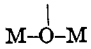
explained by oligomerization. Similar observations were made for the $HMC^-$ chelates.[14] It is most likely that the oligomers contain $HMNC^-$ oxygens that are coordinated to two metals, thereby forming an



$$\mathrm{M{-}\overset{|}{O}{-}M}$$

bridging system. The remaining octahedral coordination sites, *i.e.*, those not containing either bridging or nonbridging $HMNC^-$ oxygens, are taken by water molecules. Hence, fractional numbers of water molecules per metal atom are the result of the number of bridge bonds formed, or in other words, of the structure of the oligomeric molecule. For $Co(HMNC)_2 \cdot 0.5H_2O$, the structure which is consistent with all these data is a dimer, $Co_2(HMNC)_3(H_2O)$, containing a shared face between two basically octahedral units. The twelve coordination sites are filled by five nonbridging $HMNC^-$ oxygens, three bridging $HMNC^-$ oxygens, and one oxygen from a water molecule. For $Ni(HMNC)_2 \cdot 0.25H_2O$, the structure which is consistent with all these data is a tetramer, $Ni_4(HMNC)_8(H_2O)$, containing two shared edges and a shared face between four basically octahedral units. The twenty-four coordination sites are filled with nine nonbridging $HMNC^-$ oxygens, seven bridging $HMNC^-$ oxygens, and one oxygen from a water molecule. On the basis of structures such as these, the presence of water is understandable. It must be present to complete the pseudooctahedral coordination of all the metal ions. Furthermore, our inability to remove the water molecule can be explained, since removal without decomposition would require extensive molecular rearrangement.

**Acknowledgment.**—The authors wish to acknowledge support of this research by the National Science Foundation and Wayne State University in the form of an Academic Year Institute Fellowship (L. L. B.) and a Faculty Summer Fellowship (R. L. L.), respectively.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BAYLOR UNIVERSITY, WACO, TEXAS 76703

# Kinetics of the Spontaneous Aquation and Linkage Isomerization of the S-Bonded–N-Bonded Dithiocyanate Complex of Chromium(III)

BY LEO D. BROWN AND DAVID E. PENNINGTON*

*Received September 18, 1970*

A novel complex ion of chromium(III) containing two thiocyanate ions, one S bonded and the other N bonded, has been prepared in solution by the reaction of $Fe\mathit{N}CS^{2+}$ with $Cr^{2+}(aq)$ in the presence of free thiocyanate ion. The complex ion undergoes two spontaneous reactions, aquation and linkage isomerization, both involving the S-bonded ligand. The rate law has the form: rate $= (k_0 + k_{-1}/[H^+])[Cr(\mathit{S}CN)(\mathit{N}CS)^+]$, where $k_0 = k_0^a + k_0^i$ and $k_{-1} = k_{-1}^a + k_{-1}^i$. The rate constants at 25.0° and $\Sigma[ClO_4^-] = 1.0\ M$ followed by the enthalpies (kcal/mol) and entropies (eu) of activation in parentheses are as follows: $k_0^a = 1.09 \times 10^{-4}\ sec^{-1}$ (19.6, −9.8), $k_0^i = 8.3 \times 10^{-5}\ sec^{-1}$ (19.6, −9.8), $k_{-1}^a = 7.3 \times 10^{-6}\ M\ sec^{-1}$ (24.9, 2.6), and $k_{-1}^i = 5.5 \times 10^{-6}\ M\ sec^{-1}$ (24.9, 2.6) in the ranges 18.0–34.5° and 0.10–1.00 $M\ H^+$.

## Introduction

In the last ten years there has been considerable interest in the study of linkage isomerism involving the thiocyanate ion.[1–7] However, there have been relatively few examples of thiocyanate complexes containing both bonding modes. These are $Pd(Me_2bipy)(\mathit{S}CN)(\mathit{N}CS)$,[8] $Cu(tripyam)(\mathit{S}CN)(\mathit{N}CS)$,[9] $Pd[(C_6H_5)_2As(o\text{-}C_6H_4)P(C_6H_5)_2](\mathit{S}CN)(\mathit{N}CS)$,[10] $M_2[(C_6H_5)_2PC_2P(C_6H_5)_2]_2(\mathit{S}CN)(\mathit{N}CS)$,[11] where M = Pd(II) and Pt(II), and $Pd[(C_6H_5)_2P(CH_2)_3N(CH_3)_2](\mathit{S}CN)(\mathit{N}CS)$.[12] The last example is particularly noteworthy since the X-ray crystal structure study[12] unequivocally establishes that one thiocyanate ion is S bonded while the other is N bonded. One other related example[13] involves a binuclear complex of platinum(II) containing two bridging thiocyanate ions such that each platinum(II) ion has one S-bonded and one N-bonded thiocyanate ion.

The present study presents evidence for the formation and characterization of an S-bonded–N-bonded dithiocyanate complex ion of chromium(III), $Cr(OH_2)_4(\mathit{S}CN)(\mathit{N}CS)^+$, in solution. The kinetics of the spontaneous aquation and linkage isomerization of $Cr(OH_2)_4(\mathit{S}CN)(\mathit{N}CS)^+$ are also reported. The latter reactions parallel very closely those observed for $Cr(OH_2)_5\mathit{S}CN^{2+}$.[2,4]

## Experimental Section

**Materials.**—Chromium(II) solutions were prepared by reduction of chromium(III) perchlorate in 0.1 *M* perchloric acid with lightly amalgamated zinc. The reduction was carried out in an oxygen-free container through which prepurified argon was passed. The argon used was passed through a heated copper catalyst (BASF) at 120° to remove traces of oxygen. The chromium(II) solutions were stored under an argon atmosphere in serum bottles capped with self-sealing rubber stoppers.

---

[1] See for example ref 10–26, 34, and 35 in J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).

[2] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 4210 (1965); **88**, 434 (1966).

[3] B. R. Baker, M. Orhanović, and N. Sutin, *ibid.*, **89**, 722 (1967).

[4] M. Orhanović and N. Sutin, *ibid.*, **90**, 538, 4286 (1968).

[5] M. Orhanović, H. N. Po, and N. Sutin, *ibid.*, **90**, 7224 (1968).

[6] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

[7] D. P. Fay and N. Sutin, *ibid.*, **9**, 1291 (1970).

[8] I. Bertini and A. Sabatini, *ibid.*, **5**, 1025 (1966).

[9] G. C. Kulasingam and W. R. McWhinnie, *Chem. Ind.* (*London*), 2200 (1966).

[10] P. Nicpon and D. W. Meek, *Inorg. Chem.*, **6**, 145 (1967).

[11] A. J. Carty and A. Efraty, *Can. J. Chem.*, **47**, 2573 (1969).

[12] G. R. Clark, G. J. Palenik, and D. W. Meek, *J. Amer. Chem. Soc.*, **92**, 1077 (1970).

[13] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1416 (1961).

Stock solutions (0.2 $M$) of iron(III) perchlorate in 3.2 and 0.1 $M$ perchloric acid were prepared from reagent grade, chloride-free iron(III) perchlorate. Sodium thiocyanate stock solutions (0.2 $M$) were prepared from reagent grade material. Stock solutions of sodium perchlorate were prepared by neutralizing standardized perchloric acid with reagent grade sodium carbonate and diluting to a specified volume with triply distilled water. All other chemicals used were reagent grade. Triply distilled water was used to prepare all solutions for the stoichiometric and kinetic experiments involving $\mathrm{Cr(OH)_2)_4}(S\mathrm{CN})(N\mathrm{CS})^+$.

Dowex 50W-X8 cation-exchange resin ($\mathrm{H}^+$ form, 50–100 mesh) was treated by boiling in an alkaline hydrogen peroxide solution. The resin was then rinsed with water followed by successive treatment with 0.1 $M$ sodium citrate, 3 $M$ hydrochloric acid, 3 $M$ perchloric acid (each interspersed with an amount of water), and water until the effluent was neutral.

**Preparation of *cis,trans*-$\mathbf{Cr(OH)_2)_4}(S\mathbf{CN})(N\mathbf{CS})^+$.**—Solutions containing $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$,[14] presumably as a mixture of cis and trans isomers, were prepared by treating $\mathrm{Fe}N\mathrm{CS}^{2+}$ with chromium(II) ion in the presence of free thiocyanate ion. Preparations were carried out at both high (1–2 $M$) and low (0.05 $M$) acidities. Under these conditions substantial amounts of $\mathrm{Cr}(N\mathrm{CS})_2^+$, $\mathrm{Cr}N\mathrm{CS}^{2+}$, and $\mathrm{Cr}S\mathrm{CN}^{2+}$ were also formed. In a typical experiment a solution containing $1.03 \times 10^{-1}\ M$ $\mathrm{Cr}^{2+}$ and $\mathrm{NCS}^-$ was added dropwise to a well-stirred solution of $1.04 \times 10^{-1}\ M$ $\mathrm{Fe}^{3+}$ (in 0.1 $M$ perchloric acid) and $9.1 \times 10^{-2}\ M$ $\mathrm{NCS}^-$ maintained at 0°. All operations were carried out under an argon atmosphere with iron(III) (1.91 mmol) always in excess of the chromium(II) (1.65 mmol). An excess of potassium peroxydisulfate was used to oxidize the iron(II) produced in this reaction. The reaction mixture (~35 ml) was diluted to 250 ml with ice-cold water and percolated through two cation-exchange columns (Dowex 50W-X8, $\mathrm{H}^+$ form) in tandem. A short (20 cm) column was used to adsorb the species of charges 2+ and 3+, while the species of charge 1+ were adsorbed on a longer, ice-jacketed column (75 cm). The longer column was washed with ice-cold water until there were no traces of free thiocyanate ion, as judged by the absence of any color upon the addition of 0.3 $M$ $\mathrm{Fe}^{3+}$ to the effluent. The 1+ species (~20% based on the millimoles of chromium(II) added) were then eluted from the resin with 1.0 $M$ perchloric acid[15] and stored frozen at 77°K to prevent aquation or isomerization of the sulfur-bonded ligand in $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$.

**Analyses.**—The total chromium content of solutions was determined spectrophotometrically as $\mathrm{CrO_4}^{2-}$ (with a molar absorptivity $\epsilon$ 4815 $M^{-1}\ \mathrm{cm}^{-1}$ at 372 nm)[16] after oxidation of an aliquot of the chromium-containing solution with alkaline hydrogen peroxide. Excess hydrogen peroxide was removed by boiling the solution for 0.5 hr.

Total thiocyanate ion was determined spectrophotometrically as $\mathrm{Fe}N\mathrm{CS}^{2+}$ using the method of Haim and Sutin.[2]

Iron(III) perchlorate solutions were analyzed spectrophotometrically as $\mathrm{Fe}^{3+}$ ($\epsilon$ 4160 $M^{-1}\ \mathrm{cm}^{-1}$ at 240 nm).[17]

Stock solutions of perchloric acid were standardized by titration with standard sodium hydroxide to a phenolphthalein end point.

The concentrations of chromium(II) solutions were determined by oxidation with an excess of iron(III) followed by titration of the iron(II) produced with standard potassium dichromate.[18]

**Composition of 1+ Fraction.**—The ratio of thiocyanate to chromium was found to be 2.0 : 1.0. The amount of S-bonded complex in the mixture of 1+ species was determined indirectly by reaction with chromium(II). The fast chromium(II)-catalyzed aquation of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ yields $\mathrm{Cr}N\mathrm{CS}^{2+}$, leaving $\mathrm{Cr}(N\mathrm{CS})_2^+$ unreacted.[19] Following the air oxidation of chromium(II), which is not consumed in the reaction, $\mathrm{Cr}(N\mathrm{CS})_2^+$ was separated from $\mathrm{Cr}N\mathrm{CS}^{2+}$ by means of ion-exchange chromatography and analyzed for chromium. The $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ content was determined as the difference between the total chromium content of the 1+ fraction and the chromium content of the $\mathrm{Cr}(N\mathrm{CS})_2^+$ recovered. Unfortunately, a direct analysis of the $\mathrm{Cr}N\mathrm{CS}^{2+}$ produced in the chromium(II) reaction was not possible due to the efficient manner with which free thiocyanate ion adds to chromium(II) upon air oxidation.[2]

The isomeric content of the $\mathrm{Cr}(N\mathrm{CS})_2^+$ in the 1+ fraction was determined by taking the ratio of the absorbance at 300 nm to that at 270 nm. This ratio is 1.31 for the trans isomer and 0.96 for the cis isomer.[20]

**Spectrum of $\mathbf{Cr}(S\mathbf{CN})(N\mathbf{CS})^+$.**—A composite spectrum of the 1+ fraction was obtained from 700 to 220 nm. Using the known isomeric composition of the $\mathrm{Cr(NCS)_2}^+$ portion and the known spectra of the pure isomers,[20] the spectrum of the $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ was determined by subtracting the contributions of *cis*- and *trans*-$\mathrm{Cr}(N\mathrm{CS})_2^+$ from the composite spectrum. The analysis resulted in two peaks in the visible region at 605 nm ($\epsilon$ 55 $M^{-1}\ \mathrm{cm}^{-1}$) and 440 nm ($\epsilon$ 43 $M^{-1}\ \mathrm{cm}^{-1}$) and one in the ultraviolet region at 265 nm ($\epsilon$ $8.3 \times 10^3\ M^{-1}\ \mathrm{cm}^{-1}$).

**Stoichiometric Measurements.**—Solutions of the 1+ fraction containing $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ decompose spontaneously yielding $\mathrm{Cr}N\mathrm{CS}^{2+}$ and $\mathrm{Cr}(N\mathrm{CS})_2^+$. Duplicate samples containing $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ were kept in a thermostated bath in the dark for a time ≥10 half-lives, after which $\mathrm{Cr}N\mathrm{CS}^{2+}$ and $\mathrm{Cr}(N\mathrm{CS})_2^+$ were separated by ion-exchange chromatography and analyzed for their chromium content. These experiments were carried out at $\Sigma[\mathrm{ClO_4}^-] = 1.0\ M$ with the hydrogen ion concentration varied between 0.1 and 1.0 $M$ at 18.0, 25.0, and 34.5°.

**Kinetic Measurements.**—The spontaneous aquation and isomerization of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ were followed on a Cary Model 14 recording spectrophotometer by observing the decrease in absorbance at 264 nm. Absorbance readings were taken at various times rather than continuously. In order to minimize the possibility of photoinduced reactions, a cardboard shield was used to block the ultraviolet beam from the sample between absorbance readings. The reactions were first order in all cases. Rate constants were obtained from the slopes of plots of log $(A_t - A_\infty)$ *vs.* time, where $A_t$ and $A_\infty$ are the absorbances at times $t$ and ~10 half-lives, respectively. Measurements were made at various hydrogen ion concentrations at 18.0, 25.0, and 34.5°, $\Sigma[\mathrm{ClO_4}^-] = 1.0\ M$ (sodium perchlorate).

## Results

Various products of the reaction between $\mathrm{Fe}N\mathrm{CS}^{2+}$ and chromium(II) in the presence of added thiocyanate ion are given by reaction 1. The yield of 1+ species

$$\mathrm{Fe}N\mathrm{CS}^{2+} + \mathrm{Cr}^{2+} + \mathrm{NCS}^- \xrightarrow[0°]{0.1\ M\ \mathrm{H}^+} \mathrm{Cr}^{3+} + \mathrm{Cr}N\mathrm{CS}^{2+} + \mathrm{Cr}S\mathrm{CN}^{2+} + cis,trans\text{-}\mathrm{Cr}(N\mathrm{CS})_2^+ + cis,trans\text{-}\mathrm{Cr}(S\mathrm{CN})(\mathrm{NCS})^+ + \mathrm{Fe}^{2+} \quad (1)$$

based on chromium(II) consumed was 19%. (Although a higher yield of the 1+ fraction was obtained at 1 $M$ hydrogen ion concentration (27%), the extra 10-fold dilution of the reaction solution necessary to adsorb the 1+ species led to such long procedural times that decomposition of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ became significant.) The remainder of the chromium was distributed in the 2+ fraction (46%) and in the 3+ fraction (35%). Analysis of the 1+ fraction indicated the formation of 44% $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ and 56% $\mathrm{Cr}(N\mathrm{CS})_2^+$, the latter having a nearly statistical isomeric distribution: 85% cis and 15% trans. It is *assumed*, therefore, that the $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$ was also produced as a mixture of geometric isomers. No attempt was made to effect an isomer separation due to the thermodynamic instability of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^+$. Interestingly, the 2+ fraction consisted of 66% $\mathrm{Cr}N\mathrm{CS}^{2+}$ and 34% $\mathrm{Cr}S\mathrm{CN}^{2+}$, a reversal in yields from that reported[4] in the absence of thiocyanate ion in the chromium(II) solution.

The results of stoichiometric experiments indicate

---

[14] Coordinated water molecules in this and remaining formulations are omitted for brevity.

[15] In earlier experiments it was established that the species were moved readily with 0.2 $M$ perchloric acid. The higher concentration employed here was used both to hasten the ion-exchange separation and to concentrate the solution.

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

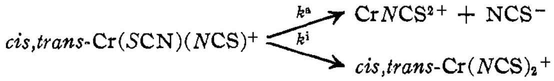
[17] R. Bastian, R. Weberling, and F. Palilla, *Anal. Chem.*, **28**, 459 (1956).

[18] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, Macmillan, New York, N. Y., 1952, p 579.

[19] Unpublished results of K. Schug cited in ref 20 indicate that $\mathrm{Cr}(N\mathrm{CS})_2^+$ reacts very slowly with chromium(II).

[20] J. T. Hougen, K. Schug, and E. L. King, *J. Amer. Chem. Soc.*, **79**, 519 (1957).

that the spontaneous decomposition of Cr(*S*CN)(*N*CS)$^+$ proceeds by two parallel reactions, aquation and linkage isomerization. These reactions are given in eq 2.



$$cis,trans\text{-Cr}(SCN)(NCS)^+ \xrightarrow{k^a} \text{Cr}NCS^{2+} + NCS^- \qquad cis,trans\text{-Cr}(SCN)(NCS)^+ \xrightarrow{k^i} cis,trans\text{-Cr}(NCS)_2^+$$

(2)

The ratio of aquation to linkage isomerization, [Cr*N*CS$^{2+}$]/[Cr(*N*CS)$_2^+$], was found to be 1.31 ± 0.054. This ratio was found to be independent of both temperature (in the range 18–35°) and hydrogen ion concentration (between 0.1 and 1 *M*). The compositon of the 1+ fraction after isomerization was 80% cis and 20% trans, which, within experimental error, is identical with the composition of the Cr(*N*CS)$_2^+$ portion prior to the isomerization.

In Table I are presented the overall first-order rate constants for aquation and isomerization of Cr(*S*CN)(*N*CS)$^+$ at different hydrogen ion concentrations and at different temperatures. It is seen that the observed constants increase with decreasing hydrogen ion concentration at each temperature. The dependence of $k_{\text{obsd}}$ upon the hydrogen ion concentration is adequately given by eq 3. Both $k_0$ and $k_{-1}$ consist of contributions from the

$$k_{\text{obsd}} = k_0 + k_{-1}/[\text{H}^+] \qquad (3)$$

aquation and linkage isomerizations, *i.e.*, $k_0 = k_0^{\text{a}} + k_0^{\text{i}}$ and $k_{-1} = k_{-1}^{\text{a}} + k_{-1}^{\text{i}}$, where $k_0^{\text{a}}$ and $k_0^{\text{i}}$ are the rate constants for aquation and isomerization of Cr(*S*CN)(*N*CS)$^+$ and $k_{-1}^{\text{a}}/K_{\text{h}}$ and $k_{-1}^{\text{i}}/K_{\text{h}}$ are the rate constants for aquation and isomerization of Cr(*S*CN)(*N*CS)OH. $K_{\text{h}}$ is the equilibrium constant for the reaction Cr(*S*CN)(*N*CS)$^+$ + H$_2$O = Cr(*S*CN)(*N*CS)OH + H$^+$.

TABLE I

OBSERVED RATE CONSTANTS FOR THE SPONTANEOUS AQUATION AND LINKAGE ISOMERIZATION OF Cr(*S*CN)(*N*CS)$^+$ AT $\Sigma[\text{ClO}_4^-] = 1.0\ M$

| [HClO$_4$], | $10^4k_{\text{obsd}}$,[a] sec$^{-1}$ | | |
|---|---|---|---|
| *M* | 18.0° | 25.0° | 34.5° |
| 1.00 | 0.88 (1) | 2.1 ± 0.02 (2) | 6.0 (1) |
| 0.25 | 1.02 (1) | 2.4 ± 0.02 (3) | 7.2 (1) |
| 0.15 | 1.11 (1) | 2.8 ± 0.16 (2) | . . . |
| 0.10 | 1.27 (1) | 3.2 ± 0.04 (5) | 10.1 (1) |

[a] Number of experiments given in parentheses; deviations are average deviations.

The fact that the ratio of aquation to linkage isomerization, $(k_0^{\text{a}} + k_{-1}^{\text{a}}/[\text{H}^+])/(k_0^{\text{i}} + k_{-1}^{\text{i}}/[\text{H}^+])$, is independent of the hydrogen ion concentration (within experimental error) requires that $k_0^{\text{a}}/k_0^{\text{i}} = k_{-1}^{\text{a}}/k_{-1}^{\text{i}} = 1.31$. Therefore, knowing the sum and the ratio of the rate constants, the various individual rate constants can be calculated. In Table II are summarized the results of the above calculations at each temperature.

TABLE II

RATE CONSTANTS FOR THE SPONTANEOUS AQUATION AND LINKAGE ISOMERIZATION REACTIONS OF Cr(*S*CN)(*N*CS)$^+$ AT $\Sigma[\text{ClO}_4^-] = 1.0\ M$

| Temp, | $10^5k_n$,[a] $M^{-n}$ sec$^{-1}$ | | | |
|---|---|---|---|---|
| °C | $k_0^{\text{a}}$ | $k_0^{\text{i}}$ | $k_{-1}^{\text{a}}$ | $k_{-1}^{\text{i}}$ |
| 18.0 | 4.8 ± 0.21 | 3.6 ± 0.16 | 0.24 ± 0.012 | 0.18 ± 0.009 |
| 25.0 | 10.9 ± 0.48 | 8.3 ± 0.37 | 0.73 ± 0.0036 | 0.55 ± 0.027 |
| 34.5 | 31 ± 1.5 | 24 ± 1.1 | 2.6 ± 0.15 | 2.0 ± 0.12 |

[a] See text for definitions of various constants. Uncertainties given are standard errors as defined by G. L. Squires, "Practical Physics," McGraw-Hill, New York, N. Y., 1968, pp 34–37.

Activation parameters for the various rate constants are presented in Table III in the Discussion. The values were derived from the slopes of plots of log *k vs.* $1/T$ and the equations $E_{\text{a}} = \Delta H^{\ddagger} + RT$ and $k = (RT/N_0h)\cdot\exp(\Delta S^{\ddagger}/R)\exp(\Delta H^{\ddagger}/RT)$.[21]

## Discussion

**The Spontaneous Aquation and Linkage Isomerization of Cr(*S*CN)(*N*CS)$^+$.**—Before discussing the kinetic and stoichiometric results it should be reemphasized that Cr(*S*CN)(*N*CS)$^+$ is probably a mixture of geometric isomers. Thus each rate constant derived for the spontaneous aquation and isomerization reactions will consist of contributions from both cis and trans isomers.

In Table III are presented comparisons of the various rate constants and associated activation parameters for the spontaneous aquation and linkage isomerization reactions of Cr(*S*CN)(*N*CS)$^+$ and Cr*S*CN$^{2+}$. The parallels between the two systems are striking. First, both systems exhibit rate laws identical in form: rate = $k_{\text{obsd}}[\text{Cr(III)}]$, where $k_{\text{obsd}} = (k_0^{\text{a}} + k_{-1}^{\text{a}}/[\text{H}^+]) + (k_0^{\text{i}} + k_{-1}^{\text{i}}/[\text{H}^+])$. Second, the hydrogen ion independent terms for aquation and linkage isomerization are at least a factor of 6 times greater than the corresponding hydrogen ion dependent terms in both systems. Third, the activation enthalpies for the hydrogen ion independent terms for aquation and isomerization are identical, as are those for the hydrogen ion dependent terms, in each system. The explanation for the last observation arises from the fact that the ratio of aquation to linkage isomerization is insensitive to temperature, at least in the range studied. Interestingly, this ratio is also insensitive to the hydrogen ion concentration in the range 0.1–1.0 *M* in both systems.

TABLE III

COMPARISON OF RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE SPONTANEOUS AQUATION AND LINKAGE ISOMERIZATION REACTIONS OF Cr(*S*CN)(*N*CS)$^+$ AND Cr(*S*CN)$^{2+}$ AT 25.0° AND $\Sigma[\text{ClO}_4^-] = 1.0\ M^a$

| Rate const[b] | System | $10^5k_n$, $M^{-n}$ sec$^{-1}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu |
|---|---|---|---|---|
| $k_0^{\text{a}}$ | Cr(*S*CN)(*N*CS)$^+$ | 10.9 ± 0.48 | 19.6 ± 0.2 | −9.8 ± 0.7 |
| | Cr(*S*CN)$^{2+}$ | 1.7 | 23.5 ± 0.3 | 1.0 ± 0.9 |
| $k_0^{\text{i}}$ | Cr(*S*CN)(*N*CS)$^+$ | 8.3 ± 0.37 | 19.6 ± 0.2 | −9.8 ± 0.7 |
| | Cr(*S*CN)$^{2+}$ | 4.2 | 23.5 ± 0.3 | 1.0 ± 0.9 |
| $k_{-1}^{\text{a}}$ | Cr(*S*CN)(*N*CS)$^+$ | 0.73 ± 0.036 | 24.9 ± 0.2 | 2.6 ± 0.7 |
| | Cr(*S*CN)$^{2+}$ | 0.27 | 27.8 ± 0.2 | 11.7 ± 0.5 |
| $k_{-1}^{\text{i}}$ | Cr(*S*CN)(*N*CS)$^+$ | 0.55 ± 0.027 | 24.9 ± 0.2 | 2.6 ± 0.7 |
| | Cr(*S*CN)$^{2+}$ | 0.69 | 27.8 ± 0.2 | 11.7 ± 0.5 |

[a] Data for Cr(*S*CN)$^{2+}$ from ref 4. [b] Rate constants defined in Results.

An examination of column 3 in Table III reveals that the rate constants for the Cr(*S*CN)(*N*CS)$^+$ system are greater than those for the corresponding reactions of Cr*S*CN$^{2+}$. It would appear at first glance that the term involving $k_{-1}^{\text{i}}$ is an exception to this trend. However, it should be noted that the tabulated values of $k_{-1}^{\text{i}}$ (and $k_{-1}^{\text{a}}$) are products of an elementary rate constant $k'_{-1}{}^{\text{i}}$ (or $k'_{-1}{}^{\text{a}}$) and a hydrolysis constant $K_{\text{h}}$ for the respective chromium(III) complex. It is then apparent that the appropriate rate comparisons involve the elementary rate constants $k'_{-1}{}^{\text{i}}$ (and $k'_{-1}{}^{\text{a}}$) for the two systems rather than the tabulated values of $k_{-1}^{\text{i}}$ (or $k_{-1}^{\text{a}}$). Although no values for the hydrolysis constants have been reported, order-of-magnitude estimates can be made from available

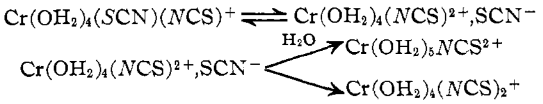
---

[21] W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Englewood Cliffs, N. J., 1963, p 298.

data. For these purposes the concentration quotients $Q_h$ for hydrolysis of $\mathrm{Cr}^{3+}$ ($8 \times 10^{-5}$ *M*)[22] and $\mathrm{CrCl}^{2+}$ ($7 \times 10^{-6}$ *M*)[23] will be used. The value of $K_h$ for $\mathrm{Cr}S\mathrm{CN}^{2+}$ will be set equal to the hydrolysis (concentration) quotient of $\mathrm{CrCl}^{2+}$. (It is unlikely that the nature of the substituent on a $\mathrm{CrX}^{2+}$ species would alter the quotient appreciably.) Since the value of $Q_h$ for $\mathrm{CrCl}^{2+}$ is nearly one order of magnitude less than that for $\mathrm{Cr}^{3+}$, it appears reasonable to assume that $Q_h$ for a 1+ species would be approximately an order of magnitude less than that for a 2+ species. The value of $K_h$ for $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ will, therefore, be taken as $7 \times 10^{-7}$ *M*. For the $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ system $k'_{-1}{}^{a} = 10\ \mathrm{sec}^{-1}$ and $k'_{-1}{}^{i} = 8\ \mathrm{sec}^{-1}$, whereas for the $\mathrm{Cr}S\mathrm{CN}^{2+}$ system $k'_{-1}{}^{a} = 0.4\ \mathrm{sec}^{-1}$ and $k'_{-1}{}^{i} = 1\ \mathrm{sec}^{-1}$. Now the rate constants for the hydrogen ion dependent linkage isomerization are in the expected order.

An examination of column 4 in Table III reveals that the observed enthalpies of activation for the aquation and isomerization reactions are identical for the hydrogen ion independent terms, as well as for the hydrogen ion dependent terms, for each system. Furthermore, it is seen (column 5 in Table III) that the entropies of activation for the $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ system are all 9–11 units less positive than the corresponding entropies for the $\mathrm{Cr}S\mathrm{CN}^{2+}$ system. The trend in the entropies of activation is that expected for a complex of lower positive charge. That the observations of such trends in the enthalpies and entropies in both systems would be fortuitous seems rather unlikely. There is most likely a similarity in mechanisms for the two systems.

The identity of the activation enthalpies for the aquation and isomerization reactions in the $\mathrm{Cr}S\mathrm{CN}^{2+}$ system led Orhanović and Sutin[4] to suggest a common activated complex for the aquation and isomerization reactions. In their mechanism the removal of S-bonded thiocyanate ion to the second coordination sphere (as a "tight" ion pair) was postulated. From there it could either escape into the solution yielding aquation or rotate and reenter the first coordination sphere *via* the nitrogen end yielding isomerization. It was demonstrated that the thiocyanate ion undergoing isomerization did not exchange with "free," labeled thiocyanate ion. Therefore, we adopt an entirely analogous mechanism for the $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ system



$$\mathrm{Cr(OH_2)_4}(S\mathrm{CN})(N\mathrm{CS})^{+} \rightleftharpoons \mathrm{Cr(OH_2)_4}(N\mathrm{CS})^{2+},\mathrm{SCN}^{-}$$

$$\mathrm{Cr(OH_2)_4}(N\mathrm{CS})^{2+},\mathrm{SCN}^{-} \begin{cases} \xrightarrow{\mathrm{H_2O}} \mathrm{Cr(OH_2)_5}N\mathrm{CS}^{2+} \\ \longrightarrow \mathrm{Cr(OH_2)_4}(N\mathrm{CS})_2{}^{+} \end{cases}$$

**Spectrum and Preparation of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$.**—It was noted in the Experimental Section that $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ has absorption maxima at 605, 440, and 265 nm. Since N-bonded thiocyanate ion is very near water in the spectrochemical series, one might have anticipated that $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ would have its first absorption maximum very near that for $\mathrm{Cr}S\mathrm{CN}^{2+}$ (620 nm).[2,4,24] Our results indicate that S-bonded thiocyanate ion lies between fluoride and chloride ions in the spectrochemical series. Further evidence in support of this assignment comes from the absorption spectrum of the recently reported $\mathrm{Co(NH_3)_5}(S\mathrm{CN})^{2+}$ ion.[6] The first absorption maximum of this ion lies at 512 nm as compared to the corresponding maxima for $\mathrm{Co(NH_3)_5F}^{2+}$ (510 nm) and $\mathrm{Co(NH_3)_5Cl}^{2+}$ (533 nm).[25]

A novel feature of the reaction given in eq 1 is that disubstituted tetraaquochromium(III) species are produced. It has already been demonstrated[2] that the reaction between $\mathrm{Fe}N\mathrm{CS}^{2+}$ and chromium(II) produces a mixture of $\mathrm{Cr}S\mathrm{CN}^{2+}$ and $\mathrm{Cr}N\mathrm{CS}^{2+}$. Moreover, the oxidations of certain chromium(II)–thiocyanate ion solutions by iron(III), oxygen, and $\mathrm{Co(NH_3)_5Cl}^{2+}$ produce substantial amounts (8–40%) of $\mathrm{Cr}N\mathrm{CS}^{2+}$.[2] In view of these observations it is not, therefore, unreasonable that the oxidation of chromium(II)–thiocyanate ion solutions by $\mathrm{Fe}N\mathrm{CS}^{2+}$ should produce a mixture of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$ and $\mathrm{Cr}(N\mathrm{CS})_2{}^{+}$. What is perhaps surprising is that the isomeric composition of the $\mathrm{Cr}(N\mathrm{CS})_2{}^{+}$ produced was 85% cis and 15% trans, a virtually statistical distribution. There are several possible mechanisms for the formation of $\mathrm{Cr}(N\mathrm{CS})_2{}^{+}$: (1) adjacent attack of $\mathrm{Cr}N\mathrm{CS}^{+}$ on $\mathrm{Fe}N\mathrm{CS}^{2+}$, although steric considerations[26] would indicate severe steric crowding, (2) incorporation of two thiocyanate ions *via* an $\mathrm{Fe}^{3+}$–$\mathrm{Cr}^{2+}$–$\mathrm{NCS}^{-}$ reaction, and (3) $\mathrm{Cr}N\mathrm{CS}^{+}$-catalyzed isomerization of $\mathrm{Cr}(S\mathrm{CN})(N\mathrm{CS})^{+}$. Unfortunately, we have been unable to determine which mechanism is operative.

**Acknowledgment.**—The authors are grateful to the Robert A. Welch Foundation for financial support of this research and to the National Science Foundation (Grant No. GP-8248) for matching funds for the purchase of the Cary 14 spectrophotometer.

---

[22] G. Mattock, *Acta Chem. Scand.*, **8**, 777 (1954).

[23] H. Wenger, Thesis, ETH Zurich, 1962; quoted by G. Schwartzenbach and B. Magyar, *Helv. Chim. Acta*, **45**, 1425 (1962).

[24] After it was discovered[4] that an error had been made earlier[2] in analyzing the composition of solutions containing $\mathrm{Cr}S\mathrm{CN}^{2+}$ and $\mathrm{Cr}N\mathrm{CS}^{2+}$, the molar absorptivities of $\mathrm{Cr}S\mathrm{CN}^{2+}$, but not the positions of the absorption maxima, were redetermined. It would appear reasonable to expect a shift toward lower wavelengths for the first absorption maximum of $\mathrm{Cr}S\mathrm{CN}^{2+}$.

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

[26] D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).