like the simple iodide in the 600–4000-cm$^{-1}$ region, except that the peaks were broad and the NH vibrations unresolved, with $\nu_{NH}$ broad and centered about 3140 while $\delta_{NH}$ was broad and centered about 1575 cm$^{-1}$ (KCl pellet).

The stability of $I_3^-$ is established;[14] $IBr_2^-$ and $ICl_2^-$ are relatively stable,[22] but $Cl_3^-$ has been reported to be thermodynamcally unstable[23] although it was prepared[24] as early as 1923 and studied since.[14,17,18,25] It is interesting to note that the present work provided a trichloride, though not very stable, with a tripositive ion while the other known cases involve large monovalent ions, except in solution studies. Also interesting is the observation that $I_2$ and $Br_2$ react no further with $[Os(en)_3]I_3 \cdot 2H_2O$ than the reaction with the anion to form trihalides. Chlorine first forms the trihalide, and, when concentrated chlorine is used or a chlorinated compound is exposed to the air, attack on the ligand and/or oxidation of the central metal ion begins.

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# The Reactions of Isothiocyanatobis(ethylenediamine)cobalt(III) Complexes with Chromium(II) and the Linkage Isomerization of the Monothiocyanate Complex of Chromium(III)[1]

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**Abstract:** The rates of reaction of chromium(II) with various *cis*- and *trans*-$Co(en)_2(NCS)X^{n+}$ complexes (where X = $H_2O$, $NH_3$, $Cl^-$, and $SCN^-$) have been measured at 25.0° and ionic strength 1.0 *M*. The chromium(II) attacks both the remote and the adjacent positions of the bound thiocyanate. Remote attack produces $CrSCN^{2+}$ while adjacent attack yields $CrNCS^{2+}$. The chromium(II)-catalyzed isomerization, the spontaneous isomerization, and the aquation of $CrSCN^{2+}$ were also studied. The mechanisms of these reactions are discussed.

It has long been believed that the transfer of an unsymmetrical bridging group in an inner-sphere, electron-transfer reaction would, under certain circumstances, yield an unstable product.[3,4] Intermediates produced in this manner have recently been detected. The reactions of $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5CN^{2+}$ with $Co(CN)_5^{3-}$ produce the unstable species $Co(CN)_5ONO^{3-}$ and $Co(CN)_5NC^{3-}$, respectively,[5] while the reaction of $Co(NH_3)_5CN^{2+}$ with chromium(II) produces $CrNC^{2+}$.[6] We have found that the sulfur-bonded chromium(III) complex $CrSCN^{2+}$ is produced in the reaction of chromium(II) with $FeNCS^{2+}$.[7] This complex reacts with chromium(II) to form the stable nitrogen-bonded isomer $CrNCS^{2+}$

$$CrSCN^{2+} + Cr^{2+} \xrightarrow{k_c} Cr^{2+} + CrNCS^{2+} \qquad (1)$$

with a rate constant of 42 $M^{-1}$ sec$^{-1}$ in 1 *M* perchloric acid at 25.0°. In the absence of chromium(II), $CrSCN^{2+}$ undergoes aquation and isomerization. We wish to report here that $CrSCN^{2+}$ is also produced in the reaction of chromium(II) with *cis*- and *trans*-$Co(en)_2OH_2(NCS)^{2+}$ and to describe some additional properties of $CrSCN^{2+}$.

## Experimental Section

**Materials.** Iron(III) perchlorate was purified by recrystallization from perchloric acid. A stock solution approximately 0.5 *M* in iron(III) and 1.5 *M* in perchloric acid was prepared from the recrystallized iron(III) perchlorate. The concentration of the iron(III) in the stock solution was determined by reduction of the iron(III) with a Jones reductor and titration of the iron(II) produced with standard cerium(IV) sulfate using ferroin as indicator. The perchloric acid concentration of the stock solution was determined by precipitating iron(III) hydroxide with excess standard alkali and back-titrating with standard acid to a phenolphthalein end point.

Stock solutions approximately $10^{-1}$ and $10^{-2}$ *M* in chromium(II) and 1 *M* in perchloric acid were prepared by the reduction of chromium(III) perchlorate solutions with amalgamated zinc. The chromium(II) concentration was determined by titration with a standard iron(III) solution containing a two- to threefold excess of thiocyanate. The disappearance of the red iron(III) thiocyanate complexes was taken as the end point. The perchloric acid concentration of the chromium(II) solution was determined by oxidiz-

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
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ing an aliquot with air and then passing the resulting chromium(III) solution through a Dowex 50W-X8 ion-exchange column in the hydrogen form. The acid concentration of the eluate was determined by titration with standard base and the perchloric acid concentration of the original chromium(II) solution obtained after correction for the zinc and chromium(II) in the solution. The zinc was determined polarographically.[8]

Sodium perchlorate solutions were prepared by neutralizing sodium carbonate with perchloric acid.

The cobalt(III) complexes were prepared from $[Co(en)_2Cl_2]Cl$[9] using published procedures: *trans*-$[Co(en)_2(NCS)_2]ClO_4$,[10,11] *cis*-$[Co(en)_2(NCS)_2]ClO_4$,[10,11] *trans*-$[Co(en)_2(NCS)Cl]Br$,[12] *cis*-$[Co(en)_2(NCS)Cl]Cl$,[13] *trans*-$[Co(en)_2(NCS)OH]SCN$,[14] *trans*-$[Co(en)_2NH_3(NCS)](SCN)_2$,[15] and *cis*-$[Co(en)_2NH_3(NCS)](SCN)_2$.[15] The complexes were purified by recrystallization and by ion exchange on a Dowex 50W-X8 column in the hydrogen form. The complexes of charge +1 were eluted with 0.5 *M* (*trans*) or 1 *M* (*cis*) perchloric acid and those of charge +2 with 2 *M* (*trans*) or 3 *M* (*cis*) perchloric acid. A solution containing an equilibrium mixture[16] of *cis*- (82%) and *trans*-$Co(en)_2OH_2(NCS)^{2+}$ (18%) was prepared by adding alkali to a solution of *cis*-$Co(en)_2(NCS)Cl^+$ and rapidly reacidifying with perchloric acid.

**Preparation of $CrSCN^{2+}$ Solutions.** Two methods were used to prepare solutions containing $CrSCN^{2+}$ for the aquation and isomerization studies. In the first method, a solution containing $1.0 \times 10^{-2}$ *M* $Cr^{2+}$ was gradually added to an equal volume of a well-stirred solution containing $1.1 \times 10^{-2}$ *M* $Fe^{3+}$ and $9.0 \times 10^{-3}$ *M* $SCN^-$. The iron(II) produced in this reaction was oxidized to iron(III) with excess sodium peroxydisulfate. In the second method a slightly less than stoichiometric amount of $Cr^{2+}$ was gradually added to a well-stirred solution $1 \times 10^{-3}$ *M* in *trans*-$Co(en)_2OH_2(NCS)^{2+}$. The $CrSCN^{2+}$ and $CrNCS^{2+}$ were adsorbed on a Dowex 50W-X8 column and eluted with 1 *M* perchloric acid. The ion-exchange procedure was carried out with chilled solutions.

The solutions obtained by elution with 1 *M* perchloric acid (which contained chromium(III) complexes of charge +2) were analyzed in the following manner. Total chromium was determined spectrophotometrically as $CrO_4^{2-}$ ($\epsilon$ $4.83 \times 10^3$ at 372 m$\mu$) after oxidation with alkaline peroxide.[17] Free thiocyanate was determined spectrophotometrically as $FeNCS^{2+}$ after the addition of excess iron(III) ($\epsilon$ $3.60 \times 10^3$ at 460 m$\mu$ when $[Fe(III)] = 3.12 \times 10^{-2}$ *M*, $[SCN^-] \sim 10^{-5}$ *M*, and $[HClO_4] = 1$ *M*). For the determination of total thiocyanate (free and bound) the solution containing $CrSCN^{2+}$ and $CrNCS^{2+}$ was made slightly alkaline prior to addition of the iron(III) and perchloric acid solutions. This treatment releases $SCN^-$ very rapidly from both $CrNCS^{2+}$ and $CrSCN^{2+}$. The $[SCN^-]/[Cr(III)]$ ratios of three different preparations were 0.99, 1.02, and 1.03.

**Analysis of Mixtures of $CrSCN^{2+}$ and $CrNCS^{2+}$.** Two methods were devised for determining the composition of solutions containing both $CrNCS^{2+}$ and $CrSCN^{2+}$. In the first method, chlorine was bubbled through the solution; this treatment converts $CrNCS^{2+}$ and $CrSCN^{2+}$ into $Cr^{3+}$ and $CrCl^{2+}$, respectively.[18] The reaction products were separated by ion exchange on a Dowex 50W-X8 column, and the chromium content of the $CrCl^{2+}$ fraction was determined. In the second method, $CrNCS^{2+}$ and $CrSCN^{2+}$ were converted into $CrNCSHg^{4+}$ and $Cr^{3+}$, respectively, by the addition of $Hg(ClO_4)_2$ in 1 *M* $HClO_4$. Following this treatment, hydrochloric acid was added to convert $CrNCSHg^{4+}$ to $CrNCS^{2+}$ and $HgCl_2$, and the concentration of $CrNCS^{2+}$ was measured spectrophotometrically ($\epsilon$ $2.90 \times 10^3$ at 292 m$\mu$[19]). After the ratio of isomerization to aquation of $CrSCN^{2+}$ had been established, the reaction mixtures were analyzed by measuring the amount of thiocyanate released in the aquation.

**Kinetic Measurements.** The oxidation–reduction reactions were studied by the use of the flow apparatus which has been described previously.[20] The disappearance of the cobalt(III) complexes[21] was followed by observing the change in absorbance in the ultraviolet and at their absorption maxima in the visible (generally near 500 m$\mu$). The chromium(II)-catalyzed isomerization of $CrSCN^{2+}$ was followed by observing the change in absorbance in the range 260 to 350 m$\mu$. A large excess of chromium(II) was present in all the above reactions. The aquation and the spontaneous isomerization of $CrSCN^{2+}$ were followed on a Cary Model 14 recording spectrophotometer by observing the decrease in absorbance at 262 m$\mu$ and at 630 m$\mu$, as well as by determining the amount of thiocyanate released. At the completion of the reaction the absorbance at 292 m$\mu$ was measured in order to determine the amount of isomerization which had taken place. In all cases the reactions were either first order or pseudo first order. The rate constants were obtained from the slopes of plots of log $(D_t - D_\infty)$ *vs.* time, where $D_t$ and $D_\infty$ are the optical densities at time *t* and at the end of the reaction, respectively. All the kinetic measurements were made at 25.0° and an ionic strength of 1.0 *M*.

The amount of thiocyanate transferred from the cobalt to the chromium in the oxidation–reduction reactions was obtained in the following manner. After the reaction between the cobalt(III) complex (usually in slight excess) and chromium(II) had proceeded to completion, the reaction mixture was analyzed for free thiocyanate and for thiocyanate bound to chromium(III). The ratio of thiocyanate bound to chromium(III) to the sum of the free and bound thiocyanate was taken as the fraction of thiocyanate transferred.

## Results

**The Oxidation–Reduction Reactions.** The second-order rate constants for the oxidation of chromium(II) by the $Co(en)_2(NCS)X^{n+}$ complexes are presented in Table I. With the exception of *cis*- and *trans*-$Co(en)_2(NCS)Cl^+$, quantitative transfer of thiocyanate from cobalt to chromium is observed, indicating that these reactions proceed *via* a thiocyanate-bridged transition state. The chloro complexes, on the other hand, react predominantly *via* a chloride-bridged transition state.

The reaction of chromium(II) with *trans*-$Co(en)_2OH_2(NCS)^{2+}$ was studied in some detail. In the presence of excess chromium(II) this reaction proceeds in two stages. The first is the reduction of the cobalt(III) complex by chromium(II) and the second is the chromium(II)-catalyzed isomerization of the $CrSCN^{2+}$ produced in the first stage. The rate constant for the isomerization reaction is 42 ± 2 $M^{-1}$ sec$^{-1}$ in 1 *M* perchloric acid, in excellent agreement with the value reported earlier.[7]

The rate of oxidation of chromium(II) by *trans*-$Co(en)_2OH_2(NCS)^{2+}$ increases with decreasing acidity. In the range $[HClO_4] = 1.0$ to $10^{-2}$ *M*, the observed rate constant is given by

$$k = k_1 + k_2K_h/[H^+] \qquad (2)$$

where $k_1$ and $k_2$ are the rate constants for the reactions of chromium(II) with *trans*-$Co(en)_2OH_2(NCS)^{2+}$ and

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[18] Blank experiments showed that less than 1% of $CrCl^{2+}$ is formed when $CrNCS^{2+}$ is treated with $Cl_2$ in 1 *M* perchloric acid. However, about 6% of $CrCl^{2+}$ is formed in 1 *M* hydrochloric acid. In this connection it is noteworthy that the reactions of nitrogen-bonded chromium(III) thiocyanate complexes with oxidants do not preserve the chromium–nitrogen bond, but result in the formation of the corresponding aquo complexes (A. Werner and J. Halban, *Ber.*, **39**, 2668 (1906)). The formation of $Cr(OH_2)_6^{3+}$ in the $CrNCS^{2+}$–$Cl_2$ reaction is therefore consistent with the above findings. By contrast, the oxidations of nitrogen-bonded cobalt(III) thiocyanate complexes occur without breaking the cobalt–nitrogen bond and produce the corresponding ammine complexes (A. Werner and H. Müller, *Z. Anorg. Allgem. Chem.*, **22**, 91 (1900)). The $CrSCN^{2+}$–$Cl_2$ reaction bears a striking resemblance to the $Cr(NH_3)_5Br^{2+}$–$Cl_2$ and $Co(NH_3)_5Br^{2+}$–$Cl_2$ reactions (A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963)) in that all these oxidations produce the corresponding chloro complexes quantitatively.

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[21] As a consequence of the ion-exchange treatment of the cobalt(III) salts perchlorate was the only anion present in these solutions.

Table I. Second-Order Rate Constants for the Reduction of Some [Co(en)$_2$(NCS)X]$^{n+}$ Complexes by Chromium(II) in 1.0 *M* Perchloric Acid at 25.0°

| Oxidant[a] | Reductant[a] | $k$, $M^{-1}$ sec$^{-1}$ | SCN$^-$ transfer, % |
|---|---|---|---|
| *trans*-[Co(en)$_2$(NCS)Cl]$^+$ ($3 \times 10^{-6}$–$1 \times 10^{-5}$ *M*) | Cr$^{2+}$ ($3 \times 10^{-5}$–$1 \times 10^{-4}$ *M*) | $(2.5 \pm 0.4) \times 10^6$ | ≤5 |
| *cis*-[Co(en)$_2$(NCS)Cl]$^+$ ($3 \times 10^{-6}$–$1 \times 10^{-5}$ *M*) | Cr$^{2+}$ ($3 \times 10^{-5}$–$1 \times 10^{-4}$ *M*) | $(1.8 \pm 0.4) \times 10^6$ | ≤5 |
| *trans*-[Co(en)$_2$OH$_2$(NCS)]$^{2+}$ ($2 \times 10^{-4}$–$1 \times 10^{-3}$ *M*) | Cr$^{2+}$ ($2 \times 10^{-3}$–$2 \times 10^{-2}$ *M*) | $(1.4 \pm 0.1) \times 10^3$ | 98–100 |
| *cis*-[Co(en)$_2$OH$_2$(NCS)]$^{2+}$ ($2 \times 10^{-4}$–$1 \times 10^{-3}$ *M*) | Cr$^{2+}$ ($2 \times 10^{-3}$–$2 \times 10^{-2}$ *M*) | $45 \pm 2$ | 98–100 |
| *trans*-[Co(en)$_2$(NCS)$_2$]$^+$ ($1 \times 10^{-3}$ *M*) | Cr$^{2+}$ ($4 \times 10^{-2}$–$1 \times 10^{-1}$ *M*) | $28 \pm 1$ | ~110 |
| *cis*-[Co(en)$_2$(NCS)$_2$]$^+$ ($1 \times 10^{-3}$ *M*) | Cr$^{2+}$ ($4 \times 10^{-2}$–$1 \times 10^{-1}$ *M*) | $30 \pm 1$ | ~110 |
| *trans*-[Co(en)$_2$NH$_3$(NCS)]$^{2+}$ ($2 \times 10^{-4}$ *M*) | Cr$^{2+}$ ($4 \times 10^{-2}$–$1 \times 10^{-1}$ *M*) | $3.8 \pm 0.2$ | ~95 |
| *cis*-[Co(en)$_2$NH$_3$(NCS)]$^{2+}$ ($5 \times 10^{-4}$ *M*) | Cr$^{2+}$ ($4 \times 10^{-2}$–$1 \times 10^{-1}$ *M*) | $3.1 \pm 0.1$ | ~95 |

[a] The numbers in parentheses are the concentration ranges used.

*trans*-Co(en)$_2$(NCS)OH$^+$, respectively, and $K_h$ is the equilibrium constant for the reaction

$$trans\text{-Co(en)}_2\text{OH}_2\text{(NCS)}^{2+} \rightleftharpoons trans\text{-Co(en)}_2\text{(NCS)OH}^{+} + \text{H}^+$$

A plot of $k$ *vs.* 1/(H$^+$) gives $k_1 = (1.4 \pm 0.1) \times 10^3$ $M^{-1}$ sec$^{-1}$ and $k_2K_h = 6.6 \pm 0.6$ sec$^{-1}$. The extent of thiocyanate transfer in the reaction was also determined at various perchloric acid concentrations. The ratio ([CrSCN$^{2+}$] + [CrNCS$^{2+}$])/[Cr$^{3+}$] decreases with decreasing acidity; in the range [HClO$_4$] = 1.0 to $10^{-2}$ *M* it is equal to $1.4 \times 10^2$[H$^+$].

Both CrSCN$^{2+}$ and CrNCS$^{2+}$ are produced when chromium(II) reacts with *trans*-Co(en)$_2$OH$_2$(NCS)$^{2+}$. The yield of CrSCN$^{2+}$, *i.e.*, the ratio [CrSCN$^{2+}$]/([CrSCN$^{2+}$] + [CrNCS$^{2+}$]), is 45 ± 2% in 1 *M* perchloric acid. It was previously found[7] that the yield of CrSCN$^{2+}$ in reaction 3 is 35 ± 5% in 1 *M* perchloric

$$\text{FeNCS}^{2+} + \text{Cr}^{2+} \longrightarrow (\text{CrSCN}^{2+} + \text{CrNCS}^{2+}) + \text{Fe}^{3+} \quad (3)$$

acid.

The rate constant for the *cis*-Co(en)$_2$OH$_2$(NCS)$^{2+}$–Cr$^{2+}$ reaction is too similar to that of the CrSCN$^{2+}$–Cr$^{2+}$ reaction to allow an accurate measurement of the yield of CrSCN$^{2+}$. However, the changes in absorption observed in the 260–280-mμ region clearly indicate that CrSCN$^{2+}$ is also produced in this reaction. No attempts were made to confirm the formation of CrSCN$^{2+}$ in the Cr$^{2+}$ reductions of Co(en)$_2$(NCS)$_2$$^+$ and Co(en)$_2$NH$_3$(NCS)$^{2+}$.

**The Spectrum of CrSCN$^{2+}$.** The absorption spectrum of CrSCN$^{2+}$ was calculated from the spectra of mixtures of CrSCN$^{2+}$ and CrNCS$^{2+}$. In common with other CrX$^{2+}$ complexes, CrSCN$^{2+}$ has two maxima in the visible [620 mμ (ε 36), 435 mμ (ε 28)]. In addition, CrSCN$^{2+}$ has an absorption maximum in the ultraviolet [262 mμ (ε ~$1.1 \times 10^4$)]. A comparison of the spectra of CrSCN$^{2+}$, CrI$^{2+}$ [650 mμ (ε 36.1), 474 mμ (ε 32.6)],[22] CrBr$^{2+}$ [622 mμ (ε 19.9), 432 mμ (ε 22.4)],[23] CrCl$^{2+}$ [609 mμ (ε 16.4), 428 mμ (ε 20.8)],[22] and CrF$^{2+}$ [595 mμ (ε 12.2), 417 mμ (ε 11.8)][22] shows that sulfur-bonded thiocyanate is adjacent to bromide in the spectrochemical series. On the other hand, nitrogen-bonded thiocyanate [570 mμ (ε 31.4), 410 mμ (ε 33.5)] lies among the nitrogen-bonded complexes, CrN$_3$$^{2+}$ [585 mμ (ε 67.5), 434 mμ (ε 66.4)],[24] CrNO$^{2+}$ [559 mμ (ε 28), 449 mμ (ε 120)],[25] CrNC$^{2+}$ (560–545 mμ),[6] and CrNH$_3$$^{3+}$ [545 mμ (ε 22.1), 397 mμ (ε 21.8)].[26]

**The Chromium(II)-Catalyzed Isomerization of CrSCN$^{2+}$.** We have previously studied the rate of the chromium(II)-catalyzed isomerization of CrSCN$^{2+}$ in 1 *M* perchloric acid. These measurements have now been extended to lower acidities. The acid dependence of the observed rate constant in the range [HClO$_4$] = 1.0 to $10^{-2}$ *M* is described by

$$k' = k_1' + K_h'k_2'/[\text{H}^+] \qquad (4)$$

where $k_1'$ and $k_2'$ are the rate constants for the reactions of chromium(II) with CrSCN$^{2+}$ and Cr(SCN)OH$^+$, respectively, and $K_h'$ is the equilibrium constant for the reaction

$$\text{CrSCN}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Cr(SCN)OH}^{+} + \text{H}^+ \qquad (5)$$

A plot of $k'$ *vs.* 1/[H$^+$] gives $k_1' = 40 \pm 2$ $M^{-1}$ sec$^{-1}$ and $k_2'K_h' = 2 \pm 0.2$ sec$^{-1}$. In contrast to the reaction of *trans*-Co(en)$_2$(NCS)OH$^+$ with chromium(II), the reaction of Cr(SCN)OH$^+$ with chromium(II) produces only CrNCS$^{2+}$.

**The Spontaneous Isomerization and Aquation Reactions of CrSCN$^{2+}$.** In the absence of chromium(II), CrSCN$^{2+}$ undergoes aquation and isomerization. The over-all rate constants for these reactions are presented in Table II. The acid-dependence of the over-all rate constant is given by

$$k = (k_a + k_i) + (k_a' + k_i')K_h'/[\text{H}^+] \qquad (6)$$

where $k_a$, $k_a'$, $k_i$, and $k_i'$ are the rate constants for the aquation and isomerization of CrSCN$^{2+}$ and Cr(SCN)OH$^+$, respectively. A plot of $k$ *vs.* 1/[H$^+$] gives $(k_a + k_i) = 6.3 \times 10^{-5}$ sec$^{-1}$ and $(k_a' + k_i')K_h' = 1.45 \times 10^{-5}$ $M^{-1}$ sec$^{-1}$. The ratio $k_a/k_i$, determined from the amounts of Cr$^{3+}$ and CrNCS$^{2+}$ produced in the reaction, is equal to 1.8 ± 0.2 and is independent of the acidity. Consequently $k_a = 4.0 \times 10^{-5}$ sec$^{-1}$, $k_i = 2.3 \times 10^{-5}$ sec$^{-1}$, $k_a'K_h' = 9.3 \times 10^{-6}$ $M^{-1}$ sec$^{-1}$, and $k_i'K_h' = 5.2 \times 10^{-6}$ $M^{-1}$ sec$^{-1}$. The effect of chloride on the product distribution of the reactions was studied at [H$^+$] = 1.0 *M*, [Cl$^-$] = 0.8 *M*, and [ClO$_4$$^-$] = 0.2 *M*. The yield of CrNCS$^{2+}$ was not affected by the addition of chloride while the yield of

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**Table II.** Spontaneous Isomerization and Aquation of $CrSCN^{2+}$ at 25.0° and $\mu$ = 1.0 $M$[a]

| $[HClO_4]$, $M$ | $[CrSCN^{2+}]$, $M$ | $k$, $sec^{-1}$ |
|---|---|---|
| 1.0 | $2.3 \times 10^{-4}$ | $7.2 \times 10^{-5}$ |
| 1.0 | $2.3 \times 10^{-4}$ | $7.5 \times 10^{-5}$ [b] |
| 1.0 | $5.7 \times 10^{-4}$ | $7.8 \times 10^{-5}$ [c] |
| $5.0 \times 10^{-2}$ | $5.7 \times 10^{-6}$ | $3.62 \times 10^{-4}$ |
| $2.0 \times 10^{-2}$ | $5.7 \times 10^{-6}$ | $7.7 \times 10^{-4}$ |
| $2.0 \times 10^{-2}$ | $1.7 \times 10^{-6}$ | $7.3 \times 10^{-4}$ |
| $2.0 \times 10^{-2}$ | $1.7 \times 10^{-5}$ | $7.9 \times 10^{-4}$ |
| $1.25 \times 10^{-2}$ | $5.7 \times 10^{-6}$ | $1.22 \times 10^{-3}$ |

[a] Measurements at 262 m$\mu$ except where indicated. [b] Measurements at 460 m$\mu$ by following the release of thiocyanate. [c] Measurements at 630 m$\mu$.

**Table III.** Comparison of the Rate of Reduction of Some $[Co(en)_2XY]^{n+}$ Complexes by Chromium(II) and Iron(II)[a] at 25.0°

| | | Relative rate constants | | |
|---|---|---|---|---|
| Oxidant | Reductant | *trans*-X / *cis*-X | *cis*-X / *cis*-$NH_3$ | *trans*-X / *trans*-$NH_3$ |
| $[Co(en)_2NH_3(NCS)]^{2+}$ | $Cr^{2+}$ | 1.2 | 1.0 | 1.0 |
| $[Co(en)_2(NCS)_2]^+$ | $Cr^{2+}$ | $9 \times 10^{-1}$ | 4.8[b] | 3.7[b] |
| $[Co(en)_2OH_2(NCS)]^{2+}$ | $Cr^{2+}$ | $3 \times 10^1$ | $1.5 \times 10^1$ | $3.7 \times 10^2$ |
| $[Co(en)_2NH_3Cl]^{2+}$ | $Fe^{2+}$ | 3.7 | 1.0 | 1.0 |
| $[Co(en)_2(NCS)Cl]^+$ | $Fe^{2+}$ | $8 \times 10^{-1}$ | 10 | 2 |
| $[Co(en)_2OH_2Cl]^{2+}$ | $Fe^{2+}$ | $5.2 \times 10^2$ | $2.6 \times 10^1$ | $3.6 \times 10^3$ |

[a] Data from ref 27. [b] Corrected for statistical factor.

$CrCl^{2+}$, based on the amount of $CrSCN^{2+}$ initially present, was 2.2%.

## Discussion

**The Oxidation-Reduction Reactions.** The rates of the $Co(en)_2(NCS)X^{n+}$–Cr(II) reactions measured in the present work are compared in Table III with the rates of some $Co(en)_2ClX^{n+}$–Fe(II) reactions.[27] Although the chromium(II) reactions proceed *via* thiocyanate-bridged transition states, while the iron(II) reactions are believed to proceed *via* chloride-bridged transition states, the general trends in the two series are remarkably similar. First, for X = $NH_3$ or $SCN^-$, only minor differences between the rates of the *cis* and *trans* isomers are observed. Second, replacement of $NH_3$ by $SCN^-$ in either the *cis* or *trans* positions results in a modest increase in rate. Third, replacement of $NH_3$ by $H_2O$ results in a large increase in rate, especially for the *trans* compounds. The similarity in the trends provides additional support for the view that the iron(II) reductions are chloride bridged.[28,29] Further evidence for this view comes from a somewhat more direct comparison of the rates. The rates of the $Co(NH_3)_5Cl^{2+}$–$Fe^{2+}$ and $Co(NH_3)_5Cl^{2+}$–$Cr^{2+}$ reactions have been related[30] by the equation[31]

$$\frac{k_{12}}{k_{13}} = \left(\frac{k_{22}K_{12}f_{12}}{k_{33}K_{13}f_{13}}\right)^{1/2} \tag{7}$$

where $k_{12}$ and $K_{12}$ are the rate constant and equilibrium constant, respectively, for the $Co(NH_3)_5Cl^{2+}$–$Cr^{2+}$ reaction, $k_{13}$ and $K_{13}$ are the corresponding quantities for the $Co(NH_3)_5Cl^{2+}$–$Fe^{2+}$ reaction, and $f_{12}$ and $f_{13}$ have been defined by Marcus.[31] In these systems $f_{12}/f_{13} \approx 1$ and therefore eq 7 reduces to $k_{12}/k_{13} = (k_{22}K_{12}/k_{33}K_{13})^{1/2}$. The rate constants for the chromium(II) reactions calculated using this expression are presented in Table IV. It is necessary to emphasize that eq 7 was derived for outer-sphere electron-transfer reactions only. Nevertheless, the agreement between observed and calculated rates, especially in the pentaammine series, is encouraging, suggesting that an expression of the form of eq 7 may be applicable also to inner-sphere reactions. A similar calculation for the $Co(NH_3)_5Cl^{2+}$–$V^{2+}$ reaction, which is believed to proceed by an outer-sphere mechanism, yields a rate constant which differs from the observed one by a factor of about $10^3$. This disagreement is not surprising since the comparison involves two reactions with different mechanisms.

**Table IV.** Rate Constants for Some Reactions of Chromium(II) and Iron (II) with Cobalt(III) Complexes at 25.0° and $\mu$ = 1.0 $M$

| Reaction | Log $k_i$[a] | Log $k_{obsd}$ | Log $k_{calcd}$[b] | Ref |
|---|---|---|---|---|
| $Co(NH_3)_5Cl^{2+} + Fe^{2+}$ | 1.3 | −2.9 | ... | *c, d* |
| $Co(NH_3)_5Cl^{2+} + Cr^{2+}$ | ~1.7 | 6.4 | 6.6 | *e, f* |
| $Co(NH_3)_5F^{2+} + Fe^{2+}$ | 1.6 | −2.2 | ... | *d, g* |
| $Co(NH_3)_5F^{2+} + Cr^{2+}$ | −1.6 | 5.9 | 5.5 | *e, f* |
| $Co(NH_3)_5N_3^{2+} + Fe^{2+}$ | 3.9 | −2.0 | ... | *h, i* |
| $Co(NH_3)_5N_3^{2+} + Cr^{2+}$ | 0.8 | 5.5 | 5.7 | *j, k* |
| *cis*-$Co(en)_2(NCS)Cl^{2+} + Fe^{2+}$ | 1.3 | −3.8 | ... | *c, l* |
| *cis*-$Co(en)_2(NCS)Cl^{2+} + Cr^{2+}$ | 1.7 | 6.3 | 5.7 | *e, m* |
| *trans*-$Co(en)_2(NCS)Cl^{2+} + Fe^{2+}$ | 1.3 | −3.9 | ... | *c, l* |
| *trans*-$Co(en)_2(NCS)Cl^{2+} + Cr^{2+}$ | 1.7 | 6.4 | 5.6 | *e, m* |

[a] $i$ = 2 for chromium; $i$ = 3 for iron. [b] Calculated from $k_{12}/k_{13} = (k_{22}K_{12}/k_{33}K_{13})^{1/2}$. [c] N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961). [d] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965). [e] Reference 4. [f] Reference 36. [g] J. Hudis and A. C. Wahl, *J. Am. Chem. Soc.*, **75**, 4153 (1953). [h] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961). [i] A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963). [j] Reference 40. [k] Reference 33. [l] Reference 27. [m] This work.

The dependence of the rate of reduction of *trans*-$Co(en)_2OH_2(NCS)^{2+}$ upon $[H^+]$ is given by eq 2. The acid-dependent term can be interpreted in terms of the reaction of *trans*-$Co(en)_2(NCS)OH^+$ with chromium(II).

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(27) P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

(28) Direct evidence for a chloride-bridged mechanism in the $CoCl^{2+}$–$Fe^{2+}$ reaction has been obtained.[29]

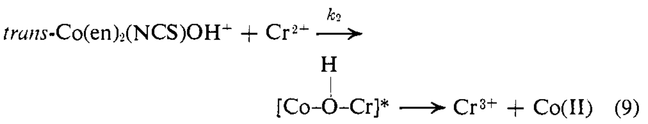
(29) T. J. Conocchioli, G. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

(30) N. Sutin, Symposium on Exchange Reactions, International Atomic Energy Agency, Brookhaven National Laboratory, June 1965.

(31) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

Substitution of $K_h \approx 5 \times 10^{-7}\ M$[32] gives $k_2 \approx 1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. It is possible to determine whether $SCN^-$ or $OH^-$ is the bridging group by considering the dependence of the thiocyanate transfer on the acidity. If it is assumed that *trans*-$Co(en)_2OH_2(NCS)^{2+}$ reacts with chromium(II) entirely *via* a thiocyanate-bridged intermediate and that *trans*-$Co(en)_2(NCS)OH^+$ reacts with chromium(II) entirely *via* a hydroxide-bridged intermediate

$$trans\text{-}Co(en)_2OH_2(NCS)^{2+} + Cr^{2+} \xrightarrow{k_1} [Co{-}NCS{-}Cr]^* \longrightarrow (CrSCN^{2+} + CrNCS^{2+}) + Co(II) \quad (8)$$



$$trans\text{-}Co(en)_2(NCS)OH^+ + Cr^{2+} \xrightarrow{k_2} [Co{-}\overset{\overset{\displaystyle H}{|}}{O}{-}Cr]^* \longrightarrow Cr^{3+} + Co(II) \quad (9)$$

then the dependence of the ratio $([CrSCN^{2+}] + [CrNCS^{2+}])/[Cr^{3+}]$ on the acidity can be readily calculated. This ratio is equal to $k_1[H^+]/k_2K_h = 2.1 \times 10^2[H^+]$, in fair agreement with the value $1.4 \times 10^2[H^+]$ obtained from the product analysis. If the difference between these two values is significant, it suggests that some water-bridging occurs in the acid-dependent path. This conclusion is not unreasonable since $SCN^-$ is a better bridging ligand than $H_2O$ by a factor of only 40. (The rate constants for the $Co(NH_3)_5NCS^{2+}$–$Cr^{2+}$ and $Co(NH_3)_5OH_2^{3+}$–$Cr^{2+}$ reactions are 19 $M^{-1}$ sec$^{-1}$ and 0.5 $M^{-1}$ sec$^{-1}$, respectively,[33] at 25.0°.) It is of interest that the rate constant for reaction 9 ($k_2 \sim 1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$) is similar to that for reaction 10 ($2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$).[34] Oxygen-tracer studies have es-

$$Co(NH_3)_5OH^{2+} + Cr^{2+} \longrightarrow Cr^{3+} + Co(II) \quad (10)$$

tablished that reaction 10 proceeds *via* a hydroxide-bridged intermediate.[35]

While an acid-dependent path is present in the reaction of *trans*-$Co(en)_2OH_2(NCS)^{2+}$ with chromium(II) it is absent in the *trans*-$Co(en)_2OH_2Cl^{2+}$–Fe(II) reaction. This difference may be due partly to the weaker acidity of *trans*-$Co(en)_2OH_2Cl^{2+}$ ($pK = 7.2$)[32] compared to *trans*-$Co(en)_2OH_2(NCS)^{2+}$ ($pK = 6.3$)[32] and partly to the better bridging ability of chloride compared to thiocyanate. (The rate constants for the reduction of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5NCS^{2+}$ by chromium(II) are $2.6 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ [36] and 19 $M^{-1}$ sec$^{-1}$,[33] respectively, at 25.0°.) A detailed study of the acid dependence of the *cis*-$Co(en)_2OH_2(NCS)^{2+}$–Cr(II) reaction was not undertaken. However, preliminary experiments indicate a slight increase in rate and decrease in the fraction of thiocyanate transferred in 0.1 $M$ compared to 1.0 $M$ perchloric acid.

These studies also show the effect of chelation of the nonbridging ligands on the reaction rate. A comparison of the rate constants for the reduction of *cis*- and *trans*-$Co(en)_2NH_3(NCS)^{2+}$ and -$Co(NH_3)_5NCS^{2+}$ by chromium(II) ($k$ = 3.1, 3.8, and 19 $M^{-1}$ sec$^{-1}$ at 25.0°, respectively) shows that the replacement of four ammonia molecules by two ethylenediamine molecules decreases the reaction rate by a factor of about 5. The rates of reaction of $Co(en)_2NH_3(SO_4)^+$ and $Co(NH_3)_5SO_4^+$ with chromium(II) also differ by a similar factor.[37]

The formation of $CrSCN^{2+}$ in the reduction of *trans*-$Co(en)_2OH_2(NCS)^{2+}$ presumably arises from the attack of the chromium(II) on the sulfur atom of the thiocyanate ligand. It is more difficult to account for the $CrNCS^{2+}$ formed in this reaction. Some possible explanations are: (a) the $CrNCS^{2+}$ is formed in the chromium(II)-catalyzed isomerization of $CrSCN^{2+}$ during the reaction of chromium(II) with *trans*-$Co(en)_2OH_2(NCS)^{2+}$. However, it can readily be seen that this explanation cannot account for all the $CrNCS^{2+}$ produced. If the $CrNCS^{2+}$ is produced only in reaction 1 then the ratio $[CrNCS^{2+}]/[CrSCN^{2+}]$ at the end of the *trans*-$Co(en)_2OH_2(NCS)^{2+}$–Cr(II) reaction can be calculated from

$$\frac{[CrNCS^{2+}]_\infty}{[Cr(II)]_0} = 1 - \frac{k_1[Co(III)]_0}{k_c[Cr(II)]_0}\left\{1 - \exp\left[-\frac{k_c[Cr(II)]_0}{k_1[Co(III)]_0}\right]\right\} \quad (11)$$

Since under the conditions of the experiments $k_1[Co(III)]_0/k_c[Cr(II)]_0 > 10^2$, $[CrNCS^{2+}]/[CrSCN^{2+}] \approx 0$. (b) The $CrNCS^{2+}$ is formed by the incorporation of "free" thiocyanate. This reaction appears to proceed very efficiently. For example, $CrNCS^{2+}$ is quantitatively produced in the thiocyanate-catalyzed iron(III)–chromium(II) reaction which does not involve $FeNCS^{2+}$ as a reactant.[7] For example, on mixing a solution $2 \times 10^{-2}\ M$ in NaSCN and $4.2 \times 10^{-1}\ M$ in chromium(II) with an equal volume of a solution $5.2 \times 10^{-1}\ M$ in iron(III), the yield of $CrNCS^{2+}$ based on the thiocyanate was 22%. The value predicted from the rate constants for the $Fe^{3+}$–$Cr^{2+}$ and $Fe^{3+}$–$Cr^{2+}$–$SCN^-$ reactions is 26%. Air oxidation of chromium(II) solutions containing thiocyanate also produces $CrNCS^{2+}$ in good yield. Thus, bubbling $O_2$ through a solution $1 \times 10^{-2}\ M$ in NaSCN and $2.1 \times 10^{-1}\ M$ in chromium(II) produces about 40% of $CrNCS^{2+}$, based on the amount of thiocyanate initially present. Similarly, when $1.2 \times 10^{-3}\ M$ $Co(NH_3)_5Cl^{2+}$ reacts with $1 \times 10^{-3}\ M$ chromium(II) in the presence of $1.0 \times 10^{-3}\ M$ NaSCN, the yield of $CrNCS^{2+}$ is 8%. Although these effects are quite striking, they can account for only a small proportion of the $CrNCS^{2+}$ formed in the *trans*-$Co(en)_2OH_2(NCS)^{2+}$–Cr(II) reaction. (c) The chromium(II) attacks the nitrogen atom of the thiocyanate ligand. The steric restrictions of this type of attack are severe and $Cr(H_2O)_6^{2+}$ probably has to lose two of its coordinated water molecules in order to form a bond to the nitrogen.[4] Nevertheless, adjacent attack of the thiocyanate offers the most reasonable explanation of the $CrNCS^{2+}$ produced. Since the ratio of $[CrSCN^{2+}]/[CrNCS^{2+}]$ is not significantly increased on going from 25.0 to 0°, this interpretation requires that the entropies and heats of activation for adjacent and remote attack of thiocyanate not be very different. This implies that the unfavorable steric factor for the adjacent attack

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[32] Unpublished results of M. Baldwin quoted by M. L. Tobe, *Sci. Progr.*, 48, 483 (1960). The reference gives $K_h = 5 \times 10^{-7}\ M$ at 20° and an unspecified ionic strength.

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

[34] H. Taube, *Advan. Inorg. Chem. Radiochem.*, 1, 1 (1959).

[35] R. K. Murmann, H. Taube, and F. A. Posey, *J. Am. Chem. Soc.*, **79**, 262 (1957).

[36] J. P. Candlin and J. Halpern, *Inorg. Chem.*, 4, 766 (1965).

[37] R. T. M. Fraser, *ibid.*, **2**, 954 (1963).

is largely compensated by the increase in entropy accompanying the loss of the two water molecules coordinated to the chromium(II). Moreover, although adjacent attack yields stable $CrNCS^{2+}$, this favorable enthalpy change appears to be largely cancelled by the energy required to remove the coordinated water molecules.

In our previous communication,[7] we suggested that the stable isomer of iron(III) was nitrogen bonded. However, since both $CrNCS^{2+}$ and $CrSCN^{2+}$ were formed in the reaction between chromium(II) and the iron(III) thiocyanate complex, we mentioned the possibility of forming $CrSCN^{2+}$ by adjacent attack on the sulfur-bonded isomer $FeSCN^{2+}$. In view of the formation of both $CrSCN^{2+}$ and $CrNCS^{2+}$ in the reaction of $Cr^{2+}$ with $Co(en)_2OH_2(NCS)^{2+}$, a complex in which thiocyanate is definitely nitrogen bonded, we can now conclude that the stable monothiocyanate complex of iron(III) is nitrogen bonded.

**Chromium(II)-Catalyzed Isomerization.** The chromium(II)-catalyzed isomerization of $CrSCN^{2+}$ (eq 1) proceeds by attack of chromium(II) at the nitrogen atom. The position of attack of the chromium(II) on $CrNCS^{2+}$ in the $Cr^{2+}$–$CrNCS^{2+}$ exchange reaction[4] is less certain. As has been seen, chromium(II) attack occurs at the nitrogen and sulfur atoms of $CoNCS^{2+}$ and $FeNCS^{2+}$ with roughly equal probability. It is therefore likely that the $CrNCS^{2+}$–$Cr^{2+}$ exchange also proceeds by both adjacent and remote attack. Under these conditions the rate constant for the exchange of labeled chromium between $CrNCS^{2+}$ and $Cr^{2+}$ is equal to the sum of the rate constants for adjacent and remote attack, *i.e.*

$$k_{ex} = (k_n + 2k_s) \qquad (12)$$

where $k_n$ and $k_s$ are defined by the reactions

$$CrNCS^{2+} + Cr^{2+} \underset{k_n}{\overset{k_n}{\rightleftharpoons}} CrNCS^{2+} + Cr^{2+} \qquad (13)$$

$$CrNCS^{2+} + Cr^{2+} \underset{k_c}{\overset{k_s}{\rightleftharpoons}} CrSCN^{2+} + Cr^{2+} \qquad (14)$$

The coefficient 2 in eq. 12 is necessary because the reactants and products of the remote attack, but not of the adjacent attack, are different.[38] If it is assumed that the ratio $k_n/k_s$ is the same for the $CrNCS^{2+}$–$Cr^{2+}$ and $FeNCS^{2+}$–$Cr^{2+}$ systems then $k_{ex} = 4k_s$. Since $k_{ex} = 1.4 \times 10^{-4}\ M^{-1}\ sec^{-1}$ at 25.0°,[4] we estimate that $k_s = 3.5 \times 10^{-5}$ and $k_n = 7.0 \times 10^{-5}\ M^{-1}\ sec^{-1}$ at 25.0°. For purposes of comparison we may correct the rate constants for any differences in the standard free energy changes of the reactions. This can be accomplished by means of the Marcus relation[31,39]

$$k_{12} = (k_{11}k_{22}K_{12})^{1/2} \qquad (15)$$

where $k_{12} = k_s$, $K_{12} = k_s/k_c$ (or $k_c$ and $k_c/k_s$, respectively), and $k_{11} = k_{22} = k^0_{ex}$, the rate constant for the *hypothetical* exchange reaction involving remote attack of $Cr^{2+}$ on $CrSCN^{2+}$ to give $CrNCS^{2+}$ and $Cr^{2+}$ (or *vice versa*) *with zero free energy change*. We thus obtain $k^0_{ex} = k_{12}K_{12}^{-1/2} = 4 \times 10^{-2}\ M^{-1}\ sec^{-1}$. Comparison of $k^0_{ex}$ with $k_n$ shows that for zero free energy change, remote attack on thiocyanate is approximately $10^3$ times more favorable than adjacent attack. It is noteworthy that $k^0_{ex}$ is smaller than the rate constant for the $CrN_3^{2+}$–$Cr^{2+}$ reaction (6.1 $M^{-1}\ sec^{-1}$ at 25.0°).[40] This suggests that the azide-bridged reaction is faster than the thiocyanate-bridged reaction even after allowance is made for the difference in the standard free energy changes of the reactions. In other words, this comparison suggests that, in the chromium(II)–chromium(III) system, azide is a better bridging ligand than a "symmetrized" thiocyanate group. The above argument also implies that remote attack of chromium(II) on $CrN_3^{2+}$ is about $10^3$ times more favorable than adjacent attack.

An acid-dependent path similar to the one found in the $CrSCN^{2+}$–$Cr^{2+}$ reaction

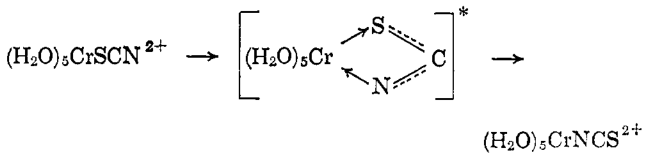
$$Cr(SCN)OH^+ + Cr^{2+} \longrightarrow Cr^{2+} + Cr(NCS)OH^+ \qquad (16)$$

has not been observed in other $CrX^{2+}$–$Cr^{2+}$ exchanges.[4,40] The rapid rate of reaction 16 ($k > 2 \times 10^4\ M^{-1}\ sec^{-1}$ if $K_h'$ is greater than the hydrolysis constant of $Cr(H_2O)_6^{3+}$ [19]) indicates a large effect of hydroxide as a nonbridging ligand or, more likely, perhaps, a double-bridged (hydroxide and thiocyanate) transition state. A double-bridged transition state, with hydroxide as one of the bridging groups, has been proposed for the *cis*-$Co(NH_3)_4OH(OAc)^+$–Cr(II) reaction.[41]

**Aquation and Isomerization of $CrSCN^{2+}$.** The rates of aquation of $CrX^{2+}$ complexes decrease in the order $I^-$ [22] $> SCN^- > Br^-$ [42] $> Cl^-$ [22] $> NCS^-$.[19] Azide and fluoride are not included in this series since there is some evidence that $CrN_3^{2+}$ and $CrF^{2+}$ dissociate into $CrOH^{2+}$ and $HN_3$, and $CrOH^{2+}$ and HF, respectively.[22,24,43] As expected from Pearson's theory[44] the complexes formed between the hard acid chromium(III) and the soft bases $I^-$ and $SCN^-$ are not very stable and dissociate relatively rapidly. The above order of the ligands is similar to the spectrochemical series $I^- > Br^- \sim SCN^- > Cl^- > NCS^-$ and suggests that, in these systems at least, the same factors are important in determining the order of the ligands.

The rate of isomerization of $CrSCN^{2+}$ is comparable to its rate of aquation. For the isomerization to occur it is necessary that the chromium–nitrogen bond be formed before the thiocyanate leaves the sphere of influence of the chromium(III). Some mechanisms satisfying this requirement will next be considered.

**(a) Intramolecular Isomerization.** In this case the isomerization proceeds *via* a seven-coordinated transition state



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[38] R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

[39] The rates of a large number of outer-sphere electron-transfer reactions have been successfully correlated by means of this expression. See, for example, R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1091 (1964). The validity of this expression as applied to inner-sphere reactions has not yet been established.

[40] R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964).

[41] K. D. Kopple and R. R. Miller, *Proc. Chem. Soc.*, 306 (1962).

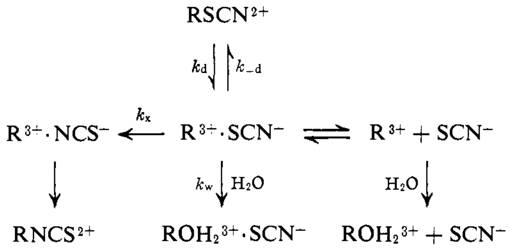
[42] F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

[43] D. Seewald and N. Sutin, *ibid.*, **2**, 643 (1963).

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

A similar transition state has been proposed for the isomerization of nitritopentaamminecobalt(III).[45,46] This mechanism, although reasonable in the nitrito case, is not likely in the thiocyanate system because of the prohibitive amount of energy required to bend the linear thiocyanate group. On the other hand, a seven-coordinated transition state, in which an entering water molecule assists the removal of thiocyanate, cannot be ruled out for the aquation of $CrSCN^{2+}$. A solvent-assisted dissociation has been proposed for the aquation of other complexes.[47]

**(b) Ion-Pair Mechanism.** In this case a five-coordinated intermediate is formed. A reasonable mechanism of this type is



where R stands for $Cr(OH_2)_5$. If the dissociation of the ion pair into $R^{3+}$ and $SCN^-$ is relatively slow compared to the internal return of the ion pair, then, in the absence of added thiocyanate, $k_i = k_dk_x/(k_{-d} + k_x + k_w)$ and $k_a = k_dk_w/(k_{-d} + k_x + k_w)$. The assumption that the dissociation of the ion pair is relatively slow is supported by our observation that when the aquation–isomerization is carried out in the presence of 0.8 *M* $Cl^-$ the yield of $Cr(OH_2)_5Cl^{2+}$ is appreciably less than the amount calculated from data on the competition of $H_2O$ and $Cl^-$ for $Cr(OH_2)_5{}^{3+}$.[48] This type of mechanism, namely the formation of an ion-pair intermediate which dissociates to only a small extent, has also been proposed for the isomerization of benzhydryl thiocyanate in acetonitrile.[49–51]

The ratio of the rates of aquation to isomerization is independent of acidity. This implies that the two ion-pair intermediates $Cr(H_2O)_5{}^{3+}Cl^-$ and $Cr(H_2O)_4OH^{2+}Cl^-$ are in rapid equilibrium or, more likely, that the branching ratios $k_x/k_w$ are the same for the two intermediates.

The behavior of $CrSCN^{2+}$ may be contrasted with that of $CrNC^{2+}$. The isomerization of $CrSCN^{2+}$, but not that of $CrNC^{2+}$,[6] is catalyzed by chromium(II). Moreover while the aquation and isomerization of $CrSCN^{2+}$ proceed at similar rates, $CrNC^{2+}$ undergoes only isomerization.[6]

Finally, other linkage isomers of thiocyanate have recently been reported. Palladium(II) forms $Pd(As(C_6H_5)_3)_2(SCN)_2$ and $Pd(bipy)(SCN)_2$ as well as $Pd(As(C_6H_5)_3)_2(NCS)_2$.[52] Manganese forms the linkage isomers $Mn(CO)_5SCN$ and $Mn(CO)_5NCS$[53] and there is evidence that cadmium forms sulfur-bonded and nitrogen-bonded thiocyanate complexes in solution.[54–56] It is of interest that the rate of isomerization of $Pd(As(C_6H_5)_3)_2(SCN)_2$ in chloroform solution is too rapid to be studied by conventional techniques.[52]

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(45) R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **78**, 4886 (1956).

(46) R. G. Pearson, P. M. Henry, J. G. Bergman, and F. Basolo, *ibid.*, **76**, 5920 (1954).

(47) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(48) M. Ardon, *ibid.*, **4**, 372 (1965).

(49) P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

(50) A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *ibid.*, **83**, 2729 (1961).

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(54) A. Tramer, *J. Chim. Phys.*, **59**, 232 (1962).

(55) R. A. Plane, quote in ref. 52.

(56) O. W. Howarth, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc.*, 3335 (1964).