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Carbon-13 Chemical Shifts of Substituted Pentacyanoferrate(II) Complexes Correlated with Mössbauer and Electronic Spectra

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Profound changes in the bonding and reactivity of octahedral iron(II) are produced upon substitution of cyano ligands for the water molecules in $[Fe(OH_2)_6]^{2+}$, to form $[Fe(CN)_6]^{4-}$. The stability of the iron–cyano bonds results from strong donor–acceptor interactions between cyanide and the metal ion. We and others have employed carbon-13 magnetic resonance [1–3], UV–visible [4–6] and Mössbauer [6–10] spectroscopy to probe these interactions in a series of iron(II) cyanides $[Fe(CN)_5L]^{n-}$, for which the σ-donor and π-acceptor properties of the ligands L are varied. Recently we obtained heretofore unreported spectra of the complexes where L is imidazole, glycine or carbon monoxide. In this article we present correlations of Mössbauer and UV–visible spectra with the observed ^{13}CN chemical shifts. The results indicate that ^{13}CN chemical shift measurements can be employed to study the distribution of electrons in this series of cyano complexes.

Typical ^{13}C NMR spectra of diamagnetic $[Fe^{II}(CN)_5L]^{n-}$ species are seen in Figure 1. The characteristic ^{13}CN peaks, in the 130–190 ppm range, present *ca.* 4:1 intensity patterns which are consistent with *cis* and *trans* assignments, respectively. We note that the *trans*-CN resonance is found slightly downfield of the *cis* in the CO complex. The reverse is true for all other substituted pentacyanoferrate(II) species thus far reported.

In Table I, ^{13}CN chemical shifts are given along with electronic and Mössbauer spectra. The d–d transition energy (E_{dd}) refers specifically to the lowest energy band ($^1A_1 \rightarrow {}^1E(1)$), which itself is directly related to the D_q parameter of the ligand L [6]. A salient feature of the data is that downfield shifts of the ^{13}CN resonances are accompanied by regular decreases in E_{dd} and by increases in the isomer shift. Figure 2 presents plots of these quantities *versus* δ (^{13}CN, *cis*).

The trends in UV and Mössbauer spectra show decreasing ligand field strength as one moves down the series of complexes in Table I. This is observed directly in the relative values of E_{dd} for complexes 1

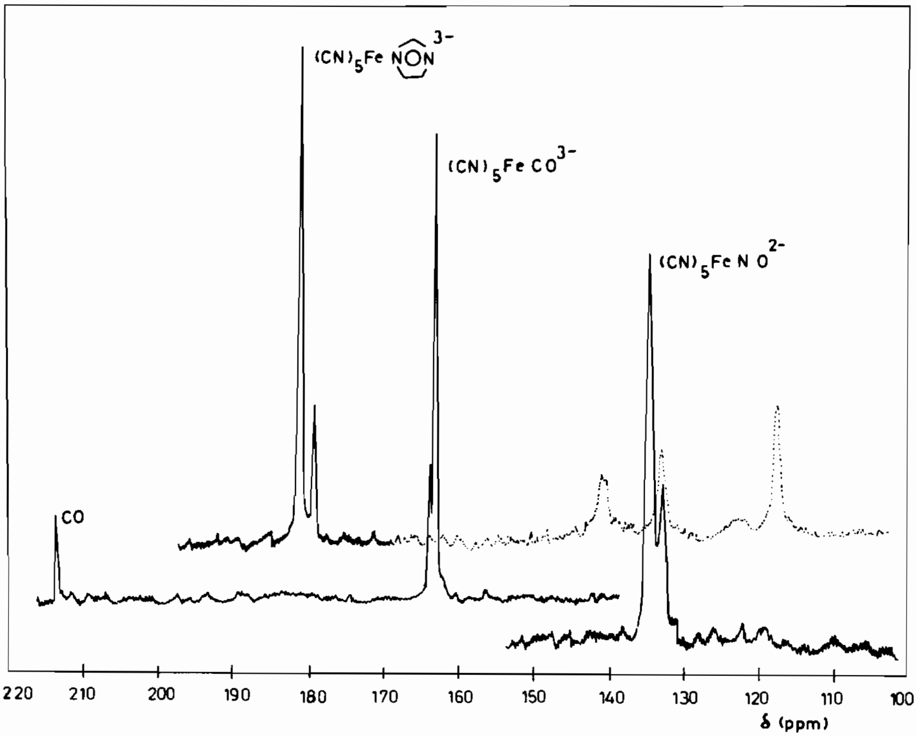


Fig. 1. ^{13}C NMR spectra of pentacyanoferrate(II) complexes of imidazole, CO and NO^+ (aqueous solution, 33 °C, measured *versus* methanol, referred to TMS).

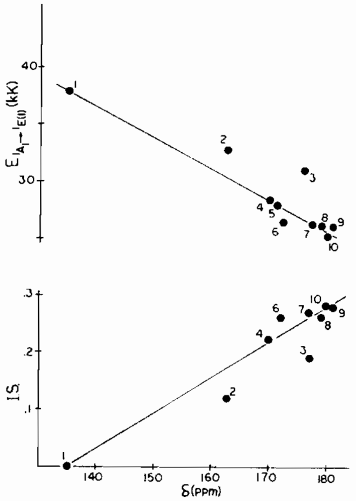


Fig. 2. Correlations of *cis*-^{13}CN chemical shifts of Fe^{II}-(CN)$_5$L complexes with the Mössbauer isomer shifts (mm/s) and the energies of the electronic d–d transition.

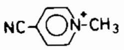
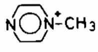
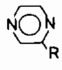
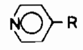
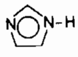
to 10. The increase in isomer shift (I.S.) along the series indicates decreasing 4s electron density at the iron nucleus, which also is consistent with a diminution in the overall ligand field. Furthermore, the order given is roughly that of decreasing stability of the complexes with respect to ligand exchange and to oxidation (Fe(II) → Fe(III)). It is especially interesting that the Bronsted basicities of the ligands L (except for cyanide) are largest at the bottom of the table. These variations in basicity indicate a weaker tendency for ligands high in the table to donate σ-electrons in a coordinate bond, relative to those at the bottom. In order to account for the complexes' properties it is necessary to introduce the π-acceptor capabilities of the ligands L, which vary from excellent π-acceptors (*e.g.*, NO$^+$) to poor or nonacceptors (imidazole, glycine).

For the [Fe(CN)$_5$L]$^{n-}$ species in Table 1 we see that the strong field ligands, which are mostly poor σ-donors and good π-acceptors, induce a pronounced upfield shift in the cyano resonances. It is highly probable that this shift accompanies increasing polarization of cyano electrons toward iron(II). We suggest that the shift is caused largely by the same factors responsible for the shift of HCN (110.9 ppm) [11] upfield with respect to that of aqueous cyanide ion (168.8 ppm) [12]. Similar upfield dislocations with increasing polarization of a cyano ligand are found in a series of cyanocobalamins for which the chemical shifts are 161.5, 139.6 and 110.1 ppm, respectively, when the ligands *trans* to CN$^-$ are CH$_3^-$, CN$^-$ and H$_2$O [13].

According to the Karplus–Pople MO treatment [14–17], carbon chemical shifts are dominated by the paramagnetic screening term:

$$\sigma_p = -\frac{K}{\Delta E}\langle r^{-3}\rangle_{2p}\,[Q_{AA} + Q_{BB}]$$

TABLE I. Comparison of ^{13}CN Chemical Shifts of Fe^{II}(CN)$_5$L Complexes with Mössbauer and Electronic Spectral Data.[a]

L	δ_{cis} ^{13}CN ppm	δ_{trans} ^{13}CN ppm	E_{dd} kK	I.S. mm/s
1. NO$^+$	134.8[b] 135.1[e] 135.0[f]	132.8[b] 133.2[e] 132.8[f]	37.7[c,i]	0.00[d]
2. CO	162.8[b]	163.4[b]	32.7[b]	0.118[d]
3. CN$^-$	177.0[e]		31.0[c]	0.192[d]
4. *S*O(CH$_3$)$_2$	170.0[e]	167.0[e]	28.5[c]	0.226[d]
5. 	171.3[f]	163.8[f]	28.2[b]	–
6. 	172.3[e]	166.2[e]	26.5[b]	0.262[d]
7. 	177–178[b]	173–174[b]	26.3[b]	0.27[d]
8. 	179–180[e]	174–177[e]	26.3[g]	0.26[d]
9. 	181.1[b]	179.1[b]	26.1[b]	0.28[h]
10. *N*H$_2$CH$_2$CO$_2^-$	180.2[b]	178.4[b]	25.2[b]	0.28[h]

[a] Room temperature data, E_{dd} refers to the $^1A_1 \to {}^1E(1)$ transition (1 kK = 1000 cm^{-1}). [b] This work. [c] Ref. 6, energy associated with the $^1A_{1g} \to {}^1T_{1g}$ transition in the O_h complex. [d] Ref. 10. [e] Ref. 1. [f] Ref. 3. [g] Estimated. [h] H. E. Toma and J. M. Martins, to be published. [i] Ref. 4.

Here, ΔE is an average excitation energy, $\langle r^{-3} \rangle$ is the mean inverse cubed radius of the 2p orbitals and the Q terms contain elements of the charge density, bond order matrix. We have noted that as L is replaced by ligands with increasing σ-donor/π-acceptor ratios the electron density at iron is shifted towards the CN^- ligands. In analogy with a series of metal carbonyl complexes [17], this might be expected to produce a progressive decrease in ΔE. If $\langle r^{-3} \rangle_{2p}$ were constant the result would be an increase in magnitude of σ_p, leading to the observed downfield shift. However, the nature of the change in $\langle r^{-3} \rangle_{2p}$ is not clear. An increase in the polarization of the iron–carbon bond towards carbon would produce a decrease in $\langle r \rangle$. Simultaneously, the accompanying polarization of the C≡N bond towards N would increase $\langle r \rangle$.

At this time a definitive theoretical treatment of the ^{13}CN chemical shift data is not available. However, our results show that magnetic resonance experiments provide insight regarding the distribution of charge in metal cyanide complexes. The evidence for the $[Fe(CN)_5L]^{n-}$ series suggests that increases in the ligand field, sometimes associated with strong $d\pi$–$p\pi$ backbonding to L, often are accompanied by increasing donation of electrons from the cyano ligands to the metal center. Indeed, it seems very likely that this increased donation by CN^- contributes to the increase in the ligand field. Thus, we postulate that the strong field ligands which are very weak bases (Table I, ligands 1, 2 and 4–6) owe their ligand field strength, at least in part, to an ability to induce electron donation by coordinated cyanide. A similar mechanism has been proposed by Fenske and DeCock [18] in their analysis of intramolecular environmental effects in complexes $[M(CN)_5NO]^{n-}$.

In Figure 2 it is noteworthy that the strong field complexes of CO and CN^- do not conform to the straight line which fits the nitrogen bases. The direction of the deviations indicates that, in relation to their ligand field strengths, these carbon bases do not polarize the $Fe(CN)_5^{3-}$ moiety as effectively as do the nitrogen bases. For CN^-, which is a strong σ-donor, this behavior appears quite reasonable. A similar argument may apply for the CO complex. We point out that plots of E_{dd} *versus* I.S., which both are indicators of ligand field strength, show a behavior which is more closely linear [6].

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