potassium cyanide react with the tricarbonatocobaltate(III) and then letting ammonium chloride and ammonia react with the product in the presence of activated charcoal. The main difference between the procedure for synthesizing the monocyano complex and that for the tricyano complex is in the amounts of potassium cyanide and ammonium chloride used. These amounts are exactly the factors that decide the end products. The amount of activated charcoal is also important; if it is too small the final product will be a red sirup, and if too large, potassium hexacyanocobaltate(III) will result.

Very recently, potassium pentanitroamminecobaltate(III) was used for the infrared study of the nitroammine series by Nakagawa and Shimanouchi.[13] The tricyanotriamminecobalt(III) was also investigated by Tanaka, Sugi, and Fujita,[14] and they assigned the *cis-trans* form to the complex.

[13] I. Nakagawa and T. Shimanouchi, presented at the 13th Symposium on Coordination Compounds, Nagoya, Japan, Oct. 14, 1963.

[14] S. Tanaka, H Sugi, and J. Fujita, presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1, 1964.

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The Kinetics of Exchange of Thiocyanate between Tetrathiocyanatonickelate(II) and Free Thiocyanate Ion in Aqueous Solution[1]

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Received May 21, 1964

Rate data are reported for the exchange of NCS^- with an assumed $Ni(NCS)_4(H_2O)_2{}^{2-}$ species in aqueous solution. For the rate law $R = 4k_1[Ni(NCS)_4(H_2O)_2{}^{2-}]$, k_1 is $6.9 \pm 0.3 \times 10^5$ sec.$^{-1}$ at 25°, $\Delta H^* = 8.6 \pm 0.7$ kcal./mole, and $\Delta S^* = -5 \pm 3$ e.u. A shift of the N^{14} resonance in NCS^- was observed and gave a scalar coupling constant, A/h, of 2.27×10^7 c.p.s. The effect of thiocyanate concentration, pH, and cation on the rate was studied and the rate of exchange of water was determined through the O^{17} resonance. Possible mechanisms are discussed and it is concluded that a dissociation type mechanism is the most plausible.

Introduction

Measurement of the rates of exchange of ligands in labile complexes is of considerable importance in assessing the role of electronic structure of metal ions in the kinetic behavior of complexes. Several methods are currently being employed in the study of rapid reactions, among them being the use of n.m.r. line-broadening effects.[3,4] We have begun a study of NCS^- complexes and report results on the $Ni(NCS)_4{}^{2-}$–NCS^- exchange reaction in aqueous solution. These results are compared with studies on other Ni(II) complexes using various experimental techniques.

Experimental

The n.m.r. spectrometer used employed a variable, regulated magnetic field of *ca.* 9300 gauss, a Pound–Knight–Watkins marginal oscillator, and a phase-sensitive detector. Square wave field modulation at 30 c./sec. was used rather than the more usual sine wave type. The N^{14} n.m.r. absorption signal was observed on a recorder at *ca.* 2.85 Mc./sec. by sweeping the magnetic field. The observed recorder trace consisted of two identical Lorentzian absorption curves, one inverted with respect to the other and overlapping the first on the field axis. Calibration of the recorder chart in terms of gauss/cm. was effected using the known separations of the N^{14} n.m.r. lines in NH_4NO_3 (347 p.p.m.). The significant information to be obtained from the recorded absorption lines is the line width at half-maximum height (W'). Several factors must be taken into account in order to obtain the correct values for W'. First, the radiofrequency power level must be kept low enough to avoid saturation phenomena. Curves were run as a function of the power level to enable determination of the point at which saturation effects become important. Runs were then made at levels below this point. Second, the modulation frequency and amplitude must be properly chosen to avoid artificial line broadening. The 30 c./sec. frequency used causes no significant error in our results. The modulation amplitude effects were studied, and it was found that large amplitudes caused eddy currents in the magnet pole pieces. Amplitudes used were kept below these levels. Third, because of the overlapping nature of the observed curves (at the modulation amplitudes used) it was necessary to correct the observed heights and widths of such curves. These corrections were obtained graphically by constructing true Lorentzian curves and by measuring the distortion caused by their overlapping. Fourth, field inhomogeneities cause artificial broadening. In our experiments this broadening amounted to *ca.* 0.15 gauss, a value relatively small compared to the line widths of interest. It was assumed that this error would effectively cancel when differences in widths were taken. The over-all precision in the W' measurements was found to be *ca.* ±10%. Samples were run in 12-mm. Pyrex test tubes using a constant volume of solution which just filled the oscillator coil. Sample temperatures were controlled to ±0.5° using a thermostated N_2 gas flow system. Measurements of temperature were made using a glass-protected thermocouple placed directly in the solution.

Solutions were prepared from distilled water. The thiocyanate salts were analytical reagent grade. Thiocyanate concentration was determined by silver titration. Some experiments were done using $K_4Ni(NCS)_6 \cdot 4H_2O$ prepared using the method of

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[1] This work supported in part by U.S.A.E.C. Contract AT(45-1)-1031.

[2] To whom inquiries may be addressed.

[3] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[4] J. P. Hunt, H. W. Dodgen, and F. Klanberg, *Inorg. Chem.*, **2**, 478 (1963).

TABLE I

LINE-BROADENING DATA IN KNCS

t, °C.	Δ'^{c}	T'_{2p} (×10^5)
	0.0097 M^{a} Ni^{2+}; 8.38 M NCS^-	
18.5	0.90 ± 0.25	1.12 ± 0.30
28	0.82 ± 0.15	1.23 ± 0.23
30	0.73 ± 0.07	1.38 ± 0.13
73	0.213 ± 0.03	4.74 ± 0.6
29	0.765 ± 0.06	1.32 ± 0.11^{d}
−9	0.39 ± 0.10	2.59 ± 0.6^{e}
−9	0.62 ± 0.06	1.63 ± 0.16^{e}
−2	0.48 ± 0.10	2.10 ± 0.5^{e}
−2	0.70 ± 0.15	1.44 ± 0.3^{e}
10	1.11 ± 0.08	0.91 ± 0.07^{e}
46	0.60 ± 0.04	1.69 ± 0.1^{e}
29	0.79 ± 0.15	1.28 ± 0.25^{d,e}
	0.020 M^{b} Ni^{2+}; 8.48 M NCS^-	
1	1.27 ± 0.10	1.63 ± 0.13
30	1.46 ± 0.18	1.42 ± 0.18
32	1.305 ± 0.1	1.58 ± 0.1
40	1.17 ± 0.14	1.77 ± 0.2
50	0.955 ± 0.19	2.16 ± 0.4
61	0.71 ± 0.05	2.91 ± 0.2
68	0.57 ± 0.08	2.62 ± 0.4
74	0.502 ± 0.04	4.12 ± 0.3
	0.020 M^{b} Ni^{2+}; 8.42 M NCS^-	
−15.5	0.77 ± 0.20	2.68 ± 0.7
10.5	2.00 ± 0.2	0.97 ± 0.1
29.5	1.38 ± 0.08	1.50 ± 0.09
31.3	1.255 ± 0.17	1.65 ± 0.2
41	1.015 ± 0.08	2.04 ± 0.16
55	0.71 ± 0.08	2.91 ± 0.3
	0.0202 M^{a} Ni^{2+}; 8.44 M NCS^-	
−3	1.10 ± 0.2	1.90 ± 0.35
19	2.07 ± 0.25	1.01 ± 0.12
29	1.805 ± 0.15	1.16 ± 0.08
29	1.795 ± 0.15	1.16 ± 0.08^{d}
−9.5	0.90 ± 0.08	2.32 ± 0.2
−9.5	0.91 ± 0.08	2.30 ± 0.2^{e}
−2	1.23 ± 0.07	1.70 ± 0.1^{e}
−2	1.15 ± 0.20	1.82 ± 0.3^{e}
4	1.55 ± 0.05	1.35 ± 0.04^{e}
4	1.81 ± 0.30	1.15 ± 0.20^{e}
10.5	1.86 ± 0.30	1.12 ± 0.2^{e}
10.5	1.81 ± 0.20	1.15 ± 0.12^{e}
30	1.69 ± 0.40	1.23 ± 0.3^{e}
29	1.60 ± 0.3	1.30 ± 0.25^{d,e}
	0.0381 M^{a} Ni^{2+}; 8.55 M NCS^-	
18.5	3.62 ± 0.20	1.09 ± 0.06
29	3.00 ± 0.03	1.31 ± 0.013
30.5	3.57 ± 0.50	1.10 ± 0.18
74	1.04 ± 0.08	3.79 ± 0.3
29	2.87 ± 0.05	1.36 ± 0.025^{d}
−10	1.70 ± 0.2	2.32 ± 0.3^{e}
−10	1.56	2.52^{e}
46.5	1.80 ± 0.20	2.18 ± 0.25^{e}

[a] Solution prepared from $K_4Ni(NCS)_6 \cdot 4H_2O$. [b] Solution prepared from $Ni(NO_3)_2 \cdot 6H_2O$. [c] Errors represent the extremes among about four sweeps through the resonance. [d] pH ~3.5. [e] Antisymmetric square wave modulation used.

Rosenheim.[5] Identical results were obtained using analytical reagent grade $Ni(NO_3)_2 \cdot 6H_2O$.

Treatment of Data and Results

The theoretical treatment of line-broadening effects in relation to kinetics of fast reactions has been given in detail previously.[3,4] For our present experiments we use the relation $1/T_2 - 1/T_{2A} \equiv 1/T_{2p} = \gamma\Delta'/2$ where T_2 is the observed transverse relaxation time for the N^{14} nucleus in free NCS^- in the presence of paramagnetic ions, T_{2A} is the same quantity in the absence of paramagnetic ions, γ is the magnetogyric ratio for N^{14} (1934 gauss^{-1} sec.$^{-1}$), and Δ' is the line broadening (in gauss) measured at half-maximum absorption using the *n.m.r.* absorption curves. Since Δ' is proportional to total nickel concentration at constant thiocyanate concentration, we have referred the measurements to 1 M nickel concentration, thus $\gamma\Delta'/2[\mathrm{Ni}] = 1/T_{2p}[\mathrm{Ni}] \equiv 1/T'_{2p}$ or $T'_{2p} \equiv 2[\mathrm{Ni}]/\gamma\Delta'$. When the line broadening is controlled by the rate of chemical exchange we obtain the relation $R = C(p_0/p_4) \cdot \gamma(\Delta'/2)$ (analogous to the one previously derived[4]) where R is the total rate of exchange (M sec.$^{-1}$) of NCS^- between the complex and the free NCS^- in solution, C is the total concentration of N^{14} in the complex, p_0 is the atom fraction of N^{14} in free NCS^-, p_4 is the atom fraction of N^{14} present in the complex, and γ and Δ' are defined as above. The data are given in Tables I and II. A plot of log T'_{2p} *vs.* $10^3/T$ (for the 8.4 M NCS^- data) is given in Fig. 1. From this it can be seen that only below *ca.* 10° is the broadening determined by the rate of chemical exchange. Above this temperature, nuclear relaxation rates in the complex are important. Experiments in 3.40 M KNCS below 10° are consistent with the 8.4 M data with respect to the slope of the log T'_{2p} *vs.* $10^3/T$ plot.

In order to treat the data it is necessary to consider the species which may be present. Fronaeus[6] has given the formation constants (at 20° and $\mu = 1$) $K_1 = 15$, $K_2 = 2.9$, and $K_3 = 1.5$. If K_4 were *ca.* 0.5, *ca.* 80% $Ni(NCS)_4^{2-}$ and 20% $Ni(NCS)_3^-$ would be present in 8.4 M NCS^-. Some spectrophotometric studies were made by us on the Ni^{2+}–NCS^- solutions. $Ni(H_2O)_6^{2+}$ has weak absorption bands at 3950, 7200, and 11,700 Å. For Ni^{2+} in 8.4 M NCS^-, absorption bands occur at 3970, 6370, and 11,000 Å., which suggests that these green solutions contain approximately octahedral species with three or four water molecules replaced by thiocyanate. Beer's law was found to be obeyed with respect to nickel concentration in 8.4 M NCS^- at 3970 and 6370 Å. The 6370 Å band is the most clearly resolved and optical density measurements were made as a function of NCS^- concentration. Using 2×10^{-2} M Ni^{2+} the optical density increased approximately linearly from 3 to 8.4 M NCS^- (a factor of *ca.* 1.5 was observed). If the total salt concentration was kept constant at 8.4 M by addition of $NaClO_4$ the increase was only *ca.* 1.08-fold over the same range of NCS^-. These results,

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(5) A. Rosenheim and R. Cohn, *Z. anorg. allgem. chem.*, **27**, 292 (1901).

(6) S. Fronaeus, *Acta Chem. Scand.*, **7**, 21 (1953).

TABLE II

LINE-BROADENING DATA IN KNCS, NaNCS, AND NH_4NCS AT VARIOUS THIOCYANATE CONCENTRATIONS

Ni, *M*	NCS^-, *M*	*t*, °C.	Δ′	$T'_{2p} \times 10^5$	T'_{2p} (cor. to 0°) $\times 10^5$
0.02	3.40	7.5	1.66 ± 0.42	1.24 ± 0.3[a]	
0.02	3.40	0.5	0.80 ± 0.24	2.58 ± 0.75[a]	2.58 ± 0.75
0.04	3.40	0.5	2.18 ± 0.24	1.90 ± 0.2[a]	1.90 ± 0.2
0.02[d]	4.28	−2	0.76 ± 0.14	2.72 ± 0.5[a]	2.57 ± 0.5
0.02[d]	5.94	−2.5	1.07 ± 0.16	1.93 ± 0.3[a]	1.73 ± 0.3
0.0051[d]	7.61	−1	0.46 ± 0.16	1.15 ± 0.4[b]	1.05 ± 0.4
0.02	8.48	3	1.92 ± 0.48	1.08 ± 0.25[b]	1.21 ± 0.25
0.0192	3.40	2.5	1.18 ± 0.23	1.68 ± 0.3[c]	1.78 ± 0.3
0.0192	3.40[e]	3	2.58 ± 1.2	0.77 ± 0.4[c]	0.90 ± 0.4
0.0192	6.80	3	1.76 ± 0.3	1.13 ± 0.2[c]	1.26 ± 0.2
0.02	8.48	1.5	1.76 ± 0.6	1.17 ± 0.4[c]	1.23 ± 0.4

[a] KNCS. [b] NH_4NCS. [c] NaNCS. [d] Indicates solution was prepared from $K_4Ni(NCS)_6 \cdot 4H_2O$; all other solutions prepared from $Ni(NO_3)_2 \cdot 6H_2O$. [e] 6.80 *M* Na^+ by addition of $NaClO_4$.

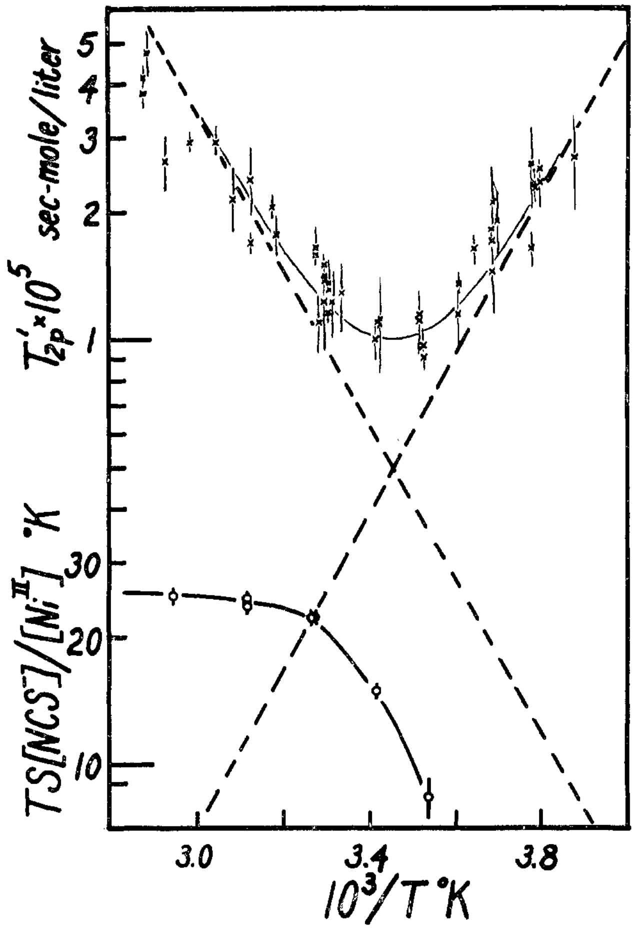

Fig. 1.—Plot of T'_{2p} *vs.* $1/T$ and $TS[NCS^-]/[Ni^{II}]$ *vs.* $1/T$. Dashed lines were used to calculate the solid curves drawn through the T'_{2p} and shift data.

along with the formation constants obtained by Fronaeus, suggest an equilibrium involving tri- and tetrathiocyanato complexes and perhaps approach to saturation of the tetra complex at the high total salt concentration.

The T'_{2p} data of Fig. 1 can be fitted assuming a single species which obeys cases 10a and 10b of Swift and Connick.[3] Assuming this species to be the tetra complex the appropriate equation for T'_{2p} is

$$T'_{2p} = [Ni]p_0/p_4\tau_{40}\Delta\omega_4{}^2 + [Ni]p_0\tau_{40}/p_4$$

where p_4 is the atom fraction of N^{14} in the tetra complex, τ_{40} is the mean life of a NCS^- for change from the tetra complex to the "free" state, and $\Delta\omega_4$ is the resonance frequency of N^{14} in the tetra complex minus the resonance frequency in the free state. The two dashed straight lines in Fig. 1 represent the two terms of the above equation and the solid curve their sum.

TABLE III

N^{14} RESONANCE SHIFT DATA

Ni, *M*	NCS^-, *M*	*t*, °C.	Shift, p.p.m.	$TS[NCS^-]/[Ni]$
0.020	8.42	9	70 ± 9	8.3 ± 1.0[a]
0.020	8.42	17.5	121 ± 7	14.8 ± 0.9[a]
0.0381	8.55	31.5	324 ± 10	22.1 ± 0.6[a]
0.020	8.48	32.5	169 ± 5	21.9 ± 0.6[b]
0.0381	8.55	47.5	339 ± 15	24.4 ± 1.0[a]
0.02	8.48	47.5	172 ± 6	23.4 ± 0.8[b]
0.0381	8.55	65.8	327 ± 15	24.9 ± 1.0[a]

[a] KNCS. [b] NH_4NCS.

In order to be able to construct more accurately the curve given in Fig. 1, some shift measurements were performed. The shift of the N^{14} line in NCS^- was measured relative to the signal from a saturated NH_4NO_3 solution contained in a small tube placed concentrically in the sample tube. The shift measurements are given in Table III and the quantity $TS[NCS^-]/[Ni]$ is plotted against $10^3/T$ in Fig. 1. The theory[3] of the chemical shift consistent with the assumptions made above for calculating T'_{2p} leads to the equation

$$S = \Delta\omega/\omega_0 = p_4\Delta\omega_4/p_0\omega_0(1 + \tau_{40}{}^2\Delta\omega_4{}^2)^{-1}$$

where ω_0 is the resonance frequency of N^{14} in thiocyanate with no Ni added and $\Delta\omega$ is the change in resonance frequency upon addition of Ni. Noting that $p_4 = 4f_4[Ni]/[NCS^-]$, where f_4 is the atom fraction of nickel in the tetra complex, we can write

$$TS[NCS^-]/[Ni] = 4f_4(\Delta\omega_4 T/\omega_0)/p_0(1 + \tau_{40}{}^2\Delta\omega_4{}^2)^{-1}$$

By noting that $\tau_{40}{}^2\Delta\omega_4{}^2 = ([Ni]p_0\tau_{40}/p_4)/([Ni]p_0/p_4 \cdot \tau_{40}\Delta\omega_4{}^2)$ one can see that $(1 + \tau_{40}{}^2\Delta\omega_4{}^2)$ can be calculated from the dashed straight lines in Fig. 1. Assuming $\Delta\omega_4$ obeys Curie's law and that f_4 and p_0 are essentially unity, the quantity $4f_4(\Delta\omega_4 T/\omega_0)/p_0$ may be regarded as constant and the solid curve through the shift points can then be calculated from the two dashed straight lines. It is worth noting that the quantity $TS[NCS^-]/[Ni]$ falls to one-half its high-temperature

TABLE IV

N^{14} AND O^{17} RESONANCE DATA[a]

t, °C.	$[Ni]\tau_{NCS^-}$, M sec.	$[Ni]\tau_{H_2O}$, M sec.	τ_{H_2O}/τ_{NCS^-}
27	$<1.1 \times 10^{-5}$	1.4×10^{-4}	>13
	$(2.9 \times 10^{-6})^b$		$(48)^b$
5	$<1.1 \times 10^{-5}$	$>1.8 \times 10^{-4}$	>16
	$(0.9 \times 10^{-5})^b$	$(7.0 \times 10^{-4})^b$	$(78)^b$

$[Ni]\tau_{H_2O}$ (6.6 M $NaClO_4$, 27°) $= 2.7 \times 10^{-4}$

$[Ni]\tau_{H_2O}$ (0.1 M $HClO_4$, 27°) $= 2.6 \times 10^{-4}$ (ref. 3)

[a] Ni^{2+} in 6.59 M NaNCS solution, $[H_2O]/[NCS^-] = 5.94$.

[b] See text for explanation of the values in parentheses.

limiting value at the temperature corresponding to the minimum in the T'_{2p} curve. The final fitting process involved adjusting the two dashed lines to give the best over-all fit of the T'_{2p} and shift data. The high-temperature T'_{2p} points suggest that another species may be starting to exchange at a significant rate at the higher temperatures.

It should be stressed that the above data-fitting process involves the assumption that the temperature variation of $\Delta\omega_4$ and p_4 may be ignored in the equation for T'_{2p}. The precision of the data does not warrant attempting to take this into account.

Assuming the tetrathiocyanatodiaquo species to be predominant, and ignoring possible differences between the isomers of this species, first-order rate constants for the 8.4 M NCS^- data below 10° were calculated from the equation $R = 4k_1[Ni]$ or $k_1 = [NCS^-]/4T'_{2p}$. This leads to $k_1 = 6.9 \pm 0.3 \times 10^5$ sec.$^{-1}$ (at 25°), $\Delta H^* = 8.6 \pm 0.7$ kcal./mole, and $\Delta S^* = -5 \pm 3$ e.u. The shift data yield $\Delta\omega_4/\omega_0 = 0.0222$ (at 25°) and $A/h = (\Delta\omega_4/\omega_0 h)3kT\gamma/S(S+1)\gamma_e = 2.27 \times 10^7$ c.p.s.[7] In this equation A is the scalar coupling constant, h Planck's constant, k Boltzmann's constant, γ the N^{14} magnetogyric ratio, S the resultant electron spin of Ni^{2+}, and γ_e the electron magnetogyric ratio.

Some experiments were also performed observing the O^{17} and N^{14} resonances in the same Ni–NCS^- solutions and the results are summarized in Table IV. The results are given in terms of the mean lives (τ) of the free species indicated multiplied by the total nickel concentration. The results at the bottom of the table show that addition of 6.6 M $NaClO_4$ has little effect on the exchange rate of water with $Ni(H_2O)_6{}^{2+}$. In the 6.6 M NaNCS solution the values given at 27 and 5° for the quantity $[Ni]\tau_{NCS^-}$ are upper limits since at 27° the nuclear relaxation process is limiting rather than the exchange process and at 5° both processes are contributing to the line width. The values in parentheses are the values expected for chemical exchange obtained using the temperature coefficient data given in Fig. 1. The value for $[Ni]\tau_{H_2O}$ at 5° in the 6.6 M NaNCS solution is reported as a lower limit since the water exchange rate had been slowed by cooling so that no broadening was observed. The value in parentheses for 5° was obtained from the value at 27° assuming the temperature coefficient in the 6.8 M NaNCS solution is the same as that observed by Swift and Connick[3] in 0.1 M $HClO_4$. The fourth column gives the ratio of the mean lives of free H_2O and NCS^- in the solution inferred from the data. Further implications of these O^{17} results will be presented later in the Discussion.

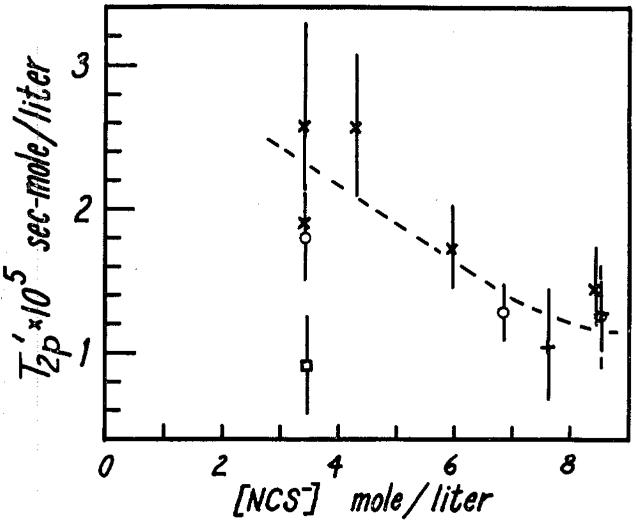

Fig. 2.—Plot of T'_{2p} *vs.* $[NCS^-]$: ×, KNCS; O, NaNCS; □, NaNCS + $NaClO_4$; +, NH_4NCS.

The pH of the solution was varied from 3.5 to 6.5 by addition of dilute nitric acid with no observable effects at 29° where the relaxation process is controlling the line width.

The same rate, within experimental error, is observed in 8.4 M solutions of sodium, potassium, and ammonium thiocyanates (see Table II), indicating no large specific cation effects.

Discussion

Interpretation of the results is greatly complicated by the weakness of the nickel–thiocyanate complexes and the accompanying uncertainty as to species present. The data can be most simply understood in terms of exchange of NCS^- with a complex of the formula $Ni(H_2O)_2(NCS)_4{}^{2-}$. The results of Ahmed and Wilkins[8] on ammine complexes suggest that higher complexes exchange more rapidly than lower ones, so that the tetra complex may be responsible for the exchange even if not completely formed. The data are all consistent with a rate law having a first-order dependence of rate on nickel concentration. The order with respect to thiocyanate is more difficult to determine. The high salt concentrations are very likely to cause important medium effects. Values of T'_{2p} appear to decrease with increasing NCS^- concentration if the total salt concentration is not kept constant (Table II and Fig. 2). On the other hand, for the two solutions with 6.8 M Na^+, T'_{2p} remains constant or increases slightly. If one can assume that activity coefficients are constant in the 6.8 M media some conclusions might be drawn concerning the dependence of rate on NCS^- concentration. Since for chemical exchange $T'_{2p} = \tau_{NCS^-}[Ni]$ and $\tau_{NCS^-} = [NCS^-]/R$ where τ_{NCS^-} is the mean life for free thiocyanate ion

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[7] Equation No. 11 in ref. 3 needs to be multiplied by $^3/_4 I(I+1)$ on the right.

[8] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 2901 (1960).

TABLE V

RATE DATA FOR LABILE Ni(II) COMPLEXES AT 25°

Reaction	k_1, sec.$^{-1}$	μ	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.	Ref.
$Ni(NH_3)_6^{2+}(aq) + NH_3(aq)$	5.6×10^4	0.3	9.5	−5	4
$Ni(NH_3)^{2+}(aq)$ (dissociation)	6	...	14	...	*b*
$Ni(NH_3)_6^{2+}(l) + NH_3(l)$	9.8×10^4	...	11.3	+2	*c*
$Ni(H_2O)_6^{2+} + H_2O(l)$	2.7×10^4	0.3	11.6	+0.6	3
$Ni(NCS)_4^{2-}(aq) + NCS^-(aq)$	6.9×10^{5a}	8.4	8.6	−5	This work
$Ni(NCS)^+(aq)$ (dissociation)	*ca.* 10^2	0.5	*ca.* 10	...	*d*

[a] Extrapolated value. [b] G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962). [c] Results of Dr. Hans H. Glaeser and Dr. G. A. Lo in this laboratory; submitted to *Inorg. Chem.* [d] A. G. Davies and W. MacF. Smith, *Proc. Chem. Soc.*, 380 (1961).

and R is the exchange rate, the dependence of T'_{2p} on NCS^- can be calculated for various possible rate laws. If one further assumes a tri–tetra equilibrium for the nickel thiocyanate complexes, processes of the following type will account for the variation in T'_{2p} at 6.8 M Na^+.

(a) $Ni(H_2O)_3(NCS)_3^- + NCS^- \rightleftharpoons Ni(H_2O)_2(NCS)_4^{2-} + H_2O$ (equilibrium)

(b) $Ni(H_2O)_2(NCS)_4^{2-} \longrightarrow [Ni(H_2O)_2(NCS)_3 \text{ - - - - - } NCS]^{2-}$ ("dissociation")

Processes which would appear not to fit the data are, for example

(c) $Ni(H_2O)_2(NCS)_4^{2-} + NCS^- \rightleftharpoons Ni(H_2O)_2(NCS)_4^{2-} + NCS^-$

(d) $Ni(H_2O)_3(NCS)_3^- \longrightarrow [Ni(H_2O)_3(NCS)_2 \text{ - - - - } NCS]^-$

These conclusions are reached as follows: Taking k_a, k_b, k_c, k_d as the forward rate constants for the four processes given above, the variation of T'_{2p} with thiocyanate concentration is

(a) $T'_{2p} = 1/k_a(1 + K_4[NCS^-])$

(b) $T'_{2p} = 1/k_b(1/K_4 + [NCS^-])$

(c) $T'_{2p} = 1/k_c(1/K_4[NCS^-] + 1)$

(d) $T'_{2p} = 1/k_d([NCS^-] + K_4[NCS^-]^2)$

Cases (a) and (b) can be made consistent with the observed T'_{2p} values using reasonable values of K_4. Case (d) appears to be excluded. Case (c) predicts a decrease in T'_{2p} with increasing NCS^- concentration, or no change in T'_{2p} if K_4 is sufficiently large; and so exclusion of (c) is sensitive to the values of stepwise association constants used and the magnitude of the experimental error.

Some further information on the mechanism can be obtained from experiments in which both O^{17} and N^{14} line broadenings are observed in the same solution. From these measurements the ratio τ_{H_2O}/τ_{NCS^-} can be obtained where τ_{H_2O} is the mean life of a free H_2O in the nickel–thiocyanate solution and τ_{NCS^-} is the mean life of a free NCS^- in the same solution. Process (a) above, for example, predicts that in 6.6 M NCS^- the ratio τ_{H_2O}/τ_{NCS^-} would be 5.94.

Our measured values, given in Table IV, are 48 at 27° and 78 at 5°. Thus, the water exchange is not directly involved in the thiocyanate exchange rate-determining step and process (a) is not significant. Process (b) is consistent with the measured values since the water exchange rate can be much slower than the thiocyanate exchange rate (and thus $\tau_{H_2O} >> \tau_{NCS^-}$). The data can then be qualitatively interpreted rather reasonably in terms of a tetrathiocyanato complex exchanging *via* a "dissociation" type mechanism. Some data for comparison purposes are given in Table V.

The data in Table V support the notion that the higher complexes have higher reaction rates than the lower ones. The rate parameters are fairly similar for the higher aqueous complexes. The faster rate for NCS^- may be due to weaker bonding with this ligand.

Similar studies are underway on thiocyanate complexes of Mn(II), Co(II), V(III), and Fe(III). Several new features seem to exist for these but it seems quite clear that the order of exchange rates is Mn(II) > Co(II) > Ni(II) > Fe(III) > V(III) in general agreement with the water exchange data. Comparisons of this sort may be the most useful application of the n.m.r. method.

It would be highly desirable to have more data on complex formation at high salt concentrations in order to take greater advantage of the n.m.r. techniques. Comparisons between similar ions may be valid even if true thermodynamic data are not available for high concentrations.