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Photosubstituted synthesis, characterization and thermal kinetics of potassium hexacyanoferrate with monoethanolamine

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ABSTRACT

Photoinitiated substitution complex of K_4 [Fe(CN)₆] and monoethanolamine has been synthesized and characterized on the basis of elemental analysis, UV, FTIR, TA and DSC. The complex has been assigned as K₂[Fe(CN)₃(OH)(MEOA)]H₂O. The presence of different moieties is confirmed by the appearance of characteristics IR absorption peaks. The photoaquation of K₄[Fe(CN)₆] is confirmed by recording UV spectra before and after irradiation. Irradiation of aqueous solution of metal cyanides leads to the formation of the primary photoadduct where a CN⁻ ion is replaced by OH⁻, which undergoes subsequent thermal substitution by entering ligand (MEOA). Thermal kinetics of the complex has been studied by TG and DSC techniques. The thermal analysis has been carried out in nitrogen atmosphere up to 800°C. Thermograms obtained confirm IR data, hence supports the empirical formula. On the basis of thermal data, thermal decomposition mechanism has been proposed for the complex. Thermodynamic parameters like activation energy (E_a), preexponential factor (A) and entropy of activation ($\Delta S^{\#}$) has been calculated for each decomposition step, using Dolye's, Coats and Redfern and Arrhenius method. The reaction enthalpy is obtained from DSC technique.

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Introduction

A survey of literature reveals that a considerable amount of work has been carried out on the ethanolamine derivatives of transition and non transitions metals [1]. The coordination chemistry of amino alcohols with metal ions deserves further study because they play important roles in nature, for example, in hormones and in amino sugars [2-4]. Though the complexes have been reported more than sixty years ago, but subject is still under observation, due to its importance in various fields like catalysis, inhibitors, ion exchangers, additives in building materials, electroplating and dyes [5-8]. MEOA acts monodentate as well as bidentate ligand [9-13]. Potassium hexacyanoferrate $K_4[Fe(CN)_6]$ has got an extreme photochemistry [14-16]. On one hand keeping the fascinating flexibility of K₄[Fe(CN)₆] for photoaquation, photosubstitution and photoaddition process and on the other hand the interesting coordinating behavior of MEOA, prompted us to investigate the study. The complex has been synthesized as a result of Photoinitiation followed by secondary thermal reactions. The complex was characterized with various spectroscopic techniques and thermal kinetics of the complex was studied. Experimental

The reagents $K_4[Fe(CN)_6]$, monoethanolamine (MEOA) were of AR grade and the solutions were prepared in double distilled water. Photocomplexation of K₄[Fe(CN)₆] with MEOA was carried out by irradiating solution of $K_4[Fe(CN)_6]$ under UV light. On irradiation the solution changes its color from red to green and then to blue. Precipitation was observed by adding MEOA dropwise into the irradiated solution of $K_4[Fe(CN)_6]$ and the solution was kept over night for complete precipitation. The precipitate was filtered, washed repeatedly with ethanol and then water. The precipitate was dried over fused calcium chloride.

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UV visible spectra were taken on Shimadzu UV-190 double beam spectrophotometer. Irradiation was done with the help of Osram UV photolamp. Elemental analysis was done on Elementar Analysensysteme Gmbh Vario EL CHNS. The FTIR spectrum of the solid complexes was recorded in Perkin Elmer RXI IR spectrophotometer in the range of 200-4000 cm⁻¹ using KBr disc techniques. Thermal analysis was carried on universal V4.1 DTA instrument. The treatment was made in a dynamic nitrogen atmosphere with a rate of 50 ml/min. between ambient temperature to 800 °C at a heating rate of 10 °C/min. DSC was taken on universal V4.1 DTA instrument. The temperature repeatability of the instrument is ± 0.1 °C and of Δ H is equal to \pm 0.2mW.

Results and discussion

The complex was analyzed for C, H and N and was assigned the formula K₂[Fe(CN)₃(OH)(MEOA)]H2O for which the observed values of C, H and N are 18.81, 3.14 and 17.6 against calculated values as 18.86, 3.21and 17.56 respectively. The electronic absorption spectra of $K_4[Fe(CN)_6]$ shown in Fig.1. shows a characteristic peak at 325 nm, assigned as metal to ligand charge transfer transition.



Figure 1: The UV-VIS spectrum of K₄[Fe(CN)₆] (A) before and (B) after irradiation.

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On exposure the solution turns red and then green and on prolonged exposure it turns blue with absorption maximum at 590 nm, which is assigned as d-d transition. The unexposed solution of $K_4[Fe(CN)_6]$ shows a d-d transition at 605 nm. On irradiation the d-d band shows a shift of about 15 nm towards higher frequency which justifies the photoaquation reaction and availability of aqua ligands for further substitution.

The complex characterization was done by FTIR spectroscopy and is shown in Fig. 2 and 3. The observed peaks of FTIR are in conformity with the composition of the complex and support the presence of individual moieties present. First the presence of water molecule as moisture is shown by a strong absorption peak at 3494 cm⁻¹ assigned to v (O-H), v(H-O-H) [17]. The presence of this water as water of lattice is latter confirmed by TA analysis. The presence of cyanide is confirmed by the presence of strong peak at 2115 and 1634 cm⁻¹, assigned as $v(-C \equiv N)$ and v(=C=N-) respectively. The presence of cyanide in (Fe-C=N) has been observed at 2090 cm⁻¹[18]. The presence of MEOA in the complex is confirmed by the appearance of absorption peaks at 1382,1430,1517cm⁻¹ which is assigned as v (-CH2-) and 1100, 1139 cm⁻¹ for (-C-O-). The presence of hydroxyl is shown by v (O-H) which appears as a broad peak at 514 cm⁻¹[19]. The peaks observed at 384, 249 cm⁻¹ is because of metal cyanide v (M-CN)[20]. MEOA in the complex is coordinating via both nitrogen and oxygen, is evident by the M-N stretching frequencies and M-O presence of both stretching frequencies which are observed at 721, 847 cm⁻¹ and 531, 562, 574, 591, 600 cm⁻¹ respectively, which is further verified by the appearance of absorption peak at 1100cm⁻¹, due to M-O-H bending mode [21-22].



Fig.2. FTIR of the complex K₂[Fe(CN)₃(OH)(MEOA)]H2O in the spectral range from 500-4000 cm⁻¹



Fig.3. FTIR spectra of the K₂[Fe(CN)₃(OH)(MEOA)]H2O in the spectral range from 200-600 cm⁻¹

The TG curve can be explained by considering the two stages with two different maximum temperatures. Initiating from the initial temperature of 23.74°C to 150.63°C with maximum temperature of 57.66°C, complex shows a significant weight loss equivalent to 11.14% which can be as a result of loss of water moiety along with hydroxyl. The calculated weight loss for these moieties is 11%. The presence of water as lattice water confirmed from IR is assured by temperature range of thermal

analysis at which weight loss equivalent to water moiety occurs. The second thermal decomposition step is initiating from 198.03 to 794.25°C with DTG maximum of 631°C giving a weight loss of 31.67% against 31.84%, accounts for the removal of 1 mole of MEOA and one mole of CN. The curve shows that the decomposition is incomplete, because of presence of KCN, as decomposition temperature of KCN is 1625°C [23]. Since the temperature range of analysis is from ambient to 800°C, therefore the residue left at 800°C is 2KCN+ Fe, the calculated weight loss of which is 57.33 against observed weight loss of 56.21%. The thermo analytical data is given in table 1. DSC curve of this complex is shown in Fig. 5. It involves one endothermic peak in the temperature range of 39.04°C to 70°C with maximum at 57.56°C giving Δ H=20.33 J/g. This peak is due to the release of H2O and OH molecules. The second peak is wide as being exothermic peak from 73.08°C to 883.72°C with maximum at 331.02 °C, which is because of release of other moieties from the complex. The heat flow during the transition is 4511 J/g.



Fig.4. TG Curve of the complex K₂[Fe(CN)₃(OH)(MEOA)]H2O



Fig.5. DSC curve of the complex K₂[Fe(CN)₃(OH)(MEOA)]H2O

On the basis of these studies, following scheme is proposed for thermal decomposition of complex. Scheme:

 $K_2[Fe(CN)_3(OH)(MEOA)]H_2O \rightarrow K_2[Fe(CN)_3(MEOA)]+H_2O+OH \rightarrow 2KCN+CN+Fe+MEOA.$

Three different methods viz. Doyle's (-Log α vs 1/T×103K), Coats and Redfern (- Log[-ln(1- α)/T2 vs1/T × 103K) and Arrhenius (- Log K vs 1/T × 103K) were employed for evaluation of kinetic data (table 2). Thermodynamic parameters like activation energy (Ea), pre-exponential factor (A), and entropy of activation (Δ S#) for different decomposition steps of the complex were calculated and are given in table 2. From the calculated thermodynamic parameters (table 2) and thermal analysis mechanism, the order of thermal stability of different moieties present in the complex is in accordance with the spectrochemical series. Lowest value of Ea and maximum value of (Δ S#) for stage I corresponds to the release of water and hydroxyl at the very onset of thermal decomposition process

justifying the weak bonding with central metal ion. The stage II corresponding to the release of one mole of MEOA and one mole of CN, gives the maximum value of Ea and lowest value of $(\Delta S^{\#})$ shows their strong co-ordination with iron, the same must be true for frequency factor according to Eyring's equation A α $e\Delta S\#/R$ is verify from the data also (table 2). After removal of one mole of cyanide and MEOA, the rest two cyanide moieties are present as two moles of potassium cyanide. The residue left at 800°C includes iron and two moles of KCN, which is supported by the fact that the decomposition temperature of KCN and Fe is 1625°C and 1537°C respectively 20 which is beyond the analysis range, hence showing incomplete thermal decomposition and is treated as residue. The thermal decomposition data using different methods is plotted in Fig.6 and it is evident that the trend is same for all the methods used and are linear, hence follow first order kinetics.



Fig.6. (A) Plot of (1) - Log α (2) - Log[-ln(1- α)/T2] and (3) - Log K versus 1/T × 103 K for stage I (B). Plot of (1) - Log α (2) - Log[-ln(1- α)/T2] and (3) - Log K versus 1/T × 103 K for stage II

Conclusion:

The Photosubstituted synthesis of potassium hexacyanoferrate with monoethanolamine (MEOA) has been successfully achieved. The complex has been characterized by various spectroscopic methods. The empirical formula of the complex has been ascertained by elemental analysis and has been justified by IR and thermal characterization. MEOA acts as a bidentate ligand in the characterized complex. On the basis of thermal data, thermal decomposition mechanism has been proposed for the complex. Thermodynamic parameters have been calculated using various methods. The complex has been found to be thermally stable above 800 °C.

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Table1. Thermoanalytical data for the decomposition of the complex K2 [Fe(CN)3(OH)(MEOA)]H2O

Temp. range in ⁰ C	Max. Temp. in DTG ⁰ C	Obsd. Wt. Loss %	Calc.wt. loss %	Remarks Removal of					
23.74 - 150.63	57.56	11.14	11	1 mole of water + 1 mole of OH					
198.03-794	631	31.84	31.67	1 mole of MEOA + 1 mole of CN					

Residue is Fe + 2KCN Calc. (57.33), observed. (56.21)

Table2. Activation energy (E_a), pre-exponential factor (A) and entropy of activation ($\Delta S^{\#}$) forthe complex [Fe (CN)₃(MEOA)(OH)] H₂O.

Stage	DTG max. in K	Parameters	Doyle	Coats and Redferm	Arrhenius
1.	330.56	$E_a(KJmol^{-1})$	23.6	16.1	36.4
		$A(S^{-1})$	4.3	1.8×10^{-22}	8.0
		$\Delta S^{\#} (JK^{-1}mol^{-1})$	-234.2	-662.4	-229.0
II	904	E_a (KJ mol ⁻¹)	70.6	74.1	72.0
		$A(S^{-1})$	0.6	1.3×10^{-30}	2.6
		$\Delta S^{\#}(JK^{-1}mol^{-1})$	-254.1	-769.4	-254.6