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# The Kinetics of the Mercury(II) Catalyzed Isomerization and Aquation of the Thiocyanatopentaamminecobalt(III) Ion[1a]

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*Mercury(II) reacts with the $Co(NH_3)_5SCN^{2+}$ ion to form $Co(NH_3)_5(SCN)Hg^{4+}$ which undergoes aquation and isomerization to yield $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5NCSHg^{4+}$. The stability constant of the binuclear complex is 1.2 $M^{-1}$ and the corresponding $\Delta H_0$ and $\Delta S_0$ values are –5.2 kcal $mol^{-1}$ and –17 cal $mol^{-1}$ $K^{-1}$, respectively, at $\mu$ = 1.00M and 25° C. Rate parameters $k$ = 0.23 $s^{-1}$ at 25° C, $\Delta H^{\ddagger}$ = 21.4 kcal $mol^{-1}$, and $\Delta S^{\ddagger}$ = 10 cal $mol^{-1}$ $K^{-1}$ were obtained for the aquation and isomerization of the binuclear complex. The two cobalt(III) products are formed at approximately equal rates. The mechanism of the reaction is discussed in terms of the formation of a common intermediate in the isomerization/aquation processes.*

## Introduction

In acidic aqueous solution the $Co(NH_3)_5SCN^{2+}$ ion undergoes spontaneous isomerization to the more stable nitrogen-bonded isomer, $Co(NH_3)_5NCS^{2+}$, with a yield of >98%.[2] We find that this process is catalyzed by mercury(II), but the catalyzed isomerization is accompanied by a significant aquation path to form the $Co(NH_3)_5H_2O^{3+}$ ion. The kinetics of the analogous process for the $Cr(H_2O)_5SCN^{2+}$ ion have been studied previously.[3] A two-stage mechanism for the mercury(II) catalyzed reaction was proposed involving a fast equilibrium between the reactants to form the $Co(H_2O)_5(SCN)Hg^{4+}$ complex* (K), followed by the rate determining aquation and isomerization of this binuclear complex (k). There was not sufficient build-up of the complex under the conditions employed in the earlier study to allow resolution of the composite second-order rate constant kK into the stability constant K and the rate constant k.

Here we report a kinetic study of the mercury(II) catalyzed aquation and isomerization of the $Co(NH_3)_5SCN^{2+}$ ion:

$$Co(NH_3)_5SCN^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} Co(NH_3)_5(SCN)Hg^{4+}$$

$$\xrightarrow{k} \begin{cases} \rightarrow Co(NH_3)_5NCSHg^{4+} \\ \rightarrow Co(NH_3)_5H_2O^{3+} + Hg(II) \end{cases}$$

The build-up of the binuclear complex in this reaction is high enough to permit the determination of both K and k.

## Experimental

### *Materials*

Crude $[Co(NH_3)_5NCS](SCN)_2$ was prepared by the method of Carlin and Edwards.[4] The material obtained contained a significant amount of +1 and 0 charged species (probably the bis- and tris-isothiocyanato complexes) which were not readily removed by repeated recrystallizations from dilute $HClO_4$. The crude material was therefore purified on a column of BioRad AG50W-X2 cation exchange resin. The poorly soluble complex readily precipitated on the column when elution with $NaClO_4$, $HClO_4$, NaCl, or HCl $\geqq$ 0.6*M* was attempted. The complex was therefore eluted with 0.2*M* HCl, the eluate concentrated on a rotary evaporator at 25–30° C, and the $[Co(NH_3)_5NCS]Cl_2$ precipitated by cooling the solution to 0° C. The cobalt(III) content was determined by flame photometry or as cobalt(II) by the Kitson method[5] after reduction of the cobalt(III) by europium(II). Thiocyanate in the reduced solution was determined spectrophotometrically as $FeNCS^{2+}$ after the addition of excess iron(III).[6] The $[Co(NH_3)_5NCS]Cl_2$ prepared in the above manner had molar absorptivities of 178.1 and 1541$M^{-1}$ $cm^{-1}$ at 498 and 306 nm, the absorption band maxima, in very good agreement with absorptivities of 177.4 and 1550$M^{-1}$ $cm^{-1}$ at 497 and 305 nm, respectively, reported by Schug *et al.*[7] for the complex prepared in a different way. The literature controversy concerning the molar absorptivities of the $Co(NH_3)_5NCS^{2+}$ ion cited by Schug[7] thus appears to be resolved.

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* Note that the formulations $Cr(H_2O)_5(SCN)Hg^{4+}$ and $Co(NH_3)_5(SCN)Hg^{4+}$ have only stoichiometric and not structural significance.

The sulfur-bonded isomer $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5\ H_2O$ was prepared by the literature method.[2] The purity of the complex was ascertained from absorption measurements in aqueous solution. The amount of the $Co(NH_3)_5NCS^{2+}$ component (0–3%) present as a preparative impurity and formed by the isomerization process was calculated from absorption measurements at 512 and 288 nm using molar absorptivity values of 74 and $15{,}600 M^{-1}$ $cm^{-1}$ for $Co(NH_3)_5SCN^{2+}$,[2] and 161.4 and $1232 M^{-1}$ $cm^{-1}$ for $Co(NH_3)_5NCS^{2+}$, respectively.

$[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared using a previously described procedure[8] and its purity checked spectrophotometrically.[8]

The other chemicals were all reagent grade and were used without further purification. Triply distilled water was used throughout.

### *Kinetic Measurements*

The kinetics were followed at 288 nm, an absorbance maximum for $Co(NH_3)_5SCN^{2+}$. A Cary 14 instrument which was equipped with a thermostated cell compartment fitted with a magnetic stirrer was used for the measurements. All of the reaction components except the cobalt(III) were placed in a modified 10 cm cell containing a stirring bar, the cell was thermostated to the reaction temperature, and the reaction was initiated by injecting 1 ml of a $[Co(NH_3)_5SCN]Cl_2$ solution into the stirred reaction mixture. The cobalt(III) concentration in the runs was (5–7) × $10^{-6}M$, and the concentration of $Hg(ClO_4)_2$ was high enough so as to remain constant during a run. The pseudo-first-order rate constants, $k_{obsd}$, for the runs were calculated from the straight lines obtained by plotting $\log(A_t - A_\infty)$ *vs.* t, where $A_t$ and $A_\infty$ are the absorbances at time t and after 10 half-lives of the reaction, respectively. The ionic strength was maintained at $1.00M$ by the addition of $Mg(ClO_4)_2$ or $NaClO_4$.

### *Product Analysis*

The $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5H_2O^{3+}$ produced in the reaction were determined spectrophotometrically using a 10 cm cell. For this purpose runs with (5–7) × $10^{-4}M$ $[Co(NH_3)_5SCN]Cl_2$ and 0.1 or $0.01M$ $Hg(ClO_4)_2$ were performed. The spectrum of the $Co(NH_3)_5NCS^{2+}$ product depends on the mercury(II) concentration.[9] For runs with $0.01M$ Hg(II) the concentration of mercury(II) in the "infinite time" solution was increased to $0.1M$ prior to the spectrophotometric measurements to ensure complete formation of the $Co(NH_3)_5NCSHg^{4+}$ adduct.[10] This binuclear complex is very inert, the half-life for its aquation being >10 days. Its visible–near UV spectrum has not been well-defined previously.[9,10] In a solution containing $0.1M$ $HClO_4$, $0.2M$ $Mg(ClO_4)_2$, and $0.1M$ $Hg(ClO_4)_2$ we find absorbance maxima at 476 and 336 nm with molar absorptivities of 85.2 and 79.0 $M^{-1}$ $cm^{-1}$, respectively. If free thiocyanate is present in solution as the counter ion of the complex and/or as preparative impurity, the maximum at 336 nm is obscured by the absorption of mercury(II)–thiocyanate species.

The relative amounts of $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5H_2O^{3+}$ produced in the mercury(II) induced reaction were calculated from the absorption measurements at 476 nm using $\varepsilon = 45.6$ and $85.2M^{-1}$ $cm^{-1}$ for the $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_5NCS^{2+}$ ions, respectively, in the media employed.

## Results

### *Kinetics*

In the presence of excess $Hg(ClO_4)_2$ the rate of disappearance of $Co(NH_3)_5SCN^{2+}$ is given by

$$-d\frac{[Co(NH_3)_5SCN^{2+}]}{dt} = k_{obsd}[Co(NH_3)_5SCN^{2+}]$$

Figure 1 is a plot of $k_{obsd}$ (25° C, ionic strength $1.00M$ with sodium perchlorate) as a function of mercury(II) concentration. The broken line shown there (slope $0.30 M^{-1}$ $sec^{-1}$) was drawn on the basis of the first five entries in Table I (which are not shown in Figure 1). These lie in the region of low mercury(II) concentration ($2.26 \times 10^{-4}$ to $6.67 \times 10^{-3}M$) in which $k_{obsd}$ is linearly dependent on [Hg(II)]. Significant departure from linearity is observed in Figure 1 at the higher mercury(II) concentrations. It is not likely that the high mercury(II) behavior is due to a medium effect, as the same kind of behavior is found with magnesium perchlorate as supporting electrolyte (in Table I, note the diminishing value of $k_{obsd}$/[Hg(II)] as [Hg(II)] increases).

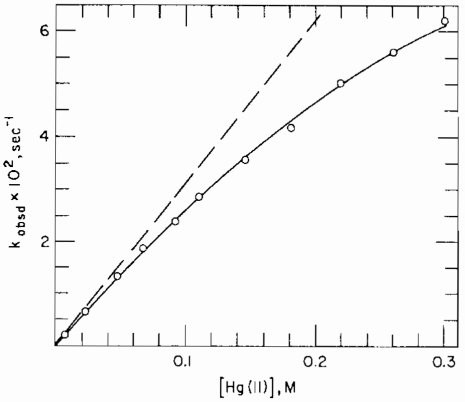

Figure 1. Pseudo-first-order rate constants for the mercury(II) catalyzed aquation and isomerization of $Co(NH_3)_5SCN^{2+}$ as a function of $Hg(ClO_4)_2$ concentration in $0.1M$ $HClO_4$ and $\mu = 1.00M$ $(NaClO_4)$ at 25° C.

TABLE I. Rate Constants for the Mercury(II) Catalyzed Aquation and Isomerization of $Co(NH_3)_5SCN^{2+}$ Ion at $0.1\,M$ $HClO_4$ and $\mu = 1.0\,M$[a, b].

| T<br>°C | $(Hg^{2+})$<br>m$M$ | $k_{obsd} \times 10^3$<br>$sec^{-1}$ | $10 \times k_{obsd}/(Hg^{2+})$<br>$M^{-1}\,sec^{-1}$ |
|---|---|---|---|
| 25.0 | 0.226 | 0.0671[c] | 2.97[c] |
| 25.0 | 0.667 | 0.217[c] | 3.21[c] |
| 25.0 | 2.26 | 0.704[c] | 3.12[c] |
| 25.0 | 2.26 | 0.72[c, d] | 3.19[c, d] |
| 25.0 | 6.67 | 2.10[c] | 3.10[c] |
| 25.0 | 0.361 | 0.105 | 2.91 |
| 25.0 | 0.451 | 0.130 | 2.87 |
| 25.0 | 0.677 | 0.188 | 2.78 |
| 25.0 | 1.58 | 0.458 | 2.90 |
| 25.0 | 4.51 | 1.26 | 2.80 |
| 25.0 | 14.9 | 4.20 | 2.82 |
| 25.0 | 35.0 | 9.06 | 2.59 |
| 25.0 | 79.6 | 20.7 | 2.60 |
| 25.0 | 125 | 31.4 | 2.51 |
| 25.0 | 157 | 37.2 | 2.37 |
| 25.0 | 187 | 43.3 | 2.31 |
| 25.0 | 215 | 49.8 | 2.32 |
| 25.0 | 260 | 55.5 | 2.14 |
| 25.0 | 300 | 62.1 | 2.07 |
| 38.6 | 0.150 | 0.142 | 9.45 |
| 38.6 | 0.350 | 0.324 | 9.25 |
| 38.6 | 0.702 | 0.653 | 9.3 |
| 38.6 | 1.60 | 1.51 | 9.4 |
| 38.6 | 5.00 | 4.62 | 9.25 |
| 38.6 | 15.0 | 13.9 | 9.3 |
| 38.6 | 35.1 | 30.4 | 8.65 |
| 38.6 | 79.8 | 65 | 8.2 |
| 38.6 | 100 | 93 | 8.25 |
| 10.85 | 1.49 | 0.099 | 0.665 |
| 10.85 | 1.99 | 0.131 | 0.66 |
| 10.85 | 3.02 | 0.197 | 0.655 |
| 10.85 | 4.43 | 0.295 | 0.665 |
| 10.85 | 9.91 | 0.653 | 0.66 |
| 10.85 | 19.9 | 1.31 | 0.66 |
| 10.85 | 49.5 | 3.01 | 0.61 |
| 10.85 | 80.2 | 4.62 | 0.575 |
| 10.85 | 120 | 6.61 | 0.55 |
| 10.85 | 171 | 8.4 | 0.49 |
| 10.85 | 220 | 10.5 | 0.475 |
| 10.85 | 260 | 11.9 | 0.46 |
| 10.85 | 299 | 13.5 | 0.45 |

[a] $[Co(NH_3)_5SCN]^{2+} = 5\text{–}7 \times 10^{-6}\,M$. [b] Ionic strength adjusted with $Mg(ClO_4)_2$ unless otherwise noted. [c] Ionic strength adjusted with $NaClO_4$. [d] $HClO_4 = 1.24 \times 10^{-3}\,M$.

These observations are consistent with the reaction scheme

$$Co(NH_3)_5SCN^{2+} + Hg^{2+} \overset{K}{\rightleftharpoons} Co(NH_3)_5(SCN)Hg^{4+} \xrightarrow{k} \text{products} \quad (1)$$

where the first step is a fast equilibrium and the second step is rate determining. In terms of this scheme $k_{obsd}$ is given by

$$k_{obsd} = \frac{kK[Hg^{2+}]}{1 + K[Hg^{2+}]}\,,$$

and its inverse by

$$1/k_{obsd} = 1/kK[Hg^{2+}] + 1/k\,.$$

On plotting the data in Figure 1 and Table I as $1/k_{obsd}$ *vs.* $1/[Hg^{2+}]$ straight lines are obtained. Figure 2 shows the plot for the $Mg(ClO_4)_2$ medium at 25° C. Values of K and k calculated from the slopes and intercepts of the plots are given in Table II. The lower $Hg^{2+}$ concentrations used (and the lower K) at 38.6° C precluded resolution of the kK product.

From the plot of log(kK/T) *vs.* 1/T for the three temperatures in Table II the following values for the composite reaction parameters were calculated: $(\Delta H^{\ddagger} + \Delta H_o) = 16.2$ kcal mol$^{-1}$ and $(\Delta S^{\ddagger} + \Delta S_o) = -6.7$ cal mol$^{-1}$ K$^{-1}$. Using the analogous plot, log(k/T) *vs.* 1/T for the two k entries, activation parameters $\Delta H^{\ddagger} = 21.4$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = 10$ cal mol$^{-1}$ K$^{-1}$ were obtained. The standard enthalpy and entropy changes for the formation of the binuclear complex are then $\Delta H_o = -5.2$ kcal mol$^{-1}$ and $\Delta S_o = -17$ cal mol$^{-1}$ K$^{-1}$.

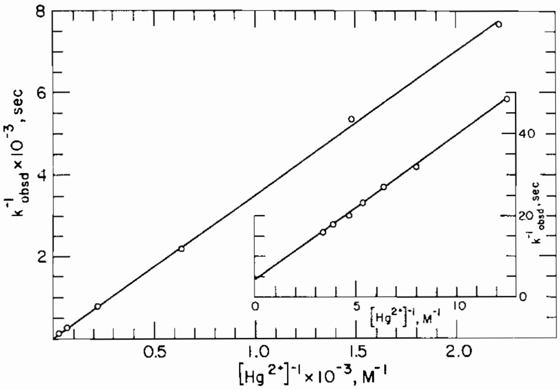

Figure 2. Plot of $k_{obsd}^{-1}$ as a function of $[Hg(II)]^{-1}$ for the mercury(II) catalyzed aquation and isomerization of $Co(NH_3)_5SCN^{2+}$ in $0.1\,M$ $HClO_4$ and $\mu = 1.00\,M$ ($Mg(ClO_4)_2$) at 25° C.

TABLE II. Rate and Equilibrium Constants for the Reaction between $Co(NH_3)_5SCN^{2+}$ and $Hg^{2+}$ at $HClO_4 = 0.1\,M$ and $\mu = 1.0\,M$.

| T<br>°C | kK<br>$M^{-1}\,sec^{-1}$ | k<br>$sec^{-1}$ | K<br>$M^{-1}$ |
|---|---|---|---|
| 10.85[a] | 0.066 | 0.036 | 1.8 |
| 25.0[a] | 0.285 | 0.23 | 1.2 |
| 38.6[a] | 0.93 | – | – |
| 25.0[b] | 0.30 | 0.23 | 1.3 |

[a] $Mg(ClO_4)_2$ medium. [b] $NaClO_4$ medium.

### *Cobalt(III) Reaction Products*

In order to perform the spectrophotometric analysis of the cobalt(III) reaction products it was necessary to resolve the literature controversy[9,10] regarding the visible–near UV absorption spectrum of $Co(NH_3)_5NCSHg^{4+}$. In the presence of $0.1M$ $Hg(ClO_4)_2$ carefully purified $[Co(NH_3)_5NCS]Cl_2$ shows absorption maxima at 476 and 336 nm, the two maxima originally reported by Larsson.[9] The existence of the maximum at 336 nm is not unexpected. The maxima in the $Co(NH_3)_5NCS^{2+}$ spectrum are lowered in intensity and displaced toward higher energies in the spectrum of $Co(NH_3)_5NCSHg^{4+}$ with the shoulder of the former ion at ~360 nm appearing in the spectrum of the binuclear complex as a maximum at 336 nm.

The spectrum of the cobalt(III) products of the mercury(II) catalyzed reaction indicates the formation of both $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5H_2O^{3+}$. At 65, 38.6, 25.0, and 10.4° C the amounts of the $Co(NH_3)_5NCS^{2+}$ isomer formed are 59, 49, 47, and 50 percent of the total cobalt(III). A relatively large experimental error introduces an uncertainty of about $\pm 4\%$ in these figures. This essentially precludes the drawing of conclusions about a possible trend in the product distribution with temperature.

## Discussion

Equilibrium constants for some mercury(II) reactions relevant to this study are collected in Table III. It is evident from this table that the equilibrium constants for mercury(II) addition to the coordinated thiocyanate in the nitrogen-bonded complexes $Co(NH_3)_5NCS^{2+}$ and $Cr(H_2O)_5NCS^{2+}$ are factors of $\sim 10^4$ and $7 \times 10^4$, respectively, less than the equilibrium constant for mercury(II) addition to free thiocyanate. In these reactions the mercury(II) presumably adds to the sulfur atom of the thiocyanate. It is also evident from Table III that the equilibrium constants for mercury(II) addition to the sulfur-bonded complexes $Co(NH_3)_5SCN^{2+}$ and $Cr(H_2O)_5SCN^{2+}$ are reduced by an additional factor of $\sim 10^5$ and $> 10^4$ compared to the constants for mercury(II) addition to the corresponding nitrogen-bonded complexes. In the sulfur-bonded complexes the mercury(II) may add to the nitrogen atom or to the sulfur atom of the coordinated thiocyanate. Consequently the reduced stabilities of the resulting binuclear complexes may reflect either the poorer affinity of $Hg^{2+}$ for the nitrogen atom or steric and electronic effects related to the binding of mercury(II) to the coordinated sulfur atom. If the affinity of $Hg^{2+}$ for free azide is taken as a measure of the stability of a nitrogen-bonded $HgNCS^+$ complex, the possibility of mercury(II) binding to the nitrogen atom of the sulfur-bonded complexes cannot be ruled out. In a study of the mercury(II) catalyzed aquation of $Cr(H_2O)_5N_3^{2+}$ the reaction was found to be first order in mercury(II) over the range of concentrations used indicating a value of $< 7M^{-1}$ at 25° C* for the stability constant of the mercury(II) adduct.[11] These comparisons show that the magnitudes of the stability constants for mercury(II) addition to the sulfur-bonded complexes do not indicate the mode of mercury(II) binding.

Additional information can be obtained from relative rate considerations. Rate constants for the aquation and/or isomerization of cobalt(III) and chromium(III) complexes containing coordinated thiocyanate are presented in Table IV. The catalytic effect of mercury(II) bound to the remote end of the thiocyanate on the rate of aquation of $Co(NH_3)_5NCS^{2+}$ and $Cr(H_2O)_5NCS^{2+}$ is seen to be $< 2.5 \times 10^3$ and $\sim 10^4$, respectively, compared to the rates of spontaneous aquation of the nitrogen-bonded complexes. Similarly, the catalytic effect of coordinated mercury(II) on the aquation/isomerization rate of $Co(NH_3)_5SCN^{2+}$ and $Cr(H_2O)_5SCN^{2+}$ is $2.9 \times 10^5$ and $> 9 \times 10^6$ compared to the rates of spontaneous aquation/isomerization of the sulfur-bonded complexes. The much larger catalytic effect of mercury(II) on the sulfur-bonded complexes suggests that in these complexes mercury(II) addition takes place to the coordinated sulfur atom

TABLE III. Stability Constants for Reactions of Mercury(II) with Some Coordinated or Free Pseudo-Halide Ligands at 25° C and $\mu = 1M$.

| Reactant | K, $M^{-1}$ | Reactant | K, $M^{-1}$ |
|---|---|---|---|
| $Co(NH_3)_5SCN^{2+}$ | 1.2[a] | $Cr(H_2O)_5SCN^{2+}$ | <1[e] |
| $Co(NH_3)_5NCS^{2+}$ | $9.8 \times 10^4$ [b,c] | $Cr(H_2O)_5NCS^{2+}$ | $1.7 \times 10^4$ [f] |
| $SCN^-$ | $1.2 \times 10^9$ [d] | $N_3^-$ | $1.4 \times 10^7$ [g,h] |

[a] This work. [b] Ref. 10. [c] $\mu = 0.1M$, $K = 2.6 \times 10^{-5}$ $M^{-1}$ in $\mu = 0.16M$ K. Schug and B. Miniatas, *Abstracts, 155th National Meeting of the American Chemical Society*, San Francisco, Calif., March 1968, No. M-136. [d] L. Ciavatta and M. Grimaldi, *Inorg. Chim. Acta, 4,* 312 (1970). [e] Ref. 3. [f] Ref. 12. [g] T. R. Musgrave and R. H. Keller, *Inorg. Chem., 4,* 1793 (1965). [h] At 28° C and $\mu = 0.25M$, the value decreases with increasing $\mu$.

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* Estimated from the upper limit of K at 60° C for the acid-independent reaction and assuming $\Delta H_o = -5$ kcal $mol^{-1}$.

TABLE IV. Rate Constants for the Isomerization and/or Aquation of Some Co(III) and Cr(III) Complexes with SCN$^-$ Ligand at 25° C and $\mu$ = 1*M*.

| Reactant | k, sec$^{-1}$ | Reactant | k, sec$^{-1}$ |
|---|---|---|---|
| $Co(NH_3)_5(SCN)Hg^{4+}$ | $0.23^a$ | $Cr(H_2O)_5(SCN)Hg^{4+}$ | $>5.4 \times 10^{2\,d}$ |
| $Co(NH_3)_5NCSHg^{4+}$ | $<10^{-6\,a}$ | $Cr(H_2O)_5NCSHg^{4+}$ | $8.5 \times 10^{-5\,e}$ |
| $Co(NH_3)_5SCN^{2+}$ | $8 \times 10^{-7\,b}$ | $Cr(H_2O)_5SCN^{2+}$ | $5.9 \times 10^{-5\,d}$ |
| $Co(NH_3)_5NCS^{2+}$ | $4 \times 10^{-10\,c}$ | $Cr(H_2O)_5NCS^{2+}$ | $9.1 \times 10^{-9\,f,g}$ |

[a]This work. [b]Ref. 2. [c]D. L. Gay and G. C. Lalor, *J. Chem. Soc. (A)*, 1179 (1966). [d]Ref. 3. [e]Ref. 12. [f]C. Postmus and E. L. King, *J. Phys. Chem.*, *59*, 1217 (1955). [g]Ionic strength 0.50*M*.

rather than to the "free" nitrogen atom of the thiocyanate.*

Another possibility that needs to be considered is the existence of a rapidly established, mercury(II)-dependent equilibrium in addition to the one observed kinetically. This adduct would not have been detected in the kinetic measurements if the stability constant for its formation were sufficiently high. However, the visible–near UV spectrum of Co(NH$_3$)$_5$SCN$^{2+}$ does not show any change in the presence of $5 \times 10^{-3}M$ Hg$^{2+}$ at 10.9° C. Since the reaction rate is slow enough under these conditions to safely allow "zero time" absorbance measurements to be made, there is no spectrophotometric evidence for the formation of a very stable complex between Hg$^{2+}$ and Co(NH$_3$)$_5$ SCN$^{2+}$.

It is likely that the intramolecular mechanism proposed previously[2,3,6] for the spontaneous and the mercury(II) catalyzed rearrangement of thiocyanate complexes applies also to the isomerization of Co(NH$_3$)$_5$SCNHg$^{4+}$. This mechanism involves breaking of the metal(III)–sulfur bond, rotation of the ligand within the solvent cage, and rebonding. Assuming the existence of a common intermediate I for the isomerization and aquation of Co(NH$_3$)$_5$(SCN)Hg$^{4+}$, the reactions of this binuclear complex can be represented by the following scheme

$$\begin{tikzcd}
Co(NH_3)_5(SCN)Hg^{4+} \arrow[r, shift left, "k_1"] & I \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_3"', "H_2O"] & Co(NH_3)_5NCSHg^{4+} \\
 & Co(NH_3)_5H_2O^{3+} + HgSCN^{+} &
\end{tikzcd}$$

The steady-state assumption for the concentration of I gives

$$k_{isom} = \frac{k_1k_2}{k_{-1} + k_2 + k_3}$$

$$k_{aq} = \frac{k_1k_3}{k_{-1} + k_2 + k_3}$$

Since the aquation and isomerization paths proceed to comparable extents, it follows that $k_2 \approx k_3$. The relative values of $k_2$ and $k_3$ are determined by at least three factors: the extent of $\pi$-bonding in the intermediate, the cage effect, and the charge of the rotating (or leaving) group. We comment on these on the basis of the data presented in Table V.

Comparison of the percentage isomerization of Co(NH$_3$)$_5$SCN$^{2+}$ and Co(NH$_3$)$_5$ONO$^{2+}$ suggests that $\pi$-bonding of the rotating group in the intermediate may not be required for high isomerization yields. A similar conclusion concerning the role of $\pi$-bonding in the isomerization of Ru(NH$_3$)$_5$N$_2$$^{2+}$ has been reached previously.[13] These considerations imply that the solvent cage rather than $\pi$-bonding is primarily responsible for $k_2/k_3 > 1$ in these systems. The relatively low percentage isomerization of Cr(H$_2$O)$_5$SCN$^{2+}$ compared with the spontaneous isomerizations of the three

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* This conclusion must be regarded as tentative at this time since the binuclear complex formed by mercury(II) addition to the nitrogen atom of the thiocyanate might also be relatively reactive because of the more favorable driving force for its aquation/isomerization.

TABLE V. Isomerization Yield for Some Metal Complexes in Aqueous Solution.

| Complex | % Isomerization | Complex | % Isomerization |
|---|---|---|---|
| $Co(NH_3)_5SCN^{2+}$ | $>98^a$ | $Co(NH_3)_5(SCN)Hg^{4+}$ | $50^e$ |
| $Co(NH_3)_5ONO^{2+}$ | $\sim98$–$\sim99^b$ | | |
| $Ru(NH_3)_5N_2^{2+}$ | $\sim98^c$ | | |
| $Cr(H_2O)_5SCN^{2+}$ | $72^d$ | $Cr(H_2O)_5(SCN)Hg^{4+}$ | $43^f$ |

[a]Ref. 2. [b]R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, *J. Am. Chem. Soc.*, *76*, 5920 (1954); Ref. 13. [c]Ref. 13. [d]Ref. 3. [e]This work. [f]Ref. 3.

other complexes shown in Table V may stem from an associative component in the activation of chromium(III). Substitution reactions of chromium(III) often feature an $I_a$ mechanism,[14] and a bond-making role of $H_2O$ in the activation for the isomerization could lead to a higher degree of aquation. The relatively lower ratio of isomerization to aquation for $Co(NH_3)_5(SCN)Hg^{4+}$ and $Cr(H_2O)_5(SCN)Hg^{4+}$ may reflect the large size and relative ease of escape of the 1+ charged $HgSCN^+$ from the solvent cage compared with the 1− charged ligand in $Co(NH_3)_5SCN^{2+}$, $Cr(H_2O)_5SCN^{2+}$ and $Co(NH_3)_5ONO^{2+}$, or the zero-charged ligand in $Ru(NH_3)_5N_2^{2+}$. On the basis of these comparisons we may conclude that in these systems the separation of the metal center and the (rotating) ligand is prevented by the surrounding solvent molecules for a time long enough for the isomerization to occur, and that, all other factors remaining constant, the isomerization/aquation ratio is higher the greater the $S_N1$ character of the initial ligand separation.

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