# Mössbauer and Infrared Spectroscopic Studies of Some Alkyl- and Arylamine Coordinated Pentacyanoferrate(II) Complexes

Ratnakar Balkrishna LANJEWAR and Amar Nath GARG*
Department of Chemistry, Nagpur University, Nagpur 440010, India
(Received December 3, 1990)

Mössbauer spectra of alkyl- and arylamine coordinated pentacyanoferrate(II) complexes, $Na_3[Fe(CN)_5L]\cdot xH_2O$ where L=$(CH_3)_3N$, $(CH_3)_2CHNH_2$, $(CH_3)_2CHCH_2NH_2$, $(CH_3)_3C-NH_2$, $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$, $C_6H_5NHC_2H_5$, $o$-$ClC_6H_4NH_2$, and $p$-$ClC_6H_4NH_2$ have been studied. All compounds exhibit a well-resolved quadrupole doublet. An unusually high quadrupole splitting is observed for isobutylamine coordinated complex ($\Delta E_Q$=1.75 mm s$^{-1}$). Other complexes show $\Delta E_Q$=0.67—0.86 mm s$^{-1}$. A correlation of $\delta$ vs. $\Delta E_Q$ suggests a positive sign of electric field gradient for isobutylamine coordinated complex and negative for all other complexes. Partial isomer shift (p.i.s.) and $\delta$ have been correlated with partial quadrupole splitting (p.q.s.). Also characteristic CN and Fe–N stretching frequencies have been correlated with $\delta$ to derive information on $\sigma$-donor and $\pi$-acceptor properties of the ligands.

Mössbauer spectroscopic studies of coordinated pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{n-}$ where L= $H_2O$, $NH_3$, CO, $NO_2$, $SO_3^{2-}$, py, $NO^+$, DMSO, $RNH_2$, $R_3N$ etc. have been reported extensively.[1—14] In these studies main emphasis has been to know the extent of deformation in octahedral geometry and correlate isomer shift ($\delta$) with quadrupole splitting ($\Delta E_Q$) to predict the sign of electric field gradient (EFG). Also bonding characteristics with regard to $\sigma$-donor and $\pi$-acceptor properties of the ligands have been investigated.[8—10] In our earlier studies on mono-, di-, and trialkylamine coordinated pentacyanoferrates(II), it has been observed that though substituted alkylamines, ($R_nNH_{3-n}$) are primarily $\sigma$-donors but in some cases indirect $\pi$-interaction is also possible.[11] In the present studies we have synthesized some new pentacyanoferrate(II) complexes, $Na_3[Fe(CN)_5L]\cdot xH_2O$ where L=$(CH_3)_3N$, $(CH_3)_2CHNH_2$, $(CH_3)_2CHCH_2NH_2$, $(CH_3)_3C-NH_2$ $C_6H_5NHCH_3$, $C_6H_5N(CH_3)_2$, $C_6H_5NHC_2H_5$, $o$-$ClC_6H_4$-$NH_2$, and $p$-$ClC_6H_4NH_2$ and studied their Mössbauer and infrared spectra. We have also attempted to see the validity $\delta$ vs. $\Delta E_Q$ correlation in predicting the sign of EFG.

## Experimental

All reagents used were AR, GR (S. Merck) or of high purity grade (Koch-Light, UK and Fluka, Switzerland). Solvents were distilled and dried before use. The complexes were prepared by slightly modified procedure described in the literature.[15,16]

**Preparation of Trimethylamine, Isopropylamine, Isobutylamine, and *t*-Butylamine Coordinated Complexes:** Three gram of sodium pentacyanonitrosylferrate(II) (1 mol) and 2 g of sodium acetate were dissolved in 20 ml water and mixed with ice cold solution of the respective amine (20—25 ml) in ethanol. The solution was continuously stirred and additional amount of amine was added till a negative test for pentacyanonitrosylferrate(II) was obtained. The mixture was kept in freezing mixture for 2—4 h during which the complexes separated out.

**Preparation of Arylamine Coordinated Complexes:** In order to prepare these complexes, sodium amminepentacyanoferrate(II), $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ (SPF) was synthesized[16] which was used for further synthesis of arylamine coordinated complexes. Freshly prepared 3 g SPF (1 mol) was dissolved in 20 ml water, cooled and mixed with an ice cold solution of respective amine (20—25 ml). The solution was continuously stirred for 3—4 h. On addition of cold absolute ethanol

Table 1. Mössbauer Parameters and Characteristic IR Frequencies in Aminepentacyanoferrate(II) Complexes, $Na_3[Fe(CN)_5L)\cdot xH_2O$

| | Complex | Isomer shift[a] $\delta$/mm s$^{-1}$ | Quadrupole splitting[a] $\Delta E_Q$/mm s$^{-1}$ | p.i.s. mm s$^{-1}$ | p.q.s. mm s$^{-1}$ | $\nu$(CN) cm$^{-1}$ | $\delta$(Fe–CN) cm$^{-1}$ | $\nu$(Fe–N) cm$^{-1}$ | $\delta$(Fe–c) cm$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| I | $Na_3[Fe(CN)_5(CH_3)_3N]\cdot H_2O$ | 0.27 | 0.78 | 0.06 | −0.45 | 2025s | 570s | 225w | 410w |
| II | $Na_3[Fe(CN)_5(i\text{-}PrNH_2)]\cdot H_2O$ | 0.24 | 0.76 | 0.03 | −0.46 | 2060s | 560m | 310w | 450m |
| III | $Na_3[Fe(CN)_5(i\text{-}BuNH_2)]\cdot 3H_2O$ | −0.04 | 1.75 | −0.25 | 0.04 | 2140s 1950s | 540s | 315w | 410w |
| IV | $Na_3[Fe(CN)_5(t\text{-}BuNH_2)]\cdot H_2O$ | 0.23 | 0.86 | 0.02 | −0.41 | 2060s | 580m | 240w | 430m |
| V | $Na_3[Fe(CN)_5(PhNH_2)]\cdot 2H_2O$ | 0.28 | 0.74 | 0.07 | −0.47 | 2040s | 570s | 280w | 400w |
| VI | $Na_3[Fe(CN)_5(PhNHCH_3)]\cdot H_2O$ | 0.29 | 0.69 | 0.08 | −0.50 | 2040s | 570m | 260w | 410w |
| VII | $Na_3[Fe(CN)_5(PhNHC_2H_5)]\cdot 3H_2O$ | 0.29 | 0.77 | 0.08 | −0.46 | 2050s | 570s | 220sh | 410b |
| VIII | $Na_3[Fe(CN)_5(p\text{-}ClC_6H_4NH_2)]\cdot H_2O$ | 0.25 | 0.82 | 0.04 | −0.43 | 2050s | 540s | 220sh | 410b |
| IX | $Na_3[Fe(CN)_5(o\text{-}ClC_6H_4NH_2)]\cdot H_2O$ | 0.26 | 0.71 | 0.05 | −0.48 | 2040s | 560m | 230w | 430w |
| X | $Na_3[Fe(CN)_5(C_6H_5NMe_2)]\cdot H_2O$ | 0.27 | 0.67 | 0.06 | −0.51 | 2040s | 560s | 240w | 420m |

a) Standard deviations are within ±0.03 mm s$^{-1}$.

complexes were precipitated. These were filtered and dried in vacuo over $CaCl_2$ in a desiccator. The complexes were characterized by the elemental analysis of C, H, N, and Fe. Number of water molecules were matched with the suggested molecular formulae (Table 1).

Mössbauer spectra were recorded on a transducer driven Mössbauer spectrometer in constant acceleration mode (Nucleonix, Hyderabad) at room temperature. A ca. 5 mCi $^{57}Co(Rh)$ source was used. The spectrometer was calibrated using natural iron foil and sodium pentacyanonitrosylferrate(II) dihydrate (SNP) was used as standard. Spectral lines were assumed to have Lorentzian line shape and the Mössbauer parameters were calculated from visual fitting. Errors were estimated from replicate spectral recording. Infrared spectra (4000—200 $cm^{-1}$) in KBr pellets were recorded on Perkin-Elmer-157 IR spectrophotometer.

## Results and Discussion

The Mössbauer spectra of all the complexes exhibit a well-resolved quadrupole doublet at room temperature. The Mössbauer parameters of all the individual complexes are listed in Table 1. Also given in the Table 1 are characteristic infrared frequencies for $\nu$(C≡N), $\delta$(Fe–CN), $\nu$(Fe–C), and $\nu$(Fe–N). Typical Mössbauer spectra of isobutylamine and *t*-butylamine coordinated complexes are shown in Fig. 1.

If one of the cyano ligands in hexacyanoferrate(II), $[Fe(CN)_6]^{4-}$ is replaced by a neutral ligand L to give $[Fe(CN)_5L]^{3-}$, then octahedral geometry remains unaffected but the symmetry is lowered from $O_h$ to approximately $C_{4v}$.[7] Even though the electronic configuration will be $t_{2g}^6$ but it will further split into $d_{YZ}$, $d_{ZX}$, and $d_{XY}$ (also called e and $b_2$). All the complexes are expected to be diamagnetic. All amines are essentially σ-donors. The five cyano ligands have vacant π* $2p_y$, $2p_z$ orbitals

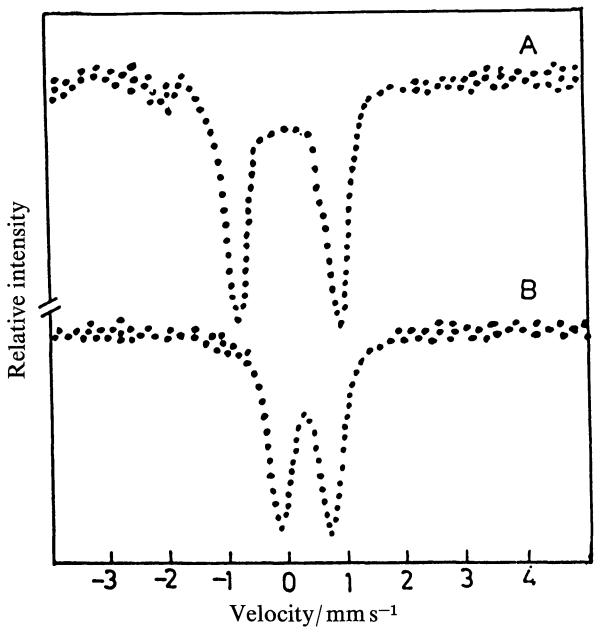


Fig. 1. Mössbauer Spectra of (A) isobutylamine and (B) *t*-butylamine coordinated pentacyanoferrate(II) complexes at room temperature.

available for back bonding, while no such orbitals are available in the case of amines. X-Ray crystal structure determination[17,18] of sodium pentacyanonitrosylferrate(II) has shown that the ligand $NO^+$ and *trans*-cyano are approximately colinear with central Fe atom slightly displaced in the direction of NO ligand from the plane of four pseudoequivalent CN ligands. Manoharan et al.[19] have studied several hexanitroferrates(II) and confirmed π* $2p_y$, $2p_z$-bonding ability of $NO_2^-$ but found it to be much less than that of $CN^-$ ligands.

**(i) Mössbauer Parameters:** All compounds show large quadrupole splitting ($\Delta E_Q$) indicating quite significant distortion in octahedral geometry. Since all the six 3d-electrons form a closed shell ($t_{2g}^6$), no quadrupole splitting is expected due to valence electron contribution. However, due to substitution of sixth cyano with an amine ligand distortion in octahedral geometry is expected. Therefore, $\Delta E_Q$ is a direct measure of the distortion due to ligand contribution although small electronic contribution may also be expected due to further lifting of degeneracy in $t_{2g}$ level as suggested by Manoharan and Gray[20] for sodium pentacyanonitrosylferrate(II). All $\Delta E_Q$ values fall in the range, 0.67—1.75 mm $s^{-1}$ and can be divided into two subgroups; Gr. I with $\Delta E_Q$=0.67—0.86 mm $s^{-1}$ and Gr. II with $\Delta E_Q$=1.75 mm $s^{-1}$. Surprisingly isobutylamine coordinated complex exhibits largest $\Delta E_Q$=1.75 mm $s^{-1}$ which is more than double compared to other complexes.

Isomer shift values of all the complexes are in the range −0.04—0.29 mm $s^{-1}$ with respect to SNP as standard. These are well within the typical range for iron(II) low spin complexes.[1–3,10] For all the six aniline coordinated complexes, the isomer shift values are within 0.27±0.02 mm $s^{-1}$ and are comparable with other alkylamine coordinated complexes. It indicates that substitution of alkyl or aryl group or even that of chloro at ortho or para position on phenyl group of aniline ligand does not have any significant effect on s-electron density at the Fe nucleus. It may be further noted that $\delta$ value for isobutylamine coordinated complex (−0.04 mm $s^{-1}$) is very low and it is almost equal to that for dibutylamine and butylamine coordinated complexes studied earlier in our laboratory.[11] It is known that on substitution with bulkier groups in $NH_3$, its basic character changes resulting in an increase in electron density and hence decrease in $\delta$ value is expected. As mentioned $\delta$ values for aniline coordinated complexes do not vary significantly indicating that change in basic character of amines may not affect the σ-donor property of the amine ligands.

As already mentioned, a strong asymmetry is generated due to the presence of sixth odd ligand L, resulting in quadrupole splitting. Earlier several workers have observed $\Delta E_Q \approx 0.80$ mm $s^{-1}$ in amine and monoalkylamine coordinated complexes.[4–11] It is suggested that since alkyl- or arylamines are only σ bonded, $d_\pi$ orbitals of iron remain distributed among five $CN^-$ ligands only. Hence the nature of alkyl or aryl groups should not

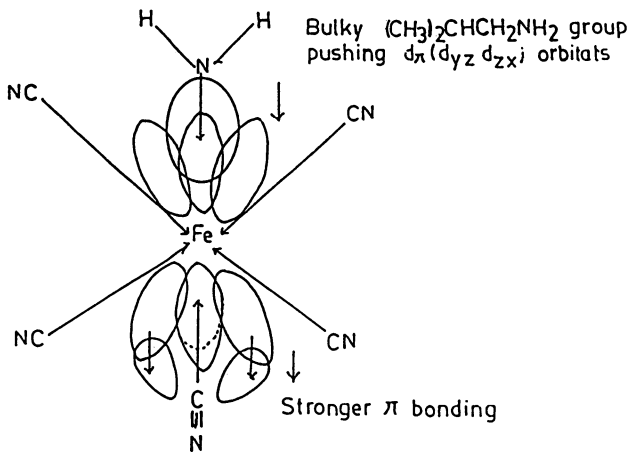


Fig. 2. Diagrammatic representation of isobutylamine ligand pushing $\pi$-orbitals (only $d_{YZ}$ and $d_{ZX}$) of Fe atom which may result in increased $\pi$-bonding with trans CN ligand.

cause any significant change in $\Delta E_Q$ values. However, for isobutylamine coordinated complex an unusually high $\Delta E_Q$=1.75 mm s$^{-1}$ is observed. It is comparable with sodium pentacyanonitrosylferrate(II) ($\Delta E_Q$=1.71 mm s$^{-1}$) where it is attributed to excessive $\pi$-bonding character of NO.[8] Therefore, in the case of isobutylamine coordinated pentacyanoferrate(II) complex also it may be possible that the central Fe atom is slightly pushed towards trans $CN^-$ by the bulkier isobutyl group and also due to greater $\pi$-bonding ability of $CN^-$. This is schematically illustrated in Fig. 2.

These observations, viz. almost similar values of $\delta$ and $\Delta E_Q$ for various monoalkyl- and arylamines in these complexes are in accordance with the observation of Ballhausen and Gray.[21]

**(ii) Correlation of $\delta$ and $\Delta E_Q$:** Several workers have attempted to correlate $\delta$ and $\Delta E_Q$ values and used this correlation in predicting the sign of EFG and bonding characteristics.[22–25] On plotting $\delta$ vs. $\Delta E_Q$ for all the complexes studied here a linear correlation is observed as shown in Fig. 3. $\Delta E_Q$ decreases with increasing $\delta$ for all the complexes of the type $[Fe(CN)_5(NH_2R)]^{3-}$ with various alkyl or aryl groups. This is based on the assumption that a positive sign of EFG exists for isobutylamine coordinated complex (similar to SNP) and a negative sign for all other coordinated complexes. However, this sign of EFG needs to be experimentally verified by a crystal orientation or magnetic perturbation method.

**(iii) Infrared Spectra:** Various vibrational modes of the complexes were assigned by comparison with those for other pentacyanoferrate(II) complexes.[5,8,13] The most important of all vibrational frequencies is the most intense C≡N stretching band which is observed in the region 2140—2040 cm$^{-1}$. Earlier three modes have been observed for $\nu$(CN) of some di- and trialkylamine coordinated complexes.[11,12] In the present studies, however, we have observed only one band at ca. 2040 cm$^{-1}$ for $\nu$(CN) in all the pentacyanoferrate(II) complexes except for isobutylamine coordinated complex where two intense bands at 2140, 1950 cm$^{-1}$ were observed. Both these bands are either at higher or lower by ca. 100 cm$^{-1}$ compared to normal $\nu$(CN) mode

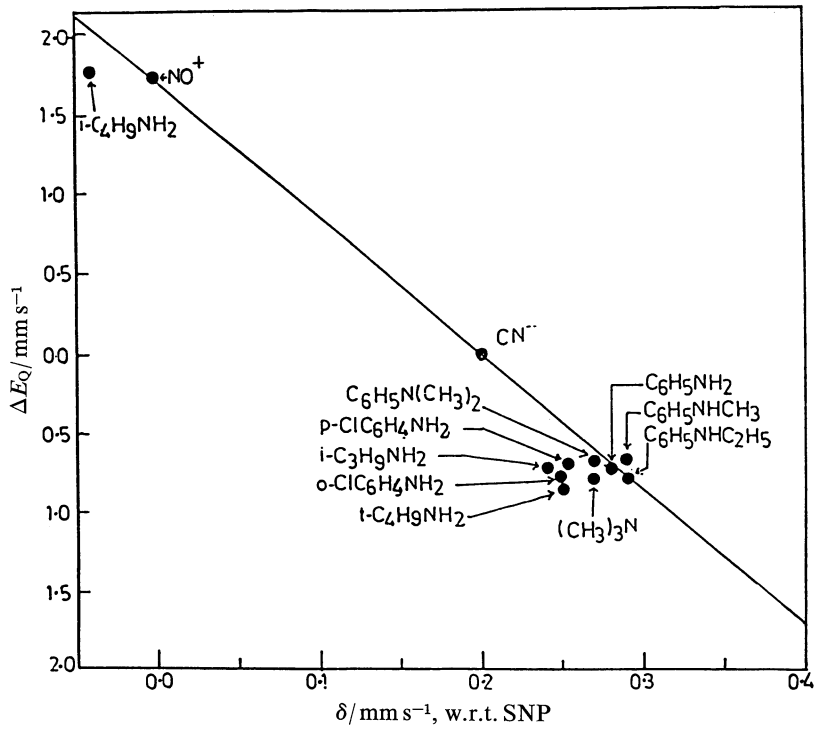


Fig. 3. Correlation of isomer shift ($\delta$) vs. quadrupole splitting ($\Delta E_Q$) values in alkyl- and arylamine coordinated pentacyanoferrate(II) complexes.

observed at ca. 2040 $cm^{-1}$. Another important characteristic mode of medium intensity is due to Fe–C≡N bending observed in the range 580—540 $cm^{-1}$. A very weak band observed in the range 450—400 $cm^{-1}$ has been assigned to Fe–C stretching vibrations in acccordance with the assignments of Fluck et al.[8] Another weak band was observed in the range 315—225 $cm^{-1}$ which may be assigned to Fe–N stretching.[8-27] A sharp medium intensity band is also observed at ca. 1600 $cm^{-1}$ and assigned to bending mode of $H_2O$ molecules occupying interstitial position. Interestingly for isobutylamine coordinated complexes $\nu$(CN), $\delta$(Fe–CN) and to some extent $\nu$(Fe–N) are shifted by ca. 100 $cm^{-1}$ in comparison with other complexes. This shift may be a sufficient indication of the difference in bonding characteristics of the isobutylamine coordinated complex compared with others. It may be noted that $\nu$(Fe–C) remains almost unaffected on substitution. Rachlewicz et al.[27] have found $\nu$(Fe–N) to be sensitive to further substitution and changes in bonding characteristics. Therefore, on the basis of $\nu$(Fe–N) and other frequencies, we can conclude that bonding in isobutylamine coordinated complex is certainly different than other complexes.

Since σ-donor and π-acceptor properties of the ligands $CN^-$ and $RNH_2$ are playing a dominant role, an attempt has been made to correlate $\nu$(CN) and $\nu$(Fe–N) with $\delta$ values of the respective complexes as shown in Fig. 4. In both cases straight line correlations have been observed indicating a decrease in $\delta$ value with both the stretching modes. Brar and Muzumdar[12] and Inoue et al.[13] have also correlated $\delta$ with $\nu$(CN) in pentacyanoferrate(II) complexes. Earlier we have observed a similar trend for $\nu$(CN) and $\delta$(Fe–C≡N) for di- and trialkylamine coordinated complexes.[10] It has been argued that if $d_\pi$–$p_\pi$ back donation from Fe to CN is reduced than Fe–C bond strength should decrease. Following the same argument Fe–N bond strength should also be affected depending on the interaction of ligand orbitals with the metal $d_\pi$ orbitals. Again a clear trend dividing the ligands into two subgroups is evident. Gr. I complexes exhibiting $\Delta E_Q \approx 0.75$ mm $s^{-1}$ show $\nu$(CN) and $\nu$(Fe–N) at lower frequencies. On the other hand isobutylamine coordinated complex exhibiting unusually high $\Delta E_Q$ shows the respective bands at higher frequencies. Almost similar kind of trend is observed for $\delta$(Fe–CN) (Table 1).

**(iv) Partial Isomer Shift and Quadrupole Splitting:** Several attempts have been made to evaluate partial isomer shift (p.i.s) and partial quadrupole splitting (p.q.s.) values of the ligands in a series of isostructural complexes and correlating them with bonding characteristics.[28,29] These values were calculated using the equations:

$$[L]_{p.i.s.} = \delta - 0.21$$
$$[L]_{p.q.s.} = 1/2(\Delta E_Q - 1.68)$$

where $\delta$ and $\Delta E_Q$ are observed values. These are listed in Table 1. Plots of p.q.s. vs. $\delta$ and p.i.s. show straight line correlations as shown in Fig. 5. In both cases p.q.s. values increase with decreasing $\delta$ or p.i.s. values. For distorted octahedral complexes of the type $[Fe(CN)_5L]^{3-}$ it has been observed that $\delta$ values are affected depending on whether L is a better σ-donor or

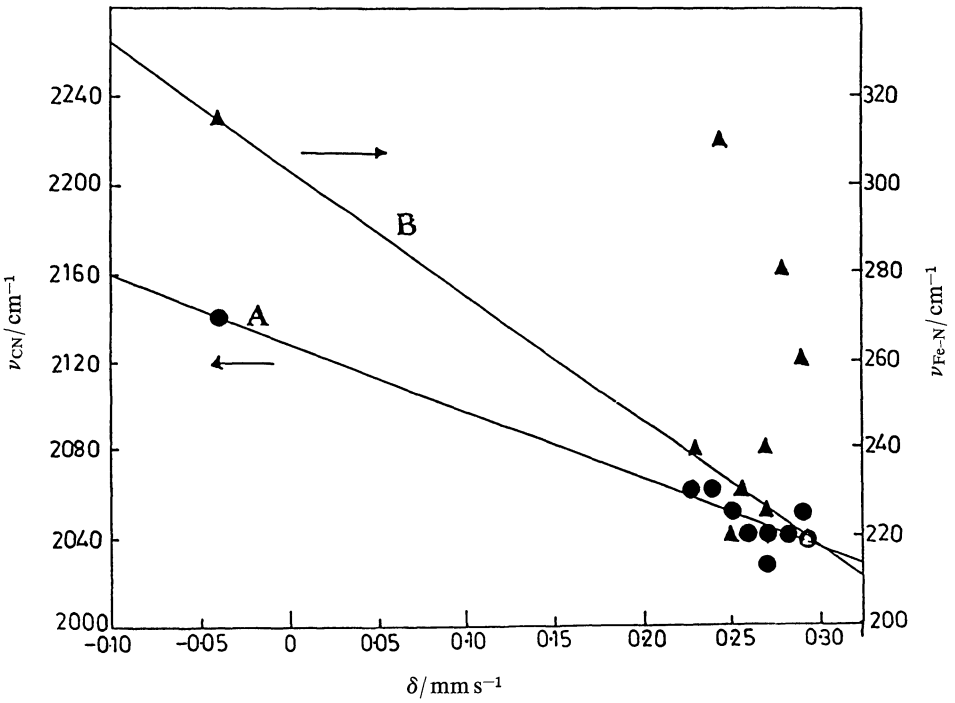


Fig. 4. Variation of isomer shift ($\delta$) with (A) $\nu$(C≡N) and (B) $\nu$(Fe–N) stretching frequencies in $Na_3[Fe(CN)_5(RNH_2)] \cdot xH_2O$ complexes.

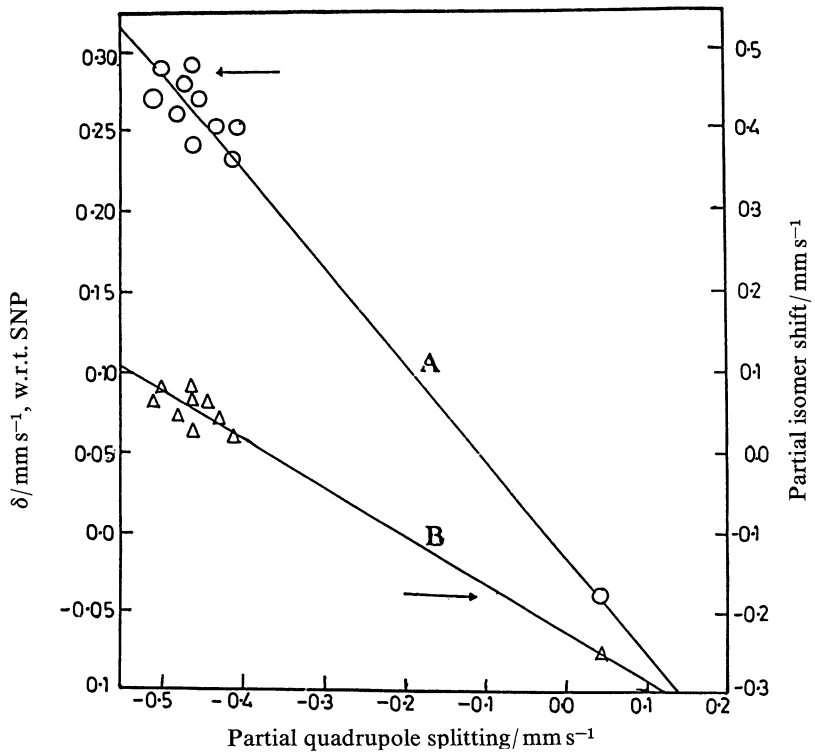


Fig. 5. Correlation of partial quadrupole splitting (p.q.s.) with (A) isomer shift ($\delta$) and (B) partial isomer shift (p.i.s.) in $Na_3[Fe(CN)_5(RNH_2)] \cdot x\ H_2O$ complexes.

π-acceptor than and $CN^-$ ligand.[26] In the present study where all the ligands are alkyl- or aryl-group substituted amines, their σ-donor property is affected by the substitution. It could be correlated with the change in base strength of amines as well. For example alkylamines with bulkier alkyl group are stronger bases and with arylamines are weaker bases than $NH_3$. However, this does not seem to affect the σ-donor property of the respective amines significantly except in the case of isobutylamine as indicated by its low values of $\delta$ and p.i.s. Presumably it is not just the σ-donor property but a combination of σ-donor and π-acceptor characteristics, both of which are operating simultaneously and can not be separated.

## Conclusion

Mössbauer spectra of alkylamine and arylamine coordinated pentacyanoferrate(II) complexes exhibit a well resolved quadrupole doublet. Isobutylamine coordinated complex exhibits unusually high $\Delta E_Q$ and low $\delta$ which are comparable with sodium pentacyanonitrosylferrate(II). Correlation of $\delta$ vs. $\Delta E_Q$ gives a straight line suggesting a positive sign of EFG for isobutylamine coordinated complex. Stretching modes of CN and Fe–N also correlate well with the isomer shift data suggesting significant differences in its bonding characteristics compared with other alkyl- and arylamine coordinated complexes.

Our grateful thanks are due to Council of Scientific and Industrial Research, New Delhi for financial assistance. Thanks are also due to RSIC, Lucknow for providing C, H, N analysis and IR spectral data.

### References

1) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem., Int. Ed. Engl.*, **2**, 277 (1963); *Z. Phys.*, **175**, 200 (1963).
2) E. Fluck, *Adv. Inorg. Chem. Radiochem.*, **6**, 433 (1964).
3) E. Fluck and P. Kuhn, *Z. Anorg. Allg. Chem.*, **350**, 263 (1967).
4) H. E. Toma, E. Giesbrecht, J. M. Malin, and E. Fluck, *Inorg. Chim. Acta*, **14**, 11 (1975).
5) J. A. Olabe and P. J. Aymonino, *J. Inorg. Nucl. Chem.*, **36**, 1221 (1974); *ibid.*, **38**, 225 (1976).
6) P. J. Aymonino, M. A. Blesa, J. A. Olabe, and E. Frank, *Z. Naturforsch., B*, **31**, 1532 (1976).
7) C. P. Monagham and J. C. Fanning, *J. Phys. Chem.*, **82**, 1045 (1978).
8) E. Fluck, H. Inoue, M. Nagao, and S. Yanagisawa, *J. Inorg. Nucl. Chem.*, **41**, 287 (1979).
9) A. N. Garg and P. N. Shukla, *Z. Naturforsch., B*, **36**, 59 (1981).
10) D. V. Parwate and A. N. Garg, *Z. Naturforsch., B*, **40**, 1495 (1985).
11) D. V. Parwate and A. N. Garg, *Polyhedron*, **5**, 999 (1986).
12) A. S. Brar adn S. K. Muzumdar, *Radiochem. Radioanal. Lett.*, **48**, 329 (1981); *Solid State Commun.*, **45**, 981 (1983).
13) H. Inoue, M. Sasagawa, E. Fluck, and T. Shirai, *Bull.*

*Chem. Soc. Jpn.*, **56**, 3434 (1983).
14) H. E. Toma and J. A. Vanin, *Inorg. Chim. Acta Lett.*, **33**, 159 (1979).
15) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Academic Press, New York (1965), Vol. 2, p. 1513.
16) D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nucl. Chem.*, **20**, 75 (1961).
17) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, **2**, 1043 (1963).
18) F. Bottomley and P. S. White, *Acta Crystallogr., Sect. B*, **35**, 2193 (1975).
19) P. T. Manoharam, S. S. Kaliraman, V. G. Jadhao, and R. M. Singru, *Chem. Phys. Lett.*, **13**, 585 (1972).
20) P. T. Manoharan and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3340 (1965).
21) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **2**, 426 (1963).
22) R. W. Grant, "Mössbauer Effect Methodology," ed by I. J. Gruverman, Plenum Press, New York (1966), Vol. 2, p. 23.
23) Y. Hazony and R. C. Axtmann, *Chem. Phys. Lett.*, **8**, 571 (1971).
24) M. G. Clark, A. G. Maddock, and R. C. Platt, *J. Chem. Soc.*, **1972**, 281.
25) D. V. Parwate and A. N. Garg, *J. Radioanal. Nucl. Chem. Lett.*, **87**, 379 (1984).
26) P. G. Rasmussen and E. A. Meyers, *Polyhedron*, **3**, 183 (1984).
27) K. Rachlewicz, J. Pietrzyk, and K. Drabent, *Polyhedron*, **4**, 1777 (1985).
28) G. M. Bancroft, M. J. Mays, and B. E. Prater, *Chem. Commun.*, **1968**, 1374; *J. Chem. Soc. A*, **1970**, 956.
29) G. M. Bancroft, "Mössbauer Spectroscopy; An Introduction for Inorganic Chemists and Geochemists," McGraw Hill, London (1973), p. 94.