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Properties and Reactivity of Some Pentacyanoferrate(II) Complexes of Aromatic Nitrogen Heterocycles

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Received May 10, 1972

Studies of a number of the properties of pentacyanoferrate(II) complexes of pyridine, pyrazine, and related aromatic nitrogen heterocycles are presented. Each complex has a strong absorption band in the visible region which is assigned to a metal-to-ligand electron-transfer transition. The calculated oscillator strengths of a number of the bands and the measured oxidation potentials of the Fe(II)-Fe(III) couples in the complexes are also reported. The complexes can be reversibly protonated, presumably at a cyanide. The measured values of the pK_a for the protonated complexes vary according to the identity of the ligand. The kinetics of ligand exchange were studied, yielding clear evidence for a limiting SN1 substitution mechanism. The spectra and the thermodynamic and kinetic data are interpreted in terms of $d\pi$-$p\pi$ back-donation from the pentacyanoferrate(II) moiety to the aromatic ligand.

Introduction

Although the complex ion pentacyanopyridineferrate(II) was first synthesized long ago,[1] surprisingly little is known of its properties and those of related pentacyanoferrate(II) complexes. This is especially intriguing in the light of the recent development of the chemistry of pentaamminepyridineruthenium(II) and analogous species in whose stability metal-to-ligand back-bonding plays a significant role.[2] Specifically, the metal centers in both series of complexes feature spin-paired, d^6 electronic configurations, with filled orbitals of the symmetry required to interact with low-lying, unoccupied ligand π orbitals. The relatively high concentration of negative charge in the $Fe(CN)_5{}^{3-}$ moiety might be expected to compensate in some measure for the requirement that 3d valence orbitals must participate in the bonding in the Fe(II) complexes, rather than the more spatially extensive 4d orbitals available in the Ru(II) case.

Accordingly, we have synthesized a number of new pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles that, together with those known previously,[1] form an interesting series. Our report and interpretation of the various spectral, thermodynamic, and kinetic properties of the complexes are presented in this paper.

Results

Visible-Uv Spectra. All of the complexes exhibited strong absorption in the visible-near-uv spectral regions. Data describing these bands, which are attributable to metal-to-ligand electron transfer,[3] are shown, along with data for the analogous pentaammineruthenium(II) complexes,[2,4] in Table I.

In assigning these bands we have employed the arguments presented by Ford, *et al.*[2] Other high-intensity absorptions are found in the uv region. One of them, as in Ford's complexes, seems to be identical with that of the free ligand. In the pentacyanoferrate(II) complexes, still other very strong absorptions occur at 230 nm and at shorter wavelengths, sometimes obscuring part of the ligand band. These very high energy absorptions are similar to those seen in hexacyanoferrate(II) ion and probably involve electron transfer between the cyanide ligands and Fe(II). The shapes of the metal-to-ligand electron-transfer bands are somewhat asymmetric, as are the reported shapes of the corresponding bands in the ruthenium(II) complexes.[2]

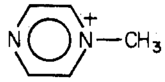
Band Intensities. The intensities of the electron-transfer bands of the pentacyanoferrate(II) complexes involving a single aromatic ring are presented in Table II. They were calculated in terms of the oscillator strength according to[5]

$$f = \frac{2.303mc(9n_0)}{\pi Ne^2(n_0{}^2 - 2)^2} \int \epsilon_i d\bar{\nu}$$

where e and m are the charge and mass of an electron, N is Avogadro's number, n_0 is the refractive index of the medium, and ϵ_i is the extinction coefficient at the ith value of the wave number. The areas of absorption bands were determined numerically, using Simpson's rule. Complexes undergoing ligand substituent equilibria (*e.g.*, hydration of coordinated p-formylpyridine to form the hemiacetal derivative) are excluded from Table II.

A considerable decrease in intensity of the electron-transfer band can be seen when the energy of the absorption increases.

Effect of pH on the Visible Spectra of the Substituted Pentacyanoferrate(II) Ions. Figure 1 shows the uv-visible spectrum of the complex ion $[Fe(CN)_5MPz^+]^{2-}$. MPz^+ is the N-methylpyrazinium ligand



As can be seen in Figure 1 the absorption maximum in the visible spectrum of the N-methylpyrazinium-substituted complex is shifted to higher energy when the hydrogen ion concentration is increased. The same behavior was found for every substituted pentacyanoferrate(II) complex examined. The spectra of the analogous pentaammineruthenium(II) complexes are, in general, not affected by changes in the hydrogen ion concentration between pH 1 and pH 7.[2]

The observed increase in energy of the metal-to-ligand transition, associated with decreasing pH, is probably due to protonation of a cyanide group coordinated to the metal ion. Similar effects were found by Schilt[6] in complexes of the type $Fe(CN)_2L_2$ (L = bipyridine, o-phenanthroline). Protonation of a cyanide in those complexes was shown by Hamer and Orgel.[7]

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[1] W. Manchot and P. Woringer, *Ber.*, **46**, 3519 (1913); also see T. A. Larue, *Anal. Chim. Acta*, **40**, 437 (1968).

[2] P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

[3] Following C. K. Jorgensen, "Oxidation States and Oxidation Numbers," Springer-Verlag, New York, N. Y., 1969, the term "electron-transfer" rather than "charge-transfer" spectra will be used here.

[4] This work.

[5] W. Kauzmann, "Quantum Chemistry," 6th ed, Academic Press, New York, N. Y., 1967, p 581.

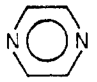
[6] A. A. Schilt, *J. Amer. Chem. Soc*, **82**, 5779 (1960).

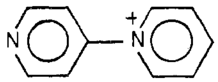
[7] N. K. Hamer and L. E. Orgel, *Nature (London)*, **190**, 439 (1961).

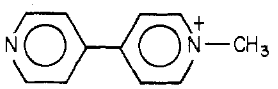
Table I. Electron-Transfer Spectra of Substituted Fe(II) and Ru(II) Complexes

	$Fe^{II}(CN)_5L$		$Ru^{II}(NH_3)_5L$		
Ligand L	λ_{max}, nm (kK)	log ϵ_{max}	λ_{max}, nm (kK)	log ϵ_{max}	Ref
$4\text{-}C_5H_4NCH_3$[a]	356 (28.1)	3.55	398 (25.1)		2
C_5H_5N	362 (27.6)	3.57	407 (24.6)	389	2
$4\text{-}C_5H_4NCl$	383 (26.1)	3.61	422 (23.8)		4
$4\text{-}C_5H_4NCH(OH)_2$	390 (25.6)		425 (23.5)		2
$4\text{-}C_5H_4NCOO^-$	415 (24.1)		457 (21.9)		2
$4,4'\text{-}(C_5H_4N)_2$	432 (23.2)	3.75	475 (21.1)		4
$4\text{-}C_5H_4NCONH_2$	435 (23.0)	3.66	479 (20.9)	4.02	2
Pyrazine[b]	452 (22.2)	3.70	472 (21.2)	4.03	2
4-Pyridylpyridinium[b]	482 (20.8)	3.58	520 (19.2)		4
$4\text{-}C_5H_4NCHO$	505 (19.8)		545 (18.4)		2
1-Methyl-4-(4-pyridyl)pyridinium[b]	520 (19.4)	3.75	570 (17.4)		4
N-Methylpyrazinium[b]	655 (15.1)	4.08	542 (18.4)	4.21	4

[a] C_5H_4N is pyridyl. [b] Structures are given below.


pyrazine


4-pyridylpyridinium


1-methyl-4-(4-pyridyl)pyridinium

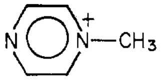

N-methylpyrazinium

Table II. Optical Oscillator Strength Values for $Fe(CN)_5L^{n-}$

L	$\bar{\nu}_{max}$, kK	*f*
$4\text{-}C_5H_4NCH_3$	28.1	0.080
C_5H_5N	27.6	0.085
$4\text{-}C_5H_4NCl$	26.1	0.090
$4\text{-}C_5H_4NCONH_2$	23.0	0.105
Pyrazine[a]	22.2	0.100
N-Methylpyrazinum[a]	15.1	0.145

[a] See Table I for structures.

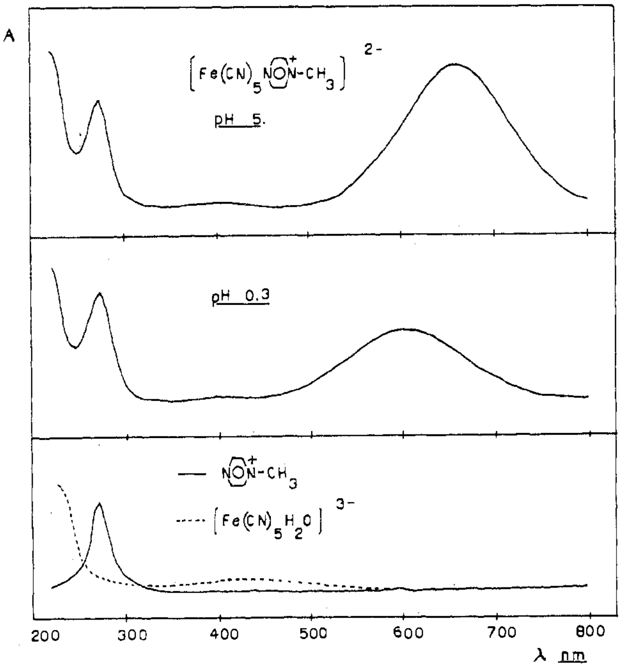


Figure 1. Uv-visible spectra of $Fe(CN)_5MPz^{2-}$.

Figure 2 shows the continuous variation with pH of the visible spectrum of the ion $Fe(CN)_5MPz^{2-}$. We note the isosbestic point at 595 nm, characteristic of the equilibrium

$$HFe(CN)_5MPz^-(aq) \rightleftharpoons Fe(CN)_5MPz^{2-}(aq) + H^+(aq) \quad (1)$$

Similar behavior was observed for the other pentacyanoferrate(II) complexes studied. Deviations (dotted line in Figure 2) from the isosbestic point were registered at very high hydrogen ion concentration. The deviations were probably related partly to higher order protonation equilibria and partly to a loss in the stability of the complexes which was noted at especially low pH.[8]

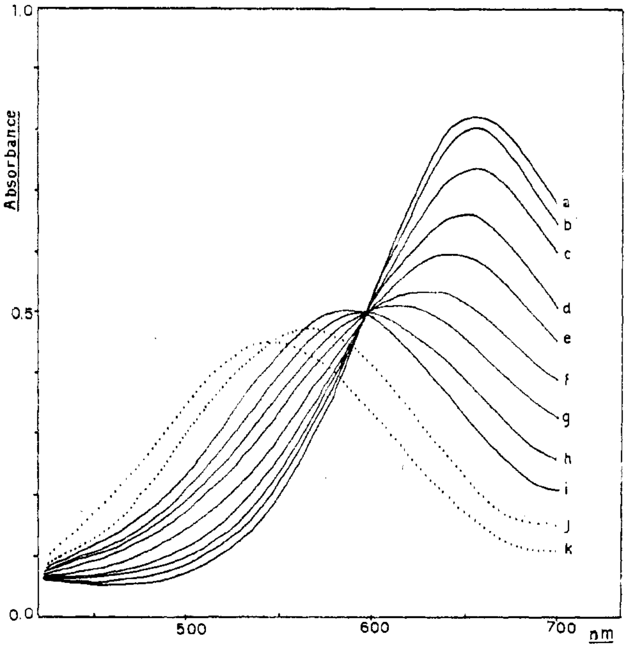


Figure 2. Variation of the visible spectrum of the ion $Fe(CN)_5MPz^{2-}$ with pH ($[Fe(CN)_5MPz^{2-}] = 6.7 \times 10^{-5}$ *M*, $\mu = 1.0$ (LiCl), 25.0°): a, pH 5.0; b, pH 3.0; c, pH 1.80; d, pH 1.30; e, pH 1.05; f, pH 0.80; g, pH 0.58; h, pH 0.32; i, pH 0.10; j, $[H^+] = 2$ *M*; k, $[H^+] = 3$ *M*.

The pK_a value was obtained graphically using the expression

$$pH = pK_a + \log \frac{[Fe(CN)_5MPz^{2-}]}{[HFe(CN)_5MPz^-]}$$

plotting pH *vs.* log $([Fe(CN)_5MPz^{2-}]/[HFe(CN)_5MPz^-])$. Excellent straight-line plots were obtained for all complexes studied, with a probable error of 0.05 in the values of the pK_a determined. The results of the studies of the hydrogen ion concentration dependence using several complexes are collected in Table III.

The shift of the electron-transfer band to higher energies when the complex is protonated can be seen in the table.

[8] At low pH an interesting secondary deviation was observed in the spectrum of the pentacyanopyrazineferrate(II) ion. The initial shift to higher energy on increasing the hydrogen ion concentration gave way to a secondary shift back to lower energy. The new peak grew at nearly 600 nm, very close to the absorption for the $HFe(CN)_5MPz^-$ species. Protonation of the free electron pair of bound pyrazine is implicated.

Table III. pH Dependence of Electron-Transfer Bands

L of $Fe^{II}(CN)_5L$	$\bar{\nu}_{max}$, kK		$\Delta\bar{\nu}$, kK	pK_a[a]
	$Fe^{II}(CN)_5L$	$HFe^{II}(CN)_5L$		
$4\text{-}C_5H_4NCH_3$	28.1	30.8	2.7	2.20
C_5H_5N	27.6	30.3	2.7	2.10
$4\text{-}C_5H_4NCl$	26.1	28.9	2.8	2.00
$4\text{-}C_5H_4CONH_2$	23.0	25.8	2.8	1.92
Pyrazine[b]	22.2	25.0	2.8	1.88
4-Pyridylpyridinium[b]	20.8	24.0	3.2	1.51
N-Methylpyrazinium[b]	15.1	17.9	2.8	0.73

[a] 25°, $\mu = 1.0$ (LiCl). [b] See Table I for structures.

From the nearly constant value of $\Delta\bar{\nu}$ one observes that the magnitude of the energy shift on protonation is almost independent of the identity of the aromatic heterocyclic ligand in the complex.

Another important effect evident in Table III is the variation of the proton association constants (K^{-1}) with the electron-transfer energies measured for the complexes. The residual basicity of cyanide coordinated to iron(II) appears to decrease when the π-acceptor power of the ligand increases. This tendency is very probably associated with the degree of removal of electron density from the metal by a process of back-donation.

Oxidation Potentials. The pentacyanoferrate(II) complexes used in this study can be oxidized by 1 molar equiv of Ce(IV), with concurrent disappearance of the characteristic electron-transfer band and appearance of a much weaker band at higher energy, which we assign to the substituted pentacyanoferrate(III) complex. The oxidation is quantitatively reversible in the presence of a small excess of the heterocycle; the color of the complex is redeveloped upon addition of a reducing agent (*e.g.*, thiosulfate). The formal oxidation potentials at 25°, $\mu = 0.1$ *M*, pH 4.5, are given in Table IV along with those of the pentaammineruthenium(II) analogs.[9-11]

Rate of Ligand Exchange. The kinetics of substitution of the *N*-methylpyrazinium ligand for other aromatic nitrogen heterocycles coordinated to pentacyanoferrate(II) were studied. MPz was chosen as the entering ligand in most of the studies because the product complex is especially stable. The reactions were followed spectrophotometrically at pH 7, $\mu = 1.00$ *M* (lithium perchlorate), at various temperatures using an initial concentration of $Fe(CN)_5L^{3-}$ equal to 5.0×10^{-5} *M*. To ensure pseudo-first-order conditions, the concentration of the leaving ligand, L, was maintained at 5.0×10^{-3} *M*. The concentration of the *N*-methylpyrazinium ion was varied from 1.0×10^{-3} to 0.15 *M*.

The dependence of the rate of formation of pentacyano-*N*-methylpyraziniumferrate(II) on the MPz concentration gave the saturation behavior shown in Figure 3. The form and limiting values of the curves for the six leaving ligands studied indicate that the rate-determining step in the reaction probably involves rupture of the original metal-ligand bond. The temperature dependence of the reactions in the region beyond saturation in the MPz concentration was measured in the 15-35° temperature interval and the saturation-limited rate constants at 25° as well as their activation parameters are presented in Table V.

Table IV. Oxidation Potentials (V) of Substituted Fe(II) and Ru(II) Complexes

L	$Fe^{II}(CN)_5L$ pot.	$Ru^{II}(NH_3)_5L$ Pot.	Ref
$4\text{-}C_5H_4NCH_3$	−0.45		
C_5H_5N	−0.47	−0.35	9
$4\text{-}C_5H_4NCl$	−0.49		
$4\text{-}C_5H_4NCONH_2$	−0.50	−0.44	10
Pyrazine[a]	−0.55	−0.51	9
4-Pyridylpyridinium[a]	−0.55		
N-Methylpyrazinium[a]	−0.78	−0.89	11

[a] See Table I for structures.

Table V. Rate Parameters for Ligand Exchange in Substituted Pentacyanoferrate(II) Complexes

L of $Fe(CN)_5L$	$\bar{\nu}_{max}$, kK	10^4k_{-1}, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$4\text{-}C_5H_4NCH_3$	28.1	11.5	24.0 ± 0.5	9 ± 2
C_5H_5N	27.6	11.0	24.8	11
$4\text{-}C_5H_4NCONH_2$	23.0	7.3	26.0	14
$4,4'\text{-}(C_5H_4N)_2$	23.1	6.2	26.5	16
Pyrazine[a]	22.2	4.2	26.4	14
N-Methylpyrazinium[a]	15.1	2.8	27.5	18

[a] See Table I for structures.

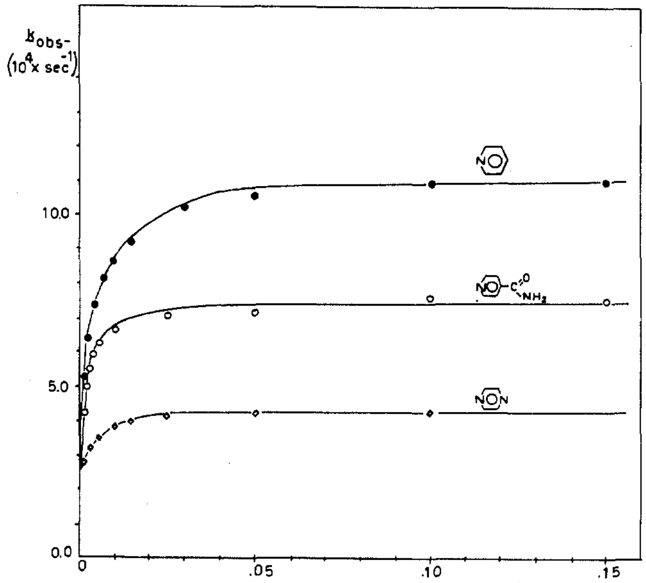


Figure 3. Plot of observed specific rate of substitution, k_{obsd}, *vs.* *N*-methylpyrazinium ion concentration for several leaving ligands.

Experimental Section

Spectra. Ultraviolet and visible range spectra were measured using a Cary 14 recording spectrophotometer, with the cell compartment thermostated at 25.0 ± 0.2°. Ir, uv, and nmr spectra showed clearly the presence of the heterocyclic ligand in the complexes.

pH Measurements. pH measurements were made with a Beckman expandomatic pH meter, Model SS-2, using commercial standard buffer solutions (pH 4.01 and 7.00 at 25.0°) as reference points. p*K* determinations were made spectrophotometrically using buffered solutions consisting of acetate-acetic acid and chloroacetate-chloroacetic acid at several proportions.

To determine the formal oxidation potentials, potentiometric titrations using Ce(IV) were monitored with the Beckman instrument utilizing calomel *vs.* platinum electrodes as reference and indicator, respectively. The method was calibrated using the quinhydrone couple.

Kinetics Experiments. The kinetics were carried out using a Cary Model 14 recording spectrophotometer or in a Durrum stopped-flow Model D-150 apparatus, according to conventional procedures. All the reactant solutions were freshly prepared for each experiment. Prior to mixing and during kinetic runs the solutions were maintained in darkness.

Preparation and Characterization of the Complexes. The majority of the heterocyclic ligands used in this work were recrystallized ac-

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(9) R. E. Shepherd, Ph.D. Dissertation, Stanford University, 1971.

(10) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

(11) H. E. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, **94**, 4039 (1972).

cording to conventional procedures. Pyridine, pyrazine, and 4-methylpyridine of high purity are commercially available and were used as supplied. *N*-Methylpyrazinium iodide was prepared by direct methylation of pyrazine (Aldrich Chemical Corp.) with methyl iodide.[12] The pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles were prepared in aqueous solution by direct mixture of recrystallized $Na_3Fe(CN)_5NH_3$ (Eastern Chemical Corp.) with a severalfold excess of the ligand. The intensities of the electron-transfer bands of the complexes were virtually independent of the ligand concentrations when the ligands were present in greater than 1:1 ratio. This observation, together with the high formation constants[13] which were estimated for the complexes, indicates that very stable adducts of 1:1 stoichiometry are formed under the conditions of this work.

Spectrophotometric analysis of all of the complexes was performed by treating each one in solution with at least a 100-fold excess of the *N*-methylpyrazinium ion, causing complete conversion of the iron complex to the *N*-methylpyrazinium-substituted derivative within 2 hr at room temperature. The ratios of extinction coefficients so obtained were checked by treating separate weighed samples of the trisodium salt of pentacyanoaminoferrate(II) with known volumes of solutions of the ligands in excess. The extinction coefficients of the complexes relative to that of the *N*-methylpyrazinium complex were thus determined by two methods which were found to agree within 2%.

The *N*-methylpyrazinium-substituted complex was chosen as the standard for the series of complexes because it is the most stable. The extinction coefficient for this complex was determined by direct weighing and subsequent dissolution of the sodium salt of the complex and was confirmed by potentiometric titration with cerium(IV).

Not all of the complexes were isolated as solid salts. Two of the species studied, the isonicotinate and the *p*-formylpyridine complexes, exist in labile equilibria with respectively their protonated and hemiacetal forms. Experimental conditions for selective precipitation of only one of these forms were not found. Furthermore, the complexes, especially with the ligands pyridine, *p*-methylpyridine, and *p*-chloropyridine, proved to be thermally and photochemically sensitive. Nevertheless it was possible to prepare the sodium salts of several of the complexes in the following way: 2.0 g of recrystallized trisodium pentacyanoaminoferrate(II)·nH$_2$O was dissolved in 10 ml of water containing a fivefold excess of the ligand, at ice bath temperature, and kept cold in the dark for *ca.* 30 min. The product was precipitated by careful addition of methanol, collected on a sintered-glass filter and recrystallized several times.

Anal. Calcd for *N*-methylpyrazinium iodide: C, 27.04; N, 12.6; H, 3.18; I, 57.2. Found: C, 27.11; N, 12.8; H, 3.22; I, 57.2. Calcd for $Na_2[Fe(CN)_5C_5H_7N_2]\cdot 4H_2O$ ($C_5H_7N_2$ = *N*-methylpyrazinium): C, 30.0; N, 24.6; H, 3.7. Found: C, 29.0; N, 24.7; H, 3.3. Calcd for $Na_3[Fe(CN)_5C_4H_4N_2]\cdot 4H_2O$ ($C_4H_4N_2$ = pyrazine): C, 26.5; N, 24.0; H, 2.9. Found: C, 25.7; N, 24.7; H, 2.7. Calcd for $Na_3[Fe(CN)_5C_6H_6N_2O]\cdot 5H_2O$ ($C_6H_6N_2O$ = isonicotinamide): C, 28.3; N, 21.0; H, 3.4. Found: C, 28.2; N, 21.4; H, 2.7. Calcd for $Na_3[Fe(CN)_5C_{10}H_9N_2]\cdot 5H_2O$ ($C_{10}H_9N_2$ = 1-(4-pyridyl)pyridine): C, 37.6; N, 20.5; H, 3.9. Found: C, 36.9; N, 20.9; H, 3.6.

Microanalysis was performed by the Stanford Microanalytical Laboratory, Stanford University. Although the analyses for carbon were uniformly low for the cyano complexes, the microanalytical results are clearly consistent with the formulations given and with the characterization of the complexes in solution. The presence of the stated number of molecules of water was confirmed in each case, using Karl Fischer reagent.

Discussion

A plot of the energy of the electron-transfer band in the visible-near-uv spectral region for a series of pentaammineruthenium(II) complexes *vs.* the energy of the band in the substituted pentacyanoferrate(II) species is shown in Figure 4. With the exception of the *N*-methylpyrazinium ligand (see Table I), the plot is strikingly linear. This close analogy with the substituted pentaammineruthenium(II) complexes, as well as the other lines of evidence being presented here, indicates almost unequivocally the electron-transfer nature of the strong visible absorption band in the pentacyanoferrate(II) complexes.

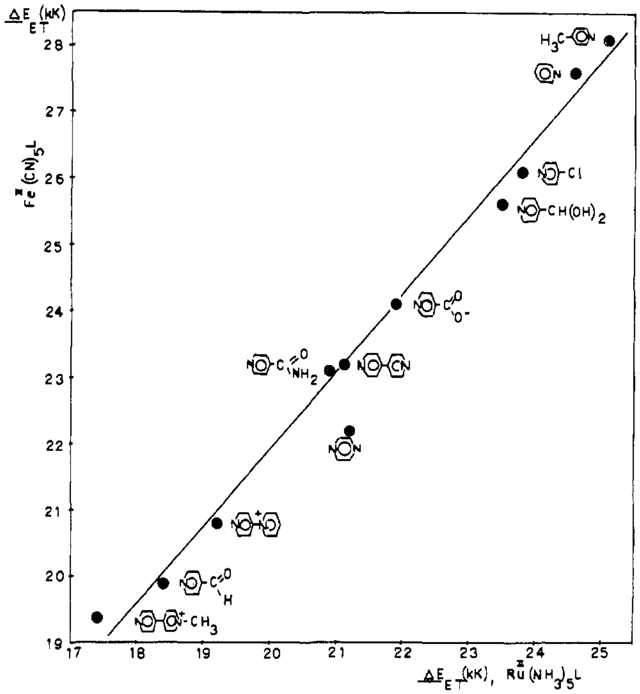

Figure 4. Energy maxima of electron-transfer bands in $Fe(CN)_5L^{n-}$ complexes plotted *vs.* the energies of the peaks in substituted pentaammineruthenium(II) complexes.

According to the simplified Murrell equation,[14] $E_{ET} = I_M - A_L + C$ (where I_M is the ionization potential of the metal ion, A_L is the electron affinity of the ligand, and C is a coulombic term approximated as the energy of the attraction which the electron transferred into the ligand orbital has for the metal ion with its charge increased by 1). When the equation is valid, one expects a nearly linear relationship between the electron-transfer energy and the electron affinity of the ligand for closely related complexes, if the C term is constant or varies linearly within the series. Such a relationship was found between the half-wave reduction potential of the free ligand and the energy of the metal-to-ligand electron-transfer band for a number of substituted pentaammineruthenium(II) complexes.[2]

The close correspondence between the energies of the transitions in the pentacyanoferrate(II) complexes and those in the Ru(II) complexes demonstrates that a similar relationship with the half-wave reduction potentials of the ligands must hold for the energies of the electron-transfer bands in the substituted pentacyanoferrate(II) complexes.

Band Intensities. In the series of pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles the transition intensity, as expressed by the measured oscillator strength, was found to increase when the energy of the electron-transfer transition decreased. According to a simplified treatment by Day and Sanders[15] of the ferrous, ferric, and cuprous *o*-phenantroline complexes (assuming a 1:1 stoichiometric model), the intensity of the electron-transfer transition depends primarily on a mixing coefficient of the ground- and excited-state wave functions. The mixing coefficient, within the HMO approximation, is proportional to the resonance

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(12) C. T. Bahner and L. L. Norton, *J. Amer. Chem. Soc.*, 72, 2881 (1950).

(13) The specific rates of formation of the heterocycle-substituted complexes from aqueous pentacyanoammineferrate(II) are more rapid than the specific rates of dissociation by a factor of approximately 10^6. This suggests that the rate of loss of the NH_3 ligand and the exchange of inner-sphere H_2O should be rapid compared to the k_{-1} step in eq 2a. The measured specific rates vary only slightly among the incoming ligands studied: H. E. Toma and J. M. Malin, submitted for publication in *Inorg. Chem.*

(14) J. N. Murrell, *Quart. Rev., Chem. Soc.*, 191 (1961).

(15) P. Day and N. Sanders, *J. Chem. Soc*, 1530 (1967).

integral β_{M-L} and varies inversely with the energy separation between metal and ligand orbitals.

The observed variation of the oscillator strength with the energy of the electron-transfer transition suggests that the degree of t_{2g}(metal)-π^*(ligand) interaction increases as we pass along the series of ligands: 4-methylpyridine, pyridine, 4-chloropyridine, isonicotinamide, pyrazine, and *N*-methylpyrazinium. A tentative molecular orbital description of the pentaammineruthenium(II) analogs can be found in ref 2. Extending the same model to our complexes, one can see that the primary contribution to back-bonding must come from the interaction of the lowest unoccupied orbital of B_2 symmetry with the d_{yz} orbital with the same symmetry. This assignment is also in agreement with the rule that electron-transfer intensity must always be polarized in the direction in which the electron is transferred.

pH Effects. Considering the results of Schilt[6] and of Hamer and Orgel,[7] and in view of the nonexistence of similar effects in analogous pentaammineruthenium(II) species, we conclude that the observed pH dependence of the visible spectra of the pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles results from protonation of coordinated cyanide.

The nearly identical values of the shifts of the visible bands to higher energies on proton association, shown in Table III and Figure 1, suggest that the electronic ground state (in which the electron to be transferred resides primarily on the metal ion) is more strongly affected by protonation than the excited state (in which the electron occupies an orbital of the ligand). The increase in the energy separation caused by proton association is probably responsible for the somewhat lower intensities of the metal-to-ligand electron-transfer bands exhibited by the protonated forms of these complexes. The ultraviolet absorption assigned to an intraligand transition ($\pi^* \leftarrow \pi$) in the heterocycle was practically unaffected by changes in pH.

The decrease in the protonation constant with decreasing energy of the $\pi^* \leftarrow t_{2g}$ transition is an especially interesting correlation. In ruthenium(II) complexes of heterocyclic ligands, the back-bonding process is considered to effect a significant removal of electron density from the metal center to the ligand.[16] In the series of substituted pentacyanoferrate(II) complexes the decreasing basicity of coordinated cyanide signifies an increasing shift of electron density away from Fe(II) as the ligand L becomes increasingly attractive to π electrons.[17]

Redox Potentials. The observed variation in the formal oxidation potentials of the substituted pentacyanoferrate(II) complexes clearly shows the varying abilities of the aromatic nitrogen heterocycles to stabilize pentacyanoferrate(II) against oxidation. Increasing stabilization of the Fe(II) state follows the order of increasing back-bonding in the complexes as indicated by the spectral and pH effects. An analogous correlation can be made between the oxidation potentials of the pentaammineruthenium(II) complexes of aromatic nitrogen heterocycles and the energies of their electron-transfer bands.

Kinetics of Ligand Exchange. The rate of substitution of *N*-methylpyrazinium ion for the ligand L in $Fe(CN)_5L^{3-}$ was seen to vary with the identity of L. In each case the reaction rate depended initially upon the *N*-methylpyrazinium ion concentration, but eventually reached a constant value which did not increase with increasing [MPz]. This type of saturation behavior can be understood in terms of rate-determining loss of L from the $Fe(CN)_5L^{3-}$ ion, with subsequent, rapid attack by the incoming ligand. The possibility that rate saturation might be due to the use of MPz as entering ligand was eliminated. The kinetics of the replacement of pyridine in the pentacyanoferrate(II) complex by pyrazine also showed saturation behavior. The saturation-limited value of k_{obsd} was, within experimental error, the same for incoming pyrazine as for *N*-methylpyrazinium ion. We therefore postulate the following mechanism as consistent with the kinetic results

$$Fe(CN)_5L^{3-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} Fe(CN)_5{}^{3-} + L \tag{2a}$$

$$Fe(CN)_5{}^{3-} + H_2O \overset{K}{\rightleftharpoons} Fe(CN)_5H_2O^{3-} \tag{2b}$$

$$Fe(CN)_5{}^{3-} + MPz \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5MPz^{2-} \tag{2c}$$

The rate law for the mechanism is

$$\frac{d[Fe(CN)_5MPz^{2-}]}{dt} = k_{obsd}\{[Fe(CN)_5L^{3-}] - [Fe(CN)_5L^{3-}]_{t=\infty}\}$$

where, applying the steady-state approximation

$$k_{obsd} = \frac{k_{-1}k_2[MPz] + k_1k_{-2}[L]}{k_1[L] + k_2[MPz]} \tag{3}$$

In the measurements a small excess of [L] over $[Fe(CN)_5L^{3-}]$ was maintained. However, one can see that the [L]-dependent terms become negligible at sufficiently high [MPz] and the observed rate constant reduces simply to k_{-1}. Similarly, as the *N*-methylpyrazinium ion concentration approaches zero, k_{obsd} should tend toward k_{-2}. Both predictions are verified in Figure 3, by the saturation behavior in MPz and by the fact that the extrapolated curves all pass through the same ordinate intercept when the *N*-methylpyrazinium ion concentration goes to zero.

The equilibrium involving water (eq 2b) is written in the mechanism because it is a likely, although nonproductive, step. The assumption that eq 2b is labile with respect to the k_{-1} and k_{-2} steps has been justified.[13]

The rate constants and activation parameters for the k_{-1} step are consistent with the proposed mechanism (eq 2). The activation entropies ($\Delta S^{\ddagger}$) are positive as expected for a dissociative type of mechanism. The rates of ligand loss (k_{-1}) decrease with the expected increase in back-bonding interaction, rather than with increasing ligand basicity. Enthalpies of activation increase in the expected order of increasing back-bonding. We note that the enthalpies of activation are very similar to those measured in a recent study, by Vaska and Yamaji,[18] in which one pyridine molecule, or a substituted pyridine, was replaced by carbon monoxide in nonaqueous solution, in a series of *trans*-$Fe(DPGH)_2(py)_2$ complexes (DPGH is the univalent, bidentate diphenylglyoximato anion). However, in that study the apparent relative rate of ligand loss decreased with increasing basicity of the leaving ligand. This difference reflects, perhaps, the higher concentration of negative charge in the $Fe(CN)_5L^{3-}$ complexes relative to that in the $Fe(DPGH)_2(py)_2$ species.

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(16) C. Creutz and A. M. Zwickel, *Inorg. Chem.*, 10, 2395 (1971).

(17) An example of considerable change in acid strength with changing formal charge on Fe(II) is found in the comparison of the $H_4Fe(CN)_6$ complex, which is weakly acidic in its third and fourth ionization steps, with the strongly acidic $H_3Fe(CN)_6$.

(18) L. Vaŝka and T. Yamaji, *J. Amer. Chem. Soc*, 93, 6673 (1971).

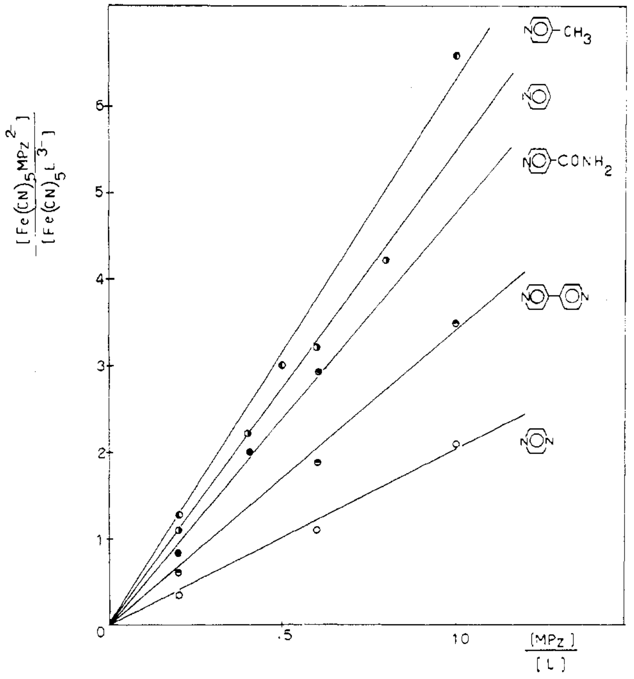

Figure 5. Plot of k_{-1}/k_{obsd} *vs.* [pyridine]/[*N*-methylpyrazinium] showing deviations at low [MPz].

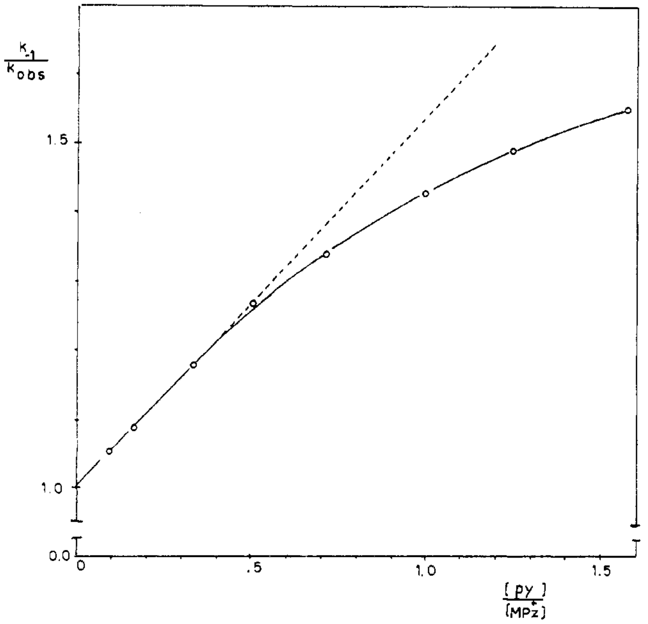

Figure 6. Dependence of product distribution on free ligand concentrations.

The experimental observations represented in Figure 3 are especially significant because they give a direct indication, of which there are relatively few,[19,20] of a limiting SN1 ligand replacement mechanism. Also, this study is, to our knowledge, the first account of the kinetics of monodentate ligand substitution in simple, low-spin iron(II) complexes in aqueous solution.

From the kinetic data it is possible to extract the relative values of the specific rates of attack, k_1, by the various leaving groups (eq 2) in the following way.

Assuming the mechanism given in eq 2 and rearranging eq 3, the relationship expressed in eq 4 is derived. At relatively high [MPz],

$$\frac{k_{-1} + k_1k_{-2}[L]/k_2[MPz]}{k_{obsd}} = 1 + \frac{k_1[L]}{k_2[MPz]} \qquad (4)$$

this expression can be simplified through the considerations that $k_1[L] \leqslant k_2[MPz]$ and $k_{-2} < k_{-1}$ yielding eq 5.

$$\frac{k_{-1}}{k_{obsd}} = 1 + \frac{k_1[L]}{k_2[MPz]} \qquad (5)$$

Applying the equation above, one might expect a linear variation of k_{-1}/k_{obsd} with [L]/[MPz] giving a unit intercept. However, as [MPz] decreases the term $k_1k_{-2}[L]/k_2[MPz]$ in eq 4 ceases to be negligible and leads to the deviation from linearity which is obtained by experiment, as shown in Figure 5. The fact that the deviation is observed is consistent with the proposed mechanism. From the initial slopes of plots such as Figure 5, the relative specific rates of attack, k_1, have been shown to vary within only a factor of less than 2 for the ligands 4-methylpyridine, pyridine, isonicotinamide, 4,4′-bipyridine, and pyrazine. Thus the reactive intermediate shows little selectivity among these ligands.[13]

According to the proposed mechanism the distribution of the complexes at equilibrium should be given by

$$\frac{[Fe(CN)_5MPz^{2-}]}{[Fe(CN)_5L^{3-}]} = \frac{k_2k_{-1}[MPz]}{k_1k_{-2}[L]}$$

A plot of the quotient $[Fe(CN)_5MPz^{2-}]/[Fe(CN)_5L^{3-}]$ *vs.* [MPz]/[L] was linear, as exemplified in Figure 6, for the five leaving ligands studied. The slopes of these plots were used to estimate the ratios of the formation constants of those complexes relative to the association constant of the $Fe(CN)_5MPz^{2-}$ species. The decreasing order of formation quotients was *N*-methylpyrazinium > pyrazine > 4,4′-bipyridine > isonicotinamide ⩾ pyridine ⩾ 4-methylpyridine. It is interesting that the increasing stability of the complexes follows the order which would be expected on the basis of increasing back-bonding interaction. However, the important effect of ligand basicity has not yet been assessed.

Conclusion

The correlation of electron-transfer energy with the energy of the unoccupied orbitals in the aromatic nitrogen heterocyclic ligands suggests a spectrochemical order of back-donation: *N*-methylpyrazinium[21] > pyrazine ~ isonicotinamide > pyridine > 4-methylpyridine.

The order seems to be common to both the pentacyanoferrate(II) and the pentaammineruthenium(II) series. In the pentacyanoferrate(II) case, the order is reflected in direct correlations[22] among electron-transfer energies, oscillator

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(19) A. Haim, R. J. Grassi, and W. K. Wilmarth, *Advan. Chem. Ser.*, No. 49, 31 (1965).

(20) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 3.

(21) While it is clear that the $Fe(CN)_5MPz^{2-}$ is the most stable of the series studied and that this is consistent with strong back-bonding in the complex, the electrostatic contribution to the complex's stability has not been assessed. Therefore, it is also interesting to compare the properties of the pentacyanoferrate(II) complex of the pyridylpyridinium ion. In the case of this latter complex, the overall charge is 2−, and the distance from the metal ion to the positively charged center of the ligand is only slightly greater. Yet in the pyridylpyridinium complex, all the indices of stability are shifted considerably toward values exhibited by the pentacyanoferrate(II) complexes of uncharged aromatic nitrogen heterocycles. The authors suggest that the special stability of the *N*-methylpyrazinium complex cannot come solely from electrostatic attraction between the pentacyanoferrate(II) group and the MPz ligand but must also involve a significant back-bonding contribution.

(22) Some similar correlations have been shown to be theoretically consistent: see, for example, R. L. Flurry, Jr., *J. Phys. Chem.*, 69, 1927 (1965); 73, 2111 (1969); P. Politzer and R. L. Flurry, Jr., *ibid.*, 73, 2787 (1969).

strengths of electron-transfer bands, proton association constants, formal oxidation potentials, and rates of dissociation.

Registry No. $Fe(CN)_5L^{3-}$ (L = 4-methylpyridine), 37475-65-3; $Fe(CN)_5L^{3-}$ (L = pyridine), 37475-75-5; $Fe(CN)_5L^{3-}$ (L = 4-chloropyridine), 37475-74-4; $Fe(CN)_5L^{3-}$ (L = isonicotinaldehyde hemiacetal), 37475-73-3; $Fe(CN)_5L^{4-}$ (L = isonicotinate), 37475-64-2; $Fe(CN)_5L^{3-}$ (L = 4,4′-bipyridine), 37475-72-2; $Na_3(CN)_5L$ (L = isonicotinamide), 37475-71-1; $Na_3Fe(CN)_5L$ (L = pyrazine), 37475-70-0; $Na_2Fe(CN)_5L$ (L = 4-pyridylpyridinium), 37475-69-7; $Fe(CN)_5L^{3-}$ (L = isonicotinaldehyde), 37475-68-6; $Fe(CN)_5L^{2-}$ [L = 1-methyl-4-(4-pyridyl)pyridinium], 37475-67-5; $Na_2Fe(CN)_5L$ (L = methylpyrazinium), 37475-66-4.

Acknowledgment. The authors gratefully acknowledge financial support from the following: the Conselho National de Pesquisas, the Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (predoctoral fellowship to H. E. T), the Atlantic Petroleum Co. of Brasil, the Agency of International Development, the National Science Foundation, the National Academy of Sciences, and the Atlantic Richfield Corp. Also acknowledged gratefully are the aid and encouragement of Professors Ernesto Giesbrecht, Pawel Krumholtz, and Henry Taube.

Contribution from the University Chemical Laboratory, Cambridge, United Kingdom, and the Department of Chemistry, University of British Columbia, Vancouver, Canada

Mossbauer Measurements of the Electric Field Gradient at Iron in Some Pentacoordinate Phosphine-Carbonyl-Iron(0) Complexes

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Received June 23, 1972

We report experimental and theoretical studies of the electric field gradient at trigonal-bipyramidally coordinated Fe in phosphine derivatives of $Fe(CO)_5$. Theoretical calculations are based on the assumption (supported by experimental evidence) that the effect of substitution may be treated as a perturbation. It is shown that, although substitution which preserves the axial symmetry has little effect on the electric field gradient at Fe, both the asymmetry parameter η and the sign of the $^{57}Fe^m$ quadrupole splitting ΔE_Q [$\Delta E_Q = {}^1/_2 e^2qQ(1 + {}^1/_3\eta^2)^{1/2}$] are very sensitive to breaking of the threefold symmetry by substitution, but $|\Delta E_Q|$ is not. Mossbauer spectra in applied magnetic fields of 35–50 kG give values for η and the sign of ΔE_Q for four derivatives of $Fe(CO)_5$. The results are considered in the light of the theoretical investigations. It is concluded that determination of η and the sign of ΔE_Q is a sensitive method for detecting lack of axial symmetry in derivatives of $Fe(CO)_5$ but cannot easily be used to answer more detailed stereochemical questions.

Introduction

An interesting feature of the Mossbauer spectra of $Fe(CO)_5$ and its pentacoordinate phosphine and arsine derivatives of the types $LFe(CO)_4$, $L_2Fe(CO)_3$, $L^{(b)}Fe_2(CO)_8$, and $L^{(c)}Fe(CO)_3$ is that the magnitude of the ^{57}Fe quadrupole splitting $|\Delta E_Q|$ is quite insensitive both to the nature of the ligand and to the symmetry of the complex. [L represents a tertiary phosphine or arsine, and $L^{(b)}$ and $L^{(c)}$ represent a di(tertiary phosphine or arsine) acting as a bridging or chelating group, respectively.] At 80°K all complexes of the above four types for which Mossbauer data are available[3-9] have $|\Delta E_Q|$ values within about ±15% of the value for $Fe(CO)_5$ itself, even when the symmetry of the complex is quite different. An examination of the Mossbauer quadrupole interaction in some of these compounds in the presence of an applied magnetic field seemed attractive, since this technique allows one to determine the sign of the electric field gradient (EFG) at the iron nucleus and to estimate the value of the asymmetry parameter η. Both of these quantities should be more sensitive than the quadrupole splitting to replacement of carbonyl groups if such substitution breaks the axial symmetry.[10]

Very few determinations of the sign of the EFG in Fe(0) complexes have been reported. For $Fe(CO)_5$, studies of oriented polycrystalline samples have shown that the quadrupole coupling constant e^2qQ is positive.[3] Collins and Travis[11] have reported the Mossbauer spectra of butadieneiron tricarbonyl and cyclobutadieneiron tricarbonyl in applied magnetic fields of 26 kG. They found that e^2qQ was negative in the butadiene compound and positive in the cyclobutadiene derivative, but a satisfactory explanation of this sign reversal was not given. Magnetic perturbation studies on a few derivatives in which the $(\pi\text{-}C_5H_5)Fe(CO)_2$ moiety is bonded to a tin atom have revealed positive signs for e^2qQ at Fe in every case.[12,13] No attempt has been made to interpret these results, since the nature of the molecular orbitals is not well understood.

The approximate invariance of $|\Delta E_Q|$ in pentacoordinate phosphine and arsine derivatives of $Fe(CO)_5$ suggests that replacement of CO may be regarded as a perturbation of the electronic structure of the Fe atom in $Fe(CO)_5$. In the next

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(3) P. Kienle, *Phys. Verh.*, 3, 33 (1963).

(4) R. L. Collins and R. Pettit, *J. Amer. Chem. Soc.*, 85, 2332 (1963); *J. Chem. Phys.*, 39, 3433 (1963).

(5) R. H. Herber and R. G. Hayter, *J. Amer. Chem. Soc.*, 86, 301 (1964).

(6) R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, 3, 101 (1964).

(7) T. C. Gibb, R. Greatrex, N. N. Greenwood, and D. T. Thompson, *J. Chem. Soc. A*, 1663 (1967).

(8) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 8, 1464 (1969).

(9) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, 2, 153 (1963).

(10) M. G. Clark, *Chem. Phys. Lett.*, 13, 316 (1972).

(11) R. L. Collins and J. C. Travis, *Moessbauer Eff. Methodol., Proc. Symp.*, 3, 123 (1967).

(12) S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc. A*, 1616 (1971).

(13) B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc. A*, 1868 (1971).