

## Synthesis and Characterization of Heterocyclic Substituted Pentacyanoferrate (II) Complexes: UV-Visible, Infrared, Mossbauer, TGA-DTG and XRD

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**ABSTRACT:** A series of substituted compounds  $Na_3[Fe(CN)_5L]_n \cdot xH_2O$  where L= nicotinic acid, nicotinamide, 2,3,4-cyanopyridine and isonicotinamide have been synthesized. These pentacyanoferrates complexes studies by UV-visible, infrared, Mössbauer spectroscopic, TGA-DTG and XRD. All complexes has an absorption band in the visible region that is assigned to **d-d** transition. The Mössbauer spectra of these pentacyanoferrates complexes exhibit quadrupole doublet  $\Delta E_Q = 0.71-0.84 \text{ mms}^{-1}$  at room temperature. The isomer shift ( $\delta$ ) values fall within  $0.00 \pm 0.02 \text{ mms}^{-1}$  suggest the iron atom in +2 low spin states. The complex start decomposing at 60 °C yielding residual weight 17.0-20.1. The Mössbauer spectra at higher temperatures and TGA/DTG of the complexes show that solids yielding into metal carbides, magnetite ( $F_3O_4(A)$  and  $F_3O_4(B)$ ) and hematite ( $F_2O_3$ ). Mössbauer spectra recorded after heating at 150, 200, 250 and 300 °C exhibit symmetric doublet suggested partial decomposition. At 500°C, a six line pattern starts appearing which on further heating at > 700 °C turns into eight or ten lines suggesting the formation of  $Fe_3O_4(A)$ ,  $Fe_3O_4(B)$  of different particle sizes and iron carbide  $Fe_3C$  along with metal phase. The XRD powder pattern of the 2,3,4-cyanopyridine substituted pentacyanoferrate complexes after heating at 950 °C showed an intense lines corresponds to the formation of  $\gamma$ - $Fe_2O_3$ .

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### I. INTRODUCTION

Mössbauer spectroscopic studies of substituted pentacyanoferrate (II) complexes of the type,  $Na_3[Fe(CN)_5L]^{n-3+n} \cdot xH_2O$  ( where L=  $H_2O$ ,  $NH_3$ ,  $NO^+$ ,  $RNH_2$  etc ) have been extensively studied<sup>1-4</sup>. Earlier we have studied several alkyl and aryl amine substituted pentacyanoferrate(II) complexes<sup>5,6</sup>. Recently special attention has been given to the study of interaction of iron with ligand of biological importance<sup>7</sup>, therefore, thermal behavior of simple and complex cyanide has been the subject matter of much work. Also ferrites formed at higher temperature are widely employed in industry as catalysts and ferromagnetic materials<sup>8</sup>. Brar and Varma<sup>9</sup> studied thermal decomposition product of sodium pentacyanoferrate(II) using Mössbauer spectroscopy.

Sielo et al have reported the thermal behavior of pentacyanoferrate(II) complexes with L= pyrazine and pyridine and proposed the water release and finally yield metal carbide. In view of this, we report the Mössbauer Spectroscopic studies of thermal decomposition products of pentacyanoferrate(II) complexes  $Na_3[Fe(CN)_5L]_n \cdot xH_2O$  where L= 2-cyanopyridine (2-CNPy), 3-cyanopyridine (3-CNPy), 4-cyanopyridine (4-CNPy) nicotinic acid (NIAC), nicotinamide (NIAM), isonicotinamide (I- NIAM), diphenylamine (Di-PhAm) and triphenylamine (Tri-Ph-Am). The complexes have been characterized by elemental analysis, UV-visible, infrared, Mössbauer spectroscopy and XRD. An attempt has been made to identify the thermal decomposition of intermediate and final products by Mössbauer spectroscopic, TGA-DTG and XRD.

### II. EXPERIMENTAL

All reagents used were of AR, GR or high purity grade. The complexes were prepared by modifying the procedure. The stoichiometric of the complexes was ascertained by elemental analysis which was well agreement with the proposed formulae.

#### II.1. Preparation of substituted pentacyanoferrate(II) complexes

A solution containing 0.47g of hydroxylamine hydrochloride and 0.54g NaOH in 20 mL water was prepared. Then 10% heterocyclic ligand in ethanol was added. The mixture was kept in ice for 1hr and then added dropwise to an ice cold solution of 2g sodium pentacyanonitrosylferrate(II) in 20mL water. In each case an oily layer separated after adding cold alcohol. The complexes were forced to solidify by through washing with absolute ethanol and then drying for 24hr over concentrated sulphuric acid in desiccator.

### III. PHYSICAL MEASUREMENTS

The Mössbauer spectra were recorded on transducer driven Mössbauer spectrometer in constant acceleration mode (ELCENT) at room temperature. A ~5 mCi <sup>57</sup>Co(Rh) source was used. The spectrometer was calibrated using a natural iron foil. The isomer shift values were reported with respect to metallic iron. The spectra were fitted with Lorentzian line shapes by using least square fitting procedure. UV-visible spectra of the heterocyclic substituted pentacyanoferrate(II) complexes were recorded in aqueous solution using Hitachi Model U-3500 spectrophotometer and 1cm path length. Infrared spectra were obtained on a sample in KBr pallets using Hitachi Nicolet Model\_I 5040 FTIR spectrophotometer. The thermogravimetric (TGA-DTA) were carried out using Seiko Instrument Inc.SSC/5200. The DSC Curve were recorded between 273K and 785K on RIGAKU Thermoflex Apparatus at scanning rate 5Kmin<sup>-1</sup>. XRD of decomposition products were recorded using MAC science MXP-18 automated diffractometer by Cu-K $\alpha$  radiation.

### IV. RESULT AND DISCUSSION

All the complexes were coloured solid and stable under normal atmospheric conditions. Analytical data, electronic spectral bands and characteristic IR frequencies due to  $\nu(\text{CN})$ ,  $\delta(\text{Fe-CN})$ ,  $\nu(\text{Fe-C})$  and  $\nu(\Delta\text{C}\equiv\text{N})$  are listed in Table 1. <sup>57</sup>Fe Mössbauer spectra of all the complexes exhibit a well resolved quadrupole doublet at room temperature. Typical Mössbauer spectra of 4- cyanopyridine, substituted pentacyanoferrate(II) complexes at room temperature and after heating at different temperatures are shown in Fig.1. UV-visible absorption spectra of 2, 3 and 4-cyanopyridine substituted complexes are shown in Fig.2. The Mössbauer parameters such as isomer shift(IS), quadrupole splitting (QS) and halfwidth ( $\Gamma_{\text{exp}}$ ) derived from the observed spectra are summarized in Table 1. The spectra consist of one doublet with small quadrupole splitting QS may be seen the same Fig.1. The values of IS and QS indicate that the iron atom in this complexes is at Fe(II) low spin state.

When one of the cyano ligands in  $[\text{Fe}(\text{CN})_6]^{4-}$  is replaced by neutral heterocyclic ligand L to give  $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$ , the octahedral geometry remain affected but symmetry is lowered from  $O_h$  to approximately  $C_{4v}$ . Even though the electronic configuration will be  $t_{2g}^6$ , it will further split into  $d_{yz}$ ,  $d_{zx}$ ,  $d_{xy}$  (also called e and  $b_2$ )<sup>11,12</sup>. All complexes are expected to be diamagnetism. The heterocyclic bases coordinating through N-atom are essentially  $\sigma$ -donors<sup>10-13</sup>. On the other hand, five CN<sup>-</sup> ligands have vacant  $\Pi_{2py}^*$ ,  $2p_z^*$  orbital available for backbonding.

#### IV.1. UV-Visible Spectra:

Aqueous solution of pentacyanoferrate (II) exhibiting an absorption in the UV-visible region. In  $d^6$  pentacyanoferrate(II) of  $C_{4v}$  symmetry for which the ground state is  $^1A_1$  and low energy excited states of the same multiplicity are  $^1A_2$  and  $1E_{(1)}$ <sup>14</sup>. Thus two  $d-d$  transitions are typically observed for such complexes  $^1E_{(1)}\leftarrow^1A_1$  and  $^1A_2\leftarrow^1A_1$ . The first band with energy and intensity considerably greater than second has been assigned to  $^1E_{(1)}\leftarrow^1A_1$  transition. The second, a weak band occurred at lower energies and should be relatively insensitive to the ligand L. The  $^1A_2\leftarrow^1A_1$  is expected at 310nm (31kK) but it is not observed for the pentacyanoferrate(II) complexes in the region 264-444 nm<sup>15</sup>. By analogy, considering their energy and intensity, the band due to  $^1E_{(1)}\leftarrow^1A_1$  in pentacyanoferrate(II) is found in the region 387-404nm. As the d-d bands have large and asymmetric form, we suggest that  $^1A_2\leftarrow^1A_1$  transitions occur superimposed on the  $^1E_{(1)}\leftarrow^1A_1$  in the spectra of the studied complexes.

#### Infrared Spectra: $\nu(\text{C}\equiv\text{N})$ , $\delta(\text{Fe-CN})$ , $\nu(\text{Fe-C})$ and $\nu(\Delta\text{C}\equiv\text{N})$

Various vibrational modes were assigned by the comparison with the other substituted pentacyanoferrate(II) complexes<sup>16-17</sup>. The most intense band due to  $\nu(\text{C}\equiv\text{N})$  observed in the range 2090-2010  $\text{cm}^{-1}$ . Earlier, three modes of  $\nu(\text{C}\equiv\text{N})$  have been observed for some di and trialkylamine substituted pentacyanoferrate(II) complexes<sup>7,11</sup>. A strong to medium intensity band due to  $\nu(\text{C}\equiv\text{N})$  was observed in the range 2010-2090  $\text{cm}^{-1}$ . Another characteristic mode of medium intensity is due to  $\delta(\text{Fe-CN})$  observed at  $\sim 575 \pm 5 \text{cm}^{-1}$ . A very weak band observed at  $430 \pm 10 \text{cm}^{-1}$  has been assigned to  $\nu(\text{Fe-C})$  according to assignments of Fluck et al<sup>18</sup>. The Fe-N could not be assigned as this is expected to be observed at  $\sim 250 \text{cm}^{-1}$ . An intense weak broad peak in the region 3580-3405  $\text{cm}^{-1}$  arose mainly due to weak bonded water molecules in the lattice. The exact assignment of various bands in this region is not possible due to several overtone and combination of bending vibrations. Similarly sharp to medium intense band at  $\sim 1600 \text{cm}^{-1}$  has been assigned due to bending mode of H<sub>2</sub>O. It has been noted that  $\nu(\text{C}\equiv\text{N})$ ,  $\delta(\text{Fe-CN})$  and  $\nu(\text{Fe-C})$  are remain affected by the different isomers of cyanopyridine ligands.

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**Table 1.** IR frequencies and Electronic spectral band for substituted pentacyanoferrate(II)

Sr. No	Complex	IR Frequencies (cm <sup>-1</sup> )			Electronic spectral band /cm <sup>-1</sup>
		$\nu(\text{C}\equiv\text{N})$	$\delta(\text{Fe-CN})$	$\nu(\text{Fe-C})$	
1	Na <sub>3</sub> [Fe(CN) <sub>5</sub> 2-CN-C <sub>5</sub> H <sub>4</sub> N] 8H <sub>2</sub> O	2055s	570m	430s	24,700
2	Na <sub>3</sub> [Fe(CN) <sub>5</sub> 3-CN-C <sub>5</sub> H <sub>4</sub> N] 3H <sub>2</sub> O	2090w	575m	455s	25,200
		2045s			
		2010w			
3	Na <sub>3</sub> [Fe(CN) <sub>5</sub> 4-CN-C <sub>5</sub> H <sub>4</sub> N] 4H <sub>2</sub> O	2080w	575s	430vw	23,800
		2046			

**Table 2.** Mössbauer parameters for substituted pentacyanoferrate(II) and its thermal decomposition products.

Complex Na <sub>3</sub> [Fe(CN) <sub>5</sub> L]	Temp/ °C	Isomer shift, $\delta$ , mms <sup>-1</sup>	Quadrupole splitting, $\Delta E_Q$ , mms <sup>-1</sup>	Heff/ kOe	Possible products
2-CNpy	25	-0.01	0.84	-	-
		0.13	0.76	-	-
	300	-0.06	-	-	-
		0.26	0.72	-	-
		-0.08	-	-	-
	500	-0.07	-	-	-
		0.30	0.02	501	Fe <sub>3</sub> O <sub>4</sub> (A)
		0.65	0.01	457	Fe <sub>3</sub> O <sub>4</sub> (B)
		0.19	0.00	209	Fe <sub>3</sub> C
		-0.05	-	-	-
	750	0.02	0.00	330	□-Fe
		0.19	0.01	208	Fe <sub>3</sub> C
		950	0.34	0.11	493
0.64			0.00	437	Fe <sub>3</sub> O <sub>4</sub> (B)
300	0.03	0.06	318	□-Fe	
	0.93	0.81	-	Fe <sub>1-x</sub> O	
3-CNpy	25	-0.01	0.87	-	-
	200	0.056	0.87	-	-
		-0.05	-	-	-
	300	0.15	0.89	-	-
		-0.07	-	-	-

	400	0.25 0.65 -0.07	-0.04 0.13 -	485 470 -	Fe <sub>3</sub> O <sub>4</sub> (A) Fe <sub>3</sub> O <sub>4</sub> (B) -
	600	0.34 0.71 0.19	0.00 -0.02 0.00	487 453 206	Fe <sub>3</sub> O <sub>4</sub> (A) Fe <sub>3</sub> O <sub>4</sub> (B) Fe <sub>3</sub> C
	800	0.02	-0.04	328	□-Fe
	950	0.18 0.01 0.40	-0.03 - -0.14	206 - 515	Fe <sub>3</sub> C □- NaFeO <sub>2</sub> □-Fe <sub>2</sub> O <sub>3</sub>
4-CNpy	25	0.02	0.80	-	-
	200	0.07 -0.04	0.88 -	- -	- -
	300	0.35 -0.08	0.75 -	- -	- -
	400	0.19 0.66 -0.07	0.07 0.10 0.02	479 468 499	Fe <sub>3</sub> O <sub>4</sub> (A) Fe <sub>3</sub> O <sub>4</sub> (B) Fe <sub>3</sub> O <sub>4</sub> (A)
	600	0.32 0.61 0.19	0.09 0.00 -0.04	469 207 328	Fe <sub>3</sub> O <sub>4</sub> (B) Fe <sub>3</sub> C □-Fe
	800	0.02 0.18 -0.01	-0.04 - -0.15	206 - 515	Fe <sub>3</sub> C - □-Fe <sub>2</sub> O <sub>3</sub>
	950	0.39			

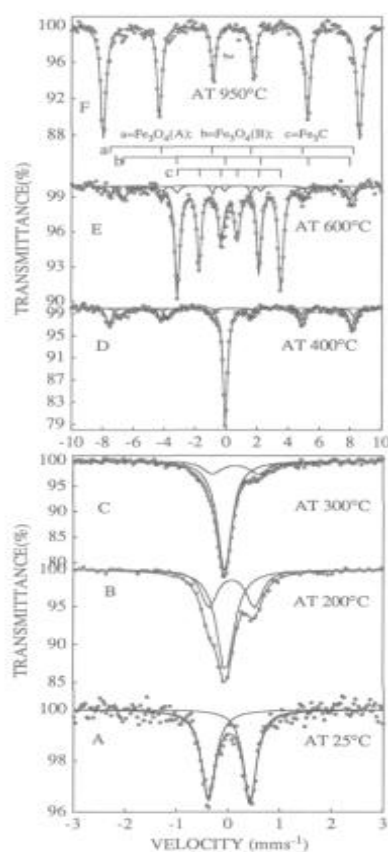


Fig.1 Mössbauer spectra of 4-cyanopyridine substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 200°C, (C) 300°C, (D) 400°C, (E) 600°C and (F) 950°C for 3hrs.