Scheme I

$$\begin{tikzcd}
{[\mathrm{Co(H}_n\mathrm{edta)(NH_3)_5}]^{(n-1)+}} \arrow[rrd] & & \\
{[\mathrm{Co(edta)}]^-} \arrow[r] & {[\mathrm{Cr(H}_n\mathrm{edta)(H_2O)_5}]^{(n-1)+}} \arrow[r] & {[\mathrm{Cr(edta)(H_2O)}]^-} \\
{[\mathrm{(NH_3)_5Co\{edtaCr(H_2O)\}}]^{2+}} \arrow[r] & {[\mathrm{(H_2O)_5Cr\{edtaCr(H_2O)\}}]^{2+}} \arrow[ru] & \\
{[\mathrm{(NH_3)_5Co\{edtaCo(H_2O)\}}]^{2+}} \arrow[r] & {[\mathrm{(NH_3)_5Co(H}_n\mathrm{edta)Cr(H_2O)_5}]^{(n+2)+}} \arrow[u] &
\end{tikzcd}$$

inner-sphere mechanisms. Although various chromium(III)–EDTA complexes are produced by the reactions, it should be noted that these products are ultimately converted to $[\mathrm{Cr(edta)(H_2O)}]^-$.

Acknowledgment. The authors wish to thank Professor Kahei Takase in this department for allowing us to use a rapid-scanning spectrophotometer. We also wish to thank the Ministry of Education for Scientific Research Grant-in-Aid No. 147043.

Registry No. $[\mathrm{Co(edta)(NH_3)_5}]^-$, 69576-62-1; $[\mathrm{(NH_3)_5Co\{edtaCr(H_2O)\}}]^{2+}$, 61813-16-9; $[\mathrm{(NH_3)_5Co\{edtaCo(H_2O)\}}]^{2+}$, 61813-10-3; $[\mathrm{Co(edta)}]^-$, 15136-66-0; $\mathrm{Cr(H_2O)_6}^{2+}$, 20574-26-9; $[\mathrm{(H_2O)_5Cr\{edtaCr(H_2O)\}}]^{2+}$, 69531-92-6; $[\mathrm{(NH_3)_5Co(H_2edta)Cr(H_2O)_5}]^{4+}$, 69596-66-3; $[\mathrm{Cr(edta)(H_2O)_5}]^-$, 69531-93-7.

References and Notes

(1) K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

(2) See for example: (a) E. S. Gould and H. Taube, *Acc. Chem. Res.*, **2**, 321 (1969); (b) H. Ogino, K. Tsukahara, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 2743 (1976).

(3) A. H. Martin, A. Liang, and E. S. Gould, *Inorg. Chem.*, **15**, 1925 (1976), and references cited therein.

(4) Abbreviations used in this paper: EDTA, ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid; NTA, nitrilotriacetic acid; IDA, iminodiacetic acid. In $[\mathrm{Co(H}_n\mathrm{edta)(NH_3)_5}]^{(n-1)+}$, the EDTA is coordinated to the $[\mathrm{Co(NH_3)_5}]^{3+}$ moiety through an acetate arm.[5] In $[\mathrm{(NH_3)_5Co\{edtaM(H_2O)\}}]^{2+}$ (M = Co(III) or Cr(III)), the EDTA acts as a quinquedentate ligand for M and a unidentate ligand for the $[\mathrm{Co(NH_3)_5}]^{3+}$ moiety.[5]

(5) H. Ogino, K. Tsukahara, and N. Tanaka, *Inorg. Chem.*, **16**, 1215 (1977).

(6) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

(7) E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

(8) K. D. Kopple and R. R. Miller, *Inorg. Chem.*, **2**, 1204 (1963).

(9) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

(10) Under the present experimental conditions, the chromium(III)–EDTA which was produced is present as the equilibrium mixture of $[\mathrm{Cr(Hedta)(H_2O)}]$ and its conjugate base form, $[\mathrm{Cr(edta)(H_2O)}]^-$, because the value of $\mathrm{p}K_\mathrm{a}$ for the acid dissociation of $[\mathrm{Cr(Hedta)(H_2O)}]$ has been determined to be 1.8.[11] For simplicity, the chromium(III)–EDTA complex is expressed as $[\mathrm{Cr(edta)(H_2O)}]^-$ throughout the paper.

(11) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975).

(12) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

(13) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

(14) H. Ogino and J. Fujita, *Bull. Chem. Soc. Jpn.*, **48**, 1836 (1975).

(15) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

(16) R. D. Cannon and J. Gardiner, *J. Chem. Soc., Dalton Trans.*, 622 (1976).

(17) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

(18) P. B. Wood and W. C. E. Higginson, *J. Chem. Soc. A*, 1645 (1966).

(19) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

(20) J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, **7**, 2431 (1968).

Contribution from the Department of Chemistry,
University of Hong Kong, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. 23. Evidence for Dissociative Substitution Reactions of Some *trans*-Acido(isothiocyanato)(1,4,8,11-tetraazacyclotetradecane)iron(III) Complexes, *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^+$, $\mathrm{X}^- = \mathrm{NCS}^-$, $\mathrm{CH_2ClCOO}^-$, $\mathrm{CHCl_2COO}^-$, Cl^-, and Br^-

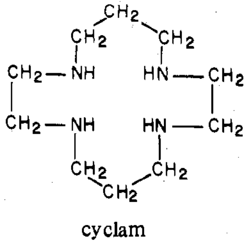
C. K. POON* and ANDREW W. M. TO

Received August 4, 1978

Mass-law retardation has been observed for the ligand substitution reactions of some low-spin *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^+$ complexes by thiocyanate (cyclam = 1,4,8,11-tetraazacyclotetradecane; $\mathrm{X}^- = \mathrm{CH_2ClCOO}^-$, $\mathrm{CHCl_2COO}^-$, Cl^-, Br^-) and *trans*-$[\mathrm{Fe(cyclam)(NCS)_2}]^+$ by a series of nucleophiles in aqueous acidic solution. These rate constants (k_{-x}) are strongly dependent on the nature of the leaving ligands but are independent of the nature and concentration of the entering groups. A plot of log k_{-x} against –log Q_x, where Q_x represents the corresponding aquation equilibrium constant, is linear over 5 logarithmic units with a slope of 1.00 ± 0.05. These results are fully consistent with a dissociative mechanism for the substitution reactions of these low-spin iron(III)–amine complexes.

Introduction

As part of our program to extend the studies of ligand-substitution kinetics and mechanisms of octahedral amine complexes to systems other than those of the extensively explored cobalt(III)[1–6] and chromium(III) systems,[6–10] we report here the reactions of some low-spin iron(III) complexes of the type *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^{n+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane; X = NCS^-, Cl^-, Br^-, $\mathrm{CH_2ClCOO}^-$, $\mathrm{CHCl_2COO}^-$, $\mathrm{H_2O}$).



cyclam

To date, there has been little systematic study on kinetics and mechanisms of ligand substitution reactions of octahedral iron(III)–amine complexes.[11] Swaddle[12] proposed that all trivalent transition-metal complexes, with the exception of cobalt(III) complexes which are well documented to react by a dissociative mechanism, underwent ligand substitution reactions by an associative mechanism. Recently, evidence has accumulated to support a dissociative mechanism for the acid hydrolysis of some amine complexes of chromium(III)[10] and ruthenium(III).[13] This paper presents some kinetic evidence to support a dissociative mechanism for the ligand substitution reactions of some low-spin iron(III)–amine complexes.

Experimental Section

Materials. The complexes *trans*-$[\mathrm{Fe(cyclam)X_2}]\mathrm{ClO_4}$ ($\mathrm{X}^- = \mathrm{NCS}^-$ and Cl^-) were prepared by published methods.[14] Sodium salts of $\mathrm{CH_2ClCOO}^-$ $\mathrm{CHCl_2COO}^-$, and $\mathrm{H_2PO_4}^-$ were prepared by neutralizing the corresponding acids with sodium hydroxide. Concentrations of ionic $\mathrm{CH_2ClCOO}^-$, $\mathrm{CHCl_2COO}^-$, and $\mathrm{H_2PO_4}^-$ were calculated from the known acid dissociation constants of these acids[15] ($\mathrm{p}K_\mathrm{a}$ = 2.86, 1.29, and 2.12, respectively).

Kinetics. The substitution reactions of *trans*-$[\mathrm{Fe(cyclam)(NCS)_2}]^+$ by various nucleophiles were followed spectrophotometrically in situ by using a Unicam SP8000 recording spectrophotometer fitted with

0020-1669/79/1318-1277$01.00/0

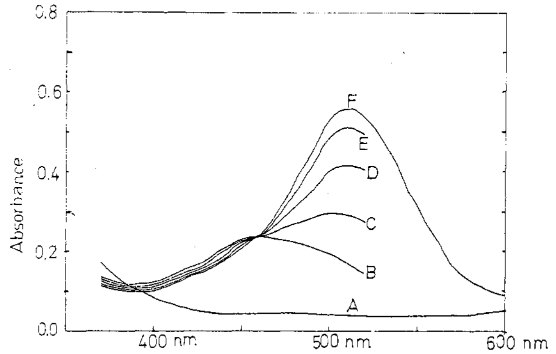


Figure 1. Spectral changes for the substitution reaction of *trans*-[Fe(cyclam)Cl_2]$^+$ by thiocyanate in the presence of a large excess of chloride: (A) initial spectrum; (B) the resulting spectrum immediately scanned after the mixing of reactants; (C–E) subsequent spectral changes; (F) the final spectrum which is identical with that of *trans*-[Fe(cyclam)$(NCS)_2$]$^+$.

a thermostated cell housing and a digital printer accessory, Weyfringe ADCP-2. Kinetic runs of the more rapid substitution reactions of *trans*-[Fe(cyclam)(NCS)X]$^+$ (X^- = CH_2ClCOO^-, $CHCl_2COO^-$, Cl^-, Br^-) by thiocyanate and anation reactions of *trans*-[Fe(cyclam)(NCS)(OH_2)]$^{2+}$ were monitored on an Aminco-Morrow stopped-flow spectrophotometer, equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. Experimental details on sampling, data collection, temperature control, and data treatment have been described previously.[16]

Physical Measurements. Visible and UV spectra of freshly prepared complex solutions were measured on a Unicam SP8000 spectrophotometer. Magnetic susceptibilities of complexes in D_2O were determined by the method of Deutsch and Poling[17] with a coaxial NMR tube and *tert*-butyl alcohol as a source of standard proton. NMR spectra were recorded on a 60-MHz Perkin-Elmer R-20 spectrometer.

Results

(1) Kinetics of Substitution Reactions of *trans*-[Fe(cyclam)(NCS)X]$^+$ by Thiocyanate (X^- = Cl^-, Br, CH_2ClOO^-, $CHCl_2COO^-$). When a solution of NaNCS was added to a cold acidic solution (pH 2) of *trans*-[Fe(cyclam)Cl_2]$^+$ containing a large excess of X^- (X^- = Cl^-, Br^-, CH_2ClCOO^-, $CHCl_2COO^-$), the absorbance of the visible spectrum instantaneously increased giving a peak at around 450 nm. This was followed by another relatively slower spectral change with a peak developing at 510 nm and an isosbestic point (X^- = Cl^-, 460 nm; X^- = Br^-, 470 nm; X^- = CH_2ClCOO^-, 462 nm; X^- = $CHCl_2COO^-$, 467 nm) maintained till the end of the reaction. The whole reaction was completed in a few seconds or minutes depending on the nature and concentration of X^- (Figure 1). The final spectrum was identical with that of an authentic sample of *trans*-[Fe(cyclam)$(NCS)_2$]$^+$. *trans*-[Fe(cyclam)Cl_2]$^+$ is very labile. Volhard titration confirmed that both chlorides were released as soon as the complex was dissolved in an acidic solution, giving *trans*-[Fe(cyclam)$(OH_2)_2$]$^{3+}$. In the presence of a large excess of X^-, the diaquo species would be immediately anated to *trans*-[Fe(cyclam)X_2]$^+$. The thiocyanate substitution reaction can be represented by eq 1 and 2, with reaction 1 much faster than reaction 2.

$$RX_2^+ + NCS^- \xrightarrow{\text{fast}} R(NCS)X^+ + X^- \quad (1)$$

$$R(NCS)X^+ + NCS^- \xrightarrow{\text{slow}} R(NCS)_2^+ + X^- \quad (2)$$

For simplicity, *trans*-[Fe(cyclam)AX]$^{n+}$ shall be written as RAX^{n+} in all subsequent equations in this paper.

These reactions were followed spectrophotometrically on an Amino-Morrow stopped-flow spectrophotometer. With a suitable choice of the sampling time, reaction 2 could be separately and conveniently followed at 510 nm. Standard semilogarithmic plots of log ($A_\infty - A_t$) against time were linear to 3 half-lives. Pseudo-first-order rate constants, k_{obsd}, are independent of complex concentration (5.0×10^{-5}–5.0×10^{-4} M), acid strength ($HClO_4$, 0.01–0.66 M), and ionic strength ($NaClO_4$, 0.15–1.26 M). Most of the reactions were followed at a constant acid strength of 0.01 M. These rate constants are, however, critically dependent on the concentration of both X^- and NCS^-. Experimental data are summarized in Table I.

Table I. Pseudo-First-Order Rate Constants, k_{obsd}, for the Substitution Reactions of *trans*-[Fe(cyclam)(NCS)X]$^+$ by NCS^- at 22.4 °C and at [H^+] = 0.01 M

X^-	[X^-]/M	[NCS^-]/M	$k_{obsd}{}^a$/s^{-1}
$CHCl_2COO^-$	0.078	0.033	0.031_0
	0.078	0.050	0.04_0
	0.078	0.10	0.058_0
	0.19	0.033	0.014_5
	0.19	0.050	0.020_5
	0.19	0.10	0.034_0
	0.25	0.033	0.012_0
	0.25	0.050	0.017_0
	0.25	0.10	0.030_0
CH_2ClCOO^-	0.035	0.033	0.019_0
	0.035	0.050	0.023_0
	0.035	0.10	0.030_0
	0.045	0.025	0.014_0
	0.083	0.050	0.016_5
	0.083	0.10	0.023_0
	0.14	0.050	0.011_0
	0.14	0.10	0.017_5
	0.21	0.033	0.0053_0
	0.21	0.050	0.0076_0
	0.21	0.10	0.013_0
Cl^-	0.10	0.050	0.95_0
	0.10	0.11	1.5_5
	0.20	0.050	0.57_0
	0.20	0.068	0.74_0
	0.20	0.11	1.0_5
	0.30	0.050	0.40_0
	0.30	0.068	0.52_0
	0.30	0.11	0.78_0
	0.50	0.068	0.34_0
	0.50	0.11	0.54_0
Br^-	0.50	0.033	2.1_0
	0.50	0.063	4.0_0
	0.50	0.10	6.3_0
	0.65	0.033	1.6_5
	0.65	0.050	2.3_0
	0.65	0.10	4.4_0
	0.65	0.25	9.2_5

[a] Values of k_{obsd} are independent of complex concentration (5.0×10^{-5}–5.0×10^{-4} M), acid strength (1.0×10^{-2}–6.6×10^{-1} M), and ionic strength (1.5×10^{-1}–1.26 M).

(2) Kinetics of Substitution Reactions of *trans*-[Fe(cyclam)$(NCS)_2$]$^+$ by X^{n-} (X^{n-} = Cl^-, Br^-, CH_2ClCOO^-, $H_2PO_4^-$, SO_4^{2-}). *trans*-[Fe(cyclam)$(NCS)_2$]$^+$ is very stable in dilute acid ($HClO_4$), and it is not possible to study the hydrolysis of this complex directly. In the presence of a large excess of X^{n-} (Cl^-, CH_2ClCOO^-, $H_2PO_4^-$, and SO_4^{2-}), the spectrum changed slowly, with the 510-nm peak gradually disappearing. The initial spectrum was identical with that of the starting *trans*-[Fe(cyclam)$(NCS)_2$]$^+$ while the final spectrum was the same as that of *trans*-[Fe(cyclam)X_2]$^{(3-2n)+}$ prepared by adding a large excess of X^{n-} to an acidic solution of *trans*-[Fe(cyclam)Cl_2]$^+$. These reactions can be represented by eq 3 and 4. The observation that the semilogarithmic plots of log ($A_t - A_\infty$) against time were linear to 3 half-lives suggested that

$$R(NCS)_2^+ + X^{n-} \xrightarrow{\text{slow}} R(NCS)X^{(2-n)+} + NCS^- \quad (3)$$

$$R(NCS)X^{(2-n)+} + X^{n-} \xrightarrow{\text{fast}} RX_2^{(3-2n)+} + NCS^- \quad (4)$$

Table II. Pseudo-First-Order Rate Constants, k_{obsd}, for the Reactions ([H$^+$] = 0.01 M)

trans-[Fe(cyclam)(NCS)$_2$]$^+$ + X^{n-} $\rightleftharpoons$ *trans*-[Fe(cyclam)(NCS)X]$^{(2-n)+}$ + NCS$^-$

X^{n-}	θ/°C	[X^{n-}]/M	[NCS$^-$]/M	$k_{obsd}{}^a$/s^{-1}	[R(NCS)$_2{}^+$]$_e$/ [R(NCS)X$^+$]$_e$	$k_{cor}{}^b$/s^{-1}
Cl$^-$	22.8	2.5	8.0×10^{-4}	$1.2_0 \times 10^{-3}$	2.1	3.9×10^{-4}
	22.8	3.0	8.0×10^{-4}	$9.7_0 \times 10^{-4}$	1.7	3.6×10^{-4}
	22.8	3.5	8.0×10^{-4}	$9.2_0 \times 10^{-4}$	1.4	3.8×10^{-4}
	22.8	4.8	8.0×10^{-4}	$8.1_0 \times 10^{-4}$	1.2	3.7×10^{-4}
	22.8	6.0	8.0×10^{-4}	$7.4_0 \times 10^{-4}$	1.0	3.7×10^{-4}
	22.8	4.0	1.0×10^{-3}	$1.0_5 \times 10^{-3}$	1.8	3.8×10^{-4}
	22.8	5.0	2.0×10^{-3}	$1.5_0 \times 10^{-3}$	3.2	3.6×10^{-4}
	22.8	9.0		$3.9_0 \times 10^{-4}$		
Br$^-$	22.8	5.7	1.6×10^{-4}	$1.1_0 \times 10^{-3}$	1.9	3.8×10^{-4}
CH$_2$ClCOO$^-$	22.8	1.9×10^{-1}	6.7×10^{-3}	$1.5_0 \times 10^{-3}$	3.0	3.8×10^{-4}
	22.8	5.2×10^{-1}		$3.7_0 \times 10^{-4}$		
SO$_4{}^{2-}$	22.8	4.0×10^{-1}		$4.0_0 \times 10^{-4}$		
H$_2$PO$_4{}^{-c}$	22.8	7.8×10^{-1}		$3.7_5 \times 10^{-4}$		
	29.7	2.1×10^{-1}		$1.0_5 \times 10^{-3}$		
	29.7	7.8×10^{-1}		$1.1_5 \times 10^{-3}$		
	29.7	2.0		$1.1_5 \times 10^{-3}$		
	36.6	7.8×10^{-1}		$3.2_5 \times 10^{-3}$		
	47.3	7.8×10^{-1}		$1.5_0 \times 10^{-2}$		
	47.3	1.41		$1.6_0 \times 10^{-2}$		

[a] Values of k_{obsd} are independent of complex concentration (5.0×10^{-5}–5.0×10^{-4} M), acid strength (0.01–0.20 M), and ionic strength (0.20–1.4 M); with the exception of those for X^{n-} = Cl$^-$, each entry represents an average of two or three independent determinations. [b] $k_{cor} = k_{obsd}/(1 + [\mathrm{R(NCS)_2}^+]_e/[\mathrm{R(NCS)X}^+]_e)$. [c] Activation parameters obtained from the least-squares plot of the Eyring equation of ln (k_{obsd}/T) against ($1/T$) are as follows: $\Delta H^{\ddagger} = 28.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 20 \pm 2$ cal K^{-1} mol^{-1}, $k_{22.4} = 3.5 \times 10^{-4}$ s^{-1}.

reaction 4 was much faster than reaction 3 and that the observed pseudo-first-order rate constant, k_{obsd}, should give the rate constant for reaction 3. These data (Table II) are independent of the nature and concentration of the entering ligand X^{n-}, complex concentration, acid strength (0.01–0.20 M), and ionic strength (0.2–1.4 M). When bromide was used as the entering ligand, however, the replacement of thiocyanate was not complete even at a 6.8 M bromide concentration. The persistence of a small absorption peak at 510 nm in the final spectrum, the absorbance of which depended inversely on the bromide concentration, suggested that the final solution still contained some coordinated isothiocyanato species. An isosbestic point was maintained throughout the entire reaction, but its position varied with the bromide concentration (e.g., at 452 nm for 6.0 M Br$^-$ and 1.0×10^{-4} M complex). These observations seemed to suggest that reaction 4 and possibly reaction 3 were reversible [i.e., eq 1 and 2 for X$^-$ = Br$^-$] and that both *trans*-[Fe(cyclam)(NCS)Br]$^+$ and *trans*-Fe(cyclam)Br$_2$]$^+$ were present in the final solution, the relative amounts of which depended on the bromide concentration. The reaction could be much simplified if a small amount of thiocyanate was introduced at the beginning of the reaction. As an example, if the reaction solution contained 1.0×10^{-4} M complex, 1.5×10^{-4} M thiocyanate, 5.6 M bromide, and 1.0×10^{-2} M HClO$_4$, the spectral change was just the reversed trace of that observed for the forward substitution reaction of *trans*-[Fe(cyclam)(NCS)Br]$^+$ by thiocyanate described previously in section (1), with an isobestic point maintained at 470 nm. The position of the isosbestic point became independent of the concentrations of bromide and thiocyanate introduced, provided that the thiocyanate concentration was greater than about 1.5×10^{-4} M. Below this thiocyanate concentration, the reaction would again become more complicated as if thiocyanate was not at all present. In other words, the substitution reaction of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ by a large excess of bromide could be made to reach an equilibrium mixture of *trans*-[Fe(cyclam)(NCS)Br]$^+$ and the starting complex (eq 5 which, in essence, is a combination of eq 3 and 2) by a suitable control of the amount of thiocyanate added.

$$\mathrm{R(NCS)_2}^+ + \mathrm{X}^- \rightleftharpoons \mathrm{R(NCS)X}^+ + \mathrm{NCS}^- \qquad (5)$$

Pseudo-first-order rate constants of approach to equilibrium, k_{obsd}, were obtained from the standard semilogarithmic plots which are linear to 3 half-lives. In order to determine the rate constant for the forward reaction of eq 5 (i.e., reaction 3), it became necessary to know the equilibrium composition of $[\mathrm{R(NCS)_2}^+]_e/[\mathrm{R(NCS)X}^+]_e$ with

$$\frac{[\mathrm{R(NCS)_2}^+]_e}{[\mathrm{R(NCS)X}^+]_e} = \frac{A_x - A_e}{A_e - A_{NCS}} \qquad (6)$$

where [complex]$_e$ represents the concentration of the corresponding complex at equilibrium, the A_{NCS}, A_e, and A_x represent, respectively for each kinetic run, the initial absorbance, absorbance at equilibrium, and the calculated absorbance of *trans*-[Fe(cyclam)(NCS)X]$^+$ if reaction 5 goes to completion to the right. In the absence of a pure sample of *trans*-[Fe(cyclam)(NCS)Br]$^+$, the value of A_{Br} (X$^-$ = Br$^-$) for a given value of A_{NCS} was determined indirectly by following reaction 2 at a sufficiently low temperature and then extrapolating the linear plot of log ($A_\infty - A_t$) against time to zero time (here $A_\infty = A_{NCS}$). Since reaction 2 was rather rapid, the average value of A_{Br} obtained at 510 nm ($A_{Br} = 0.25 A_{NCS}$) was only accurate to about 20%. Similarly, in the presence of an appropriate amount of added thiocyanate, the substitution reactions of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ by Cl$^-$ and CH$_2$ClCOO$^-$ could also be controlled to react according to eq 5 to an equilibrium mixture. The average values of A_x at 510 nm were determined in the same manner, but slightly more accurately, as that of A_{Br} ($A_{Cl} = 0.10 A_{NCS}$ and $A_{CH_2ClCOO} = 0.22 A_{NCS}$). All of the experimental results of k_{obsd} and $[\mathrm{R(NCS)_2}^+]_e/[\mathrm{R(NCS)X}^+]_e$, together with those of k_{cor}, where

$$k_{cor} = \frac{k_{obsd}}{1 + [\mathrm{R(NCS)_2}^+]_e/[\mathrm{R(NCS)X}^+]_e} \qquad (7)$$

are collected in Table II.

(3) Kinetics of Anation of *trans*-[Fe(cyclam)(NCS)(OH$_2$)]$^{2+}$ by NCS$^-$ and CHCl$_2$COO$^-$. In the absence of a pure sample of *trans*-[Fe(cyclam)(NCS)(OH$_2$)]$^{2+}$, this aquo complex was generated in solution together with a small amount of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ by adding NaNCS (about 1.2 equiv) to an acidic solution of *trans*-[Fe(cyclam)Cl$_2$]$^+$. Since *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ is unreactive relative to *trans*-

Table III. Observed Pseudo-First-Order Rate Constants k_{obsd} of the Reactions ($[\mathrm{H^+}] = 0.01$ M)
trans-$[\mathrm{Fe(cyclam)(NCS)(OH_2)}]^{2+} + \mathrm{X^-} \rightarrow$ *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^+ + \mathrm{H_2O}$

$\mathrm{X^-}$	θ/°C	I/M	$[\mathrm{X^-}]$/M	$k_{\mathrm{obsd}}{}^a$/ $\mathrm{s^{-1}}$	$B_{\mathrm{x}}{}^b$/$\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$
$\mathrm{NCS^-}$ ^{c}	17.8	0.56	0.025	1.1_5	47
		0.56	0.033	1.5_5	
		0.56	0.050	2.3_0	
		0.56	0.10	4.4_0	
	19.8	0.56	0.025	1.4_0	58
		0.56	0.033	1.9_0	
		0.56	0.050	2.8_0	
		0.56	0.10	5.1_5	
	20.6	0.56	0.025	1.5_0	62
		0.56	0.033	2.0_0	
		0.56	0.050	2.9_5	
		0.56	0.10	5.5_5	
	22.0	0.56	0.025	1.8_0	73
		0.56	0.033	2.3_5	
		0.56	0.050	3.4_5	
		0.56	0.10	6.8_5	
		0.56	0.15	$10._5$	
		1.0	0.10	6.1_0	
		0.92	0.10	6.2_0	
		0.79	0.10	6.1_5	
		0.65	0.10	6.4_0	
		0.38	0.10	7.2_5	
		0.29	0.10	7.6_0	
		0.20	0.10	8.6_0	
		0.11	0.10	$10._0$	
	24.9	0.56	0.025	2.4_5	100
		0.56	0.033	3.2_0	
		0.56	0.050	4.6_5	
		0.56	0.10	9.5_0	
	27.2	0.56	0.025	3.1_5	129
		0.56	0.033	4.1_5	
		0.56	0.050	6.3_0	
		0.56	0.10	$12._0$	
$\mathrm{CHCl_2COO^-}$	22.4	0.56	0.025	1.7_0	71
		0.56	0.033	2.3_5	
		0.56	0.050	3.4_0	
		0.56	0.25	$14._5$	
		0.56	0.50	$22._0$	

[a] Values of k_{obsd} are independent of complex concentration (5.0×10^{-5}–5.0×10^{-4} M) and acid strength (0.01–0.40 M). [b] $B_{\mathrm{x}} = k_{\mathrm{x}}K_{\mathrm{x}}$. [c] Activation parameters deduced from the Eyring plot are as follows: $\Delta H^{\ddagger} = 18.3 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = 12 \pm 2$ cal K^{-1} mol^{-1}, and $k_{22.4} = 77$ M^{-1} s^{-1}.

Table IV. Summary of Rate Constants for the Substitution Reactions of *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^+$ by $\mathrm{NCS^-}$ and the Corresponding Anation Reactions at 22.4 °C, $[\mathrm{H^+}] = 0.01$ M, and $I = 0.56$ M

$\mathrm{X^-}$	$k_{-\mathrm{x}}{}^a$/$\mathrm{s^{-1}}$	$B_{\mathrm{x}}{}^b$/ $\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$	$k_{\mathrm{x}}K_{\mathrm{x}}$/ k_{NCS}· $K_{\mathrm{NCS}}{}^a$	$k_{\mathrm{x}}K_{\mathrm{x}}{}^c$/ $\mathrm{M^{-1}}$ $\mathrm{s^{-1}}$	$Q_{\mathrm{x}}{}^d$/M
$\mathrm{NCS^-}$	3.5×10^{-4}	77			4.5×10^{-6} ^{e}
$\mathrm{CH_2ClCOO^-}$	4.4×10^{-2}		1.1_4	88	5.0×10^{-4}
$\mathrm{CHCl_2COO^-}$	1.0×10^{-1}	71	1.0_2	79	1.4×10^{-3} ^{e}
$\mathrm{Cl^-}$	3.2		1.1_6	89	3.6×10^{-2}
$\mathrm{Br^-}$	4.2×10		1.2_5	96	4.4×10^{-1}

[a] Values of $k_{-\mathrm{x}}$ and $k_{\mathrm{x}}K_{\mathrm{x}}/k_{\mathrm{NCS}}K_{\mathrm{NCS}}$ ($\mathrm{X^-} = \mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{CH_2ClCOO^-}$, $\mathrm{CHCl_2COO^-}$) were deduced from the linear plots of $1/k_{\mathrm{obsd}}$ against $[\mathrm{X^-}]/[\mathrm{NCS^-}]$ according to eq 26 using data of Table I; $k_{-\mathrm{x}}$ ($\mathrm{X^-} = \mathrm{NCS^-}$) was obtained by extrapolation of data from Table II using Eyring's equation. [b] Values of B_{x} ($=k_{\mathrm{x}}K_{\mathrm{x}}$) were determined directly from anation reactions (Table III). [c] Values of $k_{\mathrm{x}}K_{\mathrm{x}}$ were obtained by multiplying corresponding values of $k_{\mathrm{x}}K_{\mathrm{x}}/k_{\mathrm{NCS}}K_{\mathrm{NCS}}$ by B_{NCS} (77 M^{-1} s^{-1}). [d] $Q_{\mathrm{x}} = k_{-\mathrm{x}}/k_{\mathrm{x}}K_{\mathrm{x}}$. [e] These values were obtained from $k_{-\mathrm{x}}/B_{\mathrm{x}}$.

$[\mathrm{Fe(cyclam)(NCS)(OH)_2}]^{2+}$, its presence would not affect the kinetic studies of the aquo complex. The anation reactions were studied at a fixed wavelength (510 nm for $\mathrm{NCS^-}$ and 540 nm for $\mathrm{CH_2ClCOO^-}$) with an Amino-Morrow stopped-flow spectrophotometer. Ionic strength was adjusted constant with $\mathrm{NaClO_4}$. Pseudo-first-order rate constants, k_{obsd}, determined in the usual manner from semilogarithmic plots which are linear to 3 half-lives, are collected in Table III. These rate constants are dependent on the ionic strength of the solution, and most reactions were studied at $I = 0.56$ M. Occasionally, when thiocyanate was used as the entering ligand, the reaction was started directly on an acidic solution of *trans*-$[\mathrm{Fe(cyclam)Cl_2}]^+$. The first step leading to the formation of *trans*-$[\mathrm{Fe(cyclam)(NCS)(OH_2)}]^{2+}$ was so fast that it became totally separated from the second step which could then be followed accurately. The rate constants obtained agreed well with those determined on a mixture of *trans*-$[\mathrm{Fe(cyclam)(NCS)(OH_2)}]^{2+}$ and *trans*-$[\mathrm{Fe(cyclam)(NCS)_2}]^+$. Anation reactions by other ligands, such as $\mathrm{Cl^-}$, Br, and $\mathrm{CH_2ClCOO^-}$, could not be accurately followed because of the relatively very small spectral change. However, a rough estimate of their reactions showed that their second-order rate constants at a relatively low concentration of the nucleophile are rather similar to each other and also to those which have been accurately determined.

Discussion

The complexes *trans*-$[\mathrm{Fe(cyclam)(NCS)_2}]^+$ and *trans*-$[\mathrm{Fe(cyclam)Cl_2}]^+$ have been shown by magnetic measurement[14] as well as by ESR study[18] to be low spin. However, *trans*-$[\mathrm{Fe(cyclam)Br_2}]^+$ is in a state of high-spin–low-spin equilibrium with about 71% low spin at 20 °C.[14,18] *trans*-$[\mathrm{Fe(cyclam)X_2}]^+$ ($\mathrm{X^-} = \mathrm{CH_2ClCOO^-}$ and $\mathrm{CHCl_2COO^-}$) and *trans*-$[\mathrm{Fe(cyclam)(NCS)(OD_2)}]^{2+}$ (in the presence of a small amount of *trans*-$[\mathrm{Fe(cyclam)(NCS)_2}]^+$), prepared by adding a large excess of $\mathrm{X^-}$ and about 1.2 equiv of $\mathrm{NCS^-}$, respectively, to an acidic $\mathrm{D_2O}$ solution of *trans*-$[\mathrm{Fe(cyclam)Cl_2}]^+$, have also been shown by the method of NMR to be low spin. Since thiocyanate ion is much higher up in the spectrochemical series than all other ligands $\mathrm{X^-}$ in the present study, it is quite safe to conclude that all of these acidoisothiocyanato complexes *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^{n+}$ (X = Cl, Br, $\mathrm{CH_2ClCOO}$, $\mathrm{CHCl_2COO}$, NCS, $\mathrm{OH_2}$) under investigation here are low spin. Probably the assignment of a low-spin state to *trans*-$[\mathrm{Fe(cyclam)(NCS)Br}]^+$ may be less certain in view of the equilibrium spin state of the dibromo complex. However, the high-spin component in the dibromo complex is only about 30%. It seems not unreasonable to assume that the average ligand field in *trans*-$[\mathrm{Fe(cyclam)(NCS)Br}]^+$ is strong enough to make the complex low spin. In any case, the similarity in the kinetic behavior of this complex with that of other *trans*-$[\mathrm{Fe(cyclam)(NCS)X}]^+$ complexes strongly endorses that it is also low spin.

The kinetic behavior of the anation reactions of *trans*-$[\mathrm{Fe(cyclam)(NCS)(OH_2)}]^{2+}$ by $\mathrm{NCS^-}$ and $\mathrm{CHCl_2COO^-}$ is very similar to that of most aquo(amine)cobalt(III) complexes[2,19] in which the observed rate constant, k_{obsd}, depends on the concentration of the entering anion according to eq 8, where B_{x} and C_{x} are two proportionality constants

$$k_{\mathrm{obsd}} = B_{\mathrm{x}}[\mathrm{X^-}]/(1 + C_{\mathrm{x}}[\mathrm{X^-}]) \tag{8}$$

(Figure 2), or eq 9 in the reciprocal from (Figure 3). This

$$\frac{1}{k_{\mathrm{obsd}}} = \frac{C_{\mathrm{x}}}{B_{\mathrm{x}}} + \frac{1}{B_{\mathrm{x}}}\,\frac{1}{[\mathrm{X^-}]} \tag{9}$$

type of kinetic behavior has been explained[2,18] either in terms of a dissociative mechanism with extensive mass-law retardation by solvent water, i.e., eq 10–12,

$$\mathrm{R(NCS)(OH_2)^{2+}} \xrightarrow[\text{slow}]{k_1} \mathrm{R(NCS)^{2+}} + \mathrm{H_2O} \tag{10}$$

$$R(NCS)^{2+} + H_2O \xrightarrow[\text{fast}]{k_{-1}} R(NCS)(OH_2)^{2+} \qquad (11)$$

$$R(NCS)^{2+} + X^- \xrightarrow[\text{fast}]{k_2} R(NCS)X^+ \qquad (12)$$

or in terms of an ion-pair mechanism involving a slow ligand interchange between the coordinated water and the entering anion in the ion pair, i.e., eq 13 and 14. The rate law for the

$$R(NCS)(OH_2)^{2+} + X^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \{R(NCS)(OH_2)^{2+}\cdots X^-\} \qquad (13)$$

$$\{R(NCS)(OH_2)^{2+}\cdots X^-\} \xrightarrow[\text{slow}]{k} R(NCS)X^+ + H_2O \qquad (14)$$

dissociative competition mechanism is (15) or (16) and that for the ion-pair mechanism is (17) or (18). Kinetically it is

$$k_{\text{obsd}} = \frac{k_1k_2[X^-]}{k_{-1}[H_2O] + k_2[X^-]} \qquad (15)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k_{-1}[H_2O]}{k_1k_2}\,\frac{1}{[X^-]} \qquad (16)$$

$$k_{\text{obsd}} = \frac{kK[X^-]}{1 + K[X^-]} \qquad (17)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k} + \frac{1}{kK}\,\frac{1}{[X^-]} \qquad (18)$$

not possible to distinguish between these two mechanisms. In accordance with the dissociative mechanism, $B_x = k_1k_2/k_{-1}[H_2O]$ and $C_x = k_2/k_{-1}[H_2O]$. The observation that these B_x values (also see Discussion later) and, hence, the k_2 values are independent of the nature of the entering anions X$^-$ implies that the five-coordinate intermediate [Fe(cyclam)(NCS)]$^{2+}$ is very short-lived and that it cannot differentiate among various anions X$^-$. Then for the ion-pair mechanism, $B_x = kK$ and $C_x = K$ = 0.6 and 0.9 M^{-1} at 22 °C for X$^-$ = NCS$^-$ and $CHCl_2COO^-$, respectively.[20] These ion-pair association constants seem reasonable for a 2:1 electrolyte in water.[21-24] The independence of B_x (i.e., k_xK_x) on the nature of X$^-$ is also consistent with a dissociative interchange rate constant k_x within various ion pairs of the same charge nature.[25]

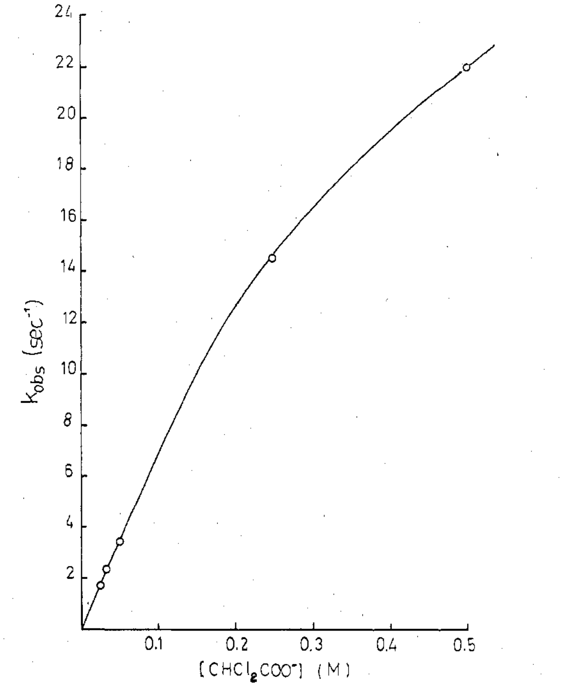


Figure 2. Plot of k_{obsd} against [$CHCl_2COO^-$] for the anation of *trans*-[Fe(cyclam)(NCS)(OH$_2$)]$^{2+}$ by $CHCl_2COO^-$ at [H$^+$] = 0.01 M, I = 0.56 M, and at 22.4 °C.

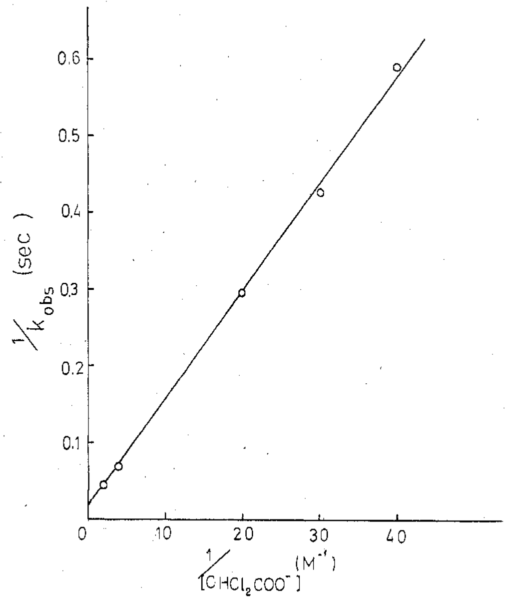


Figure 3. Plot of $1/k_{\text{obsd}}$ against $1/[CHCl_2COO^-]$ for the reaction of Figure 2.

The observation of mass-law retardation for the substitution reactions of *trans*-[Fe(cyclam)(NCS)X]$^+$ (X$^-$ = Cl$^-$, Br$^-$, CH_2ClCOO^-, $CHCl_2COO^-$) by thiocyanate strongly suggests that these reactions are clearly not of the classical bimolecular type. The observed pseudo-first-order rate constants, k_{obsd} (Table I), are dependent on the concentration of X$^-$ and NCS$^-$ according to eq 19 (Figure 4), where D an E are proportionality constants.

$$1/k_{\text{obsd}} = D + E[X^-]/[NCS^-] \qquad (19)$$

tionality constants. This kind of kinetic behavior is consistent with a competitive mechanism described by eq 20–24. The

$$R(NCS)X^+ + H_2O \xrightarrow[\text{slow}]{k_{-x}} R(NCS)(OH_2)^{2+} + X^- \qquad (20)$$

$$R(NCS)OH_2^{2+} + X^- \underset{\text{very fast}}{\overset{K_x}{\rightleftharpoons}} \{R(NCS)OH_2^{2+}\cdots X^-\} \qquad (21)$$

$$\{R(NCS)OH_2^{2+}\cdots X^-\} \xrightarrow[\text{fast}]{k_x} R(NCS)X^+ + H_2O \qquad (22)$$

$$R(NCS)OH_2^{2+} + NCS^- \underset{\text{very fast}}{\overset{K_{NCS}}{\rightleftharpoons}} \{R(NCS)OH_2^{2+}\cdots NCS^-\} \qquad (23)$$

$$\{R(NCS)OH_2^{2+}\cdots NCS^-\} \xrightarrow[\text{fast}]{k_{NCS}} R(NCS)_2^+ + H_2O \qquad (24)$$

pseudo-first-order rate constant, k_{obsd}, for the formation of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ is then given by eq 25 or 26 (see Appendix). A plot of $1/k_{\text{obsd}}$ against [X$^-$]/[NCS$^-$], therefore,

$$k_{\text{obsd}} = \frac{k_{-x}k_{NCS}K_{NCS}[NCS^-]}{k_xK_x[X^-] + k_{NCS}K_{NCS}[NCS^-]} \qquad (25)$$

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_{-x}} + \frac{k_xK_x}{k_{-x}k_{NCS}K_{NCS}}\,\frac{[X^-]}{[NCS^-]} \qquad (26)$$

yields k_{-x} and $k_xK_x/k_{NCS}K_{NCS}$. If we equate $k_{NCS}K_{NCS}$ with the value of B_{NCS} determined independently from the anation reaction, it is possible to calculate the values of other k_xK_x's. Unfortunately, it was not possible to determine the separate values of k_x and K_x from the present experimental studies. All of these data are collected in Table IV. To endorse the reliability of the k_xK_x values so determined and the accept-

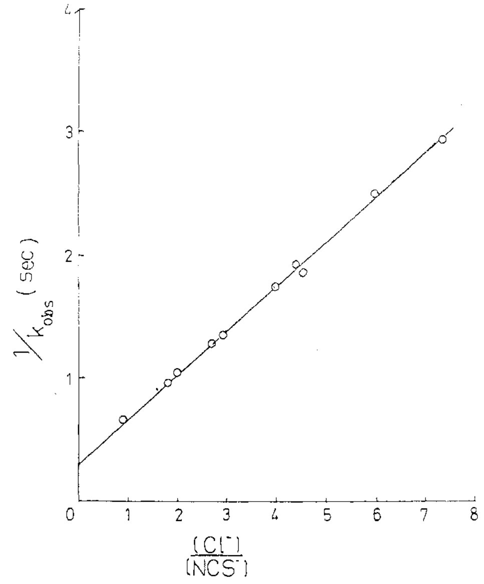


Figure 4. Plot of $1/k_{obsd}$ against $[Cl^-]/[NCS^-]$ for the substitution reaction of *trans*-[Fe(cyclam)(NCS)Cl]$^+$ by NCS^- in the presence of excess Cl^- at $[H^+]$ = 0.01 M and 22.4 °C.

ability of the proposed mechanism, the value $k_{CHCl_2COO}K_{CHCl_2COO}$ determined here is found to agree very well with the value of B_{CHCl_2COO} determined directly from the anation study. Although an accurate determination of other B_x values (X = Cl, Br, CH_2ClCOO) from direct anation study has not been successful, the order of magnitude of the constants estimated also agrees with the k_xK_x values determined here from the competition ratios.

The substitution reactions of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ by X^{n-} (X^{n-} = Cl^-, Br^-, CH_2ClCOO^-, $H_2PO_4^-$, SO_4^{2-}) appear to be a bit complicated; but they can still be explained by essentially the same mechanism discussed above. In the presence of a large excess of X^{n-} and in the absence of any added thiocyanate ion (other than those released from the original *trans*-[Fe(cyclam)(NCS)$_2$]$^+$), *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ goes completely to *trans*-[Fe(cyclam)X$_2$]$^{(3-2n)+}$ according to eq 3 and 4 with the rate-determining step $k_{-NCS} = k_{obsd}$. The observation that k_{obsd} is independent of the nature and concentration of X^{n-} (Table II, X^{n-} = Cl^-, CH_2ClCOO^-, $H_2PO_4^-$, and SO_4^{2-}) at 22.8 °C strongly supports the above deliberation. On the other hand, in the presence of a suitable amount of added thiocyanate ion as well as a large excess of X^{n-}, the substitution reaction of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ by X^{n-} approaches an equilibrium mixture of *trans*-[Fe(cyclam)(NCS)$_2$]$^+$ and *trans*-[Fe(cyclam)(NCS)X]$^+$ (X^{n-} = X^- for Br^-, Cl^-, and CH_2ClCOO^-), as given by eq 5, with the observed rate constant, k_{obsd}, given by eq 27 (see Appendix).

$$\frac{1}{k_{cor}} = \frac{1 + [R(NCS)_2{}^+]_e/[R(NCS)X]_e}{k_{obsd}} = \frac{1}{k_{-NCS}} + \frac{k_{NCS}K_{NCS}}{k_{-NCS}k_xK_x}\,\frac{[NCS^-]}{[X^-]} \qquad (27)$$

Experimentally, the effective ratio of $[NCS^-]/[X^-]$ to stop the reaction scheme from proceeding beyond reaction 3 (i.e., maintain an equilibrium of eq 5) is of the order of 10^{-2}–10^{-4} for X^- = CH_2ClCOO^-, Cl^-, and Br^-. Since $k_{NCS}K_{NCS}/k_xK_x$ is approximately unity, the second term on the right of eq 27 is negligibly small compared with the first term. Equation 27 is thus simplied to eq 28. It is clear from Table II that although individual k_{obsd} varies with the concentration of NCS^- and X^-, the corrected k_{cor} values become independent of the nature and concentration of X^- and NCS^-. Furthermore, according to eq 28 these k_{cor} values, indeed, agree very well with other k_{-NCS} values determined previously in the absence of added thiocyanate.

$$k_{cor} = \frac{k_{obsd}}{1 + [R(NCS)_2{}^+]_e/[R(NCS)X^+]_e} = k_{-NCS} \qquad (28)$$

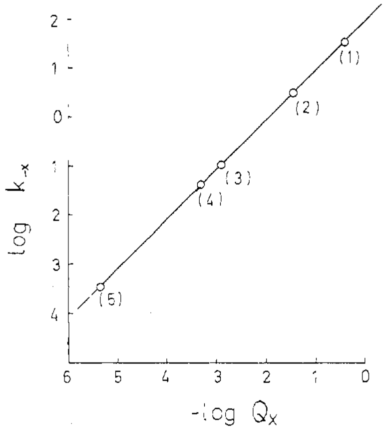


Figure 5. Plot of log k_{-x} against $-\log Q_x$ for the reaction *trans*-[Fe(cyclam)(NCS)X]$^+$ + H_2O ⇌ *trans*-[Fe(cyclam)(NCS)(OH$_2$)]$^{2+}$ + X^- at $[H^+]$ = 0.01 M, I = 0.56 M, and 22.4 °C. The numbers in parentheses indicate X: (1) Br, (2) Cl, (3) $CHCl_2COO$, (4) CH_2ClOO, (5) NCS.

As a summary, the foregoing discussion of various substitution reactions can be collectively presented in terms of reaction 29 (X^- = Cl^-, Br^-, $CHCl_2COO^-$, CH_2ClCOO^-, NCS^-).

$$trans\text{-}[Fe(cyclam)(NCS)X]^+ + H_2O \rightleftharpoons trans\text{-}[Fe(cyclam)(NCS)(OH_2)]^{2+} + X^- \qquad (29)$$

In the absence of authentic samples of *trans*-[Fe(cyclam)(NCS)X]$^+$ the thermodynamic equilibrium constants for reaction 29 cannot be directly determined. However, it has been demonstrated[10,19] in many cases that these equilibrium constants, Q_x, could be fairly reliably given by the ratio k_{-x}/k_xK_x. These relevant data are collected in Table IV. A plot of log k_{-x} against $-\log Q_x$, as shown in Figure 5, is linear over five logarithmic units with a slope of 1.00 ± 0.05. Following previous arguments for pentaammine complexes of cobalt(III)[26,27] and chromium(III),[10] such a linear free energy relationship implies that the leaving ligand X^- in the aquation reaction (29) is at most weakly bound to the iron(III) center in the transition state.

Acknowledgment. We thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for financial support and Professor M. L. Tobe for helpful discussion.

Appendix

Consider a series of reactions represented by eq A-1 to A-6

$$RX + H_2O \xrightarrow{k_{-x}} ROH_2 + X \qquad (A\text{-}1)$$

$$ROH_2 + X \overset{K_x}{\rightleftharpoons} \{ROH_2\cdots X\} \qquad (A\text{-}2)$$

$$\{ROH_2\cdots X\} \xrightarrow{k_x} RX + H_2O \qquad (A\text{-}3)$$

$$ROH_2 + Y \overset{K_Y}{\rightleftharpoons} \{ROH_2\cdots Y\} \qquad (A\text{-}4)$$

$$\{ROH_2\cdots Y\} \xrightarrow{k_Y} RY + H_2O \qquad (A\text{-}5)$$

$$RY + H_2O \xrightarrow{k_{-Y}} ROH_2 + Y \qquad (A\text{-}6)$$

(neglecting charges on the complexes) with the following assumptions: (a) [X] and [Y] are much greater than [RX] an [RY]; (b) [ROH_2] remains very small. According to assumption (b), the steady-state approximation of d[ROH_2]/dt = 0 is applicable; then

$$\frac{d[ROH_2]}{dt} = k_{-x}[RX] + k_{-Y}[RY] - \frac{k_xK_x[X][ROH_2]}{1 + K_x[X] + K_Y[Y]} - \frac{k_YK_Y[Y][ROH_2]}{1 + K_x[X] + K_Y[Y]} = 0$$

Thus

$$[ROH_2] = \frac{(k_{-x}[RX] + k_{-Y}[RY])(1 + K_x[X] + K_Y[Y])}{k_xK_x[X] + k_YK_Y[Y]} \qquad \text{(A-7)}$$

If we apply the concentration conditions:

$$\text{at } t = 0,\ [RX] = a,\ [RY] = 0$$

$$\text{at } t = t,\ [RX] = a - x,\ [RY] = x$$

$$\text{at } t = \infty,\ [RX] = [RX]_e = a - x_e,\ [RY] = [RY]_e = x_e$$

then

$$\begin{aligned}\frac{d[RY]}{dt} = \frac{dx}{dt} &= \frac{k_YK_Y[Y][ROH_2]}{1 + K_x[X] + K_Y[Y]} - k_{-Y}x \\ &= \frac{k_YK_Y[Y]\{k_{-x}(a - x) + k_{-Y}x\}}{k_xK_x[X] + k_YK_Y[Y]} - k_{-Y}x \\ &= C\{k_{-x}(a - x) + k_{-Y}x\} - k_{-Y}x \\ &= (Ck_{-Y} - Ck_{-x} - k_{-Y})x + Ck_{-x}a \qquad \text{(A-8)}\end{aligned}$$

where

$$C = \frac{k_YK_Y[Y]}{k_xK_x[X] + k_YK_Y[Y]} = \text{a constant} \qquad \text{(A-9)}$$

Also at $t = \infty$

$$d[RX]/dt = d[RY]/dt = 0 \qquad \text{(A-10)}$$

Thus

$$x_e = \frac{Ck_{-x}a}{k_{-Y} + Ck_{-x} - Ck_{-Y}} \qquad \text{(A-11)}$$

Then (A-8) becomes

$$dx/dt = (x_e - x)(k_{-Y} + Ck_{-x} - Ck_{-Y})$$

After integration and application of suitable boundary conditions

$$\ln [(x_e - x)/x_e] = -(k_{-Y} + Ck_{-x} - Ck_{-Y})t$$

The specific first-order rate constant for approach to equilibrium, k_{obsd}, is then given by

$$\begin{aligned}k_{obsd} &= k_{-Y} + Ck_{-x} - Ck_{-Y} \\ &= \frac{k_{-x}k_YK_Y[Y] + k_{-Y}k_xK_x[X]}{k_YK_Y[Y] + k_xK_x[X]} \qquad \text{(A-12)}\end{aligned}$$

Now

$$\frac{[RX]_e}{[RY]_e} = \frac{a - x_e}{x_e}$$

From (A-11)

$$\begin{aligned}\frac{[RX]_e}{[RY]_e} &= \frac{(1 - C)k_{-Y}}{Ck_{-x}} \\ &= \frac{k_{-Y}k_xK_x[X]}{k_{-x}k_YK_Y[Y]} \qquad \text{(A-13)}\end{aligned}$$

Rearranging (A-12)

$$\begin{aligned}k_{obsd} &= \frac{1 + \dfrac{k_{-Y}k_xK_x[X]}{k_{-x}k_YK_Y[Y]}}{\dfrac{1}{k_{-x}} + \dfrac{k_xK_x[X]}{k_{-x}k_YK_Y[Y]}} \\ &= \frac{1 + \dfrac{[RX]_e}{[RY]_e}}{\dfrac{1}{k_{-x}} + \dfrac{k_xK_x[X]}{k_{-x}k_YK_Y[Y]}} \qquad \text{(A-14)}\end{aligned}$$

or the "corrected rate constant", k_{cor}, is given by (A-15) In

$$\frac{1}{k_{cor}} = \frac{1 + [RX]_e/[RY]_e}{k_{obsd}} = \frac{1}{k_{-x}} + \frac{k_xK_x[X]}{k_{-x}k_YK_Y[Y]} \qquad \text{(A-15)}$$

the special case when reaction A-6 is relatively very slow compare to reactions A-1 to A-5, i.e., for an essentially nonreversible competing reaction leading to the formation of RY, eq A-8 is simplified to eq A-16

$$dx/dt = Ck_{-x}(a - x) \qquad \text{(A-16)}$$

with

$$k_{obsd} = \frac{k_{-x}k_YK_Y[Y]}{k_xK_x[X] + k_YK_Y[Y]} \qquad \text{(A-17)}$$

Registry No. *trans*-[Fe(cyclam)(NCS)($CHCl_2COO$)]$^+$, 69238-71-7; *trans*-[Fe(cyclam)(NCS)(CH_2ClCOO)]$^+$, 69238-72-8; *trans*-[Fe(cyclam)(NCS)Cl]$^+$, 69238-73-9; *trans*-[Fe(cyclam)(NCS)Br]$^+$, 69238-74-0; NCS^-, 302-04-5; *trans*-[Fe(cyclam)($NCS)_2$]$^+$, 60105-31-9; Cl^-, 16887-00-6; Br^-, 24959-67-9; CH_2ClCOO^-, 14526-03-5; SO_4^{2-}, 14808-79-8; $H_2PO_4^-$, 14066-20-7; *trans*-[Fe(cyclam)(NCS)(OH_2)]$^{2+}$, 69238-75-1; *trans*-[Fe(cyclam)Cl_2]$^+$, 60105-27-3; $CHCl_2COO^-$, 13425-80-4.

References and Notes

(1) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, 1966.
(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967.
(3) M. L. Tobe, *Acc. Chem. Res.*, **3**, 377 (1970).
(4) C. K. Poon, *Inorg. Chim. Acta, Rev.*, **4**, 123 (1970).
(5) C. K. Poon, *Coord. Chem. Rev.*, **10**, 1 (1973).
(6) C. H. Langford and V. S. Sastri, "Reaction Mechanisms in Inorganic Chemistry", M. L. Tobe, Ed., Butterworths, London, 1972, Chapter 6.
(7) C. S. Garner and D. A. House, *Transition Met. Chem.*, **6**, 61 (1970).
(8) E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, **9**, 1781 (1970).
(9) W. G. Jackson, P. D. Vowles, an W. W. Fee, *Inorg. Chim. Acta*, **19**, 221 (1976).
(10) T. Ramasami and A. G. Sykes, *Inorg. Chem.*, **15**, 2885 (1976).
(11) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **47**, 11 (1974).
(12) T. W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
(13) C. K. Poon and D. A. Isabirye, *J. Chem. Soc., Dalton Trans.*, 2115 (1977).
(14) P. K. Chan and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 858 (1976).
(15) "Handbook of Chemistry and Physics", R. C. Weast, Ed., 48th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1967, p D-90.
(16) C. K. Poon and P. W. Mak, *J. Chem. Soc., Dalton Trans.*, 216 (1978).
(17) J. L. Deutsch an S. M. Poling, *J. Chem. Educ.*, **46**, 167 (1969).
(18) A. Desideri, J. B. Raynor, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2051 (1977).
(19) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).
(20) K = intercept/slope from the linear plot of $1/k_{obsd}$ against $1/[X^-]$.
(21) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).
(22) J. A. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956).
(23) O. Nor and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1232 (1973).
(24) S. C. Chan, *J. Chem. Soc. A*, 1124 (1966).
(25) C. H. Langford and W. R. Muir, *J. Am. Chem. Soc.*, **89**, 3141 (1967).
(26) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).
(27) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).