antibonding electron in the reduction of **3** to **4**. These considerations emphasize that the resulting energy stabilization in the Ni–CO back-bonding due to the increased electronic charge more than compensates for the energy destabilization arising from the occupation of the trimetal antibonding HOMO by one or even two electrons.[40-42]

Acknowledgment. We are pleased to acknowledge the National Science Foundation for their support of this research. Thanks are also due to Mark H. Englert for performing magnetic susceptibility measurements and to Dr. Debasis Bhattacharya for obtaining an EPR spectrum of the cobalt–dinickel monoanion.

Registry No. **1**, 77460-36-7; **2**·$[K(2,2,2\text{-crypt})]^+ \cdot 0.5(n\text{-}C_5H_{12})$, 81219-11-6; **3**, 12194-69-3; **4**·$[K(2,2,2\text{-crypt})]^+$, 81219-12-7; **5**, 81316-26-9; $Na^+[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]^-$, 81219-13-8; $Li^+[Ni(\eta^5\text{-}C_5Me_5)(CO)]^-$, 81230-31-1; $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$, 69239-93-6; nickelocene, 1271-28-9; $Ni(CO)_4$, 13463-39-3.

Supplementary Material Available: Six tables lising the atomic parameters and three tables giving the observed and calculated structure factor amplitudes for $[K(2,2,2\text{-crypt})]^+[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^- \cdot 0.5(n\text{-}C_5H_{12})$, $[K(2,2,2\text{-crypt})]^+[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]^-$, and $Ni_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (51 pages). Ordering information is given on any current masthead page.

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[40] From the experimental structured data reported herein, recent calculations[41] with the Fenske–Hall MO model,[42] which is an approximate, nonempirical procedure with the only adjustable parameters being the basis sets and molecular geometries, have substantiated our experimental quantum mechanical conclusions regarding the ground-state electronic configurations of the $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]^n$ series ($n = 0, -1$).

[41] Rives, A. B.; You, X-Z; Fenske, R. F. *Inorg. Chem.*, in press.

[42] Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768–775.

Intramolecular Electron Transfer from Pentacyanoferrate(II) to Pentaamminecobalt(III): Linkage Isomers of 3- and 4-Cyanopyridine as Bridging Ligands[1]

Alek P. Szecsy and Albert Haim*

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11794. *Received July 13, 1981*

Abstract: The reactions of each linkage isomer of (3- and 4-cyanopyridine)pentaamminecobalt(III) with aquopentacyanoferrate(II) proceed in two stages. In the first stage, iron(II)–cobalt(III) binuclear complexes bridged by cyanopyridine are formed. The mechanism features rapid equilibration to produce an ion pair $Co(NH_3)_5L^{3+} + Fe(CN)_5OH_2^{3-} \rightleftharpoons Co(NH_3)_5L^{3+}|Fe(CN)_5OH_2^{3-}$, Q_{IP}, followed by inner-sphere substitution $Co(NH_3)_5L^{3+}|Fe(CN)_5OH_2^{3-} \rightarrow (NC)_5FeLCo(NH_3)_5$, k_f^{IP}. At 25 °C, ionic strength 0.10 M and pH 5.0, values of Q_{IP} and k_f^{IP} are in the range 447–872 M^{-1} and 13.3–42.0 s^{-1}, respectively. The second stage corresponds to the disappearance of the binuclear complexes via intramolecular electron transfer and/or back-dissociation to reactants followed by outer-sphere electron transfer. The binuclear complexes with the pyridine nitrogen bound to iron undergo intramolecular electron transfer with rate constants (25 °C, ionic strength 0.10 M) 0.16 ± 0.01 and $(3.0 \pm 0.2) \times 10^{-3}$ s^{-1} for 4- and 3-cyanopyridine, respectively. The binuclear complexes with the nitrile nitrogen bound to iron undergo back-dissociation to reactants with rate constants (25 °C, ionic strength 0.10 M) 0.15 ± 0.01 and 0.46 ± 0.05 for 4- and 3-cyanopyridine, respectively. The subsequent outer-sphere electron transfer proceeds via the ion pair mechanism, the internal electron transfer rate constants within the ion pair being 0.46 and 0.71 s^{-1} for 4- and 3-cyanopyridine, respectively. The mechanisms of these and related reductions by chromium(II) and ruthenium(II) are compared and discussed.

The importance of measuring rate constants for electron-transfer reactions in the intramolecular mode has been emphasized repeatedly.[2] By exploiting the high affinity[3] of the $Fe(CN)_5^{3-}$ moiety for nitrogen heterocycles, we have been able to prepare binuclear complexes of type I simply by mixing solutions of $Fe(CN)_5OH_2^{3-}$ and $Co(NH_3)_5N\text{-}N^{3+}$,[4-6] where N-N represents 4,4′-bipyridine or other symmetrical bipyridines. The binuclear complexes were found to undergo intramolecular electron transfer, as well as dissociation into the reactants (eq 1 and 2, respectively).[4-6] For a series of related conjugated bridging ligands containing identical donor atoms, rate constants for intramolecular electron transfer in I were found to correlate with the distance between the two metal centers.[6]

$$(NH_3)_5Co^{III}N\text{-}NFe^{II}(CN)_5$$

I

$$(NH_3)_5Co^{III}N\text{-}NFe^{II}(CN)_5 \rightarrow (NH_3)_5Co^{II}N\text{-}NFe^{III}(CN)_5 \tag{1}$$

$$(NH_3)_5Co^{III}N\text{-}NFe^{II}(CN)_5 + H_2O \rightarrow Co^{III}(NH_3)_5N\text{-}N^{3+} + Fe^{II}(CN)_5OH_2^{3-} \tag{2}$$

The present work was initiated in an attempt to obtain information about the effects of unsymmetrical bridging ligands on rate constants for intramolecular electron transfer. Although a fair amount of work has been done on the effects of linkage isomers on the rate constants for inner-sphere electron transfer reactions,[2,7-9] all the measurements so far have yielded second-order rate constants. Under these circumstances, the intrinsic effect of the bonding mode of the unsymmetrical ligand upon the rates of electron transfer cannot be obtained because the observed rate constants are composite quantities that include thermodynamic (equilibrium constant for formation of precursor complex) as well as kinetic (first-order rate constant for internal electron transfer) contributions. It was anticipated that, by utilizing complexes of the type $Co(NH_3)_5D\text{-}D'^{n+}$ (and their linkage isomers Co-

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[1] (a) This work was supported by Grants CHE-7610449 and CHE-7909253 from the National Science Foundation. (b) Abstracted in part from the Ph.D. Dissertation of A.P.S., State University of New York, Stony Brook, NY, 1978.

[2] Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264.

[3] Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039.

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[6] Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981**, *103*, 1679.

[7] Fay, D. D.; Sutin, N. *Inorg. Chem.* **1970**, *9*, 1291.

[8] Shea, C.; Haim, A. *Inorg. Chem.* **1973**, *12*, 3013.

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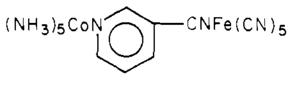
$(NH_3)_5D'{-}D^{n+})$ where D–D′ represents a ligand containing donor atoms D and D′ that exhibit a high affinity for the $Fe(CN)_5^{3-}$ moiety, it would be possible to prepare the isomeric binuclear complexes II and III and, perhaps, measure the rate constants

$$\underset{\text{II}}{(NH_3)_5Co^{III}D{-}D'Fe^{II}(CN)_5} \qquad \underset{\text{III}}{(NH_3)_5Co^{III}D'{-}DFe^{II}(CN)_5}$$

for internal electron transfer in II and III. Unfortunately, we have been unable to find unsymmetrical ligands in which the two binding sites have a high affinity for $Fe(CN)_5^{3-}$. The best we have been able to do so far is to utilize 3- and 4-cyanopyridine as bridging ligands. As already indicated, pyridine N has a high affinity for $Fe(CN)_5^{3-}$ (formation constants in the 10^6 range[3]), but nitrile N has 2 orders of magnitude less affinity.[10] It will be seen that, when the equilibrium constants for the formation of binuclear complexes such as II and/or III become small, dissociation to reactants (eq 2) and alternate outer-sphere pathways become important side reactions, and it becomes difficult, if not impossible, to obtain rate constants for internal electron transfer. Such circumstances obtain for the binuclear complexes containing 3- and 4-cyanopyridine with the nitrile N bound to the iron, structures IV and V, respectively, and therefore we could only place upper limits on the rate constants for intramolecular electron transfer. In contrast, we have been able to obtain good measurements of the rate constants for the linkage isomers of 3- and 4-cyanopyridine that contain the pyridine N bound to iron, structures VI and VII, respectively.



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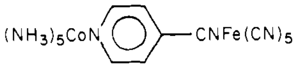
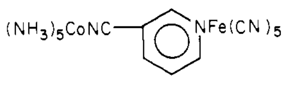
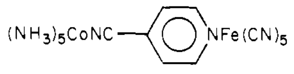


V



VI

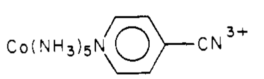


VII

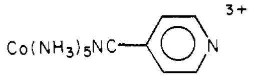
Experimental Section

Materials. Triethyl phosphate was distilled, under vacuum, from 8-mesh anhydrous calcium sulfate. The middle 70% of the distillate was used. The 3- and 4-cyanopyridine ligands were purified by recrystallization from hot 95% ethanol. Argon, water, and lithium perchlorate were purified as described previously.[6] *N*-Methylpyrazinium perchlorate was prepared as described previously.[10] All other chemicals were reagent grade and used as received.

Preparation of Complexes. Sodium amminepentacyanoferrate(II) and azidopentaamminecobalt(III) perchlorate were prepared by standard methods.[11,12] The two isomers of (4-cyanopyridine)pentaamminecobalt(III) perchorate, VIII and IX, respectively, were prepared by a



VIII

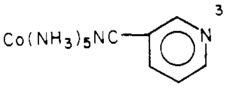


IX

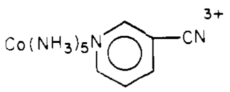
modification of the literature procedure.[13] Following the precipitation of the isomers upon addition of 2-butanol/ethyl ether, it was found convenient to do a preliminary separation by fractional dissolution. Because of its considerable lower solubility, the crude nitrile-bonded complex was retained as a solid, while the solution contained the pyridine-bonded isomer. The remainder of the literature procedure[13] followed smoothly for the pyridine-bonded isomer, which was obtained as large, deep orange crystals in 10% yield. For the nitrile-bonded isomer, the literature method yielded a product that on the basis of cobalt analyses appeared to be partially protonated at the exposed pyridine nitrogen. To circumvent this difficulty, we isolated the nitrile-bonded isomer in its protonated form by addition of cold 4 M perchloric acid to an equal volume of a cold, saturated solution of the complex. The precipitate obtained was allowed to digest at 0 °C for 15–20 min. It was then collected, washed with ethanol and ether, and then dried overnight in a vacuum desiccator.

Anal. Calcd for $[Co(NH_3)_5C_6H_4N_2](ClO_4)_3{\cdot}H_2O$ ($C_6H_4N_2$ = pyridine-bonded 4-cyanopyridine): Co, 10.44; C, 12.76; H, 3.75; N, 17.37. Found: Co, 10.45; C, 12.59; H, 3.80; N, 17.01. Calcd for $[Co(NH_3)_5C_6H_5N_2](ClO_4)_4$ ($C_6H_5N_2$ = nitrile-bonded, pyridine-protonated 4-cyanopyridine): Co, 9.11; C, 11.14; H, 3.12; N, 15.15. Found: Co, 9.03; C, 11.44; H, 3.40; N, 15.28.

The preparation of the nitrile-bonded (3-cyanopyridine)pentaamminecobalt(III) complex, X, was accomplished as described,[13] except that after the addition of 3-cyanopyridine the solution was heated at 65 °C for 30 min; yield 6%. It was reported[13] that the pyridine-bonded isomer, XI, is not produced in the above synthesis. However, we found that the filtrate from the precipitation of the crude nitrile-bonded isomer contains the pyridine-bonded isomer. The filtrate was diluted 5-fold with water and then added to a column of Sephadex CM C-25 (40–120 μm) cation-exchange resin. Elution of the complexes absorbed on the resin was accomplished with 0.30 M NaCl (unidentified red-purple product), 0.50 M NaCl (orange, deprotonated carboxamide complex $(NH_3)_5CoN(H)C(O)(3{-}C_5H_4N)^{2+}$, followed by red, unreacted $Co(NH_3)_5N_3^{2+}$), and 0.70 M NaCl (yellow, nitrile-bonded isomer followed by orange, desired pyridine-bonded isomer). The 0.70 M NaCl eluate was diluted 5-fold with water and then added to a column of Dowex 50W-X2 (50–100 mesh, H^+ form). The column was rinsed with water, and then elution was accomplished with 6 M HCl. The eluate was evaporated to near dryness at 40 °C in a rotary evaporator. The product was dissolved in a minimum amount of water and the resulting solution filtered to remove an unidentified blue impurity. The desired complex was obtained by addition of concentrated perchloric acid and cooling. The product was recrystallized by dissolution in water followed by precipitation with concentrated perchloric acid: yield, 7%; electronic spectrum: 475 and 339 nm with molar absorbances 66.7 and 47.8 $M^{-1}\,cm^{-1}$, respectively; IR (in KBr pellet) CN stretch at 2250 cm^{-1}; NMR (in $Me_2SO{-}d_6$) δ cis NH_3, 3.74; trans NH_3, 3.44; aromatic ring, 8.89, 8.72, 8.61, 7.97.



X



XI

Anal. Calcd for $[Co(NH_3)_5C_6H_4N_2](ClO_4)_3$: Co, 10.78; C, 13.19; H, 3.50; N, 17.94. Found (for $C_6H_4N_2$ = nitrile-bonded 3-cyanopyridine): Co, 10.85; C, 13.24; H, 3.90; N, 18.05. Found (for $C_6H_4N_2$ = pyridine-bonded 3-cyanopyridine): Co, 10.94; C, 13.17; H, 3.58; N, 17.75.

Analytical Methods. The cobalt complexes were decomposed by fuming with concentrated sulfuric acid. Following decomposition, a standard[6] spectrophotometric analysis was performed. Carbon, hydrogen, and nitrogen analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Kinetic Measurements. Rates of reactions with half-lives greater than ~30 s were obtained from absorbance vs. time measurements from a Cary 118 or 17 spectrophotometer. Rates of reactions with half-lives smaller than ~30 s were measured in a Durrum Model D-110 stopped-flow spectrometer. Rates of formation of the binuclear complexes were monitored at or near their absorption maxima by mixing *freshly* prepared solutions of $Fe(CN)_5OH_2^{3-}$ (obtained by aquation of $Fe(CN)_5NH_3^{3-}$) with solutions of the desired cobalt(III) complex in at least 10-fold excess concentration. For all the binuclear complexes, except VII, the redox reactions subsequent to the formation reactions were slow and presented no interference. In these cases, observed rate constants were obtained from a least-squares treatment of the linear ln $(A_\infty - A_t)$ vs. t plots. However, for VII, the rates of formation and of internal electron transfer are comparable, and the absorbance first increased, reached a maximum, and then decreased. For this system, the absorbance vs. time data were treated by a nonlinear least-squares program to evaluate the two first-order rate constants in the consecutive sequence $A \rightarrow B \rightarrow C$.

Rates of disappearance of the binuclear complexes, except VII, were measured in the absence and in the presence of methyl nicotinate. In both types of measurements, rate constants were obtained from least-squares treatment of ln $(A_t - A_\infty)$ vs. t plots. For VI, the reaction in the presence of methyl nicotinate is relatively slow, and therefore, the measurements were carried out by using ordinary mixing techniques and by monitoring the absorbance changes with a Cary 118 or 17 spectrophotometer. However, the reactions of IV and V in the presence of methyl nicotinate are too fast for conventional mixing techniques. Therefore, for these systems the binuclear complexes were prepared by mixing (syringe techniques) solutions of $Fe(CN)_5OH_2^{3-}$ and VIII or XI. The

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(10) Szecsy, A. P.; Miller, S. S.; Haim, A. *Inorg. Chim. Acta* **1978**, *28*, 189.

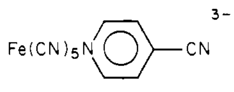
(11) Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed; Academic Press: New York, 1965; Vol. II, p 1511.

(12) Linhard, M.; Flygare, H. *Z. Anorg. Allg. Chem.* **1950**, *262*, 328.

(13) Balahura, R. J. *Can. J. Chem.* **1974**, *52*, 1762.

resulting solution was immediately transferred to one of the driving syringes of the stopped-flow apparatus and then mixed with a methyl nicotinate solution that had already been transferred to the other driving syringe.

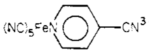
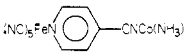
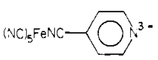
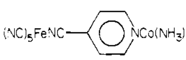
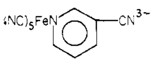
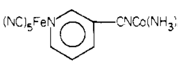
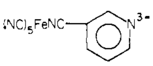
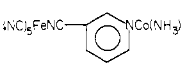
Stoichiometric Measurements. Solutions of $Fe(CN)_5OH_2^{3-}$ and the desired cobalt(III) complex were mixed, and the redox and dissociation reactions of the resulting binuclear complex were allowed to proceed to completion. The product solution was added to a column of ion-exchange resin Dowex 50W-X2, sodium ion form, to remove the excess cobalt(III) complex. To the resulting solution were added, in sequence, first *N*-methylpyrazinium perchlorate and then ascorbic acid. There is an immediate increase in absorbance at 658 nm (the maximum for $Fe(CN)_5pyzCH_3^{2+}$) (pyz-1,4-pyrazine), and this is followed by a slower increase. The rapid increase is a measure of the $Fe(CN)_5OH_2^{2-}$ produced,[5] since reduction of $Fe(CN)_5OH_2^{2-}$ to $Fe(CN)_5OH_2^{3-}$ and reaction of $Fe(CN)_5OH_2^{3-}$ with $pyzCH_3^+$ are rapid processes. The slow increase is a measure of the $Fe(CN)_5L^{2-}$ (L is the ligand originally bound to the cobalt(III) reactant) produced. The % $Fe(CN)_5OH_2^{2-}$ produced in the reaction was calculated from $A_{\text{extrap}}/A_{\text{tot}}$, where A_{extrap} is the value of the absorbance obtained by extrapolating the slow absorbance increase to the time of addition of ascorbic acid and A_{tot} is the absorbance at the completion of the slow increase. This method was applicable to the reactions of IX and X, since the corresponding pyridine-bonded iron(II) and iron(III) complexes undergo dissociation rather slowly. However, the method was not applicable to VIII and XI, since the corresponding nitrile-bonded iron(III) complexes undergo dissociation quite rapidly compared to the redox reaction, and $Fe(CN)_5OH_2^{2-}$ is the sole iron-containing product. For these systems the only parameter applicable to the determination of stoichiometry relates to the relative contributions of electron transfer and dissociation of the corresponding binuclear complexes. The method involved separating the binuclear complex from the iron complexes by ion-exchange chromatography on Sephadex CM-C-25. The binuclear complex and the excess cobalt were absorbed on the resin, and then 0.20 M 4-cyanopyridine in 0.10 M $LiClO_4$ was added to the resin. The binuclear complex was allowed to undergo reaction in the resin, and then the resulting products, XII and $Fe(CN)_5OH_2^{2-}$, were removed from the column by rinsing it with water. The absorbance at 477 nm (the absorption maximum for XII) was measured, and then ascorbic acid was added and the absorbance was measured again. The absorbance increase upon addition of ascorbic acid divided by the total absorbance gives the fraction of $Fe(CN)_5OH_2^{2-}$ produced.



XII

Results and Discussion

Table I. Metal to Ligand Charge Transfer Spectra of Cyanopyridine Complexes of Pentacyanoferrate(II)[a]

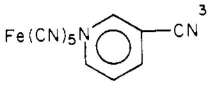
complex	λ, nm[b]	$10^{-3}A$, $M^{-1}\,cm^{-1}$ [c]
	477	5.7
	527	8.8
	405	7.4
	490	7.0
	414	3.2
	410	3.6
	370	6.0
	432	5.4

[a] In aqueous solution, [Fe(II)] = (1–2) × 10^{-5} M, [ligand] > 5 × 10^{-4} M. Values for the mononuclear complexes from ref 10. [b] Wavelength for absorption maximum. [c] Molar absorbance at absorption maximum (corrected for incomplete formation of binuclear complex when necessary).

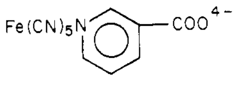
Absorption Spectra. The information of highly absorbing, transient species was observed upon mixing solutions of $Fe(CN)_5OH_2^{3-}$ with any of the four (3- or 4-cyanopyridine)pentaamminecobalt(III) complexes. Repetitive scanning of these solutions and extrapolation to the time of mixing yielded the spectra of the precursor binuclear complexes formed via the reaction

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5L^{3+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} (NC)_5Fe^{II}LCo^{III}(NH_3)_5 + H_2O \quad (3)$$

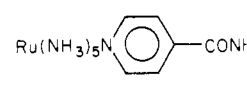
The binuclear complexes exhibit the metal to ligand charge transfer bands characteristic of pentacyanoferrate(II) complexes of pyridines[3] and aromatic nitriles.[10] The wavelengths and molar absorbances of the MLCT bands of the binuclear complexes and of the corresponding mononuclear complexes are listed in Table I. It will be seen that, except for the pyridine-bonded 3-cyanopyridine system, addition of the $Co(NH_3)_5^{3+}$ moiety to the free coordination site of the ligands results in a substantial shift of the MLCT bands to lower energies. Bathochromic shifts are expected for the introduction of electron-withdrawing substituents in the ring,[3,10,14,15] the shifts being especially large for substitution in the 2- or 4-positions by groups that can interact with the π system of the ring. Moreover, coordination of a positive center (a proton or a non-π-interacting metal center) to a substituent should result in an additional bathochromic shift, again the effect being more pronounced for conjugated positions.[5,16,17] All these trends are applicable to the present systems except for one of the isomers in the 3-cyanopyridine system. Coordination of $Co(NH_3)_5^{3+}$ to the free nitrile in XIII results in a *hypsochromic* shift. Although this result is unexpected, increases in the transition energy upon coordination of a positive center to a substituent in the 3-position are not unprecedented. Thus coordination of $Co(NH_3)_5^{3+}$ to a carboxylate oxygen in XIV and of $Cr(H_2O)_5^{3+}$ to the carbonyl oxygen of XV results in shifts of the MLCT bands from 382 to 370 nm and from 427 to 420 nm, respectively.[17,18] Perhaps as suggested previously,[17] the increased electronegativity of the ligand caused by coordination of the tripositive metal center would result in a shift of the MLCT bands toward longer wavelengths. Opposing this effect, however, is the decreased σ basicity of the pyridine N, and through the synergistic bonding mechanism, the back-bonding is also decreased. The interplay of these opposing effects evidently results in a net, small blue shift.



XIII



XIV



XV

Kinetics of Formation and Dissociation of Binuclear Complexes. When $Fe(CN)_5OH_2^{3-}$ is mixed with any of the isomeric (cyanopyridine)pentaamminecobalt(III) complexes, the absorbance increase that results after the rapid outer-sphere association is governed by the forward and reverse reactions in eq 3 as well as by the outer-sphere electron transfer process given by eq 4. The

$$Fe(CN)_5OH_2^{3-} + Co(NH_3)_5L^{3+} \xrightarrow{k_{os}} Fe(CN)_5OH_2^{2-} + Co(NH_3)_5L^{2+} \quad (4)$$

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(14) Ford, P.; DeRudd, F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

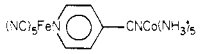
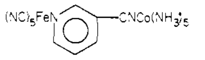
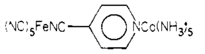
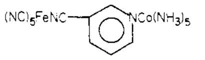
(15) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 495.

(16) Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* **1979**, *33*, 51.

(17) Jwo, J.-J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.

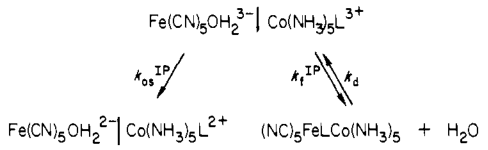
(18) Gaunder, R. G.; Taube, H. *Inorg. Chem.* **1970**, *9*, 2627.

Table II. Rate Constants for Dissociation and Intramolecular Electron Transfer of Binuclear Complexes[a]

complex	k_{obsd}, s^{-1} [b]	($k_d + k_{et}$), s^{-1} [c]	R_s [d]	k_{et}, s^{-1}
	0.16 ± 0.01[e]		0.442 ± 0.004[f]	0.16 ± 0.01
	$(5.1 \pm 0.2) \times 10^{-3}$ [g]	0.0133 ± 0.0002[h]	0.81 ± 0.02	$(3.0 \pm 0.2) \times 10^{-3}$
	$(5.1 \pm 0.2) \times 10^{-3}$ [i]	0.15 ± 0.01	0.019 ± 0.008[j]	$<1 \times 10^{-3}$
	$(7.6 \pm 0.4) \times 10^{-3}$ [k]	0.46 ± 0.05[l]	0.012 ± 0.004[j,m]	$<1 \times 10^{-3}$

[a] At 25.0 °C, ionic strength 0.10 M, pH 5.0, $[Fe(CN)_5OH_2^{3-}]_0 = (1-2) \times 10^{-5}$ M, $[Co(NH_3)_5L^{3+}] = (1.2-6) \times 10^{-4}$ M. Measurements at 525, 435, 490, and 460 nm, as listed. [b] First-order rate constant for spontaneous disappearance. [c] First-order rate constant for disappearance in the presence of 1.0 M methyl nicotinate. Each entry is the average of 3-4 replicate determination. [d] Ratio $[Fe(CN)_5OH_2^{2-}]_\infty/[Fe(CN)_5\text{-}1,3(4)\text{-}NC_5H_4CN^{2-}]_\infty$. Average of duplicate determinations. [e] Average of six measurements. Measurements at 15.0, 20.0, and 30.0 °C are 0.042 ± 0.002, 0.081 ± 0.001, and 0.334 ± 0.004 s^{-1}, respectively. [f] One measurement at 5 °C gave 0.546. [g] Average of six measurements. Measurements at 20.0, 30.0, and 35.0 °C are $(1.70 \pm 0.05) \times 10^{-3}$, $(8.02 \pm 0.10) \times 10^{-3}$, and $(15.6 \pm 0.3) \times 10^{-3}$ s^{-1}, respectively. [h] Duplicate determinations. [i] Average of 12 measurements. Measurements at 20.0, 30.0, and 35.0 °C are $(2.55 \pm 0.15) \times 10^{-3}$, $(11.7 \pm 0.2) \times 10^{-3}$, and $(20.6 \pm 0.6) \times 10^{-3}$ s^{-1}, respectively. [j] This is the ratio $[Fe(CN)_5OH_2^{2-}]_\infty/[Fe(CN)_5NC_5H_4CN^{3-}]_\infty$. See text. Two measurements at 5 °C yielded 0.073 ± 0.022. [k] Average of 12 measurements. Measurements at 15.0, 20.0, and 30.0 °C are $(1.72 \pm 0.15) \times 10^{-3}$, $(3.78 \pm 0.02) \times 10^{-3}$, and $(14.7 \pm 0.1) \times 10^{-3}$ s^{-1}; respectively. [l] Duplicate measurements at 20.0 °C are 0.25 ± 0.03 s^{-1}. [m] Measured at 5.0 °C.

Scheme I



subsequent absorbance decrease corresponds to the intramolecular electron transfer process given by eq 5 and/or the reverse of eq

$$(NC)_5Fe^{II}LCo^{III}(NH_3)_5 \xrightarrow{k_{et}} (NC)_5Fe^{III}LCo^{II}(NH_3)_5 \quad (5)$$

3 followed by the outer-sphere reaction 4. Except for the 4-cyanopyridine system with the iron bound to the pyridine nitrogen, the two stages differ in rate by at least two orders of magnitude and, therefore, were treated independently to obtain the corresponding rate constants. For the $Fe(CN)_5OH_2^{3-}$–IX system, the two stages are comparable in rate and were treated as consecutive kinetics (A → B → C) to obtain the corresponding rate constants. According to eq 3 and 4, the observed rate constant for the first stage is given by $k_{obsd} = k'_f + k_d + k'_{os}$, where k'_f and k'_{os} are the pseudo-first-order rate constants for the forward reaction in eq 3 and for reaction 4. Values of k_{obsd} for the VIII, IX, X, and XI systems are plotted in Figure 1 vs. the concentration of the cobalt(III) complex. It will be seen that the values of k_{obsd} have less than a first-order dependence with respect to the concentration of cobalt. The observations are consistent with the ion-pair mechanism depicted in Scheme I. On the basis of this scheme, the dependence of k_{obsd} with respect to the concentration of the cobalt(III) complex is given by eq 6. A nonlinear least-squares

$$k_{obsd} = k_d + \frac{(k_f + k_{os}^{IP})Q_{IP}[Co(NH_3)_5L^{3+}]}{1 + Q_{IP}[Co(NH_3)_5L^{3+}]} \quad (6)$$

program was used to fit the k_{obsd} values to the cobalt concentration, keeping k_d as a fixed parameter and floating ($k_f^{IP} + k_{os}^{IP}$) and Q_{IP}. The values of k_d were obtained from measurements of the disappearance of the binuclear complexes in the presence of a large excess of methyl nicotinate. It will be seen that the rate constants measured in this manner (listed in column 3 of Table II) are equal to $k_d + k_{et}$ since any $Fe(CN)_5OH_2^{3-}$ produced by the dissociation of a binuclear complex (reverse of eq 3) is scavenged rapidly by the methyl nicotinate (eq 7). For the binuclear complexes with

$$Fe(CN)_5OH_2^{3-} + NC_5H_4CO_2CH_3 \rightarrow Fe(CN)_5NC_5H_4CO_2CH_3^{3-} + H_2O \quad (7)$$

the nitrile N bound to iron, the stoichiometric measurements in the presence of a scavenger for $Fe(CN)_5OH_2^{3-}$ (vide infra) show that less than 2% of the reactions of the binuclear complexes result in electron transfer, and therefore the rate constants measured in the presence of methyl nicotinate are effectively measures of k_d. For the complex VI the contribution of k_d (the value of $k_d + k_{et}$ from Table II is 0.0133 s^{-1}) to k_{obsd} (values in the range 3.26–14.9 s^{-1}, Figure 1) is negligible. Because of the rapid intramolecular electron transfer in VII, we have been unable to carry out the methyl nicotinate scavenger studies for this compound (a triply fast-mixing apparatus is necessary, but unavailable). However, on the basis of the results for the analogous 3-cyanopyridine system and the low rate of dissociation of XII,[10] we assumed that the k_d contribution to k_{obsd} is negligible for the 4-cyanopyridine system as well.

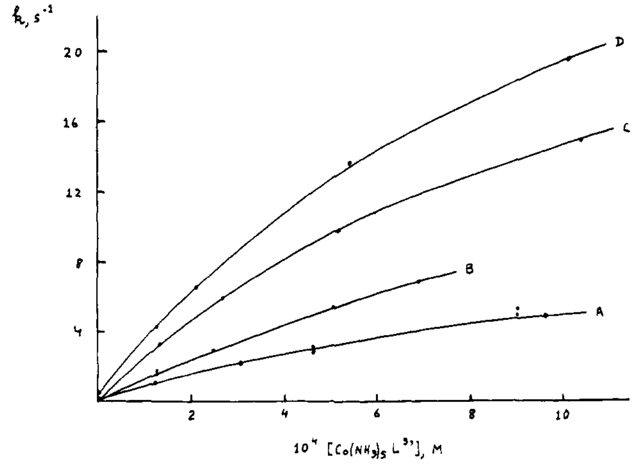
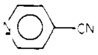
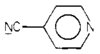
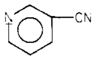
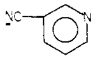


Figure 1. Pseudo-first-order rate constants vs. Co(III) concentration for formation, dissociation, and outer-sphere electron transfer for the reactions of $Fe(CN)_5OH_2^{3-}$ with $Co(NH_3)_5L^{3+}$ at 25.0 °C, ionic strength 0.10 M, pH 5.0, $[Fe(CN)_5OH_2^{3-}] = (1.0-1.1) \times 10^{-5}$ M. Each point is the average of three to four replicate measurements. (A) L = pyridine-bonded 4-cyanopyridine, measurements at 495 nm; (B) L = nitrile-bonded 4-cyanopyridine, measurements at 525 nm; (C) L = nitrile-bonded 3-cyanopyridine, measurements at 435 nm; (D) L = pyridine-bonded 3-cyanopyridine, measurements at 432 nm. Solid lines calculated by using the parameters given in the text.

It will be seen that the measured values of k_{obsd} conform quite nicely to the functional dependence given by eq 6. The values of Q_{IP} and $k_{os}^{IP} + k_f^{IP}$ obtained from the least-squares treatment are listed in Table III, and the solid lines in Figure 1 are plots of eq 6 utilizing the parameters of Table III. The agreement between experimental points and calculated curves is excellent. The values Q_{IP} obtained in the present work (447–872 M^{-1}) are near those previously measured for the ion pairs $Fe(CN)_5OH_2^{3-}$,

Table III. Ion Pair Formation Constants, Rate Constants, and Equilibrium Constants for Reactions of $Fe(CN)_5OH^{3-}$ with $Co(NH_3)_5L^{3+}$[a]

L	Q_{IP}, M^{-1} [b]	$(k_{os}^{IP} + k_f^{IP})$, s^{-1} [b]	k_f^{IP}, s^{-1} [c]	k_d, s^{-1} [c]	$Q_{IP}k_f^{IP}/k_d$, M^{-1}
	597 ± 151	13.8 ± 2.4	13.3 ± 2.4	0.15 ± 0.01	5.3×10^4
	447 ± 21	29.0 ± 1.1	20.1 ± 0.7	~4×10^{-3} [d]	2.2×10^6
	799 ± 91	42.7 ± 3.1	42.0 ± 3.1	0.46 ± 0.05	7.5×10^4
	872 ± 40	31.3 ± 0.9	26.5 ± 0.9	0.010 ± 0.001	2.3×10^6

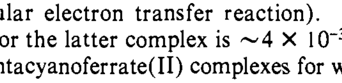
[a] At 25.0 °C, ionic strength 0.10 M, pH 5.0. [b] From nonlinear squares fitting of k_{obsd} (Figure 1) to eq 6. [c] Calculated by combining kinetic and stoichiometric data; see text. [d] Estimated; see text.

$Co(NH_3)_5(imidazole)^{3+}$[6] (302 M^{-1}) and $Fe(CN)_5OH_2^{3-}$, $Co(NH_3)_5OS(CH_3)_2^{3+}$[19] (350 M^{-1}). However, all these Q_{IP} values are substantially higher than the theoretical[20] value of 75 M^{-1} calculated by utilizing 4.5×10^{-8} and 4.7×10^{-8} cm[21] for the radii of $Fe(CN)_5OH_2^{3-}$ and $Co(NH_3)_5L^{3+}$, respectively. Perhaps, as suggested previously,[6] some specific hydrogen bonding between one hydrogen in $Fe(CN)_5OH_2^{3-}$ and the exposed cyanopyridine nitrogen in $Co(NH_3)_5L^{3+}$ provides some additional stability to the already favorable electrostatic interaction.

The composite values of $k_{os}^{IP} + k_f^{IP}$ can be dissected into their components by combining kinetic and stoichiometric data for the disappearance of the binuclear complexes. Two types of kinetic data were gathered,[5] those in the absence of a scavenger (spontaneous disappearance) and those in the presence of a scavenger for $Fe(CN)_5OH_2^{3-}$. As indicated above, the latter measurements yield values of $k_{et} + k_d$. The former measurements yield observed first-order rate constants k_{obsd} equal to $k_{et} + k_{os}^{IP} k_d/(k_{os}^{IP} + k_f^{IP})$.[5] Values of k_{obsd} and of $k_{et} + k_d$are listed in columns 2 and 3, respectively, of Table II. Two types of stoichiometric measurements, both listed in column 4 of Table I, were obtained. For the complexes with the nitrile bound to the cobalt(III) center, solutions of $Fe(CN)_5OH_2^{3-}$ and the cobalt complex were mixed, and the binuclear complex was allowed to be formed and to disappear. At the completion of the reaction, the concentrations of $Fe(CN)_5OH_2^{2-}$ (produced in the outer-sphere path, eq 4) and of XII or XIII (produced in the inner-sphere path, eq 5) were measured. For the 4-isomer, the ratio of the concentrations ($R_s = [Fe(CN)_5OH_2^{2-}]_\infty/[XII]_\infty$) is equal to k_{os}^{IP}/k_f^{IP} because the rate of internal electron transfer (k_{et} in eq 5) is so large (vide infra) that once the binuclear complex is formed, back-dissociation into the reactants (reverse of eq 3) is not competitive. From the sum and the ratio of k_{os}^{IP} and k_f^{IP}, we compute $k_f^{IP} = 20.1 \pm 0.7$ and $k_{os}^{IP} = 8.9 \pm 0.7$ s^{-1}. For VI, however, internal electron transfer is relatively slow (vide infra) and back-dissociation into reactants is relatively important. Under these circumstances, the stoichiometric ratio $R_s = [Fe(CN)_5OH_2^{2-}]_\infty/[XIII]_\infty$ is equal to $k_{os}^{IP}(k_{et} + k_d)/k_{et}k_f^{IP}$.[5] In order to obtain individual values of k_f^{IP} and k_{os}^{IP}, it is necessary to combine the measurements of $k_{os}^{IP} + k_f^{IP}$ (column 3 of Table III), $k_d + k_{et}$ (column 3 of Table II), k_{obsd} (column 2 of Table II), and R_s (column 4 of Table II). The results are $k_f^{IP} = 26.5 \pm 0.9$ s^{-1} and $k_{os}^{IP} = 4.8 \pm 0.9$ s^{-1}. Values of R_s could not be measured for the reactions of the isomers with the pyridine nitrogen bound to cobalt because the nitrile-bonded iron(III) complexes resulting from the internal electron transfer of the binuclear complexes undergo aquation[10] in the time necessary for the complete disappearance of the binuclear complexes. However, an estimate of k_{et}/k_d was made for these complexes (vide infra). Combining the three types of kinetic measurements and the stoichiometric measurements, we compute $k_f^{IP} = 13.3 \pm 2.4$ and 42.0 ± 0.31 s^{-1} for the VIII-$Fe(CN)_5OH_2^{3-}$ and XI-$Fe(CN)_5OH_2^{3-}$ systems, respectively.

It will be seen (column 4 of Table III) that the values of k_f^{IP} fall in the narrow range 13–42 s^{-1}. Previous measurements of k_f^{IP} yielded values of 20 and 4.9 s^{-1} for $Co(NH_3)_5OS(CH_3)_2^{3+}$ and $Co(NH_3)_5im^{2+}$, respectively.[6,19] The narrow range of reactivities conforms to the well-established[3] dissociative nature of the substitution reactions of $Fe(CN)_5OH_2^{3-}$. Included in Table III (last column) are the calculated values of the equilibrium constants for eq 3. The calculation requires values of k_d which were measured for all systems except VII (because of the rapidity of the intramolecular electron transfer reaction). A reasonable estimate of k_d for the latter complex is $\sim 4 \times 10^{-3}$ s^{-1}, since for all (pyridine)pentacyanoferrate(II) complexes for which data are available[5,10,17] the dissociation of a binuclear complex is about 3–5 times faster than that of the corresponding iron mononuclear complex. As found previously for mononuclear nitrile and pyridine complexes of $Fe(CN)_5^{3-}$,[10] the binuclear complexes with the nitrile bound to iron are about two orders of magnitude less stable than the binuclear complexes with the pyridine nitrogen bound to the iron. The difference in stabilities is undoubtedly determined by the considerably higher σ basicity of pyridines as compared to nitriles.[10]

It is noteworthy that the rate constants for dissociation of the binuclear complexes are larger than the rate constants for dissociation[10] of the corresponding mononuclear complexes. For both linkage isomers of 3-cyanopyridine, the rate increase is about a factor of 4, but for the 4-cyanopyridine isomer with the pyridine N bound to cobalt, the rate increase is only ~50%. The rate increase upon coordination of $Co(NH_3)_5^{3+}$ to the remote nitrogen is rationalized easily, since such coordination decreases the basicity of the adjacent nitrogen and hence weakens the Fe–N bond. The very modest rate increase for the 4-cyanopyridine system is taken to indicate the influence of two opposing effects on the strength of the Fe–N bond: a decrease in the basicity of the adjacent nitrogen and a strengthening of the π interaction by stabilization of the canonical form



Outer-Sphere and Intramolecular Electron Transfer. The rate constants, k_{obsd}, for the spontaneous disappearance of the binuclear complexes are listed in column 2 of Table II. On the basis of Scheme I and eq 5, $k_{obsd} = k_{et} + k_{os}^{IP}k_d/(k_{os}^{IP} + k_f^{IP})$.[5] For the complexes with the pyridine nitrogen bound to the cobalt, the following stoichiometric measurements were performed in an effort to obtain estimates of k_{et}. The binuclear complexes were formed by reaction of $Fe(CN)_5OH_2^{3-}$ with excess $Co(NH_3)_5L^{3+}$ and adsorbed[22] immediately on a bed of Sephadex CM-C25. The bed was rinsed rapidly to remove any unreacted $Fe(CN)_5OH_2^{3-}$ and any $Fe(CN)_5OH_2^{2-}$ produced by reaction 4, and then 0.20 M 4-cyanopyridine in 0.10 M $LiClO_4$ was added to the resin. The binuclear complex was allowed to undergo reaction to completion (internal electron transfer and dissociation), and the amounts of

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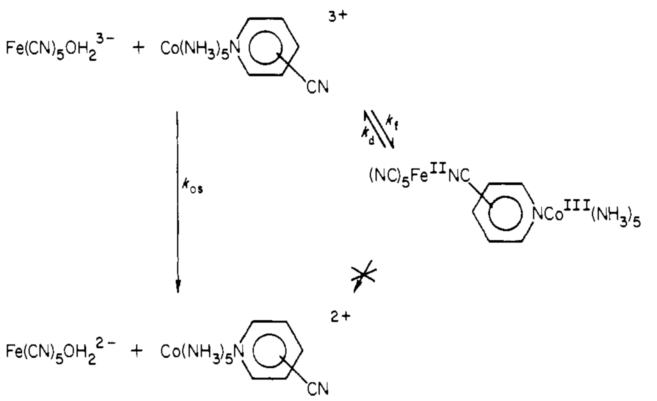
[19] Oliveira, L. A. A.; Toma, H. E.; Giesbrecht, E. *Inorg. Chim. Acta* **1977**, *22*, 269.

[20] Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

[21] The radius of the sphere equivalent to the nonspherical ions ($Co(NH_3)_5L^{3+}$.

[22] The binuclear complexes are retained by the resin, presumably because of their high zwitterionic character.

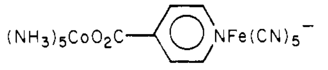
Scheme II



$Fe(CN)_5OH_2^{2-}$ (from internal electron transfer followed by rapid[10] nitrile ligand dissociation) and XII (from dissociation) produced were measured. The ratio of the two products was in the 0.01–0.02 range. These values were obtained from measurements of small absorbance increases (1–2%) superimposed over large absorbances upon addition of ascorbic acid to the mixture of iron complexes. Moreover, the dissociation and electron transfer reactions are taking place with the binuclear complex adsorbed on a bed of Sephadex resin rather than in homogeneous solution. On the basis of these considerations, we tend to discount the significance of the small yields of $Fe(CN)_5OH_2^{2-}$ measured, and we believe that for the binuclear complexes with the pyridine nitrogen bound to the cobalt, electron transfer is negligible compared to dissociation with $k_{et} < 1 \times 10^{-3}$ s^{-1}. Under these circumstances, $k_{obsd} = k_{os}^{IP}k_d/(k_f^{IP} + k_{os}^{IP})$, and from the values of $k_f^{IP} + k_{os}^{IP}$ and of k_d (columns 3 and 5 of Table III), we calculate $k_{os}^{IP} = 0.46$ and 0.71 s^{-1} and 4-cyanopyridine and 3-cyanopyridine, respectively. These values compare well with the values[23] 0.15 and 0.33 s^{-1} measured for internal, outer-sphere electron transfer in the ion pairs $Fe(CN)_6^{4-}|VIII$ and $Fe(CN)_6^{4-}|XI$, respectively. Since the reduction potentials of $Fe(CN)_6^{3-}$ (0.42 V) and $Fe(CN)_5OH_2^{2-}$ (0.39 V) are similar, the rate constants for self-exchange of $Fe(CN)_6^{3-/4-}$ and $Fe(CN)_5OH_2^{2-/3-}$ must also be similar. Using the ion pair formulation of the Marcus equation and correcting for electrostatics,[24] we find the rate constants for self-exchange in $Fe(CN)_5OH_2^{2-/3-}$ calculated from the 4-cyanopyridine and 3-cyanopyridine data are 2.2×10^5 and 6.7×10^5 M^{-1} s^{-1}, respectively, compared with 1.9×10^4 M^{-1} s^{-1} for $Fe(CN)_6^{3-/4-}$ and $\sim 7 \times 10^5$ M^{-1} s^{-1} $Fe(CN)_5NH_3^{2-/3-}$.[25]

It is noteworthy that the VIII or XI–$Fe(CN)_5OH_2^{3-}$ systems represent an additional example of the "dead-end" mechanism for inner-sphere electron transfer.[26,27] The dominant reaction between the reactants produces a precursor binuclear complex which does not undergo internal electron transfer. The binuclear complex returns to reactants which in turn yield the mononuclear products via an outer-sphere electron transfer reaction (Scheme II). It must be emphasized that in previous work the dead-end mechanism was supported on the basis of rate comparisons,[26,27] but no direct proof was provided. In contrast, the negligible yield of $Fe(CN)_5OH_2^{2-}$, the expected reaction product of internal electron transfer within the binuclear complexes, represents direct evidence for the mechanism proposed in Scheme II.

For the IX–$Fe(CN)_5OH_2^{3-}$ system, the relative rates of intramolecular electron transfer and dissociation are such that k_d is negligible compared to k_{et}, and therefore the values of k_{obsd} in Table II are identified as k_{et}. For the X–$Fe(CN)_5OH_2^{3-}$ system, both k_d and k_{et} are important, and individual values of these as well as the other two rate constants in Scheme I and eq 5 were obtained as described above. The resulting value of k_{et} is listed in column 5 of Table II. It will be seen that, as observed previously[17] for the analogous 3- and 4-pyridinecarboxylate systems, the 4 isomer, which features a conjugated system between the two metal ions, transmits electrons quite readily, whereas the 3 isomer, in which the metal ions are not conjugated, reacts 2 orders of magnitude slower. It is also interesting to compare the 4-cyanopyridine and 4-pyridinecarboxylate ligands as electron mediators. The distances between Fe and Co in VII and in XVI are not very different, and therefore the outer-sphere contributions to the respective barriers are expected[6] to be similar. The considerably slower reaction of the carboxylate complex (by ~3 orders of magnitude) as compared to the nitrile complex is then taken to be a measure of the difference in inner-sphere reorganizations and in the thermodynamic barriers. The low reactivity of the carboxylate complex is consistent with the generally accepted notion[28] that a lead-in carboxylate group is a "poor electron mediator" for inner-sphere reactions of Co(III) complexes. It is also noteworthy that the second-order rate constants for Cr^{2+} reduction of the (3- and 4-cyanopyridine)pentaamminecobalt(III) complexes (with the nitrile nitrogen bound to cobalt) differ by more than 3 orders of magnitude.[9] Since the affinity of the pyridine N for Cr^{2+} is not expected to depend on whether the coordinated nitrile is in the 3- or 4-position,[29] the difference in second-order rate constants reflects the difference in intramolecular electron transfer rates. Therefore, the ratios of rate constants for the 4 isomer to the 3 isomer are ~2500 and ~50 for Cr^{2+} and $Fe(CN)_5^{3-}$, respectively. The large difference in reactivity ratios may be rationalized on the basis of the intimate mechanism. For the Cr^{2+} reaction, there is strong evidence, at least for the 4 isomer, that electron transfer proceeds via the chemical mechanism,[9] whereas $Fe(CN)_5^{3-}$ is too weak a reductant to reduce the bridging ligand, and the resonance transfer[4] mechanism obtains. In this context, it is useful to compare the rates of reactions of pairs of linkage isomers. For the Cr^{2+} reductions of the linkage isomers of (4-cyanopyridine)pentaamminecobalt(III), the reactivity ratio is ~50,[9] the isomer with the nitrile bound to cobalt being the faster. This ratio is based on measured second-order rate constants. Since these constants include the equilibrium constant for precursor complex formation, and pyridine N is expected[9] to bind Cr^{2+} more strongly than nitrile N, the reactivity ratio, expressed as intramolecular electron transfer rates, should be closer to 1. For the reduction by $Fe(CN)_5^{3-}$, the reactivity ratio is >160, the isomer with the nitrile bound to cobalt being the faster. Again, the large difference in rate ratios is accommodated on the basis of mechanism. For Cr^{2+}, the chemical mechanism obtains[9] and little discrimination is exhibited between linkage isomers. For $Fe(CN)_5^{3-}$, the resonance mechanism obtains and the differences in thermodynamic barriers and inner-sphere reorganizations between the linkage isomers are fully displayed. By utilization of the reduction potentials of $Fe(CN)_5(pyridine)^{2-}$ (0.47 V[3]) and $Fe(CN)_5(benzonitrile)^{2-}$ (0.62 V[10]) as estimates of the relative thermodynamic barriers in VII and V, the relative rate, calculated on the basis of a $K^{1/2}$ dependence, is ~ 3×10^2 compared with the experimental result, >160. Evidently, the difference in thermodynamic barriers may be sufficient to account for the difference in rate between the linkage isomers. This result, in turn, may be taken to indicate that the electron-mediating ability of



XVI

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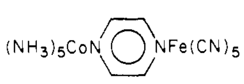
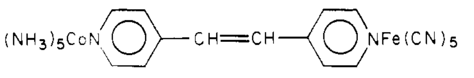
4-cyanopyridine does not depend on its bonding mode.[30]

Finally, it is noteworthy that the activation parameters for intramolecular electron transfer in VII, $\Delta H^{\ddagger} = 23.4 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = 19.2 \pm 0.2$ cal/(deg mol), compare favorably with the values for intramolecular electron transfer in the related systems XVII (24.6 ± 1.4 kcal/mol, 18 ± 5 cal/mol deg)[31] and XVIII (24.5 ± 0.3 kcal/mol, 10.6 ± 1.0 cal/(mol deg)).[5] The sizable positive entropies of activation are to be contrasted with the near-zero values measured for intramolecular electron transfer in *trans*-$(H_2O)(NH_3)_4RuLCo(NH_3)_5^{5+}$ (L = 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethylene, 3,3′-dimethyl-4,4′-bipyridine, bis(4-pyridyl) sulfide).[32] The values of $\Delta S^{\ddagger}$ are rationalized on the basis of the charge redistribution concept.[20] For the iron systems, in going from precursor to successor complex, the charge separation goes from 3+,3− to 2+,2−, whereas for the ruthenium system no change in charge separation obtains upon electron transfer, 3+,2+ being the charge separation in both precursor and successor complexes. For the iron systems, the charge redistribution would be accompanied by a decrease in solvation and, consequently, a positive entropy of activation. For the ruthenium systems, the electron transfer does not change the net charge distribution, no net change in solvation takes place, and consequently, a near-zero entropy of activation obtains.



XVII



XVIII

Registry No. $Fe(CN)_5OH_2^{3-}$, 18497-51-3; $Co(NH_3)_5NC_5H_4CN^{3+}$, 46247-07-8; $Co(NH_3)_5NCC_5H_4N^{3+}$, 53739-10-9; $Co(NH_3)_5$-1,3-$NC_5H_4CN^{3+}$, 80041-64-1; $Co(NH_3)_5NC$-3,1-$C_5H_4N^{3+}$, 53739-14-3; $(NC)_5FeNC_5H_4CNCo(NH_3)_5$, 81095-43-4; $(NC)_5FeNCC_5H_4NCo(NH_3)_5$, 81063-99-2; $(NC)_5Fe$-1,3-$NC_5H_4CNCo(NH_3)_5$, 81064-00-8; $(NC)_5FeNC$-3,1-$C_5H_4NCo(NH_3)_5$, 81064-01-9.

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[30] The differences in reduction potentials and self-exchange rates for nitrile-bound and pyridine-bound complexes of $Co(NH_3)_5^{3+}$ and 4-cyanopyridine are assumed to be small. We have no direct information on this point. However, the rates of reduction of nitrile-bound and pyridine-bound complexes of $Co(NH_3)_5^{3+}$ with 3-cyanopyridine differ by a factor of 2: Miralles, A. J.; Szecsy, A. P.; Haim, A. *Inorg. Chem.* **1982**, *21*, 697.

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X-ray Structures of Two Unexpected Complexes Isolated during CO Substitutions by Phosphine Ligands in Dinuclear Bridged d^8 Metal Complexes

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Abstract: The reaction of $[Ir_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4]$ in concentrated hexane solution with 2 mol of trimethylphosphine results in the two complexes $[Ir_2(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})(CO)_2(S\text{-}t\text{-Bu})(PMe_3)_3]$ and $[Ir_3(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})_3(CO)_4(PMe_3)_2]$, for which the structures have been determined by X-ray crystallography. The first complex crystallizes in space group $P\bar{4}2_1c$ with $a = 15.334$ (2) Å, $c = 26.623$ (4) Å, and $Z = 8$. On the basis of 2313 unique reflections, the structure was refined by full-matrix least-squares techniques to conventional indices of $R = 0.045$ and $R_w = 0.035$. The Ir–Ir separation is 2.702 (1) Å, and a CO ligand is in a bridging position whereas a S-*t*-Bu ligand is in an equatorial position. The complex $[Ir_3(\mu\text{-CO})(\mu\text{-S-t-Bu})_3(CO)_4(PMe_3)_2]$ crystallizes in space group $P2_1/c$ with $a = 16.521$ (3) Å, $b = 10.060$ (3) Å, $c = 21.295$ (4) Å, $\beta = 90.23$ (1)°, and $Z = 4$. On the basis of 1746 unique reflections, the structure was refined by full-matrix least-squares techniques to $R = 0.059$ and $R_w = 0.072$. The structure of the trinuclear entity ressembles that of $[Ir_2(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})(CO)_2(S\text{-}t\text{-Bu})(PMe_3)]$, owing to the Ir–Ir separation of 2.712 (3) Å and the presence of the bridging CO and S-*t*-Bu ligands. Infrared studies of these two complexes and of their CO loss in solution to form the disubstituted complex $[Ir_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2(PMe_3)_2]$ allow us to propose a new pathway for this type of dinuclear iridium complexes to the CO substitution by tertiary phosphine ligands.

In previous publications we have described the synthesis and the structures of dinuclear bridged d^8 metal complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ and $[Ir_2(\mu\text{-SBu})_2(CO)_2L_2]$[4,5] (L = trialkylphosphine or phosphite) obtained by addition of 2 mol of ligand L to the parent compounds $[Rh_2(\mu\text{-}SR)_2(CO)_4]$ and $[Ir_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4]$, respectively. Focusing our attention to the substitution process, we proposed for the rhodium complexes as intermediate species $[Rh_2(\mu\text{-}SR)_2(CO)_4L_2]$ with the two phosphorus ligands in the apical positions of two square pyramids sharing an edge. This structure was proposed from spectroscopic arguments.[2] Besides, examination of the IR and ^1H NMR spectra for the iridium complexes gave evidence for the labile species $[Ir_2(\mu\text{-S-}t\text{-Bu})_2(CO)_3L]$[4] in equilibrium with the non- and disubstituted complexes.

In order to gain more insight into the substitution process we found it an advantage to use the high solubility of the complex $[Ir_2(\mu\text{-S-}t\text{-Bu})_2(CO)_4]$ in any organic solvent and particularly in noncoordinating solvents such as pentane. The addition of 2 mol of ligand (in our case trimethylphosphine) was carried out in very concentrated solutions under a CO atmosphere, and a mixture

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