Correlations of Mössbauer and Visible–UV Spectra with the Aqueous Substitution Reactivity of Several Substituted Pentacyanoferrate(II) Complexes

H. E. TOMA[1a], E. GIESBRECHT[1a], J. M. MALIN[1b] and E. FLUCK[1c]

Instituto de Quimica, Universidade de São Paulo, CP 20780, S. Paulo, Brasil, Department of Chemistry, Univ. of Missouri, Columbia, Mo. 65201, USA and the Institut für Anorganische Chemie, Univ. Stuttgart, 7 Stuttgart 80, Germany

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A comparison is presented of electronic and Mössbauer spectra with the limiting S_N1 rates of ligand loss in aqueous solution for complexes $Fe(CN)_5L^{n-}$ where L is H_2O, NH_3, pyridine, pyrazine carboxylate, N-methyl pyrazinium, dimethyl and tetramethylenesulfoxide. The correlations are viewed as evidence of the bonding properties of the several saturated and unsaturated ligands empoyed.

Introduction

For a series of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{n-}$, observations of ligand substitution rates and systematic changes in electron-transfer spectra have indicated varying degrees of $d_\pi-p_\pi$ backdonation between iron(II) and a variety of ligands L[2–5]. In order to elucidate further the nature of the metal–ligand interactions we have recorded the Mössbauer spectra of a number of the complexes. The results correlate very well with the energies of the complexes' observable *d–d* transitions and also with their substitution reactivity.

Experimental

Reagents

Preparation of pentacyanoferrate(II) complexes of a variety of ligands has been described previously[2–4]. Starting materials were obtained from commercial sources and were either used as obtained or purified according to conventional procedures, as necessary.

Visible–UV Spectra

The electronic spectra of the pentacyanoferrate(II) complexes were recorded in aqueous solution using a Cary Model 17 spectrophotometer, in the presence of a slight excess of the free ligand L to prevent dissociation. The spectra of $10^{-4}–10^{-5} M$ solutions of the aquopentacyanoferrate(II) ion were measured using 10 cm path length cells and 0–0.1 expanded absorbance scale. No evidence of Beer's law deviation was observed, suggesting that in this range of concentration the formation of those binuclear species reported by Emschwiller[6] is neglegible. The samples of the aquopentacyanoferrate(II) ion were prepared starting from aqueous solutions of the aminopentacyanoferrate(II) complex neutralized with perchloric acid under argon atmosphere, or by dissolving solid $Na_3[Fe(CN)_5NH_3] \cdot 3H_2O$ in deaerated dihydrogenphosphate/hydrogen phosphate or acetic acid/acetate buffer solutions.

Mossbauer Spectra

The Mossbauer spectra of the complexes were measured at liquid nitrogen temperature using a Mossbauer Spectrometer with mechanical drive. Isomer shifts quoted here are referred to iron at room temperature.

Kinetics Measurements

The rates of dissociation of the aqueous pentacyanoferrate(II) complexes of S-bonded tetramethylenesulfoxide (tmso) and pyrazine carboxylate ($pzCO_2^-$ were measured in the manner described previously for the pyridine (py), N-methylpyrazinium (MPz^+) and S-bonded dimethylsulfoxide (dmso) complexes[2,3]. Ionic strength, $\mu = 1.0 M$, was maintained by the addition of lithium perchlorate. The rate of water exchange in the aquopentacyanoferrate(II) complex was estimated from substitution experiments performed previously[2]. To eliminate the effect of protonation of the complexes, which takes place at pH 2–4, the kinetics measurements described here were performed at pH 6–8.

Results and Discussion

Electronic Spectra

The pentacyanoferrate(II) complexes of dimethyl sulfoxide, tetramethylenesulfoxide, water and aliphatic amines each exhibit an absorption band of medium intensity ($\varepsilon \sim 10^3 M^{-1}$ cm^{-1}) in the visible–near uv

spectral region and a very strong absorption ($\varepsilon \sim 10^4$ M^{-1} cm^{-1}) below 250 nm. Electronic transitions between iron d levels are responsible for the former. The latter is due to electron transfer from iron(II) to the cyanide ligands.

In the pentacyanoferrate(II) complexes of aromatic N-heterocycles two additional bands of high intensity are seen[2]. The first, in the uv region, arises from $\pi^* \leftarrow \pi$ transitions within the heterocycle. The second, due to electron transfer from iron(II) to the heterocycle, appears in the visible region. For certain of the complexes, *e.g.,* those of pyridine, pyrazine and isonicotinamide, the metal-to-heterocycle electron transfer absorption masks the d–d band. However, for others this band can be measured directly. In Figure 1 the observable d–d bands are illustrated for several Fe(CN)$_5$L^{n-} (aq) complexes, where L = H$_2$O, NH$_3$, MPz$^+$ and dmso.

To determine the origins of these d–d bands we draw upon assignments made previously for low-spin d^6 complexes. In the ion Fe(CN)$_6^{4-}$ the d–d band observed at 31.0 kK has been assigned to a spin-allowed transition from the $^1A_1$ ground state to the $^1T_{1g}$ excited state[7]. On lowering the symmetry from O$_h$ to C$_{4v}$ as in Fe(CN)$_5$NO^{2-} the ground state symmetry is unchanged and the $^1T_{1g}$ state is split into $^1A_2$ and $^1E(1)$ states. Manoharan and Gray[8] assigned bands observed in the nitroprusside ion spectrum at 30.3 ($\varepsilon = 40 M^{-1}$ cm^{-1}) and 37.8 ($\varepsilon = 900 M^{-1}$ cm^{-1}) to transitions from

Figure 1. d–d bands of the complex ions Fe(CN)$_5$L^{n-}(aq) where L = H$_2$O (——), NH$_3$ (----), MPz+ (–..–..–) and dmso (...)

the ground state to the levels $^1A_2$ and $^1E(1)$ respectively. They pointed out that the $^1A_2 \leftarrow ^1A_1$ transition is essentially $d_{x^2-y^2} \leftarrow d_{xy}$ and that its energy should therefore be relatively insensitive to changes in L. The fact that this transition is orbitally forbidden in C$_{4v}$ symmetry accounts for its small extinction coefficient.

We note a considerable variation with changing L in the energies of the bands in Figure 1. Further, we point out that the values of ε in Figure 1 range between *ca.* 200 and 650 M^{-1}cm^{-1}. Therefore the bands are assigned in each case to the $^1E(1) \leftarrow ^1A_1$ excitation. The weaker $^1A_2 \leftarrow ^1A_1$ transition, which is expected to be found near 31 kK, does not appear and is probably masked by the nearby d–d and electron transfer bands.

Except for the nitroprusside ion, none of the pentacyanoferrate(II) complexes with which we are concerned are rigorously of C$_{4v}$ symmetry. However, the similarities in their spectra suggest that assignments based on C$_{4v}$ microsymmetry are appropriate.

Wentworth and Piper[9] have shown that it is possible to state the energy splittings of d–d bands in tetragonal, low spin d^6 complexes in terms of crystal field parameters Dq and Dt. Here Dq is the octahedral field strength of the ligand L and Dt is its tetragonal distortion parameter. Assuming as a first approximation, the crystal field model for the Fe(CN)$_5$L^{n-} complexes, the following treatment can be derived.

Within the formalism of crystal field theory, the energy of the transition $^1T_{1g} \leftarrow ^1A_{1g}$ in Fe(CN)$_6^{4-}$ is expressed by eq 1

$$E_{(^1T_{1g} \leftarrow ^1A_{1g})} = 10Dq - C \tag{1}$$

where C is a Racah electronic repulsion parameter. The energies of the two lowest energy d–d transitions in C$_{4v}$ symmetry are given by

$$E_{(^1A_2 \leftarrow ^1A_1)} = 10Dq - C \tag{2}$$

$$E_{(^1E(1) \leftarrow ^1A_1)} = 10Dq - (35/4)DT - C \tag{3}$$

Thus the splitting of the parent state $^1T_{1g}$ is expressed by the tetragonal distortion parameter Dt. Making the assumption that Dt and Dq are characteristics of a given ligand without regard to the complex in which it is found, Wentworth and Piper expressed Dt in terms of Dq. In the case of the pentacyanoferrate(II) complexes the relationship would be

$$Dt = 2/7 (Dq_{CN} - Dq_L) \tag{4}$$

Using equations 2–4 it is possible to evaluate the values of DqL and Dt if the energies of the bands $^1A_2 \leftarrow ^1A_1$ and $^1E(1) \leftarrow ^1A_1$ as well as the parameter Dq$_{CN}$ are known. The latter is 3.2 kK, from the value of 10Dq in Fe(CN)$_6^{4-}$ [10]. Unfortunately, the transition $^1A_2 \leftarrow ^1A_1$ is not observed.

To avoid this obstacle, one can choose between two approximations. In the first, the energy of the transition is assumed to be equal to that of the excitation
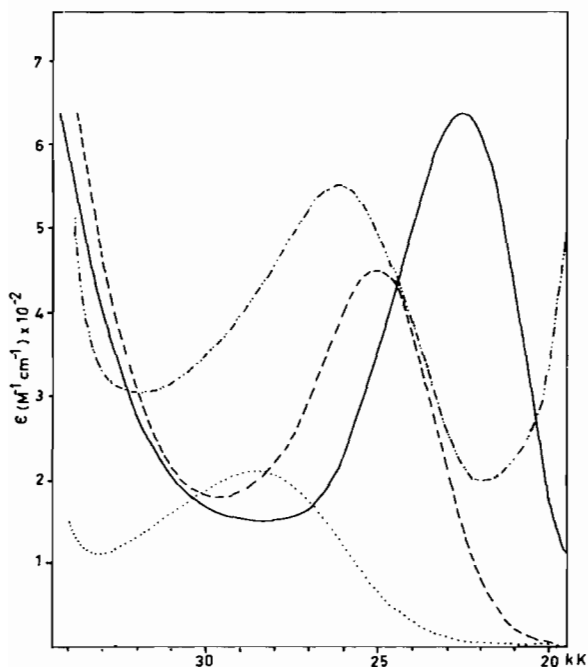
$^1T_{1g} \leftarrow {}^1A_{1g}$ in $Fe(CN)_6^{4-}$. Although an analogous approximation was favored by Wentworth and Piper for a series of cobalt(III) ammine complexes, its use in the pentacyanoferrate(II) species leads to unrealistically low values of Dq for the tetragonal ligands.

An alternate approximation is to assume that $E_{({}^1A_2 \leftarrow {}^1A_1)}$ lies between 31.0 kK and the measured energy of the $^1E(1) \leftarrow {}^1A_1$ band, and to take an average of these two values as $E_{({}^1A_2 \leftarrow {}^1A_1)} = 10$ Dq–C. If this is done a more reasonable set of values of Dq and Dt is computed. The results are presented in Table I. Although these calculations are rather speculative, as a consequence of the formalism and approximations here employed, the trends observed in the values estimated for Dq and Dt are intuitively consistent and demonstrate the sensitivity of the $^1E(1) \leftarrow {}^1A_1$ transition to the properties of the ligand L. Moving down the table, Dq decreases and Dt increases, showing that the ability of the ligands to stabilize the appropriate orbitals of π symmetry (d_{xz}, d_{yz}) relative to that of σ symmetry (d_{z^2}) diminishes.

Mossbauer Spectra

Like those of other pentacyanoferrate(II) complexes studied previously[11–20], the Mossbauer spectra of the pyridine, pyrazine carboxylate, N-methyl pyrazinium, dimethyl and tetramethylene sulfoxide complexes are doublets. Isomer shifts and quadrupole splittings calculated from the spectra are presented in Table I. The dependence of these parameters on the external cation is now well recognized[19–20] and for this reason only the sodium salts are compared in this article.

The isomer shifts and quadrupole splittings in a series of $Fe(CN)_5L^{n-}$ complexes are expected to vary according to the properties of the ligand L[12]. Ligands with π-acceptor capability are thought to remove π d-electron density from the metal causing a reduction in the shielding of the nucleus from s-electrons and resulting in a decrease in the isomer shift. The effect of an increase in σ donation from ligand to metal is expected to be an increase in the $4s$ orbital population, also yielding a decrease in measured isomer shift.

For the ligands H_2O, and NH_3 the variation in I.S. noted in Table I is consistent with the relative basicities of the two molecules. However, for the other ligands in Table I. the decrease in isomer shift is apparently dominated by the relative abilities of the ligands to accept π-electrons, rather than by their σ-donor properties.

Since the splitting of the iron d-orbitals is determined by the σ and π interactions in the complex, a correspondence between d–d band energies and isomer shifts is expected[13,18]. In Figure 2 a plot of the energy of the proposed $^1E(1) \leftarrow {}^1A_1$ band versus the isomer shift is shown to be nearly linear. Thus, even though the charge of the complexes is not held constant and the bonding properties of L must change considerably from NO^+ to H_2O, we note a striking similarity in the sensitivity of both the d–d band energies and the Mossbauer isomer shifts to the identity of the sixth ligand in $Fe(CN)_5L^{n-}$.

The quadrupole splitting of a Mossbauer absorption line is a measure of the asymmetry of the electric field at the nucleus. In Table I this asymmetry is seen to decrease in the order $L = NO^+ \rangle$ dmso $\sim$ tmso $\sim MPz^+ \rangle$ $pzCO_2^- \rangle$ py $\sim H_2O \rangle$ NH_3. For this series of complexes one expects, as Bancroft and Platt[18] have pointed out, that the quadrupole splitting should decrease as L becomes a better σ-donor or a poorer π-acceptor. Since these tendencies are correlated in the series of ligands used, no definitive position can be taken regarding the relative importance of σ versus π effects on the quadrupole splitting.

TABLE I. d–d Band Maxima[a], Crystal Field[b], Mössbauer[c] and Kinetic Parameters[d] of Some Substituted Pentacyanoferrate(II) Complexes.

$Na_n[Fe(CN)_5L^{n-}] \cdot xH_2O$ L =	$E_{{}^1E(I) \leftarrow {}^1A_1}$ (kK)	Dq' (kK)	Dt' (kK)	δ ± 0.02 (mm/s)	$\varDelta$ ± 0.02 (mm/s)	k_{obs}(lim) (s^{-1})
NO^+	37.8[e]	6.0	−0.81	−0.257[g]	1.712	−
CN^-	31.0[f]	3.2	0.00	−0.05[g]	0.00	−
dmso	28.5	2.7	0.14	0.0	1.10	0.75×10^{-4}
tmso	28.6	2.7	0.14	0.0	1.06	1.00×10^{-4}
MPz^+	26.3	2.3	0.27	0.06	1.10	2.8×10^{-4}
$pzCO_2^-$	25.9[h]	2.2	0.29	0.08	0.96	3.1×10^{-4}
py	masked	−	−	0.08	0.74	1.1×10^{-3}
NH_3	25.1	2.0	0.34	0.11[i]	0.63	1.75×10^{-2}
H_2O	22.6	1.5	0.48	0.16[i]	0.71	$(.3–.5 \times 10^3)$

[a] Measured in aqueous solutions. [b] Values estimated only for comparison purposes. [c] Measured at 77 K except as noted; isomer shifts are referred to iron at room temperature. [d] Limiting values, 25° C, $\mu = 1.0M$ LiClO$_4$, pH 6–8, references 2–4. [e] Reference 8. [f] Energy of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition. [g] Room temperature, reference 16. [h] Band which appears as shoulder on electron-transfer absorption, was resolved by decomposition into Gaussian form. [i] Reference 20.
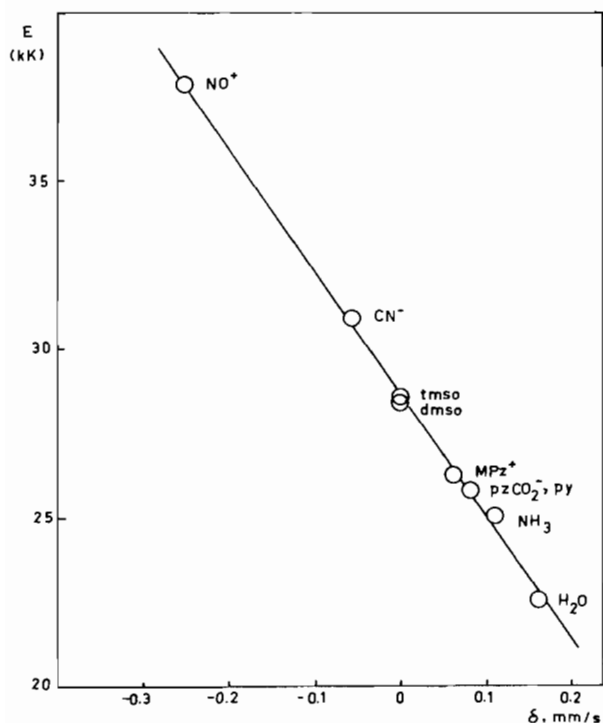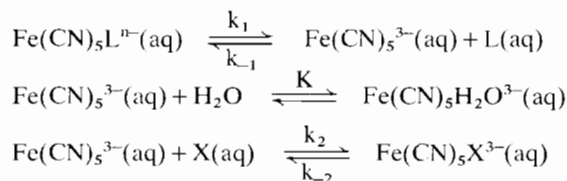
Figure 2. Plot of the energy of the $^1E(1) \leftarrow {}^1A_1$ transition versus the isomer shift for several substituted pentacyanoferrate(II) complexes.

Dissociation Kinetics

Substitution for the ligand L in $Fe(CN)_5L^{n-}$ is known to occur by a limiting S_N1 dissociative mechanism which can be represented by[2-4]:

$$Fe(CN)_5L^{n-}(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(CN)_5^{3-}(aq) + L(aq)$$

$$Fe(CN)_5^{3-}(aq) + H_2O \overset{K}{\rightleftharpoons} Fe(CN)_5H_2O^{3-}(aq)$$

$$Fe(CN)_5^{3-}(aq) + X(aq) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5X^{3-}(aq)$$

where X and L are the attacking and leaving ligands, respectively. Making the steady-state assumption for the concentration of the hypothetical intermediate $Fe(CN)_5^{3-}(aq)$, the observed rate constant k_{obs} can be expressed by

$$k_{obs} = \frac{k_{-1}k_2[X] + k_1k_{-2}[L]}{k_2[X] + k_1[L]}$$

At high concentrations of the attacking ligand X, the observed rate constant is reduced to k_1, the specifie rate of dissociation of $Fe(CN)_5L^{n-}(aq)$. Values of k_1 which were measured directly for six of the complexes discussed in this work are presented in Table I. Of these, the values for the tmso and $pzCO_2^-$ complexes have never before been reported.

The value for H_2O exchange in $Fe(CN)_5H_2O^{3-}$ (aq) is estimated using the equation $k' = Kk_{H_2O}$[21]. Here k' refers to the specific rates of substitution in $Fe(CN)_5H_2O^{3-}(aq)$ by a variety of ligands studied previously[2]. K is a proportionality factor which in this case should fall between 1 and $0.2 M^{-1}$ [22] and k_{H_2O} is the estimated specific rate of H_2O loss.

The importance of σ and π interactions in determining the dissociation rates of substituted pentacyanoferrate (II) complexes has been discussed previously[2-4]. For unsaturated ligands such as the aromatic N-heterocycles and dimethyl sulfoxide there exists considerable evidence that metal-to-ligand backdonation makes an important, but varying, contribution to the free energy of activation for the dissociation process. That evidence is supported by the interpretations of d–d and Mossbauer spectra presented here.

Acknowledgement

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