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Photo initiated Synthesis, Characterization, and Structural Analysis of photoadduct of Potassium hexacyanoferrate with Phenanthroline ligand

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ABSTRACT

This paper involves the synthesis of photoadduct of Potassium hexacyanoferrate and phenanthroline via photochemical route .The photoadduct has been synthesized by photoirradiation followed by substitution with phenanthroline ligand. The photoaquation, substitution and successful synthesis has been proved by recording pH, colour change, UV visible spectra before and after irradiation. The as synthesized photoadduct has been subjected to various spectroscopic and surface characterization techniques like elemental analysis, UV-visible spectra, XRD, and SEM. XRD of photoadduct shows crystalline structure. Moreover parameters like crystallite size (L), interplanar distance (d), micro strain (ε), dislocation density (δ) and distortion parameters (g) were evaluated from XRD data using Schrerrer and other equations for the photoadduct.

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Introduction

The synthesis of photoadducts through photochemical procedure is an easy route for its synthesis. Photochemistry of transition metal complexes especially cyanocomplexes possess a beautiful and flexible nature for further substitution and addition reactions[1].The kinetics and mechanistic studies of these photo substituted reactions has been discussed extensively in literature [2-6]. Photo reactivity of octacyanometallates of Mo (IV), W (IV), and Fe (III) with many ligands like 2,2' bipyridyl, ethylenediamine, 8-hydroxyquionoline, pyrazine, ethanolamine, imidizole has been reported [7-11]. The intermediate photoaquation reactions of these cyanocomplexes undergo substitution reactions with various ligands and provide an easy route of incorporation of desired ligands into the complex. The final product has been isolated as such, or as an adduct, by the addition of some other complexing agent or metal chloride solution. The final product, more appropriately a photoadduct, represents a combination of metal centre with very potent ligands. The photoadduct as a whole possess very significant properties which can be explored for its applications in increasing thermal and mechanical stability of polymers, lubricants etc.[12-14]

In this direction potassium hexacyanoferrate (II) has been chosen for investigation because of the fact that photoirradiation in the ligand field bands of hexacyanoferrate (II) in an alkaline medium results in the substitution of cyanide ligand by water followed by other thermal steps, which results in the formation of stable products with ligands 2, 2' bipyridyl, imidizole etc. Moreover $K_4Fe(CN)_6$ is easily available among all cyanocomplexes and is photochemically active.[15-18] Our group recently reported the photoadduct synthesis and characterization of $K_4Fe(CN)_6$ with imidizole and hexamine ligand[19-20]

Now keeping in view the potential application of these compounds, we here report the structural characterization of another photoadduct synthesized from $K_4Fe(CN)_6$ and Phenanthroline. 1,10' Phenanthroline has been used as a ligand for the reasons of possessing good coordination site , a starting material to prepare dyes and drugs, metal chelator, used in metallocene industry for the application including coordination of organometallic-complexes, redox mediators in biosensor, catalysts for the oxidative organic synthesis, molecular chemistry, disease diagnosis and treatment, water treatment, photolysis chemistry, microbiology. It is used as an indicator to determine iron. Other applications include chelating agent, cross-linking reagent, indicator, intercalating agent, neurotransmitter Agent. Keeping these application in view our aim is to study is to synthesize photoadduct of Potassium hexacyanoferrate with Phenanthroline ligand.

Experimental details

Materials

$K_4Fe(CN)_6$ and Phenanthroline was was supplied by Loba Chemicals and was used as such.. All solutions were prepared in triply distilled water.

Synthesis of Photoadducts

Solutions of $K_4Fe(CN)_6$ and phenanthroline were mixed in equimolar ratio (0.3 molar). The solution mixture was subjected to ultraviolet radiation using Osram UV photo lamp for about half an hour till the color of solution changed to deep yellow. The solution was evaporated and a yellow solid photoadduct was obtained. The photoadduct was finally isolated and dried over fused $CaCl_2$. The complex isolated is a yellow solid powder with a light yellow colour. The complex formed was analyzed for C, H and N and the empirical formula for the complex was found to be $K_2[Fe(CN)_3(OH)(C_{12}H_8N_2)]H_2O$. The observed percentages of C, H, and N are 36.15%, 2.70%, and 9.73%, respectively, against the calculated percentages C 36.17%, H 2.78%, and N 9.73%.

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Physical measurements

Elemental analysis was done on Elementar Analysen systeme Gmbh Vario EL CHNS. UV-Visible spectra were taken on Shimadzu UV-190 double beam spectrophotometer. Irradiation was done with the help of Osram UV photo lamp. Surface morphology of the samples was studied on a Hitachi SEM Model S-3600N. X-ray diffraction (XRD) was recorded on PW 3050 base diffractometer with Cu Ka radiations (1.54060 Å).

Results and discussions

Elemental Analysis

The complex formed between $K_4Fe(CN)_6$ and phenanthroline by photosubstitution process ,was analyzed for C, H and N and the empirical formula proposed for the complex was found to be $K_2[Fe(CN)_3(OH)(C_{12}H_8N_2)]H_2O$. The observed percentages of C, H, and N are 36.15%, 2.70%, and 9.73%, respectively, against the calculated percentages C 36.17%, H 2.78%, and N 9.73%.

UV Characterization

When aqueous $[Fe(CN)_6]^{4-}$ solution is irradiated with UV or visible light, Fe^{+2} ions and HCN was product with the increase in pH of the solution. The pH of equimolar solution of $[Fe(CN)_6]^{4-}$ and phenanthroline before and after irradiation was 9.78 and 11.43 respectively which shows successful photoaquation. The photoirradiation followed by substitution was further proved by recording UV spectra of this solution before and after irradiation (Fig.1). Before irradiation the peaks observed are at 400nm can be assigned as spin allowed ligand field transition $^1A_{1g} \rightarrow {}^1T_{1g}$ which shows a shift after irradiation by appearing at 420nm which can be assigned to the $^1A_{1g} \rightarrow {}^3T_{1g}$ spin forbidden ligand field transition.

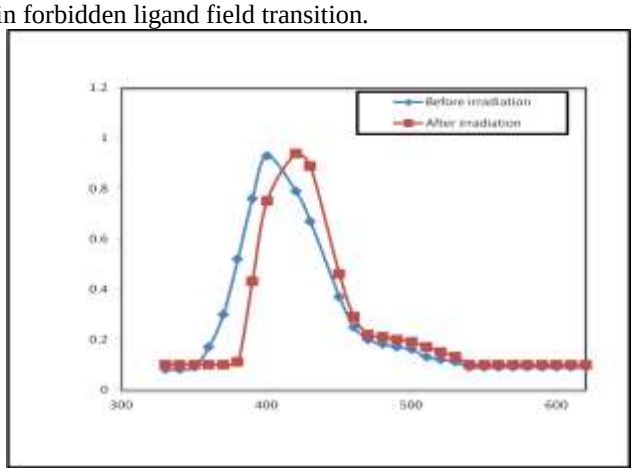

Fig.1. UV –Visible spectra of equimolar solution of potassium hexacyanoferrate

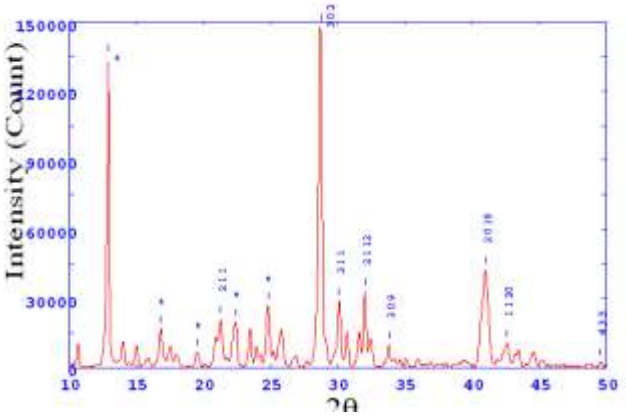

Fig.2.XRD of Photoadduct

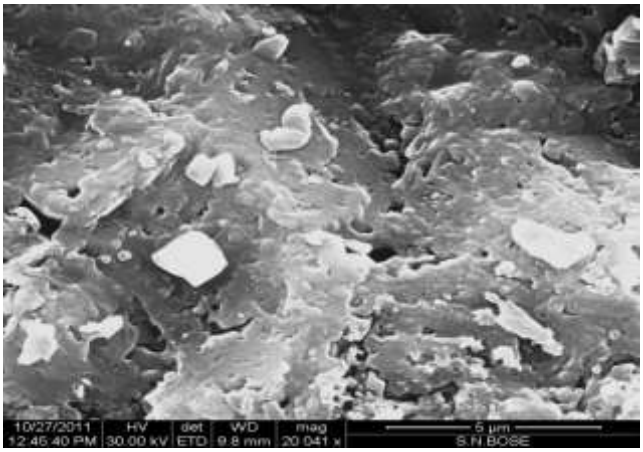

Fig.3 SEM imageof photoadduct

XRD Characterization

The XRD data has been analyzed using Powder X software. Figure 2 represents XRd graph of photoadduct. Characteristic peaks are indexed by miller indices. The appearance of sharp peaks indicates degree of crystallinity in the photoadduct. The XRD peaks of synthesized photoadduct shows tetragonal structure of potassium hexacyanoferrate. The sharp peaks due to potassium ferrocyanide in the photoadduct matches well with the JCPDS-International centre for diffraction data, file No14-0695. Moreover some extra peaks due to phenanthroline are observed which proves the successful synthesis of photoadduct. The average crystallite size of the particle is calculated by using the Debye Scherrers formula

$D=K\lambda / \beta \cos\theta$.

Where D is the crystallite size, λ =1.54Å is the wavelength of Cu Kα radiation, K is shape factor which has a value of 0.89, θ is the Bragg angle and β is the Full width at half maximum of angle of diffraction in radians. The above equation when introduced for the characteristic (302plane) peak of photoadduct viz. at 2θ =10.5732 leads to about 35.6nm.(Table1.)Various parameters like , interplanar distance (*d*), micro strain (ε), dislocation density (*δ*) and distortion parameters (*g*) were calculated for the photoadduct using these equations, $d= \lambda / 2\sin\theta$, $\varepsilon=b \cos\theta / 4$, $\delta=1 / L^2$ and $g=b / \tan\theta$, respectively, d is the interplanar distance (A^0), ε is the micro strain, *δ* is the dislocation density and g is the distortion parameter. When the values are introduced in the above equations for the most intense peak corrosponding to 302 plane gives the value of d= 3.10746, ε= 2.537, δ= 0.00065 and g=2.3462 for photoadduct. The lattice parameters have been calculated after refinement which are a=b=9.41316, c= 44.85458 with unit cell volume equal to 3974.45 and R factor equal to 0.001 for the photoadduct.The d-spacing has been calculated using the following equation.$1/d^2=a^2(1/h^2+1/k^2)+c^2/l^2$.The value of d-spacing is in agreement with the experimental d-spacing.

SEM Characterization

SEM micrograph of photoadduct is shown in figure 3. SEM photograph shows uniform structure of photoadductwith some unreacted phenanthroline which supports the photoreactivity of K4Fe(CN)6 for showing release of cyanide moieties as subjected to irradiation time, and subsequent thermal reactions.

Conclusion:

From the study it is evident that with the procedure mentioned, there is successful synthesis of photoadduct of potassium hexacyanoferrate involving phenanthroline ligand, which is proved by noting the colour change, pH and shifts in UV bands before and after irradiation.

Table 1. HKL and d-spacing values of photoadduct

Cos2θ	h	k	l	d (cal)	d (exp)
21.264	2	1	1	4.19127	4.19127
28.703	3	0	2	3.10746	3.11322
30.103	2	1	12	2.97017	2.97017
32.017	3	0	9	2.79507	2.79507
33.782	3	0	9	2.65530	2.65530
40.971	2	0	18	2.20222	2.20736
42.587	1	1	20	2.12533	2.12533
49.536	4	3	5	1.84250	1.84050

SEM images are also showing successful synthesis of composite. Various parameters like crystallite size, dislocation density, strain, d-spacing have been evaluated from XRD data using Debye Schrerrer and other equations, showing the crystalline structure of photoadduct.

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