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# Interaction of Aminopyridines with Metal Hexacyanoferrates(II)

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Copper(II) and zinc(II) hexacyanoferrates(II) have been found to be effective adsorbents for aminopyridines, such as 2-amino-, 3-amino-, and 4-aminopyridines. The maximum adsorption was found at neutral pH (pH = 7.0). The adsorption trend followed a Langmuir adsorption isotherm. The Langmuir constants, $K_L$ and $X_M$, were determined. The overall adsorption trend was found to be in the order 3-amino- > 4-amino- > 2-aminopyridine. Infrared spectral studies of the adsorption adducts indicate that adsorption takes place through an interaction between the adsorbate molecule and the outer divalent metal ion of metal hexacyanoferrates(II). The results of the present study suggest the importance of metal hexacyanoferrates(II) and metal ions in the stabilization of biomolecules from degradation on primitive earth.

Little is known about how biomonomers were concentrated from a dilute aqueous solution and condensed to biopolymers during the course of chemical evolution. However, one suggestion is that clays and other minerals may have provided surfaces onto which small molecules could be concentrated, and subsequently polymerized. Materials adsorbed on mineral surfaces would have been protected from the environment, which might have been advantageous in prebiotic synthesis. Selective adsorption provides a means for concentrating solute molecules present in traces in the primeval seas, which might have further interacted to give complex structures. The adsorption of a wide variety of organic molecules, such as amino acids,[1,2] peptides,[3—5] sugars,[6—9] and nucleotides,[10] on clays and clay minerals has been investigated in detail. Extensive studies on the reaction and polymerization of nucleotides on clays were performed by Ferris and his collaborators.[11—14]

Compounds containing pyridine rings are widely distributed in nature, and vitamin $B_6$, nicotinamide, adenine, and dinucleotide phosphate are of great biochemical importance.[15] The pyridine ring is also featured in the structural framework of many drugs, dyes, and alkaloids.[15] Harvey et al.[16,17] reported on the synthesis of nitrogen heterocycles on kaolinite from $CO_2$ and $NH_3$ under the conditions of the prebiotic era.

Kobayashi and Ponnamperuma[18] proposed that there exists a correlation between the concentration of the chemical elements in the primordial sea and their biological behavior. Further, it is assumed that divalent transition metal ions, which were in abundance in the primeval sea, would have formed complex compounds with the simple molecules readily available to them.[18,19] It is therefore reasonable to assume that transition-metal ions could easily have formed a number of soluble and insoluble complexes with abundant $CN^-$ in the primeval sea. The thus formed insoluble cyanometal complexes could have settled at the bottom of the sea or at the sea shore, and might have catalyzed a number of reactions like condensation–oligomerization, oxidation, and interaction reactions on their surfaces. The existence of hexacyanoferrate(II), ferrate(III) and metal hexacyanoferrates(II) on the primitive earth has recently been reported by Arrhenius.[20]

During the last few years, we have undertaken experimental studies on the catalytic role of cyano complexes and their possible role in chemical evolution. Recently, we prepared a number of metal(II) hexacyanoferrates(II), and studied their interaction with organic monomers in detail.[21—23] The present paper describes our studies on the interaction of aminopyridines with zinc and copper hexacyanoferrates(II). Aminopyridines belong to a special class of heterocyclic compounds that are essential in the synthesis of biomolecules under prebiotic conditions. Infrared spectral studies of adsorption adducts have indicated complex formation between the adsorbate molecule and the outer divalent metal cation of metal hexacyanoferrates(II).

## Experimental

**1. Materials.** Potassium hexacyanoferrate(II) (B.D.H.), zinc(II) chloride (B.D.H.), copper(II) sulphate (Fluka), 2-aminopyridine (Merck), 3-aminopyridine (Merck), and 4-aminopyridine (Fluka) were used as received. All other chemicals were of analytical reagent grade. Doubly distilled water was used throughout the studies.

**2. Methods.** Synthesis of metal hexacyanoferrates(II), $M_2[Fe(CN)_6]\cdot xH_2O$ (M = divalent cation): All of the metal hexacyanoferrates(II) were prepared following Kourim's method.[24] A solution of potassium hexacyanoferrate(II) (167 ml, 0.1 M, 1 M = 1 mol dm$^{-3}$) was slowly added to a solution of the respective metal salt (500 ml, 0.1 M) with constant stirring. An excess of metal salt markedly improved coagulation of the precipitate. The reaction mixture was then heated at 60 °C on a water bath for 2—3 h and kept as such for 24 h at ambient temperature. The precipitate was filtered and washed thoroughly with water and dried in an oven at 60 °C. The dried product was ground and sieved to 100 mesh size. The purity of metal hexacyanoferrates(II) was checked by comparing the X-ray diffraction data of the complex. The relative-intensity data and interplanner spacing (*d*) were in good agreement with the reported values.[25]

**3. Spectral Studies.** The electronic spectra of 2-amino-, 3-amino-, and 4-aminopyridines were recorded on a Beckman DU-6 spectrophotometer. The characteristic values of $\lambda_{\max}$ are 298, 288, and 247 nm in the case of 2-amino-, 3-amino-, and 4-aminopyridines, respectively, at pH 7.0. The infrared spectra of adsorbents, adsorbates, and adsorption adducts were recorded in KBr discs on a Perkin Elmer FTIR spectrophotometer.

**4. Adsorption Studies.** The adsorption of aminopyridines on metal hexacyanoferrates(II) as a function of the pH and concentration of the adsorbate was observed by adding 10 ml of a buffer aminopyridine solution to 0.1 g of metal hexacyanoferrates(II) each time. The buffers used to maintain the pH (4.0—5.5) were acetate buffer (0.2 M acetic acid and 0.2 M sodium acetate) and borax buffer (0.2 M boric acid and 0.05 M borax) for pH 7.0—8.5. The suspension was shaken using an Expo shaker initially for one hour, and was then allowed to equilibrate at 30 °C with intermittent shaking at fixed time intervals. The suspensions were centrifuged after 6 h. The supernatant liquid was decanted and the pH of the solution was again noted on a pH meter (model CP-90P), and was found to be unaltered. The aminopyridines concentration was determined spectrophotometrically. The amount of aminopyridines adsorbed was calculated from the difference between the aminopyridine concentrations before and after adsorption. The equilibrium concentration of aminopyridine and the amount adsorbed were used to obtain adsorption isotherms.

It was found that the species of buffer used did not become adsorbed on metal hexacyanoferrates(II). This was checked by conductivity measurements.

**5. Surface Area Measurement.** The B.E.T. method was used to determine the surface areas of metal hexacyanoferrates(II). In this technique, the surface area is determined by the physical adsorption of gases at their boiling temperatures. The calculated values of the surface areas are 412.4 and 444.7 $m^2\,g^{-1}$ in the case of zinc and copper hexacyanoferrates(II), respectively.

## Results and Discussion

A wide range of pH (4.0—9.0) was selected for preliminary adsorption sutdies of aminopyridines on zinc and copper hexacyanoferrates(II). All three aminopyridines (2-amino-, 3-amino-, and 4-aminopyridines) showed maximum adsorption at neutral pH (7.0) on both zinc and copper hexacyanoferrates(II). Therefore, subsequent studies were performed at only pH 7.0. The effect of pH on the adsorption of aminopyridines is shown in Figs. 1 and 2.

Dolezal and Kourim[26] have reported a general formula of metal hexacyanoferrates(II) as $M_2[Fe(CN)_6]$, where M represents a transition metal ion. The $M^{2+}$ ions are exchangeable divalent cations, which in our case are $Zn^{2+}$ and $Cu^{2+}$. Species $[Fe(CN)_6]^{4-}$ in metal hexacyanoferrates(II) exist with an octahedral geometry, where six $CN^-$ ligands surround the central iron atom.[27] Due to the strong field of the $CN^-$ ligands, all six electrons become paired to give the electronic configuration $t_{2g}^6$. Although the $CN^-$ ligands bond with Fe via σ-donation, there is sufficient back bonding from iron metal dπ orbitals to the $CN^-$ ligand antibonding pπ orbitals. Transition-metal hexacyanoferrates(II) complexes usually have a polymeric lattice structure with $[Fe(CN)_6]^{4-}$ anions, where the outer transition-metal ions may be coordinated through the nitrogen end of the cyanide ligand. As proposed earlier concerning on the adsorption of several biomolecules on different metal hexacyanoferrates(II), the adsorption of aminopyridines on metal hexacyanoferrates(II) is probably due to an aminopyridine interaction with the replaceable divalent metal ions present outside of the coordination sphere of the hexacyanoferrates(II).

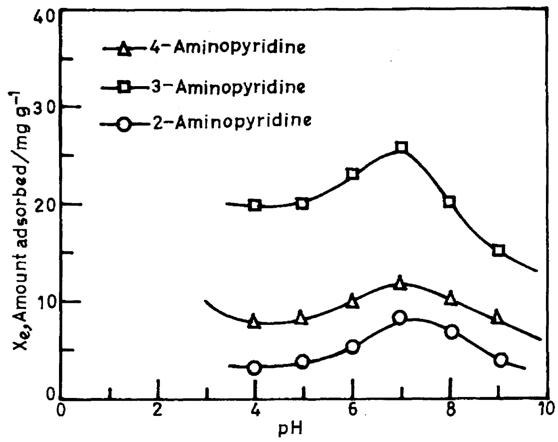

Fig. 1. Adsorption of aminopyridines on copper hexacyanoferrate(II) as a function of pH, Temp = 27 °C.

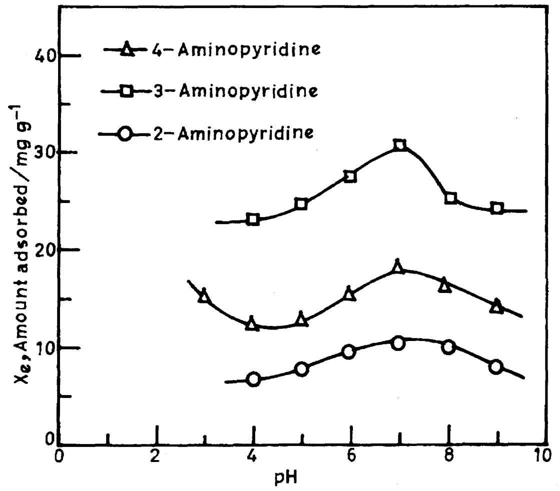

Fig. 2. Adsorption of aminopyridines on zinc hexacyanoferrate(II) as a function of pH, Temp = 27 °C.

It appears that in an acidic medium the lone pair of electrons on either of two nitrogen atoms of aminopyridine are not free, and poor adsorption takes place. The poor adsorption may be due to protonation of the nitrogen atoms. The decrease in the adsorption of aminopyridines on zinc and copper hexacyanoferrates(II) observed at higher pH (i.e. pH > 7.0) may be because coordination of the available $OH^-$ ions in the reaction medium becomes competitive with that of the aminopyridine molecules.

Adsorption isotherms were obtained at pH 7.0 by varying the concentration of the adsorbate ($1.0\times10^{-4}$—$10\times10^{-4}$ M). The thus-obtained adsorption isotherms are shown in Figs. 3, 4, and 5. The asymptotic nature of the curves suggests Langmuir-type adsorption. At higher concentrations of the adsorbate, a saturation limit of the metal hexacya-

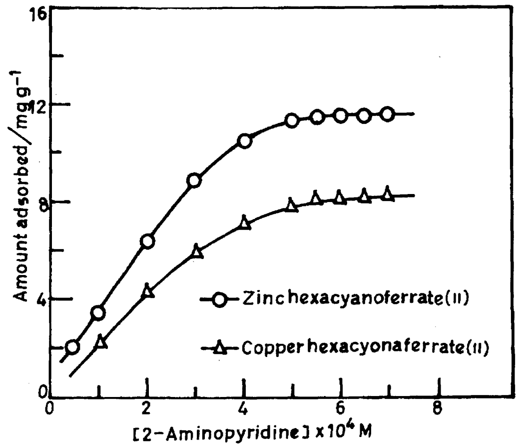

Fig. 3. Adsorption isotherms of 2-aminopyridine on metal hexacyanoferrates(II), pH = 7.0; Temp = 27 °C.

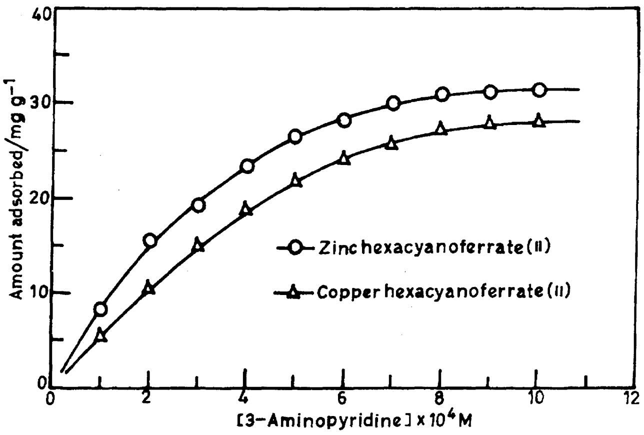

Fig. 4. Adsorption isotherms of 3-aminopyridine on metal hexacyanoferrates(II), pH = 7.0; Temp = 27 °C.

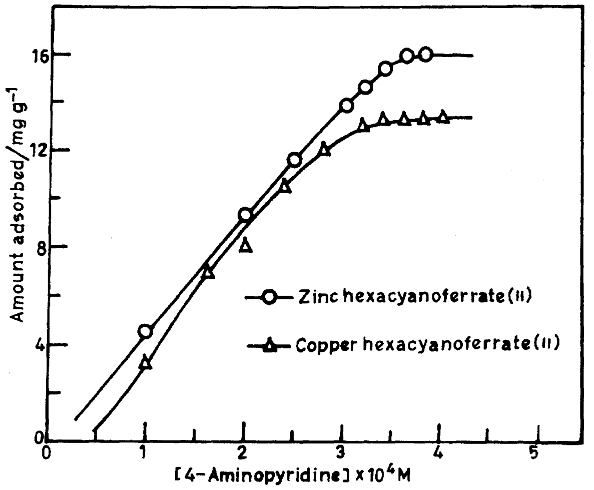

Fig. 5. Adsorption isotherms of 4-aminopyridine on metal hexacyanoferrates(II), pH = 7.0; Temp = 27 °C.

noferrates(II) was observed, i.e. as the equilibrium concentration ($C_{eq}$) increases, the amount adsorbed $X_e$ approaches that corresponding to complete monolayer formation, i.e. $X_m$ asymptotically. The adsorption data can be represented through a Langmuir adsorption isotherm which assumes the formation of a monolayer of solute molecules on the surface of the adsorbent, as given by

$$\frac{C_{eq}}{X_e} = \frac{1}{K_L X_m} + \frac{C_{eq}}{X_m},$$

or

$$\frac{1}{X_e} = \left(\frac{1}{C_{eq}}\right)\left(\frac{1}{K_L X_m}\right) + \frac{1}{X_m},$$

where $X_e$ is the amount of solute adsorbed per gram of adsorbent, $C_{eq}$ the equilibrium concentration of the solute, $X_m$ the moles of solute required per gram of weight of metal hexacyanoferrates(II) for the formation of a complete monolayer on the surface, and $K_L$ a constant related to the heat of adsorption or enthalpy.

The values of $X_m$ and $K_L$ were obtained and are given in Table 1. From the trend of the $X_m$ values, it is clear that the adsorption of aminopyridines follows the pattern

3-Aminopyridine > 4-Aminopyridine > 2-Aminopyridine.

The observed trend may also be related to the basicities of the aminopyridines. The p$K_a$ values of 4-amino-, 3-amino-, and 2-aminopyridines are 9.1, 6.6, and 7.2, respectively, showing that 4-aminopyridine is the strongest base in the series.[28]

From the resonating structure,[28] it is clear that 4-amino- and 2-aminopyridines, are more basic than 3-aminopyridine, and the availability of electrons for binding with metal hexacyanoferrates(II) is more in strong bases. However, the uptake of 3-aminopyridine is more for both metal hexacyanoferrates(II), despite the fact that 4-amino- and 2-aminopyridines are stronger bases compared to 3-aminopyridine. This is because one more adsorption site is available in the case of 3-aminopyridine: one hetero atom and another amino group. The lone pair of electrons on the amino group is not easily available for an interaction in the case of 2-amino-, and 4-aminopyridines, due to the contribution from the structures shown in Figs. 6(b) and 7(b), respectively. An alternate explanation for the lower binding of 2-aminopyridine on metal hexacyanoferrates(II) could be intramolecular hydrogen bonding.

Efforts to extract the adsorbed aminopyridines from metal hexacyanoferrates(II) either with 0.1 M $NH_4Cl$ or 0.1 M

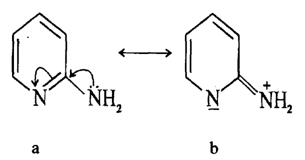

Fig. 6.

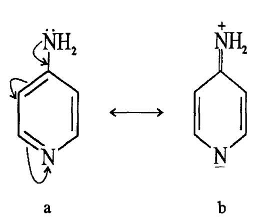

Fig. 7.

Table 1. Langmuir Constants for the Adsorption of Aminopyridines on Metal Hexacyanoferrates(II)

| Aminopyridines | Copper hexacyanoferrate(II) | | Zinc hexacyanoferrate(II) | |
|---|---|---|---|---|
| | $K_L$ (dm$^3$ mol$^{-1}$) | $X_m$ (mg g$^{-1}$) | $K_L$(dm$^3$ mol$^{-1}$) | $X_m$(mg g$^{-1}$) |
| 2-Aminopyridine | $3.5\times10^4$ | 8.1 | $8.5\times10^4$ | 11.9 |
| 3-Aminopyridine | $0.7\times10^4$ | 27.8 | $2.1\times10^4$ | 31.7 |
| 4-Aminopyridine | $23.5\times10^4$ | 12.9 | $130.5\times10^4$ | 16.4 |

aqueous ammonia gave negligible desorption. This shows that the aminopyridines are strongly bound to metal hexacyanoferrates(II). The interaction of aminopyridines with divalent metals in the framework of metal hexacyanoferrates(II) is suggested by the change in the IR characteristic frequencies of aminopyridines after adsorption. The insertion of aminopyridines in the inner coordination sphere of metal hexacyanoferrates(II) seems to be quite improbable, because aminopyridine can not replace a strong ligand, such as CN$^-$; the replacement of a cyanide by other strong ligands is found to occur only under UV light.[29] Only a negligible change in the infrared frequencies ($\nu_{\mathrm{C\equiv N}}$, $\delta_{\mathrm{Fe-CN}}$, and $\nu_{\mathrm{Fe-C}}$) is observed after adsorption (Tables 2 and 3). In view of this fact, the adsorption of aminopyridines on metal hexacyanoferrates(II) must be thought to have occurred through interactions between the aminopyridine and divalent metal ions (Zn$^{2+}$, Cu$^{2+}$) held in the lattice of the respective metal hexacyanoferrates(II). The hetero atom of the ring or the amino group in aminopyridines can provide a lone pair of electrons for interactions with metal ions.

Metal hexacyanoferrates(II) with adsorbed aminopyridines were washed with water and dried. The infrared spectra for all of the metal hexacyanoferrates(II) before and after adsorption were recorded and analyzed. The results are given in Tables 2 and 3 and Figs. 8, 9, and 10. In the case of 2-aminopyridine, the N–H and C–N stretching bands are

Table 2. Typical Infrared Spectral Frequencies (cm$^{-1}$) of Aminopyridine and Copper Hexacyanoferrate(II) before and after Adsorption[a)]

| Aminopyridines | Aminopyridine frequencies | | | | Copper hexacyanoferrate(II) frequencies | | |
|---|---|---|---|---|---|---|---|
| | Ring stretching frequencies | Amino group frequencies | | | | | |
| | | $\nu_{\mathrm{N-H}}$ | $\delta_{\mathrm{N-H}}$ | $\nu_{\mathrm{C-N}}$ | $\nu_{\mathrm{C\equiv N}}$ | $\delta_{\mathrm{Fe-CN}}$ | $\nu_{\mathrm{Fe-C}}$ |
| 2-Aminopyridine | 1412(1487) | 3472 | 1617 | 1323 | 2098 | 602 | 486 |
| | (1442) | (3471) | (1617) | (1321) | (2097) | (601) | (485) |
| | | (3398) | | | | | |
| 3-Aminopyridine | 1362(1586) | 3363 | 1615 | — | 2099 | 603 | 487 |
| | (1486) | (3380) | (1634) | (1316) | (2097) | (601) | (485) |
| | (1436) | (3333) | | | | | |
| 4-Aminopyridine | 1414(1594) | 3448 | — | (1334) | 2100 | 601 | 485 |
| | (1468) | (3434) | | | (2097) | (601) | (485) |
| | | (3390) | | | | | |

a) Bracket values show the frequencies before adsorption.

Table 3. Typical Infrared Spectral Frequencies (cm$^{-1}$) of Aminopyridine and Zinc Hexacyanoferrate(II) before and after Adsorption[a)]

| Aminopyridines | Aminopyridine frequencies | | | | Zinc hexacyanoferrate(II) frequencies | | |
|---|---|---|---|---|---|---|---|
| | Ring stretching frequencies | Amino group frequencies | | | | | |
| | | $\nu_{\mathrm{N-H}}$ | $\delta_{\mathrm{N-H}}$ | $\nu_{\mathrm{C-N}}$ | $\nu_{\mathrm{C\equiv N}}$ | $\delta_{\mathrm{Fe-CN}}$ | $\nu_{\mathrm{Fe-C}}$ |
| 2-Aminopyridine | 1410(1487) | 3474 | 1616 | 1325 | 2081 | 590 | 495 |
| | (1442) | (3471) | (1617) | (1321) | (2078) | (590) | (494) |
| | | (3398) | | | | | |
| 3-Aminopyridine | 1390(1586) | 3410 | 1620 | — | 2080 | 592 | 495 |
| | (1486) | (3380) | (1634) | (1316) | (2078) | (590) | (494) |
| | (1436) | (3333) | | | | | |
| 4-Aminopyridine | 1399(1594) | 3447 | — | 1373 | 2079 | 590 | 494 |
| | (1468) | (3434) | | (1334) | (2078) | (590) | (494) |
| | | (3390) | | | | | |

a) Bracket values show the frequencies before adsorption.

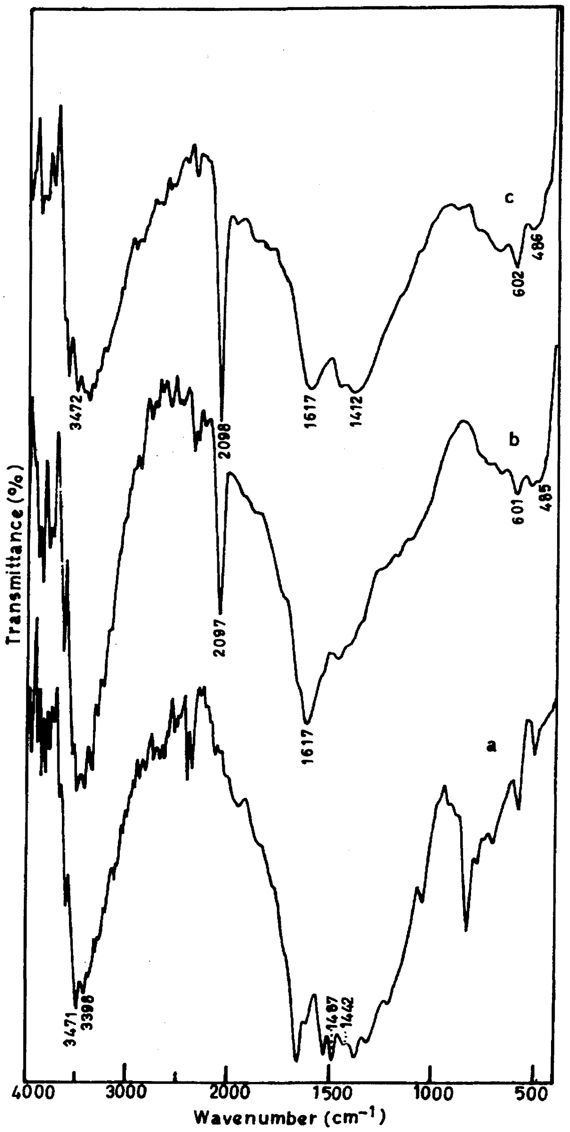

Fig. 8. Infrared Spectra of (a) 2-Aminopyridine, (b) Copper hexacyanoferrate(II), (c) Adsorption adduct of 2-Aminopyridine and copper hexacyanoferrate(II).

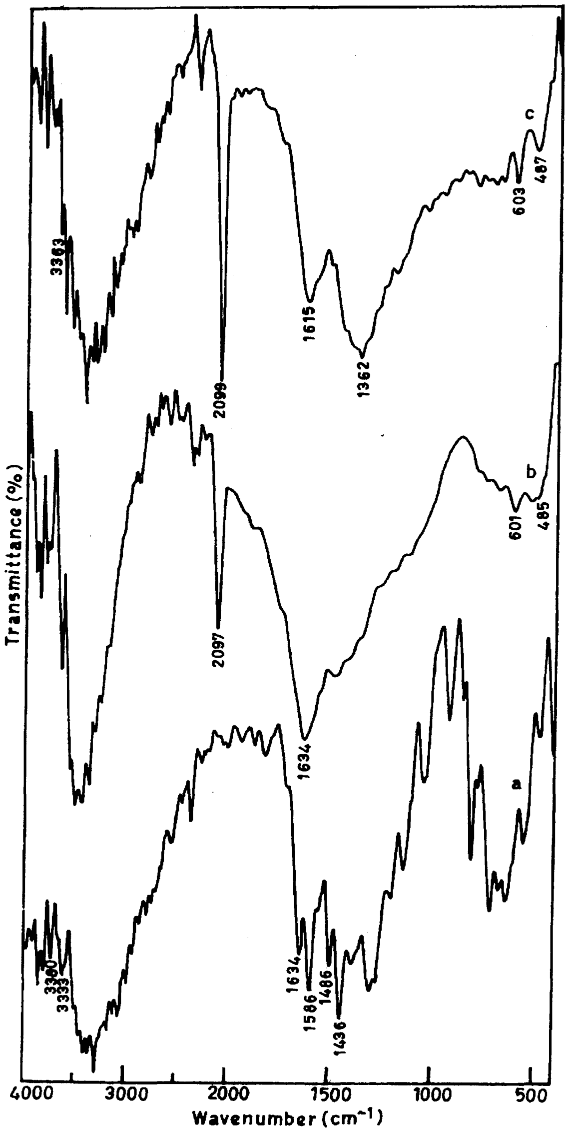

Fig. 9. Infrared Spectra of (a) 3-Aminopyridine, (b) Copper hexacyanoferrate(II), (c) Adsorption adduct of 3-Aminopyridine and copper hexacyanoferrate(II).

not at all changed after adsorption. The ring-stretching frequencies are drastically changed, and merge into a single sharp band at 1412 and 1410 cm$^{-1}$ in the case of copper and zinc hexacyanoferrates(II), respectively. This indicates that the interaction of 2-aminopyridine with hexacyanoferrates(II) takes place only through the ring, and not through the $-NH_2$ group. This may be due to the fact that the electron density on the $-NH_2$ group is the least in this case, because of intramolecular hydrogen bonding and due to a resonance hybrid structure involving the structure in Fig. 6b.[28]

In the case of metal hexacyanoferrates(II) with adsorbed 3-aminopyridine, a pronounced change was observed in the characteristic frequencies of the $-NH_2$ group as well as the ring-stretching frequencies. The $\nu_{N-H}$ stretching frequencies are shifted by 20—30 cm$^{-1}$, whereas the $\delta_{N-H}$ deformation band is also shifted by 10—15 cm$^{-1}$. $\nu_{C-N}$ at 1316 cm$^{-1}$ disappeared in the case of copper and zinc hexacyanoferrates(II) due to overlapping with the ring-stretching band. The ring-stretching frequencies also disappear in the spectra, and a new sharp well-defined and intense band was found at 1362 and 1390 cm$^{-1}$ in the case of copper and zinc hexacyanoferrates(II), respectively. The above observations suggest that the interaction of metal hexacyanoferrates(II) with 3-aminopyridine occurs through both the amino group and the ring.

The infrared spectra of metal hexacyanoferrates(II) before and after the adsorption of 4-aminopyridine showed that the $\nu_{N-H}$ stretching and $\delta_{N-H}$ bending vibrations are changed only slightly. The $\nu_{C-N}$ band overlapped with the ring band. The characteristic ring-stretching frequencies of free aminopyridine disappeared after the interaction, and a new intense sharp peak in the range of 1399—1415 cm$^{-1}$ was observed.

The above-mentioned analysis of the infrared spectra suggests that the modes of the interaction of metal hexacyano-

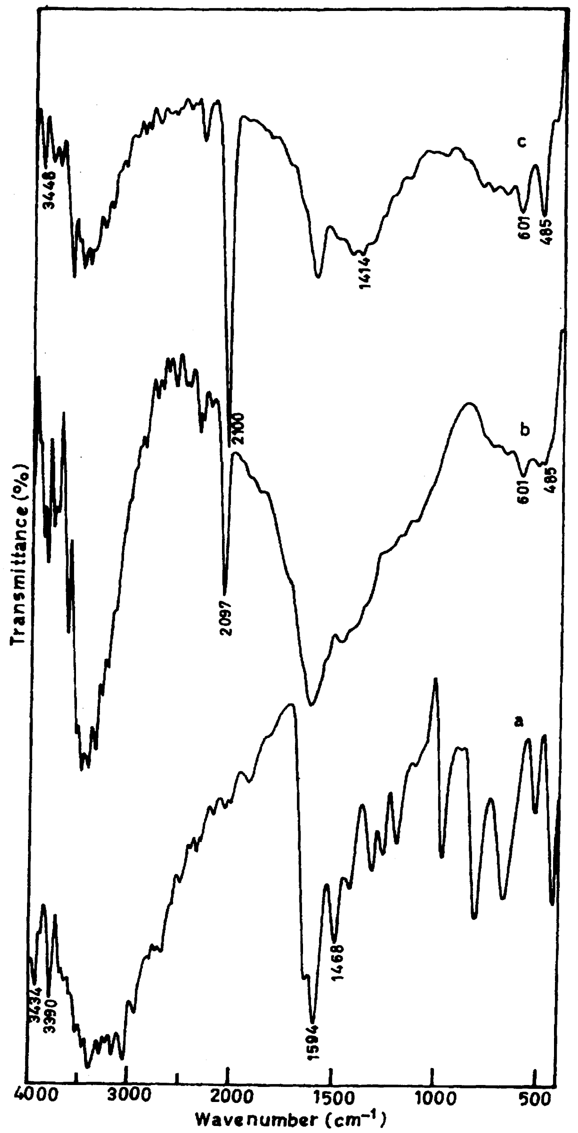

Fig. 10. Infrared Spectra of (a) 4-Aminopyridine, (b) Copper hexacyanoferrate(II), (c) Adsorption adduct of 4-Aminopyridine and copper hexacyanoferrate(II).

ferrates(II) with the hetero atom of the ring of 2-amino-, and 4-aminopyridines are similar. The characteristic bands of the pyridine ring disappeared and a new well-defined, intense, sharp band was observed. In the case of 3-aminopyridine, an interaction through the ring as well as the amino group nitrogen seems to be indicated.

Minor shifts were also observed in the characteristic frequencies of metal hexacyanoferrates(II) due to the adsorption of aminopyridines. There is a change in the $\nu_{C\equiv N}$ band by 1—4 $cm^{-1}$; the $\delta_{Fe-CN}$ and $\nu_{Fe-C}$ bands also shifted by 1—6 $cm^{-1}$. On the basis of the above results we infer that the interaction of aminopyridines occurs through the coordination of either of the nitrogen atoms with the outer metal ion of the metal hexacyanoferrates(II).

## Conclusion

In view of our present and earlier work,[21—23] we have suggested that different metal hexacyanoferrates(II) present on the primitive earth might have played a crucial role in the course of chemical evolution. Metal hexacyanoferrates(II) might have interacted with several important biomolecules in order to protect them from degradation and thus allowing them further reactions. A definite conclusion with respect to the exact binding sites of the metal hexacyanoferrates(II) and adsorbate molecules can not be concluded strictly on the basis of the infrared spectral data due to the overlapping of a large number of frequencies. Nevertheless, probable coordination sites could be proposed, as discussed.

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