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C. R. Chimie 13 (2010) 69–96

Comptes Rendus Chimie

Full paper/Mémoire

Full spectroscopic characterization of an hydrolytically stable and colored Ti(IV)-precursor in solution

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Reçu le 28 mars 2009 ; accepté après révision le 4 novembre 2009

Abstract

The orange-colored and hydrolytically stable compound $\{[Ti_2O(bhmpc)(Hbhmpc)(H_2bhmpc)].C_4H_8O_2.HX\}_2$ (with H_3bhmpc = 2,6-bis(hydroxymethyl)-*p*-cresol and X = OEt or CCl_3) has been studied by a combination of single crystal X-ray diffraction data, U.V.-vis. spectroscopy, IR and Raman spectroscopies, ^1H, ^{13}C and ^{17}O solution NMR spectroscopies, electron density and statistical thermodynamics modeling. We observed that the molecular structure found in the solid state is conserved in solution. Based on X-ray diffraction data, we also propose a complete and non-ambiguous assignment for the fully resolved ^1H and ^{13}C solution NMR spectra through the use of 2D-techniques (COSY, ROESY, HSQC, HMBC) and ^1H relaxation time measurements. The ability of the partial charge model introduced more than 20 years ago by J. Livage's group to reproduce observed ^{13}C NMR chemical shifts in solution is demonstrated. Statistical thermodynamic modeling between $Ti(OR)_4$ (monomers, trimers or tetramers) has shown that complexation was in all cases under entropy control. Possible applications of this soluble and stable precursor to the sol–gel processing of hybrid organic–inorganic are addressed. ***To cite this article: H. Senouci et al., C. R. Chimie 13 (2010).***

Keywords: U.V.-Vis. spectroscopy; IR and Raman spectroscopy; NMR; ^1H; ^{13}C; ^{17}O; COSY; ROESY; HSQC; HMBC; PACHA; Ti(IV) aryloxides; 2,6-bis(hydroxymethyl)-*p*-cresol; Hybrid organic-inorganic materials; PACHA modeling; Statistical thermodynamics

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1. Introduction

Titanium dioxide TiO_2 is a strategic material in many fields of materials chemistry [1]. Owing to its large refractive index (n_D = 2.7 and 2.55 at 590 nm for rutile and anatase polymorphs respectively), it is widely used for making white pigments [2] or high-refractive-index coatings on silica glasses [3]. With its well-sized band gap (E_g = 3.1–3.2 eV) [4], it may be used in the photoelectrolysis of water [5] and leads to economically credible photocatalysts [6], gas sensors [7] or photovoltaic devices [8]. Moreover, upon UV irradiation TiO_2-containing materials may become superhydrophilic leading to self-cleaning materials

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doi:10.1016/j.crci.2009.11.008

[9]. When mixed with an alkaline earth oxide (MgO, CaO, SrO, BaO), TiO_2 leads to a wide array of ferroelectric [10], piezoelectric [11] and pyroelectric [12] high-tech ceramics for electronic applications. Finally, if mixed with polymers, original organic–inorganic hybrid materials may be readily obtained, combining in a single phase important properties such as high transparency (glasslike), low temperature processing (polymer-like) and sufficient thermal stability (ceramic-like) [13]. In all the above applications, the starting molecular precursors of titanium oxide are usually titanium tetra-alkoxides mixed with various chemical additives in order to finely tune the hydrolytic behavior of these highly reactive species and the final processing of the resulting sol or gel phase [1]. The pioneer work of J. Livage's group in this domain is worth noticing and was initiated by suggestion from André Vioux about the use of acetic acid in order to monitor and control the hydrolysis and condensation of titanium(IV) alkoxides in order to obtain monolithic TiO_2 gels under reproducible conditions [14]. Thanks to the top-level expertise of J. Livage's group in spectroscopy, it was then quickly demonstrated through the use of ESR [15], IR [16], XANES/EXAFS [17] and ^{13}C CPMAS NMR [18] that a change of coordination number from 4 or 5 in $Ti(OR)_4$ up to 6 in $TiO_x(OR)_y(OAc)_z$ derivatives was the key point allowing orientation of the polycondensation process leading to Ti—O—Ti bonds towards a gel instead of a precipitate. With the use of acetic acid as a gelling agent, it was thus possible to synthesize not only homogenously Cr^{3+} and Al^{3+}-doped TiO_2 photoanodes for the photoelectrolysis of water [19] but also to initiate a very fundamental research through the establishment of a Partial Charge Model (PCM) putting onto a quantitative basis some crucial ideas concerning the nature of the chemical bond along the lines suggested by L. Pauling or R.T. Sanderson [20–23]. It is worth noting that this PCM approach of chemical reactivity has been validated by other groups in the case of antimonates, phosphates, molybdates, ferrates or stannates [24], silicates [25], aluminates [26] but seems to fail in the case of alkoxides bearing a lone pair such as tellurium alkoxides $Te(OR)_4$ [27]. With the help of this PCM, it was thus possible to rationalize the solution and sol–gel chemistry of most metallic species in both aqueous and non-aqueous solvents based on the sole knowledge of stoichiometric coefficients. On one hand, this was a great advantage, as in most cases, the detailed molecular structure in solution or the gel state remains unknown. On the other hand, it was soon realized by working at low hydrolysis ratios ($h = H_2O/Ti < 1$) that single-crystals could be easily grown from solutions allowing a much better understanding of the structural chemistry involved during the very first steps of a titania-based sol–gel process. The original PCM approach, unable to take into account the detailed molecular structure was thus regarded with more and more scepticism, more particularly by people deeply involved in NMR spectroscopy or in *ab initio* calculations. A survey of the literature devoted to NMR studies of crystalline titanium(IV) oxo-alkoxides show that four types of nuclei have been studied: ^1H, ^{13}C, ^{17}O and $^{47,49}Ti$. Very few results have been reported concerning ^{47}Ti and ^{49}Ti NMR owing to the rather large quadrupolar moment of these two nuclei. This comes from the fact that TiO_6 or TiO_5 polyhedra are usually strongly distorted relative to their corresponding ideal regular geometry leading to large electrical field gradients at the titanium center and thus to very broad signals. Consequently, titanium NMR is limited to symmetric tetrahedral species, such as $TiCl_4$ (NMR reference) or $Ti(O^iC_3H_7)_4$ and $Ti(OCH_2{}^tC_4H_9)_4$, characterized by $\delta(^{49}Ti) = -854$ ppm and $\delta(^{47}Ti) = -1120$ ppm [28]. Owing to the fast exchange between terminal and bridging positions, ^{17}O NMR is not very informative for non-hydrolyzed titanium alkoxides that are just characterized by a deshielding of about 250 ppm from the parent alcohol [29–30]. This is no more true for titanium oxo-alkoxides where a very clear differentiation between oxo groups is usually observed: $\delta(OTi_2) = 650–850$ ppm, $\delta(OTi_3) = 450–650$ ppm and $\delta(OTi_4,OTi_5) = 250–450$ ppm [31,32]. These characteristic signatures may thus be used to follow the start of these oxo cores during the design and synthesis of hybrid organic–inorganic materials [32]. However, a severe limitation of the technique comes from the fact that only a few signals are usually observed and that natural abundance ^{17}O NMR can be performed only on non-viscous solutions. For gels or xerogels where solid state NMR is required, isotope enrichment is mandatory, preventing tone performing routine analysis on these compounds. ^1H NMR techniques are also not very convenient owing to the very limited chemical shift range and to large dipolar couplings in the solid state. In solution one usually get either quite deceptive spectra in the fast exchange limit (0.5–0.7 ppm deshielding relative to the parent alcohol for Ti—O—CH_x protons) or very complex spectra in the slow exchange limit owing to the numerous scalar couplings. Consequently, with its one-half spin associated to a large chemical shift range and dilute