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A new polyoxo–alkoxo titanium cluster of the Keggin family: synthesis and characterization by X-ray diffraction and NMR spectroscopy

Nathalie Steunou,[a] Guido Kickelbick,[b] Kamal Boubekeur[c] and Clément Sanchez[a]*†

[a] *Chimie de la Matière Condensée, UMR CNRS 7574, 4 place Jussieu, 75252 Paris Cedex 05, France. E-mail: clems@ccr.jussieu.fr*
[b] *Institut für Anorganische Chemie der Technischen Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria*
[c] *Institut des Matériaux de Nantes, UMR CNRS 110, Université de Nantes, 2 rue de la Houssinière, 44 072 Nantes Cedex 03, France*

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The new $[Ti_{17}O_{24}(OPr^i)_{20}]$ cluster 1, that can be described as a non-charged lacunar super-Keggin complex, adopts a pseudo-D_{2d} symmetry as established by X-ray diffraction and solution NMR studies.

Transition metal alkoxides are used as precursors in sol–gel chemistry for the elaboration of a wide variety of materials including metal oxide ceramics, metal oxide nanoparticles, hybrid organic–inorganic materials and more recently mesoporous materials.[1] Nevertheless, they are highly reactive towards hydrolysis, and therefore the elaboration of metal-oxo based advanced materials needs a careful tuning of their reactivity. Substitution of some of the easily hydrolyzable alkoxide ligands by complexing bidentate ligands allows a decrease of precursor functionality and reactivity.[2] Among complexing ligands, carboxylates are often used to modify titanium alkoxides[2] and therefore to control their reactivity. A second advantage of carboxylate ligands is due to their ability to produce water *in situ* through esterification reactions with alkoxy ligands or with alcohol molecules released upon the complexation reaction.[3–5] Numerous titanium and zirconium oxo–carboxylate clusters have been obtained by reacting the metal alkoxide with the corresponding carboxylic acid.[4,5] The metal-oxo clusters are structurally similar to the first hydrolysis products and their degree of condensation leads to a moderate reactivity compared to the metal alkoxide precursor.[6] This stability seems to depend on the degree of condensation (*i.e.* the cluster size). As a consequence, further developments could be based on the use of large metal-oxo clusters as precursors for the synthesis of new ceramics or hybrid mesostructured materials.

In the present communication, the structure of a new oxo–isopropoxy titanium complex $[Ti_{17}O_{24}(OPr^i)_{20}]$ is described. This large cluster joins the group of the two larger titanium-oxo complexes already reported ($[Ti_{18}O_{22}(OBu^n)_{26}(acac)_2]$, $[Ti_{18}O_{28}H(OBu^t)_{17}]$).[7,8] It has a compact arrangement based on the Keggin[9] structure, which was first described for the heteropolyanion $[PW_{12}O_{40}]^{3-}$.[9]

A variety of stable polyoxo-tungstate and -molybdate compounds display this structure type. The arrangement has a paramount importance in the construction of metal-oxo cores in heteropolyanion chemistry.[10] The metal-oxo core of the Keggin structure consists of a central tetrahedron XO_4 (X = P, Si, transition metal) which is encapsulated in a metal–oxygen cage of twelve MO_6 octahedra. These octahedra constitute four trinuclear units M_3O_{13} of octahedra sharing edges. The trinuclear units are corner-linked to the central tetrahedron. Other compact arrangements can be derived from the Keggin structure since some square faces between the trimeric units M_3O_{13} can be capped by other polyhedra. Such an example was reported for a polyvanadate compound. Indeed, the polyanion $[PV_{14}O_{42}]^{9-}$ has a bicapped Keggin structure in which two faces are capped by two five-fold coordinated vanadium atoms.[11] These vanadium centers exhibit a trigonal bipyramidal environment. In polytitanate chemistry, only one complex, $[Ti_{18}O_{28}H(OBu^t)_{17}]$, involving the Keggin structure type was already reported.[8] This compound has a $[Ti_{18}O_{45}]^{18-}$ metal-oxo core that can be considered as a $[Ti_{13}O_{40}]^{28-}$ Keggin complex capped by five TiO^{2+} units. The compound $[Ti_{17}O_{24}(OPr^i)_{20}]$ **1** is a cluster of 17 titanium atoms coordinated to oxo and isopropoxo ligands, in which the metal-oxo framework is closely related to the Keggin structure (Fig. 1). It can be described as a $[Ti_{13}O_{40}]^{28-}$ Keggin complex which is capped by four five-coordinate titanium centres. The titanium centres present different geometries: one is a tetrahedral center, twelve have a distorted octahedral coordination and four have a distorted trigonal-bipyramidal environment. The metal-oxo core contains 4 μ_4-oxo bridges, 16 μ_3-oxo bridges and 4 μ_2-oxo bridges. The complex contains also 16 terminal isopropoxy groups and 16 bridging ones. Some of them were difficult to locate even at low temperature in the X-ray structure analysis due to thermal motion. One can notice that the complex adopts a pseudo-D_{2d} symmetry which involves the presence of a four-fold axis $\bar{4}$ located on Ti(1), two mirror planes σ_1 and σ_2 and two two-fold

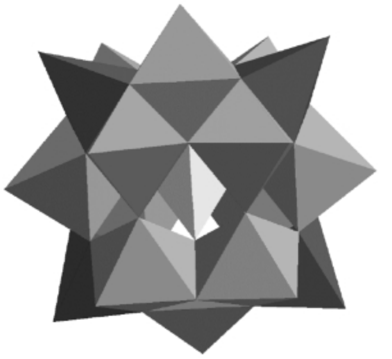

Fig. 1 Compact arrangement of complex **1**. Trigonal bipyramids correspond to the black polyhedra, octahedra to the grey polyhedra and the tetrahedron to the white polyhedron.

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3653/

Also available: ^{13}C, ^{1}H and ^{17}O NMR spectra for complex **1**. For direct electronic access see http://www/rsc.org/suppdata/dt/1999/3653/, otherwise available from BLDSC (No. SUP 57642, 4 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (http://www/rsc.org/dalton).

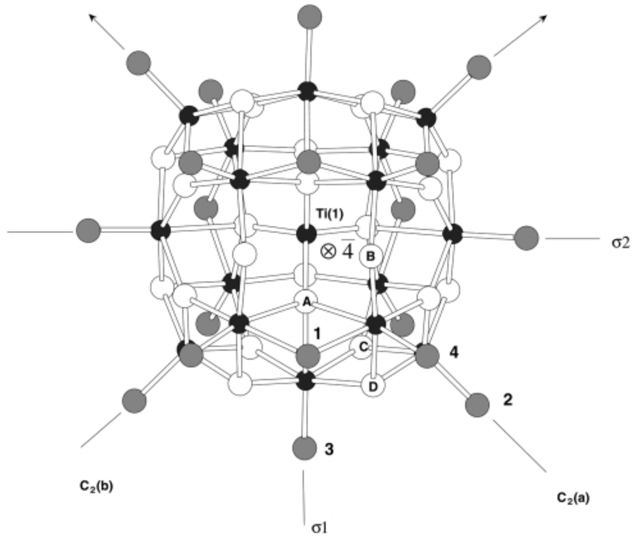

Fig. 2 D_{2d}-$[Ti_{17}O_{44}]^{20-}$ core of the D_{2d}-$[Ti_{17}O_{24}(OPr^i)_{20}]$ structure. Titanium atoms are represented by small filled spheres, oxide oxygens by large open spheres, and alkoxide oxygens by large shaded spheres. One member from each set of symmetry-equivalent oxygen atoms is labeled using numbers for alkoxide oxygens and letters for oxide oxygens.

axes C_2(a) and C_2(b) (Fig. 2). In order to validate this structural hypothesis, complex **1** was characterised by ^{17}O, ^{1}H and, ^{13}C NMR spectroscopy in solution (No. SUP 57642, 4 pp.).

The ^{17}O NMR spectrum of complex **1** displays four resonances. According to the assignments previously reported for oxo-bridges,[12] the resonance located at 436 ppm is assigned to a μ_4-oxo bridge, the two signals at 533 and 541 ppm to μ_3-oxo bridges and the remaining resonance at 711 ppm to a μ_2-oxo bridge. This spectrum is consistent with the metal-oxo core $[Ti_{17}O_{24}]^{20+}$ since the latter contains these three kinds of oxo bridges (Fig. 2). Moreover, the number and the intensity of the signals δ 436, 533, 541, 711 (respectively equal to 1, 2, 2, 1) are in agreement with the pseudo-D_{2d} symmetry. The ^{1}H and ^{13}C NMR spectra (No. SUP 57642, 4 pp.) confirm that complex **1** can be assigned to the D_{2d} structure which is indicated by X-ray diffraction. The four methine ^{1}H (and ^{13}C) resonances and the corresponding intensities are in agreement with the presence of four types of isopropoxo groups in the D_{2d} structure (Fig. 2). Furthermore, this NMR study in solution shows that complex **1** retains its structure in solution. According to the literature,[4–8,13] this cluster seems to be large enough to have an oxo core sufficiently stable towards nucleophilic species such as water. It should have the possibility to retain at least partially its titanium-oxo core during sol–gel polymerisation reactions to make new materials assembled through nano building blocks.

The $[Ti_{17}O_{24}(OPr^i)_{20}]$ complex **1** was obtained upon reacting titanium isopropoxide with acetic acid in the molar ratio 1/1.3 at 150 °C.‡ The synthesis of titanium oxo–alkoxide clusters $[Ti_{12}O_{16}(OPr^i)_{16}]$ and $[Ti_6O_4(OAc)_4(OPr^i)_{12}]$ by adding titanium isopropoxide to acetic acid in a 1/1.2 molar ratio, was already reported in the literature.[5] The source of condensation is water, generated through esterification reactions between the acetic acid and isopropoxide ligands (or the cleaved alcohol). While the $[Ti_6O_4(OAc)_4(OPr^i)_{12}]$ cluster is obtained at room temperature, the formation of $[Ti_{12}O_{16}(OPr^i)_{16}]$ requires a higher reaction temperature (80 °C). Moreover, whereas the $[Ti_6O_4(OAc)_4(OPr^i)_{12}]$ complex still contains some carboxylato ligands, such ligands are not coordinated to titanium centres in the $[Ti_{12}O_{16}(OPr^i)_{16}]$ complex.[5,13] By increasing the amount of acetic acid ($AcOH/Ti(OPr^i)_4 = 1.3$), temperature (150 °C) and pressure, a more highly condensed oxo-titanium cluster as complex **1** is obtained.

This study shows that upon using solvothermal conditions, the esterification process is particularly favored since most of the carboxylic acid molecules are transformed into isopropyl ester and water. Moreover by adjusting the temperature and the amount of acetic acid, it is possible to achieve a better control of the water generated *in-situ* and thus a better control of the metal-oxo core size of the cluster. The size of the metal-oxo cores of titanium clusters increase with the temperature and the amount of acetic acid.

Notes and references

‡ Experimental data for **1**: Titanium isopropoxide (8.4 mL, 0.0285 mol) was added to acetic acid (2.1 mL, 0.037 mol). The reaction mixture was heated in a Parr Teflon-lined acid digestion bomb of 23 mL capacity at 150 °C over 5 days. After cooling of the reaction bomb to room temperature, colourless crystals of **1** were obtained. Yield 42%. A suitable crystal was chosen for X-ray structure determination. All NMR experiments were carried out under argon in a glovebox in order to prevent hydrolysis by atmospheric water. For solution NMR spectra, fresh crystals were dissolved in C_6D_6 solvent under an argon atmosphere.

NMR data for **1**: ^{1}H NMR [300 MHz, C_6D_6, 25 °C] δ 1.45–1.47 (48 H, $^{3}J_{HH}$ 6.1 Hz, 3 overlapping doublets, CH_3), 1.53–1.57 [48 H, 2 overlapping doublets, $^{3}J_{HH}$ 6.1 Hz, CH_3], 1.83 [24 H, d, $^{3}J_{HH}$ 6.1 Hz, CH_3], 4.80 [4 H, sept, $^{3}J_{HH}$ 6.1 Hz, CH], 5.18–5.24 [12 H, 2 overlapping sept, $^{3}J_{HH}$ 6.1 Hz, CH], 5.60 [4 H, sept, $^{3}J_{HH}$ 6.1 Hz, CH] ; ^{13}C NMR [75 MHz, C_6D_6, 25 °C] δ 24.8, 25.8, 25.9, 26.0, 27.0, 27.1, [CH_3], 78.1, 81.1, 81.3, 81.8 [CH]; ^{17}O NMR [54 MHz, C_6D_6, 25 °C] δ 436 [4 O, Ti_4O], 533 [8 O, Ti_3O], 541 [8 O, Ti_3O], 711 [4 O, Ti_2O].

Crystal data for **1**: $Ti_{17}O_{44}C_{60}H_{140}$, $M = 2380.02$, colourless crystals (0.30 × 0.20 × 0.20 mm) were mounted on a Siemens SMART CCD diffractometer and measured with Mo-Kα radiation ($\lambda = 0.71073$ Å, graphite monochromated). Monoclinic, space group $P2_1/c$, $a = 26.3210(1)$, $b = 17.5855(1)$, $c = 26.9526(3)$ Å, $\beta = 114.158(1)°$, $U = 11382.89(15)$ Å^3, $Z = 4$, $D_c = 1.733$ g cm^{-3}. The data collection at 200(2) K covered a hemisphere in reciprocal space. Each exposure took 20 s and covered 0.3° ω. The collected data range was $1.42 \le \theta \le 22.50°$ ($-28 \le h \le 26$, $-18 \le k \le 18$, $-23 \le l \le 29$) with a crystal-to-detector distance of 3.85 cm. 14424 reflections were collected, and 7398 unique reflections ($R_{int} = 0.226$) were obtained after correction of Lorentz effects ($\mu = 1.189$ mm^{-1}). An empirical absorption correction with the program SADABS.[14] The structure was solved by direct methods (SHELXS86)[15] and refined by the full-matrix least-squares method based on F^2 (SHELXL93)[16] [$R_1 = 0.1467$ and $wR_2 = 0.3905$]. CCDC reference number 186/1650. See http://www.rsc.org/suppdata/dt/1999/xxxx/ for crystallographic files in .cif format.

Despite the low temperature data collection, the present X-ray structure determination reveals a very high thermal motion and a disorder on all the terminal isopropoxy groups. Due to the great number of these isopropoxy groups (20) and to the splitting of the isopropyl groups over several positions for each isopropoxy group, all attempts to introduce a disorder model were unsuccessful. However, the oxo-metallic core was determined unambiguously.

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