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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

## Shape Controlled Synthesis of Nano-Sized Titanium(IV) Metal-Organic Frameworks

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Published online: 19 Feb 2011.

To cite this article: Balram P. Baranwal, Alok K. Singh, Anand Varma & Avinash C. Pandey (2011) Shape Controlled Synthesis of Nano-Sized Titanium(IV) Metal-Organic Frameworks, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 41:2, 150-154

To link to this article: <u>http://dx.doi.org/10.1080/15533174.2010.538026</u>

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## Shape Controlled Synthesis of Nano-Sized Titanium(IV) Metal-Organic Frameworks

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A convenient method to synthesize shape controlled nano-sized metal-organic frameworks (MOFs) has been explored to prepare some novel mixed–ligand complexes of titanium(IV) with the general formula [Ti(acac)Cl<sub>2-n</sub>(OOCC<sub>15</sub>H<sub>31</sub>)(SB)<sub>n</sub>] (where Hacac = acetylacetone, HSB = Schiff bases and n = 1 or 2). They have been synthesized by stepwise substitutions of chloride ions from titanium(IV) chloride. The complexes were characterized by elemental analyses, molecular weight determinations, spectral, and TEM studies. Coordination number 7 and 8 was assigned for titanium(IV) in the complexes. The powder XRD, TEM, and SAED studies indicates that these complexes are nano-sized having poor crystalline nature.

Keywords mononuclear, multidentate ligands, nano-size, titanium(IV)

#### INTRODUCTION

Shape-controlled synthesis of titanium(IV) metal-organic frameworks (MOFs) provides novel nano- or micromaterials with opportunities in exploring their unique physical and chemical properties. Metal-organic frameworks (MOFs) composed of metal ions linked together by multidentate ligands have attracted considerable attention in recent years.<sup>[1-6]</sup> A key challenge for the industrial use of MOFs is to deliver them in a shape suitable for applications.

Most of the titanium complexes are sensitive to hydrolysis, which may cause a subsequent reduction in their catalytic property.<sup>[7]</sup> Their rate of hydrolysis can be significantly reduced by using bulky electron-rich ligands.<sup>[8,9]</sup> In this light, we have recently reported some titanium(IV) complexes having Ti-O-C bond and increased resistance towards hydrolysis.<sup>[10]</sup> We report here an easier method of synthesis of some metalorganic frameworks of titanium(IV) using multidentate ligands like acetylacetone, carboxylic acids, and Schiff bases. These ligands were chosen in accordance with the objectives that all of them act as potential chelating agents having hard oxygen donor atoms suitable for titanium(IV). These complexes are hydrolytically stable and have Ti-O-C linkage, a basic requirement for catalytic action. Their nano-size and spherical shaped particles have been observed and are being reported here.

#### **EXPERIMENTAL**

#### **Materials and Analytical Methods**

All the reactions were carried out under anhydrous conditions. Organic solvents (Qualigens) were dried and distilled before use by standard methods.<sup>[11]</sup> Sodium palmitate, acetylacetone (Aldrich), and TiCl<sub>4</sub> (BDH) were used as received. Titanium and chlorine were estimated gravimetrically as TiO<sub>2</sub> and AgCl, respectively.<sup>[12]</sup>

#### **Physico-chemical Measurements**

Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer using KBr discs. <sup>1</sup>H NMR spectra were recorded at 300 MHz on a Bruker DRX-300 NMR spectrometer in CDCl<sub>3</sub>. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermistor sensing device. Powder XRD data were collected on a PW 1710 diffractometer. The operating voltage of the instrument was 30 kV and the operating current was 20 mA. The intensity data were collected at room temperature over a  $2\theta$  range of 5.025–79.925° with a continuous scan mode. Transmission electron microscopy (TEM) images were obtained on a Tecnai 30 G<sup>2</sup>S - Twin electron microscope with an accelerating voltage of 300 kV on the surface of a carbon coated copper grid. Elemental analyses (C, H and N) were done on a Vario EL III Carlo Erba 1108 elemental analyzer. Molar conductance were measured on century CC-601 digital conductivity meter at  $10^{-2}$ - $10^{-3}$  molar solutions in nitrobenzene. Solid state conductance measurements were carried out with Keithley 6220 Precision current source and keithley 2182A Nanovoltmeter.

Received 27 May 2010; accepted 18 August 2010.

The authors are thankful to the CSIR [No. 01(2293)/09/EMR-II] and [UGC-DSA F.4-5/2006 (XI Plan/BSR) dated September 20, 2007], New Delhi for financial supports. They also thank CDRI, Lucknow for spectral and microanalysis.

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TABLE 1 Analytical results for the titanium(IV) complexes

		Product (color) (% yield)			M.p. (°C)	Found (calculated) %					Molecular
Reactants (g, mmol)						Ti Cl		C	Н	H N	weight
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> (2.10, 4.44)	$H_{31}$ ] + NaSB-1 (1.13, 4.45)	[Ti(acac)Cl(OO (Dark grey)	CC <sub>15</sub> H <sub>31</sub> (88)	( <b>1</b> )( <b>SB</b> -1)]	113	7.09 (7.16)	10.57 (10.61)	61.05 (61.08)	7.11 (7.10)	2.08 (2.10)	661 (669)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> (2.62, 5.54)	H <sub>31</sub> )] + NaSB-1 (2.81, 11.08)	[Ti(acac)(OOC (Light grey)	C <sub>15</sub> H <sub>31</sub> ) (83)	(SB-1) <sub>2</sub> ] (2)	119	5.52 (5.54)	8.18 (8.21)	65.36 (65.34)	6.53 (6.55)	3.25 (3.24)	858 (864)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> (2.43, 5.13)	H <sub>31</sub> )] + NaSB-2 (1.13, 5.16)	[Ti(acac)Cl(OO (Dark grey)	CC <sub>15</sub> H <sub>31</sub> (89)	( <b>3</b> )(SB-2)]	92	7.54 (7.55)	5.61 (5.59)	64.38 (64.40)	7.61 (7.65)	2.19 (2.21)	643 (634)
[Ti(acac)Cl <sub>2</sub> (OOCC <sub>15</sub> (2.82, 5.96)	H <sub>31</sub> )] + NaSB-2 (2.62, 11.95)	[Ti(acac)(OOC (Light grey)	$C_{15}H_{31})$ (81)	(SB-2) <sub>2</sub> ] (4)	94–97	6.01 (6.02)	_	71.02 (71.01)	7.35 (7.37)	3.51 (3.53)	789 (795)

#### Synthesis of $[Ti(acac)Cl(OOCC_{15}H_{31}) (SB-1)]$ (1)

Schiff bases HSB-1 and HSB-2 were prepared by the literature procedure.<sup>[13,14]</sup> Their sodium salts were prepared by adding the required amount of sodium metal to an excess of isopropanol (sodium isopropoxide formed in situ). The solution thus formed was added slowly to the Schiff bases in isopropanol and the contents were boiled to reflux for 2 h. Removal of excess solvent under vacuum vielded the desired sodium salts of Schiff bases. [Ti(acac)Cl<sub>2</sub>(OOCC<sub>15</sub>H<sub>31</sub>)] was prepared by treating TiCl<sub>4</sub> with one equivalent mole of acetylacetone in benzene which yielded [Ti(acac)Cl<sub>3</sub>]. To the suspension of [Ti(acac)Cl<sub>3</sub>] (2.11 g, 8.33 mmol) in benzene (40 mL), sodium palmitate (2.32 g, 8.33 mmol) was added. The contents were stirred for 8 h followed by refluxing for 2 h. The contents were filtered using G 4 sieve to remove insoluble sodium chloride formed during the reaction. The excess solvent was removed in vacuo and a yellow colored solid, [Ti(acac)Cl<sub>2</sub>(OOCC<sub>15</sub>H<sub>31</sub>)] was obtained. This composition was confirmed by the elemental analysis and infrared.<sup>[10]</sup> To a solution of [Ti(acac)Cl<sub>2</sub>(OOCC<sub>15</sub>H<sub>31</sub>)] (2.10 g, 4.44 mmol) in benzene (50 mL), NaSB-1 (1.13 g, 4.45 mmol) was added. The contents were stirred (10 h) followed by refluxing (3 h) and filtration using G 4 sieve to remove insoluble sodium chloride formed during the reaction, leaving a black colored solution. The desired product was isolated by evaporation of the solvent under reduced pressure. It was recrystallized in dichloromethane-n-hexane mixture (1:1 ratio). The substitutions and stepwise use of different types of ligands made shape controlled synthesis of titanium(IV) complexes during present investigations. Other three complexes were synthesized analogously and the details of analytical results are given in Table 1.



#### **RESULTS AND DISCUSSION**

Some metal-organic frameworks of titanium(IV) were synthesized by stepwise substitutions of chloride ions from titanium tetrachloride:

$$\operatorname{TiCl}_{4} + \operatorname{Hacac} \xrightarrow[\operatorname{Reflux}]{\operatorname{Benzene}} [\operatorname{Ti}(\operatorname{acac})\operatorname{Cl}_{3}] + \operatorname{HCl} \uparrow$$
[1]

$$[Ti(acac)Cl_{3}] + C_{15}H_{31}COONa \xrightarrow[Reflux]{Reflux} [Ti(acac) \\ \times Cl_{2}(OOCC_{15}H_{31})] + NaCl \downarrow$$

$$[Ti(acac)Cl_{2}(OOCC_{15}H_{31})] + nNaSB \xrightarrow[Reflux]{Benzene} [Ti(acac)Cl_{2-n}]{Benzene} [Ti(acac)Cl_{2-n}]{Benzene} [Ti(acac)Cl_{2-n}]{Benzene}$$

$$\times (OOCC_{15}H_{31})(SB)_n] + nNaCl \downarrow$$
[3]

(Where Hacac = acetylacetone, NaSB = NaSB-1 or NaSB-2 and n = 1 or 2)

Benzene was chosen a solvent in these substitutions because sodium chloride formed during the reaction was insoluble and the titanium(IV) complexes were soluble, which could made the separation easy. The molar conductance of complexes at  $10^{-2}-10^{-3}$  molar concentrations in nitrobenzene was obtained in the range  $1-8 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , which indicated them to be non-electrolytes.<sup>[15]</sup> The value obtained from conductance measurements ( $1 \times 10^{-8} \text{A}$  current,  $2.92 \times 10^{-2} \text{ V}$ ) in the solid form of complex **2** indicated a high resistance ( $2.92 \times 10^6 \ \Omega$  at 295 K). This may lead to the conclusion that the complex shows the property like an insulator. Elemental analyses were in good agreement with the calculated values. Ebullioscopic method of molecular weight determinations showed that all the complexes were monomeric in refluxing benzene (Table 1).

#### **Infrared Spectra**

In infrared spectra of all the complexes O-H stretching vibrations of different ligands were found absent in the region 3600-3200 cm<sup>-1</sup>. The bands at 1710 cm<sup>-1</sup> (CO stretching) and at 935 cm<sup>-1</sup> (OH deformation) of free palmitic acid were also absent in

TABLE 2 <sup>1</sup>H NMR spectral data ( $\delta$ , ppm) for titanium(IV) complexes

Complex	<sup>1</sup> H
2	0.87 [s, 3H, CH <sub>3</sub> ], 1.24 [s, 26H, 13 x (-CH <sub>2</sub> )], 1.59
	[t, 2H, (α-CH <sub>2</sub> )], 2.04 [s, 6H, acac], 5.52 [s, 1H,
	CH, acac], 8.37 [s, 2H, CH=N], 7.51-6.64 [m,
	16H, arom]
3	0.88 [s, 3H, CH <sub>3</sub> ], 1.26 [s, 26H, 13 x (-CH <sub>2</sub> )], 1.63
	[t, 2H, (α-CH <sub>2</sub> )], 2.06 [s, 6H, acac], 5.51 [s, 1H,
	CH, acac], 8.21 [s, 1H, CH=N], 7.46-6.87 [m, 9H
	arom]
4	0.88 [s, 3H, CH <sub>3</sub> ], 1.26 [s, 26H, 13 x (-CH <sub>2</sub> )], 1.61
	[t, 2H, (α-CH <sub>2</sub> )], 2.05 [s, 6H, acac], 5.51 [s, 1H,
	CH, acac], 8.29 [s, 2H, CH=N], 7.47-6.55 [m,
	18H, arom]

the spectra of the complexes. Two strong bands were observed at ~1535 cm<sup>-1</sup> and ~1435 cm<sup>-1</sup>, which could be assigned due to ( $v_{asym}$ OCO) (antisymmetric) and ( $v_{sym}$ OCO) (symmetric) vibrations of the palmitate ions, respectively.<sup>[16]</sup> The difference,  $\Delta[v_{asym}OCO-v_{sym}OCO]$  was ~100 cm<sup>-1</sup>, which indicated bidentate chelating nature of palmitate ion.<sup>[17]</sup> No band was found in 1626–1700 cm<sup>-1</sup>region indicating the CO group of acetylacetone was not free in the complexes. Two splitted new bands observed at ~1615 cm<sup>-1</sup> ( $\nu$ C==-O) and ~1530 cm<sup>-1</sup>  $(\nu C = C)$  indicated the chelating nature of acetylacetonate ion in the complexes.<sup>[18]</sup> The  $\nu_{(C-O)}$  (phenolic) bands appeared in the region 1280-1263 cm<sup>-1</sup> in free Schiff bases were shifted to higher wave number ( $\sim 20 \text{ cm}^{-1}$ ). The infrared spectra of all the free Schiff bases exhibited a strong and sharp band in the region 1631-1620 cm<sup>-1</sup>, which was shifted to lower frequencies ( $\sim 15 \text{ cm}^{-1}$ ) in complexes indicating coordination through azomethine nitrogen. This was further supported by appearance of a titanium-nitrogen (Ti–N) band around 530 cm<sup>-1</sup>. The bands around 560 cm<sup>-1</sup> could be assigned to Ti–O vibrations.<sup>[17]</sup>

#### Hydrolytic Stability of the Complexes

The precursor complex  $[Ti(acac)Cl_2(OOCC_{15}H_{31})]$  is moisture sensitive.<sup>[10]</sup> Its sensitivity towards hydrolysis is reduced by substituting chloride ions by Schiff bases. This stability was tested by dissolving the complexes in benzene, and 0.1% water was added and stirred the contents for 12 h open in the air. It was also observed that the di-substituted products were more hydrolytically stable than the mono-substituted ones.

#### <sup>1</sup>H NMR Spectra

No signal was observed in the <sup>1</sup>H NMR spectra of the complexes in the region  $\delta$  15.0 to 10.0 ppm (observed due to –OH proton), which indicated deprotonation and bonding of acetylacetone, carboxylic and Schiff bases to titanium. In the <sup>1</sup>H NMR spectrum of 1 the azomethine proton in Schiff base suffered an upfield shifting from  $\delta$  8.61 to 8.28 as a singlet which indicated coordination of azomethine nitrogen to titanium. A multiplet of phenyl protons was appeared in the region  $\delta$  7.51–6.94. A singlet was appeared at  $\delta = 0.88$  ppm (3H) corresponding to methyl protons of palmitate ion [-OOCCH<sub>2</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>3</sub>] and a singlet at  $\delta = 1.26$  ppm due to 26H of 13-CH<sub>2</sub>groups. A peak at  $\delta = 1.63$  ppm (2H) indicated the  $\alpha$  -CH<sub>2</sub> protons of palmitate ion. A singlet at  $\delta = 2.05$  ppm (6H) indicated the methyl protons of acac while the methine proton of acac was observed as a singlet at  $\delta = 5.51$  ppm (1H). An almost similar pattern of <sup>1</sup>H NMR spectra were observed for other complexes and the signal positions with assignments are listed in Table 2.

#### **Powder XRD and TEM Studies**

The pattern and results of powder XRD suggested that the complexes are showing poor crystallinity. Because of this single

	1										
Angle [xZi]	d-value 1[]	d-value 2[]	Peak width [xZi]	Peak intensity [counts]	Back. intensity [counts]	Rel. intensity [x]	Significance				
7.355	12.0096	12.0391	0.150	17	42	8.3	1.20				
13.700	6.4584	6.4743	0.150	40	29	19.7	1.59				
21.550	4.1203	4.1304	0.200	110	52	54.7	1.38				
24.050	3.6973	3.7064	0.300	41	45	20.3	1.26				
25.045	3.5527	3.5614	0.200	100	41	49.6	1.97				
27.345	3.2588	3.2669	0.200	34	36	16.7	0.86				
31.680	2.8221	2.8291	0.300	202	31	100.0	4.94				
45.370	1.9973	2.0022	0.300	121	27	60.0	2.92				
56.430	1.6293	1.6333	0.250	35	18	17.3	0.83				
66.145	1.4116	1.4151	0.400	18	15	8.7	0.77				
75.170	1.2629	1.2660	0.400	38	14	19.1	1.77				

TABLE 3Powder XRD data of complex 1



FIG. 1. Powder XRD spectrum of complex 1.

crystal XRD could not be done. Powder XRD were done for all the complexes and one spectrum for **1** along with its crystal data is given in Table 3 (Figure 1), which are comparable with titanium amide chlorate carbonate, both in diffraction intensity and position (JCPDS No. 76-2255). Particle size of the complexes was calculated by the standard Scherrer equation.<sup>[19]</sup>

$$D = K\lambda/(\beta\cos\theta)$$
[4]

Where D is the particle size; K is a constant (= 0.94);  $\lambda$  is X-ray wavelength ( $\lambda = 1.5406$  Å);  $\theta$  is Bragg diffraction angle

and  $\beta$  is integral peak width, which is converted into radian while calculation. The calculated values of particle size from maximum intensity peak for 1, 2, 3, and 4 were obtained as 29, 48, 26, and 43 nm, respectively. These values are indicative of the nano-range size for the complexes.

The morphology of the complex **1** was found to be spherical (Figure 2a) having 35 nm average diameter of the particles which is in agreement with the calculated value obtained from Scherrer's equation, i.e. 29 nm. It is also concluded that the nano particles are showing poor crystallinity on the basis of selected area electron diffraction (SAED) in Figure 2b.



FIG. 2. (a) TEM image, and (b) the SAED pattern for the complex 1.

#### CONCLUSION

In this communication, we report a novel synthetic method to prepare shape controlled mixed-ligand complexes of titanium(IV). These are metal-organic frameworks of titanium(IV) having spherical shape and nano-sized particles. Their increased hydrolytic stability was noticed, and coordination number 7 and 8 have been assigned in them.

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