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General principles driving the chemical reactivity of titanium(IV) alkoxides†

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The chemical reactivity of titanium(IV) (oxo)alkoxides towards multipodal ligands such as 1,3-propanediol and pentaerythritol is investigated. Two new complexes, $[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2\{O(CH_2)_3O\}(\mu\text{-}OEt)_6(OEt)_{12}]$ and $[Ti_4(\mu_2\text{-}OEt)_4(OEt)_8\{\mu_4\text{-}(OCH_2)_4C\}]$, have been isolated and characterized using single-crystal X-ray diffraction. The partial charge distribution in these complexes and in previously synthesized ones are described. From these results, it emerges that two general rules govern the chemical reactivity of Ti^{IV} (oxo)alkoxides. First, bridging OR-groups are systematically more basic than terminal ones and thus should be selectively attacked or substituted by protic XOH reagents. Second, a reduction in coordination is systematically associated with the more electrophilic Ti atoms and thus better solvation of the complexes.

Introduction

The monitoring of the chemical reactivity of transition metal alkoxides at the molecular scale is a crucial step in sol-gel processing of high-tech materials.[1] However, despite their widespread use, the initial steps of complexation as well as hydrolysis of these alkoxides are not well understood. The paucity of crystalline structures and the rather high nuclearity of these species are mainly responsible for the lack of theoretical studies. From an experimental point of view, most published crystal structures are obtained in a rather empirical way as mere by-products during sol-gel processing. Looking at the available molecular structures of these complexes, it seems obvious that strong connections should exist between the first molecular steps of sol-gel processes and the more rigorous approaches developed by inorganic supramolecular chemists and those involved in crystal engineering and molecular programming.[2] Using the concepts based on molecular recognition, we have recently been able to synthesize new complexes by reacting titanium alkoxides with tripodal ligands such as tris(hydroxymethyl)nitromethane[3] (thmnm) or 2,6-bis(hydroxymethyl)-*p*-cresol.[4] Moreover, using a simple point-charge approximation of density functional equations,[5] we have been able to reach a good theoretical understanding of the chemical reactivity of these polynuclear compounds.[2–4] A survey of literature devoted to titanium(IV) complexes[2] shows that most structures published by sol-gel chemists were obtained by a rather empirical "mix, bake and see" approach. It should be obvious that many more structures may be designed and synthesized if general principles based on a firm theoretical basis were available. This paper is a first attempt to derive such general principles. Our approach will be both experimental through the design and synthesis of new Ti^{IV} alkoxides and theoretical through the analysis of non-empirical partial charge distributions[5] computed not only on these new structures but also in older ones.

Strategy

Previous studies[2–4] have shown that in oligomeric titanium alkoxides $[Ti_4(OMe)_{16}]$, bridging positions (μ_n-OR with $n = 2$ or 3) are more reactive towards hydrolysis or complexation than terminal ones. This suggests our first general rule: "Upon hydrolysis or chemical modification of Ti^{IV} alkoxides bridging OR groups are selectively attacked and substituted by chemical species containing *ol* groups". Theoretical support for this rule comes from the observation that partial charges of O atoms of bridging OR groups are more negative that those of OR groups in terminal positions.[2,3] Experimental support is at the present time limited to the observation of structures obtained after reacting $Ti(OR)_4$ compounds with tripodal ligands.[3,6] One may thus wonder if our rule holds for other ligands. Another question arises when considering not only $Ti(OR)_4$ species but also oxo-alkoxides that are the very first steps of the hydrolysis/condensation processes of these compounds. A possible answer to this question is to consider, for instance, the well-known molecular structure of the first hydrolysis product of titanium ethoxide $[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_8(OEt)_{12}]$.[7–9] Using ^{17}O NMR spectroscopy, it was shown that this molecular complex was stable in toluene, but was rapidly destroyed after addition of ethanol to the toluene solution.[10] This simple observation obviously suggests that bridging OR groups have been selectively attacked by ethanol and that some chemical process, other than the simple chemical exchange ($Ti\text{–}OEt + EtO^*H \rightarrow Ti\text{–}O^*Et + EtOH$), is occurring. Consequently, it would be nice if this point could be clearly demonstrated by isolating new complexes in which these bridging OR groups have been selectively substituted by some OH-bearing ligand.

Another typical and yet unexplained aspect of $Ti(OR)_4$ chemistry concerns the reduction in coordination on going from the solid state to the solution. This point is well-illustrated by the case of titanium tetraethoxide, which is found as a tetrameric hexacoordinated form in the crystalline state,[11] but only with fivefold coordination in solution.[12] What is the driving force for such a reduction in coordination? A possible answer to this question may be obtained by trying to stabilize non-octahedral coordinations in the solid state. Then by

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† Electronic supplementary information (ESI) available: computational details, final crystal structure in CIF format and charge distribution from the PACHA output for the complexes described in the text. See http://www.rsc.org/suppdata/nj/b3/b312486j/

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looking at the partial charge distributions of these complexes displaying low coordinations, one may hope to identify some key factor. Limiting ourselves to alkyl derivatives, fivefold coordination in the solid state for non-hydrolyzed titanium alkoxides was observed only twice, in the crystal structure of $Ti_2(ONp)_8$ (titanium neopentoxide)[13] and for an ethylene glycol derivative $[Ti_5(OC_2H_4O)_5(OPr^i)_{10}]$, which displays Ti atoms with five-, six- and sevenfold coordination.[14] Unfortunately, it seems that no crystal structures are available concerning $Ti(OR)_4$ compounds known to display fourfold coordination in solution as evidenced by ^{47,49}Ti NMR spectroscopy.[15] Fortunately, single monomeric $Ti(OR)_4$ tetrahedra were found in the crystal structures of $[Ti(dipp)_4]$[16] (dipp = 2,6-diisopropylphenoxy), $[Ti(temp)_4]$[17] (temp = 2,3,5,6-tetramethylphenoxy) and $[Ti(tbp)_4]$[17] (tbp = 2-*tert*-butylphenoxy). Let us, however, notice that getting a reasonable charge distribution requires a good crystal structure determination. As far as oxo-alkoxides are concerned this imperative condition is rarely met as evidenced by the structure of the complex $[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_8(OEt)_{12}]$, which is characterized by 171 independent atomic positions in a triclinic space group with a rather badly defined molecular geometry. For example, referring to the best crystal structure available[8] (SOFTOW code in the Cambridge Structural Database), highly unrealistic bond distances of 94 (C29–C30), 111 (C13–C14), 115 (C31–C32), 122 (C9–C10) and 186 (C14–O7) pm are found. Moreover, the positions of all H atoms were not determined. Consequently, before doing partial charge calculations, some geometrical optimization is necessary.

In order to be able to treat such cases, we have used a simple approach based on our point-charge approximation of density functional equations that has proved to be useful for predicting H atom positions in ice polymorphs[18] and in microporous compounds.[19,20] First, given a starting crystal structure, a full partial charge distribution is computed as described before.[2,18] From this charge distribution, a negative electrostatic balance (EB) summing all repulsive and attractive electrostatic interactions in the crystal is computed. Then eight unit cells are generated, and from this atomic list, all short range repulsive interactions between non-bonded atoms are evaluated, leading to a positive repulsive balance (RB). In order to avoid empirical parametrizations, we have used atom-atom potentials derived from the Gordon–Kim electron gas model, which have been tabulated for s and p elements up to Kr.[21] The resulting sum $TE = EB + RB$ is then treated as a variable parameter, a function of the entire crystalline structure, which has to be minimized against suitably chosen structural variations. This last time-consuming step is easily implemented by varying atomic coordinates according to a downhill simplex method. Consequently, starting from an initial reasonable guess, a converging solution in terms of crystal structure may be readily obtained. It is worth noting that, as only non-bonded interactions are taken into account, bond lengths and bond angles must be fixed at some reasonable values before starting the optimization process. In other words, only torsional angles can be varied in an arbitrary way. A full geometric optimization would obviously have been preferable, but it requires the knowledge of *ab initio* Morse and bending potentials, which are not currently available. *Ab initio* repulsive potentials are also not yet available for transition metals and elements heavier than Kr. Consequently, for this study Ti–Ti, Ti–O, Ti–C, Ti–H interactions have been neglected.

Despite the rather severe limitations, big advantages are gained by using this approach: (i) Empirical input is limited to bond lengths and bond angles. Once selected, the method is completely self consistent, as there are no adjustable parameters needed to compute the EB or RB values. Consequently, the only required user input is a starting geometry for which coordinates, which have to be optimized, are given in terms of a *Z* matrix[22] (bond length, bond angle and torsion angle). Having defined the set of torsional angles allowed to vary with no restrictions, a simple mouse click is all that is needed to start the optimization process. (ii) Optimization can be made on molecular species in the gas phase but also directly on the asymmetric unit cell of a crystal. Consequently, derived atomic coordinates are fully converged in terms of long range electrostatic interactions. (iii) Owing to the simplicity of the involved mathematics (lattice sums, LU decompositions and downhill simplex procedures) computations can be performed on any kind of computer with reasonable computational times. Obviously, this time will considerably increase with the size of the unit cell and the number of torsion angles to be optimized. However, this problem may be easily overcome by using fast processors (a parallel version of this PACHA algorithm will soon be available).

Results

Selective substitution of bridging OR groups

Our first concern was to optimize the crystal structure of the complex $[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu\text{-}OEt)_8(OEt)_{12}]$ in order to get a reasonable partial charge distribution on an oxo-alkoxide. Among the 171 atomic coordinates required to describe the crystal structure, 107 (7 C atoms and 100 H atoms) were introduced as a *Z* matrix and the torsion angles of the 20 methyl groups and of the 5 unrealistic C atoms (C10, C14, C30, C32, C40) were selected for optimization. C–C and C–O bond lengths were fixed at 146 and 141 pm, respectively, while C–H values were either 109.6 (CH_3) or 107.3 (CH_2) pm. All unknown bond angles were assumed to be tetrahedral and fixed at 110°. The resulting 25-D simplex procedure converged after 889 energy evaluations. The time-consuming step was the evaluation of the 171 × 171 madelung matrix needed to get EB. All further computational details and the final crystal structure in CIF format are provided as Electronic supplementary information.

Fig. 1 shows the obtained optimized geometry, which can now be used for a better understanding of the chemical reactivity of this heptamer. For the present discussion, we shall focus on the partial charges q(O) borne by oxygen atoms (Table 1), as these are the sites that should be attacked by protic reagents such as water, ethanol or any OH-bearing molecule. The whole charge distribution on the 171 atoms is provided in the Electronic supplementary information.

The striking feature of Table 1 is the significant differentiation of the 24 O atoms into eight sets. The most basic set is formed by oxo bridges (μ_4 and μ_3), while the least basic one is formed by terminal OEt groups. The significantly higher electronic density found on μ_4-oxo bridges relative to μ_3-oxo ones is in agreement with the stronger shielding observed in

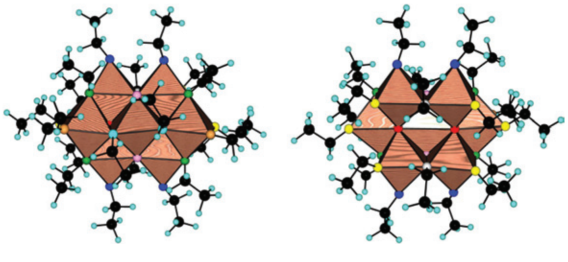

Fig. 1 Two views of the optimized molecular structure of $[Ti_7O_4(OEt)_{20}]$. μ_4-oxo in red (O11, O13), μ_3-oxo in violet (O12, O22), equatorial-μ_3-O bridging OEt in cyan (O1, O15), equatorial-μ_4-O bridging OEt in grey (O2, O10), axial bridging OEt in green (O3, O7, O17, O20), equatorial-μ_4-O terminal OEt in yellow (O5, O6, O8, O16, O19, O24), equatorial-μ_3-O terminal OEt in brown (O4, O18) and axial terminal OEt in blue (O9, O14, O21, O23) (see also Table 1).

Table 1 Averaged partial atomic charges on O atoms and corresponding pK_a distribution in [$Ti_7O_4(OEt)_{20}$]. See Fig. 1 for labels

O site	q(O)	pK_a
μ_4-O (O11, O13)	−0.927	19.3
μ_3-O (O12, O22)	−0.824	15.2
μ_2-OEt-eq4 (O2, O10)	−0.670	9.2
μ_2-OEt-ax (O3, O7, O17, O20)	−0.656	8.6
μ_2-OEt-eq3 (O1, O15)	−0.601	6.4
OEt-eq4 (O5, O6, O8, O16, O19,O24)	−0.555	4.6
OEt-eq3 (O4, O18)	−0.548	4.3
OEt-ax (O9, O14, O21, O23)	−0.538	4.0

^{17}O NMR studies: $\delta(\mu_3\text{-O}) = 537$ ppm *versus* $\delta(\mu_4\text{-O}) = 365$ ppm.[10] The corresponding rather high pK_a value also helps to explain why this Ti_7O_4 core can only be conserved in aprotic solvent. In protic solvents these oxo sites can be readily protonated, leading to destruction of the titanium oxygen core. Concerning the terminal ethoxide groups, they are found to be slightly less basic than in [$Ti_4(OEt)_{10}\{(\mu_2\text{-}OCH_2)_2(\mu_3\text{-}OCH_2)\text{-}C(NO_2)\}_2$] ($4.7 \leq pK_a \leq 5.6$).[2,3] Moreover, as in the case of [$Ti_4(OMe)_{16}$],[2,3] bridging OEt groups are found to be significantly more basic than terminal ones. In view of this charge distribution, it was hoped that bridging OEt groups could be substituted by a hydroxylated ligand displaying the right geometry to span one edge of a TiO_6 octahedron. Accordingly, as shown in Fig. 1, three types of edges are present in the [$Ti_7O_4(OEt)_{20}$] heptamer: $Ti(OEt)_2$, $Ti(OEt)(\mu_2\text{-OEt})$ and $Ti(\mu_2\text{-OEt})_2$. If the bridging positions are indeed more basic than terminal ones, substitution should preferentially occur at the (O1, O15) edge (cyan-colored O atom). For the reverse case, complexation is expected on $Ti(OEt)_2$ edges (blue-yellow or brown-yellow combinations in Fig. 1). Consequently, the 1,3-propanediol ligand was selected as a possible candidate and as expected it was found to substitute preferentially the *gem*-di-μ_2-OEt groups (Fig. 2). This experimental finding obviously brings strong support to the charge distribution given in Table 1 and extends to oxo-alkoxides our first rule derived for titanium(IV) alkoxides.

Isolation of the complex displayed in Fig. 2 raises the interesting question of what would happen if titanium alkoxides were reacted with $C(CH_2OH)_4$ (pentaerythritol). This ligand may be viewed as two dipodal arms disposed at right angles and thus could react like propylene glycol with the Ti_7 heptamer. But it may also be viewed as a tripod having an additional arm and thus could also react as thmnm. And lastly, it may also be viewed as a tetrapodal tentacular ligand that could react quite differently from either propylene glycol or thmnm. Fig. 3 displays the interesting tetrameric molecular structure that could be isolated after reaction of $Ti(OEt)_4$ with pentaerythritol in a 100:1 ratio. This structure is characterized by four μ_2-OEt groups and a fully tentacular $\mu_4\text{-}(OCH_2)_4C$ bridge.

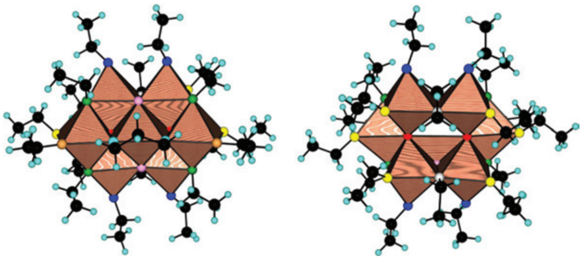

Fig. 2 Molecular structure of [$Ti_7O_4\{O(CH_2)_3O\}(OEt)_{18}$] showing the selective substitution of *gem*-di-μ_2-OEt groups in [$Ti_7O_4(OEt)_{20}$]. (Left) View of the complex with the substituting ligand at the front. (Right) View of the same complex rotated by 180° along the bottom-up direction (substituting ligand at the back).

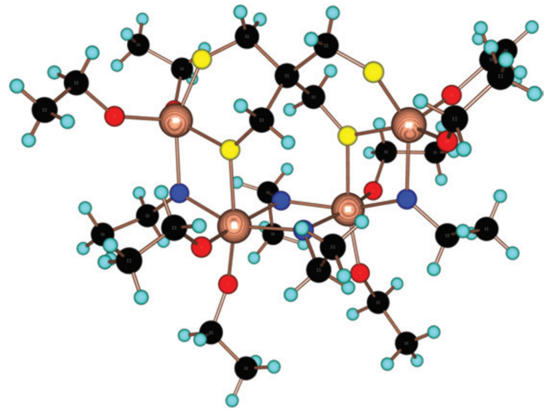

Fig. 3 Molecular structure of [$Ti_4(\mu_2\text{-OEt})_4(OEt)_8(\mu_4\text{-}(OCH_2)_4C)$] showing the two fivefold- and sixfold-coordinated titanium atoms. Atom Ti1 (right) adopts an approximate square-pyramidal conformation while atom Ti2 (left) adopts an approximate trigonal bipyramidal coordination. Selected bond distances (pm) and angles (°): Ti–OEt = 177.0(3)–181.1(3), Ti–(μ_2-OEt) = 196.8(3)–210.6(3), Ti–($\mu_4\text{-}(OCH_2)_4C$) = 181.3(3)–208.8(3), Ti–OEt–Ti = 106.0(2)–109.5(2), Ti–($\mu_4\text{-}(OCH_2)_4C$)–Ti = 107.1(2).

From a molecular standpoint, the formation of this tetramer can be readily visualized as an opening of the well-known tetrameric cyclic structure of [$Ti_4(OEt)_{16}$][11] by selective attacks of the pentaerythritol molecules on the μ_3-OEt bridges that should be the most basic sites of the structure, by analogy with the isostructural [$Ti_4(OMe)_{16}$] compound.[2,3] To the best of our knowledge, this is the second example of a μ_4 bridge, the other one being evidenced in the crystal structure of [$Ti_5(OC_2H_4O)_5(OPr^i)_{10}$].[14] Another interesting feature of this complex is the stabilization, in the solid state, of the fivefold coordination for the two outer Ti atoms by a ligand displaying no steric hindrance that could explain the observed reduction of coordination from 6 to 5. Stabilization of the fivefold coordination should then be the result of electronic effects, arising from a better overlap between Ti(3d, 4s, 4p) and O(2p) atomic orbitals upon contraction of the Ti–O bond length (188 pm for both TiO_5 polyhedra against 196 pm for TiO_6 octahedra). From the partial charge distribution (supplied as Electronic supplementary information) computed from this new molecular structure, we found a large pK_a difference between the μ_2 branches (O4, O5 = 9.3) and the chelating branches (O3, O6 = 4.9) of the pentaerythritol ligand (yellow O atoms in Fig. 3). The most basic sites are the μ_2-OEt groups bridging fivefold- and sixfold-coordinated Ti atoms (O9, O16 = 9.7). The two other groups bridging two sixfold-coordinated Ti atoms are slightly less basic (O12, O13 = 9.1). Concerning the terminal OEt groups, a difference of 0.7 pK_a units is found between those linked to the fivefold-coordinated Ti atoms (O1, O2, O7, O8 = 5.6) and those involved in the TiO_6 octahedra (O10, O11, O14, O15 = 4.9). A significant difference is also found in the partial charges for TiO_5 polyhedra (mean value +2.59) and the ones for TiO_6 octahedra (mean value +2.47). This indicates that pentacoordinated atoms should be the preferential sites for nucleophilic attack by hydroxo groups.

Chemical reactivity versus Ti coordination

In order to better understand the effect of titanium coordination on partial charge distributions we have investigated the charge distribution in $Ti_2(ONp)_8$ for which all Ti atoms are found in fivefold coordination.[13] Using the available crystal data, it was found that $q(Ti) = +2.53$, $pK_a = 9.4$ (μ_2-ONp) or 5.4 (terminal ONp). By contrast [$Ti_4(OMe)_{16}$], containing only octahedral Ti atoms, was characterized by $q(Ti) = +2.25$ +2.25 and +2.49 (mean +2.37).[2,3] For the [$Ti_5(OC_2H_4O)_5(OPr^i)_{10}$] complex that displays Ti atoms in five-, six- and sevenfold coordination,[14] it was found that atomic coordinates reported for one isopropoxy group were unrealistic (atoms C37 and C38 linked to atom C19 with bond lengths of 123 and 160 pm, respectively). Consequently, their positions have first been redefined to a standard value of 145 pm. Then, among the 155 atomic coordinates required to describe this crystal structure 92 (2 C atoms and 90 H atoms) were introduced as a Z matrix and the torsion angles of the 20 methyl groups were selected for optimization as described for the Ti_7 heptamer. C–H bond lengths were either 109.6 (methyl groups) or 107.3 (methine groups) pm. All unknown bond angles were assumed to be tetrahedral and fixed at 110°. The resulting 20-D simplex procedure converged after 368 energy evaluations. All further computational details, final crystal structure in CIF format and charge distribution are provided as Electronic supplementary information.

Fig. 4 shows the result of the optimization. Here a significant difference between pK_a values is found for the 1,2-ethanediol ligands: μ_3-O10 = 10.4, μ_4-(O3, O4) = (10.3, 9.2), μ_3-(O6, O5) = (9.2, 8.1), μ_3-(O7, O8) = (8.7, 7.5), μ_2-O1 = 8.7, O9 = O2 = 3.8. As expected the single μ_2-OPr^i group was found to be much more basic (O12 = 9.8) than the other terminal OPr^i groups: OPr^i(TiO_5) = 6.9, OPr^i(TiO_6) = 5.2 and OPr^i(TiO_7) = 4.2. This increase in basicity with decreasing coordination was found to be associated with an increase of the positive charge on the Ti atoms: $q(TiO_5) = +2.76$, $q(TiO_6) = +2.52$ and $q(TiO_7) = +2.34$.

Finally, our last concern will be the single monomeric $Ti(OR)_4$ tetrahedra found in the crystal structure of sterically crowded Ti^{IV} aryl oxides. Again, as H atoms were not localized in the case of [Ti(dipp)$_4$],[16] the crystal structure was first optimized against the 8 torsion angles characterising the isopropoxy groups. C–H bond lengths were 109.6 (methyl groups), 108.4 (aromatic protons) or 107.0 (methine groups) pm. Bond angles were 110° when H atoms were bonded to sp^3 carbons and 120° for attachment to the benzene ring. The resulting 8-D simplex procedure converged after 184 energy evaluations (Fig. 5). For the two other monomers, [Ti(temp)$_4$] and [Ti(tbp)$_4$], we have used directly the available CIF files (SOMJIN and SOMJOT codes in the CSD database).[17] From these three molecular structures it was found that $q(Ti) = +2.718$, pK_a(O) = 6.5 (dipp); $q(Ti) = +2.726$, pK_a(O) = 6.6 (temp) and $q(Ti) = +2.703$, pK_a(O) = 6.8 (tbp). As before a low coordination of the Ti atoms appears to be systematically correlated to a large positive charge on the metallic center.

Discussion

From the above results two general rules concerning partial charge distributions in titanium(IV) (oxo)alkoxides emerge. (i) Negative charge is systematically accumulated on O atoms in bridging positions relative to terminal ones. The more bonded the Ti atoms, the more negative the O atoms. (ii) Positive charge on Ti atoms decreases when coordination number increases.

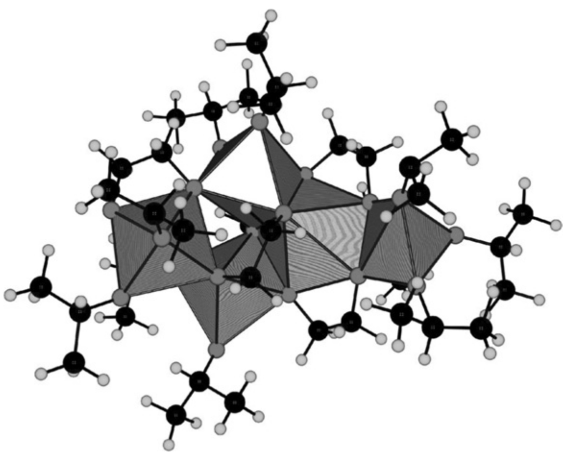

Fig. 4 Optimized crystalline structure of [$Ti_5(OC_2H_4O)_5(OPr^i)_{10}$] with Ti atoms in five-, six- and sevenfold coordination.

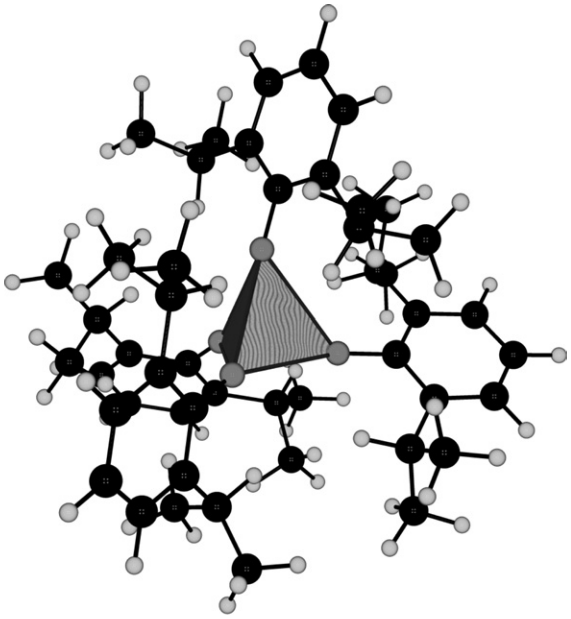

Fig. 5 Optimized crystalline structure of [$Ti\{OC_6H_3(Pr^i)_2\}_4$] with Ti atoms in fourfold coordination.

As easily anticipated these electronic effects are of crucial importance for a good understanding of the chemical reactivity of these species towards protic reagents X–OH (the very basis for an optimum control of sol-gel chemistry). For instance, the first point easily explains why currently known $Ti(OEt)_4$ hydrolysis products, [$Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_8(OEt)_{12}$],[7–9] [$Ti_{10}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OEt)_{10}(OEt)_{14}$][9] and [$Ti_4(\mu_4\text{-}O)(\mu_3\text{-}O)_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)_4(OEt)_4$]$_4$,[23] cannot be visualized as condensation oligomers of tetrameric units. This would have happened only if terminal positions were selectively attacked by water molecules upon hydrolysis. As charge distributions point rather to a selective protonation of bridging OR groups, one may expect to find rather compact clusters with oxo groups at the core of the complex and OR groups at the periphery as observed experimentally.[2] The situation is very similar for the structurally characterized Ti(OPr^i)$_4$ hydrolysis products: [$Ti_{11}(\mu_3\text{-}O)_{10}(\mu_2\text{-}O)_3(\mu_2\text{-}OPr^i)_4(OEt)_5(OPr^i)_6$],[24] [$Ti_{12}(\mu_3\text{-}O)_{14}(\mu_2\text{-}O)_2(\mu_2\text{-}OPr^i)_4(OEt)_6(OPr^i)_6$][25,26] and [$Ti_{17}(\mu_4\text{-}O)_4(\mu_3\text{-}O)_{16}(\mu_2\text{-}O)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_{16}$].[27] But the situation is worse here as the solid state structure of Ti(OPr^i)$_4$ remains unknown at the present time, in contrast with that of $Ti(OEt)_4$, which is known to be tetrameric in the solid state.[11] The second point helps to explain the observed reduction in coordination usually observed on going from the solid state to the solution. We now know that switching from sixfold coordination in [$Ti_4(OEt)_{16}$][11] to fivefold coordination in [$Ti_3(OEt)_{12}$][12] means more polar Ti–O bonds and thus most probably higher solvation energy. Nevertheless, even assuming the occurrence of an equilibrium in solution:

$$3[Ti_4(OEt)_{16}] \leftrightarrows 4[Ti_3(OEt)_{12}]$$

it remains difficult to propose a detailed condensation mechanism for the formation of the heptamer according to:

$$[Ti_4(OEt)_{16}] + [Ti_3(OEt)_{12}] + 4H_2O \rightarrow [Ti_7O_4(OEt)_{20}] + 8EtOH$$

More attention should be devoted to the elucidation of such basic condensation mechanisms so important in the field of hybrid organic-inorganic materials syntheses.[28] Work along these lines is in progress in our group using multinuclear and multidimensional NMR techniques and will be published elsewhere.

Conclusion

This very fundamental study has contributed to establish more firmly two general rules concerning the chemical reactivity of Ti^{IV} (oxo)alkoxides. First, bridging OR groups are systematically more basic than terminal ones and thus should be selectively attacked or substituted by protic XOH reagents. This explains the absence of clear structural relationships between the various hydrolysis products, but opens the route for a selective design of functionalized building blocks *via* the use of polyols such as 1,3-propanediol, tris(hydroxymethyl)-methane and pentaerythritol. Second, a reduction in coordination is systematically associated with more electrophilic Ti atoms and thus better solvation. This fact, associated to the high lability of the Ti–O bond, explains why it is so difficult to control and understand the hydrolysis behavior of Ti^{IV} (oxo)alkoxides. Here also the selective substitution of bridging positions by multipodal ligands is of a considerable help for monitoring the chemical reactivity of these sol-gel precursors. This was beautifully demonstrated by the selective dimerization through oxolation of tetrameric units in the presence of tripodal ligands.[3] We hope that more examples of such chemical control by multipodal ligands of the oxolation reaction will be provided in the very near future by the systematic use of the new complexes obtained in this study in sol-gel chemistry.

Experimental

Computational method

Non-empirical partial charge distributions[5] have been computed using our PACHA (PArtial CHArges model) software. A free copy of the software running under Windows is available upon e-mail request to M. Henry. Macintosh and Linux versions will be available soon.

Materials

All chemicals used in this study have been purchased from Fluka and used as received without any further purification.

Synthesis of the propylene glycol derivative. To a 0.5 M solution of $Ti(OEt)_4$ in toluene (40 ml, 22 mmol) were added, under vigorous stirring, 0.38 g (5 mmol) of 1,3-propanediol. After one week, large hexagonal platelet crystals are obtained in addition to some amorphous precipitate. The presence of this precipitate confirms the instability of the $[Ti_7O_4]$ core towards protic molecules. IR (KBr, cm^{-1}): 2968s ($\nu_{as}CH_3$), 2927s ($\nu_{as}CH_2$), 2863s (ν_sCH_2), 1460s ($\delta_{as}CH_3$), 1382s (δ_sCH_3), 1128vs (νC–O). ^{13}C NMR (toluene): δ 26.2 (CH_3), 27.1 (CH_3), 62.9 (CH_2), 75.9 (CH_2), 77.0–80.0 (unresolved CH_2 structure).

Synthesis of the pentaerythritol derivative. Pentaerythritol (0.024 M solution of pentaerythritol in DMSO) was reacted with $Ti(OEt)_4$ [3 M solution of $Ti(OEt)_4$ in EtOH] in a 1:1 volume ratio. Needle-like and highly hygroscopic crystals suitable for X-ray diffraction could be obtained from these solutions. IR (KBr, cm^{-1}): 3021, 2973m ($\nu_{as}CH_3$), 2925m ($\nu_{as}CH_2$), 1428s ($\delta_{as}CH_3$), 1386w (δ_sCH_3), 1216vs (νCC_4), 1108m (νC–O). ^1H NMR (DMSO-d_6): δ 0.39–0.51 (overlapping multiplets, 36 H, OCH_2CH_3), 2.83–3.21 (overlapping multiplets, 24H, OCH_2CH_3), 4.13 [singlet, 8H, $C(CH_2O)_4$]. ^{13}C NMR (DMSO-d_6): δ 17.7 (CH_3), 17.9 (CH_3), 18.4 (CH_3), 19.0 (CH_3), 19.4 (CH_3), 47.0 (CC_4), 58.1 (CH_2), 69.3 (CH_2), 69.5 (CH_2), 70.2 (CH_2), 71.0 (CH_2), 71.6 (CH_2), 71.9 (CH_2), 73.1 (CH_2), 74.4 (CH_2).

X-Ray crystallography

X-Ray data for the propylene glycol and pentaerythritol derivatives were respectively collected [$\lambda(MoK\alpha) = 0.71073$ Å] at 170 K on an Enraf Nonius CAD4 diffractometer and at 173 K with an Enraf Nonius Kappa CCD diffractometer. The structures were solved using the OpenMolen package[29] by direct methods[30] and refined by least-squares against *F*. All non-hydrogen atoms were anisotropically refined; the hydrogen atoms were positioned geometrically and refined by using a riding model in the last cycles of refinement.‡

Crystal data of the propylene glycol derivative. $C_{39}H_{96}O_{24}Ti_7$, $M = 1284.49$, triclinic, $a = 12.0601(8)$, $b = 13.733(1)$, $c = 20.595(2)$ Å, $\alpha = 105.244(6)°$, $\beta = 91.559(7)°$, $\gamma = 108.298(6)°$, $U = 3101(1)$ Å^3, $T = 173$ K, space group P-1 (no. 2), $Z = 2$, $\mu(MoK\alpha) = 0.912$ mm^{-1}, 12 914 reflections measured, 12 549 unique ($R_{int} = 0.148$). Refinement against $|F|$ [6263 reflections having $I > 3\sigma(I)$] converged at $R_1 = 0.051$, $wR_2 = 0.074$, final GOF = 1.390.

Crystal data of the pentaerythritol derivative. $C_{29}H_{68}O_{16}Ti_4$, $M = 864.46$, triclinic, $a = 9.5168(3)$, $b = 13.4861(7)$, $c = 17.8842(9)$ Å, $\alpha = 99.008(9)°$, $\beta = 90.923(9)°$, $\gamma = 105.676(9)°$, $U = 2178.6(5)$ Å^3, $T = 173$K, space group P-1 (no. 2), $Z = 2$, $\mu(MoK\alpha) = 0.756$ mm^{-1}, 18477 reflections measured, 9422 unique ($R_{int} = 0.103$). Refinement against $|F|$ [5655 reflections having $I > 3\sigma(I)$] converged at $R_1 = 0.053$, $wR_2 = 0.080$, final GOF = 1.518.

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