XANES and EXAFS Study of Titanium Alkoxides

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X-ray absorption studies (XANES-EXAFS) have been performed on four titanium alkoxides $Ti(OR)_4$ (OR = OAm^t, OPr^i, OEt, OBu^n). Only one kind of Ti-O distance of about 1.80 Å has been found for $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$ from EXAFS experiments, while two kinds of Ti-O distances of about 1.80 and 2.05 Å, respectively, attributed to terminal and bridging alkoxy groups, have been found for both $Ti(OEt)_4$ and $Ti(OBu^n)_4$. Moreover, for these latter compounds Ti-Ti correlations have been observed for the first time (about 3.1 Å), giving direct evidence of the oligomeric structure of such compounds. A model is proposed for the molecular structure of each alkoxide, based on Ti-O and Ti-Ti distances (EXAFS) together with the coordination number of titanium (XANES). $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$ are monomeric species in which the titanium atom is 4-fold coordinated (tetrahedron). $Ti(OEt)_4$ and $Ti(OBu^n)_4$ are oligomers (most probably trimers) in which each titanium atom is in 5-fold coordination.

Introduction

Metal alkoxides have been widely used during the last decade as molecular precursors for the sol-gel synthesis of glasses and ceramics.[2] Upon the use of hydrolysis and condensation reactions, a macromolecular oxide network is formed that can be converted into a dense material after drying and densification.[3a] Better ceramics will be obtained via the sol-gel process when a real understanding of the chemistry is reached. Therefore, the molecular structures of the metal alkoxide precursors have to be accurately known.

Most sol-gel work deals with silica obtained from silicon alkoxide such as TMOS ($Si(OMe)_4$) or TEOS ($Si(OEt)_4$).[4-7] In this case, Si is always 4-fold coordinated and all alkoxides are monomeric. Experiments are then focused on the hydrolysis-condensation reactions in the presence of an acid or a base catalyst.[8] The problem is much more complicated with other alkoxides such as $Ti(OR)_4$. The usual coordination number of titanium is greater than its oxidation state. Therefore oligomerization may occur in order to satisfy the full coordination of the metal atom.[2] The question then arises about the molecular structure of the molecular precursor.[3b]

X-ray diffraction (XRD) experiments performed on $Ti(OEt)_4$ single crystals show that, in the solid state, titanium ethoxide forms tetramers.[10] This is however no longer true when the ethoxide is in solution. Cryoscopic measurements carried out in benzene suggest that $Ti(OPr^i)_4$ is monomeric, while $Ti(OEt)_4$ and $Ti(OBu^n)_4$ should rather be trimeric.[9] Several molecular structures have been suggested (Figure 1), but none of them could be clearly demonstrated;[11,13] ^{1}H and ^{13}C NMR experiments were not able to solve the problem. At room temperature, a rapid exchange between terminal and bridging alkoxy groups was observed.[9] At low temperature, two sets of peaks were seen that were attributed to the formation of tetramers together with the trimers.[13,14] [47]Ti and [49]Ti NMR experiments have been performed recently on $Ti(OR)_4$ alkoxides (R = Pr^i, Bu^n, Pr^n, Bu^t).[15] Resonance peaks were observed for $Ti(OPr^i)_4$ and $Ti(OBu^t)_4$ only, which were assumed to be monomeric. Large electric field gradients occur in oligomeric structures, giving rise to very broad resonance lines. An infrared study of $Ti(OEt)_4$ was published[16] giving an assignment of the $\nu(C-O)$ and $\nu(Ti-O)$ bands arising from terminal and bridging OR groups.

This paper presents an X-ray absorption study (XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure)) of titanium alkoxides at the titanium K-edge. Four alkoxides $Ti(OR)_4$ were chosen corresponding to tertiary, $Ti(OAm^t)_4$, secondary, $Ti(OPr^i)_4$, and primary, $Ti(OEt)_4$ and $Ti(OBu^n)_4$, alkoxy groups (OR = OAm^t, OPr^i, OEt, and OBu^n, which stand respectively for *tert*-amyloxide, isopropoxide, ethoxide, and *n*-butoxide). Ti⋯Ti correlations were observed for the first time, giving direct evidence of the oligomeric structure of $Ti(OEt)_4$ and $Ti(OBu^n)_4$ alkoxides. A model is discussed for

the molecular structure of each alkoxide, based on Ti-O and Ti⋯Ti distance together with the coordination number of titanium.

Experimental Section

Samples. $Ti(OPr^i)_4$, $Ti(OEt)_4$, and $Ti(OBu^n)_4$ were purchased from Fluka and used as received. $Ti(OAm^t)_4$ was prepared from $Ti(OPr^i)_4$ by alcohol exchange according to a previously published procedure.[17]

X-ray Absorption Study. (a) Experimental Procedure. The titanium K-edge spectra were recorded at room temperature at LURE, the French synchrotron radiation facility, by using an EXAFS III spectrometer. The operating conditions in the storage ring DCI were the following: positions at energies of 1.85 GeV and intensities of about 150 mA.

The two-crystal Si 311 monochromator was detuned by about 30% from its maximum flux position to discard harmonics from the beam. The photon flux was measured by two ionization chambers flushed by a helium-neon gas mixture. The entrance slit was 0.5 mm. A 6-μm titanium metallic foil was used to check the energy calibration just before or just after each XANES spectrum. This ensures an experimental accuracy in energy better than 0.25 eV.

For the study of the Ti K-edge structure, the energy was scanned by 0.25-eV steps over the energy range 4950-5050 eV, while, for EXAFS data acquisition, the energy was scanned by 2-eV steps over the energy range 4850-5600 eV. The accumulation time was 1.6 or 2.4 s per point. The pure alkoxides were sealed into cells in order to avoid hydrolysis. The thickness of the cells was 0.15 mm, and the windows were made of X-ray-transparent Kapton.

(b) Data Analysis. Near-edge spectra were processed by subtracting a linear background computed by least-square fitting from the preedge region and normalized by using the beginning of EXAFS oscillation as a unit.

Energy calibration was made by taking the position of the first max-

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(1) (a) Laboratoire de Spectrochimie du Solide. (b) Laboratoire de Spectrochimie des Éléments de Transition. (c) LURE.
(2) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxide*; Academic: New York, 1978.
(3) (a) Third International Conference on Ultrastructure Processing of Ceramics Glasses and Composites, San Diego, CA, Feb 1987. (b) Sanchez, C.; Babonneau, F.; Doeuff, S.; Leaustic, A. Presented at the Third International Conference on Ultrastructure Processing of Ceramics Glasses and Composites, San Diego, CA, Feb 1987.
(4) Orcel, G.; Hench, L. *J. Non-Cryst. Solids* **1986,** *79,* 177.
(5) Kelts, L.; Elffinger, N.; Melpolder, S. M. *J. Non-Cryst. Solids* **1986,** *83,* 345.
(6) Pouxviel, J. C.; Boilot, J. P.; Beloeil, J. C.; Lallemand, J. Y. *J. Non-Cryst. Solids* **1987,** *89,* 345.
(7) Chen, K. C.; Tsuchiya, T.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1986,** *81,* 227.
(8) Pope, E. J. A.; Mackenzie, J. D. *J. Non Cryst. Solids* **1986,** *86,* 185.
(9) Bradley, D. C.; Holloway, C. E. *J. Chem. Soc. A* **1968,** 1316.
(10) Ibers, J. A. *Nature (London)* **1963,** *197,* 686.
(11) Martin, R. L.; Winter, G. *J. Chem. Soc. A* **1961,** 2947.
(12) Coughlan, C. N.; Smith, H. S.; Katz, W.; Hodgson, W.; Growe, R. W. *J. Am. Chem. Soc.* **1951,** *73,* 5652.
(13) Weingarten, H.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1965,** *87,* 724.
(14) Bradley, D. C.; Holloway, C. E. *Proc. Paint Res. Inst.* **1965,** *39,* 487.
(15) Hao, N.; Sayer, B. G.; Denes, G.; Bickley, D. G.; Detellier, C.; McGlinchey, M. J. *J. Magn. Reson.* **1982,** *50,* 50.
(16) Bradley, D. C.; Westlake, A. H. *Proc. Symp. Coord. Chem.,* **1964.**
(17) Bradley, D. C.; Mehrotra, R. C.; Wardlow, W. *J. Chem. Soc.* **1952,** 2027.
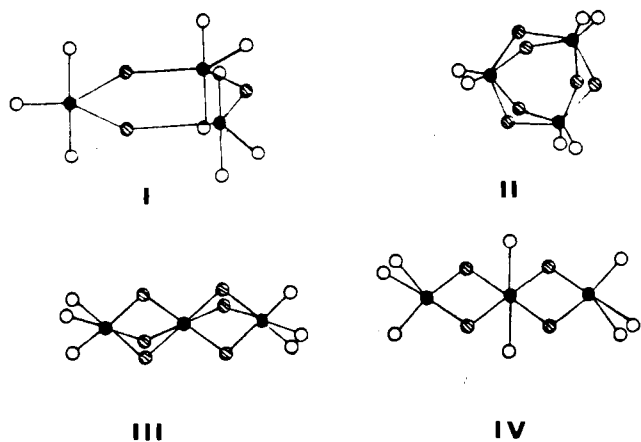
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Figure 1. Proposed structures for liquid Ti(OEt)$_4$.

Table I. Preedge Peak Parameters for Titanium Alkoxides

compd	peak position,[a] eV	peak height	half-width, eV
Ti(OAm^t)$_4$	2.8	0.74	1.6
Ti(OPr^i)$_4$	3.0	0.50	1.7
Ti(OEt)$_4$	3.4	0.32	2.2
Ti(OBu^n)$_4$	3.1	0.30	2.2

[a] The first maximum of the absorbance of the metallic titanium edge is taken as the zero energy at 4964.2 eV.

Table II. Preedge Peak Parameters for Titanium Compounds

compd	peak position,[a] eV	peak height	half-width, eV	ref
Ba$_2$TiO$_4$	3.5	0.84	1.5	24
TiCl$_4$	3.5	0.57	2.2	27
Ti[N(CH$_3$)$_2$]$_4$	3.4	0.83	2.8	24
titanyl phthalocyanine	4.5	0.79	1.9	24
TiO$_2$ anatase	1.8	0.13		this
	4.6	0.23		work
	7.4	0.22		

[a] The first maximum of the absorbance of the metallic titanium edge is taken as a reference at 4964.2 eV.

imum of the absorbance of the metallic titanium spectrum at 4964.2 eV.

Experimental data are shown in Figure 2, but energies of the main features were deduced from a fit of experimental data and an analysis of the first and second derivatives of the absorbance. EXAFS modulations were analyzed by using standard methods.[18-21] The continuous absorption background was estimated by fitting the spectrum before the edge by a Victoreen function, while the main absorption beyond the edge $\bar{\mu}(E)$ was fitted with an iterative procedure.[21] Normalization of the EXAFS signal was achieved by using $\chi(E) = (\mu(E) - \bar{\mu}(E))/\bar{\mu}(E)$. Structural information was extracted by using single-scattering theory:[20]

$$k[\chi(k)] = \sum_i \frac{N_i}{R_i^2} [f_i(k)] e^{-2\sigma^2 k^2} e^{-2R_i/\lambda_i(k)} \sin [2kR_i + \Phi_i(k)]$$

N_i is the number of atoms in the ith scattering shell at a distance R_i from the absorbing atom. σ_i is a coefficient related to thermal and static disorders. $\lambda_i(k)$ is the electron mean free path, and $f_i(k)$ and $\Phi_i(k)$ are the amplitude and the phase shift functions characteristic of the ith shell. Tabulated values of Teo et al.[22] were used.

The electron mean free path $\lambda(k)$ was approximated by $\lambda = k/\Gamma$, where Γ was a fitting parameter.

(18) Raoux, D.; Petiau, J.; Bondot, P.; Calao, G.; Fontaine, A.; Lagarde, P.; Levitz, P.; Loupias, G.; Sadoc, A. *Rev. Roum. Phys.* **1980**, *15*, 1079.
(19) Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *53*, 769.
(20) Teo, B. K. *Exafs: Basic Principles and Data Analysis*; Springer: Berlin, 1986.
(21) We used the EXAFS data analysis set of programs written in Fortran 77 and implemented by A. Michalowicz (LURE, 1985) on the Univac 1110 computer of Paris-Sud Informatique at Orsay. The programs are accessible and are available from A. Michalowicz.
(22) Teo, B. K.; Lee, P. A.; Simons, A. L.; Eisenberg, P.; Kincaid, B. M. *J. Am. Chem. Soc.* **1977**, *99*, 3854.
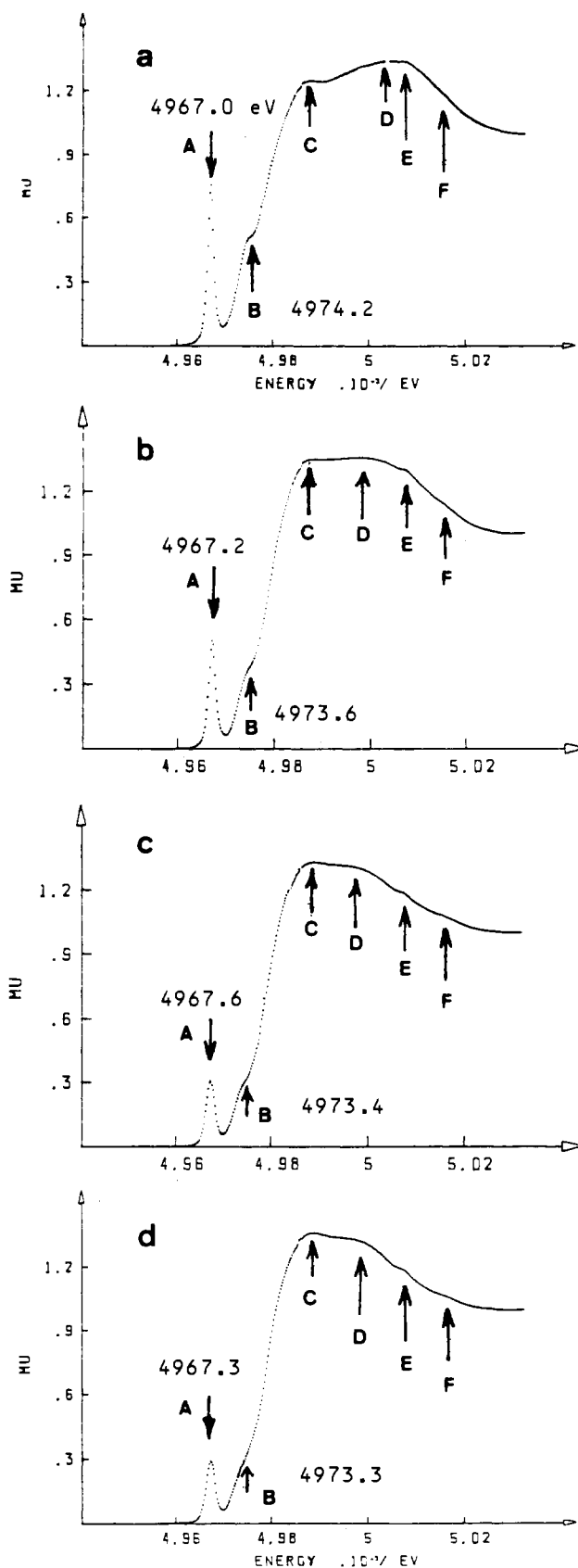

Figure 2. Ti K-edge XANES spectra: (a) Ti(OAm^t)$_4$; (b) Ti(OPr^i)$_4$; (c) Ti(OEt)$_4$; (d) Ti(OBu^n)$_4$. The letters C, D, E, and F correspond respectively to the following edge peak values (eV): (a) 4987.8, 5003.8, 5007.2, 5015.8; (c) 4988.8, 4997.8, 5007.7, 5015.8.

The reliability of the fit was determined by a weighted agreement factor $\rho = \sum W_t (\chi_{exptl} - \chi_{calcd})^2 / \sum W_t \chi_{exptl}^2$.

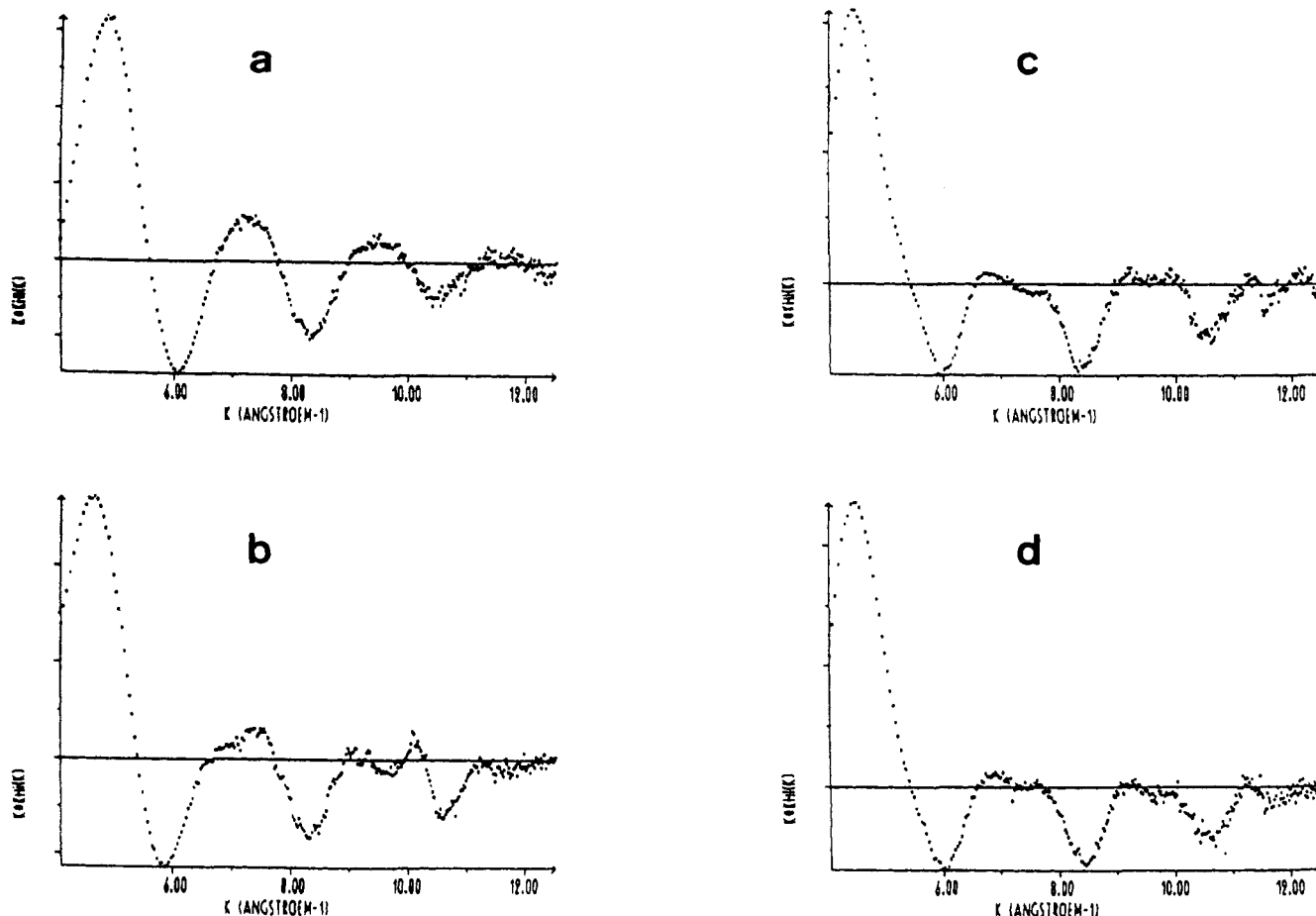The weighting factor W_t was zero below 4 Å^{-1} and equal to k^3 above 4 Å^{-1}.

Figure 3. k-Space spectra $k[\chi(k)]$: (a) Ti(OAm^t)$_4$; (b) Ti(OPr^i)$_4$; (c) Ti(OEt)$_4$; (d) Ti(OBu^n)$_4$.

Results

(a) XANES. Ti K-edge XANES spectra of the four alkoxides Ti(OR)$_4$ (OR = OAm^t, OPr^i, OEt, OBu^n) are represented in Figure 2. Details of the near-edge data are collected in Table I.

Each spectrum exhibits a single preedge peak (A) whose intensity decreases from 0.75 (Ti(OAm^t)$_4$) to about 0.30 (Ti(OEt)$_4$ and Ti(OBu^n)$_4$). Peak positions are close to each other, shifting slightly from 4967.0 to 4967.6 eV. This shift is small but beyond experimental error.

These preedge features will be discussed later, but it can already be said that the strong intensity of the preedge peak suggests that the absorbing atom does not correspond to an inversion center in the molecular structure. As for the other transitions, we can note that in Ti(OAm^t)$_4$ two main absorption edges (C and D) occur at 4987.8 and 5003.8 eV (Figure 2a), analogous to the case of other tetrahedral liquid or solution samples (aqueous MnO$_4^-$ for example). On the contrary, the two main bands in the three other spectra are not so characteristic of a known stereochemical structure (in an octahedral complex in particular, peaks C and D are well resolved).

Finally, we may point out that structures B, E, and F at 4974.2, 5007.2, and 5015.8 eV are present in all the spectra; they have low intensity, and we checked that they are not artifacts related to the monochromator used (they appear also with a Si 111 two-crystal monochromator). We propose a possible explanation in the Discussion.

(b) EXAFS. Figure 3 gives the experimental EXAFS spectra $k[\chi(k)]$ (k space) of the four Ti(OR)$_4$ alkoxides. Fourier transforms of this signal, multiplied by k_3, yield the radial distribution functions shown in Figure 4. In Figure 4b–d a first peak, due to noise, has been filtered out. On each Fourier transform, an intense peak is observed at short distances (1.4 Å) due to backscattering from the first neighbor's oxygen atoms. For Ti(OAm^t)$_4$ no other peak appears, while for the other alkoxides

Table III. Fitting Results for the EXAFS Spectra of Titanium Alkoxides

	N	R, Å	σ, Å	E_0, eV	ρ, %
		Ti(OAm^t)$_4$			
Ti–O	4.3	1.81	0.070	4995	3
		Ti(OPr^i)$_4$			
Ti–O	3.0	1.76	0.077	4981	
Ti–C	6.0	2.95	0.059	4977	3
	3.8	3.24	0.059	4977	
		Ti(OEt)$_4$			
Ti–O	3.4	1.82	0.072	4995	
	1.8	2.05	0.072	4995	5.9
Ti–Ti	1.2	3.12	0.056	5013	
		Ti(OBu^n)$_4$			
Ti–O	4.2	1.83	0.087	4994	
	2.7	2.07	0.087	4994	4.7
Ti–Ti	0.7	3.08	0.031	5008	

weaker peaks are visible at longer distances (2.5–3 Å) due to the backscattering from the neighboring carbon atoms and/or titanium atoms when the compound is an oligomer. It can be noticed that the Fourier transforms of Ti(OEt)$_4$ and Ti(OBu^n)$_4$ are quite similar with one peak around 3 Å, while the Fourier transform of Ti(OPr^i)$_4$ exhibits several peaks from 2.5 to 3.2 Å. The various peaks were filtered, and inverse Fourier transforms to k space were performed with different filtering limits: 0.5–2 Å for Ti(OAm^t)$_4$, 0.5–3 Å for Ti(OPr^i)$_4$, and 0.5–3.2 Å for Ti(OEt)$_4$ and Ti(OBu^n)$_4$. The resulting filtered data $k[\chi(k)]$ vs k, in the region 4–12.5 Å^{-1}, are shown as dashed curves in Figure 5 together with the best fit curve (full line).

The fitting results are summarized in Table III with the fitted edge energy E_0, the absorbing atom–neighbor distance R, the Debye–Waller factor σ, and the agreement factor ρ. The N value is the fitted value for the number of backscattering centers. It
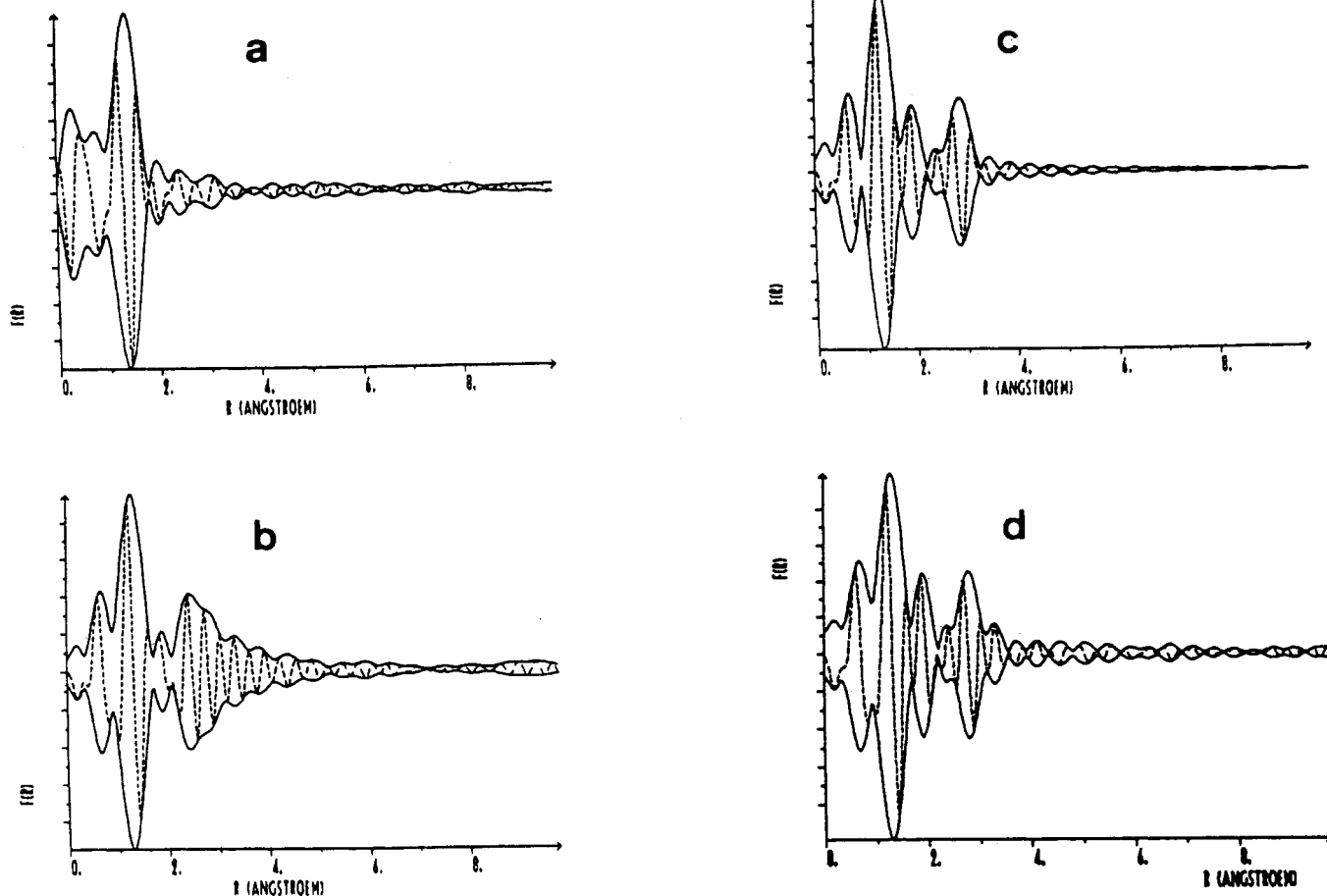
Figure 4. k^3 Fourier transform spectra: (a) Ti(OAm^t)$_4$; (b) Ti(OPr^i)$_4$; (c) Ti(OEt)$_4$; (d) Ti(OBu^n)$_4$.
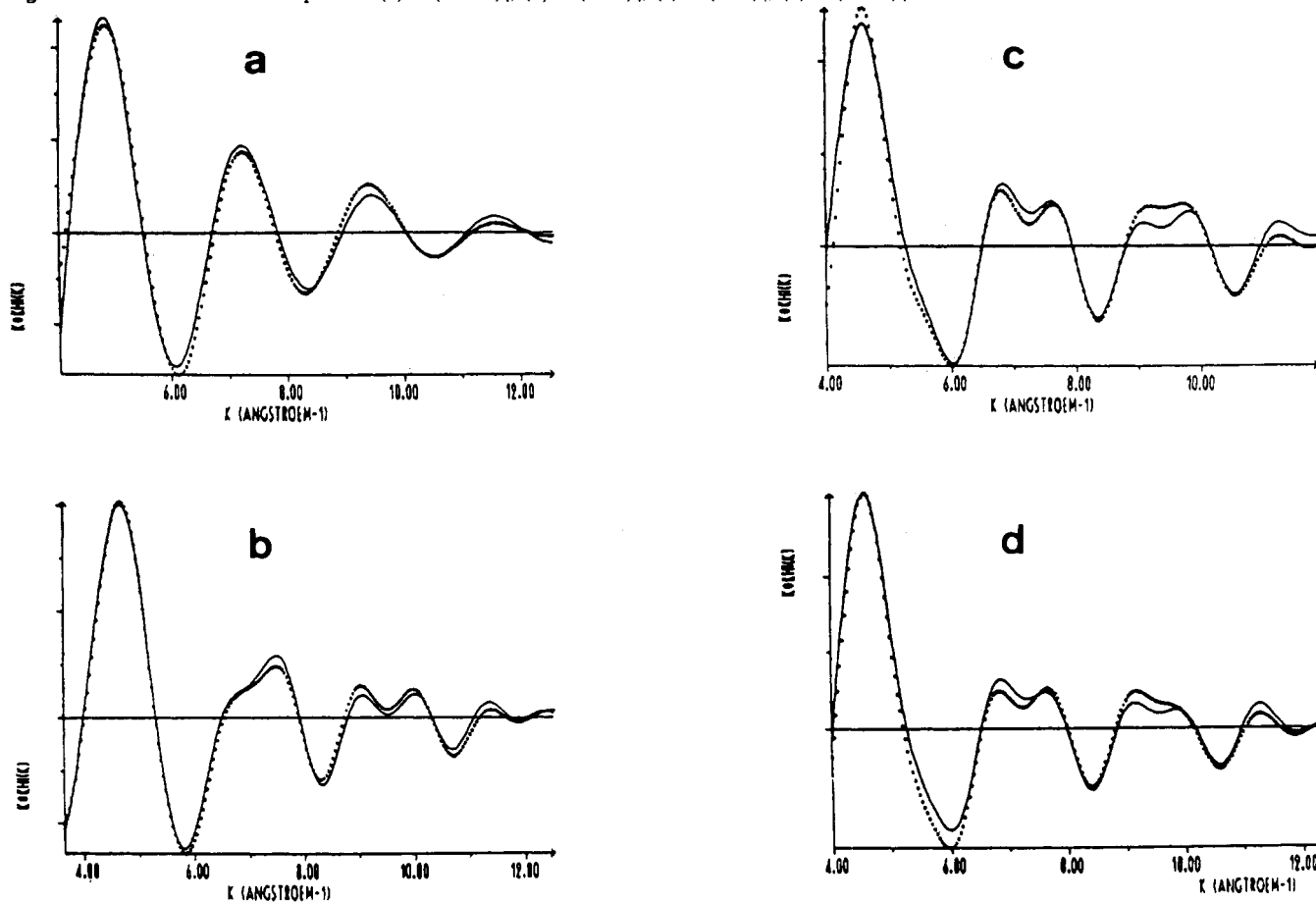
Figure 5. k-Space filtered spectra (broken curves) and fittings (solid curves): (a) Ti(OAm^t)$_4$; (b) Ti(OPr^i)$_4$; (c) Ti(OEt)$_4$; (d) Ti(OBu^n)$_4$.
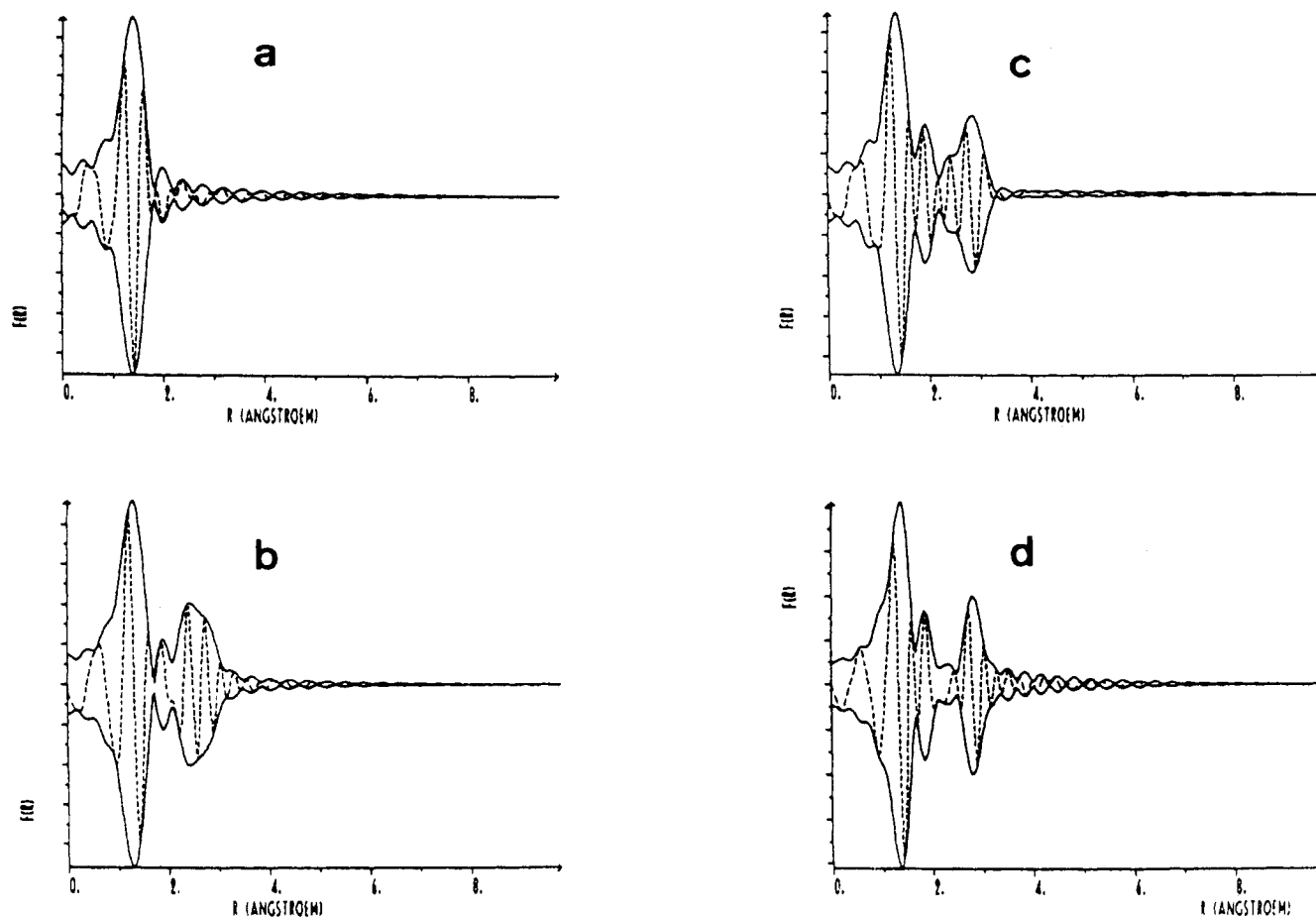
Figure 6. Simulated Fourier transforms: (a) $Ti(OAm^t)_4$; (b) $Ti(OPr^i)_4$; (c) $Ti(OEt)_4$; (d) $Ti(OBu^n)_4$.

can be affected by the quality of the samples and especially by their inhomogeneities. A rather large uncertainty is expected for this value, which should be considered as a rough estimate of the real number of neighbors. In our case, the experimental error is increased by the fact that our samples are liquids. This increases the thermal agitation and Debye–Waller factors of the remote neighbors. This can explain in particular the total absence of second-shell neighbors in the Fourier transform of $Ti(OAm^t)_4$.

Simulated Fourier transforms are shown in Figure 6. They are in rather good agreement with the experimental ones (Figure 3). For both $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$, the fitting results for the first shell show only one Ti–O distance at 1.81 and 1.76 Å, respectively, while for the other two alkoxides, two Ti–O distances appear at 1.82 and 2.05 Å for $Ti(OEt)_4$ and 1.83 and 2.07 Å for $Ti(OBu^n)_4$. As far as the longer distances are concerned, we found that the calculated Ti–Ti distances are respectively 3.08 and 3.12 Å. In $Ti(OPr^i)_4$, the peaks around 3 Å in the Fourier transform (Figure 3b) were found to be due to backscattering contributions from neighboring carbon atoms. All attempts to fit them with contributions from titanium atoms failed.

The two Ti–C distances can be assigned to the two kinds of carbon atoms present in the isopropoxy groups. No backscattering contributions of carbon atoms were seen in $Ti(OBu^n)_4$ and Ti-$(OEt)_4$. They might however exist but are probably hidden by the contributions from the titanium atoms. The three-shell fits for these two alkoxides must thus be regarded as a partial description of the structure, and this can explain the high value of the agreement factor.

Discussion

We wish to comment on three points in this discussion: (i) the XANES preedge features of the four spectra, in relation to the spectral features of well-known model compounds of tetrahedral, square-pyramidal, or octahedral symmetry, (ii) the EXAFS results in connection with the available X-ray diffraction data, and (iii) the possible structures of pure liquid alkoxides, which can be

inferred from the present data and from previous characterization by other techniques.

The near-edge spectrum of Ti(IV) is rich in information from which details on the coordination environment can be deduced. The preedge peaks are due to transitions of the photoelectron toward final states that are essentially Ti 3d bound states. These transitions are quite sensitive to the crystal field around titanium. The number, position, and intensity of these prepeaks give information about the coordination environment of titanium.[23-25]

The main reason for this can be found in the d^0 electronic configuration of titanium(IV): all the d symmetry molecular levels are vacant and available to receive the photoelectron to give a $(1s)^1(3d)^1$ excited electronic configuration. The symmetry of the final state is that of the d level since the 1s deep hole is totally symmetrical and all other shells are filled. Taking into account only dipolar electric transitions ($\hat{\delta}$ dipolar operator), the transition moment is given by the general Fermi golden rule

$$M \propto \langle \psi_{ground}|\hat{\delta}_{dip}|\psi_{excited}\rangle^2 [N(E)]\delta(h\nu - E_{ground} + E_{excited})$$

$N(E)$ is the number of vacancies in the excited states, which is 0, 1, or 2 in a molecular orbital description of a filled, singly occupied, or vacant orbital; δ is a Dirac function, and the matrix element is a complex quantum function impossible to be computed exactly in the present state of the art.

In a pure tetrahedral symmetry, one intense single peak is expected. It corresponds to a dipolar-allowed transition from the 1s to t_2 molecular levels built from the 3d and 4p metal orbitals and from neighbor's orbitals.

In an octahedral symmetry, a triplet feature is observed, the intensity of which is rather low due to the presence of an inversion

(23) Dumas, T.; Petiau, J. *J. Non-Cryst. Solids* **1986**, *81*, 201.
(24) Yarker, C. A.; Johnson, P. A. V.; Wright, A. C.; Wong, J.; Greegor, R. B.; Lytle, F. W.; Sinclair, R. N. *J. Non-Cryst. Solids* **1986**, *79*, 117.
(25) Emili, M.; Incoccia, L.; Mobilio, S.; Fagherazzi, G.; Guglielmi, M. *J. Non-Cryst. Solids* **1985**, *74*, 129.

center at the Ti site ($\Gamma_o \equiv T_{1u}$). The two peaks located at upper frequency are assigned to Laporte-forbidden $A_{1g} \rightarrow T_{2g}$ and $A_{1g} \rightarrow E_g$ transitions ($1s \rightarrow 2t_{2g}$ and $1s \rightarrow 3e_g$ levels). The weakness of the intensity is due to the absence of A_{1g} in the direct product; there is no more 3d–4p mixing for example. The presence of the two transitions may be assigned to some relaxation of the Laporte selection rules, by vibronic coupling, or to the interference of a quadrupolar mechanism, as already demonstrated in a square-planar $CuCl_4^{2-}$ complex.[26]

The assignment of the first peak is still controversial.[27,28] It appears always at the same energy ($\simeq 4966$ eV), much below the other transitions, with weak intensity, and it will not be discussed further. Nevertheless, its presence in our spectra of liquid samples allows us to rule out any interpretation of this transition based only on 3d solid-state interactions.

Preedge data for some Ti model compounds in various coordination states are given in Table II. In Ba_2TiO_4 and $Ti[N(CH_3)_2]_4$, Ti is in 4-fold coordination,[24] the preedge peak occurs around 4967.5 eV, and the peak intensity is around 0.85. In $TiCl_4$,[27] the intensity is lower (0.57). This has been analyzed in terms of decreased mixing of the 4p metal orbitals from about 17% in TiO_4^{4-} (and a Ti–O distance of 1.8 Å) to about 1.5% in $TiCl_4$ (and a Ti–Cl distance of 2.19 Å).[29]

In titanyl phthalocyanine[24] the Ti site is 5-fold coordinated in square-pyramidal surroundings. The preedge peak is unique and is shifted up to 4968.7 eV. The intensity is a bit lower. The transition corresponds here to an allowed jump into the $d_{z^2}(Ti)$ + $4p_z(Ti)$ + $2p_z(O)$ molecular orbital.

The TiO_2 anatase phase exhibits the usual triplet feature found in octahedral environments. The prepeak positions are at 4966.0, 4968.8, and 4971.6 eV, and their respective intensities are quite low (0.13, 0.23, 0.22). If the decrease in intensity when the symmetry increases is the main observable feature, the shift in energy, although weak, is significant: 1.1 eV from Ba_2TiO_4 to anatase and 0.6 eV from $Ti(OAm^t)_4$ to $Ti(OEt)_4$. Two explanations can be put forward to explain this trend: (i) the smaller overall destabilization of t_2 orbitals in a tetrahedral field compared to that in an octahedral t_{2g} one (initial-state effect) and, (ii) a stronger electron–hole interaction in the case of t_2 tetrahedral levels, containing more 4p participation than the t_{2g} octahedral ones (final-state effect). Both hypotheses must be verified with other examples.

The XANES data recorded for $Ti(OR)_4$ titanium alkoxides do not show any evidence of a pure octahedral symmetry. The position and the intensity of the prepeak seem to indicate that the symmetry is close to that for a tetrahedron. The intense prepeak of $Ti(OAm^t)_4$ at 4967 eV is in agreement with a pure tetrahedral environment. The prepeak of $Ti(OPr^i)_4$ is lower in intensity and rather similar to that of $TiCl_4$. It should still indicate a tetrahedral environment but with a lower symmetry. These two titanium alkoxides should be monomers, with a higher tetrahedral symmetry for $Ti(OAm^t)_4$ due to the presence of bulky *tert*-amyloxide groups.

The spectra of $Ti(OEt)_4$ and $Ti(OBu^n)_4$ are rather similar. The intensities of the prepeaks are lower ($\simeq 0.3$), and this could be due to a 5-fold coordination; the positions are at lower frequencies compared to that of titanyl phthalocyanine, where titanium is also in 5-fold coordination (square-pyramidal environment) but with one short distance Ti=O.

Contrary to the preceding transitions, the three humps at 4974.2, 5007.2, and 5015.8 eV cannot be used to characterize the stereochemistry of the titanium coordination sphere since they are present in all spectra at practically the same energy and intensity, and it is tempting to assign them to two-electron

transitions (shake-down for the first one, shake-off for the two last ones). But we have no experimental evidence other than their weak intensity and the constancy of their energies in the different spectra to advance this hypothesis.

We turn now to the discussion of the EXAFS results, shown in Figures 3–6 and in Table III. These results can be compared to the published X-ray diffraction study of the $Ti(OEt)_4$ crystalline structure.[10] It reveals three different Ti–O bonds: 1.77 Å for terminal ethoxy groups, 2.03 Å for bridging groups bonded to two titaniums, and 2.23 Å for bridging groups bonded to three titaniums. So it seems quite reasonable to assume that, in both $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$, terminal OR groups are only present, while, in $Ti(OBu^n)_4$ and $Ti(OEt)_4$, both terminal and bridging groups exist. This is the first indication of monomeric structures for $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$ and a possible oligomeric structure for $Ti(OBu^n)_4$. The second one is the presence of Ti–Ti correlations in the fitting results of $Ti(OBu^n)_4$ and $Ti(OEt)_4$, calculated respectively at 3.08 and 3.12 Å.

The preceding discussion placed in evidence both XANES and EXAFS results that show that $Ti(OAm^t)_4$ and $Ti(OPr^i)_4$ are monomers while $Ti(OEt)_4$ and $Ti(OBu^n)_4$ are oligomers. This is quite in agreement with previous published data.[9] But the interest of the X-ray absorption experiments is to provide direct structural information on these liquid titanium alkoxides. It is obviously impossible to propose complete descriptions of the structures, but both XANES results (stereochemistry around titanium) and EXAFS results (nature of neighboring atoms and distances) can lead to structural models for each alkoxide.

$Ti(OAm^t)_4$ behaves as a tetrahedral monomer with the four equivalent oxygen atoms attached to the *tert*-amyloxy groups at 1.81 Å from titanium. $Ti(OPr^i)_4$ also seems to be a monomer but with a lower symmetry according to the intensity of the prepeak of the XANES spectrum. Recent results of $^{47}Ti^{49}Ti$ NMR spectra recorded in our laboratory[1a] have shown single peaks for $Ti(OPr^i)_4$ and $Ti(OAm^t)_4$ and a broad signal for oligomeric species such as $Ti(OEt)_4$ and $Ti(OBu^n)_4$.

The Ti–O distance is 1.76 Å for $Ti(OPr^i)_4$. The shorter distance in the OPr^i derivative compared to that in the OAm^t derivative is consistent with the less bulky character of OPr^i groups, allowing a closer approach to titanium. For the $Ti(OPr^i)_4$ sample some information is also available on Ti–C distances. Assuming single-scattering effects only, a geometry for the isopropoxy groups may be proposed. On the basis of the C–O distance value known from the XRD structure of isopropoxy groups bonded to aluminum,[30] a Ti–C distance of 2.95 Å between Ti and the first carbon atom of the $O-CH(CH_3)_2$ group leads to a Ti–O–C angle of 135° and a distance between titanium and the carbon atoms of the methyl groups of around 3.30 Å, which is in close agreement with the fitted distance of 3.24 Å.

The fitted N values are too high compared to the N values for oxygen atoms: we must therefore be prudent with the data concerning the carbon atoms. (i) Some multiple scattering effects may occur that modify the phase and thus can affect the Ti–C distances and the corresponding N values. (ii) A two-shell fitting procedure is certainly incomplete to describe all the carbon atoms in isopropoxy groups. $Ti(OEt)_4$ was the subject of various studies in order to propose a structural model as already mentioned in the Introduction (Figure 1). Cryoscopic measurements suggest a trimeric structure. Since the number of neighboring titanium atoms N is not precisely known, EXAFS experiments cannot provide any precise information concerning the degree of condensation. The fitted value is 1.2, but the N and σ values appear correlated in the fitting procedure so that an increase of σ can lead to an increase of N without a large change in the agreement factor. If we assume a trimeric structure, some structural models shown in Figure 1 might be rejected. The XANES spectrum shows no evidence for octahedral coordination of Ti as structures II and III. Structure IV exhibits two Ti sites in 5-fold coordination and one Ti site in 6-fold coordination. Thus, the XANES

(26) Hahn, J. E.; Scott, R. A.; Hodgson, K. O.; Doniach, S.; Desjardins, S. R.; Solomon, E. *J. Chem. Phys. Lett.* **1982**, *88*, 595.

(27) Greegor, R. B.; Lytle, F. W.; Sandström, D. R.; Wong, J.; Schultz, P. *J. Non-Cryst. Solids* **1983**, *55*, 27.

(28) Poumellec, B.; Lagnel, F.; Marucco, J. F.; Touzelin, B. *Phys. Status Solidi B* **1986**, *133*, 371.

(29) Verdaguer, M.; Cartier, C. Presented at the Conference on Progress in X-ray Studies by Synchrotron Radiation, Strasbourg, France, April 1985.

(30) Garbauskas, M. F.; Wengrovius, J. H.; Going, R. C.; Kasper, J. S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1536.

spectrum should present a shoulder around 4966 eV, which is observed in all samples of an octahedral coordination. We did not see it, even in the second derivative of the spectrum.

X-ray absorption results seem to be in agreement with structure I: three equivalent Ti sites in 5-fold coordination. In such a model, titanium atoms are surrounded by three short Ti–O bonds and two long Ti–O bonds. This is in agreement with the ratio betwen short and long distances (3.4 at 1.82 Å, 1.8 at 2.05 Å) given by our EXAFS results. So, structure I appears to be more realistic for describing the $Ti(OEt)_4$ structure, but it is certainly not the only one. XANES and EXAFS results for $Ti(OBu^n)_4$ are similar to those concerning $Ti(OEt)_4$. The same structural model might then be proposed.

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Doping of Copper(II) into the Macrocyclic Amine tet a: Structural and Spectroscopic Studies

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The synthesis, X-ray structure, and electronic and EPR spectra of the Cu(II)-doped dihydroperchlorate of tet a (*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) are presented. Pale pink crystals of $(H_{1.86}Cu_{0.07}C_{16}H_{36}N_4)(ClO_4)_2 \cdot 2(CH_3)_2SO$ are monoclinic, space group $P2_1/n$, with $a = 12.330$ (4) Å, $b = 15.119$ (12) Å, $c = 8.808$ (2) Å, $\beta = 104.07$ (2)°, $Z = 2$, and R_F (R_{wF}) = 0.057 (0.078) for 2426 reflections. The structure contains Cu-doped diprotonated tet a cations $[Cu_{0.07}H_{1.86}(tet\ a)]^{2+}$ with site symmetry C_i separated by perchlorate anions and dimethyl sulfoxide solvate molecules. As determined crystallographically, 7% of the Cu sites are occupied; 93% of the cations are diprotonated amines whose structure compares favorably with that reported for the diperchlorate salt of the $H_2(cyclam)^{2+}$ cation. *Apparent* Cu–N distances are 2.117 (2) and 2.015 (2) Å for the quaternary and ternary amines, respectively. The shortest possible apical bonding distance from the center of symmetry (the Cu(II) site) involves a perchlorate O atom (Cu···O = 2.905 (2) Å). This distance is ca. 0.3 Å longer than those reported for related diperchlorate salts of Cu(II)–macrocyclic amine complexes. The observed blue shift of the doped Cu(II) species absorbance (λ_{max} = 485 (1) nm) relative to that of the reference neat Cu(tet a)$(ClO_4)_2$ (λ_{max} = 506 (1) nm) is attributed to the increased ligand field associated with the unusually weak apical bonding in the doped species. Consistent with the apparent lack of crystallographic disorder, the EPR spectra of the doped material are those of a single tetragonal Cu(II) species having $g_\parallel$ = 2.185, $g_\perp$ = ca. 2.05, and $A_\parallel^{Cu}$ = 203 × 10^{-4} cm^{-1}.

In the course of preparing stable Cu(II) aliphatic thiolates, we found it useful to displace macrocyclic ligands such as tet a[1] or tet b from Cu(II) with N_2S_2 ligands.[2,3] For example, the reaction of Cu(tet a)$(ClO_4)_2$ with *N,N'*-ethylenebis(L-cysteine) dimethyl ester yields the stable CuN_2S_2 complex and displaced tet a·2HClO$_4$. When a DMSO/water cosolvent was used, the ligand salt crystallized and occasionally exhibited a faint pink coloration. Subsequent studies yielded crystallographically identical pink crystals from solutions of tet a·2HClO$_4$ and Cu(tet a)$(ClO_4)_2$. EPR studies revealed the presence of magnetically dilute tetragonal Cu(II) ions, and electronic spectral studies suggested that the Cu(II) ions experienced a ligand field (LF) significantly greater than that of neat Cu(tet a)$(ClO_4)_2$. We have been interested in the structural, spectroscopic, and magnetic properties of Cu(II) complexes that readily dope into the structurally similar lattices of protonated amino acid ligands.[4–6] In order to determine the structural basis for the spectroscopic features of the doped Cu(II)/tet a·2HClO$_4$ system, this present study was undertaken.

Experimental Section

1. Direct Preparation of the Doped Complex (1). The meso macrocyclic amine tet a was synthesized as the dihydrate by following a pub-

lished procedure[7] and separated from the *d,l* isomer tet b by fractional crystallization. The neat copper complex was prepared by dissolving 1 mmol (0.32 g) of tet a·2H$_2$O and 1 mmol (0.38 g) of Cu(H$_2$O)$_6$(ClO$_4$)$_2$ in a mixture of 16 mL of methanol and 10 mL of H$_2$O. The mixture turned bluish purple when heated to boiling. The addition of trace amounts of NaOH resulted in rapid conversion to the stable red form. The hot solution was filtered through a fine frit and left to evaporate to dryness in air at approximately 30 °C. The product consisted exclusively of dark red six-sided plates (yield 0.462 g, 84.4%). *Caution!* Compound may explode if heated when dry.

The dihydroperchlorate salt of tet a was prepared by adding 3.2 mmol of HClO$_4$ (as a 70% aqueous solution) to a solution of 1.6 mmol of tet a·2H$_2$O in 20 mL of methanol. The initially clear solution began to deposit a colorless crystalline solid after about 5 min. The solid was collected by filtration and dried in air (yield 0.8 g). *Caution!* Compound may explode if heated when dry.

The doped material was prepared by adding a solution of Cu(tet a)(ClO$_4$)$_2$ (5 mg, 0.0091 mmol) in 1 mL of DMSO to a solution of the above salt (0.8 g, 1.25 mmol) in 20 mL of warm H$_2$O. The resulting pale pink solution was filtered through a fine frit and concentrated by evaporation at room temperature in a desiccator containing concentrated H$_2$SO$_4$. After 5 days, the resulting pale pink crystals were collected by filtration and dried in air (yield 0.6 g). Crystals obtained from this preparation, nominally doped at the 0.7% level, were uniform in color to the eye and were used for EPR and electronic spectral studies. *Caution!* Compound may explode if heated when dry.

Serendipitous, Indirect Preparation of the Doped Complex (1). A filtered, deoxygenated solution containing 80 mg (0.30 mmol) of *N,N'*-ethylenebis(L-cysteine) dimethyl ester, (–CH$_2$NHCH(CO$_2$CH$_3$)CH$_2$S-H)$_2$, in 5 mL of methanol was added to a deoxygenated solution of 120 mg (0.27 mmol) of Cu(tet a)(ClO$_4$)$_2$ in 10 mL of DMSO. The resulting solution, which turned dark red in about 5 min at room temperature, was placed in a freezer at −14 °C and allowed to stand for 1 week. Under

(1) tet a and tet b, respectively, are the meso and rac forms of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.
(2) Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1986,** *108,* 1351–2.
(3) Fikar, R. M.; Bharadwaj, P. K.; Potenza, J. A.; Schugar, H. J., unpublished results.
(4) Ou, C.-C.; Powers, D. A.; Thich, J. A.; Felthouse, T. F.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1978,** *17,* 34–40.
(5) Fawcett, T. G.; Ushay, M.; Rose, J. P.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *Inorg. Chem.* **1979,** *18,* 327–32.
(6) Fawcett, T. G. Ph.D. Dissertation, Rutgers, The State University of New Jersey, 1980.

(7) Tait, A. M.; Bush, D. H. *Inorg. Nucl. Chem. Lett.* **1972,** *8,* 491–6. Curtis, N. F.; Hay, R. W. *Chem. Commun.* **1966,** 524–5.