

Synthesis and characterization of new heteroleptic derivatives of titanium(IV) derived from 2-hydroxy-4-methoxy-benzophenone : A new precursors for the synthesis of nano sized titania

Blassan Samuel^a, Madhvesh Pathak^{*a} and Kap Jin Kim^b

^aMaterials Chemistry Division, School of Advanced Sciences, VIT University, Vellore-632 014, Tamilnadu, India

E-mail : madhveshpathak@vit.ac.in

^bDepartment of Advanced Materials Engineering for Information and Electronics, College of Engineering, Kyung Hee University, 1732, Deogyong-daero, Giheung-gu, Yongin-si, Gyeonggi-do 446-701, South Korea

E-mail : kjkim@khu.ac.kr

Abstract : A few new titanium(IV) complexes have been synthesized by the reaction among precursor $(\text{Bp})_2\text{Ti}(\text{OPr}^i)_2$ with different alkoxyalkanols and phenols/substituted phenols in 1 : 1 : 1 molar ratios in boiling toluene as mono nuclear heteroleptic titanium complexes of the type $[(\text{Bp})_2\text{Ti}(\text{L}_1\text{OR})(\text{L}_2\text{X})]$ (3a-c) (where Bp = 2-hydroxy-4-methoxy-benzophenone, $\text{L}_1 = -\text{O}-\text{CH}_2-\text{CH}_2-$; R = CH_3 , C_2H_5 ; $\text{L}_2 =$ phenol, X = H or OCH_3). The newly prepared complexes were characterized by various physico-chemical techniques such as elemental analysis, mass, UV, FTIR and NMR (^1H and ^{13}C). The mass spectra of the newly synthesized derivatives indicate their monomeric nature. Based on spectral studies *cis* hexacoordinated geometry around titanium(IV) has been proposed. By employing sol-gel techniques to all the molecules, nano sized titania was produced at 600 °C. Powder XRD analysis confirmed the formation of a mixed phase (anatase and rutile).

Keywords : Heteroleptic, titanium complexes, benzophenone, nano titania.

Introduction

The interest in the synthesis of nano sized titania is growing because of its potential applications in diverse research area such as in solar cells¹, chemical sensors², sunscreen products³ and in textiles⁴. Though titanium alkoxides are fabulous precursors for the synthesis of nano sized titania, and often it has been modified with various structural stabilizers⁵. These chemical modifiers can induce structural changes as well as control over the size of the final materials produced during calcination⁶. Sol-gel technology is one of the easy and convenient methods employed for the soft transformation of these modified precursors into pure nano structured titania⁶. This could be attained by the controlled hydrolysis of the precursor molecules which helps in the formation of porous TiO_2 in appropriate morphology⁷. 2-Hydroxybenzophenone and its derivatives are excellent structural variants due to its bidentate chelating ability, which results in the formation of number of stable and novel derivatives⁵. Motivated by

the above observation, herein we report the synthesis and characterization of a new series of heteroleptic titanium(IV) complexes derived from 2-hydroxy-4-methoxy-benzophenone and its conversion into nano sized titania at 600 °C.

Experimental

Materials and methods :

All reactions were performed under stringent moisture-free environment. Reagents used were of A.R. grade and dried prior to use. Titanium and isopropanol were estimated according to a published procedure⁸. FTIR spectra were recorded on a Shimadzu IR affinity-1 spectrometer with anhydrous KBr pellets. NMR (^1H and ^{13}C) data were collected on Bruker Advance III NMR spectrometer in DMSO at 400 MHz frequency. Mass spectral data have taken from ESI mass spectrometer. Elemental analyses of the complexes were performed on Elementar Vario EL III instrument. Powder XRD data were collected on a Bruker D8 Advance X-Ray diffractometer.

Preparation of complexes :

(a) $(Bp)_2Ti(OPr^i)_2$ (**2**) :

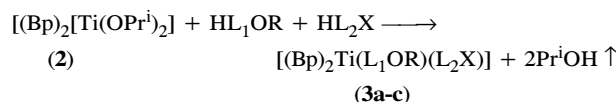
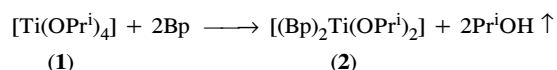
2-Hydroxy-4-methoxy-benzophenone (2.25 g, 9.86 mmol) was added to a toluene solution (~ 30 ml) of $[Ti(OPr^i)_4]$ (**1**) (1.4 g, 4.93 mmol) and reaction mixture was refluxed for 4 h. After removal of extra solvent under vacuo an orange-yellow solid (2.97 g, 97%) was obtained and got purified by washings of dried acetonitrile. [Found : $Pr^iOH = 0.570$ g, Ti = 7.9%, molecular weight = 621.8 and Calcd. : $Pr^iOH = 0.592$ g, Ti = 7.7%, molecular weight = 620.5].

(b) $[(Bp)_2Ti\{(OCH_2CH_2OR)(OC_6H_4C_6H_5)\}]$ (**3a**) :

A toluene solution of (~ 15 ml) $OH-CH_2-CH_2-OCH_3$ (0.21 g, 2.76 mmol) and C_6H_5OH (0.26 g, 2.76 mmol) were added to another solution of toluene (~ 20 ml) and $[(Bp)_2Ti(OPr^i)_2]$ (1.72 g, 2.76 mmol), and refluxed for 4–5 h. Oxidimetric titration was employed not only for monitoring the progress of the reaction but also for estimating the liberated isopropanol collected azeotropically with toluene. After the completion of reaction, excess solvents were removed *in vacuo* to furnish an orange solid, finally purified by washings of dried acetonitrile. [Found : $Pr^iOH = 0.31$ g, Ti = 7.2%, molecular weight = 670.9 and Calcd. : $Pr^iOH = 0.33$ g, Ti = 7.1%, molecular weight = 670.5], m.p. 120–122 °C. Same route has been employed for the synthesis of other analogous. The synthetic and analytical data of all the complexes have been tabulated in Table 1.

(c) Sol-gel transformation of $[(Bp)_2Ti\{(OCH_2CH_2OR)(OC_6H_4C_6H_5)\}]$ (**3a**) :

Ethylene glycol (0.22 g, 3.57 mmol) was added to a dichloromethane (~ 15 ml) solution of complex (**3a**) (1.2 g, 1.78 mmol). Stoichiometric amount of water was added (0.34 g, 1.88 mmol) to the clear solution and then stirred for 6 h. In order to ensure complete hydrolysis, excess amount of water was added (0.2 g, 1.11 mmol) and stirring was continued for 2 h more. The obtained gel was dried in a preheated (100 °C) oven and later washed with acetone. A yellow-brown powder was obtained and it was again kept at 600 °C for 2 h. An off white powder, later characterized as pure TiO_2 , was obtained. Similar route was followed for the hydrolysis of the complexes **3b** and **3c**.



(where, Bp = 2-hydroxy-4-methoxy-benzophenone, $L_1 = -O-CH_2-CH_2-$; R = CH_3 , C_2H_5 ; $L_2 =$ phenol, X = H or OCH_3)

Compound **3a** : IR (KBr, cm^{-1}) : 2936 (CH), 1607 (CO), 1505 (CC), 604 (TiO); 1H NMR (400 MHz, DMSO, ppm) δ : 3.37 (3H, s, alkoxyalkanol), 3.76 (2H, t, alkoxyalkanol), 3.82 (2H, t, alkoxyalkanol), 3.98 (6H, s, $-OCH_3$), 6.65 (2H, s), 6.85 (2H, d, J 8 Hz), 7.13 (4H, d, J 8.4 Hz), 7.27 (2H, d, J 8 Hz), 7.29 (2H, d, J 8 Hz), 7.34 (4H, t), 7.48 (2H, t), 7.74 (2H, t), 7.93 (1H, t); ^{13}C

Table 1. Synthetic and analytical data of new titanium(IV) derivatives

Complex	Reactants (g)	Color of the solid products	Liberated Pr^iOH (g)	Ti%		M.p. (°C)	Mol. wt. Found (Calcd.)
				Yield (%)	Found (Calcd.)		
	(a) $(Bp)_2Ti(OPr^i)_2$ (b) $HOCH_2CH_2OR$ (c) C_6H_4OHZ						
		New derivatives					
3a	a = 1.72, b = 0.21, R = CH_3 , c = 0.26, Z = H	$[(Bp)_2Ti\{(OCH_2CH_2OR)(OC_6H_4Z)\}]$	99.2	0.31 (0.33)	7.2 (7.1)	120– 122	670.9 (670.5)
3b	a = 1.65, b = 0.24, R = C_2H_5 , c = 0.25, Z = H	$[(Bp)_2Ti\{(OCH_2CH_2OR)(OC_6H_4Z)\}]$	98.9	0.30 (0.32)	7.1 (6.9)	128– 130	685.1 (684.5)
3c	a = 1.57, b = 0.19, R = CH_3 , c = 0.31, Z = OCH_3	$[(Bp)_2Ti\{(OCH_2CH_2OR)(OC_6H_4Z)\}]$	98.8	0.28 (0.30)	6.9 (6.8)	134– 136	701.3 (700.5)

NMR (100 MHz, DMSO, ppm) : 58.2, 60.8, 66.3, 76.4, 96.4, 104.1, 110.0, 120.8, 122.6, 126.5, 127.3, 128.1, 130.9, 131.7, 133.2, 136.7, 152.1, 154.9, 156.5, 158.8; (%) Elemental analysis : Found (Calcd.) C, 66.4 (66.3); H, 5.2 (5.1).

Compound **3b** : IR (KBr, cm^{-1}) : 2932 (CH), 1606 (CO), 1509 (CC), 606 (TiO); ^1H NMR (400 MHz, DMSO, ppm) δ : 1.17 (3H, t, alkoxyalkanol), 2.35 (2H, m, alkoxyalkanol), 3.54 (2H, t, alkoxyalkanol), 3.75 (2H, t, alkoxyalkanol), 4.04 (6H, s, $-\text{OCH}_3$), 6.38 (2H, s), 6.74 (2H, d, J 8 Hz), 7.21 (4H, d, J 8.4 Hz), 7.25 (2H, d, J 8 Hz), 7.30 (2H, d, J 8 Hz), 7.35 (4H, t), 7.45 (2H, t), 7.76 (2H, t), 7.88 (1H, t); ^{13}C NMR (100 MHz, DMSO, ppm) : 32.8, 57.9, 61.2, 66.4, 76.8, 97.1, 104.3, 110.2, 120.7, 122.8, 126.9, 127.4, 128.8, 130.7, 131.9, 132.6, 136.8, 152.4, 155.2, 156.8, 159.2; (%) Elemental analysis : Found (Calcd.) C, 66.8 (66.5); H, 5.8 (5.6).

Compound **3c** : IR (KBr, cm^{-1}) : 2940 (CH), 1608 (CO), 1503 (CC), 612 (TiO); ^1H NMR (400 MHz, DMSO, ppm) δ : 3.24 (3H, s, alkoxyalkanol), 3.38 (2H, t, alkoxyalkanol), 3.52 (2H, t, alkoxyalkanol), 3.74 (3H, s, $-\text{OCH}_3$), 3.94 (6H, s, $-\text{OCH}_3$), 6.48 (2H, s), 6.83 (2H, d, J 8 Hz), 7.21 (4H, d, J 8.4 Hz), 7.26 (2H, d, J 8 Hz), 7.32 (2H, d, J 8 Hz), 7.37 (4H, t), 7.48 (2H, t), 7.64 (2H, d, J 8.4 Hz); ^{13}C NMR (100 MHz, DMSO, ppm) : 57.6, 59.2, 65.4, 75.8, 96.1, 103.4, 109.6, 119.7, 122.8, 125.4, 126.7, 128.1, 131.2, 132.2, 133.4, 136.4, 151.3, 154.6, 156.4, 159.2; (%) Elemental analysis : Found (Calcd.) C, 65.4 (65.1); H, 5.6 (5.2).

Results and discussion

Titanium tetraisopropoxide $[\text{Ti}(\text{OPr}^i)_4]$ (**1**) reacted with 2-hydroxy-4-methoxy-benzophenone (Bp) in 1 : 2 stoichiometry in refluxing anhydrous toluene yields the precursor $(\text{Bp})_2\text{Ti}(\text{OPr}^i)_2$ (**2**). The precursor (**2**) treated with alkoxyalkanols, phenols/substituted phenols in 1 : 1 : 1 molar ratios yielded mono nuclear heteroleptic derivatives of the type $(\text{Bp})_2\text{Ti}(\text{L}_1\text{OR})(\text{L}_2\text{X})$ [where Bp = 2-hydroxy-4-methoxy-benzophenone, $\text{L}_1 = -\text{O}-\text{CH}_2-\text{CH}_2-$; $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$; $\text{L}_2 = \text{phenol}$, $\text{X} = \text{H}$ or OCH_3].

These reactions are very rapid and could be completed in 3–4 h. Completion of the reaction has been confirmed by the estimation of liberated alcohol in toluene-isopropanol azeotrope oxidimetrically⁸. All the above

complexes are orange solids and are insoluble in common organic solvents except in dimethyl sulfoxide.

Structural elucidation :

Structural characterizations of all these new derivatives were carried out by ^1H NMR, ^{13}C NMR, FT-IR, elemental analysis, mass and XRD. NMR spectra of these new molecules have been interpreted by matching it with the pure spectra of the ligands^{6,8–11}. Alkoxy alkanols and phenols produce a strong signal in the region δ 8.35–10.50 ppm. Absence of these signals in the aforesaid region is due to the deprotonation and the formation of new Ti-O bonds with the free ligands. The other δ values are obtained in the proper range.

IR spectra have been explained by comparing it with the spectra of the pure ligand used for the synthesis^{5,6,8–11}. Formation of a new band in the region of 604–612 cm^{-1} and disappearance of hydroxyl stretching from the spectra are due to the deprotonation of hydroxyl group and the formation Ti-O bond. The $\nu(\text{C}-\text{O})$ 1606–1610 cm^{-1} and $\nu(\text{C}-\text{C})$ 1501–1509 cm^{-1} bands of the complexes have shifted towards lower wave number region compared to the ligands in the IR spectra is due to the bidentate chelating nature of the benzophenone.

Mononuclear nature of the complexes has been confirmed by mass spectra and elemental analysis. Synthesis of nano sized titania was achieved by the hydrolysis of complexes **3a**, **3b** and **3c** (Fig. 1) with a bit modification in the previous report⁶. Complexes were heated at 600 °C. The XRD obtained for the titanium oxide was compared with the available literature (JCPDS card no : 00-084-1286). Formation of mixed phase (anatase and rutile) has

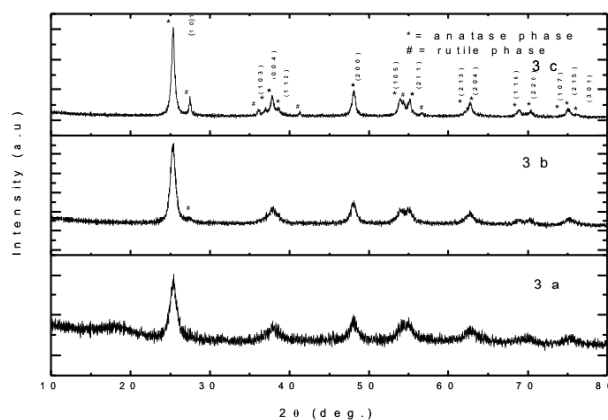


Fig. 1. XRD pattern of complex **3a-b**.

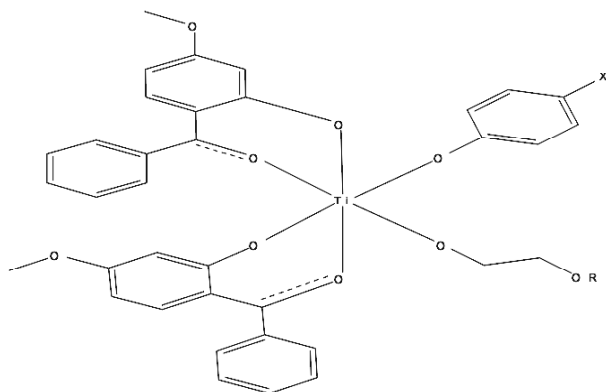


Fig. 2. Tentative structure of the newly synthesized molecule.

been confirmed by XRD. Debye-Scherrer equation¹² was used for calculating the particle size of TiO₂ from the (101) reflection of anatase for the longest peak in the XRD spectra (Complex **3a** : $2\theta = 25.28^\circ$, size = 10–15 nm, % rutile is < 5; Complex **3b** : $2\theta = 25.41^\circ$, size = 12–17 nm, % rutile is < 5; Complex **3c** : $2\theta = 25.67^\circ$, size = 25–30 nm, % rutile is < 20).

Conclusion

Based on the spectral data and available literature, we have proposed a *cis*-octahedral geometry (Fig. 2) for these newly synthesized titanium(IV) complexes of benzophenone derived from alkoxyalkanols and phenols/substituted phenols. These new complexes could be easily converted into nano materials by employing sol-gel transformation under mild experimental conditions. The ligand benzophenone not only acts as a structural modifier but precisely controls over the particle size also.

Acknowledgement

This work was supported by the National Research Foundation (NRF) grant (NRF-2008-0057632) funded by

the Korea Government (MSIP) and Industrial Source Technology Development Programs (Grant No. 10033449) funded by the Ministry of Trade, Industry and Energy of Korea. One of the authors (BS) is grateful to VIT University, India for awarding Research Associateship. We also thank VIT-TBI, VIT-SIF and STIC Cochin for sample analyses.

References

1. L. Grinis, S. Dor, A. Ofir and A. Zaban, *J. Photochem. Photobiol. (A)*, 2008, **198**, 52.
2. P. M. Faia, C. S. Furtado and A. J. Ferreira, *Sensors Actuat. B : Chem.*, 2005, **107**, 353.
3. S. Livraghi, I. Corazzari, M. C. Paganini, G. Ceccone, E. Giamello, B. Fubinia and I. Fenoglio, *Chem. Commun.*, 2010, **46**, 8478.
4. M. Montazera and E. Pakdel, *J. Photochem. Photobiol. C : Photochem. Rev.*, 2011, **12**, 293.
5. T. J. Boyle and L. A. M. Ottley, *Inorg. Chim. Acta*, 2010, **364**, 69.
6. A. Chaudhary, V. Dhayal, M. Nagar, R. Bohra, S. M. Mobin and P. Mathur, *Polyhedron*, 2011, **30**, 821.
7. N. Sharma, V. Sharma, R. Bohra, V. S. Raju, I. P. Lorenz, C. Krininger and P. Mayer, *Inorg. Chim. Acta*, 2007, **360**, 3002.
8. B. Samuel, K. Tummalapalli, P. V. Giri and M. Pathak, *Med. Chem. Res.*, in Press (DOI : 10.1007/s00044-013-0660-y).
9. M. Pathak, B. Samuel, K. Tummalapalli, P. V. Giri, S. Koppala, R. Bohra and K. J. Kim, *Adv. Mat. Res.*, 2012, **584**, 415.
10. M. Pathak, B. Samuel, K. Tummalapalli, P. V. Giri, R. Bohra and K. J. Kim, *Adv. Mat. Res.*, 2012, **584**, 411.
11. B. Samuel, K. Tummalapalli, P. V. Giri and M. Pathak, *Asian J. Chem.*, 2013, **25**, 8034.
12. B. E. Warren, "X-ray Diffraction", Dover Publication, New York, 1990.