



Alkoxyalkanol and Diol Modified Titanium Tetraisopropoxide: Synthesis and Characterization of Some Novel Precursors for Titania

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Titanium complexes of the type $[(OPr^i)_{4-n}Ti(OC_2H_4OR)_n]$, $[(acac)_2Ti(O-G-O)]$ and $[(acac)_2Ti(OPr^i)(OCH_2CH_2SH)]$ were synthesized from stoichiometric reactions between titanium tetraisopropoxide $[(Ti(OPri)_4, TPT)]$ and alkoxyalkanols $\{HOCH_2CH_2OR\}$ in 1:1 to 1:4 molar ratios, where R = Et and *n*-Bu and by the interaction of the precursor $[(acac)_2Ti(OR)_2]$ with different diols and thiol in 1:1 molar ratio, where G = $(CH_2)_2$, $(CH_2)_5$ and $C(CH_3)_2CH_2CH(CH_3)$, R = isoprop. The reactions have been carried out in refluxing benzene under anhydrous conditions to yield mononuclear derivatives. All these compounds were purified by distillation under reduced pressure. On the basis of elemental analysis, IR and NMR (1H and ^{13}C) spectral studies tetrahedral as well as a *cis* octahedral geometry around Ti(IV) is proposed.

Key Words: Titanium isopropoxide, Alkoxyalkanols, Glycols, Thioglycol, Heteroleptic, Metallacyclic.

INTRODUCTION

Metallo-organic complexes of titanium have attained the interest of researchers due to its diverse applications including as better precursors for oxide based ceramic materials^{1,2}. Highly reactive titanium alkoxides $[Ti(OR)_4]$ are often modified by β -diketones³ and oximes⁴, etc. These moieties reduce the rate of condensation and hydrolysis⁵ and these bidentate ligands have the ability to bring about the variations in coordination pattern based on steric factor as well as its hard soft acid base (HSAB) feasibility¹. These sorts of hybrid inorganic-organic materials have promised technical applications after getting processed through sol-gel method⁶. The synthesis of nano sized titania (TiO_2) via aforesaid route has led to many emerging and advanced applications in areas ranging from solar cells, optical coatings, photo catalysis to chemical sensors⁴ as well as in toothpaste, electrochromics and photochromics⁷. A recent study revealed that incorporation of nano sized TiO_2 into a waterborne acrylic coating has enhanced corrosion resistance⁸.

Thus, in view of these interesting features of titanium chemistry, we got encouraged to prepare and to report some new titanium(IV) complexes of types $[(OPr^i)_{4-n}Ti(OC_2H_4OR)_n]$, $[(acac)_2Ti(O-G-O)]$ and $[(acac)_2Ti(OPr^i)(OCH_2CH_2SH)]$.

EXPERIMENTAL

All manipulations were performed in moisture free environment and the chemicals were of analytical grade and dried before use. Titanium tetraisopropoxide^{9,10} and $[(acac)_2Ti(OR)_2]$ ¹¹ were

prepared as reported in literature. Titanium¹² and isopropanol¹³ have also been estimated as reported earlier. Infrared spectra were recorded as Nujol mulls on Nicolet Megna-550 spectrophotometer. 1H and ^{13}C NMR spectra were recorded on 90 MHz JEOL FX 90Q spectrometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$, respectively. Elemental analyses of the complexes were recorded on Elementar Vario EL III instrument. Molecular weights of the derivatives have been determined by ebullioscopically.

Preparation of $(OPr^i)Ti(OCH_2CH_2OEt)_3$ (complex 1): Benzene solution (20 mL) of $Ti(OPr^i)_4$ (0.95 g, 3.34 mmol) was added to the benzene solution (20 mL) of $HOCH_2CH_2OEt$ (0.91 g, 10.11 mmol) and the contents were refluxed for 4 h, the progress of the reaction was monitored by the estimation of liberated isopropanol with benzene azeotropically. After removal of the solvent under reduced pressure, a colourless liquid was obtained (84 %). The products derived from alkoxy alkanols were purified by vacuum distillation at around 122-125 °C/0.5 mm while complexes obtained from glycols have been washed by dried *n*-hexane. All other complexes were also prepared by similar route and the details were summarized in Table-1. NMR, IR and all other characterization details are as given below.

NMR, IR and other details of the synthesized metal complexes

Complex 1: Yield 97 %, b.p. 163-166 °C, elemental analysis (%): Found (calcd.) C = 48.2 (48.1), H = 9.3 (9.16), O = 29.7 (29.9). IR (Nujol, ν_{max} , cm^{-1}): (C-O) = 1000 (OPr^i), (Ti-O) =

TABLE-1
 SYNTHETIC AND ANALYTICAL DATA OF Ti(IV) DERIVATIVES

S. No	Reactants (g) a. Ti(OPr) ₄ b. HOCH ₂ CH ₂ OR	Molar ratio	Complex	Pr ⁱ OH(g) found (calcd.) (%)	OPr ⁱ (%)	Ti (%)
1	a. 0.95 b. R = Et, 0.91	1:3	(OPr ⁱ)Ti(OCH ₂ CH ₂ OEt) ₃	0.60 (0.61)	15.7 (15.8)	12.9 (12.8)
2	a. 0.75 b. R = Et, 0.96	1:4	Ti(OCH ₂ CH ₂ OEt) ₄	0.63 (0.64)	–	11.7 (11.8)
3	a. 1.06 b. R = Bu, 0.44	1:1	(OPr ⁱ) ₃ Ti(OCH ₂ CH ₂ OBu)	0.21 (0.22)	51.7 (51.8)	14.1 (14.0)
4	a. 1.09 b. R = Bu, 0.91	1:2	(OPr ⁱ) ₂ Ti(OCH ₂ CH ₂ OBu) ₂	0.45 (0.46)	29.3 (29.5)	11.9 (12.0)
5	a. 0.89 b. R = Bu, 1.11	1:3	(OPr ⁱ)Ti(OCH ₂ CH ₂ OBu) ₃	0.56 (0.56)	12.7 (12.9)	10.3 (10.4)
6	a. 0.78 b. R = Bu, 1.31	1:4	Ti(OCH ₂ CH ₂ OBu) ₄	0.66 (0.66)	–	9.4 (9.3)
7	a. 1.54 b. HOCH ₂ (CH ₂) ₃ CH ₂ OH, 0.35	1:1	(acac) ₂ Ti[OCH ₂ (CH ₂) ₃ CH ₂ O]	0.50 (0.51)	–	13.8, (3.7)
8	a. 1.34 b. HOC(CH ₃) ₂ CH ₂ CH(CH ₃)OH, 0.44	1:1	(acac) ₂ Ti[OC(CH ₃) ₂ CH ₂ CH(CH ₃)O]	0.44 (0.44)	–	13.2, (13.2)
9	a. 0.74 b. HOCH ₂ CH ₂ SH, 0.16	1:1	(acac) ₂ Ti(OPr ⁱ)(OCH ₂ CH ₂ SH)	0.11 (0.12)	–	12.4, (12.5)

620, (C-O) = 1085 and (C-O-C) = 1050. ¹H NMR (CDCl₃): 1.26 (d, 6H, CH₃), 4.14-4.35 (m, 1H, OCH), 1.17 (t, 9H, CH₂CH₃), 3.41-3.62 (m, 18H, OCH₂CH₂OCH₂CH₃). ¹³C NMR: 25.5 (CH₃), 61.5 (OCH₃), 22.1 (CH₃), 64.5 (OCH₂Me), 66.7 (OCH₂CH₂OEt), 71.6 (OCH₂CH₂OEt).

Complex 2: Yield 98 %, b.p. 172-175 °C, elemental analysis (%): Found (calcd.) C = 47.7 (47.5), H = 8.6 (8.9), O = 31.6 (31.6). IR (Nujol, ν_{\max} , cm⁻¹): (Ti-O) = 605, (C-O) = 1070 and (C-O-C) = 1025. ¹H NMR (CDCl₃): 1.14 (t, 12H, CH₂CH₃), 3.44-3.65 (m, 24H, OCH₂CH₂OCH₂CH₃). ¹³C NMR: 22.6 (CH₃), 64.0 (OCH₂Me), 66.5 (OCH₂CH₂OEt), 71.5 (OCH₂CH₂OEt).

Complex 3: Yield 98 %, b.p. 214-216 °C, Elemental analysis (%): Found (calcd.) C = 52.9 (52.6), H = 10.4 (10.1), O = 23.7 (23.3). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1005 (OPrⁱ), (Ti-O) = 610, (C-O) = 1090 and (C-O-C) = 1045. ¹H NMR (CDCl₃): 1.30 (d, 18H, CH₃), 4.15-4.45 (m, 3H, OCH), 1.09 (t, 3H, O(CH₂)₃CH₃), 3.36-4.12 (m, 10H, OCH₂CH₂O(CH₂)₃CH₃). ¹³C NMR: 26.4 (CH₃), 61.8 (OCH₃), 14.2 (CH₃), 25.0 (OCH₂CH₂O(CH₂)₂CH₂Me), 40.8 (OCH₂CH₂OCH₂CH₂Et), 62.6 (OCH₂CH₂O CH₂Pr), 65.2 (OCH₂CH₂OBu), 71.4 (OCH₂CH₂OBu).

Complex 4: Yield 97 %, b.p. 156-158 °C, Elemental analysis (%): Found (calcd.) C = 53.7 (54.0), H = 10.2 (10.0), O = 23.5 (23.9). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1015 (OPrⁱ), (Ti-O) = 620, (C-O) = 1075 and (C-O-C) = 1025 cm⁻¹. ¹H NMR (CDCl₃): 1.25 (d, 12H, CH₃), 4.28-4.72 (m, 2H, OCH), 1.06 (t, 6H, O(CH₂)₃CH₃), 3.28-3.92 (m, 20H, OCH₂CH₂O(CH₂)₃CH₃). ¹³C NMR: 26.9 (CH₃), 61.4 (OCH₃), 15.5 (CH₃), 25.2 (OCH₂CH₂O(CH₂)₂CH₂Me), 40.2 (OCH₂CH₂OCH₂CH₂Et), 62.7 (OCH₂CH₂O CH₂Pr), 66.0 (OCH₂CH₂OBu), 72.6 (OCH₂CH₂OBu).

Complex 5: Yield 98 %, b.p. 188-191 °C, Elemental analysis (%): Found (calcd.) C = 54.9 (55.0), H = 10.4 (10.1), O = 24.5 (24.4). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1015 (OPrⁱ), (Ti-O) = 610, (C-O) = 1080 and (C-O-C) = 1015. ¹H NMR (CDCl₃): 1.19 (d, 6H, CH₃), 4.15-4.40 (m, 1H, OCH), 1.01 (t, 9H, O(CH₂)₃CH₃), 3.12-3.70 (m, 30H, OCH₂CH₂O(CH₂)₃CH₃). ¹³C NMR: 25.7 (CH₃), 61.2 (OCH₃), 14.2 (CH₃), 25.2 (OCH₂CH₂O(CH₂)₂CH₂Me), 41.0 (OCH₂CH₂OCH₂CH₂Et), 62.7 (OCH₂CH₂O CH₂Pr), 65.1 (OCH₂CH₂OBu), 71.3 (OCH₂CH₂OBu).

Complex 6: Yield 98 %, b.p. 214-216 °C, Elemental analysis (%): Found (calcd.) C = 55.9 (55.8), H = 10.2 (10.1), O = 24.5 (24.7). IR (Nujol, ν_{\max} , cm⁻¹): (Ti-O) = 605, (C-O) = 1090 and (C-O-C) = 1040. ¹H NMR (CDCl₃): 1.05 (t, 12H,

O(CH₂)₃CH₃), 3.12-3.86 (m, 40H, OCH₂CH₂O(CH₂)₃CH₃). ¹³C NMR 14.5 (CH₃), 26.6 (OCH₂CH₂O(CH₂)₂CH₂Me), 41.3 (OCH₂CH₂OCH₂CH₂Et), 62.5 (OCH₂CH₂O CH₂Pr), 65.7 (OCH₂CH₂OBu), 72.3 (OCH₂CH₂OBu).

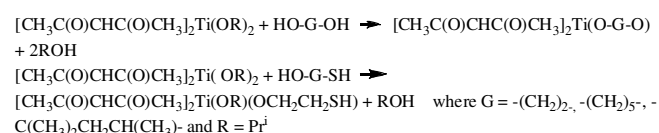
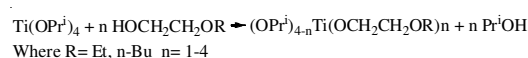
Complex 7: Yield 96 %, m.w. found. 355, calcd. 348; Elemental analysis (%): Found (calcd.) C = 51.9 (51.7), H = 7.2 (6.9), O = 27.8 (27.5). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1610, (C-C) = 1500, (C-O) = 1080 and (Ti-O) = 620. ¹H NMR (CDCl₃): 1.96, 2.01 (CH₃), 5.48 (s, CH), 3.64 (d, 4H, OCH₂), 1.54 (m, 6H, other proton); ¹³C NMR: 26.34, 26.78 (CH₃), 103.88 (CH), 191.28, 187.88 (CO), 58.40 (OCH₂), 29.52 (other carbon).

Complex 8: Yield 96 %, m.w. found. 378, calcd. 362; Elemental analysis (%): Found (calcd.) C = 53.4 (53.17), H = 7.5 (7.2), O = 26.9 (26.5). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1595, (C-C) = 1520, (C-O) = 1080 and (Ti-O) = 610. ¹H NMR (CDCl₃): 1.99, 2.08 (CH₃), 5.58 (s, CH), 4.10-4.34 (d, 1H, OCH), 1.43 (d, 2H, other proton), 1.34 (d, 3H, other proton), 1.13 (d, 6H, other proton); ¹³C NMR: 26.32, 26.86 (CH₃), 104.80 (CH), 191.28, 187.79 (CO), 69.74 (OCH), 25.80, 26.62, 51.14, 73.56 (other carbon).

Complex 9: Yield 96 %, m.w. found. 362, calcd. 382; Elemental analysis (%): found (calcd.) C = 47.5 (47.1), H = 6.4 (6.8), O = 25.3 (25.1), S = 8.4 (8.3). IR (Nujol, ν_{\max} , cm⁻¹): (C-O) = 1595, (C-C) = 1520, (C-O) = 1085, (S-H) = 2450, (C-O) = 1010 and (Ti-O) = 605. ¹H NMR (CDCl₃): 1.99, 2.05 (CH₃), 5.60 (s, CH), 1.18 (t, CH₃), 4.38-4.72 (q, CH), 3.38-3.42 (d, 4H, OCH₂), 1.45 (s, 1H, other proton); ¹³C NMR: 26.32, 26.82 (CH₃), 103.88 (CH), 191.30, 187.28 (CO), 25.68 (CH₃), 64.16 (CH), 62.82 (OCH₂), 58.44 (other carbon).

RESULTS AND DISCUSSION

Compounds of the type, [(OPrⁱ)_{4-n}Ti(OC₂H₄OR)_n], [(acac)₂Ti(O-G-O)] and [(acac)₂Ti(OPrⁱ)(OCH₂CH₂SH)] have been prepared by the reactions of titanium tetraisopropoxide and alkoxyalkanol in different molar ratios (1:1 to 1:4) and [(acac)₂Ti(OR)₂] with a variety of glycols and thioglycol in 1:1 molar ratios in refluxing anhydrous benzene as shown in the following equation:



All these reactions are highly facile and quantitative in yield and the liberated isopropanol could be removed as a benzene-isopropanol azeotrope. The completion of these reactions was checked by estimating the liberated isopropanol in the azeotrope iodometrically¹³. Alkoxy alkanol derivatives were of colourless liquids and have been purified by vacuum distillation. The glycol derivatives were yellow-orange solids or massy paste and got purified by washing with *n*-hexane. Molecular weight measurements reveal the complexes are monomeric.

IR Spectra¹⁴⁻¹⁶: IR spectral bands of these pure compounds were assigned by comparing with the spectra of free ligands. A medium intensity band at 3450 cm⁻¹ in the free ligands due to ν(OH) is absent in the spectra of all these complexes, indicating deprotonation of the alkoxyalkanols and the formation of metal-ligand bond through oxygen atom. The shifting of ν(C-O) 1595-1610 cm⁻¹ and ν(C-C) 1500-1520 cm⁻¹ towards lower wave numbers as compared to the free ligands in the IR spectra of the above derivatives indicates bidentate chelating nature of the acetylacetonate moiety. The appearance of a new band due to ν(Ti-O) is observed in the region 620-605 cm⁻¹. The medium intensity bands observed in the region 1090-1050 and 1055-1015 cm⁻¹ are assigned to alkoxyalkanolate ν(C-O) and ν(C-O-C), respectively. Appearance of ν(SH) at 2450 cm⁻¹ (as in free ligand) and absence of ν(Ti-S) stretching in the IR spectra of compound suggest that the sulphur is not coordinating to titanium atom.

¹H NMR spectra¹⁴⁻¹⁶: The ¹H NMR spectra of all these complexes exhibit characteristic peaks and the hydroxyl protons resonances of free ligands are absent, indicating deprotonation of OH group of the alkoxyalkanolate moiety and the formation of Ti-O bond. No appreciable shift was observed in the positions of alkoxyalkanolate protons as these appeared at their expected positions, ruling out the possibility of the coordination through the oxygen atom of the alkoxyalkanolate moiety. The spectra of the acetylacetonate complexes have been observed at δ 1.96-1.99, 2.01-2.08 and δ 5.45-5.60 ppm for methyl and methine protons of acetylacetonate moieties. The presence of two discrete and equivalent resonances associated with the CH₃ of the acetylacetonate is consistent with *cis* configuration for the acetylacetonate moieties.

¹³C NMR spectra¹⁴⁻¹⁶: In the ¹³C NMR spectra, the position and the number of alkoxyalkanolate carbon signals are same as expected. The fact that no significant shift was observed in the positions of alkoxy carbon of these ligand moieties further suggests that the alkoxyalkanolate is bound to titanium atom in monodentate fashion. Double peaks of CH₃ (26.28-26.38 and 26.72-26.88) and CO (191.22-191.30 and 187.28-187.88) of acetylacetonate moieties confirm the *cis* configuration of these derivatives. ¹³C NMR spectra of the above derivatives exhibit downfield shifts of OCH₂ and OCH signals of in the region δ 58.40-65.46 and 64.86-69.74 ppm, respectively, indicating bonding of the diolate moieties to Ti(IV).

In these complexes, attachments of oxygen while detachment of sulphur with titanium is justifying the HSAB rule also. The quantitative yields of the final tetra coordinated novel derivatives of titanium(IV) indicate that alcoholysis reactions are quite facile and yielding the simple tetrahedral products only.

Conclusion

On the basis of the molecular weight determinations, elemental analysis, IR and NMR (¹H and ¹³C) spectral studies a tetrahedral geometry around titanium atom has been proposed (Fig. 1) for the above compounds derived from alkoxyalkanols and a *cis* octahedral geometry is predicted in the case of diolate complexes. The work does not stop here. Sincere efforts are in the progress to get and characterize the nano structured titania from these newly synthesized metallo-organic derivatives of titanium(IV).

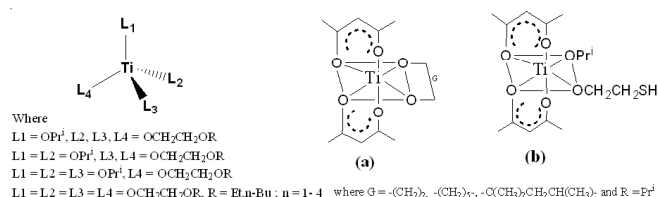


Fig. 1. Proposed structure of [Ti(OPri)_{p-n}(OC₂H₄OR)_n] and (a) [(acac)₂Ti(O-G-O)] and (b) [(acac)₂Ti(OPri)(OCH₂CH₂SH)]

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