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THERMAL STUDIES AND SPECTRAL CHARACTERIZATION OF THE CHELATE OF BIS-(η^5-CYCLOPENTADIENYL) TITANIUM(IV) WITH SALICYLIDENE-4-METHYLANILINE

Virendra Mishra[1], *D. S. Parmar*[2], *Virendra Joshi*[3] *and*
N. K. Kaushik[3]

[1]Department of Post Graduate Studies in Chemistry Nehru College, Chhibramau (U. P.)
209721, India
[2]Department of Chemistry S. G. R. College, Dobhi (U. P.), India
[3]Department of Chemistry University of Delhi, Delhi, India

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Abstract

A new chelate $(\eta^5-C_5H_5)_2Ti(SB)_2$, where SB = O, N donor Schiff base salicylidene-4-methylaniline, was synthesized. The course of thermal degradation of the chelate was studied by thermogravimetric (TG) and differential thermal analysis (DTA) under dynamic conditions of temperature. The order of the thermal decomposition reaction and energy of activation was calculated from TG curve while from DTA curve the change in enthalpy was calculated. Evaluation of the kinetic parameters was performed by Coats-Redfern as well as Piloyan-Novikova methods which gave $n = 1$, $\Delta H = 1.114\ kJ\cdot mol^{-1}$, $\Delta E = 27.01\ kJ\cdot mol^{-1}$, $\Delta S = -340.12\ kJ\cdot mol^{-1}\cdot K^{-1}$ and $n = 1$, $\Delta H = 1.114\ kJ\cdot mol^{-1}$, $\Delta E = 20.01\ kJ\cdot mol^{-1}$, $\Delta S = -342.60\ kJ\cdot mol^{-1}\cdot K^{-1}$, respectively. The chelate was also characterized on the basis of different spectral studies viz. conductance, molecular weight, IR, UV-visible and ^{1}H NMR, which enabled to propose an octahedral structure to the chelate.

Keywords: chelate complexes

Introduction

Transition metal as well as non transition metal complexes of Schiff bases have played a prominent role in the development of coordination chemistry [1]. Metal complexes with oxygen and nitrogen donor ligands have been extensively studied as one of the most interesting topics and many reports have been documented on the properties and reactivities of such complexes [2–4]. Schiff bases which find manifold applications have also been reacted with metals and studies on the resulting metal chelates have appeared in the literature in the form of

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many research publications from different laboratories [5–10]. These scanty details are limited upto the spectral characterization of the complexes. Thermal analysis which has recently evolved as an excellent analytical and investigating tool has not been exploited in these complexes. The present work includes the kinetics of the thermal decomposition of a chelate of titanium(IV) using cyclopentadiene as primary and Schiff base (derived from salicylaldehyde and 4-methylaniline) as secondary ligand, under dynamic conditions both by thermogravimetric and differential thermal analysis techniques. Evaluation of different parameters have been performed by means of Coats-Redfern [11] and Piloyan-Novikova [12] methods validating the famous Arrhenius equation. Other spectral studies eg. IR, UV-visible, NMR etc. on the chelate have also been performed for its characterization and to propose an appropriate structure to the chelate.

Experimental

Reagents and chemicals

All the reagents used were of AR grade. The solvents were dried as per literature methods [13]. Nitrobenzene was purified by the method of Fay *et al.* [14]. Metal content in the complex was determined by atomic absorption method.

Physical methods

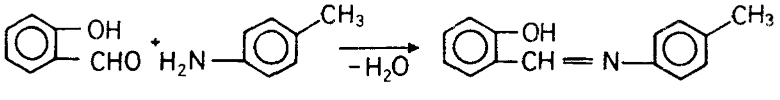
The TG and DTA curves were recorded simultaneously for powdered sample on a Rigaku 8150 thermoanalyser at the heating rate of 5 deg·min^{-1} at a chart speed of 5 mm·min^{-1}. Thermal decompositions were done using a crucible of platinum in the atmosphere of free air. α-alumina was used as a reference material. Infrared spectrum was taken on a Perkin Elmer 589 spectrophotometer in the range 4000–200 cm^{-1} in the CsI matrix while the UV-visible spectrum was run on a Backman DU-64 spectrophotometer in the range of 200–900 nm. The ^{1}H NMR studies were recorded on a Hitachi R-600 F7 NMR spectrophotometer at the sweep width of 900 Hz and the sweep time of 300 seconds using DMSO d_6 as solvent and tetrahydrofuran as internal standard.

Preparations

Bis-(η^5-cyclopentadienyl) titanium(IV) dichloride, $(C_5H_5)_2TiCl_2$, was prepared by the method of Wilkinson [15] by reacting the suspension of sodium cyclopentadiene with titanium tetrachloride in tetrahydrofuran.

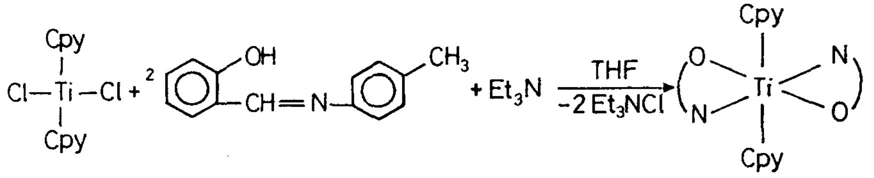
Preparation of Schiff base

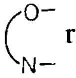
To a solution of 4-methylaniline (0.10 *M* in 100 ml alcohol) was added dropwise with vigodrous stirring. The product separated immediately. The mixture was refluxed for half an hour, then cooled in ice bath and filtered at the pump. The yellow solid was recrystallised to fine yellow needles from hot alcohol. Yield 75%; *mp.* 114°C. The reaction involved may be represented as:



Preparation of the chelate

The preparation was undertaken under strictly anhydrous conditions. The Schiff base and $(C_5H_5)_2TiCl_2$ were taken in 2:1 molar ratio in THF in the presence of triethylamine. The mixture was refluxed at 66°C for 14–15 h. The precipitated Et_3NCl was separated by filtration and then the volume of the filtrate was reduced to half of its volume by evaporation of the solvent under reduced pressure. The product was extracted from the solution with *n*-hexane and dried in vacuum at room temperature. The yellowish-brown chelate was finally recrystallised from ether. *mp.* 95°C. The complex formation reaction may be represented as follows:



where  represents deprotonated Schiff base and Cpy is cyclopentadiene

Results and discussion

The chelate was highly soluble in organic solvents like benzene, methanol, chloroform, nitrobenzene, THF etc. Its molar conductance (10^{-3} *M*) in methanol was only 0.78 $\Omega^{-1}\cdot cm^{2}\cdot mol^{-1}$. It confirmed the non electrolytic nature of the chelate. The molecular mass of the complex was determined cryoscopically in methanol. It was found to be 599.90. Chemical analysis for the chelate gave Ti 8.02%, N 4.70%, C 76.05% while $[(Cpy)_2Ti(SB)_2]$ requires Ti 7.98%, N 4.66% and C 76.01%.

Thermal studies

The chelate is stable upto 80°C and onwards it starts decomposing slowly upto 100°C after which the weight loss becomes rapid as it is clear from the TG curve in the temperature range 90–240°C (Fig. 1). The weight loss at the end of this decomposition step was calculated from the TG curve to be 60.0%. This may be represented by the following decomposition reaction:

$$(C_5H_5)_2Ti(SB)_2 \xrightarrow{90-240°C} (C_5H_5)_2Ti(CO_3) + N_2 + CO_2 + H_2O$$

This step of decomposition is also evident in the DTA curve in the temperature range 210–245°C. In this step the obtained endothermic peak is centred at 227°C. It represents the decomposition of Schiff base part of the complex and simultaneous formation of carbonates to satisfy the ionic valency of the metal.

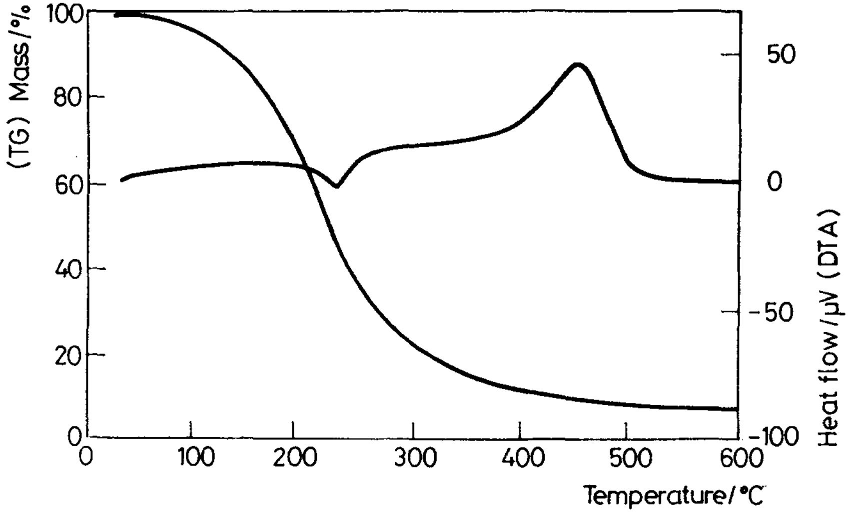


Fig. 1 Simultaneous TG (curve A) and DTA (curve B) for the thermal decomposition of the complex

The second step of decomposition starts just after the completion of the first step. In this step the cyclopentadiene part of the complex is destroyed and the chelate is converted to titanium oxide. Observed weight loss at the end of this step is 86.6%. This step completes at about 500°C and after it the TiO_2 horizontal is observed. The DTA curve shows an exothermic peak in the temperature range 387–500°C centred at 463°C. The presence of the exothermic peak indicates the decomposition of the organic material and the simultaneous oxidation of the formed compounds. The oxygen atmosphere present in the furnace is responsible for this simultaneous oxidation. Thus, the decomposition may be expressed as:

$$(C_5H_5)_2Ti(CO)_3 \xrightarrow{387\text{–}500^\circ C} TiO_2 + CO_2 + \text{oxides of nitrogen}$$

Evaluation of the kinetic parameters was performed by means of Coats-Redfern as well as Piloyan-Novikova methods assuming the rate law of the type:

$$\frac{dx}{dt} = -K(1-\alpha)^n$$

and an Arrhenius equation of the form

$$K = Z\,e^{-E/RT}$$

to be valid, where n is the order of the reaction, K is the rate constant, α the fraction decomposed and E the activation energy. The graphs for $\log[-log(1-\alpha)/T^2]$ *vs.* $10^3 1/T$ and $\log(\alpha/T^2)$ *vs.* $10^3 1/T$ gave straight lines with slopes $E/2.303R$, where R is the gas constant and T the absolute temperature. The observation of a straight line in the curves proves the order of the reaction to be one (Fig. 2). The value of heat of reaction ΔH, in microvolts has been directly given by the computer fitted thermoanalyser and it was converted in kJ·mol^{-1} using the following relationship

$$\Delta H\,(\text{kJ}\cdot\text{mol}^{-1}) = \frac{\Delta H(\mu\text{V60mol wt of chelate }10^{-6})}{1000}$$

Finally, the value of standard entropy change (ΔS) was computed by the following equation:

$$Z = \frac{kT}{h}\exp\left(\frac{\Delta S}{R}\right)$$

where k is the Boltzman constant and h is Planks constant. Z was calculated by the equation:

$$Z = \frac{E}{RT^2}\beta\,\exp\left(\frac{E}{RT}\right)$$

where β is the heating rate.

The values of the kinetic and thermodynamic parameters as calculated for the present case are:

By Coats-Redfern method:
$n = 1$, $\Delta H = 1.114$ kJ·mol^{-1},
$E = 27.01$ kJ·mol^{-1}, $\Delta S = -340.12$ kJ·mol^{-1}·K^{-1}
By Piloyan-Novikova method:
$n = 1$, $\Delta H = 1.114$ kJ·mol^{-1},
$E = 20.01$ kJ·mol^{-1}, $\Delta S = -342.60$ kJ·mol^{-1}·K^{-1}

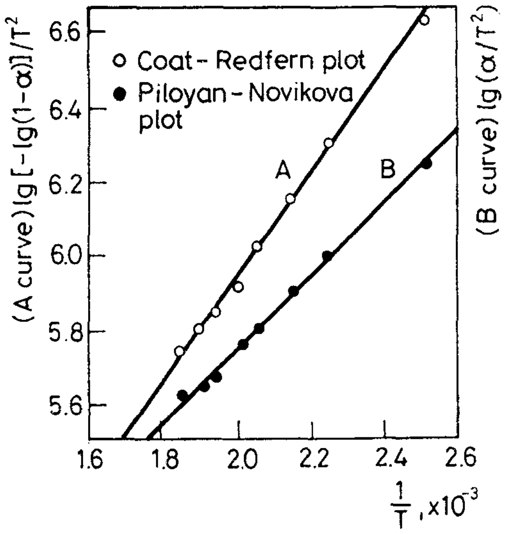


Fig. 2 Coats-Redfern (curve A) and Piloyan-Novikova (curve B) plots for the evaluation of kinetic parameters

IR spectral studies

The assignment of characteristic frequencies for the complex indicating the presence of the cyclopentadienyl groups are found at 3000 cm^{-1}(ν_{C-H}); 1480 cm^{-1}(ν_{C-C}); 1030 cm^{-1} (δ in plane C–H) and 815 cm^{-1} (δ out of plane C–H). Appearance of these cyclopentadienyl group bands in the complex indicates that the electrons in these groups remain delocalised and π bonded (η^5) to the metal [15]. Apart from this a new band at 425 cm^{-1} was assigned to the $\nu_{(Ti-C_5H_5)}$ vibration [6].

A strong band is observed at 1625 cm^{-1} in the spectrum of the Schiff base, which is characteristic of the azomethine group. Coordination of the nitrogen to the metal ion would, however, be expected to reduce the electron density in the azomethine link and thus lower the –C=N frequency. In the complex this band is, therefore, slightly shifted to lower energy side (1600 cm^{-1}) confirming the azomethine linkage. A high intensity band at 1275 cm^{-1} in the Schiff base is assignable to ν_{CO} (phenolic) [16]. In the chelate this is shifted towards higher frequency side ≈ 1300 cm^{-1}. This indicates bonding of the ligand to metal through oxygen. The disappearance of the broad $\nu_{(OH)}$ band at 3300–2975 cm^{-1} region indicates that the deprotonation of the phenolic –OH has taken place and the phenoxide ion has coordinated with the metal ion. Bands at 500 cm^{-1} and 380 cm^{-1} are attributed to the ν_{Ti-O} and ν_{Ti-N} vibrations, respectively [17].

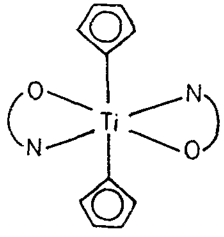
Electronic spectral studies

The electronic spectrum of the complex exhibits a broad band between 270–350 nm region which may be due to charge transfer [18–21]. There are three components of this band at 270, 320 and 340 nm corresponding to $\pi - \pi^*$ (benzoid), $\pi - \pi^*$ (azomethine) and $n - \pi^*$ (azomethine) transitions, respectively. In the Schiff base, the first two bands were found at 275 and 375 cm^{-1}. The shift of these bands may be due to donation of lone pair of electrons by the nitrogen of the azomethine group to the central metal ion [8, 17]. Absence of any d–d band in the spectrum of the chelate rules out the presence of any electron in the d-level of the metal ion and hence corresponds to the electronic configuration of the metal ion to be $(n-1)\,d^0ns^0$.

^{1}H NMR studies

The ^{1}H NMR signal due to azomethine proton appears at 7.00 ppm in the spectrum of Schiff base. It goes to downfield to 7.45 ppm in the complex indicating the deshielding of this proton as a result of coordination through nitrogen of the azomethine group to the titanium(IV) ion. A high intensity signal at 7.20 ppm in the chelate is due to the cyclopentadiene ring. The appearance of a single sharp cyclopentadiene resonance is attributed to rapid rotation of the cyclopentadiene ring about the metal-ring axis. Aromatic protons which appear at 8.45 ppm in the Schiff base also suffer downfield shift to 9.10 ppm in the chelate. This downfield shift further supports the coordination of azomethine with the metal ion. The phenolic proton signal of Schiff base spectrum at 12.5 ppm disappears in the spectrum of the chelate. It proves the deprotonation of –OH and formation of bond with metal ion as proved in the infrared spectral studies. The NMR data also indicates that titanium(IV) has a planar configuration in view of the singlet signals for HC=N (azomethine) protons.

On the basis of all the above facts, studies and observations an octahedral structure may be proposed for the chelate as follows:



where N⌒O = deprotonated Schiff base.

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Zusammenfassung — Es wurde eine neue Chelatverbindung $(\eta^5\text{-}C_5H_5)_2Ti(SB)_2$ mit der SB =O, N-Donor Schiff'schen Base Salicyliden-4-methylanilin synthetisiert. Mittels Thermogravimetrie (TG) und Differentialthermoanalyse (DTA) unter dynamischen Temperaturbedingungen wurde der Verlauf des thermischen Abbaues des Chelates untersucht. Die Reaktionsordnung der thermischen Zersetzung und die Aktivierungsenergie wurde anhand der TG-Kurve, die Enthalpieänderung anhand der DTA-Kurve berechnet. Die Bewertung der kinetischen Parameter wurde mittels der Methoden von Coats-Redfern und von Piloyan-Novikova durchgeführt, man erhielt $n=1$, $\Delta H=1.114$ kJ·mol^{-1}, $\Delta E=27.01$ kJ·mol^{-1}, $\Delta S=-340.12$ kJ·mol^{-1}K^{-1}und $n=1$, $\Delta H=1.114$ kJ·mol^{-1}, $\Delta E=27.01$ kJ·mol^{-1}, $\Delta S=-342.60$ kJ·mol^{-1}K^{-1}. Die Chelatverbindung wurde weiterhin auf der Grundlage verschiedener Spektraluntersuchungen in Abhängigkeit von Leitfähigkeit, Molekulargewicht, IR, sichtbares UV und ^{1}H-NMR charakterisiert, wodurch der Vorschlag für eine oktaedrische Struktur der Chelatverbindung ermöglicht wurde.