**Table V.** Kinetic Parameters for Water Exchange on Some Nickel(II) Complexes

| Complex | $k$, sec$^{-1}$ (25°) | $\Delta H^*$, kcal mol$^{-1}$ | $\Delta S^*$, eu | Ref |
|---|---|---|---|---|
| $Ni(OH_2)_6^{2+}$ | $3.2 \times 10^4$ | 12.1 | 2.6 | 7 |
| $Ni(NH_3)_3(OH_2)_3^{2+}$ | $2.5 \times 10^6$ | 10.2 | 5.0 | 4 |
| $Ni(terpy)(OH_2)_3^{2+}$ | $5.2 \times 10^4$ | 10.7 | −1.0 | 6 |
| $Ni(TRI)(OH_2)_3^{2+}$ | $3.8 \times 10^4$ | 10.9 | −1.9 | This work[a] |
| $Ni(en)(OH_2)_4^{2+}$ | $4.4 \times 10^5$ | 10.0 | 10 | 3 |
| $Ni(en)_2(OH_2)_2^{2+}$ | $5.4 \times 10^6$ | 9.1 | 2.6 | 3 |
| $Ni(dipy)(OH_2)_4^{2+}$ | $4.9 \times 10^4$ | 12.6 | 5.1 | 7 |
| $Ni(dipy)_2(OH_2)_2^{2+}$ | $6.6 \times 10^4$ | 13.7 | 9.2 | 7 |

[a] The average of the 60- and 100-MHz parameters from fit C, Table IV.

and obtained values of $\Delta H^*$ which were too low by 3–3.5 kcal mol$^{-1}$ and $\Delta S^*$ too negative by ~14 eu.[20,21]

The original purpose of this study was to determine the effect of a fused-ring tridendate chelate ligand on the water exchange rate. A comparison of results from this and previous work in Table V indicates that $Ni(TRI)(OH_2)_3^{2+}$ is not unusual. The $\Delta H^*$ value is certainly not unexpectedly large; therefore, it would seem that no large change in geometry occurs in the transition state for water exchange. This would be consistent with a square-based pyramidal transition state if an SN1 mechanism is assumed.

It may be noted that the variations in $\Delta H^*$ and $\Delta S^*$ in Table V do not appear to follow any obvious trends. The faster exchange of $Ni(NH_3)_3(OH_2)_3^{2+}$ and $Ni(en)(OH_2)_4^{2+}$ compared to $Ni(terpy)(OH_2)_3^{2+}$ and $Ni(TRI)(OH_2)_3^{2+}$ is largely due to a more favorable $\Delta S^*$. Therefore, simple electron withdrawal by conjugated amines, making Ni–$OH_2$ bond breaking more difficult, does not account for the rate differences. The large difference in $\Delta H^*$ for $Ni(terpy)(OH_2)_3^{2+}$ and $Ni(dipy)_2(OH_2)_2^{2+}$ is also noteworthy since these complexes might be expected to be the most similar of all those in Table V.

The results of the study have shown that steric rigidity of the chelating ligand is not a very important kinetic factor for the water exchange rates on nickel(II). However, the factors which do affect these rates remain largely unexplained.

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(21) N. A. Matwiyoff, private communication.

# Interaction between Isothiocyanatopentaaquochromium(III) and Mercury(II). Equilibrium and Kinetics[1a,b]

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**Abstract:** The isothiocyanatopentaaquochromium(III) ion reacts with mercury(II) in aqueous solution to form the binuclear complex $CrNCSHg^{4+}$. From the absorption spectrum of the complex (maxima at 565 and 398 nm with extinction coefficients 21 and 25, respectively) it is deduced that the ligand $HgSCN^+$ lies between $NCS^-$ and $NH_3$ in the spectrochemical series. The equilibrium quotient for the reaction $CrNCS^{2+} + Hg^{2+} \rightleftharpoons CrNCSHg^{4+}$ is $1.66 \times 10^4$ $M^{-1}$ at 25° and $[ClO_4^-] = 1.0$ $M$. The associated thermodynamic parameters are $\Delta H = -8.0$ kcal/mol and $\Delta S = -7.3$ eu. The relatively high formation quotient is rationalized on the basis of a stable ambidentate arrangement in which the hard and soft ends of thiocyanate are bound to hard and soft acids, respectively. The binuclear ion $CrNCSHg^{4+}$ undergoes aquation to $Cr^{3+}$ and $HgSCN^+$ by a first-order process independent of acidity. The rate constant at 25° and $[ClO_4^-] = 1.0$ $M$ is $8.5 \times 10^{-5}$ sec$^{-1}$ with $\Delta H^{\neq} = 20.4$ kcal/mol and $\Delta S^{\neq} = -8.5$ eu. Rate comparisons with related spontaneous and mercury(II)-assisted aquations of complexes of the class $CrX^{2+}$ are made. It is suggested that the aquation of $CrNCSHg^{4+}$ proceeds by a dissociative mechanism.

The mercury(II)-induced aquations of halide and pseudohalide complexes of cobalt(III)[2] and chromium(III)[3–7] have been studied extensively. The accepted mechanism for these assisted aquations is (M = Co, Cr; X = Cl, Br, I, CN)

$$MX^{n+} + Hg^{2+} \rightleftharpoons MXHg^{(n+2)+} \qquad (1)$$

rapid equilibrium, $K$

$$MXHg^{(n+2)} + H_2O \longrightarrow MOH_2^{(n+1)+} + HgX^+ \qquad (2)$$

rate determining, $k$

On the basis of eq 1 and 2, the pseudo-first-order rate coefficient $k_p$ for the disappearance of $MX^{n+}$ [free or complexed with mercury(II)] in the presence of an excess

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(1) (a) This work was supported in part by the National Science Foundation under Grant No. GP-9669; (b) abstracted in part from the B.S. thesis of J. N. Armor, The Pennsylvania State University, June 1966.

(2) C. Bifano and R. G. Linck, *Inorg. Chem.*, 7, 908 (1968), and references therein.

(3) J. H. Espenson and J. P. Birk, *ibid.*, **4**, 527 (1965).

(4) J. H. Espenson and S. R. Hubbard, *ibid.*, **5**, 686 (1966).

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

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

(7) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, **92**, 1215 (1970).

of mercury(II) is

$$k_p = \frac{kK[\mathrm{Hg^{2+}}]}{1 + K[\mathrm{Hg^{2+}}]} \qquad (3)$$

In many instances, a first-order dependence on $[\mathrm{Hg^{2+}}]$ is observed, and, consequently, $K[\mathrm{Hg^{2+}}] \ll 1$. Under these circumstances, $k_p/[\mathrm{Hg^{2+}}]$, the measured second-order coefficient, equals $kK$, and separate values of $k$ and $K$ cannot be obtained.[2-4,6] In other instances, the binuclear complex is sufficiently stable for direct detection, and individual values of $k$ and $K$ have been obtained.[2,6]

The present investigation was started in an attempt to discriminate between the equilibrium and kinetic aspects of the mercury(II) assisted aquation of $\mathrm{CrNCS^{2+}}$. Previous work[8] indicated that the interaction between $\mathrm{CrNCS^{2+}}$ and $\mathrm{Hg^{2+}}$ produces rapidly the binuclear complex $\mathrm{CrNCSHg^{4+}}$

$$\mathrm{CrNCS^{2+} + Hg^{2+} \rightleftarrows CrNCSHg^{4+}} \qquad (4)$$

$$\text{rapid equilibrium, } Q$$

In the present work we have measured the equilibrium quotient $Q$ for reaction 4 as well as the rate constant $k_1$ for reaction 5, thereby resolving the $\mathrm{CrNCS^{2+}}$–$\mathrm{Hg^{2+}}$

$$\mathrm{CrNCSHg^{4+} \longrightarrow Cr^{3+} + HgSCN^{+}} \qquad \text{slow, } k_1 \qquad (5)$$

interaction into its equilibrium and kinetic components.

## Experimental Section

**Materials.** Stock solutions of $\mathrm{CrNCS^{2+}}$ in *ca.* 1 $M$ perchloric acid were prepared by the method of King and Dismukes.[9] Chromium and thiocyanate analyses were performed as described previously.[8] The ratio of thiocyanate to chromium was 0.99. Absorption maxima were observed at 570, 410, and 292 nm with extinction coefficients of 31.9, 33.8, and $2.95 \times 10^3$, respectively, in good agreement with previously recorded values.[8,9]

Stock solutions of mercury(II) perchlorate in *ca.* 1 $M$ perchloric acid were prepared by dissolving reagent grade mercury(II) oxide in the appropriate amount of perchloric acid. A small insoluble residue was separated by filtration. The mercury(II) concentration was determined by titration with thiocyanate.[10] The measured concentration differed from that calculated on the basis of the mercury(II) oxide used by less than 1%.

Stock solutions of sodium perchlorate were prepared by neutralization of sodium carbonate with perchloric acid.

**Equilibrium Measurements.** The equilibrium quotient $Q$ for reaction 4 was determined by a spectrophotometric method. The absorbances of solutions containing the desired concentrations of $\mathrm{CrNCS^{2+}}$, mercury(II), perchloric acid, and sodium perchlorate were measured at 292 or 275 nm using a Cary 15 or 14 recording spectrophotometer equipped with a thermostated cell compartment. Because of the low concentrations of $\mathrm{CrNCS^{2+}}$ and mercury(II) used (*cf.* Table I), it was possible to maintain both the ionic strength and the total perchlorate ion concentration at 1.0 $M$. As indicated in Table I, a total of ten sets of measurements was carried out. In each set the concentration of $\mathrm{CrNCS^{2+}}$ was maintained constant at the value indicated in the first column of Table I, and the mercury(II) concentration was varied within the limits shown in the second column of Table I. The third column gives the range of absorbances covered in the measurements. The fourth column gives the number of solutions (of varying mercury(II) concentration within the range stated) which were measured for each set. As indicated below, in treating the spectrophotometric data to derive the equilibrium quotient $Q$, it is necessary to know, for each set of measurements, two additional absorbance values. These are the absorbance of a solution of the specified $\mathrm{CrNCS^{2+}}$ concentration in the absence of mercury(II) and the absorbance of a solution at the same $\mathrm{CrNCS^{2+}}$ concentration, but containing a sufficiently high mercury(II) concentration to ensure that the formation of the binuclear complex $\mathrm{CrNCSHg^{4+}}$ is essentially complete. Although these absorbance values could be calculated from the known extinction coefficients of $\mathrm{CrNCS^{2+}}$ and $\mathrm{CrNCSHg^{4+}}$ and the concentration of $\mathrm{CrNCS^{2+}}$ in each set, these values were determined directly in connection with each set of measurements. Blank measurements, *e.g.*, the absorbance of solutions containing all the components except the $\mathrm{CrNCS^{2+}}$, were carried out for each individual absorbance measurement of Table I.

**Table I.** Summary of Experimental Conditions Used to Determine the Equilibrium Quotient for Reaction 4[a]

| $[\mathrm{CrNCS^{2+}}]$, $M \times 10^4$ | $[\mathrm{Hg^{2+}}]$, $M \times 10^4$ | $A$[b] | No. of data points |
|---|---|---|---|
| 0.440 | 0.144–2.05 | 1.125–0.390 | 7 |
| 0.880 | 0.240–6.03 | 1.090–0.208 | 9 |
| 2.19 | 0.290–10.3 | 1.155–0.163 | 11 |
| 2.63 | 0.280–16.1 | 1.395–0.155 | 13 |
| 0.782[c] | 0.117–8.76 | 1.035–0.315 | 8 |
| 0.977[d] | 0.584–8.76 | 0.974–0.172 | 6 |
| 1.27[e] | 0.292–8.76 | 1.564–0.217 | 7 |
| 0.219[f] | 0.080–4.02 | 0.557–0.099 | 11 |
| 0.877[f] | 0.160–12.1 | 1.131–0.126 | 12 |
| 2.19[f] | 0.280–12.1 | 1.132–0.120 | 11 |

[a] At 25°, $[\mathrm{HClO_4}] = 1.0\ M$, and 292 nm, except where indicated. [b] Range of measured absorbances, corrected for blank absorbance. [c] At 275 nm. [d] At $[\mathrm{HClO_4}] = 0.20\ M$ and $[\mathrm{NaClO_4}] = 0.80\ M$. [e] In the presence of added $1.0 \times 10^{-5}\ M$ sodium chloride. [f] At 15°.

**Kinetic Measurements.** The rate of reaction 5 was determined by a spectrophotometric method. Solutions containing the desired concentrations of $\mathrm{CrNCS^{2+}}$, mercury(II), perchloric acid, and sodium perchlorate were kept in a constant temperature bath at 25 or 35°. At appropriate times, aliquots of the solutions were withdrawn and treated as described below, and their absorbances were recorded at the desired wavelength. Early, exploratory studies were carried out at 270 nm because at this wavelength a relatively large absorbance change (from $\mathrm{CrNCSHg^{4+}}$ to $\mathrm{HgSCN^{+}}$) occurs upon reaction. However, it was found that the absorbance at long times increased after reaction 5 was substantially complete.[11] Blank experiments with $\mathrm{HgSCN^{+}}$ (in the absence of chromium) indicated that the changes in absorbance at long times were associated with some unspecified reaction of $\mathrm{HgSCN^{+}}$. The absorbance changes at long times, although appreciable at 270 nm,[11] become very small at 292 nm and essentially negligible at 305 nm. However, at these wavelengths the differences in molar absorbancy indices between $\mathrm{CrNCSHg^{4+}}$ and $\mathrm{HgSCN^{+}}$ are extremely small, and changes in absorbance upon reaction become negligible. Therefore, the following procedure was adopted. Aliquots of the reaction mixture were added to an excess of 1 $M$ hydrochloric acid. This treatment quenches the reaction by transforming the reactive species $\mathrm{CrNCSHg^{4+}}$ into $\mathrm{CrNCS^{2+}}$ and chloromercury(II) species. Following this treatment, the absorbance of $\mathrm{CrNCS^{2+}}$ at 305 nm was measured. In this manner, large changes in absorbance were observed, since the molar absorbancy indices at 305 nm of $\mathrm{CrNCS^{2+}}$ and $\mathrm{Cr^{3+}}$ are $2.2 \times 10^3$ and *ca.* 2, respectively. The first-order rate constants $k_1$ were obtained from the linear plots of $\log (A_t - A_\infty)$ *vs.* time, where $A_t$ and $A_\infty$ are the absorbances of the solution at time $t$ and after seven to ten half-lives.

## Results

**The Absorption Spectrum of $\mathrm{CrNCSHg^{4+}}$.** The visible and ultraviolet spectrum of $\mathrm{CrNCS^{2+}}$ is profoundly altered by addition of mercury(II) ion. The maxima at 570 and 410 nm decrease in intensity and are shifted toward shorter wavelengths, whereas the maximum at 292 nm disappears completely. At sufficiently high mercury(II) concentration, the formation of $\mathrm{CrNCSHg^{4+}}$ is complete (see the equilibrium measurements below) and,

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

(9) E. L. King and E. B. Dismukes, *ibid.*, 74, 1674 (1952).

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, Macmillan, New York, N. Y., 1952, p 547.

(11) For example, the absorbances at 270 nm of a solution (25°) with $[\mathrm{CrNCS^{2+}}] = 1.75 \times 10^{-4}\ M$, $[\mathrm{Hg^{2+}}] = 1.28 \times 10^{-2}\ M$, and $[\mathrm{HClO_4}] = 1.0\ M$ were 0.918, 0.725, 0.513, 0.480, and 0.498 at times 0, 1.9, 8, 18, and 25 hr, respectively.

therefore, the spectrum of $CrNCSHg^{4+}$ can be recorded readily. Solutions containing $4.37 \times 10^{-3}$ *M* $CrNCS^{2+}$, 0.25 *M* mercury(II) perchlorate, and 1.0 *M* perchloric acid or $9.77 \times 10^{-4}$ *M* $CrNCS^{2+}$, 0.029 *M* mercury(II) perchlorate, and 1.0 *M* perchloric acid display identical spectra with maxima at 565 and 398 nm and extinction coefficients of 21 and 25, respectively.

**The Equilibrium Quotient for Reaction 4.** The following symbols are used in the treatment of the spectrophotometric data: $A_m$ = absorbance of $CrNCS^{2+}$–$Hg^{4+}$ mixtures, corrected for the absorbance of the blank; $A_1$, $A_2$ = absorbances of $CrNCS^{2+}$ and $CrNCSHg^{4+}$, respectively, at the same chromium(III) concentration as measurements of $A_m$; $\epsilon_1$, $\epsilon_2$ = extinction coefficients of $CrNCS^{2+}$ and $CrNCSHg^{4+}$, respectively; $l$ = path length of spectrophotometric cell in measurements of $A_m$, $A_1$, and $A_2$; $[Hg^{2+}]_t$ = total mercury(II) concentration; and $Q$ = equilibrium quotient for reaction 4.

As indicated above, values of $A_m$ were obtained as a function of $[Hg^{2+}]_t$ at a given concentration of $CrNCS^{2+}$ and under fixed conditions of acidity, ionic strength, and temperature. The absorbance measurements were treated on the basis of the equation

$$\frac{l[Hg^{2+}]_t}{A_1 - A_m} = \frac{l}{(A_m - A_2)Q} + \frac{1}{\epsilon_1 - \epsilon_2} \qquad (6)$$

Equation 6 can be derived readily by using the equilibrium represented by eq 4, stoichiometric considerations, and Beer's law. It must be noted that, in contrast with various equations available in the literature[12] to relate spectrophotometric data to equilibrium quotients, no assumptions other than adherence to Beer's law and the formation of a 1:1 complex are made in the derivation, and consequently eq 6 is an exact relation.

The results of the spectrophotometric measurements designed to obtain the equilibrium quotient $Q$ for reaction 4 at 25° are presented in Figure 1 in the form of plots of $l[Hg^{2+}]_t/(A_m)$ *vs.* $l/(A_m - A_2)$. Line a of Figure 1 shows the results obtained at 1.00 *M* perchloric acid and 292 nm. It is seen that in the range of $[CrNCS^{2+}]$ from 0.440 to $2.63 \times 10^{-4}$ *M* and $[Hg^{2+}]_t$ from 0.144 to $16.1 \times 10^{-4}$ *M*, the results conform reasonably well to the linear relation.[13] The inverse of the slope of line a yields the value $Q = 1.64 \times 10^4\ M^{-1}$. It must be noted, however, that the line intercepts the ordinate at a value ($3.0 \times 10^{-4}$) slightly smaller than the calculated value ($3.5 \times 10^{-4}$) of $1/(\epsilon_1 - \epsilon_2)$. Although it could be argued that the intercept, being rather small, is poorly defined, we believe that the discrepancy is outside experimental error. We have no satisfactory explanation for the discrepancy. However, it was found that addition of $1.0 \times 10^{-5}$ *M* chloride ion results in an even smaller value ($2.6 \times 10^{-4}$) of the intercept (see line b of Figure 1) without affecting the slope ($Q = 1.69 \times 10^4\ M^{-1}$), and it is conceivable that traces of chloride ion, present in our solutions, are responsible for the discrepancy between experimental and calculated intercept. Line c in Figure 1 presents the results obtained at 0.20 *M* perchloric acid, 0.80 *M* sodium perchlorate, and 292 nm, and yields a value of $1.62 \times 10^4\ M^{-1}$. Line d in Figure 1 gives $1.71 \times 10^4\ M^{-1}$ at 1.0 *M* perchloric acid and 275 nm. The agreement between the various sets is good and we conclude that, within the concentration ranges covered in Table I, the $CrNCS^{2+}$–$Hg^{2+}$ system is adequately described by eq 4, with $Q = 1.66 \times 10^4\ M^{-1}$ at 25° and ionic strength 1.0. Combining this value with the value $2.65 \times 10^4\ M^{-1}$ obtained from the measurements at 15°, we calculate the following thermodynamic quantities for reaction 4: $\Delta H = -8.0 \pm 0.3$ kcal/mol, $\Delta S = -7.3 \pm 1$ eu.

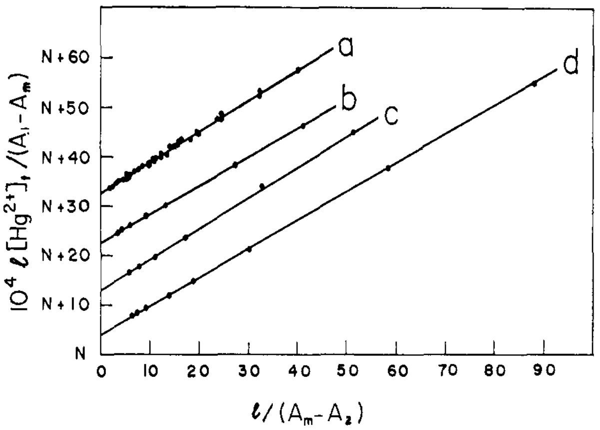

Figure 1. Plots of spectrophotometric data for reaction 4 treated according to eq 6: (a) measurements at 292 nm, $[HClO_4]$ = 1.0 *M*, $N = -30$; (b) measurements at 292 nm, $[HClO_4]$ = 1.0 *M*, $1.0 \times 10^{-5}$ *M* sodium chloride added, $N = -20$; (c) measurements at 292 nm, $[HClO_4]$ = 0.20 *M*, $[NaClO_4]$ = 0.80 *M*, $N = -10$; (d) measurements at 275 nm, $[HClO_4]$ = 1.0 *M*, $N = 0$.

**The Kinetics of Reaction 5.** The kinetic measurements summarized in Table II were carried out at a mercury(II) concentration sufficiently high to ensure essentially complete formation of $CrNCSHg^{4+}$. Under

**Table II.** Kinetics of Aquation of $CrNCSHg^{4+\ a}$

| $[Hg^{2+}]$, $M \times 10^2$ | $[HClO_4]$, *M* | $k_1 \times 10^5$, sec$^{-1}$ |
|---|---|---|
| 0.64 | 1.00 | $8.7^{b,c}$ |
| 0.64 | 1.00 | $8.4^{d}$ |
| 1.21 | 1.00 | $8.4^{e}$ |
| 1.29 | 1.00 | $8.4^{b,c}$ |
| 2.57 | 1.00 | $8.8^{b,c}$ |
| 1.21 | 0.78 | $8.6^{e}$ |
| 0.64 | 0.74 | $8.4^{d}$ |
| 1.21 | 0.70 | $8.5^{e}$ |
| 1.37 | 0.50 | $8.5^{d}$ |
| 0.64 | 0.42 | $8.5^{d}$ |
| 1.21 | 0.38 | $8.6^{e}$ |
| 1.21 | 0.18 | $8.7^{e}$ |
| 0.64 | 0.14 | $8.4^{d}$ |
| | | Av $8.5 \pm 0.1$ |
| 1.20 | 0.18–1.00 | $26.5 \pm 0.9^{f}$ |
| 1.20 | 1.00 | $26.2^{g}$ |

[a] At 25°, $[ClO_4^-]$ = 1.0 *M* and 305 nm unless stated otherwise. [b] At 292 nm. [c] $[CrNCS^{2+}] = 2.98 \times 10^{-4}$ *M*. [d] $[CrNCS^{2+}] = 3.51 \times 10^{-4}$ *M*. [e] $[CrNCS^{2+}] = 2.60 \times 10^{-4}$ *M*. [f] At 35°, $[CrNCS^{2+}] = 1.46 \times 10^{-3}$ *M*, 290–300 nm. Average of five measurements. [g] At 35°, $[CrNCS^{2+}] = 3.65 \times 10^{-4}$ *M*, 305 nm. Duplicate experiments yielded identical rate constants.

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(12) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, N. Y., 1961, Chapter 13.

(13) In one set of measurements at $[CrNCS^{2+}] = 8.8 \times 10^{-3}$ *M* and $[Hg^{2+}]_t = 1.97$–$55.5 \times 10^{-4}$ *M*, the absorbance measurements deviated considerably from the predictions of eq 6. Assuming that the deviation was caused by the formation of the trinuclear species $CrNCSHgSCNCr^{6+}$, and that the extinction coefficient of the trinuclear complex is not very different from that of $CrNCSHg^{4+}$, we estimate that the equilibrium quotient for the reaction $CrNCSHg^{4+} + CrNCS^{2+} \rightleftarrows CrNCSHgSCNCr^{6+}$ is *ca.* $10^2$. This value is sufficiently small for the measurements of Figure 1 to be unaffected by the formation of the higher complex.

these conditions the disappearance of $\mathrm{CrNCSHg}^{4+}$ obeys first-order kinetics over at least three half-lives, and the first-order rate constant is independent of $[\mathrm{Hg}^{2+}]$ over the range $0.64\text{–}2.57 \times 10^{-2}$ *M* (*cf.* the first five entries of Table II). The possible dependence of rate upon hydrogen ion concentration was also tested, and it is seen that in the range of $[\mathrm{HClO_4}]$ from 0.14 to 1.00 *M*, the value of $k_1$ remains constant within experimental error. On the basis of the above results we conclude that the rate of reaction 5 is governed by the rate law

$$\frac{-\mathrm{d}[\mathrm{CrNCSHg}^{4+}]}{\mathrm{d}t} = k_1[\mathrm{CrNCSHg}^{4+}]$$

where $k_1$ is independent of mercury(II) and hydrogen ion concentrations. At 25°, $[\mathrm{ClO_4}^-] = 1.0$ *M*, $k_1 = (8.5 \pm 0.1) \times 10^{-5}\ \mathrm{sec}^{-1}$. The associated activation parameters are $\Delta H^{\ddagger} = 20.4 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = -8.5 \pm 3$ eu.

## Discussion

The results of the present investigation provide conclusive evidence for a strong association between $\mathrm{CrNCS}^{2+}$ and $\mathrm{Hg}^{2+}$ in solution to produce the bridged, binuclear complex $\mathrm{CrNCSHg}^{4+}$. This type of interaction is apparently fairly common between nitrogen-bonded thiocyanate complexes and class b[14] or soft[15] metal ions. Thus, Werner[16] reported that the orange color of $\mathrm{Co(NH_3)_5NCS}^{2+}$ solutions is changed to yellow on addition of silver(I). Shifts toward shorter wavelengths have also been reported for a variety of cobalt(III) and chromium(III) ammine–thiocyanate complexes interacting with silver(I) or mercury(II).[17–19] In agreement with these observations, addition of mercury(II) to $\mathrm{CrNCS}^{2+}$ results in a shift of the d–d bands toward shorter wavelengths. The hypsochromic effect of mercury(II) binding to the sulfur end of nitrogen-bonded thiocyanate has been ascribed to a more purely metal–nitrogen $\sigma$ bond in the binuclear complexes than in the mononuclear isothiocyanate complexes.[18,20] However, it must be noted that the hypsochromic effect of $\mathrm{Hg}^{2+}$ on $\mathrm{Co(NH_3)_5NCS}^{2+}$ is much more pronounced than on $\mathrm{CrNCS}^{2+}$. Thus, the ligand-field strength of $\mathrm{HgSC}N^+$ is identical with that of $N\mathrm{H_3}$ for $\mathrm{Co(NH_3)_5}^{3+}$ (maxima at 498, 476, and 476 nm for $\mathrm{Co(NH_3)_5NCS}^{2+}$, $\mathrm{Co(NH_3)_5NCSHg}^{4+}$, and $\mathrm{Co(NH_3)_6}^{3+}$, respectively[19]), but $\mathrm{HgSC}N^+$ lies between $N\mathrm{CS}^-$ and $N\mathrm{H_3}$ in the spectrochemical series for $\mathrm{Cr(OH_2)_5}^{3+}$ (maxima at 570, 564, and 545 nm for $\mathrm{CrNCS}^{2+}$, $\mathrm{CrNCSHg}^{4+}$, and $\mathrm{CrNH_3}^{3+}$, respectively). On the basis of the explanation offered[18] for the bathochromacy of $N\mathrm{CS}^-$ as compared to other nitrogen ligands, the difference between the cobalt and chromium systems could be ascribed to some residual thiocyanate-to-chromium $\pi$ bonding in $\mathrm{CrNCSHg}^{4+}$. However, since $\mathrm{HgC}N^+$ has a spectrochemical position almost identical with that of $\mathrm{HgSC}N^+$ (maximum for $\mathrm{CrNCHg}^{4+}$ at 565 nm[5]), and it is unlikely that ligand-to-chromium $\pi$ bonding obtains in $\mathrm{CrNCHg}^{4+}$, residual $\pi$ bonding in $\mathrm{CrNCSHg}^{4+}$ does not provide an appealing rationalization for the difference between the chromium and cobalt systems. An alternative and, perhaps, more satisfactory explanation is that binding of the sulfur by mercury(II) induces metal-to-thiocyanate $\pi$ bonding to a larger extent in the cobalt than in the chromium system, and consequently $\mathrm{HgSC}N^+$ has a higher position in the spectrochemical series for $\mathrm{Co(NH_3)_5}^{3+}$ than for $\mathrm{Cr(OH_2)_5}^{3+}$. Some support for this explanation is obtained by recognizing that metal-to-ligand $\pi$ bonding is expected to be more important in cobalt(III) (a $\mathrm{d}^6$ system) than in chromium(III) (a $\mathrm{d}^3$ system). In addition to the effect on the ligand-field bands, binding of the sulfur by mercury(II) produces the disappearance of the strong absorption band exhibited by many thiocyanate complexes in the 320–260-nm region. Thus, the 305-nm band of $\mathrm{Co(NH_3)_5NCS}^{2+}$ and the 292-nm band of $\mathrm{CrNCS}^{2+}$ are eliminated on complexation with $\mathrm{Hg}^{2+}$. Originally, these bands had been assigned to strongly perturbed ligand transitions.[21] More recently, however, it has been suggested that, for reducible metal isothiocyanates, such as $\mathrm{Co(NH_3)_5NCS}^{2+}$ and $\mathrm{CrNCS}^{2+}$, these bands are of the charge-transfer type.[22] If we accept this assignment, then binding of the sulfur by the positive mercury(II) is expected to hinder the transfer of an electron from thiocyanate to cobalt(III) or chromium(III), and consequently a shift of the charge-transfer band toward shorter wavelengths obtains.

The equilibrium and kinetic data for the binuclear complex $\mathrm{CrNCSHg}^{4+}$ can be viewed in two different manners in order to make comparisons with the corresponding mononuclear systems $\mathrm{CrNCS}^{2+}$ and $\mathrm{HgSCN}^+$. On the one hand, we can consider the effect of chromium(III) bound to the nitrogen end of thiocyanate on the interaction between mercury(II) and the sulfur end of thiocyanate. Alternately, we can focus attention on the interaction between chromium(III) and the nitrogen end of thiocyanate, and inquire about the effect that mercury(II) binding on the sulfur end has on that interaction. More specifically, a comparison between the equilibrium quotients for reactions 1 and 7 of Table III is a measure of the effect of chromium(III) on the mercury(II)–thiocyanate interaction, and a comparison between the equilibrium quotients for reactions 2 and 5 of Table III provides the corresponding effect of mercury(II) on the chromium(III)–thiocyanate interaction. In order to make these comparisons in quantitative terms, it is necessary to have a value of $Q_{7,1}$, the formation quotient of $\mathrm{HgSCN}^+$. Unfortunately, this value has not been measured. However, an estimate can be made by recognizing that the value of $Q_{7,1}Q_{7,2}$ is $3 \times 10^{17}$ ($Q_{7,2}$ is the formation quotient of $\mathrm{Hg(SCN)_2}$ from $\mathrm{HgSCN}^+$ and $\mathrm{SCN}^-$), and that the ratio of the first to the second formation quotient for halide and pseudohalide complexes of mercury(II) varies between 2 and 80.[23] If $Q_{7,1}/Q_{7,2} = 2$, $Q_{7,1} = 8 \times 10^8$, and if $Q_{7,1}/Q_{7,2} = 80$, $Q_{7,1} = 5 \times 10^9$. Consequently, we take $Q_{7,1} \sim 2 \times 10^9\ M^{-1}$, which is certainly good

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[14] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958).

[15] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[16] A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 1 (1912).

[17] W. C. Waggener, J. A. Mattern, and G. H. Cartledge, *J. Amer. Chem. Soc.*, **81**, 2958 (1959).

[18] C. E. Schaeffer, *Chem. Soc., Spec. Publ.*, **No. 13**, 153 (1959).

[19] R. Larsson, *Acta Chem. Scand.*, **16**, 931 (1962).

[20] C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 78.

[21] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Reading, Mass., 1962, p 196.

[22] J. C. Barnes and P. Day, *J. Chem. Soc.*, 3886 (1964).

[23] L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, 112, 124, 292, 326, 341 (1964).

**Table III.** Equilibrium and Kinetic Parameters for Reactions of Chromium(III) and Mercury(II)[a]

| Reaction | $Q$ | $k_f$ | $k_r$ | Ref |
|---|---|---|---|---|
| (1) $CrNCS^{2+} + Hg^{2+} \rightleftarrows CrNCSHg^{4+}$ | $1.66 \times 10^4$ | | | *b* |
| (2) $CrNCSHg^{4+} \rightleftarrows Cr^{3+} + HgSCN^+$ | $8.5 \times 10^2$ | $8.5 \times 10^{-5}$ | $10 \times 10^{-8}$ | *b* |
| (3) $CrNCS^{2+} + Hg^{2+} \rightleftarrows Cr^{3+} + HgSCN^+$ | $1.4 \times 10^7$ | 1.4 | $10 \times 10^{-8}$ | *b* |
| (4) $CrSCN^{2+} + Hg^{2+} \rightleftarrows Cr^{3+} + HgSCN^+$ | $4.1 \times 10^{12}$ | $3.1 \times 10^2$ | $0.0076 \times 10^{-8}$ | *c* |
| (5) $CrNCS^{2+} \rightleftarrows Cr^{3+} + SCN^-$ | $7.1 \times 10^{-3}$ [d] | $9.1 \times 10^{-9}$ [d] | $73 \times 10^{-8}$ | *e, f* |
| (6) $CrSCN^{2+} \rightleftarrows Cr^{3+} + SCN^-$ | $2 \times 10^3$ | $1.7 \times 10^{-5}$ | $0.8 \times 10^{-8}$ | *c* |
| (7) $Hg^{2+} + SCN^- \rightleftarrows HgSCN^+$ | $\sim 2 \times 10^9$ | | | *g* |
| (8) $CrCl^{2+} + Hg^{2+} \rightleftarrows Cr^{3+} + HgCl^+$ | $3.8 \times 10^7$ | $4.8 \times 10^{-2}$ | $0.13 \times 10^{-8}$ | *h* |
| (9) $CrCl^{2+} \rightleftarrows Cr^{3+} + Cl^-$ | 9.1 | $2.75 \times 10^{-7}$ | $3.0 \times 10^{-8}$ | *i, j* |
| (10) $[CrNCS^{2+}]^{\ddagger} + Hg^{2+} \rightleftarrows [CrNCSHg^{4+}]^{\ddagger}$ | $1.5 \times 10^8$ [k] | | | *l* |

[a] At 25° and ionic strength 1.0 *M*, unless specified otherwise. Units of $Q$, $k_f$, and $k_r$ are of appropriate dimensions in molarities and seconds. Values of $k_r$ calculated from $Q = k_f/k_r$. [b] This work. [c] M. Orhanovic and N. Sutin, *J. Amer. Chem. Soc.*, **90,** 4286 (1968). [d] Ionic strength 0.50 *M*. [e] $Q$ and $k_f$ from C. Postmus and E. L. King, *J. Phys. Chem.*, **59,** 1217 (1955). [f] $k_r$ from J. H. Espenson, *Inorg. Chem.*, **8,** 1554 (1969). [g] Estimated; see text. [h] Reference 3. [i] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7,** 1915 (1968). [j] T. W. Swaddle and E. L. King, *ibid.*, **4,** 532 (1965). [k] This is a formal equilibrium quotient relating transition states. [l] Calculated from the ratio of $k_f$ for reaction 3 to $k_f$ for reaction 5.

within a factor of 10, and probably good within a factor of 3. By comparing the values of $Q$ for reactions 1 and 7 of Table III, it is seen that chromium decreases the affinity of thiocyanate for mercury(II) by a factor of *ca.* $10^5$. Similarly, and this is required by the fact that $Q_1/Q_7 = Q_5/Q_2$, it is seen by comparing the values of $Q$ for reactions 2 and 5 of Table III that mercury decreases the affinity of thiocyanate for chromium(III) by a factor of *ca.* $10^5$. By breaking up the equilibrium quotient $Q$ into its kinetic components $k_f$ and $k_r$, it is seen that most of the decreased stability of $CrNCSHg^{4+}$ as compared to $CrNCS^{2+}$ (reactions 2 and 5 of Table III) is associated with an approximately $10^4$ increase in the rate of aquation. In contrast, the rates of formation of $CrNCSHg^{4+}$ and $CrNCS^{2+}$ differ only by a factor of 7. Although the kinetic data are not available for the corresponding effect of chromium on the mercury(II)-thiocyanate reaction, it is likely that the same relationship obtains. Since rates of formation of mercury(II) complexes are close to diffusion controlled,[24] the decreased stability of $CrNCSHg^{4+}$ as compared to $HgSCN^+$ (reactions 1 and 7 of Table III) can be reasonably ascribed to an increase of the order of $10^5$ in the rate of dissociation of $CrNCSHg^{4+}$ as compared to $HgSCN^+$. In this context, it is noteworthy that the catalytic effect of mercury(II) on the aquation rate of $CrNCS^{2+}$ is associated with a considerable weakening of the $Cr^{3+}–NCS^-$ bond, the activation enthalpies for aquation of $CrNCSHg^{4+}$ and $CrNCS^{2+}$ being 20.4 and 27.6 kcal/mol,[25] respectively.

Although the present system appears to be the only system of the pentaaquochromium(III) class for which the interaction with mercury(II) has been resolved into the equilibrium and kinetic components, some limited comparisons with the related $CrSCN^{2+}–Hg^{2+}$ and $CrCl^{2+}–Hg^{2+}$ reactions can be made. For these two systems, the $[Hg^{2+}]$ dependence is strictly first order, and therefore only the second-order rate coefficients have been measured. However, it has been estimated[26] that $Q < 1\ M^{-1}$ for the $CrSCN^{2+}–Hg^{2+}$ interaction, and therefore the first-order rate constant for aquation of the binuclear complex[27] $Cr(SCN)Hg^{4+}$ is larger than $3.1 \times 10^2$ $sec^{-1}$ at 25°. In the study of the mercury(II)-assisted aquation of $CrCl^{2+}$, the concentration of $Hg^{2+}$ was as high as 0.20 *M* and no deviations from second-order kinetics were reported.[3] Therefore, it is possible to estimate, assuming that a 10% deviation from a first-order dependence on $[Hg^{2+}]$ would have been detected, that $Q$ for $CrCl^{2+} + Hg^{2+} \rightleftarrows CrClHg^{4+}$ is smaller than 0.5 $M^{-1}$, and consequently that the first-order rate constant for aquation of $CrClHg^{4+}$ is larger than 0.1 $sec^{-1}$ at 25°. It is seen, by comparing the pertinent first-order rate constants, that $Cr(SCN)Hg^{4+}$ and $CrClHg^{4+}$ aquate considerably faster than $CrNCSHg^{4+}$. The $CrNCSHg^{4+}–CrClHg^{4+}$ comparison emphasizes the importance of separating the $CrX^{2+}–Hg^{2+}$ interactions into their equilibrium and kinetic components. The second-order rate coefficients at 25° for the $CrCl^{2+}–Hg^{2+}$ and $CrNCS^{2+}–Hg^{2+}$ reactions are $4.8 \times 10^{-2}$ and 1.4 $M^{-1}$ $sec^{-1}$, respectively ($k_f$ for reactions 3 and 8 in Table III). On this basis, the reactivity order is NCS > $Cl^-$ and, in agreement with previous conclusions,[3] there is a correlation between second-order rate coefficients and the stability of the mercury bond being formed.[28] However, when the equilibrium component of these composite second-order rate coefficients is corrected for by allowing for the formation of the binuclear complexes, the true reactivity order becomes $Cl^- > NCS^-$, and, not unexpectedly, this order does not correlate any longer with the stability of the mercury bond formed.[29]

The increase in rate of aquation of $CrNCSHg^{4+}$ as compared to $CrNCS^{2+}$ is *ca.* $10^4$. The corresponding factors for the mercury effect on $CrCl^{2+}$ and $CrSCN^{2+}$ are $>5 \times 10^5$ and $>2 \times 10^7$, respectively. The higher factors for $CrCl^{2+}$ and $CrSCN^{2+}$ as compared to $CrNCS^{2+}$ can be rationalized satisfactorily by considering the detailed structures of the relevant binuclear complexes. For $CrNCS^{2+}$, attack by mercury(II) is undoubtedly at the remote end of the ligand, and an important increase in aquation rate obtains. For $CrCl^{2+}$, attack by mercury(II) is of necessity adjacent, and a bigger increase in aquation rate is observed in this sys-

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(24) M. Eigen and E. M. Eyring, *Inorg. Chem.*, **2,** 636 (1963).

(25) C. Postmus and E. L. King, *J. Phys. Chem.*, **59,** 1217 (1955).

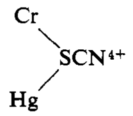
(26) M. Orhanovic and N. Sutin, *J. Amer. Chem. Soc.*, **90,** 4286 (1968).

(27) The formulation $Cr(SCN)Hg^{4+}$ is intended to indicate that there is a Cr–S bond, but the nature of the bond to mercury is left unspecified. This point is discussed later.

(28) But there is no correlation between overall free energy change and reaction rate. Compare the values of $Q$ and $k_f$ for reactions 3 and 8 of Table III.

(29) There is now a correlation between the first-order rate constants and the equilibrium constants for aquation of $CrClHg^{4+}$ and $CrNCSHg^{4+}$. The values of $Q$ and $k_f$ for $CrClHg^{4+} \rightleftarrows Cr^{3+} + HgCl^{2+}$ and for $CrNCSHg^{4+} \rightleftarrows Cr^{3+} + HgSCN^+$ are $>7.6 \times 10^7$, $>0.1$ and $8.5 \times 10^2$, $>0.1$ and $8.5 \times 10^2$, $8.5 \times 10^{-5}$, respectively.

tem. For CrSCN$^{2+}$, two alternative structures can be considered,[26] CrSCNHg$^{4+}$ and



depending on whether remote or adjacent attack obtains. On the basis of the small binding constant for mercury(II), and the very large increase in reactivity, the mechanism involving adjacent attack on CrSCN$^{2+}$ is preferred.

The aquation of CrNCSHg$^{4+}$ is independent of [H$^+$] in the range 0.14–1.0 $M$. In contrast, inverse-acid paths provide substantial contributions to the mercury(II)-assisted aquations of CrCl$^{2+}$ and CrSCN$^{2+}$ even at [H$^+$] = 1.0 $M$.[3,26] For the latter two complexes, the ratios of the rate constants for the inverse-acid paths to the rate constants for the acid-independent paths are approximately five times larger for the mercury(II)-assisted reactions than for the spontaneous aquations.[3,26,30,31] If a similar ratio obtains for CrNCSHg$^{4+}$ as compared to CrNCS$^{2+}$, then the contribution of the inverse-acid path to the aquation of CrNCSHg$^{4+}$ would not have been detected at [H$^+$] = 0.14 $M$, the lowest value used in the present work. Interestingly, the aquation of CrNCHg$^{4+}$ in the range [H$^+$] = 0.040–0.482 $M$ is also acid independent.[5] In this context, it is noteworthy that the rates of aquation of CrNCSHg$^{4+}$ and CrNCHg$^{4+}$ are remarkedly similar. At 55° and $\mu$ = 1.0 $M$, the rate constant for aquation of CrNCHg$^{4+}$ is $6.6 \times 10^{-3}$ sec$^{-1}$.[5] Extrapolation of the data obtained in the present work gives a first-order rate constant for aquation of CrNCSHg$^{4+}$ at 55° and $\mu$ = 1.0 $M$ of $2.6 \times 10^{-3}$ sec$^{-1}$. The agreement in rate laws and in rates provides indirect support for the postulated[5] linkage isomerization of CrCN$^{2+}$ when complexing with Hg$^{2+}$ to produce CrNCHg$^{4+}$.

In trying to obtain detailed information about the mechanism of substitution of complexes of the pentaaquochromium(III) class, two indirect approaches have been employed recently. Swaddle and Guastalla[32] have made use of linear free energy relationships, and Espenson[33] has tabulated rates of formation of CrX$^{2+}$ complexes. It would be of interest to consider the results obtained for CrNCSHg$^{4+}$ in the light of these two correlations. However, the charge type of CrNCSHg$^{4+}$ is radically different from that of the complexes CrX$^{2+}$ used in the approaches indicated above, and any differences observed for CrNCSHg$^{4+}$ might be ascribed to charge type rather than to mechanism.[34] Some insight into the mechanism of aquation of CrNCSHg$^{4+}$ can be obtained from a consideration of equilibrium quotients relating transition states.[35] The values of the equilibrium quotients for reactions 1, 7, and 10 of Table III are $1.66 \times 10^4$, $2 \times 10^9$, and $1.5 \times 10^8$ $M^{-1}$, respectively. The first two values represent a measure of the affinity of mercury(II) for sulfur in thiocyanate when thiocyanate is bound to chromium(III) and when thiocyanate is free, respectively. Since the value of $Q$ for reaction 10 is very similar to the value for reaction 7, it is tempting to suggest that the role of thiocyanate in reaction 10 is similar to that of free thiocyanate. The value of $Q$ for reaction 10 being, however, somewhat smaller than the value for reaction 7, it is clear that some residual binding to chromium obtains. Since it has been estimated that the separation of NCS$^-$ from CrNCS$^{2+}$ in the transition state for spontaneous aquation is about half completed,[32] the residual binding indicated above can be reasonably ascribed to the transition state [CrNCS$^{2+}$]$^{\ddagger}$, and consequently it is suggested that the Cr–N bond is essentially completely broken in the transition state [CrNCSHg$^{4+}$]$^{\ddagger}$. Some support for the proposed interpretation is obtained by considering the affinity of mercury(II) for free chloride ion, chloride in CrCl$^{2+}$, and chloride in the transition state for spontaneous aquation of CrCl$^{2+}$. The values of $Q$ are $4.2 \times 10^6$,[23] $<0.5$, and $1.7 \times 10^5$ $M^{-1}$,[36] respectively. The pattern is entirely analogous to that for thiocyanate. The affinity of mercury(II) for chloride in the transition state [CrCl$^{2+}$]$^{\ddagger}$ is substantially bigger than for chloride in the ground state CrCl$^{2+}$, but somewhat smaller than the affinity for free chloride. The suggested interpretation is that the Cr–Cl bond is essentially completely broken in the transition state [CrClHg$^{4+}$]$^{\ddagger}$. This conclusion is consistent with the recent finding of a common intermediate, presumably the ion Cr(OH$_2$)$_5{}^{3+}$, in the mercury-assisted aquations of CrCl$^{2+}$, CrBr$^{2+}$, and CrI$^{2+}$.[7]

Finally, it is useful to inquire about the high stability of the configuration CrNCSHg$^{4+}$. In this binuclear complex, the soft (S) and hard (N) ends of the ambidentate ligand thiocyanate interact with soft [mercury(II)] and hard [chromium(III)] acids, respectively, and therefore it is not surprising, given the high affinity of mercury(II) for sulfur, that a stable configuration obtains. In contrast, when mercury(II) interacts with CrSCN$^{2+}$ where the soft end of thiocyanate is already bound to the hard acid chromium(III), an unstable situation obtains, and aquation and isomerization to the more stable structure CrNCSHg$^{4+}$ takes place. An entirely analogous situation has been reported previously for the chromium(III)–mercury(II)–cyanide system.[5] The stable binuclear complex has the arrangement CrNCHg$^{4+}$, and this is attained directly from CrNC$^{2+}$ and Hg$^{2+}$, or *via* isomerization by reaction between CrCN$^{2+}$ and Hg$^{2+}$.[5] In order to achieve comparable stability with bridging ligands such as Cl$^-$ or N$_3{}^-$ that do not have an extremely high affinity for mercury(II),[23,37] it appears that doubly bridging such as

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[30] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

[31] This trend is perhaps not unexpected since, because of the proximity of the positive charge of mercury(II) to the chromium(III) center, the binuclear complexes CrXHg$^{4+}$ are undoubtedly stronger acids than the corresponding mononuclear CrX$^{2+}$ species.

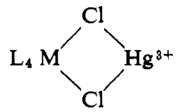
[32] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 7, 1915 (1968).

[33] J. H. Espenson, *ibid.*, **8**, 1554 (1969).

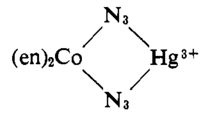
[34] In fact, CrNCSHg$^{4+}$ does not obey the linear free energy relationship. This can be seen by comparing the experimental value $8.5 \times 10^2$ for the equilibrium quotient of reaction 2 in Table III with the value $1.0 \times 10^5$ calculated from the experimental aquation rate and the relation $\log k_f = -6.87 + 0.56 \log Q$ obtained from the plot given by Swaddle and Guastalla.[32] However, the rate constant for the Cr$^{3+}$–HgSC$N^+$ reaction ($k_r$ for reaction 2 of Table III) is $10 \times 10^{-8}$ $M^{-1}$ sec$^{-1}$, a value which falls well within the range $(0.08–73) \times 10^{-8}$ $M^{-1}$ sec$^{-1}$ given by Espenson[33] for typical entering uninegative ligands. Interestingly, the rate constant for the Cr$^{3+}$–HgCl$^+$ reaction ($k_r$ for reaction 8 of Table III) is $0.13 \times 10^{-8}$ $M^{-1}$ sec$^{-1}$, again a value which falls within the range given above. It is noteworthy that the latter reaction appears to proceed by an S$_N$1 mechanism.[7]

[35] A. Haim, *Inorg. Chem.*, 7, 1475 (1968); **9**, 426 (1970).

[36] This is the ratio of $k_f$ for reaction 8 of Table III to $k_f$ for reaction 9 of Table III.



(where $L_4$ M = $(en)_2Co$, $(H_2O)_4Cr)^{2,6}$ or[38]



is necessary before sufficient stability is conferred for direct detection.[39]

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[37] T. R. Musgrave and R. N. Keller, *Inorg. Chem.*, **4**, 1793 (1965).

[38] D. A. Loeliger and H. Taube, *ibid.*, **5**, 1376 (1966).

[39] NOTE ADDED IN PROOF. After this paper was submitted, a measurement of the equilibrium quotient for reaction 7 of Table III was published: L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta*, **4**, 312 (1970). These authors report a value of $1.2 \times 10^9$ at 25° and ionic strength 1.0 (sodium perchlorate), to be compared with our estimated value of $\sim 2 \times 10^9$. With the more accurate value for $Q_7$, the following quantities can be calculated: $Q$ and $k_r$ for reaction 2, $5.1 \times 10^2$ and $17 \times 10^{-8}$; $Q$ and $k_r$ for reaction 3, $8.5 \times 10^6$ and $17 \times 10^{-8}$; $Q$ and $k_r$ for reaction 4, $2.4 \times 10^{12}$ and $0.013 \times 10^{-8}$.

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# Chelated Biscarborane Transition Metal Derivatives Formed through Carbon–Metal σ Bonds

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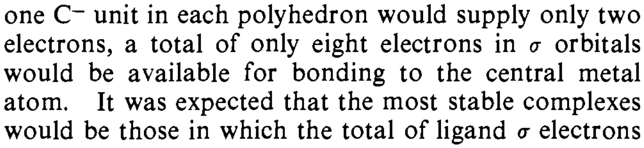
*Received August 3, 1970*

**Abstract:** Biscarborane [1-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$] reacts with 2 mol equiv of *n*-butyllithium in ethyl ether to form 2,2′-dilithiobiscarborane. Dilithiobiscarborane (2 mol equiv) reacts with transition metal halides to form a series of unusually stable anionic chelated transition metal biscarborane derivatives containing metal-carbon σ bonds. The preparation, characterization, reactions, and proposed structures and bonding of these complexes are discussed.

Numerous π-bonded transition metal complexes with $B_9C_2H_{11}^{2-}$, $B_7C_2H_9^{2-}$, and $B_6C_2H_8^{2-}$ ligands have been prepared in this laboratory.[1-9] In addition, several examples of σ-bonded transition metal complexes involving single carbon-metal bonds with 1,2-$B_{10}C_2H_{11}^-$, 1,7-$B_{10}C_2H_{11}^-$, and 1,10-$B_8C_2H_9^-$ and their C-monosubstituted derivatives have been reported.[10,11] In addition, a transition metal complex of the bidentate σ-bonding 1,10-$B_8C_2H_8^{2-}$ ion has been described.[11] One of the bipolyhedral carborane systems, biscarborane [1-(1′-1′,2′-$B_{10}C_2H_{11}$)-1,2-$B_{10}C_2H_{11}$][12] (Figure 1), offered the additional opportunity to form the first examples of chelated transition metal carborane complexes through formation of a ring consisting of the metal ion and the four carbon atoms of the two connected polyhedra. The latter study comprises the subject of this paper.

Dupont and Hawthorne[12] reported that biscarborane reacts with 2 mol equiv of *n*-butyllithium in diethyl ether to form *n*-butane and 2,2′-dilithiobiscarborane [1-(1′-2′-Li-1′,2′-$B_{10}C_2H_{10}$)-2-Li-1,2-$B_{10}C_2H_{10}$] as follows



We subsequently observed[13] that the reaction of two of these 2,2′-dilithiobiscarborane units with anhydrous transition metal halides afforded the first examples of ionic σ-bonded[14] transition metal complexes. Since one $C^-$ unit in each polyhedron would supply only two electrons, a total of only eight electrons in σ orbitals would be available for bonding to the central metal atom. It was expected that the most stable complexes would be those in which the total of ligand σ electrons and metal ion d electrons approached 18. Thus, metal ions with $d^6$, $d^7$, $d^8$, $d^9$, and $d^{10}$ configurations appeared feasible for study. Attempts were made to

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[14] For the sake of brevity and clarity, we have chosen to represent these unusually stable complexes as simple σ-bonded chelates containing $M^{n+}$ ions and 2,2′-biscarboranyl$^{2-}$ ligands. However, $^{11}B$ nmr, electronic spectra, and electrochemical data strongly indicate that further bonding involving π-type orbitals on both ligand and metal combine to give these complexes their unusual stability not found in other systems containing simple carbon-metal σ bonds. The accessibility of multiple oxidation states for each metal also indicates that electron delocalization in the ligand polyhedra is important in the formation of these complexes.