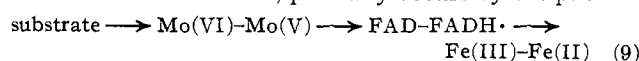


ably will be enhanced by the substitution of a flavin radical for Q⁻.⁴³

Consideration of the total collection of nonaqueous electrochemical data permits tabulation of a set of formal potentials, E' , for oxidation-reduction couples that are relevant to the chemistry of the flavoproteins; Table II summarizes such potentials (*vs.* sce) in DMSO with 0.1 *F* TEAP as the supporting electrolyte. The values represent the average between the cathodic and anodic peak potentials (from cyclic voltammetry) and $E_{r/4}$ values (from chronopotentiometry). In addition, the peak potentials at a scan rate of 0.1 V/sec are presented for several irreversible couples. Reference to the potentials in Table II indicates that

(43) L. S. Meriwether, W. F. Marzluff, and W. A. Hodgson, *Nature (London)*, **212**, 465 (1966).

the electron-transfer mechanism of metalloflavins, in the absence of other factors, probably occurs by the path



This is in agreement with the proposals by several investigators of the flavin enzymes^{1,2,10,14} and lends support to the proposal that the electron-transfer steps occur in an aprotic environment. Additional studies of the molybdenum-flavin system are in progress to further elucidate the detailed mechanism of electron transfer for the metalloflavin enzymes.

Acknowledgments.—This work was supported by the National Science Foundation under Grant No. GP-16114. We are grateful for an NSF traineeship awarded to A. F. I., Jr.

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Kinetic Studies on the Formation of a Cyanide-Bridged Adduct of Two Cationic Metal Complexes^{1a}

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Kinetic studies have been carried out on the formation of Cr-NC-Hg⁴⁺ by the reaction of CrCN²⁺ with Hg²⁺, which occurs at a rate given by

$$\frac{d[\text{Cr-NC-Hg}^{4+}]}{dt} = \frac{A + B[\text{Hg}^{2+}]}{1 + C[\text{Hg}^{2+}]} [\text{CrCN}^{2+}]_T$$

with values $A = 2.8 \times 10^{-8} \text{ sec}^{-1}$, $B (M^{-1} \text{ sec}^{-1}) = 0.62 + 0.25/[\text{H}^+]$, and $C = 24.2 \pm 2.2 M^{-1}$ at 25.0° and $\mu = 2.0 M$. The rate constant A represents a correction for a minor pathway; the proposed mechanism for the main pathway involves a rapid association between the two cations, followed by an internal rearrangement or isomerization to yield the final product. Spectrophotometric measurements on the solutions immediately after mixing gave independent evidence for the prior association complex, whose stability constant is represented by C . These studies permit the independent evaluation of C as $28.4 \pm 2.5 M^{-1}$ and generate the visible absorption spectrum of the intermediate. The steps in the mechanism are discussed, and some conjectures are made concerning the structure of the rapidly formed association complex.

Introduction

Polyvalent cationic complexes do not commonly associate with one another to an appreciable extent in aqueous solution. Not only do their like charges destabilize the interaction, but the coordinating strength of a polar solvent which is capable of dissolving and ionizing the parent compounds usually outweighs the stability of a $[\text{MXM}']^m+$ dinuclear species. Stable association can occur, however, when an ambidentate ligand having both hard base and soft base donor atoms simultaneously associates with a hard and a soft metal ion. This is the case²⁻⁵ with adducts of metal-isothiocyanate complexes and mercury(II), as in eq I.



The equilibrium quotients at 25° are $1.7 \times 10^4 M^{-1}$

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2799. (b) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

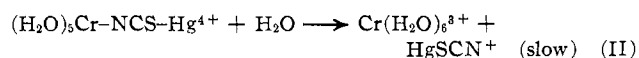
(2) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

(3) M. Orhanović and N. Sutin, *ibid.*, **90**, 538, 4286 (1968).

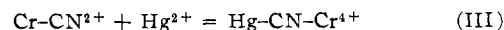
(4) J. N. Armor and A. Haim, *ibid.*, **93**, 867 (1971).

(5) (a) K. Schug and B. Miniatas, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p M136; (b) L. C. Falk and R. G. Linck, *Inorg. Chem.*, **10**, 215 (1971).

for CrNCS²⁺ ($\mu = 1.0 M$)⁴ and $9.8 \times 10^4 M^{-1}$ for Co(NH₃)₅NCS²⁺ ($\mu = 0.10 M$).^{5b} The driving force for reaction I resides in the hard acid-hard base interaction, Cr-N, and (especially) the soft-soft interaction, Hg-S. This reaction occurs "instantaneously"; a further reaction slowly takes place,⁴ which preserves all the features of stability associated with reaction I, while relieving the electrostatic repulsions associated with the 4+ adduct, as in the reaction



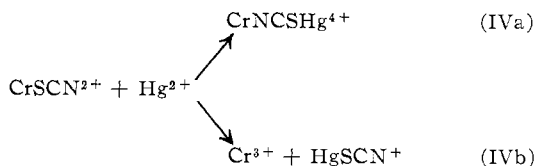
A somewhat different sequence of events transpires when the reactant with Hg²⁺ is the cyano complex Cr-CN²⁺. A stable association occurs⁶ accompanied by a rearrangement reaction, linkage isomerization of cyanide ion. This process (reaction III) does not occur



instantaneously, unlike reaction I. In the present paper we report the results of kinetic and spectrophotometric studies in the mechanism of reaction III.

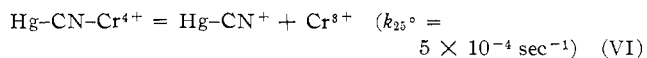
(6) J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).

Related to reaction III is the similar isomerization noted by Orhanović and Sutin³ during the reaction of the S-bonded thiocyanatochromium(III) ion with Hg^{2+} , also driven by the interaction of a soft acid (Hg^{2+}) and a soft base (S), although in their case two reactions occur concurrently



The analogy between reactions III and IVa is not complete, however, because, of the linkage isomers, CrCN^{2+} is more stable than CrNC^{2+} ,⁷ whereas CrSCN^{2+} is less stable than CrNCS^{2+} .² Consequently the linkage isomerization of the thiocyanate complex in reaction IVa is favored by conversion of a Cr-S to a Cr-N bond as well as by the Hg-S bond strength. In contrast, the Cr-C to Cr-N conversion is an added barrier, overcome only by the stable Hg-C association.

Two other reactions should be referred to. The isocyano complex of Cr(III),⁷ Cr-NC^{2+} , reacts "instantaneously" with Hg^{2+} to form the same adduct formed more slowly in III, and the adduct slowly decomposes⁷ in a process analogous to reaction IV. These reactions are



Experimental Section

Materials.—Potassium hexacyanochromate(III) was prepared either by the procedure of Schaap, *et al.*,⁹ or by reducing a $\text{Cr}(\text{ClO}_4)_3$ solution with amalgamated zinc, adding it to a KCN solution with a CN^-/Cr ratio of *ca.* 6–7, and oxidizing the resulting solution with air. Solutions of the monocyano complex were prepared by dissolving $\text{K}_2\text{Cr}(\text{CN})_6$ (3.25 g, 0.01 mol) in 1.0 M perchloric acid (50 ml, 0.05 mol). After *ca.* 10 min, 0.2 M $\text{Cr}(\text{ClO}_4)_2$ (0.5 ml, 0.1 mmol) was added to catalyze the aequation of $\text{Cr}(\text{CN})_6$ and $\text{Cr}(\text{CN})_5^+$ to CrCN^{2+} .⁹ After these reactions were complete (*ca.* 5 min), the solution was cooled to 0° to precipitate potassium perchlorate. The filtrate was passed through a column of cation-exchange resin (Dowex 50W-X8, 50–100 mesh, H⁺ form) which was kept near 0° by circulation of ice water through a condenser-type jacket. The column was rinsed with at least three column volumes of water to eliminate free cyanide as HCN, and CrCN^{2+} was eluted with 1 *F* perchloric acid. The central fraction (typically 40 ml, 3.2 mmol) of CrCN^{2+} was collected for the rate studies, although the actual yield would have been higher had the dilute fractions been collected. The spectrum of CrCN^{2+} prepared in this manner had the following maxima and minima: λ_{max} 525 nm (ϵ 25.4 $M^{-1} \text{ cm}^{-1}$), λ_{min} 450 (7.16), λ_{max} 393 (20.1); this spectrum is in good agreement with published determinations.^{7,9,10}

Solutions of CrCN^{2+} were subsequently analyzed based on the molar absorptivities cited at the maxima; the concentration was also checked in some preparations by oxidation to chromate ion with hydrogen peroxide in sodium hydroxide solution, analyzing the CrO_4^{2-} spectrophotometrically.¹¹ Stock solutions of CrCN^{2+} could be stored without noticeable decomposition for several weeks frozen in Dry Ice.

Barium perchlorate (G. F. Smith) was recrystallized three times. The preparation and analyses of the other reagents have

(7) J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 1153 (1968).

(8) W. B. Schaap, R. Krishnamurthy, D. K. Wakefield, and W. F. Coleman in "Coordination Chemistry," Plenum Press, New York, N. Y., 1969, pp 177–206.

(9) J. P. Birk and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 2266 (1968).

(10) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

(11) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

been described in an earlier publication.¹² Conductivity water was used throughout.

Kinetics Experiments.—The reaction between Hg^{2+} and CrCN^{2+} was followed using a Cary Model 14 spectrophotometer. The cylindrical Pyrex or silica cells were thermostated during the reaction by circulating water through coils surrounding the water-filled cell holder. In studies carried out below room temperature, a continuous stream of dry nitrogen was passed through the cell compartment to prevent water condensation.

A suitable electrolyte medium for studying the reaction of two dipositive cations at high concentration is not obvious, because a single added electrolyte cannot simultaneously maintain constant ionic strength and constant $[\text{ClO}_4^-]$, which appears to be the most likely way to avoid undesired medium effects. Toward this end, a procedure used before^{12,13} was adopted, wherein both a 2:1 electrolyte, $\text{Ba}(\text{ClO}_4)_2$, and a 1:1 electrolyte, LiClO_4 , were added. This permits a reasonable range of the important concentration variables $[\text{Hg}^{2+}]$, $[\text{CrCN}^{2+}]$, and $[\text{H}^+]$ at constant μ and constant $[\text{ClO}_4^-]$. To this end, all solutions were maintained at a constant ionic strength of 2.00 *M* and a constant total perchlorate ion concentration of 1.67 *M*, using both barium and lithium perchlorates to maintain the divalent ions (CrCN^{2+} , Hg^{2+} , Ba^{2+}) at 0.333 *M* and the univalent ions (H^+ , Li^+) at 1.00 *M*.

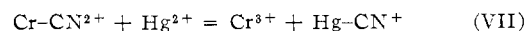
The kinetics experiments were generally performed under conditions where Hg^{2+} was at least 10-fold higher in concentration than CrCN^{2+} . Pseudo-first-order rate plots of $\ln(D - D_\infty)$ vs. time (D = absorbance) were constructed, and found to be linear for at least 3 half-lives. Typically two to six repeat determinations were made, in which the average deviation from the mean was generally $\leq 3\%$. The pseudo-first-order rate constants proved to be independent of the initial concentration of CrCN^{2+} , confirming that the reaction followed pseudo-first-order kinetics over the range of Hg^{2+} and CrCN^{2+} concentrations studied. In practice it proved desirable to evaluate the rate constants from first-order plots constructed according to the method of Guggenheim,¹⁴ because the "infinite-time" absorbance reading could not be relied upon to be exactly correct, especially at low $[\text{Hg}^{2+}]$, owing to the slow decomposition process shown in reaction VI.

Wavelengths between 510 and 525 nm proved the most convenient for following the reaction, as the absorbance changes were the largest. Other experiments were made at several wavelengths between 390 and 610 nm with no evident difference in rate at the different wavelengths. In many of the experiments the spectrophotometer recorder scale was expanded to cover 0.1 absorbance unit full scale.

Results

Stoichiometry.—The spectrum of CrCN^{2+} changes upon addition of Hg^{2+} but remains constant above a 1:1 ratio of Hg^{2+} to CrCN^{2+} as in reaction III. For ratios $\text{Hg}^{2+}/\text{CrCN}^{2+} < 1$, however, the spectrum is not simply the sum of that of CrCN^{2+} and CrNCHg^{4+} , indicating a third species, which may be $[\text{CrNC}]_2\text{Hg}^{6+}$ by analogy with $[(\text{NH}_3)_3\text{CoNCS}]_2\text{Hg}^{6+}$.⁵ A detailed analysis under these conditions was not carried out, and all the kinetic data refer to experiments with excess Hg^{2+} .

Experiments were carried out to learn whether CrCN^{2+} and Hg^{2+} associate exclusively as shown in eq III or whether the process in reaction VII, analogous to



eq IVb, is also important. Product solutions containing various added amounts of Cr^{3+} were passed through a column of cation-exchange resin (Dowex 50W-X8, H⁺ form). The band of Cr^{3+} occurred immediately below that of the 4+ product. No band was noted for solutions to which Cr^{3+} had not been added nor for solutions with a Cr^{3+} concentration less than *ca.* 10% of that of CrNCHg^{4+} . These experiments do not give

(12) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **4**, 527 (1965).

(13) J. H. Espenson and S. R. Helzer, *ibid.*, **5**, 686 (1966).

(14) E. A. Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).

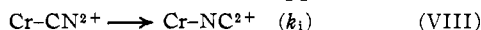
an exact determination of the stoichiometry but suffice to establish that CrNCHg^{4+} is produced in $\geq 90\%$ yield; a process corresponding to reaction VII is unimportant within these limits.

Kinetics.—At $[\text{H}^+] = 1.00 \text{ M}$, kinetic measurements were made over the concentration range $0.010 \leq [\text{Hg}^{2+}]_0 \leq 0.30 \text{ M}$. Pseudo-first-order behavior was followed at all $[\text{Hg}^{2+}]$, with half-times 20–80 sec in these experiments which are summarized in Table I.

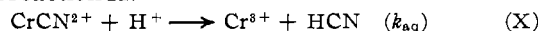
$[\text{Hg}^{2+}]_0$, ^b M	$10^3 k_{\text{app}}$, ^{c,d} sec ⁻¹	$k_{\text{app}}/[\text{Hg}^{2+}]_{\text{av}}$, M ⁻¹ sec ⁻¹
0.0100	0.879 ± 0.009 (2)	0.925
0.0111	0.954 ± 0.012 (2)	0.900
0.0133	1.17 ± 0.01 (2)	0.914
0.0167	1.22 ± 0.02 (2)	0.753
0.0200	1.28 ± 0.02 (5)	0.674
0.0230	1.37 ± 0.01 (4)	0.623
0.0271	1.51 ± 0.07 (5)	0.581
0.0328	1.71 ± 0.03 (4)	0.538
0.0400	1.89 ± 0.03 (5)	0.483
0.0600	2.12 ± 0.05 (6)	0.358
0.100	2.61 ± 0.07 (6)	0.264
0.300	3.06 ± 0.01 (5)	0.102

^a At 25.0°, $\mu = 2.00 \text{ M}$. ^b $[\text{CrCN}^{2+}]_0 \leq 0.1[\text{Hg}^{2+}]_0$. ^c $k_{\text{app}} = -d \ln [\text{CrCN}^{2+}]/dt$. ^d The uncertainty is the average deviation from the mean of repeat determinations, the number of runs being given in parentheses.

Before considering the dependence of that rate constant upon $[\text{Hg}^{2+}]$ it is necessary to apply a correction for two side reactions. The first sequence, reactions VIII–IX, is known to occur to an appreciable albeit minor extent. The second is the aquation of CrCN^{2+} shown in reaction X.



The second is the aquation of CrCN^{2+} shown in reaction X.



The rate constants are known independently. The value $k_i = 2.3 \times 10^{-3} \text{ sec}^{-1}$ was calculated from the rate constant for the reverse of reaction VIII and the estimated equilibrium constant.^{9,15} The apparent first-order rate constant for the aquation process is $4.9 \times 10^{-4} \text{ sec}^{-1}$ under these conditions.⁶ The overall correction, $k_i + k_{\text{aq}}$, is $2.8 \times 10^{-3} \text{ sec}^{-1}$, which we designate A .

In considering the kinetic data it is helpful to anticipate some of the results, for sake of clarity in the procedure used. We find that a part of the CrCN^{2+} added is very rapidly converted to another form by reaction with Hg^{2+} ; only the portion of the CrCN^{2+} that is *not* so changed is subject to the side reactions referred to above. Therefore, only a fraction of the correction $k_i + k_{\text{aq}}$ should be applied to the apparent rate constant.

The algebraic form of the rate law suggested by an inspection of the variation of k_{app} with $[\text{Hg}^{2+}]$ is given by eq 1, in which A designates the parameter correcting for known side reactions.

$$\frac{-d[\text{CrCN}^{2+}]}{dt} = \frac{A + B[\text{Hg}^{2+}]}{1 + C[\text{Hg}^{2+}]} [\text{CrCN}^{2+}]_{\text{T}} = k_{\text{app}} [\text{CrCN}^{2+}]_{\text{T}} \quad (1)$$

(15) The difference in medium between the present experiment and that in the earlier work⁷ is ignored because k_i is expected to be relatively medium independent and because this sequence of reactions constitutes a relatively small correction.

Rearrangement yields eq 2, which can be tested by

$$\frac{1}{k_{\text{app}} - A} = \frac{C}{B - AC} + \frac{1}{B - AC} [\text{Hg}^{2+}]^{-1} \quad (2)$$

a plot of $(k_{\text{app}} - A)^{-1}$ vs. $[\text{Hg}^{2+}]^{-1}$. The data do follow the linear form (Figure 1) required by eq 2, using $A =$

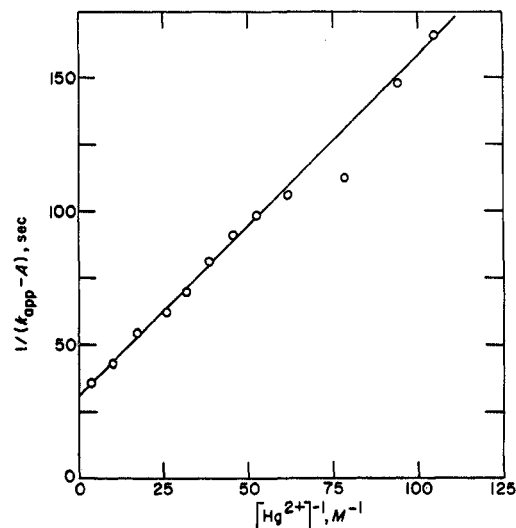
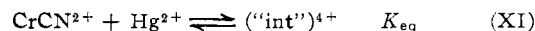


Figure 1.—Plot of the kinetic data according to eq 2. The line corresponds to the least-squares fit of the data to eq 2.

$2.8 \times 10^{-3} \text{ sec}^{-1}$. The least-squares fit gives $B = 0.85 \pm 0.06 \text{ M}^{-1} \text{ sec}^{-1}$ and $C = 24.2 \pm 2.2 \text{ M}^{-1}$.

The Prior Equilibrium.—The denominator in the rate equation is of the form $1 + C[\text{Hg}^{2+}]$, suggesting a preequilibrium step in which the reactants form an intermediate (“int”)



The existence of such a very rapid step was confirmed spectrophotometrically. The absorbance of a CrCN^{2+} solution changes suddenly upon addition of Hg^{2+} , increasing or decreasing depending on wavelength. Consider first a series of experiments done at $\lambda 565 \text{ nm}$, which is an isosbestic point for CrCN^{2+} and the product CrNCHg^{4+} . The absorbance increases instantly on addition of Hg^{2+} and then decreases with time back to the starting value. The initial rapid increase, which is too rapid to measure even using the stopped-flow method, corresponds to reaction XI. The slow decrease represents the formation of the final product from the rapidly formed intermediate (designated “int” in reaction XI). Clearly “int” absorbs more strongly than either CrCN^{2+} or CrNCHg^{4+} at $\lambda 565 \text{ nm}$. These observations suggest a means of evaluating the equilibrium constant for reaction XI.

The absorbance decrease was extrapolated to the time of mixing using the customary pseudo-first-order plot of $\ln(D - D_\infty)$ vs. time. The intercept at the time of mixing was evaluated as accurately as possible in each run. This intercept ΔD corresponds to $D_0 - D_\infty$, where D_0 represents the absorbance of the equilibrium mixture of CrCN^{2+} and “int” according to reaction XI, and D_∞ is the absorbance corresponding to complete conversion to CrNCHg^{4+} . Because of the isosbestic condition, D_∞ also represents the initial absorbance of CrCN^{2+} . The stability constant for reac-

tion XI is related to the instantaneous absorbance change ΔD by the equation

$$\Delta D / [\text{CrCN}^{2+}]_T [\text{Hg}^{2+}] = K_{\text{eq}} (\Delta D / [\text{CrCN}^{2+}]_T) + K_{\text{eq}} b (\epsilon_{\text{int}} - \epsilon_0) \quad (3)$$

where ϵ_0 is the molar absorptivity of CrCN^{2+} , and b is the optical path length, generally 10 cm. $[\text{CrCN}^{2+}]_T$ and $[\text{CrCN}^{2+}]$ are related by the equations $[\text{CrCN}^{2+}]_T = [\text{CrCN}^{2+}] + [\text{"int"}]$ and $[\text{CrCN}^{2+}] / [\text{CrCN}^{2+}]_T = (1 + K_{\text{eq}} [\text{Hg}^{2+}])^{-1}$. Figure 2 presents the data at

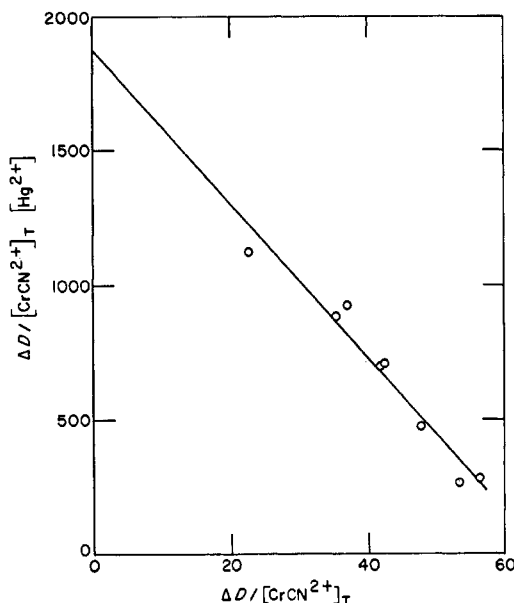


Figure 2.—Spectrophotometric evaluation of the equilibrium constant for reaction XI using the plot suggested by eq 3. The line shown represents the least-squares fit.

25.0° in graphical form according to eq 3; a least-squares fit gives $K_{\text{eq}} = 28.5 \pm 2.5 \text{ M}^{-1}$ and $\epsilon_{\text{int}} - \epsilon_0 = 6.6 \text{ M}^{-1} \text{ cm}^{-1}$.

The spectrophotometric determination of K_{eq} gives a value 18% larger than the value of C derived from the kinetic data: 28.5 ± 2.5 compared to $24.2 \pm 2.2 \text{ M}^{-1}$. Considering the level of uncertainty associated with each determination, however, it can be concluded the two values agree within the experimental error.

Spectrum of the Intermediate.—The kinetics of the reaction was evaluated under one particular set of conditions: 0.100 M Hg^{2+} , 1.00 M H^+ , 2.00 M ionic strength, at 25.0° at 23 wavelengths between 390 and 610 nm. The average value of k_{app} was 0.025 sec^{-1} , independent of the wavelength used to follow the reaction. At each wavelength the pseudo-first-order rate plot was extrapolated to the time of mixing, and a value was calculated for the zero-time absorbance reading, D_0 , which permits the calculation of ϵ_{int} according to

$$\epsilon_{\text{int}} = D_0 [1 + K_{\text{eq}} [\text{Hg}^{2+}]] [\text{CrCN}^{2+}]_T^{-1} - b \epsilon_0 [\text{Hg}^{2+}]^{-1} \quad (4)$$

using the known value of K_{eq} and ϵ_0 for CrCN^{2+} at the wavelength under consideration. The intermediate shows a spectrum typical of a Cr(III) complex, displaying absorption maxima at λ 535 nm (ϵ 27.8) and 395 (ϵ 20.1). Figure 3 depicts the spectrum of the intermediate along with those of CrCN^{2+} , CrNCHg^{4+} , and Cr^{3+} for comparison.

Hydrogen Ion Dependence.—The variation in rate

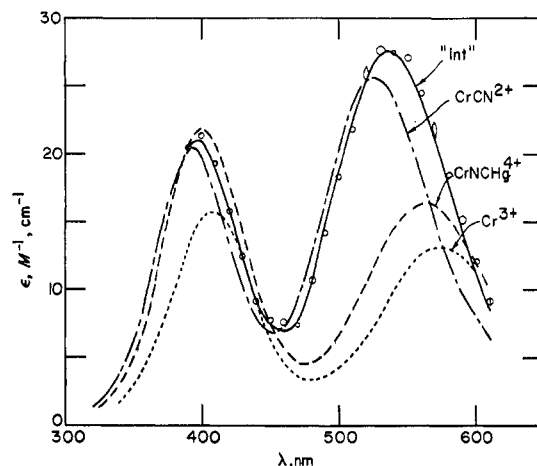


Figure 3.—Absorption spectra of the reactant, intermediate, and product and of Cr^{3+} .

with $[\text{H}^+]$ was studied between 0.10 and 1.0 M H^+ , with the results shown in Table II. The rate effects

TABLE II
EFFECT OF HYDROGEN ION CONCENTRATION^a

$[\text{H}^+]$, M	$[\text{Hg}^{2+}]_{\text{av}}$, M	$10^2 k_{\text{app}}$, sec^{-1}	B^b , $\text{M}^{-1} \text{ sec}^{-1}$
1.00	0.85
0.500	0.0220	1.82	1.15
0.500	0.0391	2.38	1.12
0.250	0.320	2.50	1.63
0.250	0.0391	3.50	1.68
0.100	0.0220	4.70	3.17

^a At 25.0°, $\mu = 2.00 \text{ M}$. ^b Calculated from eq 1, using $C = 24.2 \text{ M}^{-1}$ and $A = 2.3 \times 10^{-3} + 4.9 \times 10^{-4} [\text{H}^+] \text{ sec}^{-1}$.

noted are attributed largely to the B term, as $C (= K_{\text{eq}})$ is presumed not to be significantly dependent on $[\text{H}^+]$. This was confirmed directly using the zero-time spectrophotometric method outlined above. The correction for the side reactions represented by the value of A is only slightly different at the hydrogen ion concentrations considered. The values of B , which are given in Table II, were calculated using $C = 24.2 \text{ M}^{-1}$ and $A = 2.3 \times 10^{-3} + 4.9 \times 10^{-4} [\text{H}^+] \text{ sec}^{-1}$. A plot of

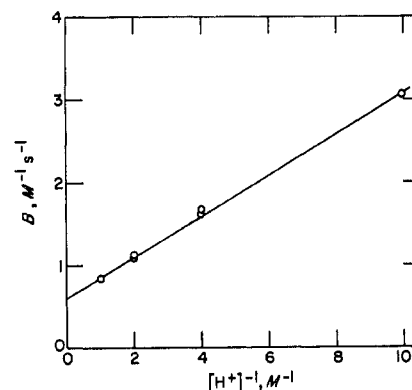


Figure 4.—Hydrogen ion dependence of rate parameter B as in eq 5.

B vs. $[\text{H}^+]^{-1}$ is linear, as shown in Figure 4, and leads to the equation

$$B = a + b [\text{H}^+]^{-1} \quad (5)$$

with $a = 0.62 \text{ M}^{-1} \text{ sec}^{-1}$ and $b = 0.25 \text{ sec}^{-1}$.

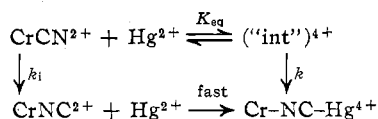
Temperature Dependences.—A limited number of kinetic runs were carried out at each of two other temperatures at 1.00 M H^+ . Plots of $(k_{app} - A)^{-1}$ vs. $[Hg^{2+}]^{-1}$ were made; as before, the choice of A is not particularly critical and it was estimated as 0.0015 and 0.0050 sec^{-1} at 16.8 and 33.3°, respectively, based on approximate temperature coefficients of the contributing rate constants. The resulting linear plots give B ($M^{-1} sec^{-1}$) = 0.38 at 16.8° and 1.87 at 33.3° and C (M^{-1}) = 29 at 16.8° and 23 at 33.3°. The derived values of k at these temperatures are, therefore, 0.013 and 0.081 $M^{-1} sec^{-1}$, respectively.

The temperature dependence of K_{eq} gives the values $\Delta H^\circ = 1.9$ kcal mol^{-1} and $\Delta S^\circ = 0.1$ cal $mol^{-1} deg^{-1}$ for reaction XI. These values can be compared with those cited for the thermodynamics of other complexes formed between two cations, which have been summarized by Newton and Baker.¹⁶ Considering the range of values of ΔH° and ΔS° represented by their survey, the present values do not appear unreasonable to attribute to this interaction.

At $[H^+] = 1.0$ the rate constant a makes the major contribution to k . Assuming the ratio b/a is approximately constant over 16–33°, activation parameters for a were computed: $\Delta H^\ddagger = 19$ kcal mol^{-1} and $\Delta S^\ddagger = -14$ cal $mol^{-1} deg^{-1}$.

Interpretation and Discussion

Reaction Mechanism.—The reaction scheme



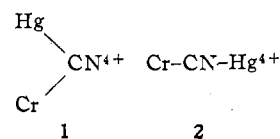
leads to a kinetic expression in accord with the experimental rate expression given in eq 1 with $C = K_{eq}$ and $B = kK_{eq}$. The major pathway for the reaction proceeds *via* the intermediate, with a relatively minor fraction going by way of prior isomerization of $CrCN^{2+}$ to $CrNC^{2+}$.

The dependence of B on $[H^+]$ given by eq 5 and its identity in the proposed mechanism lead to an expression for the rate constant for rearrangement of the intermediate to the product

$$k(sec^{-1}) = 0.026 + 0.010[H^+]^{-1} \quad (6)$$

The inverse acid dependence of one term of this rate constant is consistent with the nature of the reaction purported to be involved. The substitution reactions of $(H_2O)_6CrX^{2+}$ complexes generally show specific hydroxide ion catalysis.¹⁷ The present rearrangement reaction, where a Cr–C bond is converted to a Cr–N bond, must possess many features in common with ligand substitution. The role of the inverse acid term of eq 6 is consequently attributed to the same process by which the acceleration of ligand substitution is accounted for—a small concentration of a hydroxo form which is more reactive than the predominant aquo species owing to the nature of the OH^- group in a position trans with respect to the rearranging group.

The Reaction Intermediate.—Two likely structures of the intermediate can be considered (1 and 2). Some

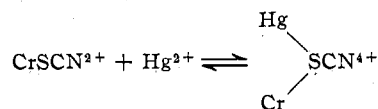


infrared measurements were attempted, but the intensities in the vicinity of the expected C–N stretching frequencies were too small for meaningful measurements even at rather high concentrations.

Structure 1, in which CN^- bridges with the same stereochemistry as the isoelectronic CO , leads to an economy of bond breaking and bond making in going to the product $Cr-NC-Hg^{4+}$. The values of k and its associated activation parameters are not unreasonable considering what is known⁷ for the interconversion of $CrNC^{2+}$ and $CrCN^{2+}$.

The second structure, on the other hand, is also a reasonable one: N donors from moderately stable complexes with Hg^{2+} and linear cyanide bridged structures are well known.¹⁸ It is not easily explained on this basis, however, why either structure should have a stability constant as high as 27 M^{-1} , considering the very weak association of $Cr-SCN^{2+}$ and Hg^{2+} for which $K_{eq} \leq 1 M^{-1}$.³

In their study of the reaction of $CrSCN^{2+}$, Orhanović and Sutin³ proposed a sulfur-bonded binuclear complex as a reaction intermediate



although they could not rule out attack at nitrogen, giving an intermediate $Cr-SCN-Hg^{4+}$. In fact, in their system the association of the two reactants is so weak, $K_{eq} \leq 1$, that no deviation from second-order kinetics was noted. The significant deviations in the present instance give a clear indication of such an intermediate as shown in reaction XI, the existence of which can be independently confirmed and whose stability constant can be determined by two independent methods from the kinetics and from the zero-time spectral studies.

A relatively stable association of Hg^{2+} with metal complexes has been noted for the reactions with *cis*- $Co(en)_2Cl_2^+$ ¹⁹ and *cis*- $Cr(H_2O)_4Cl_2^+$,²⁰ with association constants 6.5×10^2 and $(1.3 \pm 0.4) \times 10^2 M^{-1}$, respectively. In contrast to the fate of these complexes, which is necessarily dissociation, the reaction of $Cr-SCN^{2+}$ leads only to partial dissociation, and in the present case the conversion of the intermediate to $Cr-NCHg^{4+}$ appears to predominate to a considerable extent over its dissociation to $Cr^{3+} + HgCN^+$, the latter being an unimportant reaction as far as we can determine.

Related Reactions.—Table III presents the known thermodynamic and kinetic information on the monocyano complexes of Cr(III) and Hg(II) and their interactions. In part, the table serves simply to summarize these data, illustrating the reactions which are possible under different circumstances. It does appear fruitful to make certain comparisons between different reac-

(16) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **4**, 1166 (1965).

(17) J. H. Espenson, *ibid.*, **8**, 1554 (1969).

(18) D. B. Brown, D. F. Shriver, and L. H. Schwartz, *ibid.*, **7**, 77 (1968); D. F. Shriver, S. A. Shriver, and S. E. Anderson, *ibid.*, **4**, 725 (1965).

(19) C. Bifano and R. G. Linck, *ibid.*, **7**, 709 (1968).

(20) J. P. Birk, *ibid.*, **9**, 735 (1970).

TABLE III
 KINETIC AND EQUILIBRIUM PARAMETERS FOR CYANO COMPLEXES OF Cr(III) AND Hg(II)

Reaction	Temp, °C	μ , M	Q^a	k_i^b	Ref
(A) Cr-CN ²⁺ + Hg ²⁺ ⇌ Cr-NC-Hg ⁴⁺	25	1.0	≥ca. 10 ⁶	<i>b</i>	<i>c</i>
(B) Cr-CN ²⁺ + Hg ²⁺ ⇌ Cr(CN)Hg ⁴⁺ ("int")	25	2.0	26 ± 3	"Fast"	<i>d</i>
(C) Cr(CN)Hg ⁴⁺ ("int") ⇌ Cr-NC-Hg ⁴⁺	25	2.0	>ca. 4 × 10 ³	0.026 + 0.101[H ⁺] ⁻¹	<i>d</i>
(D) Cr-NC-Hg ⁴⁺ ⇌ Cr ³⁺ + HgCN ⁺	25	2.0	≥10 ³ (?)	1.4 × 10 ⁻⁴	<i>e</i>
	55	1.0		6.6 × 10 ⁻³	<i>f</i>
(E) Cr-NC ²⁺ + Hg ²⁺ ⇌ Cr-NC-Hg ⁴⁺	Room	1-2	≥ca. 2 × 10 ⁶	"Fast"	<i>g</i>
(F) Cr-NC ²⁺ ⇌ CrCN ²⁺	25	1.0	≥21	4.9 × 10 ⁻² (<i>Q</i> / <i>k</i> _{rev})	<i>h</i>
(G) Cr-NC ²⁺ + *Cr ²⁺ ⇌ Cr ²⁺ + *Cr-CN ²⁺	25	1.0	≥21	1.60	<i>h, i, j</i>
(H) Cr-CN ²⁺ + H ⁺ ⇌ Cr ³⁺ + HCN	55	1.0	>10 ⁴	9.7 × 10 ⁻⁴ + 8.0 × 10 ⁻³ [H ⁺]	<i>k</i>
	25	2.0		{1.1 × 10 ⁻⁵ + 5.9 × 10 ⁻⁴ [H ⁺]} / {1 + 0.19[H ⁺]}	<i>l</i>
(I) Cr-CN ²⁺ + *Cr ²⁺ + H ⁺ ⇌ Cr ²⁺ + *Cr ³⁺ + HCN	55	1.0	>10 ⁴	2.8 × 10 ⁻³ [H ⁺] ⁻¹	<i>f</i>
(J) Cr-NC ²⁺ + H ⁺ ⇌ CrNCH ³⁺	25	1.0	0.94	"Fast"	<i>h</i>
(K) Cr-CN ²⁺ + H ⁺ ⇌ CrCNH ³⁺	25	2.0	0.185	"Fast"	<i>l</i>
(L) Hg ²⁺ + CN ⁻ ⇌ HgCN ⁺	20	0.1	10 ¹⁸	"Fast"	<i>m</i>

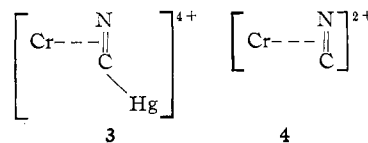
^a The designation "fast" for *k_i* indicates a process that is immeasurably fast using the stopped-flow method and may well be diffusion controlled; units of molarity and sec for *Q* and *k_i* appropriate to each. ^b No direct reaction—see eq 1. ^c Reference 6 for *Q*. ^d This work. ^e *Q* estimated from the lack of stability toward this reaction and from reactions A, H, and K; *k_i* from this work. ^f Reference 6. ^g Combining data for reactions A and F. ^h Reference 7. ⁱ Reference 9. ^j *k*_{rev} = 0.077 M⁻¹ sec⁻¹. ^k Reference 6. At low [H⁺] an additional term, 5.8 × 10⁻⁷[H⁺]⁻¹, is also important. ^l D. K. Wakefield and W. B. Schaap, *Inorg. Chem.*, **8**, 512 (1969). ^m G. Anderegg, *Helv. Chim. Acta*, **40**, 1022 (1957).

tions, however. First of all, what is the effect of Cr(III) coordination on the affinity of -CN for Hg(II)? A comparison of reactions E and L indicates that the stability is reduced by a factor of <5 × 10¹¹ on coordination of Cr³⁺ to -NC⁻. (Actually, although we can cite only a lower limit for the stability constant of reaction F, and therefore also of E, mechanistic arguments have been advanced that the lower limit of 21 for *Q_E* in fact represents its value.^{7,9}) The basis for this very large thermodynamic difference between reactions E and L, which amounts to stating that Δ*G*^o for the association of Hg²⁺ + CN⁻ is more negative than that for Hg²⁺ + CrCNC²⁺ by ca. 16 kcal mol⁻¹, is apparently to be found in the σ bond between -NC⁻ and Cr(III) formed in reaction L. The consequent flow of σ-electron density toward the tripositive Cr(III) center greatly reduces the σ-donating strength of -CN⁻ toward Hg(II). These arguments suggest that the stability of the latter interaction is, not unexpectedly, largely the consequence of the σ-bonding strength of cyanide ion and not of its π acidity. Related to this question of the effect of Cr(III) coordination on the basicity of cyanide ion, we can also compare reaction J with the corresponding reaction for free CN⁻: CN⁻ + H⁺ ⇌ HCN with *Q* ≈ 10¹⁰. The equilibrium quotients here differ by ca. 10¹⁰, which indicates that remote Cr(III) coordination affects the basicity of -CN⁻ toward both hard and soft acids to approximately the same extent. One further observation on this point appears useful: reaction E can be compared with the corresponding reaction⁴ for Cr-NCS²⁺ (eq 1), for which *Q* is 1.7 × 10⁴ M⁻¹. The formation constant for the cyanide-bridged adduct exceeds that for the thiocyanate by ≥10², whereas the relative constants for free CN⁻ and SCN⁻ differ by ~10⁹ in favor of cyanide (reaction L and ref 21). However, the actual value of *Q* for reaction E may be a great deal larger than the lower limit cited in Table III.

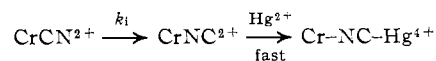
The enormous rate difference between reactions A (proceeding mechanistically *via* reactions B + C), on the one hand, and E on the other, despite comparable stability constants, reflects the structural change of cyanide linkage isomerization necessary for the former

but not the latter. Reaction E represents apparently a process no more complicated than substitution at Hg(II), a conclusion which is supported by the very high rate at which it occurs, as expected for a d¹⁰ metal ion.

The main mechanistic feature of the present reaction is the intramolecular rearrangement of the labile association complex Cr(CN)Hg⁴⁺ to the stable product, reaction C. Whatever the structure of that intermediate, its transformation to Cr-NC-Hg⁴⁺ undoubtedly is likely controlled by many of the same factors which govern the interconversion of CrCN²⁺ and CrNC²⁺ as in reaction F. The comparable rate constants for C and F are to be noted. These reactions perhaps involve transition states with a π-bonded structure, such as 3 and 4 for the respective reactions.



Finally, the question must be raised as to why the main reaction does not proceed largely by the sequence



In fact, this succession of steps *is* a minor pathway and was included as a part of the rate term represented by parameter *A*. That it is not, however, the major reaction pathway must be considered in the light of both the structure of the detected reaction intermediate, 1 or 2, and the transition state, 3, for conversion of the metastable intermediate to the product. Assume that the spontaneous isomerization process has as its mechanism the rate-determining conversion of Cr-CN²⁺ to the transition state 4. The reaction is rather slow with *k_i* = 2.3 × 10⁻³ sec⁻¹, as the energy of the π-bonded structure is likely to be considerably above that of Cr-CN²⁺. What assistance can Hg²⁺ offer? Relative to either of the likely structures which have been suggested, 1 and 2, the transition state 3 may well appear less high in energy because it has gained the

formation of a sterically uncrowded Hg-C σ bond. Naturally, the π configuration is less favored than that in the product Cr-NC-Hg⁴⁺, so that further rearrangement of **3** should be facile. It should, of course, be noted that the mechanisms invoked for all the processes considered here necessarily proceed *without* the complete cleavage of a chromium-cyanide bond, because under the acidic conditions considered re-formation of a

bond to chromium is prohibited thermodynamically. Of course, one cannot rule out the intervention of intermediates such as a solvent-separated ion pair in preference to the π -bonded possibilities.

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Fermi Contact and Dipolar Nuclear Magnetic Resonance Shifts in Paramagnetic Ion-Paired Systems. Studies on Some Anionic Lanthanide Complexes

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The observation of ¹⁴N contact shifts in ion-paired systems requires that the nature of the geometrical models used to describe the ion-pairing process be reevaluated. The relative contribution of both Fermi contact and dipolar shifts to the total isotropic shift is discussed for a new series of anionic lanthanide complexes and for the previously studied tetrahalometalate(II) complexes.

The chemical shifts which result from delocalization of very small fractions of an unpaired electron from a paramagnetic metal ion onto a ligand or from through-space dipolar coupling between electron and nucleus have begun to shed light on the nature of relatively weak interactions in solution.¹⁻⁶ In particular nmr studies of solutions containing ion pairs having one paramagnetic ion, usually the anion, have given rise to information on ion-pair geometries in solution.

The total isotropic resonance shift in the nmr due to the presence of unpaired electrons can be expressed as the sum of two parts, the Fermi contact shift, $\Delta\nu_f$, and the dipolar shift, $\Delta\nu_{dip}$, thus¹

$$(\Delta\nu)_i = (\Delta\nu_f)_i + (\Delta\nu_{dip})_i \quad (1)$$

where

$$(\Delta\nu_f)_i = \frac{A_i \chi_M}{Ng_N \beta_N} \quad (2)$$

and

$$(\Delta\nu_{dip})_i = \frac{|\beta|^2 \nu S(S+1)}{45kT} F(g) \left[\frac{3 \cos^2 \chi_i - 1}{R_i^3} \right] \quad (3)$$

Here, A_i is the electron-nuclear hyperfine coupling constant, χ_M is the paramagnetic susceptibility of the complex, and $F(g)$ is a function of $g_{||}$ and g_{\perp} , the parallel and perpendicular components of the g tensor of the paramagnetic complex. The exact form of $F(g)$ depends critically on the relative magnitudes of the electron Zeeman anisotropy energy, the electronic relaxation time, and the molecular tumbling correlation time.¹

The term at the far right of eq 3 is the so-called "geometric factor" (GF) and contains the structural information we desire. χ_i is the angle made by the i th proton with the principal magnetic axis of the complex (the axis of $g_{||}$). R_i is the distance between proton and electron, the latter assumed to be located on the center of the metal complex. The other symbols have their usual meanings.² In the absence of a specific knowledge of the g tensors for a paramagnetic complex or of the relaxation times involved, geometrical information is usually obtained by noting that, for two distinguishable protons

$$(\Delta\nu_i)_{dip}/(\Delta\nu_j)_{dip} = (GF)_i/(GF)_j \quad (4)$$

The principal interest to most of the workers in this area has been in the behavior of the symmetrical tetra- n -alkylammonium cations in solution. Larsen and Wahl⁴ studied D₂O solutions of $[(CH_3)_4N]_3Fe(CN)_6$ and of $K_3Fe(CN)_6$ containing R_4NBr ($R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9$). The interionic distance, which can be defined as the distance between the metal and the central nitrogen atom of the cation, A , was estimated at 8–9 Å; further studies on the system $R_4N^+Cr(CN)_6^{3-}$ using line broadening techniques⁶ estimated A as 11 Å. The interionic distances so derived are found to be independent of the alkyl chain length.

Studies on the system $(C_4H_9)_4N^+(C_6H_5)_3PCoI_3^-$ by La Mar^{1,2} yielded A values of 3.8 Å in chloroform, while similar results were obtained in the system $(C_4H_9)_4NCo(acac)_3$ studied by Horrocks, *et al.*,³ in chloroform and carbon tetrachloride.

These ion-pairing distances were estimated on the reasonable assumption that the tetraalkylammonium cation contains no orbitals through which covalent bonding between anion and cation can take place. Since the Fermi contact shift requires some form of covalency between metal and ligand, the earlier workers

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