

Linear Titanoxanes via the Assembling of Bridging and Terminal Oxo–Titanium(IV) Fragments

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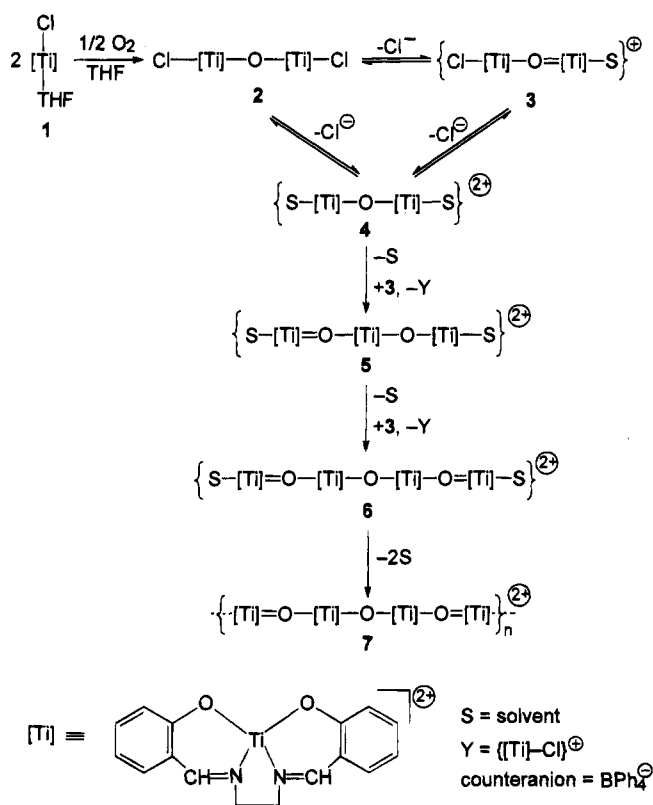
Titanoxanes³ well exemplify, within the context of metal–oxo chemistry,⁴ the move from molecular to solid state properties,⁵ via the formation of differently shaped aggregates. This move depends basically on our knowledge of two facts: (i) the genesis and the chemistry of the titanium–oxygen functionality,⁶ (ii) the dependence of the molecular topology of the aggregate on the ancillary ligands used around the metal.

The simplest titanium–oxygen functionalities which can be considered as building blocks for this goal are the quite common, unreactive, dimeric [Ti–O–Ti]⁶⁺ unit⁷ and the very rare titanyl [Ti=O]²⁺ moiety.⁷ In our design of linear oligomeric and polymeric titanoxanes, we take advantage of the relationship, reported here, between the terminal and the bridging titanium–oxo species.

The starting material we employed is the chlorobis(salicylideneiminato)titanium(III) complex [Ti(salen)Cl·THF], **1**,^{8,9} engaged in a series of oxidation and ionization reactions summarized in Scheme 1.

All of the compounds in Scheme 1 have been characterized, including 5–7, which have undergone X-ray analysis.¹⁰ We should emphasize some important observations related to Scheme 1: (i) conventional hydrolysis has never been used for accessing titanoxanes; (ii) the ionization of **2**¹¹ is the key step converting the dimeric [Ti–O–Ti]⁶⁺ unit into the titanyl or into

Scheme 1



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- (9) The synthesis of **1** is available as supplementary material.
- (10) Details are given only for **7**; Ti–O distances for **5** and **6** are reported in the text.
- (11) The synthesis of **2** is available as supplementary material.

a source of the titanyl functionality, i.e. [Ti=O–Ti]⁶⁺. To obtain a good yield of the polymeric species, an excess of NaBPh₄, which promotes the ionization of the Ti–Cl bond, has to be used. The Cl[–] ion either is removed as NaCl or remains bonded to a [Ti(salen)] fragment.

In Scheme 1 the titanyl unit, which has a high intrinsic basicity compared to that of [VO]²⁺,¹² competes with THF, acetone, the oxygen atoms from the Schiff base, and eventually H₂O in binding the cationic forms. We were able to trap the titanyl unit, which is still considered almost a curiosity, in complexes 5–7. Such a relatively long life of the titanyl unit allowing it to be trapped could be ascribed to the absence of protic sources during the reactions carried out under nonhydrolytic conditions. It is well-known that titanyl undergoes very facile proton-assisted transformations.^{12,13} The kinetic lability of titanium(IV), especially in the cationic forms, allows the simultaneous presence of the various species reported in Scheme 1, as shown by NMR. Under thermodynamic control, however,

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a single compound is obtained in the solid state. In fact, it is possible to isolate the three products **5**–**7** on the basis of their behavior in each of the three different solvents. Compound **5** is synthesized in THF, while compound **7** is isolated from dry acetone and compound **6** is isolated from acetone/H₂O. The reported Brønsted basicity of these solvents is in the order H₂O > THF > acetone,¹⁴ and for this reason each solvent competes differently with the oxygen of the titanyl unit. The replacement of a σ - and π -donating ligand such as Cl⁻ in **2** by a pure σ -donating solvent makes possible the rearrangement to the titanyl form in **3**, where the bridging oxygen establishes now a double bond with the titanium having lost Cl⁻. Such a species becomes a titanyl source. In a very competitive solvent such as THF a single solvent molecule will be replaced in **4** by the titanyl from **3** leading to **5**, which can be isolated only in the case of THF. When the reaction is carried out in less competitive solvents, such as acetone, the replacement of both solvent molecules in **4** occurs, leading to **6**. In the case of dry acetone, the two terminal weakly bonded solvent molecules are lost by **6**, leading to the polymeric form **7**, while when wet acetone is used instead, the polymerization is prevented and the tetramer **6**, having two terminal water molecules, is isolated. The transformation of **6** to **7** implies the replacement of the terminal solvent molecules by the oxygens from the Schiff base of another tetrameric unit. Complex **7**¹⁵ should be considered as derived from the polymerization of the tetrameric unit **6**. Details are given only for the structure of **7**, containing the three building blocks, the Ti–O–Ti, Ti=O, and oxygen from neighboring Schiff base, mentioned above, in a titanoxane structure.

The structure of **7**¹⁶ consists of linear tetramers (Ti(1),Ti(2),Ti(2''),Ti(1'')) linked in zigzag chains by bridging salen units (see Ti(1')) (Figure 1). The sequence of the Ti–O(oxo) distances and Ti–O–Ti angles, in agreement with the proposed structure of **7**, is particularly significant: Ti(1)–O(5), 1.672(6) Å; Ti(2)–O(5), 2.046(6) Å; Ti(2)–O(6), 1.815(2) Å; Ti(1)–

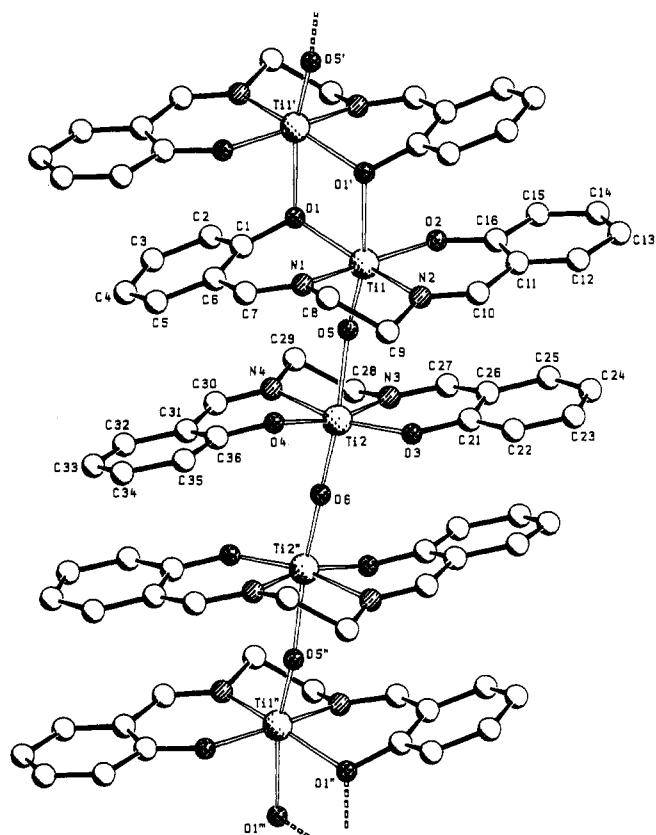


Figure 1. SCHAKAL view showing the tetrameric (Ti(1),Ti(2),Ti(2''),Ti(1'')) cations in complex **7** running along the [001] axis assembled in a polymeric form *via* the Schiff base oxygen shared with another tetrameric unit (see Ti(1')). Selected bond lengths (Å) and angles (deg): Ti(1)–O(1') = 2.297(6), Ti(1)–O(5) = 1.672(6), Ti(2)–O(5) = 2.046(6), Ti(2)–O(6) = 1.815(2); O(1')–Ti(1)–O(5) = 167.9(2), Ti(1)–O(5)–Ti(2) = 163.1(3), O(5)–Ti(2)–O(6) = 167.8(1), Ti(2)–O(6)–Ti(2'') = 180.0(–). Prime and double prime denote transformations of $-x$, $-y$, $-z$ and $1-x$, $-y$, $-z$, respectively.

O(5)–Ti(2), 163.1(3)°; Ti(2)–O(6)–Ti(2''), 180°. They should be compared with the Ti–O and Ti=O sequences in **5** [Ti–O_{av}, 1.92(2) Å; Ti=O, 1.72(2) Å; S = THF] and **6** [Ti–O, 1.817(1) Å; Ti–O, 2.036(4) Å; Ti=O, 1.701(4) Å; S = H₂O]. Appropriate recent references to the Ti–O and Ti=O bond distances are found in refs 6e,f.

This report deals with a simple strategy to generate a rare titanyl species from a quite conventional fragment and how to assemble them with the assistance of an appropriate ancillary ligand in a linear titanoxane.

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Supplementary Material Available: Text giving the preparations of **1** and **2** and a description of the structure of **7** and tables giving crystal data and details of the structure determination, fractional atomic coordinates, thermal parameters, bond lengths, and bond angles for complex **7** (11 pages). Ordering information is given on any current masthead page.

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(15) Procedure for **7**: To a THF (100 mL) suspension of **2** (1.38 g, 1.75 mmol) was added a THF (100 mL) solution of NaBPh₄ (0.85 g, 3.5 mmol). A red suspension was obtained which was refluxed for 12 h. The red suspension was extracted with the mother liquor in order to remove NaCl (see ref 9 for the procedure), the volume of the red solution was then reduced to 100 mL, and the resulting red solid was collected, dried, and suspended in dry acetone (100 mL). The red suspension was then stirred at room temperature for 12 h, and the solid was filtered off. The solution was evaporated to dryness and the red residue treated with Et₂O (100 mL) to yield a red product (55%). Crystals suitable for X-ray analysis were grown in deuterioacetone, and they contain acetone of crystallization in a titanium:acetone = 2:1 ratio. Anal. Calcd for C₁₁₂H₉₆B₂N₈O₁₁Ti₄: C, 69.23; H, 4.98; N, 5.77. Found: C, 69.67; H, 5.51; N, 5.64. ¹H NMR ((CD₃)₂CO, room temperature): δ 3.8–4.6 (m, 16 H, C₂H₄), 6.4–7.0 (m, 24 H, Ph), 7.1 (t, 16 H, BPh₄), 7.2–7.4 (m, 8 H, Ph), 7.4–7.6 (m, 24 H, BPh₄), 8.32 (s, 4 H, CH), 8.34 (s, 4 H, CH).

(16) Crystal data for **7**: C₆₄H₅₆N₈O₁₁Ti₂·2C₂₄H₂₀B·2C₃D₆O, $M = 2055.2$, monoclinic, space group $P2_1/n$, $a = 13.816(3)$ Å, $b = 16.611(6)$ Å, $c = 22.262(4)$ Å, $\beta = 101.47(2)^\circ$, $V = 5007(2)$ Å³, $Z = 2$, $D_c = 1.363$ g cm⁻³, $F(000) = 4404$, Mo K α radiation ($\lambda = 1.54178$ Å, $\mu = 31.80$ cm⁻¹), crystal dimensions 0.08 × 0.14 × 0.18 mm. The structure was solved by SHELX 89 and anisotropically refined for all the non-hydrogen atoms. For 4476 unique observed reflections [$I > 2\sigma(I)$] collected at $T = 123$ K ($5 < 2\theta < 140^\circ$) and corrected for absorption, the final R value was 0.073 (unit weights).