

Diazocoupling on Some β -Ketoaminoato Ti^{IV} Chelates

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ABSTRACT

The electrophilic substitution of p-chlorophenyldiazonium ion on β -ketoaminoato Ti^{IV} chelates, derived from β -dicarbonyl compounds (acetylacetonate, ethylacetoacetate, benzoylacetone) and 2-aminoethanol, with quasi-aromatic ring, was studied. The coupling products were isolated and characterized by elemental analysis, conductivity and magnetic susceptibility measurement and electronic, IR, ¹H NMR spectral studies. The parent chelates had undergone coupling at methine carbon of the chelated ligand. The geometry around the metal ion of the product was octahedral as that of parent chelates.

Key words: Aryldiazonium ion, Metalloaromaticity, β -ketoaminoato Ti^{IV} chelates, Electrophilic substitution

INTRODUCTION

Metalloaromaticity is the manifestation of aromatic properties in the chelate metallocycle as introduced by Calvin and Wilson in 1945 to explain the stability of Cu(II)-1, 3-diketonate complexes (Masui, 2001). Synthesis and structures of β -diketonates were reviewed when the possibility of creating diverse metal complexes with various modes of coordination of typical chelating ligands was discussed (Skopenko et al., 2004). Acetylacetonatozinc and trifluoroacetylacetonatozinc chelates have been prepared by electrolysis and ligand exchange (Vinokurov et al., 2007). Titanium(IV) β -diketonate complexes with various β -diketones, acetylacetonate, benzoylacetone, ethylacetoacetate were synthesised by the authors (Chowdhury and Uddin, 2000).

The central hydrogen atom on metal β -diketonate chelate C,O,M ring systems can be replaced by several groups under apparently electrophilic conditions such as halogenation, thiocyanogenation, arylsulfenylation, chlorosulfenylation, nitration, acylation, formylation, chloromethylation and dimethylaminomethylation (Collman, 1965). Electrophilic substitution of the phenyldiazonium ions at 2, 4-pentanedionates of aluminum(III), chromium(III), copper(II) and palladium(II) was reported (Krishnantutty and Micheal, 1991, 1993). Electrophilic substitution of the phenyldiazonium ions at titanium(IV) β -diketonates complexes of acetylacetonate, benzoylacetone, ethylacetoacetate was reported by authors (Chowdhury and Uddin, 2000).

Synthesis of β -ketoaminato complexes of metals, Ru(II) (Thangadurai and Natarajan, 2001), Ti(IV) (Tang et al., 2005), Co(II) (Woods et al., 2004) with Schiff bases derived from β -diketones by condensation of amines is recognised.

Furthermore, likewise β -diketones metal, β -ketoamines complexes having quasi-aromatic ring systems undergo many electrophilic substitutions, typical of aromatic compounds. Trinuclear/polynuclear metal complexes resulted from Schiff base, derived by the condensation of azolo (thiazolo and triazolo)-2, 4-pentanedione and *o*-phenylenediamine (Mishra et al., 1993, 1997) and 2-aminophenol and 2-aminothiophenol (Krishnankutty, et al., 2007) were established. The electrophilic substitution of aryl diazonium ion on the Cu^{II} and Ni^{II} chelates of bis-(acetylacetonate)ethylenediamine in aqueous medium have been studied (Sadasivan and Alaudeen, 2006). Previously, titanium(IV) complexes with dibasic tridentate ligands derived from various β -diketones, acetylacetonate (acac), benzoylacetone (bzac), ethylacetoacetate (etacac) and 2-aminoethanol (AET) were reported (Chowdhury and Uddin, 1998). In continuation, electrophilic substitution of chlorobenzene diazonium ions on β -ketoaminato titanium(IV) chelates of these compounds is included in this study.

MATERIALS AND METHODS

Physical Measurements

Melting point of the ligands and complexes was determined on an electrothermal melting point apparatus. UV-absorption spectra were recorded on a Shimadzu UV-visible recording spectrophotometer (model-160). Infrared spectra were recorded on KBr pellets with Perkin-Elmer infrared spectrophotometer (Model-883). NMR spectra were recorded with JNM-PMX 60 NMR spectrophotometer using CDCl₃ as solvent. Magnetic moments were determined by the Gouy method. Conductivity measurements were performed on Philips conductivity meter (model-WPA CM-25) made by WPA, Saffron Walden, England.

Elemental Analyses

Elemental analyses of some of the complexes were performed from Central Drug Research Institute (C.D.R.I), Lucnow, India. Titanium content of the diazo-coupled products was determined spectrophotometrically, following the standard procedure (Dee Snell and Biffen, 1972). All chemicals used were obtained from Aldrich Chemical Co. Ltd. Physical and analytical data for the diazo-coupled compounds are given in Table 1.

Table 1. Physical and analytical data for the diazocoupled compounds.

Compl.	Colour	MP/°C	Analysis (%) (found/calcul.)		μ_{eff} (BM)	χ_M Ohm ⁻¹ cm ² mole ⁻¹		
			CH	Ti				
Ti(^C BZ-Acac-AET) ₂	Dark red	250 d	C-50.87 (51.24) H-5.06 (4.96)		8.20 (7.86)	dia	3.6	
Ti(^C BZ-Etacac-AET) ₂	Dark red	250	---		7.46 (7.18)	--	5.0	
Ti(^C BZ-Bzac-AET) ₂	Dark red	250 d	---		--	dia	10.2	
	Characteristics infra-red frequencies (cm ⁻¹)						Electronic spectral bands (nm)	
	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{C-N})$	$\nu(\text{C-O})$	$\nu(\text{Ti-N})$		$\nu(\text{Ti-O})$
Ti(^C BZ-Acac-AET) ₂	1620 m	1580 m	1400 m	1380 m	1240 m	500 m	415 w	370, 302, 270
Ti(^C BZ-Etacac-AET) ₂	1600 s	1510 m	1490 w	1370 s	1260 s	540 w	415 s	370, 300, 272
Ti(^C BZ-Bzac-AET) ₂	1640 m	1580 s	1390 s	1350 m	1270 m	510 w	410 s	368, 300, 273

s = strong, m = medium, w = weak

Ligand Preparation

β -dicarbonyl compounds (acetylacetonone, ethylacetoacetate, benzoylacetonone) (50 mmol) in ethanol (50 mL) were refluxed with 2-aminoethanol (50 mmol) for about one hr. This was cooled and allowed to stand for crystallization when crystal separated out was filtered, washed with ethanol and dried under vacuum over silica gel (Chowdhury and Uddin, 1998).

Complex Preparation

To a solution of the Schiff base ligand (4 mmol) in dry methanol, Ti(OPⁱ)₄ (2 mmol) was added and the mixture was refluxed for 45 min. The precipitate formed was filtered hot, washed with hot methanol and petroleum spirit (40-60°C) and dried under vacuum over calcium chloride (Chowdhury and Uddin, 1998).

Diazonium Ion Preparation

Benzenediazonium chloride (^CBz) was obtained through the diazotization of aniline, using sodium nitrite and hydrochloric acid. The solution of aryldiazonium salt thus obtained was immediately used for further reactions, because the salt tends to decompose slowly even at ice-bath temperature. Excess nitrous acid present in the diazonium salt solution was destroyed by adding urea (Krishnantutty and Micheal, 1991, 1993).

Diazo-coupling Reaction

The coupling reaction was carried out as follows. To a solution of titanium complex (2 mmol) in methanol (10 mL), kept below 5°C in an ice-salt bath, was added slowly with stirring a cold aqueous solution of the diazonium salt (4 mmol). A solution of NaOH (10⁻³ M) was used to maintain the pH of the mixture between 8 and 9. The precipitated product was filtered, washed with water, sucked dry, recrystallized from hot ethanol and dried in vacuum.

RESULTS AND DISCUSSION

The completion of the formation of aryldiazonium salt was indicated by the presence of un-reacted nitrous acid in the reaction vessel. The addition of sodium nitrite was stopped as soon as the reaction mixture just gave a blue colour with the starch potassium iodide paper. Excess nitrous acid interferes with subsequent reaction of diazonium salt produced in solution. The dry diazonium salts are unstable and explosive in nature and are seldom isolated (Bhal and Bhal, 1993). Strict care was taken for the isolation of the diazocoupled products. All the products were washed thoroughly with water to make them free from the diazonium salt. The electrophilic aryldiazonium ions were made to react with titanium chelates to yield the desired diazocoupled products. Elemental analyses of the diazo coupled products indicated that substitution had occurred on all the β -ketoaminato chelate rings of the metal complexes. Infrared spectra of the diazo-coupled products of Ti^{IV} complexes were in accord with structure shown in Figure 1.

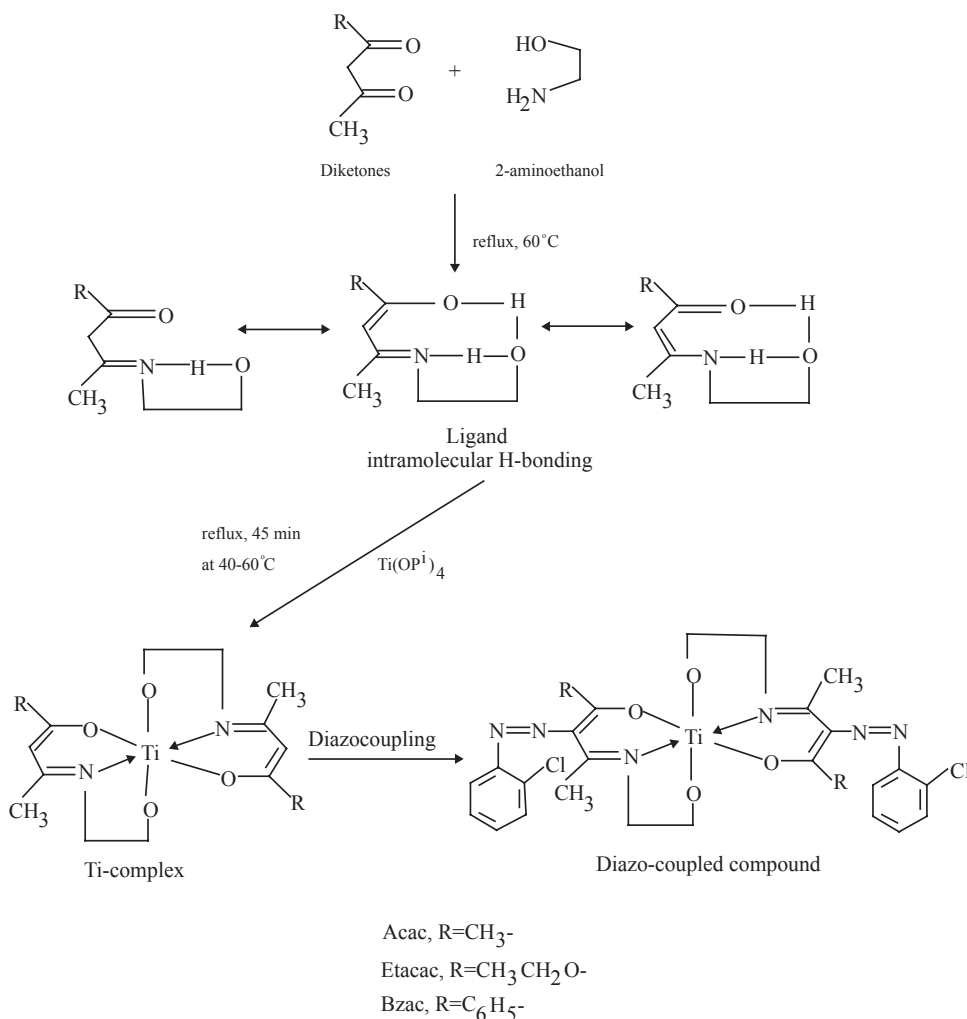


Figure 1. Schematic presentation for the reaction mechanism.

Infrared Spectra

The assignments were made by comparing the spectra of the complexes with those of the free ligands. The IR spectra of ligands showed strong bands at $\approx 1670\text{ cm}^{-1}$ and $\approx 1655\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ vibrations, respectively (Thangadurai and Natarajan, 2001, Tang et al., 2005). The $\nu(\text{C}=\text{C})$ vibrations of the aromatic rings were observed as several medium intensity bands in the $1480\text{--}1490\text{ cm}^{-1}$ region (Woods et al., 2004). The broad absorption bands around 3500 cm^{-1} were assigned to the $\nu(\text{OH})$ frequency while the bands around $3265\text{--}3406\text{ cm}^{-1}$ were assigned to the $\nu(\text{NH})$ frequency due to the intra-molecular hydrogen-bonded N–H proton (Thangadurai and Natarajan, 2001, Tang et al., 2005). The expected strong IR bands resulting from uncoordinated $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ vibrations shifted to a lower wave number and appeared as a new band at between 1510 and 1640 cm^{-1} in the spectra of all the complexes, which showed coordination of the metal atom to the nitrogen and oxygen atoms, respectively, in the C=N and the C=O moieties. Furthermore, the intra-molecularly hydrogen-bonded O–H and N–H protons were replaced by the metal ion as confirmed by the disappearance of the broad free ligand band in the region $3200\text{--}3500\text{ cm}^{-1}$, giving an indication of coordination of the carbonyl oxygen and amino nitrogen to the metal ion. Instead, several medium intensity bands assignable to various aliphatic and aromatic $\nu(\text{C-H})$ vibrations appeared in the region $2851\text{--}3107\text{ cm}^{-1}$, both in the ligands and complexes as expected. A new medium intensity band at $1390\text{--}1400\text{ cm}^{-1}$ was assigned to $\nu\text{N}=\text{N}$ vibrations (Chowdhury and Uddin, 2000). On the basis of the literature studies, bonds in the regions $1240\text{--}1270\text{ cm}^{-1}$ and $1350\text{--}1380\text{ cm}^{-1}$ are assigned to $\nu(\text{C-O})$ and $\nu(\text{C-N})$, respectively. The spectra of all the complexes showed additional medium intensity bands in the $410\text{--}415\text{ cm}^{-1}$ and $500\text{--}540\text{ cm}^{-1}$ regions, presumably due to $\nu(\text{Ti-O})$ and $\nu(\text{Ti-N})$ vibrations (Chowdhury and Uddin, 1998). Important bands which appeared in the spectra of the complexes are given in Table 1.

$^1\text{H-NMR}$ Spectra

The $^1\text{H-NMR}$ spectra of the diamagnetic titanium(IV) chelates also supported the formulations. Thus, the methine proton signal expected ($\delta 6.25\text{ ppm}$) for the metal chelates was absent in the spectra of the diazocoupled compounds, a fact that it was replaced by electrophilic substitution of diazonium ions.

Electronic Spectra

The UV spectrum of the compound showed bands with maxima between 450 nm and 270 nm . In the complexes these absorption maxima shifted appreciably to lower wave numbers. Lower energy bands might be assigned to the ligand-to-metal charge-transfer and other bands were due to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. The complexes were coloured only through their intense charge transfer transition. The absence of bands due to d-d transition indicated the $(n-1)d^0ns^0$ electronic configuration of titanium(IV) in the complexes.

Magnetic and Conductance Measurement

The measured μ_{eff} values suggested their diamagnetic behaviour supporting $3d^0$ electronic configuration consistent with the $4+$ oxidation state and octahedral geometry of complexes. And the low molar conductance values of the complexes obtained in DMF showed them to be non-electrolytes as that of parent complexes.

CONCLUSION

The analytical, IR, $^1\text{H-NMR}$ spectral data of diazocoupled compounds of titanium(IV) ketoaminato chelates suggested that coupling at methine carbon of the chelated ligand had undergone without decomposition. Together with the diamagnetic and non-electrolytic nature, 1:2 metal ligand stoichiometry of compounds as that of parent complexes conformity with Figure 1 obviously be suggested.

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