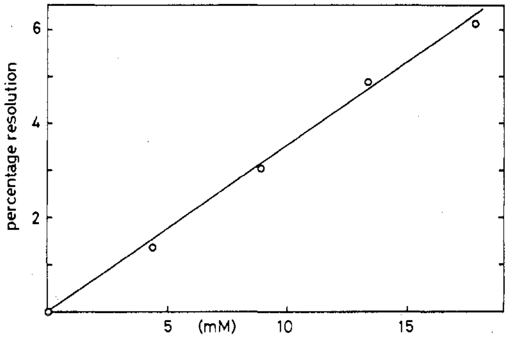

Figure 3. Dependence of the percentage resolution on the concentration of Λ-$[Co(phen)_3]^{3+}$ for the $[Cr(ox)_3]^{3-}$ (7.54 mM) system.

electric constant of the medium will lead to enhanced electrostatic association of $[Cr(ox)_3]^{3-}$ or $[Co(ox)_3]^{3-}$ with Λ-$[Co(phen)_3]^{3+}$.

In Figure 3 is plotted the percentage resolution for the $[Cr(ox)_3]^{3-}$ system as a function of the amount of added Λ-$[Co(phen)_3]^{3+}$, the amounts of the racemic complex and added dioxane being kept constant (7.54 mM and 10 mL/25 mL of solution, respectively). It is seen that the percentage resolution is enhanced almost linearly with the amount of the chiral environment substance, as is usually the case.[2]

There have already appeared two Pfeiffer-active systems with a metal complex as an environment in the literature. One is the $[Zn(phen)_3]^{2+}$–Λ-$[Co(en)_3]^{3+}$ system in water.[9] However, strong electrostatic repulsion between the two cationic complexes will prohibit their favorable interaction. Then, the $[Ni(phen)_3]^{2+}$–Λ-$[Co(en)_3]^{3+}$ system was examined in place of the zinc complex system. An aqueous mixture of the two complexes kept standing for 2 weeks[10] was subjected to a column chromatography (SP-Sephadex C-25 in Na^+ form) with aqueous NaCl (0.1 M) as an eluent. Only the first band corresponding to the nickel complex was collected, but it was found CD inactive. This result is consistent with the earlier finding[11] that no difference is observed in the racemization rates of Δ- and Λ-$[Ni(phen)_3]^{2+}$ in the presence of Λ-$[Co(en)_3]^{3+}$. Therefore, the $[Zn(phen)_3]^{2+}$–Λ-$[Co(en)_3]^{3+}$ system is supposed to be also Pfeiffer-inactive.[12]

The other is the $[Ni(acac)_3]^-$–Λ-$[Co(en)_3]^{3+}$ system in water, which was recently proposed to be Pfeiffer-active by Pollock et al.[13] However, the $[Co(acac)_3]^-$–Λ-$[Co(en)_3]^{3+}$ system similar to the above system was found Pfeiffer-inactive in our previous study.[1] Since they could not detect directly the CD spectrum due to $[Ni(acac)_3]^-$, their proposal is open to question. On the other hand, the $[Co(acac)_3]^-$–Λ-$[Co(phen)_3]^{3+}$ and the present $[Cr(ox)_3]^{3-}$– or $[Co(ox)_3]^{3-}$–Λ-$[Co(phen)_3]^{3+}$ systems are undoubtedly Pfeiffer-active systems with a dissymmetric metal complex as an environment substance.

Registry No. $[Cr(ox)_3]^{3-}$, 15054-01-0; $[Co(ox)_3]^{3-}$, 15053-34-6; Λ-$[Co(phen)_3]^{3+}$, 24501-38-0; dioxane, 123-91-1.

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Protonation of the Pentacyanoaquaferrate(II) Ion, $Fe(CN)_5OH_2^{3-}(aq)$

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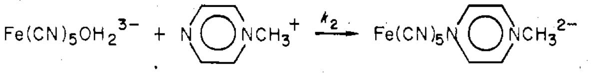
Recently, a number of studies involving kinetics of complexation by the pentacyanoaquaferrate(II) ion, $Fe(CN)_5OH_2^{3-}(aq)$, have been made.[1–6] Like other complexes involving the pentacyanoferrate(II) moiety,[7] the aqua complex is expected to behave as a weak base, protonatable at cyanide. However, the pK_a of its conjugate acid and also the substitution reactivity of that species have remained unknown. Because the aqueous pentacyanoaquaferrate(II) ion is a reactant used in a new class of electron-transfer "precursor" intermediates,[1c,5] a knowledge of its properties in the protonated form is especially important.

Complications introduced by formation and protonation of polynuclear species, e.g., $Fe_2CN_{10}^{6-}(aq)$,[6,8] make direct measurement of the pK_a by pH titration extremely difficult. Therefore, we have studied the kinetics of the aqueous substitution reaction, eq 1, within the pH range 1.0–7.5 at 25 °C,



(1)

μ = 0.1 M ($LiClO_4$). The complexing agent *N*-methylpyrazinium ion (Me(pyr)$^+$) neither gains nor loses a proton within this pH interval. The results show that the pK_a of $HFe(CN)_5OH_2^{2-}$ is 2.63 ± 0.12, under the experimental conditions. A striking diminution in substitution reactivity is seen in the protonated form.

Experimental Section

Materials and Methods. Doubly distilled water containing appropriate buffers, reagent grade perchloric acid, and lithium perchlorate were the reaction medium. pH values were measured using an Orion 801 pH meter.

N-Methylpyrazinium iodide was prepared by methylation of pyrazine.[9] Anal. Calcd for $C_5H_7N_2I$: C, 27.05; H, 3.18; N, 12.62. Found: C, 26,86; H, 3.27; N, 12.61.[10] In the kinetics experiments, control of pH in the reaction mixture was accomplished by adding acetate or phosphate buffers, or perchloric acid, to the Me(pyr) solutions.

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepared as described previously,[11] washed with methanol, and stored in vacuo in the dark. Anal. Calcd for $Na_3FeC_5H_9N_6O_3$: C, 18.24; H, 2.78; N, 25.78. Found: C, 18.18; H, 2.84; N, 25.71. For the kinetics studies, solutions of $Fe(CN)_5OH_2^{3-}$ were produced by dissolving ca. 1.5×10^{-5} mol of the above salt in 250 mL of water at pH ~10 (unbuffered). A 5.00-mL sample of this solution was added immediately to 45.00 mL of dilute lithium perchlorate solution, also at pH ~10, for use in the Durrum D-110 stopped-flow instrument. Syringe-transfer techniques, N_2 blanketing gas, and low light levels were employed to minimize the decomposition of the reactant iron(II) complex. Experiments were performed within the shortest possible time after dissolving the pentacyanoferrate(II) salt. Because of these precautions, little evidence was found of the slowly reacting polynuclear iron(II) cyanides that have been described previously.[1a,5,6,8] Slow, secondary absorbance increases could be

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Table I. pH Dependence of the Rate of Formation of $Fe(CN)_5OH_2^{3-}(aq)^a$

Run	10^4 [Me(pyr)$^+$], M	k_{obsd}, s^{-1}	pH	10^3k_2,^{b} M^{-1} s^{-1}
1	1.93	0.454	7.52	2.35
2	1.92	0.488	6.56	2.54
3	1.92	0.460	4.5	2.40
4	4.27	0.899	4.0	2.10
5	4.27	0.798	3.5	1.87
6	4.35	0.619	3.0	1.42
7	4.35	0.456	2.3	1.05
8	6.44	0.321	2.0	0.50
9	4.27	0.062	1.3	0.15
10	4.16	0.028	1.0	0.067

[a] [Fe(II)] = (2–5) × 10^{-6} M, 25.0 ± 0.3 °C, $\mu = 0.1$ M, λ 650 nm. [b] Accuracy ±4%.

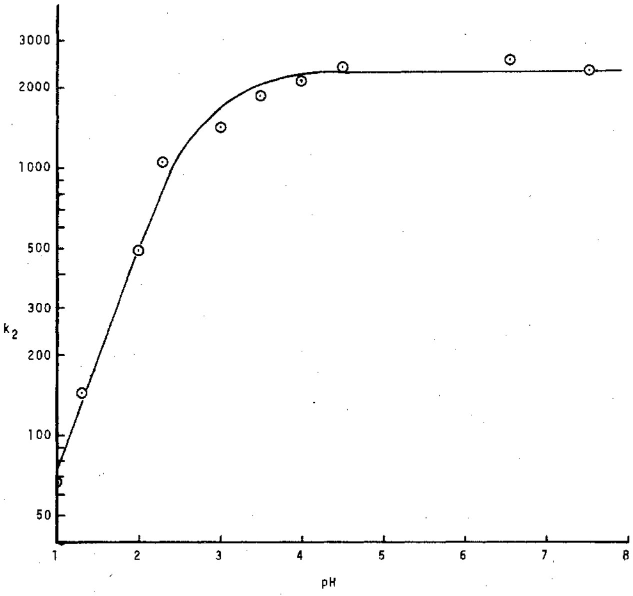

Figure 1. pH dependence of k_2.

induced, however, by decreasing the pH of the iron(II) reactant solution or by working at higher concentrations of pentacyanoferrate(II).

The reaction conditions always involved a substantial excess of Me(pyr)$^+$. Pseudo-first-order rate constants were computed by iterative, least-squares fitting of the absorbance vs. time curves to the first-order decay equation. Fits were excellent over at least 3 half-lives. Error limits given for individual rate constants are the computed standard deviations. The reaction rate was observed not to vary with spectrophotometer slit width. In computing the best fit to eq 2, the values of k_2 for runs 1, 2, and 3 were weighted 50-fold, 25-fold, and 10-fold, respectively, to compensate for the relatively small values of these rate constants. The weighting had a small effect on the calculated values of k_A, k_{AH}, and k_H.

Results and Discussion

The kinetics data are listed in Table I. Figure 1 presents a plot of log k_2 vs. pH. The points in the figure were determined by experiment, while the solid curve gives the best least-squares fit to eq 2.

$$k_2 = \frac{k_{AH}[H^+] + k_AK_{AH}}{[H^+] + K_{AH}} \tag{2}$$

A generalized mechanism for the reaction is

$$\begin{tikzcd}
HFe(CN)_5OH_2^{2-} + Me(pyr)^+ \arrow[r, shift left, "k_{AH}"] \arrow[d, shift left, "-H^+, K_{AH}"] & HFe(CN)_5Me(pyr)^- \arrow[l, shift left, "k_{-AH}"] \arrow[d, shift left, "-H^+, K'_{AH}"] \\
Fe(CN)_5OH_2^{3-} + Me(pyr)^+ \arrow[r, shift left, "k_A"] \arrow[u, shift left, "H^+"] & Fe(CN)_5Me(pyr)^{2-} \arrow[l, shift left, "k_{-A}"] \arrow[u, shift left, "H^+"]
\end{tikzcd}$$

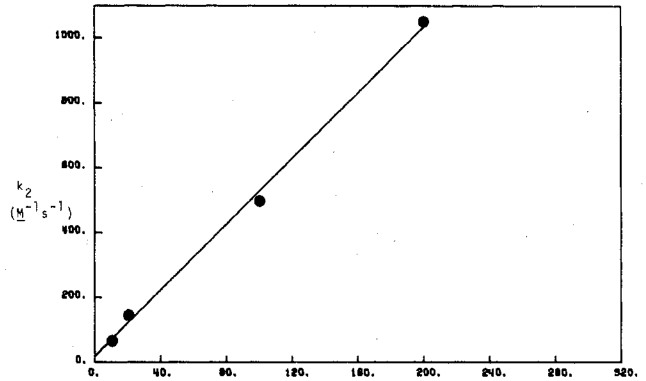

Figure 2. Plot of k_2 vs. 1/[H^+] at low pH.

Protonation of the products and reactants may be assumed to be rapid and reversible. The dissociation steps (k_{-AH} and k_{-A}) are negligibly slow on the time scale of the formation reaction. The values of k_A, k_{AH}, and K_{AH} were computed to be (2.35 ± 0.11) × 10^3 M^{-1} s^{-1}, 23 ± 42 M^{-1} s^{-1}, and (2.35 ± 0.61) × 10^{-3} M, respectively, at 25.0 ± 0.3 °C, $\mu = 0.10$ M.

Under the conditions employed, the pK_a of protonated pentacyanoaquaferrate(II) is 2.63 ± 0.12. For comparison, the values for $HFe(CN)_6^{3-}$ and $H_2Fe(CN)_6^{2-}$ are 3.16 and 1.22, respectively.[12] As expected on the basis of relative charge, the exchange of a cyano group in ferrocyanide for a water ligand results in a decrease in the basicity of the remaining cyano groups. For the protonated pentacyanoferrate(II) complexes of several aromatic N-heterocycles the pK_a values are 2.1, 1.9, and 0.73, respectively, for the ligands pyridine, isonicotinamide, and Me(pyr)$^+$ at $\mu = 1.0$ M. The value of k_A in the present work is in excellent agreement with that ((2.4 ± 0.08) × 10^3 M^{-1} s^{-1}) found previously by Toma and Malin at $\mu = 0.10$ M.[1a]

A surprising result of this work is that protonation of pentacyanoaquaferrate(II) decreases the rate of its reaction with Me(pyr)$^+$ by a factor of at least 50. In Figure 2 is presented a plot of k_2 vs. 1/[H^+] in the low-pH region. The ordinate intercept is 21 ± 30 M^{-1} s^{-1}. In view of the large relative error in the extrapolation, the finite intercept should be regarded only as an approximate upper limit for k_{AH}. Part of the striking decrease in specific rate must be due to the diminished negative charge of the protonated pentacyanoaquaferrate(II) reactant. The influence of electrostatic effects upon the kinetics of reactions producing pentacyanoferrate(II) complexes has been noted previously.[1a,3] An additional factor is probably the increase in positive charge carried by iron(II) in the protonated aqua complex. This would have the effect of strengthening the iron(II)–oxygen bond. Since the complex appears to react by a dissociative mechanism, a decrease in reactivity would be observed.

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Registry No. $Fe(CN)_5OH_2^{3-}$, 18497-51-3; Me(pyr)$^+$, 17066-96-5.

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^{14}N Nuclear Quadrupole Resonance Spectra of Coordinated 1,2-Dipiperidinoethane[1a]

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With the advent of double resonance methods for the determination of ^{14}N nuclear quadrupole resonance (NQR) spectra,[2] it has become possible to study in unprecedented detail changes in electronic charge distribution which accompany coordination of nitrogen to diamagnetic Lewis acid sites. We have previously reported on the ^{14}N NQR spectra of coordinated glyoximes, pyridine, and phenanthroline.[3-5] We have developed a coordination model, based on modification of the Townes–Dailey model, which accounts very well for changes in the electric field gradient (efg) parameters of the pyridine nitrogen upon coordination.[4] This model is applicable also to the ^{14}N NQR data for coordinated phenanthroline.[5] With slight modifications a similar coordination model is applicable to coordination of other planar, aromatic nitrogen systems such as imidazole.[6]

The coordination model provides, with a minimum of parameterization, a measure of the relative degree of charge transfer from nitrogen to the Lewis acid. A similar model should be applicable to aliphatic nitrogen ligands. However, very few systematic NQR data are available for complexes containing such ligands. We report the ^{14}N NQR spectra of several complexes of 1,2-dipiperidinoethane, $C_5H_{10}NCH_2CH_2NC_5H_{10}$ (EDP), a bidentate chelating ligand.

Experimental Section

Materials. 1,2-Dipiperidinoethane (EDP) was obtained from the Reilly Tar and Chemical Co. with a stated purity of 98%. The compound was also prepared by condensing 1,2-dichloroethane and piperidine in refluxing benzene.[7,8] EDP was distilled through a 10-cm Vigreaux column at 98 °C and 10 mmHg. Satisfactory analyses were obtained for the ligand and for all complexes whose preparations are described below.

$Zn(EDP)Cl_2$ and $Zn(EDP)Br_2$. When EDP was added in slight excess to a 2,2-dimethoxypropane solution of either $ZnCl_2 \cdot 6H_2O$ or $ZnBr_2 \cdot 6H_2O$, the corresponding $Zn(EDP)X_2$ complex precipitated.[9]

$Zn(EDP)(NO_3)_2$ and $Zn(EDP)(NO_2)_2$.[8] $Zn(NO_3)_2 \cdot H_2O$ in 2,2-dimethoxypropane reacted with EDP to form $Zn(EDP)(NO_3)_2$. When treated with $NaNO_2$ in a cold bath before EDP was added, the product was $Zn(EDP)(NO_2)_2$.

$Cd(EDP)Cl_2$. $CdCl_2$ (1.65 g, 10 mmol) was dissolved in H_2O; a precipitate formed when a slight excess of EDP was added. The precipitate was washed with small portions of H_2O and ether and then Soxhlet-extracted with CH_2Cl_2. The solvent was removed with a rotary evaporator to give 1.25 g of $Cd(EDP)Cl_2$.

$Cd(EDP)Br_2$. $CdBr_2 \cdot 4H_2O$ (3.5 g, 10 mmol) was dissolved in H_2O and reacted with EDP as described for the corresponding chloro complex, to yield 2.3 of $CD(EDP)Br_2$.

$Cd(EDP)I_2$. CdI_2 (3.65 g, 10 mmol) (Baker) was dissolved in CH_3OH and reacted with EDP. The resulting precipitate was washed with small portions of CH_3OH and ether and then extracted in a Soxhlet extractor using CH_2Cl_2, to yield 4.80 g of $Cd(EDP)I_2$.

Table I. ^{14}N Quadrupole Resonance Transitions (kHz) and Calculated Electric Field Gradient Parameters in EDP Compounds at 77 K

Compd	ν_+	e^2Qq/h	η
$Zn(EDP)Cl_2$	2583	3444	0
$Zn(EDP)Br_2$	2543	3391	0
$Zn(EDP)(NO_3)_2$	2476	3301	0
$(NO_3)^-$ group	552	695	0.178
	($\nu_- = 490$)		
$Zn(EDP)(NO_2)_2$	2580	3440	0
$(NO_2)^-$ group	550		
	(ν_- not seen)		
$Cd(EDP)Cl_2$	2676	3568	0
$Cd(EDP)Br_2$	2652	3538	0
$Cd(EDP)I_2$	2627	3503	0
$Hg(EDP)Cl_2$	2505	3340	0
$Hg(EDP)Br_2$	2490	3320	0
$(EDPH_2)(ClO_4)_2$	850	1133	0

$Hg(EDP)Cl_2$. $HgCl_2$ (2.6 g, 9.5 mmol) was dissolved in CH_3CH_2OH; a white precipitate formed when EDP was added. The precipitate was filtered and washed with small portions of CH_3CH_2OH and ether and then Soxhlet extracted with CH_2Cl_2. The solvent was removed with a rotary evaporator to give 1.95 g of $Hg(EDP)Cl_2$.

$Hg(EDP)Br_2$. $HgBr_2$ (5.4 g, 15 mmol) was dissolved in CH_3OH. Synthesis proceeded as for the corresponding iodide complex, except that CH_3OH replaced CH_3CH_2OH; yield 4.5 g of $Hg(EDP)Br_2$.

$(EDPH_2)^{2+}(ClO_4^-)_2$. EDP (2.6 mL, 12 mmol) was mixed with 15 mL of CH_3OH; 2 mL (24 mmol) of 70% $HClO_4$ was added drop by drop with stirring. The solution was filtered after several hours. The precipitate was washed with several small portions of CH_3OH and ether. The product was dried under vacuum to give 3.9 g of $(EDPH_2)^{2+}(ClO_4^-)_2$.

NQR Spectra. The ^{14}N NQR spectra were obtained as described elsewhere.[3,4]

Results and Discussion

The measured ^{14}N quadrupole resonance transitions, in kilohertz, for all of the complexes studied are listed in Table I. In every instance, only one transition ascribable to coordinated EDP was observed. The electronic environment about each nitrogen in EDP should possess approximate axial symmetry, since there are three nearly equivalent N–C bonds involved. It is noteworthy that for *N*-methylpiperidine $\eta = 0.036$.[10] From inspection of a molecular model it appears that the five-membered ring formed upon coordination of EDP to a metal ion is relatively free of strain. The M–N internuclear vector should lie roughly along the pseudo-threefold axis through the nitrogen. Thus, it is reasonable to expect that η should be near 0 in the complexes formed by EDP. In keeping with this, as noted above, only one transition ascribable to the coordinated nitrogen was observed in each complex. The calculated quadrupole coupling constant based on the assumption that $\eta = 0$ is listed in Table I for each compound.

Unfortunately, all attempts to obtain the NQR spectrum for the free EDP ligand were unsucessful, because the proton T_1 and T_{1d} are too short at 77 K. Apparently, some low-frequency motion persists in the solid at this temperature, providing a relatively facile pathway for relaxation. However, from the observed e^2Qq/h values of 5.01 and 4.99 MHz for triethylamine[11] and *N*-methylpiperidine,[10] respectively, we can assume a value of $e^2Qq/h = 5.00$ MHz for the free EDP ligand.

Assuming threefold symmetry at the nitrogen, the nitrogen 2p orbitals in free EDP are involved in three equivalent carbon–nitrogen bonds and one lone pair orbital. We designate the effective occupancy of the nitrogen orbital in the N–C σ bonds as δ_0, and denote the lone pair orbital occupancy as σ. In the free ligand $\sigma = \sigma_0 = 2.00$. Upon coordination the occupancy of the lone pair orbital decreases. Correspondingly, the occupation number of the three equivalent orbitals involved

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