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Spectroscopic investigations of nano-sized titanium(IV) complexes containing electron-rich oxygen-based ligands

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Manuscript deals an easier method of synthesis for nano-sized titanium(IV) complexes.
- They have high hydrolytic stability.
 They possess Ti-O-C linkage a
- requisite for their use as a catalyst.Particles are spherical in shape by
- Coordination number of titanium is
- Coordination number of fitanium is assigned seven or eight in the complexes.

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ABSTRACT

A convenient method has been explored to synthesize some nano-sized, mixed-ligand complexes of titanium(IV) with the general formula $[Ti(acac)Cl_{2-n}(L)_n(OOCC_{15}H_{31})]$ (where Hacac = acetylacetone, HL = dibenzoylmethane or benzoylacetone and n = 1 or 2). They have been synthesized by stepwise substitutions of chloride ions from titanium(IV) chloride with straight chain carboxylic acid and β -diketones. These were characterized by elemental analyses, molecular weight determinations, spectral (electronic, FTIR, ¹H NMR and powder XRD) and TEM studies. Conductance measurements indicated their non-conducting nature which may behave like insulators. Bidentate chelating nature of carboxylate and β -diketones anions in the complexes was established by their infrared spectra. LMCT bands were observed in the electronic spectra. Molecular weight determinations indicated the particles of these were lying in the nano-size range. The complexes exhibited high resistance to hydrolysis. On the basis of these studies, coordination number 7 or 8 is assigned for titanium in the synthesized complexes.

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1. Introduction

Cisplatin, the first inorganic compound approved as an anticancer agent, is widely used worldwide along with its derivatives [1–3]. Nevertheless, its disadvantages relating to high toxicity and limited activity range encourage extensive research aimed at finding new inorganic complexes of other metal centers that may lead to different and improved anticancer drugs [4–7]. Among others, titanium(IV) complexes have shown high antitumor activity, where in particular titanocene dichloride (Cp₂TiCl₂) and budoti-

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tane ((bzac)₂Ti(OEt)₂), followed by their improved derivatives with different substitutions, demonstrated promising activity toward cisplatin-sensitive and -resistant cells with relatively minor toxicity [8–12]. The main disadvantage of the titanium(IV) complexes is, however, their relatively rapid hydrolysis in biological environment [8,9,13], where the labile ligands of Cp₂TiCl₂ and (bzac)₂. Ti(X)₂ (X = Cl or OEt) dissociate within seconds to minutes while the inert ligands (Cp, diketonato) hydrolyze within hours to give undefined aggregates, thus hampering mechanistic investigations and applicability. Due to sensitivity towards hydrolysis most of the titanium complexes may cause a subsequent reduction in their catalytic property [14]. Their rate of hydrolysis can significantly be reduced by using bulky electron-rich ligands resulting in better

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photocatalytic activity [15,16]. In this light we have reported some titanium(IV) complexes having Ti–O–C bond with increased resistance towards hydrolysis [17].

Keeping in view of these objectives, we report here an easier method of synthesis for nano-sized, mixed-ligand complexes of titanium(IV) in which titanium is attached with all the different type of four ligands. Carboxylic acid and β -diketones have been used in the light that incorporation of these ligands in titanium(IV) complexes may enhance the cytotoxicity providing a better candidate for anticancer agents [18,19]. These ligands act as potential chelating agents providing hydrolytically stable nature of the products. The complexes are hydrolytically stable bearing Ti–O–C linkage, a basic requirement for catalytic action. The complexes are characterized using different spectral techniques and their coordination behavior is discussed.

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 [20]. Sodium palmitate, acetylacetone, benzoylacetone, dibenzoylmethane (Aldrich) and TiCl₄ (BDH) were used as received. Titanium and chlorine were estimated gravimetrically as TiO₂ and AgCl respectively [21].

2.2. Physico-chemical measurements

¹H NMR spectra were recorded at 300 MHz on a Bruker DRX-300 NMR spectrometer in CDCl₃. Electronic spectra were recorded on Hitachi U-2000 spectrophotometer in toluene. Infrared spectra were recorded on a Perkin-Elmer RX1 FTIR spectrophotometer using KBr discs. 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 2θ range of 5.025–79.925° with a continuous scan mode. Transmission electron microscopy (TEM) images were obtained on a Tecnai 30 G²S - Twin electron microscope with an accelerating voltage of 300 kV on the surface of a carbon coated copper grid. 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 2182 A Nanovoltmeter. Magnetic moment was measured on a Gouy balance using Hg[Co(SCN)₄] as a calibrant. Elemental analyses (C, H) were done on a Vario EL III Carlo Erba 1108 elemental analyzer. Molecular weights were determined in a semi-micro ebulliometer (Gallenkamp) with a thermistor sensing device.

Table 1

Analytical results for the titanium(IV) complexes.

2.3. Synthesis of $[Ti(acac)Cl(dbzm)(OOCC_{15}H_{31})]$ (1)

Sodium salts of B-diketones 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 β -diketones in isopropanol and the contents were boiled to reflux for 2 h. Removal of excess solvent under vacuum yielded the desired sodium salts of β-diketones. To the suspension of [Ti(acac)Cl₃] [22] (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 an yellow coloured solid, [Ti(acac)Cl₂(OOCC₁₅₋ H_{31} (A) was obtained. This composition was confirmed by the elemental analysis and infrared spectral study [17]. To a solution of A (1.82 g, 3.90 mmol) in benzene (50 mL), sodium salt of dibenzoylmethane (Nadbzm) (0.95 g, 3.90 mmol) was added. The contents were stirred for 9 h followed by refluxing for 3 h. Insoluble sodium chloride formed during the reaction was filtered out. Excess solvent from the soluble part was removed in vacuo to yield a dark yellow solid. It was purified in dichloromethane-n-hexane mixture (1:1 ratio). An analogous procedure was adopted to synthesize other titanium(IV) complexes and details of analytical results are given in Table 1.

3. Results and discussion

Some mixed-ligand complexes of titanium(IV) were synthesized by stepwise substitutions of chloride ions from titanium tetrachloride as depicted below:

$$\begin{split} & \text{TiCl}_4 + \text{Hacac}_{\substack{\text{Reflux}\\ \text{Reflux}}}^{\substack{\text{Benzene}\\ \text{Reflux}}} [\text{Ti}(\text{acac})\text{Cl}_3] + \text{CoNa}_{\substack{\text{Reflux}\\ \text{Reflux}}}^{\substack{\text{Benzene}\\ \text{Reflux}}} [\text{Ti}(\text{acac})\text{Cl}_2(\text{OOCC}_{15}\text{H}_{31})] + \text{NaCl} \downarrow \\ & \textbf{A} + n\text{NaL}_{\substack{\text{Benzene}\\ \text{Reflux}}}^{\substack{\text{Benzene}\\ \text{Reflux}}} [\text{Ti}(\text{acac})\text{Cl}_{2-n}(L)_n(\text{OOCC}_{15}\text{H}_{31})] + n\text{NaCl} \downarrow \end{split}$$

where Hacac = acetylacetone; NaL = Sodium salt of dibenzoylmethane (Hdbzm) or benzoylacetone (Hbzac) and n = 1 or 2.

Benzene was chosen as a solvent in these substitutions because sodium chloride formed during the reaction was insoluble and the titanium(IV) complexes were soluble which could make the separation easy. The molar conductance of complexes at $10^{-2}-10^{-3}$ molar concentrations in nitrobenzene was obtained in the range $2-8 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ which indicated them to be non-electrolytes [23]. Solid state conductance measurements were done for all the complexes and were found in the range $1.8 \times 10^6 - 3.2 \times 10^6 \ \Omega$ at 295 K using current 1×10^{-8} A and voltage 1.4×10^{-2} V. This clearly indicated them to show high resistance or they could be said to behave like insulators. Room temperature magnetic

Reactants ^a (g, mmol)	Product (colour) (% yield)	MP (°C)	Found (calculated)%				Molecular weight found (calcd.)
			Ti	Cl	С	Н	
[Ti(acac)Cl ₂ (OOCC ₁₅ H ₃₁)] + Nadbzm	[Ti(acac)Cl(dbzm)(OOCC ₁₅ H ₃₁)]	138	7.18	5.29	65.48	7.57	652
(1.82, 3.90) (0.95, 3.90)	(Dark yellow) (83) (1)		(7.24)	(5.36)	(65.40)	(7.49)	(661)
[Ti(acac)Cl ₂ (OOCC ₁₅ H ₃₁)] + Nadbzm	[Ti(acac)(dbzm) ₂ (OOCC ₁₅ H ₃₁)]	146	5.48		72.28	7.19	854
(1.91, 4.0) (1.9, 8.1)	(Yellow) (85) (2)		(5.64)		(72.15)	(7.14)	(848)
[Ti(acac)Cl ₂ (OOCC ₁₅ H ₃₁)] + Nabzac	[Ti(acac)Cl(bzac)(OOCC ₁₅ H ₃₁)]	116	8.02	5.82	62.16	7.88	610
(2.1, 4.40) (0.82, 4.41)	(Dark yellow) (88) (3)		(7.99)	(5.92)	(62.15)	(7.92)	(599)
[Ti(acac)Cl ₂ (OOCC ₁₅ H ₃₁)] + Nabzac	[Ti(acac)(bzac) ₂ (OOCC ₁₅ H ₃₁)]	124	6.49		67.87	7.69	733
(1.8, 3.81) (1.40, 7.63)	(Yellow) (81) (4)		(6.61)		(67.94)	(7.80)	(724)

^a Reflux about 3-4 h.

Table 2 Significant IR bands and their assignments* for the titanium(IV) complexes.

Complex	v _{asym} (OCO)	v _{sym} (OCO)	Δv	v(C===0)	v(C==C)	Ti-0
1 2 3	1557 1558 1555 1559	1448 1448 1450 1452	109 110 105 107	1567 1578 1583 1590	1511 1506 1495 1499	560 560 562 562
4	1559	1452	107	1590	1499	562

*Absorptions are in cm⁻¹.

moment measurements indicated diamagnetic nature of the complexes, showing absence of unpaired electrons in these complexes. 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).

3.1. Electronic spectra

Two bands were observed in the range 204-209 nm and 283-298 nm in the electronic spectra of the complexes which could be assigned to $\pi - \pi^*$ and $n - \pi^*$ transitions, respectively. The electronic transitions observed in the range 354-438 nm are due to strong charge-transfer absorption from ligand π -orbital to vacant titanium orbital (ligand to metal charge-transfer, LMCT bands) which are strongly affected by the chemical nature of the ligands giving colours to the complexes [24].

3.2. Infrared spectra

In infrared spectra of all the complexes, no band was observed in the region 3600–3300 cm⁻¹. This indicated the absence of O–H stretching vibrations of palmitic acid and β-diketones. The bands at 1710 cm^{-1} (CO stretching) and at 935 cm^{-1} (OH deformation) of free palmitic acid were also absent in the spectra of the complexes. Two strong bands were observed at ${\sim}1555$ and ~1450 cm⁻¹ which could be assigned due to (v_{asym} OCO) (antisymmetric) and $(v_{sym}OCO)$ (symmetric) vibrations of the palmitate ion, respectively [25]. The Δ value [$v_{asym}OCO - v_{sym}OCO$] was \sim 105 cm⁻¹. This indicated that –COOH group of palmitic acid was coordinated to titanium in a bidentate chelating mode involving both the oxygen atoms [25]. No band was found in 1600-1700 cm⁻¹ region indicating the CO group of β -diketones was not free in the complexes. Two splitted new bands observed in the region 1590–1567 cm⁻¹ (vC==-O) and 1511–1495 cm⁻¹ (vC==-C) indicated the chelating nature of β -diketonate ion in the complexes [26]. The band observed around 560 cm^{-1} could be assigned to Ti-O vibrations [25]. The significant infrared bands and their assignments for the complexes are given in Table 2.

3.3. Hydrolytic stability of the complexes

The complex $[Ti(acac)Cl_2(OOCC_{15}H_{31})]$ (A) is moisture sensitive [17]. Its sensitivity towards hydrolysis is considerably reduced by substituting chloride ions with *B*-diketones like benzovlacetone and dibenzovlmethane. This was tested by dissolving the complexes in benzene (1% solution) and 0.5% water was added. The contents were stirred 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.

3.4. ¹H NMR spectra

No signal was observed in the ¹H NMR spectra of all the complexes in the region δ 15.0–10.0 ppm (observed due to –OH proton), which indicated deprotonation and bonding of β -diketones and palmitic acid to titanium. In the spectrum of 1 (Fig. 1) a singlet was appeared at δ = 0.89 ppm (3H) corresponding to methyl protons of palmitate ion [-OOCCH₂(CH₂)₁₃CH₃] and a singlet at δ = 1.26 ppm due to 26H of 13-CH₂ groups. A peak at δ = 1.64 ppm (2H) indicated the α -CH₂ protons of palmitate ion. A singlet at δ = 2.07 ppm (6H) indicated the methyl protons of ace-



Table 3

¹H NMR spectral data (δ, ppm) for titanium(IV) complexes.

Complex	¹ H
2 3 4	0.90 (s, 3H, CH ₃), 1.26 (s, 26H, $(-CH_{2})_{13}$), 1.65 (t, 2H, $\alpha - CH_{2}$), 2.08 (s, 6H, acac), 5.58 (s, 1H, CH, acac), 6.89 (s, 2H, CH, dbzm), 7.93–6.99 (m, 20H, arom) 0.90 (s, 3H, CH ₃), 1.27 (s, 26H, $(-CH_{2})_{13}$), 1.65 (t, 2H, $\alpha - CH_{2}$), 2.06 (s, 6H, acac), 5.58 (s, 1H, CH, acac), 6.35 (s, 1H, CH, bzac), 7.31–7.04 (m, 5H, arom) 0.90 (s, 3H, CH ₃), 1.27 (s, 26H, $(-CH_{2})_{13}$), 1.65 (t, 2H, $\alpha - CH_{2}$), 2.06 (s, 6H, acac), 5.59 (s, 1H, CH, acac), 6.39 (s, 2H, CH, bzac), 7.47–6.92 (m, 10H, arom)



Fig. 2. Powder XRD spectrum of 1.



Fig. 3. TEM image of 1.

tylacetonate ion while its methine proton was observed as a singlet at $\delta = 5.59$ ppm (1H). A multiplet of phenyl protons was appeared in the region δ 7.51–7.03 ppm of dibenzoylmethanate anion while its methine proton was observed as a singlet at $\delta = 6.85$ ppm [27]. The signal positions observed in the spectra for other complexes are given in Table 3.

3.5. Powder XRD and TEM studies

Powder XRD was done for all the complexes. The pattern and results of XRD suggested that the crystals of the complexes are not perfect but lying in between amorphous and crystalline character. Due to this reason, the complexes were not found suitable for single crystal XRD. A representative spectrum of complex **1** is given in Fig. 2. Particle size for the complexes was calculated using maximum intensity peak by the standard Scherrer equation [28]:

 $D = \frac{K\lambda}{(\beta\cos\theta)}$

where *D* is the particle size; *K* is a constant (=0.94); λ is X-ray wavelength (λ = 1.5406 Å); θ is Bragg diffraction angle and β is integral

peak width which is converted into radian while calculation. The values obtained for all the complexes were in the range 36–75 nm which indicated that the particles were of nano-size.

TEM image for the complex **1** is given in Fig. 3. The morphology of complex was observed to have spherical particles of 40 nm average diameter. This is lying in good agreement with the calculated value (36 nm) obtained from Scherrer's equation.

4. Conclusions

In this communication, we report a novel synthetic route to prepare nano-sized, mixed-ligand complexes of titanium(IV) with carboxylic acid and β -diketones. These complexes are semi-crystalline in nature possessing Ti–O–C linkage. Their high value of hydrolytic stability makes them suitable for different applications.

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