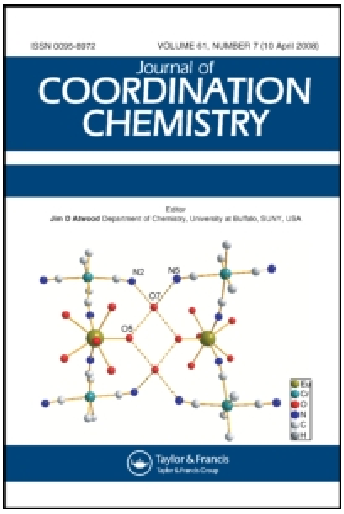

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KINETICS AND MECHANISM OF ANATION OF *CIS*-TETRAAMMINEDIAQUACOBALT(III) BY THIOCYANATE

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The anation of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with NCS^- has been studied at 40–60°. The reaction proceeds in a stepwise manner leading to the formation of *cis*-$[Co(NH_3)_4(NCS)_2]^+$. Under pseudo-first-order conditions having $[NCS^-]$, = 0.05–0.5 M, pH = 2.00 and I = 0.51 M ($NaClO_4$), the following rate law is obeyed for each step, $k_{obs} = k_0 + k[NCS^-]$, where k_0 is the rate constant for the reverse (aquation) reaction and k is the second-order anation rate constant. The activation enthalpy and entropy values corresponding to k_1, k_2, $k_0{}^{I}$ and $k_0{}^{II}$ paths are $\Delta H_1{}^{\neq} = 143 \pm 7$ kJ mol^{-1}, $\Delta S_1{}^{\neq} = 141 \pm 11$ J K^{-1} mol^{-1}, $\Delta H_2{}^{\neq} = 111 \pm 6$ kJ mol^{-1}, $\Delta S_2{}^{\neq} = 29 \pm 8$ J K^{-1} mol^{-1}, $\Delta H_0{}^{I\neq} = 102 \pm 7$ kJ mol^{-1}, $\Delta S_0{}^{I\neq} = 3 \pm 5$ J K^{-1} mol^{-1}, $\Delta H_0{}^{II\neq} = 91 \pm 8$ kJ mol^{-1} and $\Delta S_0{}^{II\neq} = -58 \pm 7$ J K^{-1} mol^{-1}, respectively. The first-step reaction rate shows a strong inverse dependence on $[H^+]$ indicating that the base form of the complex, *cis*-$[Co(NH_3)_4(OH)(H_2O)]^{2+}$, is some 10^3 times more reactive than the conjugate acid form, *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$. Within experimental error the second-step reaction rate is found to be pH independent in the pH range covered (2.00–3.36). At high ionic strength (*I* = 2.01 M), ion pairing occurs which is revealed from the tendency towards rate saturation at high $[NCS^-]$. The reaction is believed to operate through an I_d mechanism.

INTRODUCTION

Anation reactions of $[Co(NH_3)_5H_2O]^{3+}$ have been studied for a variety of entering ligands during the last few years.[1,2] These reactions are considered to proceed through a disssociative interchange (I_d) mechanism. Kinetic investigations on substitution reactions of the *cis*-tetraamminediaquacobalt(III) complex with either mono- or bidentate ligands have, however, rarely been studied except for a few recent reports.[3,4] In an attempt to better understand the reaction patterns of a diaquacobalt(III) complex, the present study was undertaken. For a complex like this two kinetically distinct steps are expected and the entering nucleophile may play some significant role depending on its electron donating or withdrawing power towards the substrate. Another interesting feature which could have been observed here is the unusually large *cis*-labilisation effect by hydroxide ion as has been detected in several thiocyanate anation reactions of diaquachromium(III) complexes.[5,6]

EXPERIMENTAL

Materials

Cis-tetraamminediaquacobalt(III) perchlorate was prepared following the method described in the literature[7] and its purity was checked by elemental and spectral analyses. Recrystallised sodium thiocyanate was used. Ionic strength was held constant by using appropriate amounts of recrystallised sodium perchlorate. All other chemicals were of 'AnalaR'or extrapure grade. All pH measurements were made with a digital Beckman pH meter (model 4500).

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Kinetics

The spectral changes observed during the reaction of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with NCS^- did not show any isosbestic point over the wavelength range 340 to 660 nm. The absorption maximum of the spectrum after completion of the reaction having $[NCS^-] \geq 0.05$ M was at 510 nm ($\varepsilon = 174$ M^{-1} cm^{-1}) which agreed very well with the species *cis*-$[Co(NH_3)_4(NCS)_2]^+$, isolated recently by Kanamori.[8] The kinetics of the reaction were followed at 510 nm in the thermostatted cell-compartment of a Pye-Unicam SP8-150 spectrophotometer using matched 1 cm quartz cells. Plots of log $(A_\infty - A_t)$ against time (where A_∞ and A_t stand for the absorbances at the completion of the reaction and at time t respectively) clearly indicated an initial curvature before becoming linear at high values of t. This behaviour is illustrated in the Figure and is reminiscent of that expected for a consecutive reaction scheme. It was possible to resolve such plots into two straight lines by the use of conventional procedures as described elsewhere.[9]

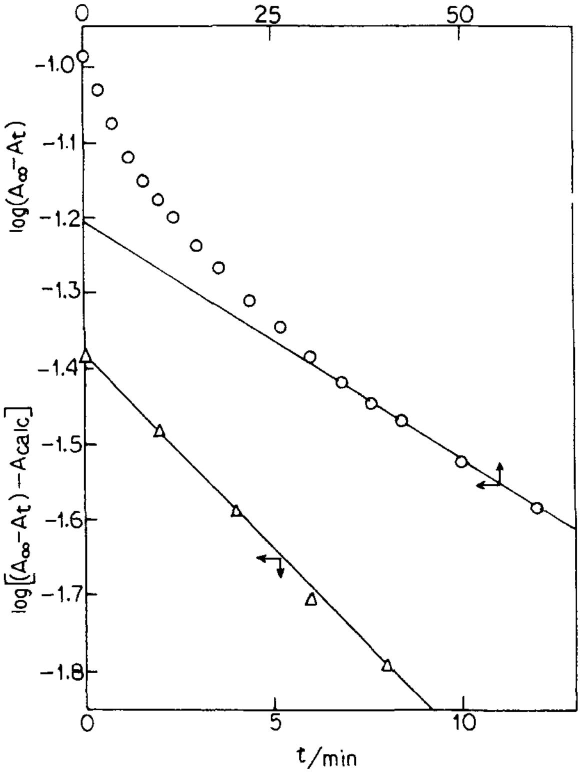

FIGURE 1 A typical kinetic plot for the reaction of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with NCS^- having [complex] = 1×10^{-3} M, $[NCS^-]$ = 0.2 M, pH = 2.00, temp = 60° and I = 0.51 M ($NaClO_4$), (open circles). A_{calc} at different times are extracted from the linear portion of the curve after extrapolation to zero time and used in the evaluation of first-step reaction rate, as shown by the open triangles.

RESULTS AND DISCUSSION

To get an idea about the $[NCS^-]$ dependence on the present reaction, kinetic experiments were performed at pH = 2.00 and I = 0.51 M in the temperature range 40–60°. At this pH, protonation of NCS^- is negligible and decomposition of HSCN

TABLE I

Rate parameters[a] for the anation of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ by NCS^-.

Temp	$10^2[NCS^-]$(M)	$10^4 k_{obs}{}^{I}$(sec^{-1})	$10^5 k_{obs}{}^{II}$(sec^{-1})
40.0 ± 0.1°	5	0.54	0.77
	10	0.69	1.42
	20	1.04	2.23
	20[b]	1.31	2.88
	30	1.14	3.04
	40	1.43	3.77
	40[b]	2.33	4.32
	50	1.67	4.56
	70[b]	3.10	6.97
	100[b]	4.99	9.34
	150[b]	5.32	12.28
	200[b]	5.89	13.82
$k_1 = (2.44 \pm 0.07) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (8.20 \pm 0.17) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0{}^{I} = (0.45 \pm 0.05) \times 10^{-4}$ sec^{-1};		$k_0{}^{II} = (0.51 \pm 0.07) \times 10^{-5}$ sec^{-1}.	
50.0 ± 0.1°	5	1.77	2.69
	10	2.19	3.93
	20	3.65	9.02
	30	4.73	12.28
	40	5.69	15.35
	50	6.40	19.00
$k_1 = (10.66 \pm 0.29) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (36.62 \pm 0.73) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0{}^{I} = (1.32 \pm 0.13) \times 10^{-4}$ sec^{-1};		$k_0{}^{II} = (1.42 \pm 0.28) \times 10^{-5}$ sec^{-1}	
60.0 ± 0.1°	8	10.20	12.95
	10	12.44	17.27
	20	19.38	23.80
	30	25.91	39.02
$k_1 = (70.16 \pm 0.72) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (110.79 \pm 1.46) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0{}^{I} = (5.06 \pm 0.37) \times 10^{-4}$ sec^{-1};		$k_0{}^{II} = (4.43 \pm 0.51) \times 10^{-5}$ sec^{-1}	

[a] pH = 2.00 (adjusted by adding required amount of dilute $HClO_4$). [Diaqua complex] = 1×10^{-3} M. I = 0.51 M ($NaClO_4$). Activation parameters computed from these are: $\Delta H_1^{\neq} = 143 \pm 7$ kJ mol^{-1}, $\Delta S_1^{\neq} = 141 \pm 11$ J K^{-1} mol^{-1}, $\Delta H_2^{\neq} = 111 \pm 6$ kJ mol^{-1}, $\Delta S_2^{\neq} = 29 \pm 8$ J K^{-1} mol^{-1}, $\Delta H_0^{I\neq} = 102 \pm 7$ kJ mol^{-1}, $\Delta S_0^{I\neq} = 3 \pm 5$ J K^{-1} mol^{-1}, $\Delta H_0^{II\neq} = 91 \pm 8$ kJ mol^{-1} and $\Delta S_0^{II\neq} = -58 \pm 7$ J K^{-1} mol^{-1}.

[b] All other conditions remaining the same but I = 2.01 M ($NaClO_4$). Kinetic parameters computed from these are, $K_{IP(1)} = 0.22$, $k_i{}^{I} = (2.15 \pm 0.07) \times 10^{-3}$ sec^{-1}, $K_{IP(2)} = 0.13$ and $k_i{}^{II} = (6.68 \pm 0.31) \times 10^{-4}$ sec^{-1}.

did not interfere.[10] The complex also exists in the pure diaqua form as was expected from its known pK_1 (= 5.69 at 20°).[11] At $[NCS^-] \geq 0.05$ M, constant A_∞ values were obtained but for $[NCS^-] < 0.05$ M this was not so; the greater the ligand concentration, the more complete the reaction. Such a feature generally occurs for an equilibrium reaction. This was further verified by an analysis of the kinetic data. Plots of k_{obs} *vs* $[NCS^-]$ gave straight lines having non-zero intercepts for each of the steps. Under pseudo-first-order conditions, relation (*1*) holds for each step

$$k_{obs} = k_0 + k[NCS^-] \qquad (1)$$

where k_0 denotes the rate constant for the reverse (aquation) reaction (obtained from the intercepts of the plots of k_{obs} *vs* $[NCS^-]$) and k is the second order anation rate constant (obtained from the slopes of such plots). The least-squares

TABLE II

Observed rate constants (k_{obs}) as a function of [NCS^-] and pH
Temp = 40°. I = 0.51 M ($NaClO_4$). [Diaqua Complex] = 1 × 10^{-3} M.

pH	10^2[NCS^-](M)	$10^4 k_{obs}^{I}$(sec^{-1})	$10^5 k_{obs}^{II}$(sec^{-1})
2.15 ± 0.02	10	0.83	1.66
	15	1.01	2.21
	20	1.22	2.56
	30	1.48	2.78
	40	1.77	3.58
	50	2.03	4.22
$k_1 = (2.96 \pm 0.05) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (5.96 \pm 0.10) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0^{I} = (0.57 \pm 0.08) \times 10^{-4}$ sec^{-1};		$k_0^{II} = (1.20 \pm 0.10) \times 10^{-5}$ sec^{-1}	
2.30 ± 0.03	5	0.43	1.00
	10	0.57	1.49
	20	1.08	2.15
	30	1.37	2.49
	40	1.77	3.28
	50	1.92	3.95
$k_1 = (3.48 \pm 0.11) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (6.27 \pm 0.27) \times 10^{-5}$ sec^{-1} M^{-1}.	
$k_0^{I} = (0.29 \pm 0.10) \times 10^{-4}$ sec^{-1};		$k_0^{II} = (0.77 \pm 0.13) \times 10^{-5}$ sec^{-1}.	
2.50 ± 0.05	10	1.09	1.12
	15	1.36	1.38
	20	1.71	1.57
	30	2.34	2.11
	40	2.92	2.53
	50	3.53	2.98
$k_1 = (6.14 \pm 0.30) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (4.66 \pm 0.19) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0^{I} = (0.47 \pm 0.09) \times 10^{-4}$ sec^{-1};		$k_0^{II} = (0.67 \pm 0.08) \times 10^{-5}$ sec^{-1}.	
2.80 ± 0.08	10	2.57	1.18
	20	3.76	1.63
	30	4.91	2.14
	40	5.99	2.56
$k_1 = (11.41 \pm 0.57) \times 10^{-4}$ sec^{-1} M^{-1};		$k_2 = (4.65 \pm 0.13) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0^{I} = (1.46 \pm 0.39) \times 10^{-4}$ sec^{-1};		$k_0^{II} = (0.72 \pm 0.05) \times 10^{-5}$ sec^{-1}	
3.36 ± 0.12	10	4.22	1.15
	20	8.44	1.73
	30	11.90	1.98
	40	15.35	2.50
k_1 = ([illegible] ± 1.71) × 10^{-4} sec^{-1} M^{-1};		$k_2 = (4.30 \pm 0.14) \times 10^{-5}$ sec^{-1} M^{-1}	
$k_0^{I} = (0.77 \pm 0.06) \times 10^{-4}$ sec^{-1};		$k_0^{II} = (0.77 \pm 0.09) \times 10^{-5}$ sec^{-1}	

values of k_0 and k are also listed in Table I. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values corresponding to the k_1, k_2, k_0^{I} and k_0^{II} paths, evaluated with the help of the Eyring equation using the respective anation and aquation rate constants at different temperatures are also presented in Table I.

Sets of kinetic experiments (at 40°) with varying [NCS^-] were done at some other pH values (2.15–3.36) and the results are shown in Table II. The data clearly indicate that for the first reaction step the base form of the complex, *cis*-$[Co(NH_3)_4(OH)(H_2O)]^{2+}$, is orders of magnitude more reactive towards NCS^- substitution than is the acid form of the complex, *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$. We determined the pK_1 (5.30) of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ at 40° and at ionic strength

0.5 M ($NaClO_4$) by the pH-titration method and it agrees well with that obtained by Schwarzenbach[11] (pK_1 = 5.69 at 20° and I = 0.1 M). Thus at the highest experimental pH (3.36) although 1.2% of the complex is in the base form, more than 97% of the observed rate is accounted for by it. Such a strong $[H^+]^{-1}$ dependence of k_{obs} for the reaction of *cis*-$[Co(NH_3)_4(H_2O)_2]^+$ with the conjugate base of a strong acid like HSCN indicates the operation of a conjugate base pathway. This type of base-catalysed substitution process has been encountered by Pavelich[12] in the chloride anation of the *trans*-diaquabis(ethylenediamine)rhodium(III) complex. In a very recent study, Ramaswamy *et al.*,[6] also have noticed a remarkable rate acceleration due to the conjugate base [Cr(salen)(OH)(H_2O)] (salen = *N*, *N'*-ethylenebis(salicylidenimine)) toward NCS^- and this is believed to arise from the strong π-donating ability of OH^-. The extraordinary lability of the aquahydroxo species compared to the diaqua complex has also been found for the isomerisation[13] and ammonia substitution[14] reactions of the dihydroxotetraamminecobalt(III) complex. An exact parallel in the reactivity trend is also found for the analogous aquahydroxobis(ethylenediamine)cobalt(III) ion.[15] The pH dependence of rate for the second-step reaction was rather insignificant although a slight decreasing tendency of k_{obs}^{II} with an increase in pH was noticed. Since the pK of *cis*-$[Co(NH_3)_4(NCS)(H_2O)]^{2+}$ may be estimated to be higher (*ca* > 6) than that of the diaqua species, the existence of any hydroxothiocyanate species is practically negligible in the pH range covered and we may ignore its contribution towards the anation process. Moreover, Balt[16] has shown that the intermediate *cis*-$[Co(NH_3)_4(OH)(NCS)]^+$ plays no role in the overall rate process during the reaction of dihydroxotetraamminecobalt(III) ion with thiocyanate in ammoniacal medium. It may be mentioned here that the k_0 values obtained from the intercepts of k_{obs} *vs* [NCS^-] plots for both the steps are subject to large uncertainties. Still, these could be treated as more or less pH-independent. This pH independency of the reverse aquation path is supported by the earlier studies of Adamson and Wilkins[17] on the aquation of $[Cr(NH_3)_5(NCS)]^{2+}$, $[Co(NH_3)_5(NCS)]^{2+}$ and *trans*-$[Co(en)_2(NCS)_2]^+$. The results of thiocyanate and pH variation studies could then be schematically represented as follows

$$[Co(NH_3)_4(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} [Co(NH_3)_4(OH)(H_2O)]^{2+} + H^+$$

$$[Co(NH_3)_4(H_2O)_2]^{3+} + NCS^- \underset{k_0^{I}}{\overset{k_{AH}}{\rightleftharpoons}} [Co(NH_3)_4(NCS)(H_2O)]^{2+} + H_2O$$

$$[Co(NH_3)_4(OH)(H_2O)]^{2+} + NCS^- \underset{k_0^{I}}{\overset{k_{A}}{\rightleftharpoons}} [Co(NH_3)_4(OH)(NCS)]^{+} + H_2O$$

$$[Co(NH_3)_4(NCS)(H_2O)]^{2+} + NCS^- \underset{k_0^{II}}{\overset{k_{2}}{\rightleftharpoons}} [Co(NH_3)_4(NCS)_2]^{+} + H_2O$$

$$[Co(NH_3)_4(OH)(NCS)]^{+} + NCS^- \longrightarrow \text{No reaction}$$

The value of K_1 at 40° is 5.01×10^{-6}. Since $[H^+] >> K_1$, the second order rate constant (k_1) for the first step anation path at varying $[H^+]$ can be expressed as shown in (*2*)

$$k_1 = k_{AH} + k_A K_1 [H^+]^{-1} \qquad (2)$$

The values of k_{AH} and k_A computed from the experimental data at 40° are $k_{AH} = 8.47 \times 10^{-5}\ s^{-1}\ M^{-1}$ and $k_A = 3.15 \times 10^{-1}\ s^{-1}$ showing the ratio $k_A/k_{AH} = 3.72 \times 10^3$.

With increasing concentration of NCS^- ion, no rate saturation was observed. Hence the bimolecular rate term k does not provide us with compelling evidence for the reaction to proceed through a dissociative path. But for bimolecular processes having very low ion-pair formation constants, a dissociative interchange mechanism is not entirely inconsistent. In order to ascertain whether any ion-pairing preequilibrium is present or not, some kinetic experiments were conducted at 40°, $I = 2.01$ M, $pH = 2.00 \pm 0.01$ and varying the $[NCS^-]$ from 0.2 to 2.0 M; the results obtained are collected in Table I. Plots of k_{obs} *vs* $[NCS^-]$ clearly indicate a tendency towards rate saturation at higher $[NCS^-]$ in addition to a small intercept. The experimental results for each step are consistent with rate equation (*3*), rearrangement of which gives (*4*)

$$k_{obs} = k_{-i} + \frac{k_i K_{IP} [NCS^-]}{1 + K_{IP} [NCS^-]} \qquad (3)$$

$$\frac{1}{k_{obs} - k_{-i}} = \frac{1}{k_i K_{IP} [NCS^-]} + \frac{1}{k_i} \qquad (4)$$

The computed k_i and K_{IP} values[18] for both steps are presented in Table I. The K_{IP} values are comparable to the corresponding values of NCS^- ($K_{IP} = 0.43$)[19] and N_3^- ($K_{IP} = 0.26$)[20] in the substitution reactions of $[Co(NH_3)_5(H_2O)]^{3+}$. From the above consideration our assumption that the thiocyanate substitution process in our system actually operates through an I_d path is justified. Balt[16] has also claimed that the rate determining step for the thiocyanate substitution in the dihydroxotetraamminecobalt(III) complex in moderately basic medium involves outer-sphere complexation between the aquahydroxotetraamminecobalt(III) cation (as the reactive species) and the thiocyanate anion. The reaction is believed to occur through an I_d path whereby the activated state is achieved by a substantial weakening of the $Co\text{-}OH_2$ bond followed by coordination of the immediately available ligand.

The $\Delta H_1^{\neq}$ and $\Delta H_2^{\neq}$ values obtained (see Table I) are comparable to the $\Delta H^{\neq}$ value obtained by Ashley *et al.*,[21] for the thiocyanate substitution of α, β, γ, δ -tetra(4-*N*-methylpyridyl)porphinediaquacobalt(III) ion. The fact that $\Delta H_2^{\neq}$ is a little lower than $\Delta H_1^{\neq}$ is consistent with the greater electron-withdrawing power of NCS^- in the intermediate aquathiocyanato species than H_2O in the diaqua species,[22] causing the second step reaction to be a little slower. The $\Delta H_0^{\neq}$ values obtained for both the steps and the $\Delta S_0^{11\neq}$ value are comparable to the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values obtained by Adamson *et al.*,[17] for the aquation of the $[Co(NH_3)_5(NCS)]^{2+}$ ion. The strong *cis* labilisation by OH^- observed for the first reaction step possibly arises from the positive $\Delta S_1^{\neq}$[21] whereas the less positive value of $\Delta S_2^{\neq}$ indicates that the water-for-thiocyanate substitution at the cobalt(III) centre is stereoretentive.[23]

REFERENCES

1. R.G. Wilkins, 'The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes' (Allyn and Bacon Inc., Boston, 1974) p. 188.
2. P. Moore, 'Inorganic Reaction Mechanisms', (Specialist Periodical Report, The Chemical Society of London, Vol. 5, 1977) p. 223.
3. M.B. Davies, *J. Inorg. Nucl. Chem.*, **43,** 1277 (1981).
4. M.C. Ghosh and P. Banerjee, *Bull. Chem. Soc. Japan*, **56,** 2871 (1983).
5. J.G. Leipoldt, S.S. Basson and D.R. Rabie, *J. Inorg. Nucl. Chem.*, **43,** 3239 (1981).
6. D.R. Prasad, T. Ramasami, D. Ramaswamy and M. Santappa, *Inorg. Chem.*, **21,** 850 (1982).
7. J. Springborg and C.E. Schaffer, *Inorg. Synth.*, **18,** 83 (1978).
8. K. Kanamori and K. Kawai, *Bull. Chem. Soc. Japan*, **55,** 764 (1982).
9. J.A. Weyh and R.E. Hamm, *Inorg. Chem.*, **8,** 2298 (1969).
10. Only 0.01% of the thiocyanate is protonated as can be estimated from $K_a = 70$. See H.H. Krause and F. Wasgestian, *Inorg. Chim. Acta*, **76,** L295 (1983).
11. G. Schwarzenbach, J. Boesch and H. Egli, *J. Inorg. Nucl. Chem.*, **33,** 2141 (1971).
12. M.V. Pavelich, *Inorg. Chem.*, **14,** 982 (1975).
13. S. Balt, *Rec. Trav. Chim.*, **91,** 1026 (1972).
14. S. Balt, *Inorg. Chim. Acta*, **7,** 453 (1973).
15. S.C. Chan and G.M. Harris, *Inorg. Chem.*, **10,** 1317 (1971).
16. E.G.A.M. Bohte and S. Balt, *J. Inorg. Nucl. Chem.*, **38,** 2265 (1976).
17. A.W. Adamson and R.G. Wilkins, *J. Am. Chem. Soc.*, **76,** 3379 (1954).
18. The k_{-1} values were extracted from the intercept obtained by a least-squares fit of the data for lower $[NCS^-]$ since the k_{obs} values at this region were almost linearly dependent on $[NCS^-]$ without any rate saturation.
19. C.H. Langford and W.R. Muir, *J. Am. Chem. Soc.*, **89,** 3141 (1967).
20. T.W. Swaddle and G. Guastalla, *Inorg. Chem.*, **8,** 1604 (1969).
21. K.R. Ashley, M. Berggrem and M. Cheng, *J. Am. Chem. Soc.*, **97,** 1422 (1975).
22. Z. Bradić, M. Birus. D. Pavlović, M. Pribanić and S. Asperger, *J. Chem. Soc.*, 2514 (1973).
23. M.L. Tobe, *Inorg. Chem.*, **7,** 1260 (1968).