

# Preparation & Characterization of Some Mixed Ligand Complexes of Fe(II) & Fe(III)

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Solutions of Fe(II) and (III) react with glycine and *I*-histidine in the presence of KCN to give the following mixed ligand complexes:  $[\text{Fe}^{\text{III}}(\text{CN})_3(\text{NH}_2\text{CH}_2\text{COOH})_3]$ ;  $\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{NH}_2\text{CH}_2\text{COO})]$ ;  $\text{K}[\text{Fe}^{\text{III}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2]$ ;  $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2]$ ;  $\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{Histidine})]$ ;  $\text{K}_3[\text{Fe}^{\text{II}}(\text{CN})_4(\text{histidine})]$ . The complexes have been characterized by chemical analysis, magnetic measurements and IR, Mössbauer, UV and visible spectral data.

POTASSIUM hexacyanoferrate(II) undergoes substitution reactions with strong donor groups<sup>1,2</sup> like OH<sup>-</sup>. However, recently Malik *et al.*<sup>3-5</sup> observed that aminoacids, which have weaker donor power, also substitute cyano groups in potassium hexacyanoferrate(II) on irradiation with UV light. These studies have now been extended to the preparation and characterization of some mixed ligand complexes of Fe(II) and (III) with KCN and glycine and histidine.

Solutions of ferric ammonium sulphate, ferrous ammonium sulphate and KCN (all Analar grade, BDH) were prepared in doubly distilled water and standardized as usual<sup>6</sup>. Glycine and histidine (BDH products) were tested for their purity by paper chromatography. Their solutions were prepared by dissolving weighed amounts in doubly distilled water or KOH-borax buffer<sup>7</sup> of pH 10.

Spectrophotometric measurements were carried out on Unicam SP 500 spectrophotometer using matched silica cells of 10 mm path length. A bench type Cambridge pH meter with a glass-SCE electrode assembly was used for pH measurements. Conductance measurements were made on a Toshniwal (India) conductivity bridge, type CLOI/OIA.

Magnetic measurements were carried out at room temperature ( $30^\circ \pm 1^\circ$ ) by Guoy's method. The relative precision of the magnetic susceptibility values after applying the diamagnetic correction was 1-3%. The IR spectra were recorded in KBr discs using Beckman IR20 spectrophotometer. Mössbauer spectra of the complexes were recorded on a Mössbauer spectrometer MBS 35 (ECL, Hyderabad). It consisted of a single channel analyser and an electronic linear velocity loud speaker drive using a 3 mCi/<sup>57</sup>Co source in copper matrix. The spectrometer was calibrated against standard sodium nitroprusside and iron foil. The counting was carried out for 200 sec at each channel and the spectra recorded in triplicate at  $20^\circ \pm 1^\circ$ .

The complexes were identified by determining their composition spectrophotometrically and by chemical analysis. The modified continuous variation method used by Schill<sup>8,9</sup> and others<sup>10,11</sup>, for three component systems, was adopted to determine the composition of the complexes in solution. Solid complexes were analysed (Table 1). Iron was estimated spectrophotometrically using 1, 10-phenanthroline<sup>6</sup> after decomposing the complexes by boiling with hydrochloric acid.

TABLE 1 — CHEMICAL ANALYSIS AND MAGNETIC DATA OF THE MIXED LIGAND COMPLEXES

Complex	Formula	H <sub>2</sub> O (%)	Fe (%)	N (%)	C (%)	μ <sub>eff</sub> (BM)
I	$[\text{Fe}^{\text{III}}(\text{CN})_3(\text{NH}_2\text{CH}_2\text{COOH})_3]$	* ( —	15.59 15.44	23.39 23.11	30.08)* 29.93	5.61
II	$\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{NH}_2\text{CH}_2\text{COO})] \cdot 2\text{H}_2\text{O}$	(10.34 10.00	16.09 16.34	20.11 20.46	20.68) 20.17	2.42
III	$\text{K}[\text{Fe}^{\text{III}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$	(10.87 10.58	16.91 16.70	16.91 16.68	21.75) 21.51	5.74
IV	$\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$	(9.72 9.51	15.13 15.00	15.13 15.34	19.45) 19.11	4.72
V	$\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$	(8.41 8.13	13.08 13.41	22.89 22.46	28.03) 27.69	2.39
VI	$\text{K}_3[\text{Fe}^{\text{II}}(\text{CN})_4(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)] \cdot 2\text{H}_2\text{O}$	(7.70 7.34	11.99 11.34	20.98 20.51	25.69) 25.11	0.56

\*Calculated values are given in parentheses.

*Preparation of the complexes*—The complexes were prepared using the stoichiometric ratios of the reactants. In the case of Fe(III) complexes, on adding an excess of absolute ethyl alcohol an oily layer separated out on standing for about 10 min which was triturated several times with absolute ethyl alcohol to give a fine powder. The complex was recrystallized from ice cold water using absolute ethyl alcohol. The recrystallized product was washed with ether and dried in vacuum over anhydrous calcium chloride.

The Fe(II) complexes were isolated by the addition of 1:1 acetone-alcohol mixture and allowing the solutions to stand for 30 min. The product was recrystallized from ice cold water using 1:1 acetone-alcohol mixture, washed with alcohol, ether and finally dried over anhydrous calcium chloride.

The following complexes have been prepared:

(a) *Tricyano-tris(glycine)ferrate (III)*—A red complex was obtained on adding ferric ammonium sulphate to a solution of glycine (pH ~5.5). It analysed for  $[\text{Fe}^{\text{III}}(\text{NH}_2\text{CH}_2\text{COOH})_6]_2(\text{SO}_4)_3$ . This complex on treatment with a conc. solution of KCN (in equivalent amounts, i.e. 1 mole of the complex for 3 moles of KCN) gave a deep red coloured compound whose spectrum showed a strong absorption band at 520 nm. It was found to be a 1:3 complex, and analysed for  $[\text{Fe}^{\text{III}}(\text{CN})_3(\text{NH}_2\text{CH}_2\text{COOH})_3]$ .

(b) *Tetracyano(glycinato)ferrate (III)*— $[\text{Fe}^{\text{III}}(\text{NH}_2\text{CH}_2\text{COOH})_6]_2(\text{SO}_4)_3$  on treatment with an excess of conc. solution of KCN gave a pink coloured solution with a strong absorption band at 620 nm. A similar product with a strong absorption band at 620 nm was obtained on adding a mixture of KCN and glycine (pH 10) to a solution of ferric ammonium sulphate. Initially the reaction mixture was yellow but changed to red and finally pink on standing for about 10 min. The pink complex was found to be  $\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$ .

(c) *Dicyano-bis(glycinato)ferrate (III)*—A mixture of glycine and ferric ammonium sulphate solution on heating for 10 hr on a boiling water-bath gave a yellowish brown insoluble precipitate. The reaction was accompanied by a decrease in pH from 5.5 to 1.5. Elemental analysis showed the product to be  $[\text{Fe}^{\text{III}}(\text{NH}_2\text{CH}_2\text{COO})_3]$ . When this complex was heated with a conc. solution of KCN on a water-bath for 3 hr, a yellow solution with an absorption maxima at 335 nm. The solid obtained analysed for  $\text{K}[\text{Fe}^{\text{III}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$ .

(d) *Dicyano-bis(glycinato)ferrate (II)*—Dropwise addition (with shaking) of a solution of ferrous ammonium sulphate to a mixture of KCN and glycine (pH 10.0) gave a yellow solution with an absorption maxima at 345 nm. A 1:2 complex corresponding to  $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_2(\text{NH}_2\text{CH}_2\text{COO})_2] \cdot 2\text{H}_2\text{O}$  was obtained.

(e) *Tetracyano(histidinato)ferrate (III)*—A light yellow coloured solution, having an absorption maxima at 295 nm was obtained on dropwise addition, with shaking, of ferric ammonium sulphate to a mixture of KCN and histidine (pH 10.0). A 1:1 complex corresponding to  $\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{histidinato})] \cdot 2\text{H}_2\text{O}$  was formed.

(f) *Tetracyano(histidinato)ferrate (II)*—A yellow coloured solution, with an absorption band at 415

nm was obtained on dropwise addition, with shaking, of ferrous ammonium sulphate solution to a mixture of KCN and histidine solutions (pH 10.0). A 1:1 complex corresponding to  $\text{K}_2[\text{Fe}^{\text{II}}(\text{CN})_4(\text{histidinato})] \cdot 2\text{H}_2\text{O}$  was formed.

## Results and Discussion

*Magnetic properties*—The magnetic susceptibilities of the various complexes are given in Table 1. The complexes obtained from Fe(III) are paramagnetic. The magnetic susceptibilities of complexes I and III show that both are spin-free<sup>12</sup>. Complex (IV) is also a spin-free complex showing 4 unpaired electrons. This behaviour is understandable considering weak donor power of the amino acids. The effective magnetic moments of the other two Fe(III) complexes lie between 2.3 and 2.5 which are well within the range 2.0-2.5 reported for Fe(III) spin-paired complexes<sup>13,14</sup>.  $\text{K}_2[\text{Fe}^{\text{III}}(\text{CN})_4(\text{histidinato})]$  is diamagnetic and hence a spin-paired complex. In these three complexes, the 4 CN<sup>-</sup> groups provide a sufficiently strong ligand field for spin-pairing.

*Infrared spectra* ( $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ )—All the complexes, except  $[\text{Fe}^{\text{III}}(\text{CN})_3(\text{glycine})_3]$ , show a broad band around 3500 corresponding to lattice water. Glycine and histidine show  $\nu\text{NH}_2$  around 3100. On coordination, this band disappears and the  $\text{NH}_2$  band appears around 3200 indicating that coordination has taken place through the amino group of the amino acid<sup>15</sup>. This is further supported by the shift<sup>16</sup> in the  $\nu\text{C}-\text{N}$  appearing at 1150. The appearance of the  $\nu_{\text{as}}\text{COO}^-$  around 1600 and the absence normal  $\nu\text{CO}$  of  $\text{COOH}$  group around 1700 provide further evidence that the amino acid is bound to iron through the carboxylic group<sup>17-19</sup>. That histidine is bidentate in these complexes is borne out by the fact that the  $\text{C}-\text{N}$  and  $\text{C}=\text{N}$  bands due to ring nitrogen do not show any shift<sup>16</sup>.

The characteristic  $\nu\text{C}\equiv\text{N}$  appears around 2000 and 2100 in Fe(II) and Fe(III) complexes respectively<sup>20</sup>. The strong band in the 610-640 region may be assigned to the  $\nu\text{Fe}-\text{C}$  and the one at 575 to  $\nu\text{Fe}-\text{N}$ <sup>15</sup>. The  $\nu\text{Fe}-\text{O}$  appears around 400 (ref. 21). The appearance of  $\nu\text{Fe}-\text{N}$  and  $\nu\text{Fe}-\text{O}$  suggests binding through  $\text{NH}_2$  and  $\text{COO}^-$  groups.

Unlike other complexes, in  $[\text{Fe}^{\text{III}}(\text{CN})_3(\text{glycine})_3]$ , the glycine molecule is monodentate and is bound to iron through the carbonyl oxygen of the carboxylic group. Similar complexes with cobalt and glycine<sup>22</sup> have also been prepared wherein cobalt is coordinated<sup>22-24</sup> to glycine through  $\text{COO}^-$  group. The IR spectrum of this complex spectra shows a strong band at 1665 which is assigned to the  $\nu\text{OCO}$  of the carboxylic group<sup>22</sup>. The  $\nu\text{Fe}-\text{O}$  appears at 400, while the  $\nu\text{Fe}-\text{N}$  band is absent. In addition, the  $\text{NH}_2$  group appears at 3300 the normal region for uncoordinated  $\text{NH}_2$  stretch and the  $\nu\text{C}-\text{N}$  stretching at 1130  $\text{cm}^{-1}$  does not show any shift.

*Mössbauer spectra*—The Mössbauer spectral data of the complexes is given in Table 2. The high spin character of the complexes I, III and IV (which contain only two CN<sup>-</sup> groups) as evidenced by the magnetic data is further supported by the high values of the Mössbauer isomer shift<sup>25,26</sup>. The low

TABLE 2 — UV, VISIBLE AND MOSSBAUER SPECTRAL DATA OF THE MIXED LIGAND COMPLEXES

Complex	Mossbauer		UV and visible		Assignment
	Isomer shift mm/sec	Quadrupole splitting mm/sec	nm	( $\epsilon$ )	
I	0.31	—	275	(1250)sh	$A_1 \rightarrow A_2$ (CT)
			320	(365)	$A_1 \rightarrow A_1$ (CT)
			520	(83)	$A_1 \rightarrow A_1$ (dd)
II	0.09	0.48	220	(22,250)	$A \rightarrow B$ (CT)
			330	(415)	$A \rightarrow A$ (CT)
			620	(92)	$A \rightarrow A$ (dd)
III	0.33	—	335	(425)	$A_g \rightarrow B_g$ (CT)
			415	(150)	$A_g \rightarrow {}^2A_g$ (CT)
IV	0.28	0.61	220	(20,670)	$A_g \rightarrow E_u$ (CT)
			345	(385)	$A_g \rightarrow A_g$ (dd)
			400	(170)	$A_g \rightarrow {}^2B_g$ (dd)
V	0.08	0.37	215	(20,250)	$A \rightarrow B$ (CT)
			295	(395)sh	$A \rightarrow A$ (CT)
			325	(380)	$A \rightarrow A$ (CT)
			360	(385)	$A \rightarrow A$ (CT)
VI	0.04	0.27	220	(21,500)	$A \rightarrow B$ (CT)
			300	(390)	$A \rightarrow A$ (dd)
			415	(160)	$A \rightarrow A$ (dd)

spin complexes II, V and VI (which contain 4 CN-groups) show low isomer shifts.

*Ultraviolet and visible spectra* — The ultraviolet and visible spectral characteristics of the complexes and their assignments are given in Table 2. In the case of  $K_3Fe(CN)_6$ , only one band at 550 nm has been assigned to ligand field, while all others are charge-transfer transitions<sup>27</sup>. Calculations by Naiman<sup>27</sup> showed that the expected ligand field bands are expected to occur in regions where they would be obscured by the more intense charge-transfer bands. All the transitions observed in the Fe(III) complexes, are therefore, assigned to charge-transfer, except the band at 520 nm for I and 620 nm for II. In the case of Fe(II) complexes a strong charge-transfer band appears at 220 nm while the two other transitions around 300 and 400 nm are assigned to *d-d* transitions<sup>28</sup>.

*Solubility of neutral tricyano-tris(glycine)ferrate (II)* — The complex  $[Fe^{III}(CN)_3(NH_2CH_2COOH)_3]$  could also be formulated as:  $[Fe^{III}(CN)_6][Fe^{III}(NH_2CH_2COOH)_6]$  and the two isomers cannot be differentiated either by analysis of IR spectra. Its molar conductivity ( $= 46.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ) suggests the presence of only one ion in solution, thereby ruling out its formulation as  $[Fe^{III}(CN)_6][Fe^{III}(NH_2CH_2COOH)_6]$  whose conductivity would be due to two ions.

The solubility of the complex in water appears to be related to the ability of the solvent to either associate through hydrogen bonding with the complex or to produce a charged species of the complex by hydrogen ion donation. The second possibility is more consistent with the conductivity data which shows the presence of only one ion in solution. The complex may act as an electrolyte due to the presence of the amino group which can be protonated easily.

*Configuration of the complexes* — A close examination of the IR spectrum of complex I shows that the Fe—C $\equiv$ N stretching observed at 640 does not show any splitting hence it has a meridional configuration.

Complexes III and IV show similar absorption spectra (with similar  $\epsilon$  values) and hence have similar configurations<sup>30</sup>. The IR spectra of these complexes shows that there is no splitting in the Fe—C $\equiv$ N band at 615 hence they are *trans*-isomers (*cis*-isomer shows greater multiplicity of peaks than the *trans*-form<sup>29,30</sup>).

## References

1. ASPERGER, S., *Trans. Faraday Soc.*, **28** (1952), 617.
2. ASPERGER, S., MURATI, I. & CUPAHIN, O., *J. chem. Soc.*, (1953), 1041.
3. MALIK, W. U. & ASLAM, M., *J. electroanal. Chem.*, **25** (1970), 147.
4. MALIK, W. U. & ASLAM, M., *J. Indian chem. Soc.*, **47** (1970), 736.
5. MALIK, W. U. & BEMBI, R., *Proc. XVIIth international conference on coordination chemistry, Dublin, 1974*, 3.41.
6. VOGEL, A. I., *A text book of quantitative inorganic analysis* (Longmans Green, London), 1968.
7. BRITTON, H. T. S., *Hydrogen ions*, Vol. 1 (Van Nostrand, Princeton), 1964.
8. SCHILT, A. A., *J. Am. chem. Soc.*, **79** (1957), 5421.
9. SCHILT, A. A., *J. Am. chem. Soc.*, **82** (1960), 3000.
10. SEGAL, L., JANASSEN, H. B. & REEVES, R. F., *J. Am. chem. Soc.*, **77** (1955), 2667; **78** (1956), 273.
11. EICHORN, G. L. & MARCHAND, N. D., *J. Am. chem. Soc.*, **78** (1956), 2688.
12. LEWIS, J. & WILKINS, R., *Modern coordination chemistry* (Interscience, New York), 1960.
13. KRONKHE, E., *Chem. Ber.*, **83** (1950), 35; **87** (1954), 1126; **88** (1955), 863.
14. KRONKHE, E. & VOGEL, I., *Chem. Ber.*, **86** (1953), 1132.
15. MALIK, W. U. & BEMBI, R., *Indian J. Chem.*, **14A** (1976), 211; **14A** (1976), 542.
16. MALIK, W. U., SHARMA, C. L., JAIN, M. C. & ASHRAF, Y., *J. inorg. nucl. Chem.*, **33** (1971), 4333.

17. MOTAKAITIS, R. J. & MARTELL, A. E., *Inorg. Chem.*, **13** (1974), 550.
18. LEGG, J. I. & NEAL, J. A., *Inorg. Chem.*, **12** (1973), 1805.
19. FISH, R. H., WINDLE, J. J., GARFIELD, W. & SCHNER, J. R., *Inorg. Chem.*, **12** (1973), 855.
20. NAKAMOTO, K., *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), 1962.
21. TEOTIA, M. P., RASTOGI, D. K. & MALIK, W. U., *Inorg. chim. Acta*, **7** (1973), 339.
22. BRUBAKER, G. R. & SCHAEFEV, D. P., *Inorg. Chem.*, **10** (1971), 811.
23. FUJITA, J., YASUI, J. & SHIMURA, Y., *Bull. chem. Soc., Japan*, **38** (1965), 654.
24. MARZILLI, L. G. & BUCKINGHAM, D. A., *Inorg. Chem.*, **6** (1967), 1042.
25. GOLDANSKII, V. I. & HERBER, R. H., *Chemical applications of mossbauer spectroscopy* (Academic Press, New York), 1968.
26. MALIK, W. U., BEMBI, R. & DWIVEDI, J. K., *J. Indian chem. Soc.*, **52** (1975), 1157.
27. NAIMAN, C. S., *J. chem. Phys.*, **35** (1961), 323.
28. JAFFE, H. H. & ORCHIN, M., *Theory and applications of ultraviolet spectroscopy* (John Wiley, New York), 1964.
29. NAKAMOTO, K., in *Coordination chemistry*, Vol. I, edited by A. E. Martell (Van Nostrand, New York), 1971.
30. BRASTED, R. C. & COOLEY, W. E., cited in *The chemistry of coordination compounds*, edited by J. C. Bailar, Jr (Reinhold, New York), 1956.