

Notes

Infrared & Mössbauer Spectral Studies on Organic Base Hydroferrocyanides

WAHID U. MALIK, RAMESH BEMBI & P. P. BHARGAVA

Department of Chemistry, University of Roorkee, Roorkee

Received 25 April 1975; accepted 4 October 1975

Organic bases and hydrogen hexacyanoferrate(II) react in ethanolic medium to give basic salts of the general formula $(\text{base-H})_x\text{H}_{4-x}[\text{Fe}(\text{CN})_6]_y\cdot z\text{H}_2\text{O}$, where $x=2, 3$ or 4 . The infrared spectral studies support the above protonated formulation. The appearance of doublet, triplet or quadruplet $\nu\text{C}\equiv\text{N}$ bands in the complexes has been explained on the basis of unsymmetrical hydrogen bonding which is supported by Mössbauer studies.

CUMMING¹ was the first to prepare hydroferrocyanides of aniline, pyridine, quinoline and dimethylaniline etc. Use of hydroferrocyanides as fungicides and bactericides has been recently reported². However, comprehensive studies regarding their structures have not been undertaken so far. In this paper the results of our studies on the infrared and Mössbauer spectra of these compounds are reported.

All the organic bases were BDH products and were purified by crystallization or distillation before use. $\text{K}_4\text{Fe}(\text{CN})_6$ was a BDH product (AR). Doubly distilled ethanol was used as solvent for the preparation of the complexes.

Preparation of the complexes — $\text{H}_4\text{Fe}(\text{CN})_6$ was prepared³ in the laboratory by treating $\text{K}_4\text{Fe}(\text{CN})_6$ with HCl and precipitating it as the etherate. A solution of 0.1M $\text{H}_4\text{Fe}(\text{CN})_6$ (20 ml) in ethanol was added to 20 ml of an ethanolic solution of 0.5M

organic base and the resultant solution further diluted to 50 ml with ethanol. Precipitation occurred immediately in majority of the cases, while it took about 15 min in other cases. In the case of methylamine, the precipitate appeared on dilution with ethanol to about 250 ml. The precipitate was filtered off, washed liberally with ethanol and finally with ether. The product was dried *in vacuo* over anhydrous calcium chloride. The entire process was carried out in the dark, since $\text{H}_4\text{Fe}(\text{CN})_6$ is light-sensitive. In the case of dimethylaniline and quinoline a slightly different procedure was adopted. An acidic solution of $\text{K}_4\text{Fe}(\text{CN})_6$ in water was added to a solution of the organic base in fairly concentrated HCl solution. The complex so formed was precipitated by the addition of excess HCl, filtered, washed with HCl, ethanol and finally with ether. The product was dried *in vacuo* over anhydrous calcium chloride.

The complexes were decomposed by prolonged boiling with a mixture (1:10) of concentrated HCl and HNO_3 . The solution was evaporated to dryness and the residue extracted with dilute H_2SO_4 . Iron in the resulting solution was estimated spectrophotometrically⁴ using 1,10-phenanthroline after reducing Fe(III) to Fe(II) with hydroxylamine hydrochloride.

Water of crystallization was determined by desiccation at 110°. Carbon and nitrogen were estimated by microanalytical methods.

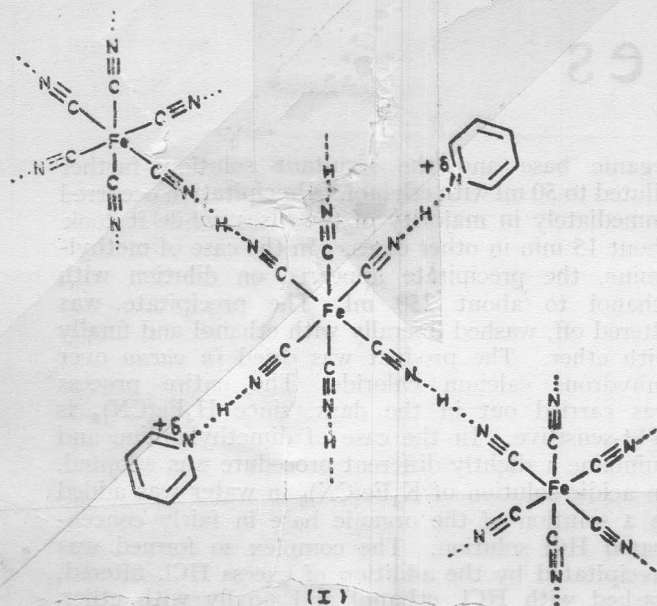
Magnetic measurements were carried out at room temperature (25°) using Gouy's method. IR spectra of the complexes were recorded in KBr on Beckmann IR 20 spectrophotometer. The Mössbauer spectra were recorded using a ⁵⁷Co source in Pd matrix with initial activity of 1 m Ci, and a linear velocity drive Mössbauer spectrometer

TABLE 1 — ANALYTICAL DATA OF THE ORGANIC BASE HYDROFERROCYANIDES*

Complex	Fe (%)		N (%)		C (%)		H (%)	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$\text{H}_4\text{Fe}(\text{CN})_6[\text{MeAn}]_2\cdot\text{H}_2\text{O}$	9.47	9.41	21.32	21.65	54.80	54.68	6.26	6.21
$\text{H}_4\text{Fe}(\text{CN})_6[\text{An}]_3\cdot 2\text{H}_2\text{O}$	10.54	10.62	23.73	23.62	54.24	54.13	5.46	5.50
$\text{H}_4\text{Fe}(\text{CN})_6[o\text{-Tol}]_2\cdot 2\text{H}_2\text{O}$	12.01	11.89	24.02	23.91	51.50	51.62	5.58	5.52
$\text{H}_4\text{Fe}(\text{CN})_6[\text{DiMeAn}]_2\cdot\text{H}_2\text{O}$	11.77	11.61	23.52	23.72	55.46	55.57	5.88	5.97
$\text{H}_4\text{Fe}(\text{CN})_6[\text{Py}]_2\cdot 2\text{H}_2\text{O}$	13.65	13.53	27.30	27.28	46.82	46.75	4.39	4.33
$\text{H}_4\text{Fe}(\text{CN})_6[\text{Qui}]_2\cdot 0.5\text{H}_2\text{O}$	11.59	11.76	23.18	23.03	59.65	59.52	3.93	4.01
$\text{H}_4\text{Fe}(\text{CN})_6[\text{MethoAn}]_2\cdot 2\text{H}_2\text{O}$	10.03	10.00	20.07	20.21	47.32	47.45	5.38	5.44
$\text{H}_4\text{Fe}(\text{CN})_6[\text{As}]_2\cdot\text{H}_2\text{O}$	11.66	11.52	23.23	23.01	50.00	50.11	5.00	4.95
$\text{H}_4\text{Fe}(\text{CN})_6[\text{HyQui}]_2\cdot 0.5\text{H}_2\text{O}$	10.87	10.71	21.75	21.96	55.91	55.79	3.69	3.77
$\text{H}_4\text{Fe}(\text{CN})_6[\text{MeAm}]_4\cdot 3\text{H}_2\text{O}$	14.21	14.36	35.53	35.42	30.46	30.59	7.61	7.51
$\text{H}_4\text{Fe}(\text{CN})_6[\text{AmPy}]_2\cdot 2\text{H}_2\text{O}$	12.73	12.62	31.81	31.70	43.63	43.72	4.54	4.46
$\text{H}_4\text{Fe}(\text{CN})_6[\text{DiPhAm}]_2\cdot\text{H}_2\text{O}$	9.79	9.91	19.51	19.58	62.95	62.82	4.90	4.81
$\text{H}_4\text{Fe}(\text{CN})_6[\text{Bz}]_2\cdot 2\text{H}_2\text{O}$	9.03	9.16	22.58	22.42	58.06	58.17	5.15	5.08
$\text{H}_4\text{Fe}(\text{CN})_6[\text{AmPl}]_2\cdot 2\text{H}_2\text{O}$	11.91	11.81	23.83	23.67	45.96	45.96	4.68	4.59
$\text{H}_4\text{Fe}(\text{CN})_6[\text{PhDiAm}]_2\cdot\text{H}_2\text{O}$	12.44	12.58	31.11	31.31	48.00	48.15	4.89	5.01

*Satisfactory analysis for water molecules was obtained.

MeAn = N-methylaniline; An = aniline; o-Tol = o-toluidine; DiMeAn = 2,5-dimethylaniline; Py = pyridine; Qui = quinoline; MethoAn = 2,5-dimethoxyaniline; As = p-anisidine; HyQui = 8-hydroxyquinoline; MeAm = methylamine; AmPy = 2-aminopyridine; DiPhAm = diphenylamine; Bz = benzidine; AmPl = p-aminophenol; and PhDiAm = p-phenylenediamine.



MBS 35 of E. C. India Ltd, Hyderabad. Sodium nitroprusside was used as the calibrant.

The analytical data conform to the general formulae, $(\text{base-H})_x\text{H}_{-1}[\text{Fe}(\text{CN})_6]_y\text{H}_2\text{O}$, where $x = 2, 3$ or 4 (Table 1). The complexes are diamagnetic in character.

The organic base hydroferrocyanides show the $\nu\text{C}\equiv\text{N}$ band around 2000 cm^{-1} . The splitting of $\nu\text{C}\equiv\text{N}$ band either as a doublet or a triplet may be explained on the basis of unsymmetrical hydrogen bonding⁵⁻⁷ between nitrogen of the cyano group and hydrogen of the protonated base as shown in structure (I). A similar explanation⁸⁻¹¹ has been given earlier for the appearance of a doublet in the case of $\text{H}_4\text{Fe}(\text{CN})_6$. Considering the typical case of the pyridine complex, two CN^- groups will be hydrogen bonded to the two organic base molecules, two CN^- groups will be hydrogen bonded to the hydrogen atoms of the complex itself (intramolecular hydrogen bonding) and the remaining two CN^- groups will be hydrogen bonded to the hydrogen atoms of surrounding hydroferrocyanide molecules (intramolecular hydrogen bonding). Although this predicts a triplet for the $\nu\text{C}\equiv\text{N}$ band, only a doublet is observed. This may be because of the very low difference between energies of the intermolecular and intramolecular hydrogen bonds in the present case. However, in complexes of bulky bases like benzidine and *p*-phenylenediamine etc. the $\nu\text{C}\equiv\text{N}$ appears as a triplet. The quadruplet splitting in aniline complex and methyl amine complex is due to the fact that three and four molecules respectively of the bases are involved in complex formation.

Infrared spectra also provide positive evidence for the protonation of the base in these complexes. An appreciable shift in the ring deformation and C—H deformation (in-plane) modes of vibrations in IR spectra support the protonation of the bases^{12,13}.

The other important infrared bands observed are in the regions $3200\text{--}3500\text{ cm}^{-1}$ and 1600 cm^{-1} due to water of hydration associated with the complex, and a band in the region $600\text{--}550\text{ cm}^{-1}$ due to $\nu\text{Fe—C}$.

TABLE 2 — MÖSSBAUER SPECTRAL DATA OF ORGANIC BASE HYDROFERROCYNANIDES

Ligand	Number of ligands	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)
Aniline	3	-0.150	—
Methyl amine	4	-0.149	0.042
<i>o</i> -Toluidine	2	-0.192	—
2,5-Dimethoxyaniline	2	-0.150	—
<i>p</i> -Anisidine	2	-0.147	0.066
2-Aminopyridine	2	-0.150	—
<i>p</i> -Aminophenol	2	-0.120	—
8-Hydroxyquinoline	2	-0.170	—
<i>p</i> -Phenylenediamine	2	-0.147	—
Diphenylamine	2	-0.120	—
Pyridine	2	-0.204	—
Dimethylaniline	2	-0.182	0.036
Quinoline	2	-0.186	—
$\text{K}_4\text{Fe}(\text{CN})_6$	—	-0.138	—
$\text{H}_4\text{Fe}(\text{CN})_6$	—	-0.136	0.23

The complexes of dimethylaniline, *p*-anisidine and methylamine show small quadrupole splittings (Table 2). A three dimensional model with four hydrogens strongly bonded than others in the crystal lattice¹¹ may be proposed for the present complexes. This asymmetry around the $\text{Fe}(\text{CN})_6^{4-}$ unit results in a net electric field gradient at the iron nucleus and hence a doublet is observed. The small magnitude of the quadrupole splitting indicates that the distortion is very minor. A similar behaviour has been observed¹¹ for $\text{H}_4\text{Fe}(\text{CN})_6$. Since the distortion of octahedral symmetry is very small, the absence of quadrupole splitting in other complexes may be due to low resolving power of the instrument.

The isomer shift decreases in the order: pyridine > *o*-toluidine > quinoline > dimethylaniline > 8-hydroxyquinoline > benzidine = 2,5 dimethylaniline > methylaniline > aniline = 2-aminopyridine = methylamine. The decrease in the isomer shift is in the order of their decreasing basic character. Since the isomer shift is influenced by the $4s$ electron density¹⁴ around the iron nucleus, such a behaviour is expected. Due to unsymmetrical hydrogen bonding, the base in the vicinity of the cyanide group will increase the electron density on the latter. This would decrease the extent of back donation from the t_{2g} orbitals of the iron to the vacant p_{π}^* antibonding orbitals of the cyano group, thereby changing the $4s$ electron density and hence the isomer shift.

References

- CUMMING, W. M., *J. chem. Soc.*, (1923), 2457.
- LAMB, G., *US Pat.* (to American Cyanamid Co.), 2,291,684 (Cl 167-23), Dec. 13, 1966; *Chem. Abstr.*, **66** (1967), 85071j.
- BRAUER, G., *Handbook of preparative inorganic chemistry*, Vol. 2 (Academic Press, London), 1965, 1509.
- VOGEL, A. I., *Text book of quantitative inorganic analysis* (Longmans, Green, London), 1961.
- EVANS, D. F., JONES, D. & WILKENSEN, G., *J. chem. Soc.*, (1964), 3164.
- BECK, W. & SMEDEL, H. S., *Nature*, **20** (1965), 109.
- GINSBERG, A. P. & KOUBECK, E., *Inorg. Chem.*, **4** (1965), 1186.
- PIEROTT, M. & KERN, R., *Acta Crystallogr.*, **17** (1964), 1612.
- VASTANOV, S. S., *Kristallografiya*, **1** (1956), 328.

10. PERIOTT, M., KERN, R. & WIESS, W., *Acta Crystallogr.*, **20** (1966), 425.
11. GARG, A. N. & GOEL, P. S., *J. inorg. nucl. Chem.*, **31** (1969), 697.
12. MITCHELL, P., *J. inorg. nucl. Chem.*, **21** (1961), 382.
13. GREENWOOD, N. N. & WADE, K., *J. chem. Soc.*, (1960) 1130.
14. BANCROFT, G. M., *Mössbauer spectroscopy for inorganic chemists and geochemists* (McGraw-Hill, New York), 1973.

Emission Spectra of Isomeric Trifluorotoluidines

M. R. PADHYE & S. A. AGNIHOTRY

Department of Chemical Technology, Matunga
Bombay 400019

Received 27 June 1975; accepted 25 August 1975

Fluorescence and phosphorescence spectra of isomeric trifluorotoluidines ($\text{CF}_3\text{C}_6\text{H}_4\text{NH}_2$) have been studied. The solution fluorescence at room temperature shows that the emission is maximum under neutral conditions and is reduced under acidic conditions. Under alkaline conditions, it gives an additional band on the longer wavelength due to the corresponding anions. At liquid nitrogen temperature, all the isomers show a strong phosphorescence in 450 nm region and relative quantum efficiencies of the two emissions vary in the three isomers.

CONSIDERABLE amount of work has been reported on the fluorescence spectra of aniline and its derivatives. Berlman¹ and McClure² has recently reviewed the fluorescence and effect of solvent on the fluorescence spectrum of aniline. It has been shown that the substitution at the amino group shifts the benzene fluorescence to longer wavelength side and enhances its intensity. This has been partly attributed to the contribution of the charge transfer states arising from the donor NH_2 group to the benzene π states. Near ultra-violet emission spectrum of aniline vapour in the region of 287 to 315 nm has been reported by Kahane-Pailous³. Similarly fluorescence of benzo-trifluoride vapour has been studied by Sastri and Sponer⁴. The emission characteristics of aniline when substituted by a strong electron withdrawing group like the CF_3 group has not been studied so far. The fluorescence spectra of isomeric trifluorotoluidines (TFT) at room temperature as well as the effect of solvent and pH on fluorescence have been studied and the results reported in this paper. The emission spectrum of TFT at low temperatures in solid glass has also been studied. The results are compared with those for aniline.

Fluorescence, phosphorescence and total emission spectra were recorded on an Aminco Bouman spectrofluorometer. Total emission at low temperature was studied in evacuated cylindrical cells without the phosphoscope attachment and the phosphorescence with the rotating cylinder phosphoscope attachment. The excitation and emission monochromator slits were 0.5 mm which were the narrowest possible. Excitation wavelength was set at the position where maximum emission is recorded.

The compounds obtained from Fluka, Switzerland, were used Spectragrade, cyclohexane, ethanol and distilled water were used to prepare the solutions after checking for solvent fluorescence. To study the effect of pH on luminescence properties, Analar H_2SO_4 and NaOH solutions were added to aqueous solutions of TFT in distilled water.

The absorption spectra of isomeric TFT in solution phase show two absorption maxima, one in the range 245-250 nm and the other near 290 nm. Solution fluorescence at room temperature of the three isomers lies in the range 310 to 410 nm and wavelengths of emission maxima are given in Table 1. It is observed that the fluorescence intensity is higher for the same solution when the excitation wavelength corresponds to the longer wavelength absorption region. It is observed that the wavelengths of the fluorescence maxima are in the order $m > o > p$ which is also the order of the longest wavelength absorption band.

It is known that solvents and pH bring about some changes in the fluorescence spectra which give some insight into the effect of substituents on the parent molecules as well as the nature of the excited state. The fluorescence spectra studied in different solvents at room temperature show that the wavelengths of the fluorescence maxima for all three isomers follow the order water > alcohol \approx cyclohexane. Solvent effect on the longest wavelength absorption, however, shows that for all the three isomers the maximum is at longest wavelength for ethanol and in water and cyclohexane, it is about the same. Thus the shift in the absorption and fluorescence maxima is largest in water. It is known that due to charge transfer contribution from the donor substituent like NH_2 to the first excited singlet state, the molecule in this state has a greater dipole moment than in the ground state. This gives a larger solute solvent interaction from the excited state and as such the Franck-Condon transition from the equilibrated excited state is expected to be at considerably longer wavelengths than the corresponding absorption. Mataga

TABLE 1 — SOLUTION FLUORESCENCE AND EMISSION MAXIMA OF ISOMERIC TFT IN DIFFERENT SOLVENTS

Solvent	Absorption maximum (nm)	Excitation maximum (nm)	Fluorescence maximum (nm)	Phosphorescence maximum (nm) in EPA glass at liquid N_2 temp.
<i>ortho</i> -TFT				
Alcohol	241, 298	298	338	425
Cyclohexane	236, 295	296	332	
Water	235, 294	298	350	
<i>meta</i> -TFT				
Alcohol	242, 299	302	340	430
Cyclohexane	238, 295	308	336	
Water	235, 290	294	352	
<i>para</i> -TFT				
Alcohol	252, 288	291	332	412
Cyclohexane	244, 286	282	324	
Water	237, 282	290	340	