or seven-coordinate intermediates having one apical and one equatorial CN⁻. Some angular motions during vibrational relaxation of the excited state are therefore definitely precluded. This limitation may again depend on the fact that in the $^4B_{2g}$ state the electron density along the z axis is unchanged relatively to the ground state and preserves rigidity in the CN–CN direction.

In conclusion, although dissociative mechanisms cannot be completely ruled out, the present stereochemical findings seem more compatible with either associative or concerted pathways. This view is in agreement with earlier mechanistic results[14]

and with solvent-dependence studies[46,47] on other chromium-(III) cations.

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Laser-Flash-Induced Dissociation and Recombination of Aqueous Pentacyano(2-methylpyrazine)ferrate(II) Ion

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Metal-to-ligand charge transfer (MLCT) excitation of pentacyano(2-methylpyrazine)ferrate(II) ion in solution has been investigated, employing pulsed laser light of wavelengths 440–530 nm. Bleaching of the MLCT absorption due to loss of the heterocycle occurs in less than 20 ns. In the presence of excess heterocycle the starting material is regenerated via two intermediates, characterized by their substitution kinetics. One of the intermediates is the ion pentacyanoaquaferrate(II), for which the rates of recombination with 2-methylpyrazine were measured in the concentration range 0.0025 M ≤ [2-Mepyr] ≤ 9.6 M. The rate law for the process when [2-Mepyr] ≤ 1 M is rate = k_f[Fe(CN)₅OH₂³⁻][2-Mepyr] (k_f = 475 ± 25 M⁻¹ s⁻¹, 25 °C, μ = 0.1 M LiTFMS, ΔH^* = 16.0 ± 0.3 kcal/mol, ΔS^* = 7.7 ± 1 cal mol⁻¹ deg⁻¹). The rate of this reaction is independent of pH in the range 6.6 ≤ pH ≤ 11.4. At [2-Mepyr] > 1 M the apparent order in that reagent's concentration increases markedly. The second intermediate decays via a much smaller absorbance change than the first and exhibits a tendency toward rate saturation in its substitution kinetics. This species is identified tentatively as the sterically hindered N-1 isomer of pentacyano(2-methylpyrazine)ferrate(II).

Introduction

Irradiation of metal-to-ligand charge-transfer (MLCT) bands has been shown to labilize the ligand L, an aromatic N heterocycle, in complexes of the type Ru(NH₃)₅L²⁺,[1] W(CO)₅L,[2] and Fe(CN)₅L³⁻.[3] All of these are low-spin, d⁶, octahedral species which are inert to substitution in their ground states.

A great deal of work has been undertaken to conceptualize the events leading to loss of the ligand L.[1–7] The primary MLCT* excited states are described as reduced ligand/oxidized metal species which should not be especially reactive to substitution during their short (probably less than 10⁻⁹ s) lifetimes. However, the complexes possess low-lying excited ligand field states (LF*) which should be strongly labilizing.[6] Thus, various workers have invoked internal conversion of MLCT* to LF* to explain observations of moderately efficient photosubstitution. Strong support is given to these arguments by the fact that the quantum yield for labilization of L, Φ_L, is diminished substantially in cases where E(MLCT*) < E(LF*).[1–3]

Rather less attention has been focused upon the events which follow ejection of L from the complex, although flash photolysis studies of the ruthenium(II) ammines have been reported recently.[7] In the present work we discuss the substitution kinetics of two intermediates formed in aqueous 2-methylpyrazine (2-Mepyr) solution after flash MLCT photolysis of Fe(CN)₅(2-Mepyr)³⁻. The speed of the photolysis technique permitted investigation at concentrations of 2-Mepyr up to 9.6

M. At high concentrations of the ligand, the rate of water replacement in the ion Fe(CN)₅OH₂³⁻, which is one of the intermediates, is accelerated markedly.

Experimental Section

Materials. The pentacyanoferrate(II) complexes were prepared as solid sodium salts according to published methods and characterized by their visible spectra.[8] Stock solutions of the complexes were diluted to desired concentrations with lithium trifluoromethylsulfonate (LiTFMS) solution and excess free ligand. Except for the pH-dependence experiments, no buffers were added and the pH was allowed to vary in the range 6–8. Removal of dissolved oxygen by deaerating the solutions with argon gas was shown not to affect the kinetics. N-Methyl-4,4′-bipyridinium iodide was synthesized by adding an excess of 4,4′-bipyridine to methyl iodide in benzene solution. Ligands 2-methylpyrazine, isonicotinamide, and 4,4′-bipyridine were purchased from Aldrich Chemical Co. The first of these was used as supplied while the second and third were purified, respectively, by recrystallization from water or benzene. Water was triply distilled.

Measurements. Most of the flash measurements were made with a dye laser system that has been described previously.[9] The untuned broad-band output of coumarin dye (~440 nm) was employed with

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Table I. Specific Rates of Principal Reaction[a]

solu-tion	[2-Mepyr], M	k_{obsd}, s^{-1}		
		1 °C	25 °C	50 °C
1	0.0025		1.09 (3)	
2	0.0125		5.67 (3)	
3	0.025		10.8 (3)	
4	0.10	5.58 (6)	42.2 (5)	554 (4)
5	0.20	10.5 (5)	101 (5)	1020 (4)
6	0.30	14.0 (4)	153 (4)	1560 (3)
7	0.50		248 (4)	2310 (3)
8	0.70	31.2 (5)	309 (4)	
9	0.90	41.4 (6)	436 (4)	3470 (5)
10	2.13	106 (5)	1332 (6)	8487 (5)
11	4.27	372 (4)	2830 (3)	
12	6.41	818 (4)	6300 (4)	
13	8.54	2678 (3)	18200 (4)	
14	9.61	4697 (4)	31500 (4)	

[a] pH 8–10 unbuffered, $\mu = 0.10$ M LiTFMS or LiClO$_4$, λ = 440–470 nm, [Fe(CN)$_5$(2-Mepyr)$^{3-}$] = (1.2–2.3) × 10^{-4} M. Runs 1–3 were by stopped-flow technique; others were by laser flash photolysis. The number of measurements is given in parentheses. The error limits in these rate constants are ±5% (estimated).

a pulse width of 0.6 μs. Experiments also were performed with a frequency-doubled neodymium laser system developing a 20-ns pulse of 530-nm light.[10] Temperature in the cell compartments of the photolysis systems was controlled within ±0.3 °C. Stopped-flow measurements were made with a Durrum D-110 instrument. Cary Model 14 and 17 spectrophotometers were used for the absorbance measurements.

Results

Preliminary Observations. Pulsed irradiation of aqueous Fe(CN)$_5$(2-Mepyr)$^{3-}$ (ca. 10^{-4} M) within the MLCT envelope was found to produce transient bleaching. The effect was observed at excitation wavelengths between 410 and 550 nm, by employing various concentrations of ligand in excess. With 530-nm light generated by a frequency-doubled neodymium laser, it was established that the bleaching occurs within the time frame of a 20-ns pulse. Although quantum yields for bleaching were not measured, estimates based on the power of the pulses indicate that Φ(bleaching) is of the same order of magnitude as that measured by Petersen and co-workers[3] for photoinduced ligand exchange ($\Phi_L = 0.35$ for pyrazine).

After bleaching, the absorbance was observed to be redeveloped at rates depending upon the concentration of the free ligand. For 2-Mepyr, this process occurred in two resolvable, pseudo-first-order steps, the more rapid of which accounted for ca. 90% of the total absorbance change. When relaxation was complete, the final absorbance values were equal to those measured before the pulse. Only one relaxation process, leading directly to the prepulse absorbance value, was found for photolysis of the complexes of isonicotinamide and N-methyl-4,4'-bipyridinium. These observations, together with the clear assignment of the faster 2-Mepyr relaxation to substitution in Fe(CN)$_5$OH$_2$$^{3-}$, have led us to postulate that the slower reaction is rearrangement of the unstable, N-1 complex of 2-Mepyr to form the N-4 isomer.

Kinetics of the Principal Reaction. Specific rates of the principal reaction, measured over a wide range of ligand concentrations (0.0025–9.6 M) are given in Table I. Although most experiments were done in unbuffered solutions, a series of runs employing phosphate buffers or sodium hydroxide solutions showed that the rate of this reaction is independent of pH over the range from pH 6.5 to 11.4. Figure 1 presents a plot of k_{obsd} vs. [2-Mepyr] for concentrations of the ligand below 1 M, while the dependence over the entire range is given
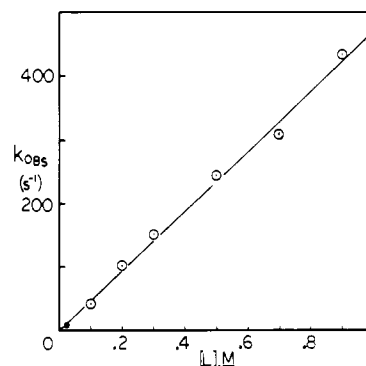
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Figure 1. k_{obsd} vs. [2-Mepyr] at [2-Mepyr] < 1.0 M, t = 25 °C, μ = 0.10 M.

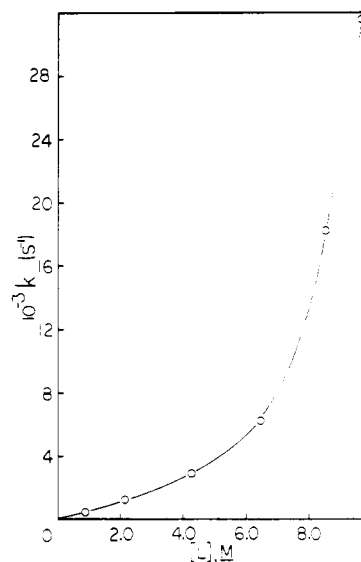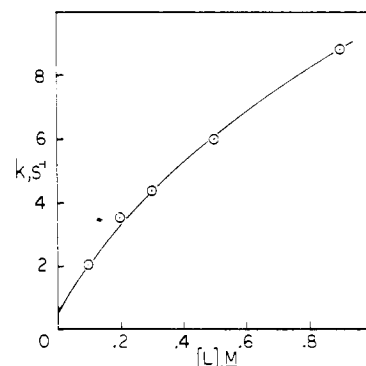**Figure 2.** k_{obsd} vs. [2-Mepyr] over a wide concentration range (t = 25 °C, μ = 0.10 M).

Figure 3. k_{obsd} for linkage isomerization reaction vs. [2-Mepyr] (t = 25 °C, μ = 0.10 M).

in Figure 2. Table I includes values of k_{obsd} obtained by stopped flow for the reaction of pentacyanoaquaferrate(II) with aqueous 2-methylpyrazine and by flash technique. Plots of data obtained at 1 and 50 °C were, like Figure 1, linear up to [2-Mepyr] $\approx$ 1 M but showed clear deviations from linearity at [2-Mepyr] $\geq$ 2 M. Within the linear portion of the plots, the rate law was

$$\frac{d[Fe(CN)_5(2\text{-Mepyr})^{3-}]}{dt} = k_f[Fe(II)_{free}][2\text{-Mepyr}] \qquad (1)$$

The iron(II) species denoted Fe(II)$_{free}$ displayed a reactivity identical with Fe(CN)$_5$OH$_2$$^{3-}$ (aq), as measured by stopped

flow. Values of k_f at 1, 25, and 50 °C were respectively, 44 ± 2, 475 ± 25, and 4550 ± 200 M^{-1} s^{-1}, leading to activation parameters $\Delta H^* = 16.0 \pm 0.3$ kcal/mol and $\Delta S^* = 7.7 \pm 1.0$ cal mol^{-1} deg^{-1}.

Kinetics of the Second Reaction. Specific rates of the second reaction are shown in Figure 3. We note that k_{obsd} increased, with a slight curvature, as [2-Mepyr] increased. This reaction was not studied systematically at concentrations of 2-Mepyr larger than 1 M.

Solvent Composition and Spectra. As the concentration of 2-Mepyr increased, λ_{max} for the MLCT band in the 2-methylpyrazinium complex was observed to move progressively from 448 (dilute 2-Mepyr) to 507 nm (9.6 M 2-Mepyr). A concurrent increase in ϵ_{max} was observed. The results are summarized in Table II.

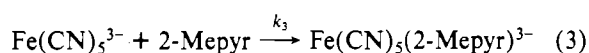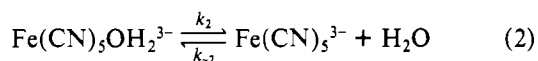**Discussion**

The experiments employing a 20-ns pulse showed that light-induced ejection of 2-Mepyr from $(NC)_5Fe(2\text{-Mepyr})^{3-}$ occurs within the pulse time. The primary photoproduct expected is $Fe(CN)_5^{3-}$, a coordinatively unsaturated intermediate that should be highly reactive toward nucleophiles in solution. Because no transients were found that could not be ascribed clearly to reactions of other, subsequently formed species, we conclude that $Fe(CN)_5^{3-}$ itself reacts too rapidly to be observed in a 10^{-8}-s time frame. Under the conditions of the experiment, three products could be expected from $Fe(CN)_5^{3-}$. These are the aqua substituted complex, the starting material, and the sterically hindered 1-isomer (I) of the starting material.

I
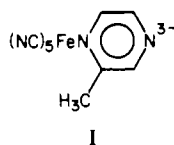
For the larger and more rapid of the two absorbance changes, the data in Table I, which were obtained both by stopped flow and by flash photolysis technique, are in full agreement as to the rate law and specific rates. The values agree closely with specific rates of substitution that have been determined for many neutral, unhindered ligands in reaction with $Fe(CN)_5OH_2^{3-}$.[11] Known rates of substitution vary only over a limited range, from 200 to 600 M^{-1} s^{-1}, at 25 °C. Similarly, the activation parameters are rather uniform for the class of ligands under discussion. These observations support the view that the substitution process is largely a bond-breaking one and that a dissociative mechanism occurs. Thus, in the present instance, the kinetics parameters show that the major absorbance increase is due to substitution of 2-Mepyr in $Fe(CN)_5OH_2^{3-}$.

On the basis of a dissociative mechanism

$$Fe(CN)_5OH_2^{3-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(CN)_5^{3-} + H_2O \qquad (2)$$

$$Fe(CN)_5^{3-} + 2\text{-Mepyr} \xrightarrow{k_3} Fe(CN)_5(2\text{-Mepyr})^{3-} \qquad (3)$$

the rate of the reaction becomes[12]

$$\text{rate} = \frac{k_2k_3[Fe(CN)_5OH_2^{3-}][2\text{-Mepyr}]}{k_{-2}[H_2O] + k_3[2\text{-Mepyr}]} \qquad (4)$$

At low concentrations of 2-Mepyr, we must suppose that $k_{-2}[H_2O] \gg k_3[2\text{-Mepyr}]$. The activation energy corresponding to k_{-2} and k_3 is likely to be much the same, and thus

Table II. Variation of λ(MLCT) with Concentration of 2-Methylpyrazine

[2-Mepyr],[a] M	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm	[2-Mepyr],[a] M	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm
0.01	5.97	448	2.1	6.65	477
0.10	6.02	454	4.3	6.99	489
0.29	6.05	455	6.4	7.72	499
0.48	6.09	460	8.5	8.10	504
0.67	6.18	463	9.6	9.30	507
1.1	6.34	465			

[a] Aqueous mixtures, [Fe(II)] $\simeq 10^{-4}$ M, 0.10 M $LiClO_4$ or LiTFMS, $t = 22$ °C.

Table III. Values of f at Various Concentrations of 2-Mepyr

[2-Mepyr], M	[H_2O], M	f^a	[2-Mepyr], M	[H_2O], M	f^a
1.07	50.9	1.09	6.41	23.8	2.05
2.13	45.3	1.21	8.54	13.0	2.97
4.27	35.1	1.52	9.61	6.8	3.96

$^a f = (55.45 + [2\text{-Mepyr}])/([H_2O] + [2\text{-Mepyr}])$.

the activation energy for all reactions is nearly that for step 2.

In this study an attempt was made to raise the concentration of 2-Mepyr, so that $k_3[2\text{-Mepyr}]$ would approach the value of $k_{-2}[H_2O]$, leading to a direct determination of k_2. As seen in Figure 2, this experiment was unsuccessful. Several factors may have contributed to the dramatic rate increase shown in Figure 2. First, we note that, if k_{-2} and k_3 are nearly equal (diffusion controlled), k_{obsd} should be affected by the change from a compact solvent (H_2O, 55.45 M neat concentration) to a less compact one (2-Mepyr), 10.6 M pure). As solvent water is diluted, the rate (eq 4) would reflect the factor $f = (55.45 + [2\text{-Mepyr}])/([H_2O] + [2\text{-Mepyr}])$. In Table III values of f are given which were computed from the measured concentrations of the solvents. One notes that significant positive deviation (upward) from linearity is predicted on this basis and that the effect becomes equal to 10% of the measured rate constant when [2-Mepyr] reaches 1 M.

In addition to the dilution effect, we note that an increase in [2-Mepyr] must eventually destroy existing hydrogen bonds between H_2O as solvent and the cyano ligands of the penta-cyanoferrate(II) complex. When this occurs, the cyano ligands can be expected to donate increased negative charge to the iron(II) center. A likely result is a weakening of the $Fe-OH_2$ interaction, with a resulting increase in lability of the bound water molecule. In a related example, Malin and Koch[13] have shown that protonation of $Fe(CN)_5OH_2^{3-}$ at cyanide has a strongly delabilizing effect on the water ligand.
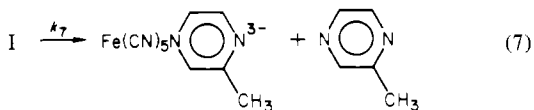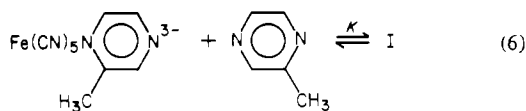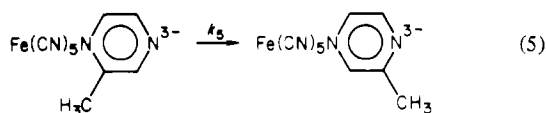
Kinetics of the Second Reaction. As we have noted, the slower relaxation process was not observed in flash photolysis experiments employing ligands other than 2-methylpyrazine. In the 2-Mepyr reaction, this second process yielded values of k_{obsd} which increased nonlinearly with increasing [2-Mepyr] (see Figure 3). This behavior is typical of ligand–replacement reactions in $Fe(CN)_5L^{3-}$.[8] The reactive iron(II) species is identified tentatively as the unstable N-1 isomer of the pentacyano(2-methylpyrazine)iron(II) complex ion. Use of a dissociative mechanism leads to an expression for k_{obsd} that is independent of [2-Mepyr]. Because this is not observed, an alternate mechanism, which does account for the dependence in [L], is postulated; see eq 5–7. In this case the rate law is $-d[\text{N-1}]/dt = k_{obsd}[\text{N-1}]$, where [N-1] represents the concentration of the N-1 bonded isomer and k_{obsd} is given

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$$Fe(CN)_5N\underset{H_3C}{\overset{}{\bigcirc}}N^{3-} \xrightarrow{k_5} Fe(CN)_5N\underset{CH_3}{\overset{}{\bigcirc}}N^{3-} \qquad (5)$$

$$Fe(CN)_5N\underset{H_3C}{\overset{}{\bigcirc}}N^{3-} + N\underset{CH_3}{\overset{}{\bigcirc}}N \underset{}{\overset{K}{\rightleftharpoons}} I \qquad (6)$$

$$I \xrightarrow{k_7} Fe(CN)_5N\underset{CH_3}{\overset{}{\bigcirc}}N^{3-} + N\underset{CH_3}{\overset{}{\bigcirc}}N \qquad (7)$$

by eq 8. The first path in the proposed mechanism (eq 5)

$$k_{obsd} = \frac{k_5 + k_7K[2\text{-Mepyr}]}{1 + K[2\text{-Mepyr}]} \qquad (8)$$

is a unimolecular linkage isomerization step, while the second is a bimolecular process involving rapid formation of an associative intermediate (eq 6) and its subsequent decomposition (eq 7). Values of k_5, k_7, and K computed by nonlinear least-squares analysis are respectively $0.8 \pm 0.5 \text{ s}^{-1}$, $22 \pm 10 \text{ s}^{-1}$, and $0.7 \pm 0.4 \text{ M}^{-1}$. The rather wide error limits are highly correlated and due principally to the uncertainty in K. In particular, the presence of the k_5 term cannot be regarded as proved, and the value quoted is considered to be an upper limit. The line drawn in Figure 3, which fits the data well, was computed employing these rate and equilibrium constants.

Although the value of k_5 is an approximate one, it compares favorably with rate constants known for dissociation of several strained complexes of pentacyanoferrate(II). For example, k_d for the quinoxaline and the 2-cyanopyridine complexes are 0.62 and 1.1 s^{-1}, respectively.[14,15] For the hindered N-1

complex of histidine the specific rate is 0.109 s^{-1}.[16] Thus, our estimate of k_5 is in reasonable agreement with results for similar reactions.

Appearance of the [2-Mepyr]-dependent term in eq 8 is noteworthy because linkage isomerization reactions normally do not occur by bimolecular pathways for octahedral complexes.[17] However, in Table II evidence is presented that indicates a weak association between the free 2-Mepyr ligand and the parent pentacyano(2-methylpyrazine)iron(II) complex ion. In the table, one notes a growing shift in the MLCT band to longer wavelength as [2-Mepyr] is increased. The effect begins to be seen within the range of concentrations over which the second relaxation process was studied (0.1–0.9 M). We suggest that a weak charge-transfer interaction between bound and free 2-Mepyr molecules is responsible for the shifts in MLCT energies and that this interaction facilitates the linkage isomerization process.

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# Kinetics of the Oxidation of Iodide by the Nickel(III) Complex of Tri-α-aminoisobutyric Acid

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The nickel(III)–deprotonated-peptide complex of tri-α-aminoisobutyric acid, Aib$_3$, oxidizes iodide by two reaction pathways to produce Ni(II) and I$_3^-$. The rate of loss of Ni(III) equals $2(k_C + k_C^H[H^+] + k_B/[Ni^{II}(H_{-2}Aib_3)^-])[I^-]^2[Ni^{III}(H_{-2}Aib_3)]^2$, where k_C, k_C^H, and k_B are $3.0 \times 10^{10} \text{ M}^{-3} \text{ s}^{-1}$, $3.8 \times 10^{11} \text{ M}^{-4} \text{ s}^{-1}$, and $2.5 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$, respectively. Path B, which is inhibited by excess Ni(II), occurs by two discrete one-electron-transfer steps and accounts for 30% or less of the observed rate. In the major reaction path (path C) two electrons are transferred in one concerted reaction step that proceeds by a transition-state complex composed of two nickel ions and two iodides.

Introduction

The nickel(III) complex of tri-α-aminoisobutyric acid Aib$_3$, I, has a Ni(III) → Ni(II) reduction potential, $E_{III,II}$, of 0.84

I   Ni^{III}(H$_{-2}$Aib$_3$)
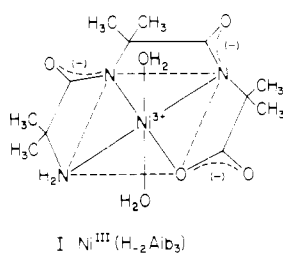
V (vs. NHE). In the absence of light this complex is kinetically resistant to acid, solvent substitution, and self-redox (intra-

molecular ligand oxidation) and is stable in neutral and acid solutions for extended periods of time (days to weeks).[1]

ESR,[2,3] electrochemical,[4–6] and crystallographic[7–9] studies of a wide variety of copper– and nickel–deprotonated-peptide

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