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Articles

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Synthesis and Solid- and Liquid-State Characterization of a Hexameric Cluster of Titanium(IV): $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OCOCH}_3)_8$

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Hexameric $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OCOCH}_3)_8$ has been prepared and the molecular structure established by single-crystal X-ray diffraction. The crystal is monoclinic $P2_1/c$ with a = 18.508 (3) Å, b = 10.818 (2) Å, c = 17.831 (8) Å, β = 104.00 (2)°, and Z = 2. The molecule is centrosymmetric and contains six octahedrally coordinated titanium atoms. ^{13}C CPMAS, ^{13}C, and ^{1}H NMR and IR spectroscopies show that the molecular structure of the cluster is conserved in solution. Such a compound plays a key role for sol–gel chemistry and is an interesting reference for NMR studies. Moreover, it exhibits reversible photochromic properties. Under visible irradiation it behaves as a class II mixed-valence compound.

Introduction

The sol–gel process offers new approaches to the synthesis of glasses and ceramics.[2-4] From molecular precursors, such as alkoxides, a molecular oxide network is obtained via inorganic polymerization reactions. It appears that the main properties of the resulting material strongly depend on the chemistry of the sol–gel process: nature of the molecular precursor, acid or base catalyst, and chemical additives.

It has recently been shown that some of the most common additives, such as acetic acid or acetylacetone, may chemically react with alkoxides at a molecular level, giving rise to new molecular precursors; therefore, the whole hydrolysis–condensation process is modified.[5,6]

Better control of the process requires an accurate characterization of the chemical species formed all along the process, from the molecular precursor to the gel and xerogel. However, most of these species do not exhibit any long-range order. For this reason many spectroscopies have to be used simultaneously, NMR, XANES, and EXAFS among them. As a consequence, well-characterized reference compounds are needed.

$\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OCOCH}_3)_8$ is an hydrolyzed derivative of a titanium(IV) alkoxide chemically modified by the acetic acid. As a result, the title compound constitutes a good structural and spectroscopic reference (liquid NMR and XANES (X-ray absorption near-edge structure) spectroscopies) for the study of the chemical modifications that occur in the sol–gel processing.

Hexanuclear compounds of titanium are not very common. Therefore, such a small-size cluster (the number of atoms is approximately 150 and the diameter approximately 30 Å) is of interest for NMR studies as a model compound. Moreover, these crystals also exhibit the property of reversible photochromism.

This paper describes the synthesis and the solid- and the liquid-state characterization of this hexameric cluster of titanium(IV).

Experimental Section

1. Preparation of the Crystal. Mixing acetic acid (100% Prolabo) drop by drop with pure titanium tetrabutoxide (Fluka) ($\text{Ti(OBu}^{\text{n}})_4$) in a 1:2 molar ratio while stirring leads to the growth of transparent colorless crystals in a few days. The solution obtained must be kept in a closed vessel because of its air–moisture sensitivity. The single-crystal is put in a glass capillary immediately after being removed from the mother liquor in order to avoid hydrolysis.

Table I. Crystallographic Data for $\text{Ti}_6(\mu_2\text{-O})_2(\mu_3\text{-O})_2(\mu_2\text{-OC}_4\text{H}_9)_2(\text{OC}_4\text{H}_9)_6(\text{OCOCH}_3)_8$

formula	$\text{Ti}_6\text{C}_{48}\text{H}_{96}\text{O}_{28}$	Z	2
fw	1408	ρ_{calcd}, g cm^{-3}	1.35
space group	$P2_1/c$ (No. 14)	μ(Mo Kα), cm^{-1}	8.6
a, Å	18.508 (3)	temp, °C	20
b, Å	10.818 (2)	radiation, Å	0.7107 (Mo Kα)
c, Å	17.831 (8)	R	0.055
β, deg	104.00 (2)	R_{w}	0.057
V, Å^3	3454		

2. X-ray Structure Data. The molecular structure has been determined by single-crystal X-ray diffraction. Analysis of preliminary Laue and precession photographs yielded a monoclinic unit cell. The space group $P2_1/c$ was established by systematic absences. Unit cell parameters were determined and refined from 25 randomly selected reflections. Crystal data, data collection parameters, and residuals from the refinements are given in Table I. During the intensity data collection, two standard reflections were measured periodically and showed no apparent variation in intensity. Intensities were corrected for Lorentz and polarization factors. Absorption corrections were not performed due to the low absorption coefficient. All the refinements were carried out by using SHELX76 programs.[9] Scattering factors were taken from the *International Tables*, including $\Delta f'$ and $\Delta f''$ for Ti.

The structure was solved by direct methods. Subsequent Fourier series revealed all oxygen and carbon atoms of the acetate groups and the butoxy chain O(40) (O(40)–C(44) atoms). At this time of the refinement (R = 0.16) a difference map revealed four chains of disordered $-\text{OC}_4\text{H}_9$. The occupancies and displacement parameters of the carbon atoms of the disordered moiety were refined alternately (in a least-squares analysis including the entire structure) with fractional site oc-

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(1) (a) Laboratoire de la Matiere Condensee, Universite Paris VI. (b) Laboratoire de Chimie des Metaux de Transition, Universite Paris VI. (c) Bu$^{\text{n}}$ = $\text{CH}_3(\text{CH}_2)_3$–, Ac = CH_3CO–, Me = CH_3–, Et = CH_3CH_2–, Pr$^{\text{i}}$ = $(\text{CH}_3)_2\text{CH}$–, and Am$^{\text{t}}$ = $\text{CH}_3\text{CH}_2\text{CCH}_3\text{CH}_3$–.

(2) *Proc. Int. Workshop Glasses Glass Ceram. Gels, 4th* (*J. Non-Cryst. Solids* **1988**, 100).

(3) *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; New York, 1988.

(4) *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds., North-Holland: New York, 1984.

(5) Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F. *J. Non-Cryst. Solids* **1987**, *100*, 65.

(6) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.*, in press.

(7) Doeuff, S.; Henry, M.; Sanchez, C.; Livage, J. *J. Non-Cryst. Solids* **1987**, *89*, 206.

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(9) Sheldrick, G. M. "SHELX-76. Program for Crystal Structure Determination", Cambridge University, 1976.

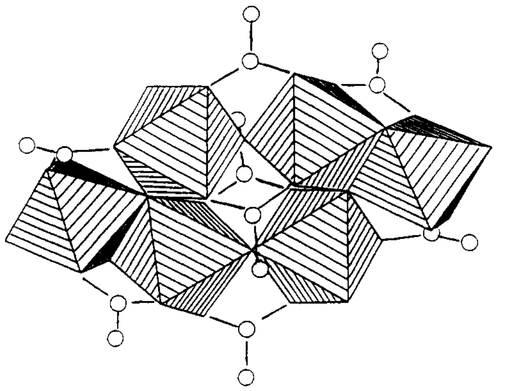

Figure 1. Molecular geometry of $Ti_6(OBu^n)_8(OCOCH_3)_8O_4$.

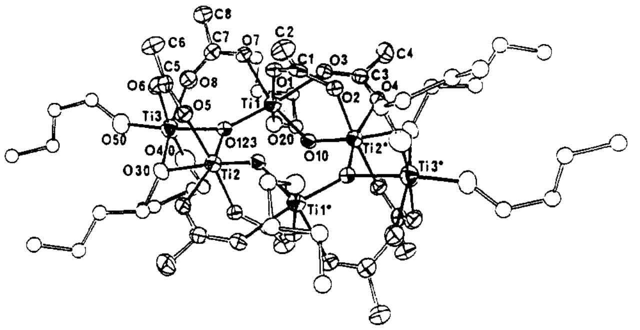

Figure 2. Crystal structure (ORTEP drawing) of the Ti hexamer. (The superscript dot refers to an atom in the $1 - x, -y, 1 - z$ equivalent position relative to the x, y, z set.

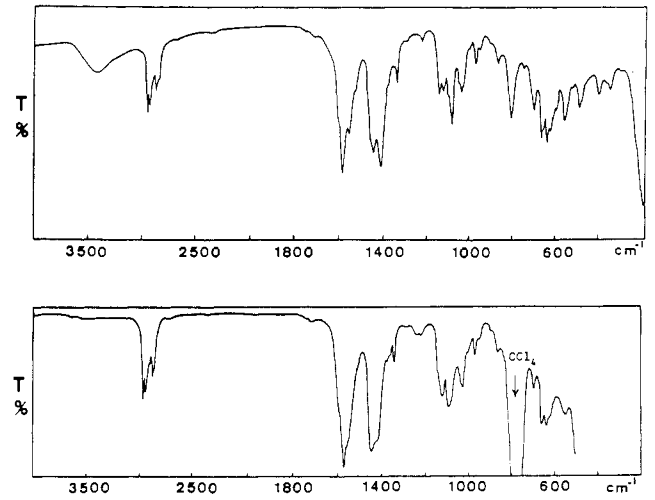

Figure 3. IR spectra: (a, top) crystal powder in KBr; (b, bottom) crystal dissolved in CCl_4.

cupancies: C(31)–C(34), two chains with site occupancies 0.5 and 0.5; C(42)–C(44), two chains with site occupancies 0.5 and 0.5; C(51)–C(54), two chains with site occupancies 0.6 and 0.4.

The final least-squares calculation, in which the disordered moieties were not refined, converged with residuals as given in Table I. The hydrogen atoms were included in fixed positions (C–H = 0.95 Å) and the isotropic thermal parameters U_{iso} fixed at 1.2 times the last U_{equ} of the parent carbon atom. A final difference map showed no residual electron density greater than 0.26 e Å^{-3}.

The final atomic coordinates are listed in Table II. Bond distances and angles are given in Table III. The molecular geometry and the crystal structure are respectively shown in Figures 1 and 2.

3. Characterization of the Compound. a. Infrared Spectroscopy. The IR spectra were recorded on a Perkin-Elmer 783 spectrometer in the 4000–200-cm^{-1} range. The crystals were studied both as a powder dispersed in a KBr pellet (Figure 3a) and as a solution of crystals dissolved in CCl_4 (Figure 3b).

b. X-ray Absorption Spectroscopy (XANES: X-ray Absorption Near-Edge Structure). The titanium K-edge spectra were recorded at room temperature at LURE, the French synchrotron radiation facility, by using the EXAFS III spectrometer.

Table II. Fractional Atomic Coordinates with Esd's in Parentheses

atom	x/a	y/b	z/c
Ti(1)	0.58002 (7)	−0.1341 (1)	0.60208 (7)
Ti(2)	0.59026 (7)	0.1508 (1)	0.52025 (7)
Ti(3)	0.74087 (7)	0.0610 (1)	0.62557 (8)
O(10)	0.5061 (2)	−0.1306 (4)	0.5089 (2)
O(123)	0.6283 (2)	0.0120 (4)	0.5837 (2)
O(1)	0.5082 (3)	−0.0247 (4)	0.6484 (2)
O(2)	0.3953 (3)	−0.0581 (5)	0.5727 (3)
C(1)	0.4412 (5)	0.0028 (7)	0.6239 (4)
C(2)	0.4121 (5)	0.1144 (8)	0.6558 (5)
O(3)	0.5202 (3)	−0.2831 (5)	0.6341 (3)
O(4)	0.4170 (3)	−0.3117 (4)	0.5408 (3)
C(3)	0.4651 (5)	−0.3450 (7)	0.6008 (4)
C(4)	0.4536 (5)	−0.4694 (8)	0.6333 (5)
O(5)	0.5877 (3)	0.2480 (4)	0.6157 (3)
O(6)	0.6899 (3)	0.1738 (5)	0.6976 (3)
C(5)	0.6312 (5)	0.2348 (7)	0.6830 (5)
C(6)	0.6082 (5)	0.3005 (8)	0.7472 (4)
O(7)	0.6353 (3)	−0.1366 (5)	0.7175 (3)
O(8)	0.7452 (3)	−0.0593 (5)	0.7139 (3)
C(7)	0.7013 (5)	−0.1105 (7)	0.7482 (4)
C(8)	0.7310 (5)	−0.144 (1)	0.8308 (5)
O(20)	0.6401 (3)	−0.2449 (5)	0.5769 (3)
C(21)	0.6508 (6)	−0.3710 (9)	0.5644 (6)
C(22)	0.6831 (9)	−0.441 (1)	0.6366 (9)
C(23)	0.7589 (8)	−0.411 (1)	0.6714 (9)
C(24)	0.7871 (9)	−0.484 (2)	0.747 (1)
O(30)	0.7031 (3)	0.1850 (5)	0.5454 (3)
C(31a)	0.7440 (8)	0.291 (1)	0.5270 (8)
C(32a)	0.782 (1)	0.236 (2)	0.468 (1)
C(33a)	0.810 (2)	0.311 (4)	0.413 (2)
C(34a)	0.882 (2)	0.373 (4)	0.450 (2)
C(31b)	0.743 (1)	0.224 (2)	0.487 (1)
C(32b)	0.793 (1)	0.327 (2)	0.509 (1)
C(33b)	0.837 (1)	0.370 (2)	0.457 (1)
C(34b)	0.885 (2)	0.475 (3)	0.494 (2)
O(40)	0.7751 (3)	−0.0438 (6)	0.5686 (3)
C(41)	0.7786 (5)	−0.119 (1)	0.5089 (8)
C(42a)	0.852 (1)	−0.188 (2)	0.519 (2)
C(43a)	0.908 (1)	−0.088 (3)	0.510 (2)
C(44a)	0.983 (2)	−0.150 (4)	0.521 (3)
C(42b)	0.850 (1)	−0.123 (2)	0.487 (1)
C(43b)	0.907 (2)	−0.180 (4)	0.553 (2)
C(44b)	0.937 (2)	−0.296 (3)	0.527 (2)
O(50)	0.8261 (3)	0.1334 (6)	0.6698 (3)
C(51a)	0.870 (1)	0.181 (2)	0.734 (1)
C(52a)	0.945 (1)	0.235 (3)	0.744 (2)
C(53a)	0.985 (2)	0.211 (3)	0.685 (2)
C(54a)	1.053 (2)	0.294 (3)	0.694 (2)
C(51b)	0.903 (2)	0.129 (3)	0.692 (2)
C(52b)	0.938 (1)	0.256 (3)	0.695 (2)
C(53b)	1.019 (2)	0.249 (4)	0.734 (3)
C(54b)	1.053 (2)	0.360 (4)	0.706 (3)

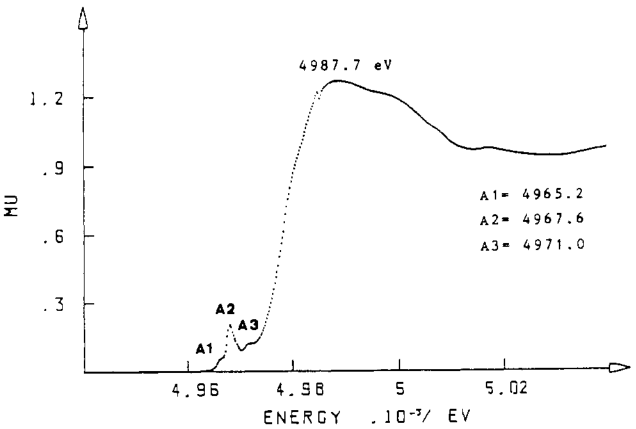

Figure 4. Ti K-edge XANES spectrum of $Ti_6(OBu^n)_8(OCOCH_3)_8O_4$ in the solid state.

The XANES spectrum of the crystalline compound, shown in Figure 4, has been recorded by putting the ground solid between two pieces of

Table III. Interatomic Distances (Å) and Bond Angles (deg) with Esd's in Parentheses

Ti(1)–O(1)	2.093 (5)	Ti(1)–O(3)	2.111 (5)
Ti(1)–O(7)	2.064 (4)	Ti(1)–O(10)	1.880 (4)
Ti(1)–O(20)	1.765 (5)	Ti(1)–O(123)	1.883 (5)
Ti(2)–O(2*)	2.010 (5)	Ti(2)–O(4*)	2.040 (5)
Ti(2)–O(5)	2.010 (5)	Ti(2)–O(10*)	1.746 (5)
Ti(2)–O(30)	2.061 (5)	Ti(2)–O(123)	1.909 (4)
Ti(3)–O(6)	2.148 (6)	Ti(3)–O(8)	2.029 (6)
Ti(3)–O(30)	1.962 (5)	Ti(3)–O(40)	1.742 (7)
Ti(3)–O(50)	1.767 (5)	Ti(3)–O(123)	2.104 (4)
O(1)–Ti(1)–O(20)	169.6 (2)	O(3)–Ti(1)–O(123)	171.9 (2)
O(7)–Ti(1)–O(10)	163.8 (2)	O(1)–Ti(1)–O(3)	84.3 (2)
O(1)–Ti(1)–O(7)	79.8 (2)	O(1)–Ti(1)–O(10)	86.6 (2)
O(1)–Ti(1)–O(123)	88.2 (2)	O(3)–Ti(1)–O(7)	83.5 (2)
O(3)–Ti(1)–O(10)	86.4 (2)	O(3)–Ti(1)–O(20)	87.4 (2)
O(7)–Ti(1)–O(20)	93.1 (2)	O(7)–Ti(1)–O(123)	92.5 (2)
O(10)–Ti(1)–O(20)	99.0 (2)	O(10)–Ti(1)–O(123)	96.0 (2)
O(20)–Ti(1)–O(123)	99.8 (2)		
O(2*)–Ti(2)–O(5)	173.8 (2)	O(4*)–Ti(2)–O(123)	162.6 (2)
O(10*)–Ti(2)–O(30)	174.5 (2)	O(2*)–Ti(2)–O(4*)	89.4 (2)
O(2*)–Ti(2)–O(10*)	91.2 (2)	O(2*)–Ti(2)–O(30)	86.5 (2)
O(2*)–Ti(2)–O(123)	89.6 (2)	O(4*)–Ti(2)–O(5)	89.6 (2)
O(4*)–Ti(2)–O(10*)	91.0 (2)	O(4*)–Ti(2)–O(30)	84.0 (2)
O(5)–Ti(2)–O(10*)	94.9 (2)	O(5)–Ti(2)–O(30)	87.3 (2)
O(5)–Ti(2)–O(123)	89.5 (2)	O(10*)–Ti(2)–O(123)	106.3 (2)
O(30)–Ti(2)–O(123)	78.7 (2)		
O(6)–Ti(3)–O(40)	173.4 (3)	O(8)–Ti(3)–O(30)	160.8 (2)
O(50)–Ti(3)–O(123)	166.1 (2)	O(6)–Ti(3)–O(8)	80.8 (2)
O(6)–Ti(3)–O(30)	85.3 (2)	O(6)–Ti(3)–O(50)	87.5 (2)
O(6)–Ti(3)–O(123)	79.4 (2)	O(8)–Ti(3)–O(40)	94.8 (3)
O(8)–Ti(3)–O(50)	94.3 (2)	O(8)–Ti(3)–O(123)	87.9 (2)
O(30)–Ti(3)–O(40)	97.8 (3)	O(30)–Ti(3)–O(50)	98.3 (2)
O(30)–Ti(3)–O(123)	76.5 (2)	O(40)–Ti(3)–O(50)	97.9 (3)
O(40)–Ti(3)–O(123)	95.6 (2)		
Ti(1)–O(10)–Ti(2*)	137.1 (3)	Ti(1)–O(123)–Ti(2)	129.8 (2)
Ti(1)–O(123)–Ti(3)	128.4 (2)	Ti(2)–O(123)–Ti(3)	101.8 (2)
C(1)–O(1)	1.248 (9)	C(5)–O(6)	1.24 (1)
C(1)–O(2)	1.269 (8)	C(5)–O(5)	1.282 (9)
C(1)–C(2)	1.49 (1)	C(5)–C(6)	1.49 (1)
C(3)–O(3)	1.245 (9)	C(7)–O(7)	1.245 (9)
C(3)–O(4)	1.266 (8)	C(7)–O(8)	1.26 (1)
C(3)–C(4)	1.50 (1)	C(7)–C(8)	1.49 (1)
O(1)–C(1)–O(2)	124.2 (7)	O(5)–C(5)–O(6)	125.0 (8)
O(1)–C(1)–C(2)	118.7 (6)	O(5)–C(5)–C(6)	115.7 (7)
O(2)–C(1)–C(2)	117.0 (7)	O(6)–C(5)–C(6)	119.2 (7)
Ti(1)–O(1)–C(1)	132.0 (5)	Ti(2)–O(5)–C(5)	126.6 (5)
Ti(2)–O(2)–C(1)	130.8 (5)	Ti(3)–O(6)–C(5)	131.6 (5)
O(3)–C(3)–O(4)	125.3 (7)	O(7)–C(7)–O(8)	124.5 (7)
O(3)–C(3)–C(4)	118.3 (7)	O(7)–C(7)–C(8)	117.8 (8)
O(4)–C(3)–C(4)	116.4 (7)	O(8)–C(7)–C(8)	117.6 (7)
Ti(1)–O(3)–C(3)	134.8 (5)	Ti(1)–O(7)–C(7)	129.2 (5)
Ti(2)–O(4)–C(3)	129.4 (5)	Ti(3)–O(8)–C(7)	138.7 (5)

tape. All of the conditions for data collection and analysis are described in a previous paper.[10]

c. NMR Spectroscopy. Solid-State NMR. The ^{13}C NMR cross-polarization spectrum was recorded on a Model AM 400 Bruker spectrometer by using freshly synthesized ground crystals. The reference was glycine ($\delta(CH_2/TMS)$ = 38.4 ppm). The ^{13}C high-resolution spectrum of the crystal is represented in Figure 5.

Liquid-State NMR (^{13}C, ^{1}H, 2D ^{13}C–^{1}H). The fresh crystals dissolve easily in organic solvents. ^{13}C and ^{1}H (Figure 6) and two-dimensional ^{13}C–^{1}H NMR spectra (Figure 7) of crystal/CD_2Cl_2 solutions were recorded on a Model AM 500 Bruker spectrometer.

d. Optical Spectroscopy. The optical spectra were recorded on a Beckman DK2A spectrometer. The crystals were dissolved in CCl_4.

e. EPR Spectroscopy. EPR spectra were recorded on a VARIAN E-19 spectrometer at the X-band frequency (ν = 9.5 GHz).

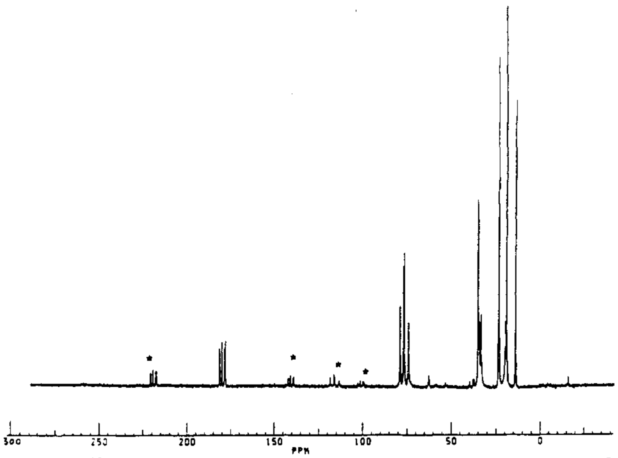

Figure 5. ^{13}C CPMAS NMR spectrum of $Ti_6(OBu^n)_8(OCOCH_3)_8O_4$. Asterisks indicate spinning bands.

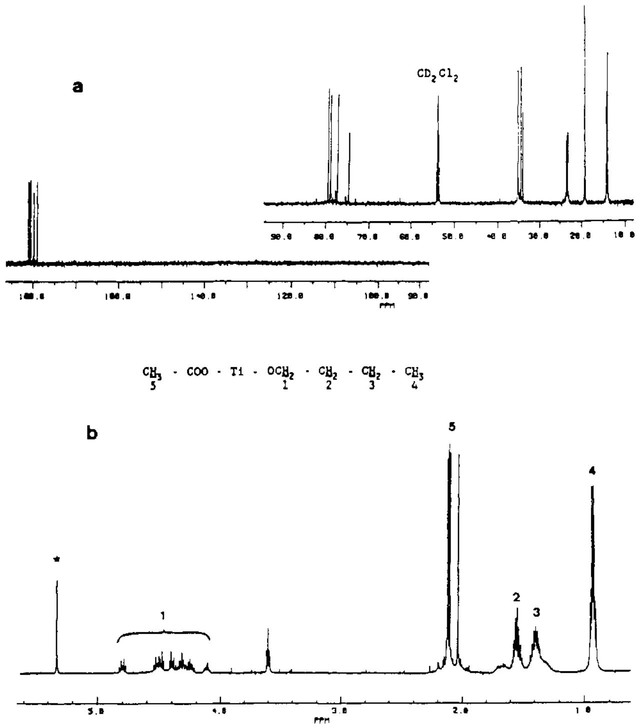

Figure 6. NMR spectra of a $Ti_6(OBu^n)_8(OCOCH_3)_8O_4/CD_2Cl_2$ solution: (a) ^{13}C; (b) ^{1}H (asterisk indicates resonance due to residual CH_2Cl_2).

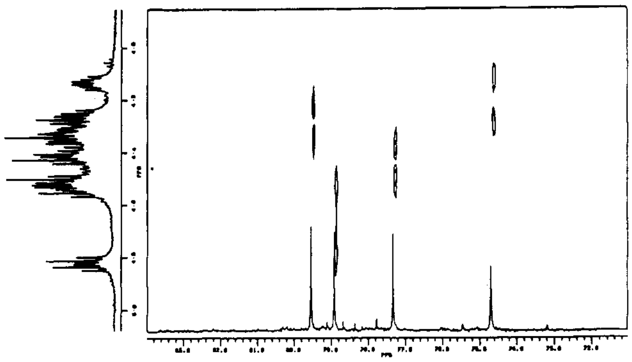

Figure 7. COSY ^{13}C–^{1}H NMR spectrum of a $Ti_6(OBu^n)_8(OCOCH_3)_8O_4/CD_2Cl_2$ solution.

Results

1. Description of the Structure. The crystal is a hexameric unit of formula $Ti_6(OBu^n)_8(OAc)_8O_4$. Each molecule is centrosymetric and contains six titanium atoms, each being 6-fold-coordinated.

The structure can be described by two Ti_2O_{10} (two edge-sharing octahedra) units linked by two corner-sharing octahedra (Figure 1).

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[10] Babonneau, F.; Doeuff, S.; Leaustic, A.; Sanchez, C.; Cartier, C.; Verdaguer, M. *Inorg. Chem.* **1988**, *27*, 3166.

There are four oxygen atoms in bridging positions between Ti_2O_{10} and the edge-sharing octahedra: two are triply bridging oxygen atoms (μ_3-oxo), O(123) and O(123*), and two are doubly bridging oxygen atoms (μ_2-oxo), O(10) and O(10*).

In the structure, all the acetate groups bridge two titanium atoms. Two types of butoxy groups can be distinguished: six terminal butoxy groups O(20), O(40), and O(50) and O(20*), O(40*), and O(50*); two bridging butoxy groups O(30) and O(30*).

The titanium atoms have nonequivalent environments. They are all bonded to a triply bridged oxygen atom, O(123), and each of them has a coordination number of 6 completed as follows. Ti(1): three oxygen atoms of the acetate groups in facial positions, one oxygen atom of a terminal butoxy group, one bridging oxygen atom μ_2-oxo-shared by Ti(2*). Ti(2): three oxygen atoms of the acetate groups in equatorial positions, one oxygen atom of the bridging butoxy group shared by Ti(3), one bridging oxygen atom μ_3-oxo-shared by Ti(1*). Ti(3): two oxygen atoms of the bridging acetate groups in cis positions, two oxygen atoms of the terminal butoxy groups, one oxygen atom of the bridging butoxy group shared by Ti(2).

In the different titanium octahedra, the bond lengths Ti–O vary from 1.742 to 2.148 Å (average 1.962 Å). The Ti–O bonds of the terminal butoxy groups are short (average 1.758 Å) and are associated with Ti–O–C angles having large values (145.3–160.6°). As a result, one can observe the lengthening of the opposite Ti–O bond by trans influence.

In contrast, the Ti–O bonds of the bridging butoxy group O(30) are medium (1.962 Å) or long (2.061 Å). In correlation, Ti–O–C angles have smaller values (123.3, 130.4°).

The long bond Ti(2)–O(30) is located in the trans position of the very short bond (1.746 Å) engaging the oxygen atom μ_2-oxo O(10). This can be explained by a π transfer from the oxygen atom O(10) to the d orbitals of Ti(2). This transfer could explain the lengthening of the Ti(2)–O(30) bond by trans influence.

The geometry of the oxygen atom O(123) bonded to three titanium atoms is remarkable. The summation of the angles around O(123) yields a value of 360.0°, and Ti(1)–Ti(2)–Ti(3) are almost perfectly planar.

The oxygen atom O(123) has a free lone pair of electrons and a geometry able to promote an interaction with the empty d orbitals of the three metallic atoms.

The carbon–oxygen bond distances of the acetate groups vary from 1.24 to 1.28 Å. The short C–O bonds (1.24 Å) correspond to oxygen atoms in the position trans from either terminal butoxy groups or the oxo oxygen atoms O(2) and O(5) where the Ti–O bonds are the longest.

2. XANES Analysis. The titanium K preedge features give information about the environment of the metallic atoms. The prepeaks correspond to transitions of the photoelectron from deep states to final states, the d-metallic levels. These transitions are sensitive to the crystal field around the titanium atom.[11-13]

A titanium atom in octahedral symmetry exhibits a characteristic triplet[11,12] with peaks of relatively weak intensity. The weak intensity of the peaks is due to the presence of an inversion center in the octahedral symmetry.

The XANES spectrum of titanium in the tetrahedral symmetry exhibits an intense lone prepeak at lower energy in contrast to the one in the octahedral symmetry.[13] The lack of an inversion center in this symmetry explains the high intensity of the peak.

The XANES spectrum of titanium in a 5-fold coordination is similar to that of titanium in a 4-fold coordination but with weaker intensity.[10]

The titanium K-edge XANES spectrum of the crystals is represented in Figure 4. The preedge peaks are weak and are located at 4965.2, 4967.6, and 4971.0 eV.

Table IV. Acetate IR Bands of the Crystal (Solid State)

wavenumber, cm^{-1}	assgnt	$\Delta\nu$		
1600	ν_{as}(COO)			155
1580			135	
1555		110		
1445	ν_s(COO)			
1415	$\delta(CH_3)$			
1340	$\delta(CH_3)$			

Table V. CPMAS ^{13}C NMR Chemical Shifts

δ(C), ppm	assgnt	δ(C), ppm	assgnt
	Butoxy Chain		
13.66	$CH_3(CH_2)_3O$	33.21	$CH_3CH_2CH_2CH_2O$
13.86		34.0	
≃13.96		34.73	
18.85	$CH_3CH_2(CH_2)_2O$	35.07	
19.76		74.10	$CH_3(CH_2)_2CH_2O$
		76.46	
		77.14	
		79.08	
	Acetate Group		
22.87	CH_3	178.08	CO
23.25		178.59	
23.68		180.10	
		181.46	

The XANES spectrum of $Ti_6(OBu^n)_8(OAc)_8O_4$ is characteristic of titanium atoms in octahedral symmetry. The position and intensity of the prepeaks are close to those observed for TiO_2 anatase.[11,12]

3. Infrared Spectroscopy. The IR spectrum of the crystal dispersed in KBr is shown in Figure 3a. The main features of the spectrum are the bands of C–H (ν(C–H) at 2900 cm^{-1}) and C–O (ν(C–O) around 1000 cm^{-1}) of the butoxy groups and the bands of C–O (ν_s(C–O) and ν_{as}(C–O) stretching vibration mode) and CH_3 ($\delta(CH_3)$ bending mode) of the acetate groups in the region 1400–1600 cm^{-1}. Some of the bands at low wavenumbers are due to the Ti–O vibrations.

The acetate ligand has several modes of coordination including monodentate and bidentate (chelating, bridging, polymeric).[14] The crystal structure has revealed the presence of only one chemical type of acetate group. They are all bridging two titanium atoms quite symmetrically (Ti–O bond distances are from 2.010 Å for the shortest to 2.148 Å for the longest).

The IR bands located at 1600, 1580, and 1555 cm^{-1} are assigned to the stretching vibrations ν_{as} of the COO^-.[14] The splitting of the $\nu_{as}(COO^-)$ band can be explained by the variations of the OCO angle (121–123°) observed for the acetate groups.[15]

The bands located at 1445 and 1415 cm^{-1} correspond to ν_s(COO) and $\delta(CH_3)$. Their labeling is more difficult.[16,17] Deuteration of the acetate groups of the crystal does not lift the ambiguity of the assignment of these two bands.

The position of these characteristic bands depends also on the nature of the metallic atom. As a result, the assumption was made that $\nu_s(COO) > \delta(CH_3)$. Indeed, an IR study[18] shows that titanium compounds exhibit ν_s(COO) at 1430 cm^{-1} for a bridging acetate. The complete band assignments of the acetate group are summarized in Table IV. The $\Delta\nu$ separations between ν_{as} and ν_s for the COO vibrator around 110–155 cm^{-1} are in close agreement with the values reported by Nakamoto.[14]

The spectrum of the crystals dissolved in CCl_4 (Figure 3b) is quite identical with that of the solid compound (Figure 3a). Only an intensity inversion of the bands located at 1445 and 1415 cm^{-1} due to the acetate groups is observed.

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Table VI. ^{13}C Liquid NMR Chemical Shifts

$\delta(^{13}C)$, ppm	assgnt	$\delta(^{13}C)$, ppm	assgnt
	Butoxy Chain		
13.94	$\mathit{C}H_3(CH_2)_3O$	34.03	$CH_3CH_2\mathit{C}H_2CH_2O$
14.04		34.48	
14.25		35.09	
19.22	$CH_3\mathit{C}H_2(CH_2)_2O$	35.28	
19.30		74.61	$CH_3(CH_2)_2\mathit{C}H_2O$
19.34		77.24	
19.36		78.82	
		79.44	
	Acetate Group		
23.15	$\mathit{C}H_3$	178.98	$\mathit{C}O$
23.21		179.74	
23.40		180.54	
23.60		181.03	

The IR bands characteristic of the bridging acetate groups and those due to the butoxy groups bound to the metal are still present, while bands due to free butanol or acetic acid are absent.

4. NMR Spectroscopy. a. Solid State. The high-resolution ^{13}C CPMAS spectrum of the crystals in the solid state is shown in Figure 5. The observed chemical shifts are reported in Table V.

The four carbon atoms of the butoxy group lead to four sets of resonance lines located around 13, 19, 35, and 77 ppm. Each set of resonance peaks is multiple, in particular the resonance peaks corresponding to O-$\mathit{C}H_2$ of the butoxy chain: their number is 4. This shows the existence of four different butoxy groups (from the NMR spectrum) in the crystal.

The resonance peaks due to the acetate groups are located in two different sets. The first one located around 23 ppm corresponds to the methyl groups and the other around 180 ppm is characteristic of the carbon atom of the COO groups.

These two sets of resonances are multiplets. The carbon atom COO shows four lines of equal intensity, indicating the presence of four different acetate groups.

This overall 4-fold multiplicity outlines the centrosymmetry of the crystal $Ti_6(OBu^n)_8(OAc)_8O_4$.

b. Liquid State. The crystal dissolves very easily in organic solvents. In order to study the crystal structure in solution and, in particular, in order to check if the structure is conserved in the liquid state, the ^{13}C and ^1H NMR spectra of a solution of crystals dissolved in CD_2Cl_2 have been recorded (Figure 6). The ^{13}C observed chemical shifts are reported in Table VII.

^{13}C Spectrum. The observed chemical shifts and their assignments are reported in Table VI. Like the ^{13}C solid-state spectrum, the spectrum of the crystals in solution exhibits well-resolved peaks due to the butoxy and acetate groups. The chemical shifts are similar to those found in the solid state (Table VI). Four types of butoxy groups and four types of bridging acetate groups are in evidence.

These results suggest that the crystal structure is globaly conserved when solvated in a chlorinated solvent. However, a weak peak is shown at 62.7 ppm characteristic of the carbon atom $\mathit{C}H_2$-O of free butanol. This seems to indicate that a partial hydrolysis of the compound occurs in solution.

^1H Spectrum. The proton spectrum (Figure 6b) reflects the same features, though with less resolution than the ^{13}C one. Peaks related to the four crystallographic sites (four acetate, four butoxy groups) tend to overlap. An interesting exception is the protons of the O-CH_2 butoxy groups. These peaks overlap slightly but are resolvable at 500 MHz.

In order to assign the ^{13}C and ^1H chemical shifts of the OCH_2 from the four butoxy groups, two other NMR experiments have been performed. The first was a two-dimensional (2D) NMR experiment. This ^{13}C–^1H COSY sequence allows one to observe the proton–carbon correlation of each CH_2 group. The second was the measurement of the spin–lattice relaxation times T_1 of carbon atoms O-CH_2. The COSY spectrum is shown Figure 7; the T_1 values are reported in Table VII.

Butoxy Group Assignment. The COSY experiment shows the systematic correlation of each carbon atom –O$\mathit{C}H_2$– with two multiplets of the ^1H NMR spectrum, labeled AA′, BB′, CC′, and DD′.

From ^{13}C T_1 measurements, two different types of butoxy groups can be distinguished: the most shielded (high-field) carbon atom O$\mathit{C}H_2$ relaxes with a time T_1 two to three times shorter (0.26 s) than those of the three other carbon atoms O$\mathit{C}H_2$ (0.60, 0.76, 0.87 s).

This particular carbon atom must belong to the less mobile butoxy group (i.e. the unique bridging butoxy group, oxygen atom O(30)), as usually reported.[19] Therefore, the three other ^{13}C NMR peaks are due to the carbon atoms O$\mathit{C}H_2$ of three terminal butoxy groups (O(20), O(40), O(50)).

From the COSY experiment all the protons of the OCH_2 butoxy groups appear inequivalent. Using this inequivalence as a rough measure of local field fluctuations, we assign the butoxy group containing O(20), the only single-bonded butoxy titanium group, to the strongest doublet inequivalence. The two butoxy groups O(40) and O(50) are the other OCH_2 groups.

The values of $\Delta\delta$ are reported in Table VII together with coupling constants J, which values are in agreement with the literature.[20]

Two of the four O–CH_2– butoxy group have been definitely assigned. The last two are the two twin terminal chains bound to Ti(3). These two species may tentatively be assigned with chemical shift positions. The Ti(3)–O(50) distance is 1.767 Å, slightly longer than the Ti(3)–O(40) distance, which is 1.742 Å. So, the electronic density of O(50)–CH_2– is higher than that of O(40)–CH_2–. Therefore, O(50)–CH_2– should be more shielded than O(40)–CH_2–; this is what is observed in both ^{13}C and ^1H NMR spectroscopy. So, we propose the assignment of the four O–CH_2– groups as reported in Table VIII.

We focus now our attention on the assignment of the acetate groups as follows: The ^{13}C and ^1H NMR spectra show the presence of four different acetate groups, but because they are chemically very comparable, it is difficult to differentiate them. We therefore propose an assignment on the basis of inductive effects. These can be transposed in a bond distance analysis. We consider the average effect on the distances by making the summation of the four distances ($\sum d = d(\text{Ti–O} + \text{O–C} + \text{C–O} + \text{O–Ti})$). Then if the distance $\sum d$ shortens, the Ti–O bond strength will increase on both side of the COO group. The ^{13}C NMR signal of the carbonyl will therefore be deshielded. These assignments are reported in Table IX.

The assignments of the $\delta(^1H)$ and $\delta(^{13}C)$ of the methyl groups of the acetate are more difficult and could eventually be done through a ^{13}C–^1H COSY long-range experiment.

5. Physical Properties of $Ti_6(OBu^n)_8(OAc)_8O_4$. Solutions of crystals of $Ti_6(OBu^n)_8(OAc)_8O_4$ dissolved in CCl_4 exhibit an interesting optical property. The initially colorless solution takes an intense blue color when irradiated with a Hg lamp (450 W) for a few minutes. This coloration is stable for several weeks but disappears rapidly when the blue solution is placed in contact with oxygen. After the decoloration, a second irradiation will again yield the blue coloration. This property of reversible photochromism has been studied by optical and EPR spectroscopies.

The optical spectra of the crystal/CCl_4 solution before irradiation (colorless) and after irradiation (blue color) have been recorded. Under irradiation, the appearance in the UV–visible spectrum of a very broad line centered around 700 nm (15 300 cm^{-1}) can be related to the blue color. This transition has been qualitatively assigned to an intervalence band Ti^{4+}–Ti^{3+} by comparison with published optical spectra of mixed-valence compounds.[21,22]

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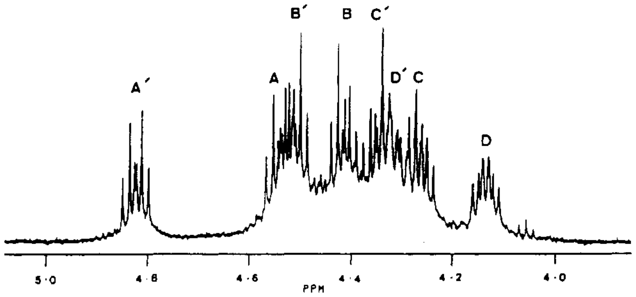
Table VII. Parameters Obtained from the ^1H and ^{13}C NMR Spectral Analysis



	D	D′	C	C′	B	B′	A	A′
$\delta(^1H)$,[a] ppm	4.107 4.119	4.288 4.298	4.228 4.251	4.318 4.341	4.383 4.405	4.478 4.500	4.508 4.531	4.791 4.816
J_{ab}, Hz	12.2			11.4		11.1		11.6
J_{ba}, Hz			11.6		11.1		11.6	
J_{ac}, Hz	9.5			6.9		6.6		
J_{ac}, Hz	5.5							
J_{bc}, Hz			6.5		6.6		6.8	6.9
$\Delta\delta$,[b] ppm	0.18 (2)		0.09 (0)		0.09 (6)		0.28 (4)	
$\delta(^{13}C)$, ppm	74.61		79.44		77.24		78.92	
T_1, s	0.26		0.60		0.87		0.76	

[a] Value of the triplet's central peak. [b] Value of the gap (ppm) between the signals of the two protons carried by the same carbon atom.

Table VIII. ^{13}C and ^1H Liquid NMR Spectral Assignment of the Four Butoxy Chains

Bridging Butoxy Chain (DD′)

$\delta(O{-}CH_2) = 74.61$ ppm; $\delta(O{-}CH_2) = 4.113$ (H_a), 4.293 ppm (H_b)

Terminal Butoxy Chains

	$\delta(OCH_2{-})$, ppm	$\delta(OCH_2{-})$, ppm H_a	$\delta(OCH_2{-})$, ppm H_b	label
O(30)	78.92	4.519	4.803	AA′
O(40)	79.44	4.239	4.329	CC′
O(50)	77.24	4.394	4.489	BB′

Table IX. Distance–Chemical Shift Correlation for the Acetate Groups

acetate group[a]	$\sum d$, Å	assgnd $\delta(COO)$, ppm	acetate group[a]	$\sum d$, Å	assgnd $\delta(COO)$, ppm
1	6.729	178.98	3	6.664	180.54
2	6.675	179.74	4	6.651	181.03

[a] Key: (1) Ti(3)–O(6)–C(5)–O(5)–Ti(2); (2) Ti(1)–O(3)–C(3)–O(4)–Ti(2); (3) Ti(1)–O(1)–C(1)–O(2)–Ti(2); (4) Ti(3)–O(8)–C(7)–O(7)–Ti(1).

The EPR spectrum of the irradiated crystal/CCl_4 solution recorded at −160 °C is characteristic of a Ti^{3+} ion in an orthorhombic ligand field. The central intense signal is due to the ^{48}Ti isotope (natural abundance 73.98%), which has no nuclear spin. The satellite lines seen on each side of the Zeeman signal are poorly resolved. They are due to the hyperfine interaction between the electronic spin $S = {}^1/_2$ and the nuclear spins $I = {}^5/_2$ and ${}^7/_2$ of the isotopes ^{47}Ti and ^{49}Ti (natural abundances 7.75% and 5.51%).

The values of the g factors obtained by the EPR spectrum analysis are $g_x = 1.81$, $g_y = 1.89$, and $g_z = 1.95$. These values are relatively close to the g factor of the free electron; this shows that the fundamental state of the electron can be expressed as a singlet orbital term (no first-order $L{\cdot}S$ coupling). These values are characteristic of a Ti^{3+} ion in which the lone electron is in a d_{xy} orbital ($^2B_2$ term).

When the temperature is increased (above −100 °C), the EPR lines broaden. At room temperature the spectrum disappears. The broadening of the EPR lines can be associated with an electronic transfer between Ti^{3+} and Ti^{4+} centers.[22] The evolution of the EPR spectrum with temperature is characteristic of a mixed-valence compound whose fundamental state is localized at low temperature. In the classification proposed by Robin and Day,[23] this behavior is typical of a mixed-valence compound belonging to class II.

Discussion

The crystalline $Ti_6(OBu^n)_8(OAc)_8O_4$ is obtained from the alkoxide precursor $Ti(OBu^n)_4$.[1c]

The X-ray crystal structures of a few titanium(IV) alkoxides have been determined ($Ti(OMe)_4$,[24] $Ti(OEt)_4$,[25] $Ti(OMe)_3OEt$[26]). In each case, a tetramer involving octahedral coordination around the titanium atoms has been found.

In the liquid state, titanium alkoxides are not tetramers. Their degree of association depends on the size of the alkoxy group.[27] Those with bulky alkoxy groups are monomeric (OR = OPr^i, OAm^t); consequently, the titanium atom is in 4-fold coordination, while those with primary alkoxy groups such as $Ti(OEt)_4$ and $Ti(OBu^n)_4$ are trimers with 5-fold-coordinated titanium atoms.[10]

The strong reactivity of these alkoxides is under the control of two main parameters; the electrophilic power of the metal atom and the degree of unsaturation of the metal (the full coordination of the titanium atom is not satisfied).

Acetic acid is an important additive used in the sol–gel processing of transition-metal oxide gels.[5] It is added to prevent precipitation during the processing of TiO_2.[7] When acetic acid is added to a titanium alkoxide prior to hydrolysis, stable transparent sols and gels can reproducibly be obtained. These colloidal solutions can be easily deposited onto a substrate, leading to electrochromic TiO_2 coatings.[30]

The chemical role of the acetic acid in the control of the sol–gel processing has been recently pointed out.[7,8] The results presented in these papers give a complete and definite confirmation of its role.

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Crystals of $Ti_6(OBu^n)_8(OAc)_8O_4$ are obtained by adding 2 mol of acetic acid to 1 mol of titanium tetrabutoxide ($Ti_3(OBu^n)_{12}$). The chemical formula of the title compound shows that only 1.33 CH_3COOH/Ti has reacted. As a consequence, the excess of acetic acid can promote an esterification reaction (the presence of butyl acetate has been characterized by infrared spectroscopy), leading to the formation of H_2O molecules. Therefore, hydrolysis and condensation reactions occur.

The formation of $Ti_6(OBu^n)_8(OCOCH_3)_8O_4$ can be schematized by the four following chemical reactions that all occur during the sol–gel processing:

modification

$$6Ti(OBu^n)_4 + 12CH_3COOH \rightarrow Ti_6(OAc)_8(OBu^n)_{16} + 8Bu^nOH + 4AcOH$$

esterification

$$8Bu^nOH + 4AcOH \rightarrow 4Bu^nOAc + 4H_2O + 4Bu^nOH$$

hydrolysis

$$Ti_6(OAc)_8(OBu^n)_{16} + 4H_2O \rightarrow Ti_6(OAc)_8(OBu^n)_{12}(OH)_4 + 4Bu^nOH$$

oxolation

$$Ti_6(OAc)_8(OBu^n)_{12}(OH)_4 \rightarrow Ti_6(OAc)_8(OBu^n)_8O_4 + 4Bu^nOH$$

The overall reaction can be written

$$2Ti_3(OBu^n)_{12} + 12CH_3COOH \rightarrow Ti_6(OAc)_8(OBu^n)_8O_4 + 12Bu^nOH + 4Bu^nOAc$$

The structure presented in this paper clearly indicates the important role played by the acetic acid. It increases the coordination number of the titanium atom up to 6. As a consequence, the reactivity and the functionality of this new precursor are completely modified.

Moreover, the hydrolysis of the different ligands (butoxy or acetate) is differentiated: the butoxy groups would be the first to be hydrolyzed[7,8] and condensation between these buildings blocks will start between the OH bonds leading to a preferential structure of the Ti–O–Ti skeleton.

The structure of the title compound also emphasizes that the bridging mode is the preferred coordination of the acetate ligand in all the titanium alkoxo–acylate compounds.[28-30]

Conclusion

The sol–gel chemistry main trends exemplified in this paper are as follows:

Certain coordination changes are allowed by the metal in transition-metal alkoxide (here titanium) complexes. These coordination possibilities are governed by two main parameters, the electrophilic power of the metal atom and its degree of unsaturation.

The choice of the starting alkoxides can allow a change in the degree of association of the precursor that leads to the different structures of the hexameric titanium alkoxide acetates.

The role of acetic acid is now depicted in detail. It increases the coordination of the titanium atom up to six. Its acts as a bridging, network former, organizing the order of polyhedra. It also modifies the reactivity and the functionality of the new precursors toward hydrolysis.

There is preferential hydrolysis of the butoxy groups, which are replaced by oxo bridges.

Though on the basis of a specific well-defined crystalline compound $Ti_6(OAc)_8(OBu^n)_8O_4$, in this study, we believe that these above steps are quite general in the sol–gel chemistry, with the emphasis on the identification of reactive sites toward hydrolysis.

The mastering of this differentiation in reactivity leads to the control of the preferred structure in gels and therefore of the final materials.

Registry No. $Ti_6(OBu^n)_8(OCOCH_3)_8O_4$, 123288-92-6.

Supplementary Material Available: Table SI, listing the crystal data, intensity collection data, and structure refinement parameters (1 page); a table of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.