



Nano-sized titanium(IV) ternary and quaternary complexes with electron-rich oxygen-based bidentate ligands

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ABSTRACT

Some novel ternary and quaternary complexes of titanium(IV) of general formula $[\text{Ti}(\text{acac})\text{Cl}_{3-n}(\text{OOCR})_n]$ ($\text{R} = \text{C}_{15}\text{H}_{31}$ or $\text{C}_{17}\text{H}_{35}$ and $n = 1-3$) have been synthesized by stepwise substitution of chloride ions of $[\text{Ti}(\text{acac})\text{Cl}_3]$ by straight chain carboxylic acid anions. The complexes are characterized by their elemental analyses, spectral (infrared, FAB mass, ^1H NMR and powder XRD) studies, molecular weight determination and molar conductance measurements. Infrared spectra suggested bidentate chelating nature of both acetylacetonate and carboxylate anions in the complexes. Monomeric nature of the complexes was confirmed by their molecular weight determination and FAB mass spectra. Molar conductance values indicated the complexes to be non-electrolytes in DMF. The complexes exhibited high resistance to hydrolysis. Their powder XRD data indicated the nano-size for the complexes. The coordination number of titanium(IV) in these complexes were found to be six, seven and eight which has been discussed in detail.

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1. Introduction

Titanium nano-particles are known for a long time, which are extensively studied during the last decade because of various applications of these nanomaterials [1–3]. Titanium(IV) complexes are widely studied for a variety of purposes, mainly serving as a catalyst in different organic reactions as well as for antitumor activity [4]. Titanium alkoxides are excellent precursors for the deposition of metal oxides used in optoelectronics, high- T_c superconductors and ceramic materials [5]. These systems are effective catalysts in the Diels–Alder reactions [6], C–C bond forming reactions [7], esterification reactions and others [8–10]. However, since titanium alkoxides are very sensitive to hydrolysis it possesses a great problem in the catalytic reactions and cleavage of Ti–OR bonds due to reaction with water is observed in esterification reactions [11]. The rate of hydrolysis of $[\text{Ti}(\text{OR})_4]$ can be significantly reduced by the presence of bulky or chelating ligands [12,13]. Therefore, synthesis of titanium(IV) complexes exhibiting high hydrolytic stability is extremely valuable. Straight chain fatty acids are electron-rich oxygen-based ligands which may lead to resistance towards hydrolysis. Titanium(IV) complexes with higher coordination numbers (more than six) have been reported recently [14,15] for their applications in many chemical reactions. Literature also reveals that mixed-ligand complexes of titanium(IV) with acetylacetone and straight chain fatty acids have not been reported so far. In this paper we describe the synthesis of hydrolytically sta-

ble ternary and quaternary complexes of titanium(IV) with oxygen donor bidentate ligands like acetylacetonate and carboxylate anions. The coordination number of titanium in these complexes varies from six to eight. Their nano-size has been determined from powder XRD data.

2. Experimental

2.1. 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 [16]. Sodium salts of fatty acids (palmitic and stearic), acetylacetone (Aldrich) and TiCl_4 (BDH) were used as received. Titanium and chlorine were estimated gravimetrically as TiO_2 and AgCl , respectively [17].

2.2. Synthesis of $[\text{Ti}(\text{acac})\text{Cl}_2(\text{OOC}_{17}\text{H}_{35})]$

The complex $[\text{Ti}(\text{acac})\text{Cl}_3]$ was synthesized by the reported method [18]. To the suspension of $[\text{Ti}(\text{acac})\text{Cl}_3]$ (3.38 g, 13.34 mmol) in benzene (50 mL), sodium stearate (4.1 g, 13.38 mmol) was added. The contents were stirred for 8 h followed by refluxing for 2 h at 100 °C. The contents were filtered using G4 sieve to remove insoluble sodium chloride formed during the reaction. A reddish brown solution was thus obtained. After removing excess of solvent *in vacuo*, a yellow coloured powder was obtained (yield = 81%). Other complexes were synthesized following the same procedure and the results are given in Table 1.

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Table 1
Analytical results for titanium(IV) complexes.

Reactants ^a (g, mmol)	Product (colour) (% yield)	Found (calculated) %				Molecular weight
		Ti	Cl	C	H	
[Ti(acac)Cl ₃] (4.82, 19.03) + C ₁₅ H ₃₁ COONa (5.32, 19.11)	[Ti(acac)Cl ₂ (OOC ₁₅ H ₃₁)] (dark yellow) (85) (1)	10.10 (10.11)	14.80 (14.98)	53.40 (53.29)	8.10 (8.11)	487 (473)
[Ti(acac)Cl ₃] (1.35, 5.33) + C ₁₅ H ₃₁ COONa (2.98, 10.70)	[Ti(acac)Cl(OOC ₁₅ H ₃₁) ₂] (light yellow) (88) (2)	6.98 (6.91)	5.05 (5.11)	64.30 (64.10)	10.08 (10.05)	679 (693)
[Ti(acac)Cl ₃] (2.70, 10.66) + C ₁₅ H ₃₁ COONa (8.96, 32.18)	[Ti(acac)(OOC ₁₅ H ₃₁) ₃] (light yellow) (82) (3)	5.21 (5.24)		69.65 (69.71)	11.05 (11.10)	931 (913)
[Ti(acac)Cl ₃] (3.38, 13.34) + C ₁₇ H ₃₅ COONa (4.1, 13.38)	[Ti(acac)Cl ₂ (OOC ₁₇ H ₃₅)] (dark yellow) (81) (4)	9.46 (9.55)	14.00 (14.14)	55.20 (55.10)	8.40 (8.46)	486 (501)
[Ti(acac)Cl ₃] (2.34, 9.24) + C ₁₇ H ₃₅ COONa (5.68, 18.53)	[Ti(acac)Cl(OOC ₁₇ H ₃₅) ₂] (light yellow) (85) (5)	6.35 (6.39)	4.60 (4.73)	65.75 (65.71)	10.40 (10.38)	735 (749)
[Ti(acac)Cl ₃] (2.6, 10.26) + C ₁₇ H ₃₅ COONa (9.48, 30.93)	[Ti(acac)(OOC ₁₇ H ₃₅) ₃] (light yellow) (89) (6)	4.80 (4.79)		71.00 (71.04)	11.30 (11.34)	984 (997)

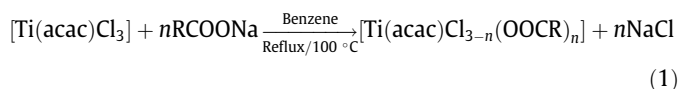
^a Reflux about 2–4 h.

2.3. Physico-chemical measurements

Infrared spectra were recorded on a Varian 3100-FTIR Excalibur series spectrophotometer using KBr discs. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermistor sensing device. FAB mass was done on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. ¹H NMR spectra were recorded at 250.17 MHz on a Bruker DPX 250 NMR spectrometer in CDCl₃. Molar conductance was measured on a century CC-601 digital conductivity meter at 10⁻²–10⁻³ molar concentrations in DMF. Elemental analyses (C, H) were done on a Carlo-Erba 1108 elemental analyzer. Magnetic moment was measured on a Gouy balance using Hg[Co(SCN)₄] as a calibrant. Powder X-ray diffraction data were collected on a PW 1710 diffractometer.

3. Results and discussion

Some mixed-ligand ternary and quaternary complexes of titanium(IV) were synthesized by the stepwise substitutions of chloride ions of [Ti(acac)Cl₃] by straight chain carboxylic acid anions:



where R = C₁₅H₃₁, Pal or C₁₇H₃₅, Stea; *n* = 1–3.

Benzene was chosen a solvent in these substitutions because during the reaction there was formation of sodium chloride which was insoluble in benzene in which the titanium(IV) complexes were soluble. This made the separation easy. After substitution of chloride ions, the colour of the complexes became lighter and the complexes [Ti(acac)(OOCR)₃] were of light yellow colour. Molar conductance of the complexes at 10⁻²–10⁻³ molar concentrations in DMF was obtained in the range 11–19 Ω⁻¹ cm² mol⁻¹ and the results indicated them to be non-electrolytes [19]. Magnetic moments of all the complexes at room temperature indicated them to be diamagnetic, ascertaining titanium is present in 4+ oxidation state with no unpaired electron.

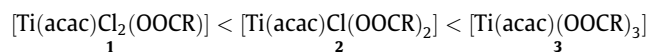
3.1. Infrared spectra

In infrared spectra of all the complexes O–H stretching vibrations of carboxylic acid were found absent near 3400 cm⁻¹. The bands at 1710 (CO stretching) and at 935 cm⁻¹ (OH deformation) of free carboxylic acids were also absent in the spectra of the complexes. Two strong bands were found in the range 1562–1530 cm⁻¹ and 1440–1430 cm⁻¹ which could be assigned due to (ν_{asym}OCO)

(antisymmetric) and (ν_{sym}OCO) (symmetric) vibrations of the carboxylate ions, respectively [20]. The differences between the symmetric and antisymmetric stretches, Δ[ν_{asym}OCO – ν_{sym}OCO] were found in the range 100–122 cm⁻¹ which indicated bidentate chelating nature of carboxylate ligands [21]. In the infrared spectra of the complexes, no band was found in 1626–1700 cm⁻¹ region indicating the CO group of acetylacetonate was not free in the complexes. Two splitted new bands observed at 1615–1590 cm⁻¹ ν_{C=O} and 1530–1515 cm⁻¹ ν_{C=C} indicated the chelating nature of acetylacetonate ion in the complexes [22]. The bands around 670 and 470 cm⁻¹ could be assigned to ring deformation ν_{Ti–O} and ν_{Ti–O} vibrations, respectively [21].

3.2. Hydrolytic stability of the complexes

Complex [Ti(acac)Cl₃] is extremely moisture sensitive and hydrolyses easily. The final product of hydrolysis is TiO₂ [18]. However, complexes [Ti(acac)(Pal)₃] and [Ti(acac)(Stea)₃] exhibit a high hydrolytic stability and are air stable for a longer time. This stability was tested by dissolving the complexes in benzene and 0.01% water is added. After stirring the contents for 12 h, no precipitate was appeared even after keeping the contents open in to air for 2 months. In contrast, the complexes [Ti(acac)Cl₂(Pal)] and [Ti(acac)Cl₂(Stea)] were precipitated while tested under same conditions. Complexes [Ti(acac)Cl(Pal)₂] and [Ti(acac)Cl(Stea)₂] showed slow precipitation after 7 days under the same conditions. This clearly indicates that the stepwise removal of chloride ion by higher fatty acid anions is directly related to the hydrolytic stability of the complexes. When all the chloride ions are removed, the complexes become highly stable to hydrolysis. In other way we can say that the substitution of chloride ions by oxygen donor long-chain fatty acid anions is directly proportional to the hydrolytic stability of the complexes. Therefore, the hydrolytic stability order of the complexes was concluded as:



3.3. ¹H NMR spectra

In the ¹H NMR spectrum of [Ti(acac)Cl₂(OOC₁₅H₃₁)] a triplet appeared at δ = 0.89 ppm (3H) corresponded to methyl protons of fatty acid while a singlet corresponding to 26H of the 13-CH₂ groups was observed at δ = 1.26 ppm interpreted for palmitate ion [–OOCCH₂(CH₂)₁₃CH₃] of the complex. A peak at δ = 1.64 ppm (2H) indicated the α-CH₂ protons of palmitate ion. A singlet at δ = 2.06 ppm (6H) indicated the methyl protons of acac while the methine proton of acac was observed as a singlet at δ = 5.51 ppm

(1H). Integration of the peaks corresponded to the total number of protons in the complex. The ^1H NMR data for other complexes are given in Table 2.

3.4. Molecular weight, FAB mass and powder XRD

The molecular weight determinations showed that all the complexes of titanium(IV) synthesized during present investigation were monomeric in refluxing benzene (Table 1). In FAB mass spectrum of complex $[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{15}\text{H}_{31})_2]$ the first peak observed at m/z 699 corresponded to its monomeric nature. The peaks at m/z 655 and 554 showed the loss of chloride and acetylacetonate ion, respectively (calculated m/z ; 657 and 558).

A peak observed at m/z 307 in the spectrum showed the presence of $[\text{Ti}(\text{OCC}_{15}\text{H}_{31})]^{3+}$ unit (calculated m/z ; 303). Some peaks on lower range may be due to the decomposed ions of indefinite compositions. FAB mass data of other complexes (given in Table 3) were also observed to follow the similar fragmentation pattern.

Powder X-ray diffraction were done for all the complexes and one spectrum along with its crystal data for $[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{15}\text{H}_{31})_2]$ is given in Fig. 1 (Table 4). Particle size of this complex was calculated using the standard equation of Scherrer [23]:

$$D = K\lambda/(\beta \cos \theta) \quad (2)$$

Table 2

NMR spectral data (δ , ppm) for titanium(IV) complexes.

Complex	^1H
$[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{15}\text{H}_{31})_2]$	0.89 (t, 6H, $2 \times \text{CH}_3$), 1.26 (s, 52H, $(-\text{CH}_2)_{26}$), 1.64 (t, 4H, $(\alpha\text{-CH}_2)_2$), 2.06 (s, 6H, acac), 5.51 (s, 1H, CH, acac)
$[\text{Ti}(\text{acac})(\text{OCC}_{15}\text{H}_{31})_3]$	0.90 (t, 9H, $3 \times \text{CH}_3$), 1.27 (s, 78H, $(-\text{CH}_2)_{39}$), 1.64 (t, 6H, $(\alpha\text{-CH}_2)_3$), 2.07 (s, 6H, acac), 5.52 (s, 1H, CH, acac)
$[\text{Ti}(\text{acac})\text{Cl}_2(\text{OCC}_{17}\text{H}_{35})]$	0.89 (t, 3H, CH_3), 1.26 (s, 30H, $(-\text{CH}_2)_{15}$), 1.64 (t, 2H, $\alpha\text{-CH}_2$), 2.06 (s, 6H, acac), 5.51 (s, 1H, CH, acac)
$[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{17}\text{H}_{35})_2]$	0.89 (t, 6H, $2 \times \text{CH}_3$), 1.26 (s, 60H, $(-\text{CH}_2)_{30}$), 1.64 (t, 4H, $(\alpha\text{-CH}_2)_2$), 2.06 (s, 6H, acac), 5.51 (s, 1H, CH, acac)
$[\text{Ti}(\text{acac})(\text{OCC}_{17}\text{H}_{35})_3]$	0.90 (t, 9H, $3 \times \text{CH}_3$), 1.27 (s, 90H, $(-\text{CH}_2)_{45}$), 1.64 (t, 6H, $(\alpha\text{-CH}_2)_3$), 2.07 (s, 6H, acac), 5.52 (s, 1H, CH, acac)

Table 3

FAB mass data of titanium(IV) complexes.

Complex	Peak position	Expected fragmentation species	Calculated molecular weight
$[\text{Ti}(\text{acac})\text{Cl}_2(\text{OCC}_{15}\text{H}_{31})]$	439	$[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{15}\text{H}_{31})]^+$	438
	404	$[\text{Ti}(\text{acac})(\text{OCC}_{15}\text{H}_{31})]^{2+}$	402
	302	$[\text{Ti}(\text{OCC}_{15}\text{H}_{31})]^{3+}$	303
$[\text{Ti}(\text{acac})(\text{OCC}_{15}\text{H}_{31})_3]$	812	$[\text{Ti}(\text{OCC}_{15}\text{H}_{31})_3]^+$	814
	560	$[\text{Ti}(\text{OCC}_{15}\text{H}_{31})_2]^{2+}$	558
	303	$[\text{Ti}(\text{OCC}_{15}\text{H}_{31})]^{3+}$	303
$[\text{Ti}(\text{acac})\text{Cl}_2(\text{OCC}_{17}\text{H}_{35})]$	465	$[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{17}\text{H}_{35})]^+$	466
	433	$[\text{Ti}(\text{acac})(\text{OCC}_{17}\text{H}_{35})]^{2+}$	430
	335	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})]^{3+}$	331
$[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{17}\text{H}_{35})_2]$	716	$[\text{Ti}(\text{acac})(\text{OCC}_{17}\text{H}_{35})_2]^+$	713
	613	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})_2]^{2+}$	614
	335	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})]^{3+}$	331
$[\text{Ti}(\text{acac})(\text{OCC}_{17}\text{H}_{35})_3]$	900	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})_3]^+$	898
	612	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})_2]^{2+}$	614
	333	$[\text{Ti}(\text{OCC}_{17}\text{H}_{35})]^{3+}$	331

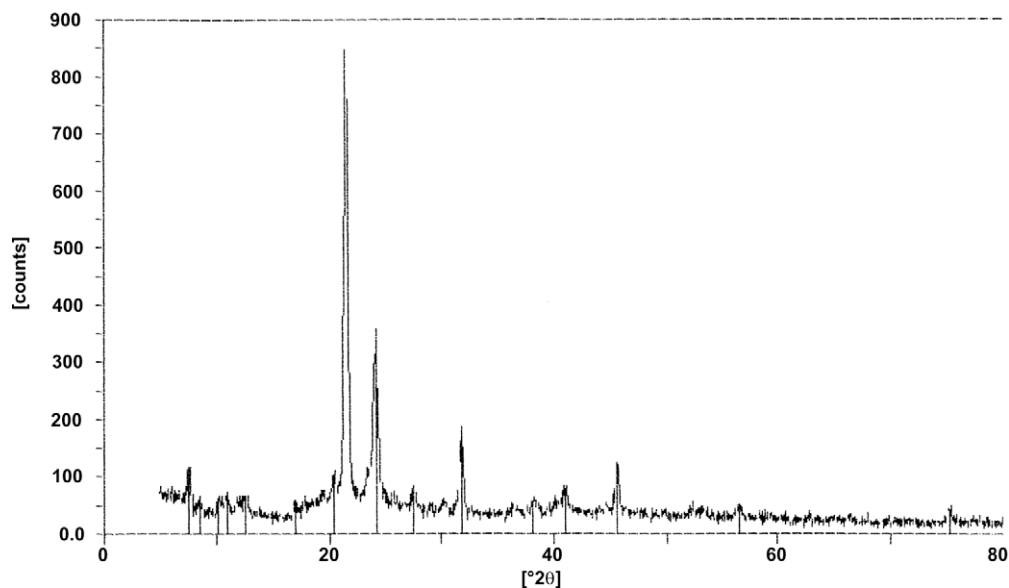


Fig. 1. Powder XRD spectrum of $[\text{Ti}(\text{acac})\text{Cl}(\text{OCC}_{15}\text{H}_{31})_2]$.

Table 4
Powder XRD data of $[\text{Ti}(\text{acac})\text{Cl}(\text{OOC}\text{C}_{15}\text{H}_{31})_2]$.

Angle [x λ]	d-Value 1 [Å]	d-Value 2 [Å]	Peak width [x λ]	Peak intensity [counts]	Backscattering intensity [counts]	Relative intensity [x]	Significance
7.605	11.6153	11.6439	0.250	62	53	8.2	1.79
8.535	10.3517	10.3771	0.300	13	44	1.7	0.85
10.230	8.6400	8.6613	0.400	23	37	3.0	0.86
11.035	8.0115	8.0312	0.300	29	37	3.8	0.89
12.690	6.9701	6.9872	0.300	30	35	4.0	1.32
16.935	5.2313	5.2442	0.300	14	36	1.8	0.86
20.450	4.3394	4.3500	0.300	46	55	6.1	1.17
21.695	4.0931	4.1032	0.350	762	56	100.0	12.63
24.255	3.6666	3.6756	0.350	292	59	38.4	5.16
27.495	3.2414	3.2494	0.400	29	45	3.8	1.26
31.830	2.8092	2.8161	0.300	137	37	18.0	2.83
36.540	2.4571	2.4632	0.800	9	32	1.2	0.87
38.130	2.3582	2.3641	0.600	21	34	2.8	1.42
40.960	2.2016	2.2070	0.400	40	37	5.2	1.09
45.510	1.9915	1.9964	0.250	66	38	8.6	1.29
56.530	1.6266	1.6307	0.300	22	27	2.9	0.86
75.290	1.2612	1.2643	0.300	19	19	2.5	1.13

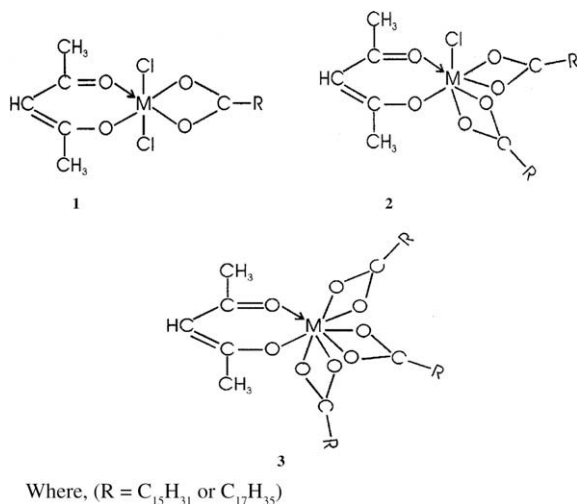


Fig. 2. Different geometries around titanium(IV) in complexes **1**, **2** and **3**.

where D is the particle size of the crystal grain; K is a constant ($=0.94$); λ is X-ray wavelength ($=1.5406 \text{ \AA}$); θ is Bragg diffraction angle and β is integral peak width which is converted into radian during calculation for particle size. The particle size for the complex was obtained to be 24 nm from the XRD data which indicated the nano-size range for this complex.

4. Conclusions

This paper describes the synthesis of some ternary and quaternary titanium(IV) complexes of the type $[\text{Ti}(\text{acac})\text{Cl}_{3-n}(\text{OOCR})_n]$. The complexes have been characterized and on the basis of physico-chemical studies, it is concluded that both acetylacetonate and carboxylate anions act as bidentate chelating ligands and a geometry around titanium(IV) in each complex is established. All the geometries are given in Fig. 2 in which the coordination num-

ber of titanium is suggested to be 6, 7 and 8 in complexes **1**, **2** and **3**, respectively. The hydrolytic stability of the complexes and a stability order is also sought. The complexes are monomeric and their powder XRD suggests them to be of nano-size.

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