and the averaging procedure is approximate. However, we are only interested in approximate values (10%). This procedure is more rigorous than taking an arithmetic average or using the 0°,0° results and considerably simpler than a detailed quantum mechanical approach. At 15° from the staggered CH_2–NH_2 configuration, and at all angles tried except 0°, the difference between the staggered methyl group and the value obtained by the above weighting procedure is less than 4%. Therefore, this weighting procedure is utilized only in determining the average shift for the configurations with staggered (0°) CH_2 and NH_2 protons.

Next let us consider rotation about the N–C bond. As can be seen from the data in Table VI, significant variations occur in the values of the spin density at the CH_3 and CH_2 protons when this bond is rotated.

The CH_3/CH_2 ratios of spin densities ranged from 0.911 (0°,0°) to 0.014 (100°,0°). Therefore, we built a Courtauld atomic model of $[Ni(C_2H_5NH_2)_6]^{2+}$ in an attempt to estimate which rotamers would be preferred in the complex. From this model we decided that only three configurations would be stable: a 0°,0° and configurations corresponding to rotation about the N–C bond, from 0°,0° to ±70° (with an error of ±5°). No intermolecular barrier to rotation appears to be imposed on the CH_3 groups in the model. The 0°,0° configuration is less sterically hindered and should be a more probable configuration. We found that, when the probability of the 0° rotameter is two and one-half times as great as the ±70° rotamers, a good fit is obtained for the ratio of the methyl and methylene coupling constants in the ethylamine complex. Admittedly, an additional check is needed on this procedure for we are in a position to vary the ratio of the rotamers and drastically affect the ratio of the coupling constants to fit that observed. Such a check is provided by the methylamine complex.

Since Δ is almost identical[12] for the $[Ni(CH_3NH_2)_6]^{2+}$ and $[Ni(C_2H_5NH_2)_6]^{2+}$ complexes, and since the amines are structurally similar, one may expect the spin delocalization mechanism to be almost identical in the two complexes. Thus, one may test the reasonableness of the assumptions for ethylamine by calculating the ratio $CH_2(C_2H_5NH_2)/CH_3(CH_3NH_2)$ from coefficients of the highest filled mo in CH_3NH_2. If we are forcing a fit in ethylamine by our averaging procedure, this calculated ratio will be in poor agreement with experimental. The excellent agreement in the ratios reported in Table VII lends credibility to our previous estimates.

Table VII. Final Ratios of Spin Densities

Group (ligand)	Ratio (calcd)	Ratio (exptl)
$CH_3(C_2H_5NH_2)/CH_2(C_2H_5NH_2)$	0.268	0.284
$CH_2(C_2H_5NH_2)/CH_3(CH_3NH_2)$	0.471	0.475

We were able to calculate the experimentally observed attenuation in the spin densities of our σ system. Consequently, in more complex systems where the ligand can undergo both σ and π bonding with the metal, calculations of the type described here may be of help in sorting out the relative importance of these various mechanisms.

Acknowledgment. The authors acknowledge with thanks the financial support of this research by the National Science Foundation through Grant GP-5498. One of us (R. J. F.) is also indebted to Dr. Donald H. Dugre for his aid and helpful discussions throughout the course of the theoretical part of this problem.

The Kinetics of the Reaction of Cobalt(III) and Iron(III) Hematoporphyrin with Cyanide and Thiocyanate. Evidence for a Dissociative Mechanism

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Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois. *Received October 2, 1967*

Abstract: The kinetics of reaction between cobalt(III) and iron(III) hematoporphyrin with the anions thiocyanate and cyanide were followed with a stopped-flow system. The kinetic data fit a reaction mechanism scheme that involves a dissociative mechanism with a five-coordinate intermediate. The cobalt(III) hematoporphyrin is very labile with respect to substitution reactions compared to the usual inert behavior of Co(III) complexes.

The reaction of metalloporphyrins with the ligands cyanide and thiocyanate has been investigated in order to determine the mechanism of this substitution reaction and also to obtain data in order to understand the unusual lability of the Co(III) ion toward substitution reactions when it is coordinated to porphyrins[2] or porphyrin-like compounds.[3]

The over-all reaction[4] that takes place can be represented by

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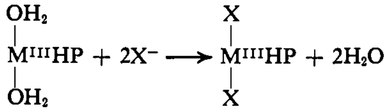
(1) Alfred P. Sloan Fellow.

(2) P. Hambright, Ph.D. Thesis, University of Chicago, 1966, p 164.

(3) W. C. Randall and R. A. Alberty, *Biochemistry*, **6**, 1520 (1967); **5**, 3189 (1966).

(4) Abbreviations used in this study: HP = hematoporphyrin IX, $M^{III}HP$ = metal(III) hematoporphyrin IX complex, AC ≡ aquocobalamin. The over-all charge on the metalloporphyrin molecule is not shown; the porphyrin side chains have a 2− charge due to two ionized carboxyl groups.



$$\overset{OH_2}{\underset{OH_2}{M^{III}HP}} + 2X^- \longrightarrow \overset{X}{\underset{X}{M^{III}HP}} + 2H_2O$$

The complexes studied were the Co(III), Mn(III), and Fe(III) hematoporphyrins. This porphyrin was chosen because of its availability and presumably monomeric character in solution.[5] Figure 1 shows the structure of the $M^{III}HP$ complex,

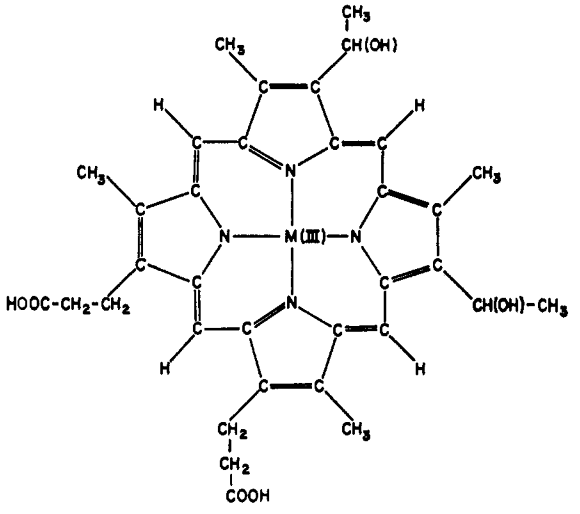


Figure 1. M(III) hematoporphyrin IX.

Experimental Section

The iron, cobalt, and manganese hematoporphyrins were synthesized and purified by literature methods.[5,6]

Anal. Calcd for cobalt(III) hematoporphyrin acetate trihydrate: C, 56.1; N, 7.3; H, 6.1; Co, 7.7. Found: C, 56.0; N, 7.7; H, 5.1; Co, 8.1.

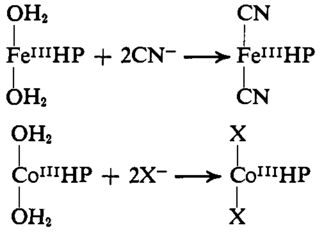
Anal. Calcd for iron(III) hematoporphyrin acetate pentahydrate: C, 54.5; N, 7.1; H, 5.8; Fe, 6.9. Found: C, 54.1; N, 6.8; H, 5.5; Fe, 6.5.

Anal. Calcd for manganese(III) hematoporphyrin acetate: C, 60.7; N, 7.9; H, 5.8; Mn, 7.7. Found: C, 60.7; N, 8.3; H, 5.9; Mn, 7.9.

The reactions were followed using a stopped-flow system that has previously been described.[7,8] The apparatus was tested using the ceric–ferrous phenanthroline reaction.[9] All the reactions were carried out at 25.0°; the metalloporphyrin concentrations were always about 2×10^{-6} *M*. The reactions were run at constant ionic strength. The sum of the ligand (CN^- or SCN^-) concentration plus sodium perchlorate was kept at 0.15 *M*. The reactions were followed by monitoring the change in their visible spectrum; the Soret region was usually followed (390–420 mμ). The pH 7.2 buffer was prepared by adding 26.5 g of Na_2HPO_4 and 8.49 g of KH_2PO_4 to 4.0 l. of distilled water. All reactions were run under pseudo-first-order conditions; the individual rate constants obtained are the average of at least four runs. The average deviation from the average of these runs is about 5%.

Results

The following reactions were studied.



$$\overset{OH_2}{\underset{OH_2}{Fe^{III}HP}} + 2CN^- \longrightarrow \overset{CN}{\underset{CN}{Fe^{III}HP}}$$

$$\overset{OH_2}{\underset{OH_2}{Co^{III}HP}} + 2X^- \longrightarrow \overset{X}{\underset{X}{Co^{III}HP}}$$

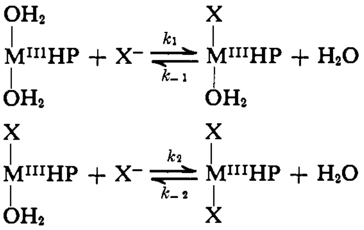
$X^- = CN^-, SCN^-$

The products of these reactions were identified by their visible absorption spectrum.[10,11] The reactions of $Mn^{III}HP$ with CN^-, N_3^-, and SCN^- were tried but there was no evidence for any reactions taking place.

The reactions were first order in the metalloporphyrin for all the cases studied; the pseudo-first-order rate constants for the various reactions are listed in Table I. The plots of the first-order rate constants, k_{obsd}, against anion concentration are given in Figures 2 and 3 for the $Co^{III}HP$–CN^- reaction and the $Co^{III}HP$–SCN^- reaction. The plot of k_{obsd} against anion concentration for the $Fe^{III}HP$–CN reaction is linear.

There are several reasonable mechanisms for this ligand metalloporphyrin anation reaction. The three most likely mechanisms will be given and then the evidence for the most consistent one will be discussed.

Mechanism I



$$\overset{OH_2}{\underset{OH_2}{M^{III}HP}} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{X}{\underset{OH_2}{M^{III}HP}} + H_2O$$

$$\overset{X}{\underset{OH_2}{M^{III}HP}} + X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \overset{X}{\underset{X}{M^{III}HP}} + H_2O$$

The above mechanism is an associative type of mechanism in the Langford and Gray[12a] terminology or an

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[5] P. A. Loach and M. Calvin, *Biochemistry*, 2, 361 (1963).

[6] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

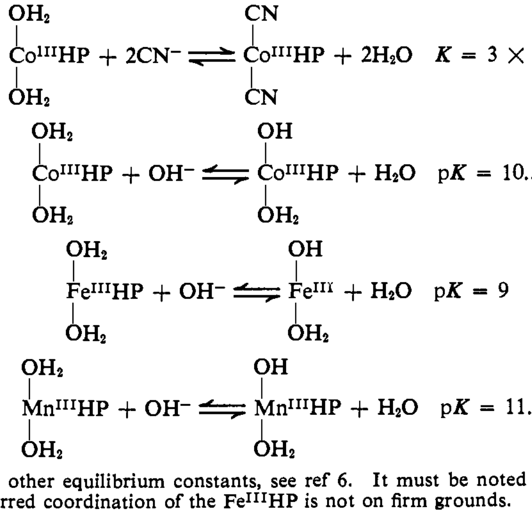
[7] J. Candlin, J. Halpern, and D. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[8] G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

[9] G. Dulz, Ph.D. Thesis, Columbia University, 1962.

[10] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 2979 (1960).

[11] Some of the equilibrium constants for the reactions studied were measured. The reactions all proceed to completion under the conditions employed in this study.



$$\overset{OH_2}{\underset{OH_2}{Co^{III}HP}} + 2CN^- \rightleftharpoons \overset{CN}{\underset{CN}{Co^{III}HP}} + 2H_2O \quad K = 3 \times 10^9$$

$$\overset{OH_2}{\underset{OH_2}{Co^{III}HP}} + OH^- \rightleftharpoons \overset{OH}{\underset{OH_2}{Co^{III}HP}} + H_2O \quad pK = 10.5$$

$$\overset{OH_2}{\underset{OH_2}{Fe^{III}HP}} + OH^- \rightleftharpoons \overset{OH}{\underset{OH_2}{Fe^{III}}} + H_2O \quad pK = 9$$

$$\overset{OH_2}{\underset{OH_2}{Mn^{III}HP}} + OH^- \rightleftharpoons \overset{OH}{\underset{OH_2}{Mn^{III}HP}} + H_2O \quad pK = 11.9^5$$

For other equilibrium constants, see ref 6. It must be noted that the inferred coordination of the $Fe^{III}HP$ is not on firm grounds. There is evidence in the literature that some metalloporphyrins exist as dimers or aggregates in solution and that even Calvin's[5] deduction of the monomeric nature of Mn^{III} hematoporphyrin is based only on a Beer's law plot. We can only say that, if these dimers or aggregates do exist, they do not seem to influence the ligand reactions studied in this paper.

[12] (a) C. Langford and H. B. Gray, "Ligand Substitution Reactions," W. A. Benjamin Inc., New York, N. Y., 1965; (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

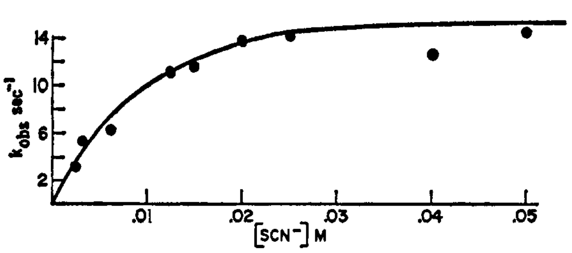
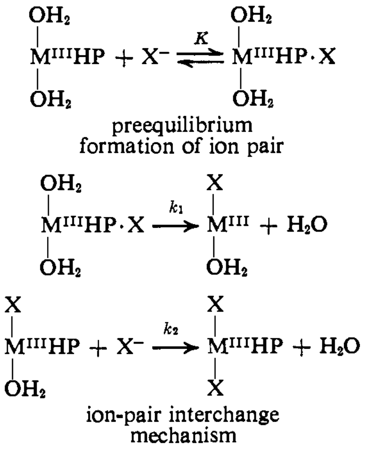


Figure 2. k_{obsd} *vs.* thiocyanate concentration for the reaction between $\mathrm{Co^{III}HP}$ and $\mathrm{SCN^-}$ 25.0°, pH 7.2. The line was calculated from the rate constants in Table III.

SN2 in the terminology of the earlier convention for classifying reaction mechanisms.[12b]

Mechanism II



$$\underset{\mathrm{OH_2}}{\overset{\mathrm{OH_2}}{\mathrm{M^{III}HP}}} + \mathrm{X^-} \overset{K}{\rightleftharpoons} \underset{\mathrm{OH_2}}{\overset{\mathrm{OH_2}}{\mathrm{M^{III}HP\cdot X}}}$$

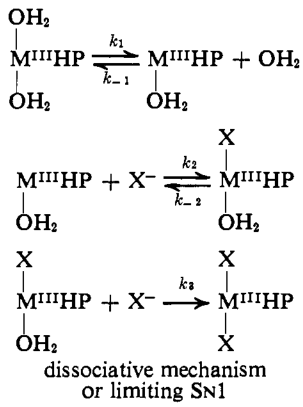
preequilibrium
formation of ion pair

$$\underset{\mathrm{OH_2}}{\overset{\mathrm{OH_2}}{\mathrm{M^{III}HP\cdot X}}} \xrightarrow{k_1} \underset{\mathrm{OH_2}}{\overset{\mathrm{X}}{\mathrm{M^{III}}}} + \mathrm{H_2O}$$

$$\underset{\mathrm{OH_2}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}} + \mathrm{X^-} \xrightarrow{k_2} \underset{\mathrm{X}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}} + \mathrm{H_2O}$$

ion-pair interchange
mechanism

Mechanism III



$$\underset{\mathrm{OH_2}}{\overset{\mathrm{OH_2}}{\mathrm{M^{III}HP}}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathrm{OH_2}}{\mathrm{M^{III}HP}} + \mathrm{OH_2}$$

$$\underset{\mathrm{OH_2}}{\mathrm{M^{III}HP}} + \mathrm{X^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\mathrm{OH_2}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}}$$

$$\underset{\mathrm{OH_2}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}} + \mathrm{X^-} \xrightarrow{k_3} \underset{\mathrm{X}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}}$$

dissociative mechanism
or limiting SN1

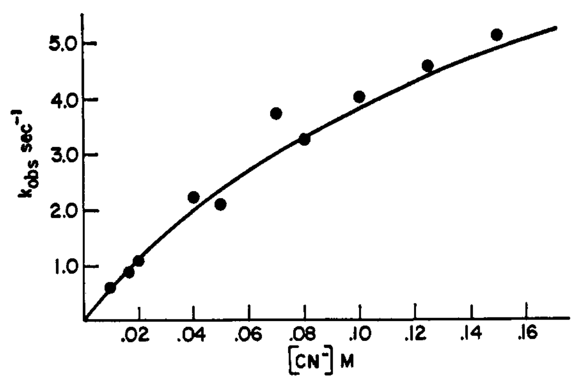
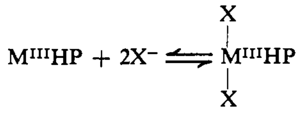


Figure 3. k_{obsd} *vs.* cyanide concentration for the reaction between $\mathrm{Co^{III}HP}$ and cyanide at 25.0°, 0.1 *N* NaOH. Line was calculated from the rate constants in Table III.

If we assume that (1) the intermediate $\mathrm{M^{III}(X)(OH_2)HP}$ is in very low concentration and (2) this intermediate reacts much faster with $\mathrm{X^-}$ than does the diaquoporphyrin complex, then we can test the observed data to see which mechanism fits best. These assumptions hold very well for this system as shown by spectrophotometric titrations[6] of metalloporphyrins and by previous kinetic studies. If the incorporation of the first anion into the metalloporphyrin did not labilize the uptake of the second, more complicated kinetics than were observed would be obtained.[13] Thus in our discussion of the rate law for these mechanisms, we will be assuming that the last step of the reaction, the addition of the second anion, plays no role in the rate-determining steps of the reaction and therefore does not appear in the rate law. With these assumptions in mind the following observations can be made. Mechanism I predicts that the rate is first order in $\mathrm{X^-}$ at all concentrations of $\mathrm{X^-}$. Since we see a fall-off of k_{obsd} with $[\mathrm{X^-}]$ for the $\mathrm{Co^{III}HP\text{-}CN}$ and $\mathrm{Co^{III}HP\text{-}SCN}$ reactions (Figures 2 and 3), mechanism I cannot be operating. Of course, we cannot rule out this mechanism for the $\mathrm{Fe^{III}HP\text{-}CN^-}$ reaction, but we will adhere to the principle that these reactions all follow a similar mechanism.

Table I. First-Order Rate Constants for the Reaction[a]



$$\mathrm{M^{III}HP} + 2\mathrm{X^-} \rightleftharpoons \underset{\mathrm{X}}{\overset{\mathrm{X}}{\mathrm{M^{III}HP}}}$$

Compound	Anion	pH	Concn of anion, *M*	First-order k_{obsd}, sec^{-1}
$\mathrm{Fe^{III}HP}$	$\mathrm{CN^-}$	0.10 *N* NaOH	0.10	8.0
		0.10 *N* NaOH	0.085	6.4
		0.10 *N* NaOH	0.050	3.8
		0.10 *N* NaOH	0.043	3.0
		0.10 *N* NaOH	0.025	1.9
		0.10 *N* NaOH	0.013	1.1
		1.0 *N* NaOH	0.050	0.33
		0.50 *N* NaOH	0.050	0.68
		0.05 *N* NaOH	0.050	8.8
$\mathrm{Co^{III}HP}$	$\mathrm{SCN^-}$	7.2	0.050	14.6
		7.2	0.040	12.4
		7.2	0.025	14.2
		7.2	0.0150	13.8
		7.2	0.0125	11.2
		7.2	0.0063	6.4
		7.2	0.0041	5.5
		7.2	0.0025	3.2
$\mathrm{Co^{III}HP}$	$\mathrm{CN^-}$	0.10 *N* NaOH	0.150	5.2
		0.10 *N* NaOH	0.125	4.6
		0.10 *N* NaOH	0.100	4.0
		0.10 *N* NaOH	0.080	3.2
		0.10 *N* NaOH	0.070	2.7
		0.10 *N* NaOH	0.050	2.1
		0.10 *N* NaOH	0.040	2.5
		0.10 *N* NaOH	0.020	1.1
		0.10 *N* NaOH	0.017	0.88
		0.10 *N* NaOH	0.010	0.67

[a] At 25°; $[\mathrm{M^{III}HP}] = 2 \times 10^{-5}\ M$.

Mechanisms II and III both predict a falling-off of the k_{obsd} with increasing concentration of the incoming

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(13) A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p 178.

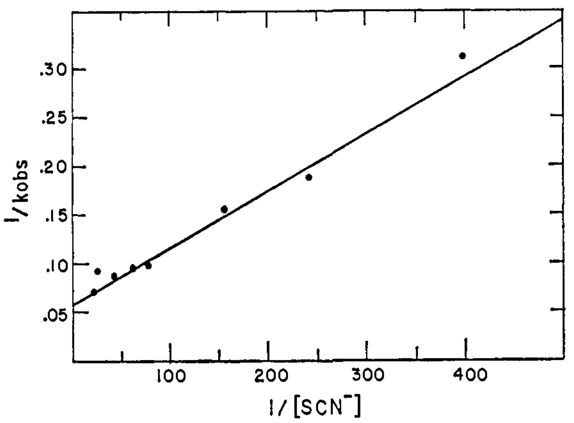

Figure 4. $1/k_{obsd}$ *vs.* $1/[SCN^-]$ for the reaction between $Co^{III}HP$ and SCN^-.

anion. Mechanism II gives

$$k_{obsd} = \frac{k_1K[X^-]}{1 + K[X^-]}$$

where K is the ion-pair equilibrium constant. This equilibrium constant can be estimated[14] and usually is in the range of 2–5 for 1+ electrolytes in water at an ionic strength of 0.1.[15,16] Of course, this constant is difficult to calculate for metalloporphyrins but probably should be smaller than usual because of the large size of the molecule. Our data would result in a K in the range of 6–100 M for this constant. Although this is larger than one might expect this constant to be, it is not large enough to definitely rule out mechanism II.

Since the calculated K is larger than expected, and anions of similar shape and charge have different effects, we feel that mechanism II is not as consistent with the data as mechanism III. Mechanism III gives the following dependence of k_{obsd} with respect to $[X^-]$.[17]

$$k_{obsd} = \frac{k_1[X^-]}{(k_{-1}/k_2) + [X^-]}$$

If one plots $1/k_{obsd}$ *vs.* $1/[X^-]$, a straight line should result with a slope of k_{-1}/k_2k_1 and an intercept of $1/k_1$. In the case where k_{obsd} does not fall off with $[X^-]$, we can only obtain k_2k_1/k_{-1} from the slope of k_{obsd} *vs.* $[X^-]$. Figures 4 and 5 show the data plotted in this fashion, and the constants that were obtained by this method are given in Table II. Using the data in Table II we back-calculated the smooth curves in Figures 2 and 3. The data are consistent with the proposed mechanism III, a dissociative mechanism or limiting SN1 mechanism.[18] This type of mechanism has been demonstrated previously by Haim and Wilmarth[19] for substitution in $Co(CN)_5H_2O^{2-}$ and by Halpern[20] for substitution in $Co(NH_3)_4SO_3X$ complexes.

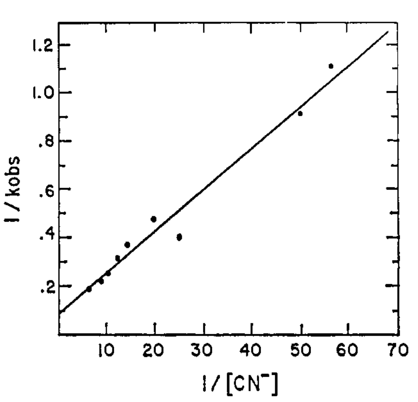

Figure 5. $1/k_{obsd}$ *vs.* $1/[CN^-]$ for the reaction between $Co^{III}HP$ and CN^-.

The reactions studied in this paper can be compared to similar ones that have been published. In general, the rates of substitutions on hemoglobin and myoglobin, iron–porphyrin-containing materials, are very rapid; $k \sim 10^6$ M^{-1} sec^{-1}.[21,22] This is probably due to the labilizing effect of the imidazole, which is on the fifth coordination position of the Fe(III) in these compounds, on the rate of substitution in the sixth position. This also substantiates the assumption made in our studies that the substitution of the second anion is very fast compared to the reaction of the first anion.

Table II. Rate Constants for the Reaction of $M^{III}HP$ with Various Anions[a]

Reaction	k_1k_2/k_{-1}, M^{-1} sec^{-1}	k_1, sec^{-1}	k_{-1}/k_2
$Fe^{III}HP + CN^-$	75		
$Co^{III}HP + CN^-$	65	11.0[b]	0.17
$Co^{III}HP + SCN^-$	1850	17.4	0.010

[a] These constants have been calculated assuming mechanism III is operative. [b] The rate k_1 of the first step of the reaction is different for the CN^- and the SCN^- because the SCN^- reaction was carried out at pH 7.2 where the cobalt porphyrin complex is in the form of the diaquo complex, whereas the CN^- reaction was carried out in 0.1 N NaOH where the complex is in the form of the hydroxyaquo species (see ref 11).

Alberty has studied the reaction of aquocobalamin with various ligands.[3,4] He found a linear dependence of the k_{obsd} with ligand concentration. The aquocobalamin has a benzimidazole group bound to the fifth site on the Co(III) ion. A comparison of the rate constants for the aquocobalamin with thiocyanate, under similar conditions as the Co(III) hematoporphyrin reactions were run, show the aquocobalamin reactions to be faster. (k_{2nd}[3,4] for cobalamin for N_3^- = 790 M^{-1} sec^{-1} and SCN^- = 5000 M^{-1} sec^{-1} compared to those for the $Co^{III}HP$ of 140 and 1850 M^{-1} sec^{-1}.) This is again due to the labilizing effect of a nonaquo ligand in the fifth position.

One of the interesting and unsolved questions concerning the reaction of $Co^{III}HP$ is the great lability toward substitution reactions compared to the usual inertness that Co(III) complexes exhibit. A good com-

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(14) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(15) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

(16) C. Langford and W. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).

(17) This assumes as previously that the last step in the mechanism is very rapid and that the equilibrium lies far to the right; both of these assumptions hold in these reactions.

(18) The data reported here do not clearly differentiate between mechanisms II and III. Future studies of this system will be carried out to attempt to clarify the mechanism of this reaction.

(19) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

(20) J. Halpern, R. Palmer, and L. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

(21) G. Duffey, B. Chance, and G. Czerlinski, *Biochemistry*, **5**, 3514 (1966).

(22) D. Goldsack, W. S. Everlen, and R. A. Alberty, *J. Biol. Chem.*, **240**, 4312 (1965).

parison is the reaction of nitroaquobis(dimethylglyoximato)cobalt(III) with SCN^- and N_3^-.[23]

The second-order rate constants for N_3^- and SCN^- are respectively 5.7×10^{-4} and 5.8×10^{-4} M^{-1} sec^{-1}. These rates are about 10^6 slower than those observed for the Co(III) hematoporphyrin reactions. The geometry and charge of these complexes are similar; thus a steric reason cannot be invoked to explain the lability of the metalloporphyrins. The metal ions in metalloporphyrins are so involved in the delocalized orbitals of the porphyrin molecule that they lose their transition metal ion character.[24] Thus Co(III) complexes, which exhibit low-spin d^6 configurations that have orbitals containing these electrons that are "predominantly" metal orbitals, should be kinetically inert toward substitution reactions as are the majority of Co(III) complexes. When the Co(III) ion becomes involved in a macrocyclic that has a "delocalized" electronic structure, the complex might be kinetically labile. The lability follows the breakdown of the Co(III) oxidation-state formalism. The problem of the oxidation state of transition metals in complexes with delocalized electronic structures has been a very active one recently.[25,26]

At present there is no way to give a quantitative description of the electronic structure of cobalt complexes to be able to determine *a priori* which complexes will be labile and which inert.[27]

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(23) D. N. Hague and J. Halpern, *Inorg. Chem.*, 6, 2059 (1967).

(24) M. Zerner and M. Gouterman, *Theoret. Chim. Acta*, 4, 44 (1966).

(25) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, 88, 43 (1966).

(26) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, 5, 1542 (1966).

(27) This research was supported by a Grant from the National Institutes of Health.

Kinetics and Mechanism of Substitution Reactions of Dinitrosyldicarbonyliron(0)

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Abstract: Dinitrosyldicarbonyliron(0) undergoes carbon monoxide substitution reactions in the presence of phosphines, phosphites, and triphenylarsine to give the monosubstituted derivatives, $Fe(NO)_2(CO)L$. The preparation and spectra of several mono- and disubstituted derivatives are reported. The rates of these reactions depend on the concentration and nature of reagent. For reagents with the same donor atom, the rates of reaction increase with increasing basicity (or polarizability) of the reagents. The results obtained support a bimolecular displacement mechanism with nucleophilic attack by the entering reagent on the class b or soft iron(0). This is discussed in terms of the nature of the chemical bonding in $Fe(NO)_2(CO)_2$.

Studies of the kinetic behavior of metal carbonyls is a subject of considerable current interest.[2] Many of the metal carbonyl substrates studied are found to undergo CO substitution reactions by a first-order process. From reactions of this type one can obtain information on the factors which affect the reactivities of different substrates but not on factors that contribute to the nucleophilic strengths of various reagents toward metal carbonyls.

Since Heck[3] reported briefly that the rate of the reaction of $Co(NO)(CO)_3$ with $(C_6H_5)_3P$ was first order in both substrate and reagent concentrations, there has been a continued effort to investigate metal carbonyl systems which undergo CO substitution reactions by a second-order process. From reactions of this type, one obtains information on the factors which affect the reactivities of different substrates, but, more important, one can also obtain useful information concerning the factors which contribute to the nucleophilic strength of various reagents toward these substrates.

Recent studies on $Co(NO)(CO)_3$[4,5] and $Mn(NO)_3(CO)$[6] have shown that these two members of the pseudo-tetracarbonylnickel series undergo CO substitution reactions in part by a second-order process. This is in contrast to the CO substitution[3,7] and ^{14}CO exchange[7,8] reactions of the isoelectronic and isostructural $Ni(CO)_4$. Both of these reactions were found to be first-order in $Ni(CO)_4$ and independent of the concentration of the entering reagent.

This paper reports the kinetic data concerning the first step of CO substitution of $Fe(NO)_2(CO)_2$

$$Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO \qquad (1)$$

where L = phosphines, phosphites, or triphenylarsine. This is an extension of a study of the kinetic behavior of members of the pseudo-tetracarbonylnickel series. Previously it had been reported[9] that the ^{14}CO exchange

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(1) Taken in part from the Ph.D. Thesis of D. E. Morris, Northwestern University, 1967.

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