together through disordered nitro groups leading to a 1D van der Waals network. From an electronic point of view, this network is more electronegative ($\langle EN \rangle = 13.03$ eV) and less ionic ($\langle GI \rangle = 25.8\%$) than the one based on $[Ti_4(OMe)_{16}]$ tetramers. Owing to some disorder around the nitro groups it is not possible to give a reliable estimation of the van der Waals energy. However, it should be fairly weak as the electrostatic balance of the whole network is found to be $\langle EB \rangle_{net} = -153.87$ eV, a value comparable to that obtained for the free tetramer ($\langle EB \rangle_{mol} = -153.99$ eV). More interesting are the predicted pK_a values for oxygen atoms of the ligand. These range from -8 for the nitro group to $+11.0$ for the μ_3-OCH$_2$ moiety of the THMNM ligand. Terminal OEt groups are found to be more basic than OMe groups ($4.7 \le pK_a \le 5.6$), whereas for the remaining μ_2-OCH$_2$ moieties a value around 8.6 is obtained.

In a very similar way, the tetrameric unit of **2** may be described as $[Ti_4(OPr^i)_{10}\{(\mu_2\text{-}OCH_2)_2(\mu_3\text{-}OCH_2)C(NO_2)\}_2]$. As before, these units are further associated in the solid state through nitro groups leading to a 1D van der Waals network (Fig. 4). From an electronic point of view, this network is more electronegative ($\langle EN \rangle = 13.22$ eV) and less ionic ($\langle GI \rangle = 21.77\%$) than the one with ethoxide-based tetramers. As nitro groups are found to be ordered in **2**, it is possible to compare the electrostatic balance of the whole network ($\langle EB \rangle_{net} = -154.95$ eV) to that of the free tetramer ($\langle EB \rangle_{mol} = -154.67$ eV). Van der Waals crystal packing forces are found to be 7 times stronger (-27.4 kJ mol^{-1}) for the THMNM-substituted tetramer than for the $[Ti_4(OMe)_{16}]$ tetramers. Predicted pK_a values for oxygen atoms of the ligand range from -7.8 for the nitro group up to $+10.8$ for the μ_3-OCH$_2$ moiety of the THMNM ligand. Terminal OPr^i groups are found to be slightly less basic than OEt groups ($4.3 \le pK_a \le 5.4$), whereas for the remaining μ_2-OCH$_2$ moieties a pK_a value of *ca.* 8.6 is obtained. This value is almost the same as that obtained for the ethoxy-based THMNM tetramer.

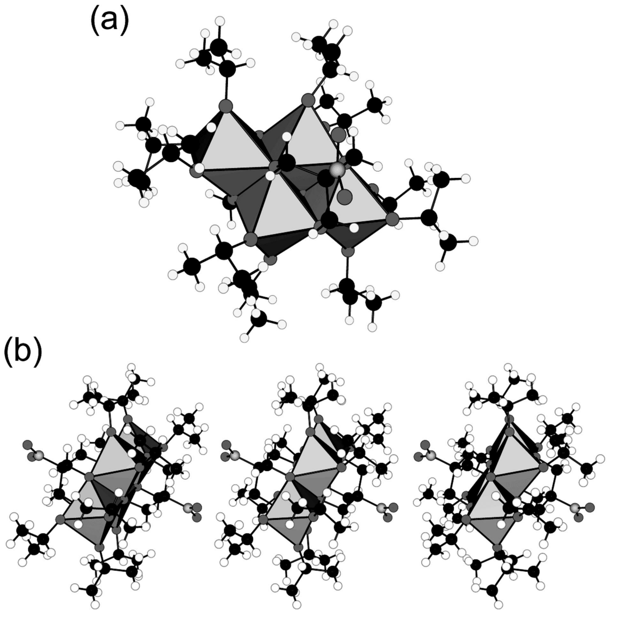

Fig. 4 (a) Molecular structure of compound **2**. (b) van der Waals chain through nitro groups based on **2**. Selected distances (Å) and angles (°): Ti–OPr^i 1.757(3)–1.819(3), Ti–(μ_2-OPr^i) 1.953(3)–2.155(3), Ti–(μ_3-OPr^i) 2.258(3); Ti–(μ_3-OPr^i)–Ti 98.1(1)–106.2(1), Ti–(μ_2-O)–Ti 109.5(1)–111.0(1), Ti–O–Pr^i 128.6(1)–164.9(1).

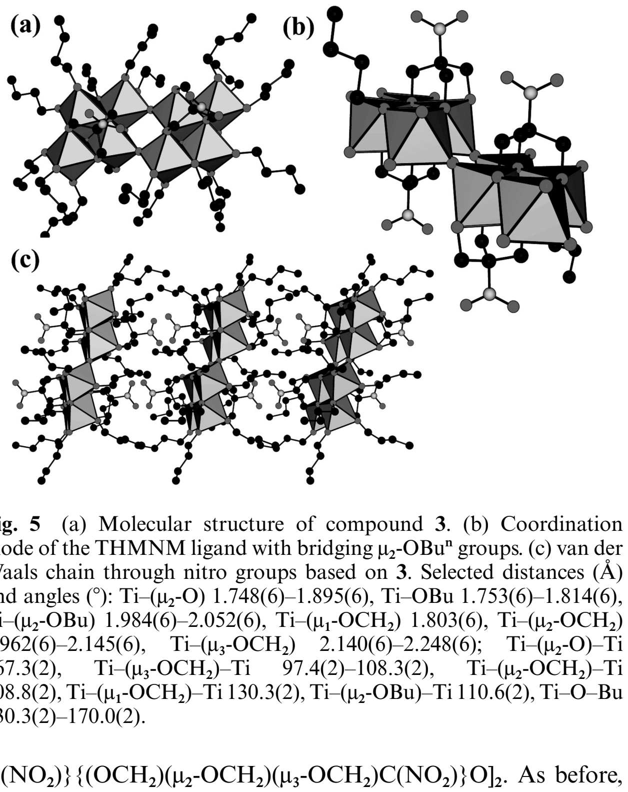

Fig. 5 (a) Molecular structure of compound **3**. (b) Coordination mode of the THMNM ligand with bridging μ_2-OBu^n groups. (c) van der Waals chain through nitro groups based on **3**. Selected distances (Å) and angles (°): Ti–(μ_2-O) 1.748(6)–1.895(6), Ti–OBu 1.753(6)–1.814(6), Ti–(μ_2-OBu) 1.984(6)–2.052(6), Ti–(μ_1-OCH$_2$) 1.803(6), Ti–(μ_2-OCH$_2$) 1.962(6)–2.145(6), Ti–(μ_3-OCH$_2$) 2.140(6)–2.248(6); Ti–(μ_2-O)–Ti 167.3(2), Ti–(μ_3-OCH$_2$)–Ti 97.4(2)–108.3(2), Ti–(μ_2-OCH$_2$)–Ti 108.8(2), Ti–(μ_1-OCH$_2$)–Ti 130.3(2), Ti–(μ_2-OBu)–Ti 110.6(2), Ti–O–Bu 130.3(2)–170.0(2).

In contrast with **1** or **2** compound **3** is a hydrolyzed product. Interestingly enough, it displays exactly the same basic structural unit with a butoxy group replacing the ethoxy and isopropoxy groups respectively, except that two such units are fused through two μ_2-oxo groups (Fig. 5). The octameric unit of **3** may be described as $[Ti_4(OBu^n)_7(\mu_2\text{-}OBu^n)\{(\mu_2\text{-}OCH_2)_2(\mu_3\text{-}OCH_2)C(NO_2)\}\{(OCH_2)(\mu_2\text{-}OCH_2)(\mu_3\text{-}OCH_2)C(NO_2)\}O]_2$. As before, these units are further associated in the solid state through nitro groups leading to a 1D van der Waals network. As hydrogen coordinates are not available for this refinement, no electronic signature for this compound may be given.

Discussion

Based on the above mentioned observations, one may propose some mechanistic conclusions concerning the hydrolysis and condensation of these THMNM-based titanium alkoxides. Although primary and secondary titanium alkoxides are known to have different molecular structures, the same tetrameric form is obtained after reacting these alkoxides with THMNM-H$_3$

indicating a strong structuring role of the THMNM ligand. Thus, the present contribution shows that it is possible to change the OR group while maintaining the molecular structure. Moreover, the overall affinity of oxygen atoms for protons is not significantly modified after complexation. Consequently, and in agreement with other experiments,[17] these complexed titanium alkoxides are as reactive towards hydrolysis as uncomplexed ones. As evidenced by our NMR data, the overall susceptibility towards hydrolysis was found to be $Bu^n >> Pr^i > Et$, and one may ask for a simple explanation for such a behavior. On purely electronic grounds, partial charge calculations made on these $Ti_4(OR)_{10}(THMNM)_2$ tetramers ($R = Et, Pr^i$) show that the two compounds are virtually indistinguishable: $q[Ti(OR)_3] = +2.512$ ($R = Et$), $+2.497$ ($R = Pr^i$) and $q[Ti(OR)_2] = +2.397$ ($R = Et$), $+2.396$ ($R = Pr^i$). Very similar values are also found for the terminal OR groups: $\langle q(OEt)\rangle = -0.572$ and $\langle q(OPr^i)\rangle = -0.562$. Consequently, solvation effects are expected to play a major role to explain the different hydrolytic behavior of the two tetramers. A possible explanation would then be that hydrogen bonding interactions between the ethoxy-based tetramer and ethanol should be more important than hydrogen bonding between the isopropoxy-based tetramer and isopropanol. Further calculations including interactions with solvent molecules are thus needed to clarify further this point.

Nevertheless, our results also show that there is a clear benefit for substituting bridging OR groups with a multidentate ligand. This substitution, obviously, does not alter the affinity of oxygen for water, but does prevent the rapid elimination of the THMNM ligand. Accordingly, the removal of such a ligand would require the simultaneous attack of three water molecules upon a single tetramer, a rather unlikely process for entropic reasons. Finally, the fact that the THMNM ligand is effectively attacked by water molecules is demonstrated by the butoxide-based structure. The observed octamer is obviously made after partial hydrolysis and further oxolation of four terminal butoxy groups between two complexed tetramers. If the THMNM ligand was significantly inert in this process, the octamer would have displayed only terminal butoxy groups. As shown in Fig. 4 this is not the case as two butoxy ligands are found in bridging positions. The occurrence of these μ_2-OBu^n groups may be explained by assuming that the μ_3-OCH_2 moiety have been first hydrolyzed as suggested by our predicted pK_a values. Since the THMNM ligand is still linked by its remaining two arms to the tetramer, it is not eliminated and the uncomplexed arm is able to react with a neighbouring terminal butoxy group to form a new link between the OCH_2 moiety and titanium. A fast cyclic permutation between three neighouring μ_2-$OCH_2 \rightarrow \mu_3$-$OH \rightarrow \mu_1$-OBu^n groups should then lead to a hydroxo group in the terminal position (μ_1-OH), ideally placed for undergoing the final oxolation reaction and to the final observed structure: μ_2-OBu^n and μ_3-OCH_2.

Conclusion

These results are highly relevant with respect to the sol–gel processing of titania-based materials. Accordingly, we consider we have demonstrated that bridging positions for OR groups are sites of preferential attack for substitution by OH and/or OX groups. We also have demonstrated that the basic structure of the Ti_4O_{16} core can be conserved upon hydrolysis and can be used as a building block for building complexes of higher nuclearity. These findings are then in deep constrast with previous results concerning the hydrolysis and condensation of unsubstituted titanium alkoxides,[2–5] where no evident structural relationship is found after partial hydrolysis of OR groups. Obviously, these preliminary results call for the search for new ligands that provide a better protection of titanium atoms against hydrolysis. For example, we have recently been able to show that the Ti_4O_{16} core can be fully preserved even after a complete substitution of OR groups by 2,6-bis(hydroxymethyl)-*p*-cresol (BHMPC) molecules.[18] In contrast with the compounds reported here, this new Ti_4O_{16} core was found to be completely inert towards hydrolysis, allowing its possible use as a building block in various supramolecular architectures. Work along these lines is currently under progress, in particular using other types of structuring organic ligands.

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