Inorg. Chem. **2000,** *39,* 1635−1638

Titanium Alkoxide Complexes: Condensed Phase and Gas Phase Comparisons

Steven M. Damo,[†] Kin-Chung Lam,[‡] Arnold Rheingold,[‡] and Marc A. Walters*,[†]

Departments of Chemistry, New York University, New York, New York 10003, and
University of Delaware, Newark, Delaware 19716

Received July 16, 1999

The complex [Ti(2,4-dimethyl-2,4-pentanediolate)$_2$]$_2$ (**1**) has been synthesized from [Ti(O^{i}Pr)$_4$] by transesterification with a stoichiometric amount of 2,4-dimethyl-2,4-pentanediol. We have characterized complex **1** in the solid state by single-crystal X-ray diffraction and in the gas phase by desorption chemical ionization mass spectrometry (DCI-MS). The structural and mass spectrometric data show complex **1** to be stable as a dimer in both the solid and gas phases. The retention of dimeric nuclearity in the gas phase sets complex **1** apart from other simple titanium alkoxide complexes [Ti(O^{i}Pr)$_4$] and [Ti(OMe)$_4$]$_4$ that give rise to respective families of molecular ions in the DCI-MS experiment. The highest mass molecular ions for Ti alkoxide complexes in the gas phase may reveal the highest nuclearity that these complexes achieve in condensed phases. According to this interpretation the complex [Ti(O^{i}Pr)$_4$] is principally dimeric in the gas phase and probably also in the pure liquid phase and should be represented by the formula [Ti(O^{i}Pr)$_4$]$_2$.

Introduction

Titanium alkoxide complexes have been prepared from a variety of alcohol precursors.[1] The simple titanium tetraalkoxides are all volatile, including the titanium tetramethoxide, which is a solid at room temperature that sublimes at 190 °C.[2] Despite their simplicity of composition the nuclearities of the titanium alkoxides have been the subject of debate. The titanium methoxide and ethoxide complexes are tetrameric in the solid state.[3,4] By contrast, there is strong evidence that [Ti(OEt)$_4$] is trimeric in both the liquid state and in solution.[5]

The nuclearity of Ti alkoxides is of technological relevance because the simple titanium alkoxide complexes, [Ti(OR)$_4$] (R = Me, Et, ^{i}Pr, etc.), are well-known precursors for TiO$_2$, formed by hydrolysis in sol−gel applications, or thermolysis in the process of chemical vapor deposition (CVD).[6−11] Titanium isopropoxide, [Ti(O^{i}Pr)$_4$], is the most volatile of the titanium alkoxides, a property that it owes to its low molecular weight and the steric effects of the ligand which restricts the nuclearity (molecular complexity) of the complex.[1] Titanium isopropoxide is a liquid at or above ambient temperature, and its nuclearity has long been accepted as being approximately 1.2.[12,13]

In this paper we report on the synthesis and structural characterization of a new titanium alkoxide complex [Ti(2,4-dimethyl-2,4-pentanediolate)$_2$]$_2$, [Ti(DMPD$_2$)]$_2$ (**1**), that was synthesized as part of our research on chalcogenide complexes. Qualitatively, complex **1** is relatively stable under ambient conditions, as might be expected for a crystalline solid.[14] However, it is sufficiently volatile at elevated temperature to be studied by soft ionization mass spectrometry in the gas phase. We compare its solid-state molecular structure and gas-phase speciation with those of other simple titanium alkoxide complexes, [Ti(OMe)$_4$]$_4$ and [Ti(OPr^i)$_4$]. The experiments on complex **1** provide a unique window to the gas phase coordination chemistry of homoleptic titanium alkoxides. The species observed in the gas phase by mass spectrometry are related to the complexes in condensed phases, either liquid or solid state. The results of our work highlight the utility of mass spectrometric methods for the study of Ti alkoxide complexes whose nuclearity and structures are known only approximately.[15,16]

Experimental Section

All syntheses were carried out under an inert atmosphere of nitrogen using a glovebox or standard Schlenk line techniques. Solvents were dried by conventional methods and degassed before use. The complexes [TiCl$_4$] (99.9%) and [Ti(O^{i}Pr)$_4$] (97%) were purchased from Aldrich and used without further purification. Melting points are uncorrected. Proton NMR data was collected on a 200 MHz Varian Gemini 200 spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of 2,4-Dimethyl-2,4-pentanediol (DMPDH$_2$). The ligand 2,4-dimethyl-2,4-pentanediol (DMPDH$_2$) was synthesized by published procedures.[17,18] Iodomethane (27.49 g, 190 mmol) was dissolved in

---

[†] New York University.

[‡] University of Delaware.

[1] Bradley, D. C.; Mehrotra, R. C.; Gaur, P. D. *Metal Alkoxides*; Academic Press: New York, NY, 1978.

[2] Varma, I. D.; Mehrotra, R. C. *J. Chem. Soc. (London)* **1960**, 2966−2969.

[3] Ibers, J. A. *Nature* **1963**, *197*, 686.

[4] Wright, D. A.; Williams, D. A. *Acta Crystallogr.* **1968**, *B24*, 1107.

[5] Caughlan, C. N.; Smith, H. S.; Katz, W.; Hodgson, W.; Crowe, R. W. *J. Am. Chem. Soc.* **1951**, *73*, 5652−5654.

[6] Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1988**, *18*, 259−341.

[7] Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996**, *25*, 1−23.

[8] Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317.

[9] Taylor, C. J.; Gilmer, D. C.; Colombo, D. G.; Wilk, G. D.; Campbell, S. A.; Roberts, J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1999**, *121*, 5220−5229.

[10] Hug, S. J.; Sulzberger, B. *Langmuir* **1994**, *10*, 3587−3597.

[11] Rajh, T.; Ostafin, A. E.; Micic, O. I.; Tiede, D. M.; Thurnauer, M. C. *J. Phys. Chem.* **1996**, *100*, 4538−4545.

[12] Bradley, D. C.; Mehrotra, R. C.; Wardlaw, W. *J. Chem. Soc.* **1952**, 5020−5023.

[13] Bradley, D. C.; Holloway, C. E. *J. Chem. Soc. A* **1968**, 1316−1319.

[14] Kemmitt, T.; Daglish, M. *Inorg. Chem.* **1998**, *37*, 2063−2065.

[15] Martin, R. L.; Winter, G. *Nature* **1963**, *197*, 687.

[16] Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Finnie, K. S.; Bartlett, J. R.; Wolfrey, J. L. *Inorg. Chem.* **1998**, *37*, 2741.

[17] Kohn, F. *Chem. Ber.* **1904**, *37*, 4731.

[18] Alagui, A.; Apparu, M.; Pasqualini, R.; Vidal, M. *Bull. Soc. Chim. Fr.* **1991**, 286.

10.1021/ic990844n CCC: $19.00 © 2000 American Chemical Society
Published on Web 03/31/2000

diethyl ether (120 mL) and added dropwise to magnesium turnings (4.61 g, 190 mmol) in refluxing ether (20 mL) containing a catalytic amount of iodine crystals. After the formation of the Grignard reagent, $IMgCH_3$, the solution was cooled to room temperature and 4-hydroxy-4-methyl-2-pentanone (10.00 g, 86.4 mmol) in ether (50 mL) was added dropwise. The resulting solution was stirred for 6 h, and then quenched with 1 N HCl at 0 °C. The organic layer was collected, and the aqueous layer was extracted twice with chloroform. The organic layers were combined, washed with brine, dried over anhydrous sodium sulfate, and concentrated on a rotary evaporator to yield $DMPDH_2$ as a yellow oil. The product was purified by distillation from potassium carbonate under reduced pressure (bp 65 °C/0.1 mm) to give 8.88 g (78% yield). ^1H NMR (ppm) ($CDCl_3$): 1.34 ($-CH_3$), 1.75 ($-CH_2-$), 3.43 ($-OH$).

Synthesis of $[Ti(DMPD)_2]_2$ (1) from Titanium(IV) Isopropoxide. $DMPDH_2$ (2.01 g, 15.2 mmol) was added to titanium(IV) isopropoxide (2.16 g, 7.60 mmol) in 40 mL of toluene and stirred at room temperature for 12 h. The 2-propanol liberated during the reaction was removed by distillation, and the solvent was removed under vacuum leaving a slightly yellow amorphous solid. The crude product was dissolved in warm heptane from which it separated as a white crystalline solid after the solution was cooled and concentrated under vacuum. The solid was collected by filtration and dried under vacuum yielding 2.11 g of product (90% yield). Colorless, transparent blocks suitable for single-crystal X-ray diffraction were obtained from a saturated $CHCl_3$ solution of complex **1** that was maintained at 10 °C for 2−3 days. Mp: 148−150 °C. The product obtained by this low-temperature method is the chloroform solvate, $[Ti(DMPD)_2]_2{\cdot}2CHCl_3$. ^1H NMR (ppm) ($CDCl_3$): 1.35 ($-CH_3$), 1.76 ($-CH_2-$). MS: $m/z = 617$. Anal. Calcd for $C_{30}H_{58}Cl_6O_8Ti_2$ (855.26): C, 42.13; H, 6.84. Found: C, 42.65; H, 7.09.

Synthesis of $[Ti(DMPD)_2]_2$ (1) from Titanium(IV) Chloride. Titanium(IV) chloride (0.722 g, 3.80 mmol) was added dropwise to a solution of $DMPDH_2$ (1.00 g, 7.60 mmol) and pyridine (0.60 g, 7.60 mmol) in 30 mL of benzene. The solution was stirred at room temperature for 2 h. Anhydrous NH_3 was then bubbled through the solution. The resulting ammonium salt was removed by filtration, and the solution was extracted with two 10 mL portions of benzene. The extracts were combined, and the solvent was removed under vacuum leaving a slightly yellow powder that was purified by sublimation ∼189 °C/0.09 mm to yield 1.09 g (93% yield) of microcrystalline material. Mp: 148−150 °C. MS: $m/z = 617$.

Synthesis of $[Ti(OMe)_4]_4$. $[Ti(OMe)_4]_4$ was synthesized by published procedures.[1] Titanium(IV) isopropoxide (5.00 g, 17.6 mmol) was added to excess methanol. A white solid immediately precipitated from solution, and the resulting slurry was stirred for 4 h. The solvent was removed under vacuum leaving a white crystalline solid that was purified by recrystallization from hot methanol to yield 2.91 g (96% yield) of titanium(IV) methoxide. Mp: 205−206 °C.

Crystal Structure Determination. Crystal data for $[Ti(DMPD)_2]_2{\cdot}2CHCl_3$ are given in Table 1. A goodness-of-fit of 1.425 was achieved for 7454 observed independent reflections ($4° \leq 2\theta \leq 50°$). Intensity data were collected on a standard P4 X-ray diffractometer equipped with a SMART CCD area detector and a graphite monochromator ($\lambda = 0.710\,73$ Å). The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and all hydrogen atoms were treated as idealized solutions.

All software and sources of the scattering factors are contained in the SHELXTL (5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Desorption Chemical Ionization Mass Spectrometry. Metal complexes were characterized by desorption chemical ionization (DCI) mass spectrometry which minimizes fragmentation and favors observation of the molecular ion. Mass spectrometric data were recorded on a Nermag R-10-10 quadrupole mass spectrometer in desorption chemical ionization mode using NH_3 as the reactant gas. The sample probe was heated with a tungsten filament to volatilize solid samples. The filament current was increased at a rate of 30 mA/s to a maximum of 300−400 mA. The corresponding probe temperature was in the range of 220−500 °C.

Table 1. Crystallographic Data for $[Ti(DMPD)_2]_2$ (**1**)

chem formula	$C_{30}H_{58}Cl_6O_8Ti_2$
fw	855.26
space group	$P2_1/c$
a, Å	14.1105(2)
b, Å	17.0887(2)
c, Å	18.2851(2)
α, deg	90
β, deg	101.5583(3)
γ, deg	90
V, Å^3	4319.68(6)
Z	4
T, K	173(2)
ρ_{calcd}, g cm^{-3}	1.315
μ, cm^{-1}	7.81
$R(F)$,[a] %	4.92
$R_w(F^2)$,[a] %	16.26

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2,0)]/3$.

Table 2. Selected Bond Lengths and Angles for $[Ti(DMPD)_2]_2$ (**1**)[a]

Bond Distances (Å)

Ti(1)−O(1)	1.8158(18)	Ti(2)−O(6)	1.8113(18)
Ti(1)−O(3)	2.1375(18)	Ti(2)−O(8)	2.1528(17)
Ti(1)−O(2)	1.8051(19)	Ti(2)−O(5)	1.8015(19)
Ti(1)−O(4)	1.8329(18)	Ti(2)−O(7)	1.8366(19)
Ti(1)−O(8)	1.9542(16)	Ti(2)−O(3)	1.9572(17)

Bond Angles (deg)

O(1)−Ti(1)−O(3)	174.12(7)	O(6)−Ti(2)−O(8)	174.08(7)
O(2)−Ti(1)−O(4)	114.28(9)	O(5)−Ti(2)−O(7)	112.72(9)
O(4)−Ti(1)−O(8)	124.50(8)	O(3)−Ti(2)−O(7)	124.44(8)
O(2)−Ti(1)−O(8)	117.46(8)	O(5)−Ti(2)−O(3)	118.72(8)
O(2)−Ti(1)−O(1)	92.45(8)	O(5)−Ti(2)−O(6)	92.81(9)
O(4)−Ti(1)−O(1)	96.73(8)	O(7)−Ti(2)−O(6)	96.82(8)
O(8)−Ti(1)−O(1)	99.75(8)	O(3)−Ti(2)−O(6)	100.16(8)
O(2)−Ti(1)−O(3)	90.31(8)	O(5)−Ti(2)−O(8)	90.62(8)
O(4)−Ti(1)−O(3)	86.86(8)	O(7)−Ti(2)−O(8)	86.29(7)
O(8)−Ti(1)−O(3)	74.36(7)	O(3)−Ti(2)−O(8)	73.95(7)
Ti(1)−O(3)−Ti(2)	103.86(8)	Ti(2)−O(8)−Ti(1)	103.40(7)

Results and Discussion

Synthesis and Crystal Structure. Compound **1** was synthesized by two related methods, with similar results (i) by displacement of $^iPrO^-$ from titanium tetraisopropoxide, ["$Ti(O^iPr)_4$"] by the diol $DMPDH_2$ and (ii) by displacement of Cl^- in $TiCl_4$ by $DMPDH_2$.[1] Crystallographic results (Tables 1 and 2) show **1** to be dimeric in the solid state with approximate overall C_2 symmetry. Two diolate ligands provide terminal coordination of Ti(1) and Ti(2), respectively. In each of the other two ligands one oxygen atom provides terminal ligation while the other oxygen atom serves to bridge the metal ions. The Ti atoms each occupy a trigonal bipyramidal coordination site (Figure 1). Axial ligation is provided by O(1) and O(3) on Ti(1) and by O(6) and O(8) on Ti(2). The respective axial O−Ti−O angles for Ti(1) and Ti(2) are 174.12(7) and 174.08(7)°. Atoms O(3) and O(8) also bridge between the Ti atoms and provide equatorial ligation for Ti(2) and Ti(1), respectively. The axial bonds to the bridging oxygens are relatively long, with an average value of 2.146 Å as compared with 1.814 Å for the axial bonds of the terminal oxygen atoms. Correspondingly, the equatorial bonds to bridging oxygen atoms have an average value of 1.956 Å, which is somewhat longer than the average value of 1.819 Å observed for the equatorial bonds to the terminal oxygen donor atoms.

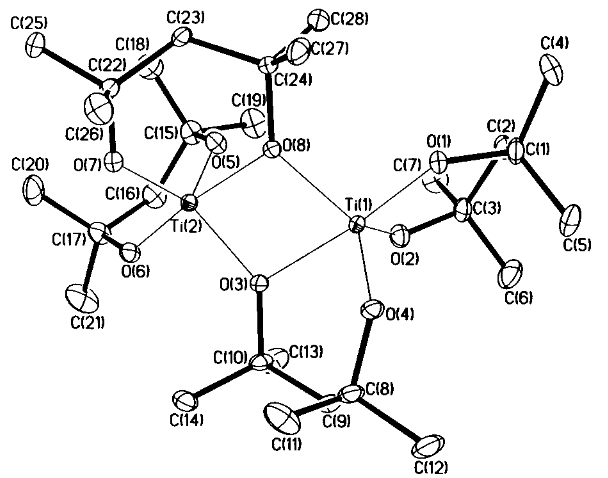

Figure 1. ORTEP diagram of $[Ti(DMPD)_2]_2{\cdot}2CHCl_3$ (**1**), showing the atom-labeling scheme. Thermal ellipsoids are at 30% probability. The solvent molecules and hydrogen atoms were omitted for clarity.

Among the structurally characterized DMPD complexes is an Al complex, $[Me_5Al_3(DMPD)_2]$.[19] This is a linear trinuclear molecule whose terminal Al^{3+} ions are coordinated by two terminal methyl groups and two μ-alkoxide oxygen atoms. The central Al atom is five coordinate with a square-based pyramidal geometry formed by four μ-oxygen atoms of the DMPD ligands in the basal plane and an axial methyl group. As in complex **1**, the low coordination number of the central Al atom results from the steric constraints imposed by the gem dimethyl groups.

The recently reported titanium neopentyl alkoxide dimer, $[Ti(ONp)_4]_2$ (Np = neopentyl), is structurally related to complex **1**.[20] The coordination environment of Ti^{4+} in the neopentoxide complex is identical to that of complex **1** with trigonal bipyramidal coordination about each Ti^{4+} ion. The average bond lengths of $[Ti(DMPD)_2]_2$ and $[Ti(ONp)_4]_2$ are nearly identical, with values of 1.86 Å (axial), 1.96 Å (equatorial) and 1.85 Å (axial), 1.94 Å (equatorial), respectively. However, the average axial bond angles of the two complexes {174°, $[Ti(DMPD)_2]_2$; 156°, $[Ti(ONp)_4]_2$ } are quite different, which results from the steric properties of the $DMPD^{2-}$ and ONp^{-} alkoxide ligands.

The DMPD ligand with its tertiary alkoxide groups limits the nuclearity and prevents oligomerization of its metal complexes. Further, the binding of this ligand to Ti^{4+} reduces the coordination number below the optimal value of six observed in complexes that incorporate primary alkoxides as in "$Ti(OEt)_4$", "$Ti(OMe)_4$", and the propanediol-containing complexes $[TiCl(HOCH_2CH_2CH_2O)(OCH_2CH_2CH_2O)_2]_2$ and $[TiCl_2(OCH_2CH_2CH_2O)(THF)]_2$.[1,3,4,21−23] The latter two complexes are closely related to **1** by virtue of the respective η^2 and μ,η^2 coordination patterns of their diolate ligands. If 2 equiv of HCl were removed from the monodeprotonated-diol complex above, the coordination geometry about Ti would be reduced from pseudooctahedral to the approximate trigonal bipyramidal structure of **1**.

Proton NMR Spectroscopy. Complex **1** gave two signals at 1.35 and 1.76 ppm, corresponding to the ligand methyl and methylene groups, respectively. The absence of discrete peaks for bridging, equatorial, and axial methyl groups is consistent with rapid exchange in solution which is characteristic of titanium alkoxide complexes.[13,20]

Table 3. Anionic and Cationic Species Obtained from Desorption Chemical Ionization Mass Spectrometry of the Idealized Neutral Monomeric Complexes $Ti(OMe)_4$, $Ti(O^iPr)_4$, and "$Ti(DMPD)_2$" (**1**)[a,b]

compd	ion	*m*/*z*	rel peak height (%)
$Ti(OMe)_4$, neg ion[c]	$[M_2]^{-\bullet}$	344, 348	85.7
	$[M_3]^{-\bullet}$	516	100.0
	$[M_4]^{-\bullet}$	688	100.0
$Ti(OMe)_4$, pos ion[c]	$[M_2 - MeOH]^{+\bullet}$	313	48.2
	$[M_3 - MeOH]^{+\bullet}$	485	60.7
$Ti(O^iPr)_4$, neg ion	$[M]^{-\bullet}$	284	45.3
	$[M_2]^{-\bullet}$	568	100.0
$Ti(O^iPr)_4$, pos ion	$[M_2 - O^iPr]^{+\bullet}$	509	100.0
$Ti(DMPD)_2$, neg ion[c]	$[M]^{-\bullet}$	308	6.8
	$[M_2]^{-\bullet}$	616	100.0
$Ti(DMPD)_2$, pos ion[c]	$[M_2 + H]^{+\bullet}$	617	100.0

[a] For the sake of simplicity the titanium complexes are all represented by monomeric formulas. These monomers are represented by M in the molecular ion formula. [b] Only molecular ions and closely related fragmentation products are shown. [c] Data acquired with heated probe.

Mass Spectrometry. We have studied the gas-phase speciation of complex **1** and two related complexes by means of desorption chemical ionization mass spectrometry (DCI-MS). This is a soft ionization method in which ion fragmentation is minimized. DCI mass spectrometry is a proven method for the determination of hydrolytically labile ions, particularly in the electron capture mode.[24] Because of variable nuclearity in the gas phase, we discuss the relevant complexes in terms of their respective empirical formulas $Ti(OMe)_4$, $Ti(O^iPr)_4$, and $Ti(DMPD)_2$ (**1**) (Table 3). For the simple alkoxide complexes, metal−ligand bond scission accounts for the fragments that are observed among both positive and negative ions. The fragmentation product peaks are accompanied by relatively intense peaks assignable to molecular ions $[M_n]^{+/-\bullet}$ and corresponding dissociation products of lower nuclearity $[M_{n-m}]^{+/-\bullet}$, $m = 1, 2, 3$ .... In the discussion that follows we focus on peaks assignable to species of integral nuclearity and closely related ions.

On the basis of single-crystal X-ray crystallography, the complex "$Ti(OMe)_4$" is a tetramer whose actual formula is $[Ti(OMe)_4]_4$.[4] DCI-MS data acquired with a heated probe shows that the tetrameric composition is partially sustained in the gas phase with a corresponding peak at *m*/*z* 688 ($[M_4]^{-\bullet}$, 100%) in negative ion data. Related species of lower nuclearity are observed at *m*/*z* 516 ($[M_3]^{-\bullet}$, 100%) and 344 ($[M_2]^{-\bullet}$, 85%). Other readily assignable species appear in the positive ion data at *m*/*z* 485 ($[M_3 - MeOH]^{+\bullet}$) and 313 ($[M_2 - MeOH]^{+\bullet}$). The appearance of ions of lower nuclearity in the gas phase of the DCI-MS apparatus likely results from spontaneous fragmentation during the process of sublimation. Fragmentation is extensive, with appearance of nearly equal amounts of $[M_4]^{-\bullet}$, $[M_3]^{-\bullet}$, and $[M_2]^{-\bullet}$ species.

Negative ion data on the title complex, "$Ti(DMPD)_2$", acquired with probe heating, reveals two peaks, one for an ion at *m*/*z* 616 ($[M_2]^{-\bullet}$, 100%) and another for a minor monomeric dissociation product at *m*/*z* 308 ($[M]^{-\bullet}$, 6.8%). The $[M_2]$ ion is the sole positive ion species detected with an *m*/*z* value of 617

---

(19) Ziemkowska, W.; Pasynkiewicz, S.; Glowiak, T. *J. Organomet. Chem.* **1998**, *562*, 3.

(20) Boyle, T. J.; Alam, T. M.; Mechenbier, E. R.; Scott, B. L.; Ziller, J. W. *Inorg. Chem.* **1997**, *36*, 3293.

(21) Thoms, H.; Epple, M.; Froba, M.; Wong, J.; Reller, A. *J. Mater. Chem.* **1998**, *8*, 1447.

(22) Huang, Y.; Stephan, D. W. *Can. J. Chem.* **1995**, *73*, 956.

(23) Winter, C. H.; Sheridan, P. H.; Heeg, M. J. *Inorg. Chem.* **1991**, *30*, 1962−1964.

(24) Forest, E.; Marchon, J. C.; Ulrich, J.; Virelizier, H. *Inorg. Chem.* **1986**, *25*, 3570.

($[M_2 + H]^{+\bullet}$, 100%). While fragmentation is extensive among the simple monohapto alkoxide complexes, it is negligible for the DMPD complex (**1**). The molecular ion again is readily assignable to the highest mass species $[M_2]$.

Negative ion data on the isopropoxide complex "$Ti(O^iPr)_4$" show assignable peaks at *m*/*z* 568 ($[M_2]^{-\bullet}$) and 284 ($[M]^{-\bullet}$). In keeping with data from complex **1** and the Ti methoxide complex, discussed above, we assign the highest mass titanium isopropoxide species to the molecular ion, $[M_2]^{-\bullet}$. The dimeric and monomeric ions, $[M_2]^{-\bullet}$ and $[M]^{-\bullet}$, have relative peak heights of 100% and 45%, respectively, indicative of extensive dissociation of the $[M_2]^{-\bullet}$ ion. In the positive ion mode the sole fragmentation product has a *m*/*z* value of 509, which corresponds to the ion $[M_2 - O^iPr]^{+\bullet}$. The negative ion data allow the possibility that significant amounts of monomer exist in the neat liquid. However the absence of a positive ion species corresponding to a monomeric molecular ion strongly supports the idea that "$Ti(O^iPr)_4$" exists principally as a dimer, $[Ti(O^iPr)_4]_2$, in the neat liquid at room temperature. Such a formulation would be in keeping with data reported on the titanium neopentoxide complex which is dimeric despite the greater steric hindrance of the tertiary alkoxide ligands.[20]

The results from DCI-MS analysis are in general agreement with earlier electrospray-MS data on "$Ti(OEt)_4$" in dry ethanol in which the following negative ion complexes of high nuclearity are observed: $[Ti_3(OEt)_{13}]^{-\bullet}$, $[Ti_4(OEt)_{17}]^{-\bullet}$, and $[Ti_5(OEt)_{21}]^{-\bullet}$.[25] Whereas a pentameric complex is formed in the electrospray experiment, only the tetramer is observed in the solid state by X-ray crystallography.[3] Both the increase in nuclearity relative to the crystalline solid and the occurrence of odd numbers of ligands may be artifacts of the electrospray mass spectrometric method.

The DCI-MS data reported here are relevant to earlier discussions on the nuclearity of Ti alkoxide complexes. EXAFS measurements have been interpreted to show one type of Ti−O bond in "$Ti(O^iPr)_4$", corresponding to a monomeric complex with T_d symmetry.[26] However, vibrational spectroscopic data on "$Ti(O^iPr)_4$" (neat liquid) show bands that provide evidence for an associated species[16] whose nuclearity decreases with dilution, consistent with the early results of Martin and Winter on "$Ti(OEt)_4$" and "$Ti(OBu)_4$".[15] Our DCI-MS data support the argument that as a pure liquid the complex "$Ti(O^iPr)_4$" exists predominantly as an associated species that yields a gas-phase dimer with the formula $[Ti(O^iPr)_4]_2$. This dimer is the likely precursor to TiO_2 in MOCVD applications. The association of monomeric species to form dimeric compounds in the gas phase would likely be marked by a higher abundance of monomer molecular ions in the DCI experiment. Our experiment does not rule out the possibility of higher nuclearity. The existence of $[Ti(O^iPr)_4]$ as a dimer in the condensed phase would be consistent with the observed dimeric forms of complex **1** and the neopentoxide complex $[Ti(ONp)_4]_2$. The latter two complexes incorporate tertiary alkoxide ligands that, because of their steric effects, are expected to be more restrictive on complex nuclearity than isopropoxide, a secondary alkoxide.

Summary

The X-ray crystallographic and DCI-MS data presented here show that the composition of the complex **1** is relatively insensitive to phase. It is dimeric in the solid state and undergoes negligible dissociation in the gas phase, unlike the titanium methoxide or isopropoxide complexes. Because of its relative stability among the titanium alkoxide complexes, **1** can serve as a benchmark for the study of liquid- and/or gas-phase stabilities of Ti alkoxide complexes. Simple neutral Ti alkoxide complexes may have variable nuclearity in the liquid phase, which would result in the appearance of a family of molecular ions in mass spectrometric data. Alternatively, polynuclear molecular ions of these alkoxides may undergo unimolecular dissociation in the gas phase, which would likewise result in the appearance of a family of Ti(IV)-containing ions in the gas phase. In either case, there is strong evidence from DCI-MS data that $[Ti(O^iPr)_4]$ is a dimeric complex in the gas phase and probably also as a neat liquid and is therefore best represented by the formula $[Ti(O^iPr)_4]_2$.

Acknowledgment. We wish to thank Ms. Vinka Parmakovich (Columbia University) for the acquisition of DCI-MS data. This investigation was supported by Grant 32208-AC3 from the American Chemical Society.

Supporting Information Available: Figures and complete listings of mass spectrometric data and on electronic listing of the X-ray CIF file for the structure determination of $[Ti(2,4\text{-dimethyl-}2,4\text{-pentanediolate})_2]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990844N

---

(25) Lover, T.; Henderson, W.; Bowmaker, G. A.; Seakins, J. M.; Cooney, R. P. *J. Mater. Chem.* **1997**, *7*, 1553.

(26) Babonneau, F.; Doeuff, S.; Leaustic, A.; Sanchez, C.; Cartier, C.; Verdaguer, M. *Inorg. Chem.* **1988**, *27*, 3166.