carried out in the 200 cm. absorption column in this particular region. Also it is realized that only a small part of the first transition has been examined for the effect of pressure. However, since the rotational structure fails to cause any apparent pressure dependence in the part observed, there is no reason why the remainder of the transition should show a pressure dependence.

The effect of pressure was investigated also in analogous transitions of C_2H_2 and C_2D_2 which occur with maxima at 65790 and 65880 cm.$^{-1}$. The electronic transition in the two molecules is surely the same, and involves excitation of an electron from the C≡C bond, possibly to a Rydberg $3d\delta$ orbital.[6] Hence it is expected that integrated absorption coefficient and *f*-number should be the same in the two molecules. However, the rotational spacing should be smaller in C_2D_2, and there should be about 38% more rotational lines in a slit width than with C_2H_2. If rotational structure has an effect on integrated absorption coefficients in this transition, it should become apparent in a difference in the *f*-numbers for the two molecules at the same pressure. It was found, however, that the *f*-numbers were exactly the same within experimental error. Furthermore, *f*-numbers for the two molecules were individually pressure independent, and the values were not modified by moderate additions of helium. C_2D_2 was studied only at two pressures because of the limited supply. The electronic transition contains in each case three broad resolved vibrational transitions, and the coefficients at the peaks of the latter are considerably higher than coefficients in SF_6. For this reason the upper pressure limit of acetylene was set at a low value, so that points near the top of the peaks could be measured. Data are given in Table III.

TABLE III

INTEGRATED ABSORPTION COEFFICIENT EXPRESSED AS *f*-VALUE FOR THE 65800 CM.$^{-1}$ TRANSITION IN C_2D_2 AND IN C_2H_2

C_2D_2 (ν_{max} = 65880 cm.$^{-1}$)			C_2H_2 (ν_{max} = 65790 cm.$^{-1}$)		
$p_{C_2D_2}$	p_{He}	*f*	$p_{C_2H_2}$	p_{He}	*f*
0.0026	0	0.128	0.0022	0	0.130
0.0050	0	0.132	.0037	0	.128
			.0022	26	.128
			.0022	44	.127
			.0022	80	.130

It may be argued that the range of pressures in every case considered here was too limited to show any variation of *f* with pressure. But it must be pointed out that the range of equivalent path lengths here is as wide, and has the same order of magnitude as in the infrared measurements, where very definite pressure dependence is found. It must be concluded in the cases examined here that sufficient reduction of the intensity peaks of rotational lines must have occurred at very low pressures, and that the *f*-numbers for these cases are not seriously in error because of this factor. This conclusion certainly should not be generalized, even to include other electronic transitions in the molecules considered here.

Finally, a correction should be made to the previous work on measurement of *f*-numbers in acetylene,[7] where the value $f = 0.062$ was reported for the transition discussed above, and the value $f = 0.13$ is found here. In the former work, the acetylene was introduced from a large calibrated volume into the spectrograph through a small bore stopcock, and it is believed that insufficient time was allowed for diffusion, and perhaps not all the measured volume of acetylene entered the spectrograph. In the present work this error was avoided. The corrected value agrees more closely with the theoretical value given in the former work.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Exchange and Aquation Studies with Thiocyanato Complexes[1]

BY ARTHUR W. ADAMSON AND R. G. WILKINS

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The first-order aquation rate constants for the replacement of thiocyanate by water have been determined for the complex ions $Cr(NH_3)_5(SCN)^{++}$, $Co(NH_3)_5(SCN)^{++}$ and *trans*-Co $en_2(SCN)_2^+$. For the first two, the respective values in min.$^{-1}$ are $k = 1.17 \times 10^{13} \exp(-24{,}900/RT)$ and $k = 0.85 \times 10^{13} \exp(-26{,}800/RT)$, with $\Delta S^{\ddagger} = -7.8, -8.4$ e.u. The rate of bimolecular exchange of thiocyanate ion with the $SC^{14}N$ labeled complexes was found to be not more than a few per cent. of the aquation rates, being undetectable against the aquation background. The aquation of $Co(NH_3)_5(SCN)^{++}$ was found to be catalyzed by thiocyanate ion while for $Cr(NH_3)_5(SCN)^{++}$ no such enhancement of rate was found. An interpretation of this and other aspects of ligand replacement with trivalent chromium and cobalt complexes is presented whereby it is inferred that an S_N2 mechanism holds for chromium complexes and an S_N1 mechanism for those of cobalt.

During recent years renewed interest has developed in the nature of the mechanisms whereby one ligand replaces another in covalently bonded complex ions. Evidence has been sought in exchange studies and in the kinetics of net reactions. Thus the rapid exchange of ligand with $Ni(CN)_4^{-2}$,[2,3] $Pd(CN)_4^{-2}$ [2] and PtX_4^{-2} [2,4] ions has been thought to result from a ready bimolecular reaction involving a five coördinated transition state employing the available outer p-orbital.[5,6]

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[1] These investigations were carried out under contract N6onr 23809 between the University of Southern California and the Office of Naval Research. They were presented at the Symposium on Coördination Chemistry, Copenhagen, August, 1953.

[2] A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

[3] F. A. Long, *ibid.*, **73**, 537 (1951).

[4] A. A. Grinberg and L. E. Nikolskaya, *Zhur. Priklad. Khim.*, **24**, 893 (1951).

[5] A. W. Adamson, J. P. Welker and W. B. Wright, THIS JOURNAL, **73**, 4786 (1951).

[6] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

A similar interpretation has been made of the data on the exchange of ligand with hexacyano complexes.[5–7]

The alternative to the bimolecular or S_N2 mechanism would be a dissociation or S_N1 type process leading to an intermediate of $(n - 1)$ coördination number. Actually, neither the above work nor the various other studies that have been made of the kinetics of ligand replacement in aqueous systems have permitted a clear-cut decision as to mechanism.[8,9] The difficulty is that either the solvent was directly involved, as in aquation and water exchange studies, or it was not possible to rule out exchange through an aquo or hydroxy intermediate.

Recently, Brown, Ingold and Nyholm[10] found partial second-order kinetics for certain ligand replacement reactions with *cis*-$\mathrm{Co\,en_2Cl_2}$ in methanol solution and concluded that the S_N2 mechanism prevailed, although an alternative interpretation is given under Discussion.

The present work was initiated in an attempt to make a more telling test for some second-order character in the kinetics of ligand replacement with hexacoördinated complexes. The particular choice was to study the exchange of thiocyanate ion with the complexes $\mathrm{Cr(NH_3)_5(SCN)^{++}}$, $\mathrm{Co(NH_3)_5(SCN)^{++}}$ and *trans*-$\mathrm{Co\,en_2(SCN)_2{}^+}$. An exchange of the anion of a strong acid with a positively charged complex ion was chosen on the grounds that the rates should then be *p*H independent on the acid side, and that the opposing charges might favor a bimolecular process. The thiocyanate system was selected because of the greater stability toward aquation (as compared to the corresponding halogen complexes). Finally, any background of aquation should be simpler to treat with a mixed acido amine type of complex for which it would be limited to one or two steps, as opposed to the situation with the hexacyanide complexes for which aquation, once initiated, generally proceeded to a complete hydrolysis.

Experimental

Preparation of Materials. (a) *trans*-$\mathrm{[Co\,en_2(SCN)_2]SCN}$ and *trans*-$\mathrm{[Co\,en_2(SCN)_2]ClO_4}$.—*trans*-$\mathrm{[Co\,en_2(SCN)_2]SCN}$ was prepared from the corresponding dichloro compound by treatment of the latter with concentrated thiocyanate solution in boiling water, as described by Fernelius.[11] The active complex was prepared by admixing some $\mathrm{KSC^{14}N}$ of high specific activity with the inactive thiocyanate. The water of crystallization was removed by heating at two hours at 120° and the anhydrous salt was employed throughout. Treatment of the thiocyanate salt of the complex in aqueous solution with sodium perchlorate yielded the slightly soluble perchlorate salt. *Anal.* Calcd. for $\mathrm{[Co\,en_2(SCN)_2]ClO_4}$: Co, 14.9. Found: Co 15.0; ionic thiocyanate, trace. Calcd. for $\mathrm{[Co\,en_2(SCN)_2]SCN}$: Co, 16.9; ionic SCN, 16.1. Found: Co, 16.7; ionic SCN, 16.4.

(b) $\mathrm{[Co(NH_3)_5(SCN)](SCN)_2}$ and $\mathrm{[Co(NH_3)_5(SCN)](ClO_4)_2}$.—$\mathrm{[Co(NH_3)_5Br]Br_2}$ was prepared according to reference 12. By treatment with a slight excess of freshly precipitated silver carbonate in aqueous suspension, conversion into $\mathrm{[Co(NH_3)_5(OH)]CO_3}$ was effected, and then to $\mathrm{[Co(NH_3)_5(SCN)]SO_4}$ by the method of Werner and Muller.[13] The sulfate salt was converted to the perchlorate by precipitation with sodium perchlorate, and to the thiocyanate salt by saturating the solution with sodium thiocyanate. *Anal.* Calcd. for $\mathrm{[Co(NH_3)_5(SCN)](ClO_4)_2}$: Co, 14.7. Found: Co, 14.8. Calcd. for $\mathrm{[Co(NH_3)_5(SCN)](SCN)_2}$: ionic SCN, 36.4. Found: ionic SCN, 36.7.

(c) $\mathrm{[Cr(NH_3)_5(SCN)](SCN)_2}$ and $\mathrm{[Cr(NH_3)_5(SCN)](ClO_4)_2}$.—$\mathrm{[Cr(NH_3)_5Cl]Cl_2}$ was prepared according to the method of Werner and Halban,[14] and was converted to $\mathrm{Cr(NH_3)_5(SCN)^{++}}$ by heating a solution *ca.* 2 *M* in sodium thiocyanate and acidified with acetic acid for a (very) few minutes at 90°. The mixture was quenched when the color change from rose to orange was complete for a test sample of precipitate obtained periodically by filtering off a small portion of the reaction mixture. Either the thiocyanate or the perchlorate salt was obtained, depending upon whether or not sodium perchlorate had also been added to the reaction mixture. In view of the large excess of free thiocyanate required for this reaction the labeled complex was prepared by boiling for a few minutes a concentrated solution of $\mathrm{[Cr(NH_3)_5(SCN)](SCN)_2}$ with a small amount of sodium radiothiocyanate and then precipitating the perchlorate salt. *Anal.* Calcd. for $\mathrm{[Cr(NH_3)_5(SCN)](ClO_4)_2}$: total SCN, 14.3. Found: total SCN, 14.7, and a trace of ionic SCN.

(d) Conversion of the perchlorate salts of the complexes to the thiocyanate salts: Although the thiocyanate salts of $\mathrm{Co(NH_3)_5(SCN)^{++}}$ and $\mathrm{Cr(NH_3)_5(SCN)^{++}}$ could be prepared directly, it was difficult to do so by the normal methods if it was desired that only the inner thiocyanate be labeled. Such complexes were prepared from the corresponding active perchlorate salts either by passing a solution through the thiocyanate form of an anion exchanger, or by adsorbing the salt on a cation exchanger and eluting with concentrated sodium thiocyanate solution. Since by the former method, the resulting solution was quite dilute because of the slight solubility of the original perchlorate salt, excess sodium thiocyanate was added, and an extraction into a much smaller volume of cyclohexanone carried out. The solid complex was recovered by precipitation from the cyclohexanone solution by the addition of ether and toluene, then washed and dried.

(e) **Sodium Radiothiocyanate.**—Potassium radiocyanide was obtained as such from Tracerlab, Inc., and converted to radiothiocyanate by refluxing with powdered sulfur in acetone containing a few drops of water (50 mg. of KCN, 50 mg. of S, 8 ml. of acetone). After an hour, the solution was evaporated to dryness, acetone added, and the product altered to remove unreacted potassium cyanide. The filtrate was again evaporated to dryness, and the residue boiled a few minutes with animal charcoal suspended in a small amount of water and then filtered. The potassium radiothiocyanate obtained upon evaporating the filtrate to dryness was either used as such, or converted to sodium radiothiocyanate by passage through the sodium form of a cation exchanger.

Analytical Procedures. (a) **Cobalt.**—The cobalt complexes containing ethylenediamine were decomposed by boiling (gently) with a mixture of perchloric and nitric acids for three hours, then for an hour with added sulfuric acid. The resulting cobaltous sulfate solution was diluted and determined by the method of Laitinen and Burdett.[15] The pentammine complexes were decomposed by fuming to dryness with sulfuric acid, diluting and adjusting the *p*H to near neutrality. The cobalt was then determined by the method of Cartledge and Nichols.[16]

(b) **Ionic Thiocyanate.**—The ionic or unbound thiocyanate present in a solution was determined by adding a meas-

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(7) A. W. Adamson, THIS JOURNAL, **73**, 5710 (1951).

(8) (a) J. N. Brönsted and R. Livingston, *ibid.*, **49**, 435 (1927); (b) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949); (c) F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1947); **34**, 1088 (1938); (d) F. Basolo, J. G. Bergman and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952); (e) H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953); (f) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1950); (g) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **18**, 757 (1950), and R. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(9) A. Rutenberg and H. Taube, *ibid.*, **20**, 823 (1952).

(10) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2675 (1953); D. D. Brown and C. K. Ingold, *ibid.*, 2680 (1953); D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953).

(11) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 223.

(12) W. C. Fernelius, *ibid.*, Vol. I, p. 186.

(13) A. Werner and H. Muller, *Z. anorg. Chem.*, **22**, 101 (1900).

(14) A. Werner and J. V. Halban, *Ber.*, **39**, 2668 (1906).

(15) H. A. Laitinen and L. W. Burdett, *Anal. Chem.*, **23**, 1268 (1951).

(16) G. H. Cartledge and P. M. Nichols, *ibid.*, **13**, 20 (1941).

ured volume to a much larger one of a standard reagent 0.5 *f* in ferric nitrate and 0.5 *f* in perchloric acid, giving a thiocyanate formality of *ca.* 10^{-4}. The optical density of the resulting ferric thiocyanate complex was determined at 460 mμ with a model DU Beckman spectrophotometer and compared with that of a standard.

(c) Total Thiocyanate.—Coördinately bound plus ionic thiocyanate was determined for the chromium complexes by destroying the compound in hot concentrated alkali The resulting deep green solution was acidified with perchloric acid, chromic hydroxide precipitated out with alkali, and after centrifugation, the supernatant was acidified and the thiocyanate ion concentration determined as in (b). It was found necessary to dissolve and reprecipitate the first precipitate twice, analyzing each supernatant for the additional small portions of free thiocyanate that were present.

It was not possible to determine bound thiocyanate for the cobalt complexes; destruction of the complex was accompanied by oxidation of much of the bound thiocyanate.

Counting and Sample Preparation Procedures.—The C^{14} radioactive samples were counted by means of a flow counter and conventional scaling circuit. An adoption of the method employed by Haissinsky and Pullman[17] of counting "infinitely thick" samples, was used. About 60 mg. of material to be counted, a washed and dried precipitate of reproducible composition, was gently spread in a cylindrical depression 1.4 cm. in diameter and 0.2 cm. deep which was machined out of a thick aluminum disk. A steel cylinder of diameter slightly less than that of the depression was then carefully pressed against the sample, and by sharply hitting the cylinder with a mallet, the sample was compressed to a compact mat. Any surplus solid on the rim of the disk was carefully wiped off. This technique was found to be as accurate and more rapid than the thin sample one employed in earlier work.[2] Since the samples are thicker than the range of the β-particles from C^{14} the measured activity is proportional to the *specific activity* of the material.

Ionic thiocyanate was counted as cuprous thiocyanate obtained by adding a small amount of cuprous chloride in 6 *N* hydrochloric acid to an acidified solution containing the radiothiocyanate, then washing the precipitate with water, alcohol and ether, and drying it at 100°. Where the starting solution contained radioactive complex it was necessary to remove it very completely to avoid coprecipitation with the cuprous thiocyanate. This was accomplished by first precipitating the perchlorate salt of the complex, then extracting the remainder by three successive extractions with cyclohexanone. The resulting water-white solution was freed of cyclohexanone (which tended to react with the cuprous salt) by two ether extractions, the ether removed by boiling the water layer gently, and then, finally, the cuprous thiocyanate was precipitated as described above.

Radiocobalt containing complexes were counted by determining the activity of a standard volume of the solution of the complex when placed in a standard size test-tube and inserted in the well of a scintillation counter. The isotope was Co^{60}, supplied by the Oak Ridge National Laboratory.

Experimental Procedures. (a) **Aquation Runs.**—A solution of the perchlorate salt of the complex being studied, usually 0.02 *M*, was acidified with perchloric acid to a *p*H of *ca.* 2.5, and then thermostated to within 0.1° of the desired temperature. Small additional amounts of acid were added as needed to maintain the *p*H during the course of the run; it was found that *p*H control was not critical provided the *p*H was not allowed to rise beyond four or five. Aliquots were withdrawn and the free thiocyanate present determined spectrophotometrically. In some cases the samples when cooled to room temperature were supersaturated with respect to complex, in which case the complex was partially removed by perchlorate precipitation prior to the thiocyanate analysis. Concentrations given for the various runs are accurate to 1%.

(b) **Exchange Runs.**—The runs with C^{14} active complexes were carried out as above, except that the perchlorate salt of the complex was precipitated, washed with water, alcohol and ether, dried and counted, or cuprous thiocyanate samples were prepared from the free thiocyanate present, as described in the preceding section. For the runs at high complex concentration, the inactive thiocyanate salts of the active complex were employed, and thiocyanic rather than perchloric acid was employed to adjust the *p*H.

For the runs with $Co^{60}(NH_3)_5(SCN)^{++}$, it was necessary to count the resulting few per cent. of $Co^{60}(NH_3)_5(H_2O)^{+++}$ formed. By means of a controlled precipitation, about 95% of the thiocyanato complex could be removed as the perchlorate salt, leaving about 95% of the aquo complex in the supernatant. Inactive thiocyanato complex was then added to this supernatant, the solution warmed slightly, and $[Co(NH_3)(SCN)](ClO_4)_2$ again precipitated. By means of three such "washings" with inactive thiocyanato complex, about 85% of the active aquo complex remained and only *ca.* 0.1% of the original active thiocyanato complex.

Experimental Results

Preliminary conventional exchange experiments, employing radiothiocyanate ion and inactive *trans*-$Co\,en_2(SCN)_2^+$ are shown in Fig. 1. Not until 80° was there an appreciable rate of appearance of activity in the complex, and the McKay plots[18] shown in the figure failed to show linear behavior unless some two days of pre-equilibration were allowed before adding the small amount of radiothiocyanate to the solution of complex plus inactive thiocyanate. In this figure, y and y_∞ denote the amounts of activity in the complex at time t and at exchange equilibrium. That this behavior resulted from a gradual attainment of aquation equilibrium was made probable by the results of separate aquation rate studies, shown in Fig. 2. It is seen that the rates are commensurate with the pre-equilibration times found necessary for the exchange runs. The data may be represented to within *ca.* 10% by an equilibrium constant of 0.030 for the first stage of aquation, and a first-order aquation constant of 0.060 hr.$^{-1}$; these are approximate because of the lack of ionic strength buffering, the presence of some extent of the second stage of aquation and the probable *trans* to *cis* isomerization also occurring.

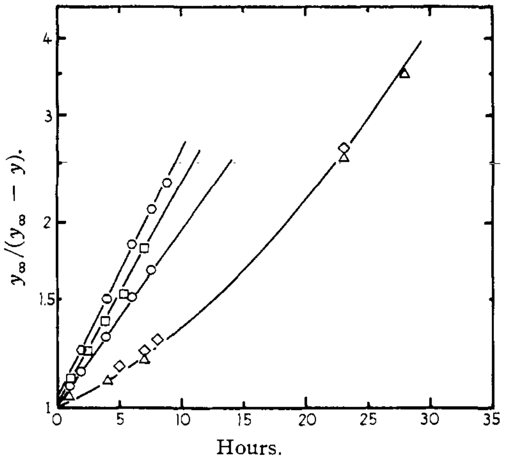

Fig. 1.—"Equilibrium" exchange between SC^*N^- and 0.038 *M* *trans*-$[Co\,en_2(SCN)_2]^+$ at 80°, *p*H 6.5: ◇, Δ, $(SC^*N^-) = 0.277$ *M*, 2 hr. pre-equilibration; □, 2 days pre-equilibration; ○, 4 days pre-equilibration; ⬡ ——, $(SC^*N^-) = 0.157$ *M*, 4 days pre-equilibration.

These and similar preliminary results with $Cr(NH_3)_5(SCN)^{++}$ indicated that any bimolecular exchange would be comparable in rate to that through the aquation path, and that a means of

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[17] M. Haissinsky and B. Pullman, *J. phys. rad.*, Ser. VII, 8, No. 2, 33 (1947).

[18] H. A. C. McKay, *Nature*, **142**, 997 (1938).

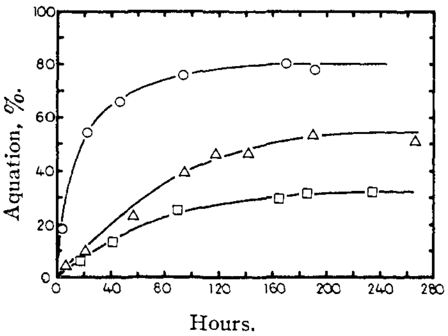

Fig. 2.—Aquation of *trans*-[Co en$_2$(SCN)$_2$]$^+$, A, at 80°, pH 6.5: ○, A = (ClO$_4^-$) = 0.0125 M; △, A = (SCN$^-$) = 0.01 M; □, A = (SCN$^-$) = 0.0500 M.

detecting the former against a high background of the latter would be necessary. Conventional exchange studies with equilibrium systems were ruled out, since the time required to reach aquation equilibrium also sufficed for some further decomposition of the complex. Exchange was therefore studied at temperatures such that the aquation was known accurately, but for times short enough that only a few per cent. aquation would occur. If radiothiocyanate ion were used, and the rate of appearance of activity in the complex determined, then, ideally, a non-zero initial exchange rate would be attributable to a direct or bimolecular exchange. Experimentally, such a non-zero initial rate was found but was due to the fact that even upon repeated recrystallizations 1 or 2% of aquocomplex would remain as an impurity in the thiocyanato complex. Thus with 0.02 M Cr(NH$_3$)$_5$(SCN)$^{++}$ and 0.0059 M SC^{14}N$^-$ at 70°, d(S/S^0)/dt = k was 0.019 hr.$^{-1}$, where S is the specific activity of the complex at time t, and S^0 the value corresponding to the initial specific activity of the radiothiocyanate. On repeating the experiment with 10% or 0.002 M added aquo complex present initially, k rose to 0.066 hr.$^{-1}$ and the first results could therefore be due to the presence, on the average, of a few per cent. of aquo complex. That this was true was shown by the results described below, which set a much lower limit to the maximum rate of any direct exchange.

The procedure finally adapted involved the use of radioactive complex and the determination of the rate of increase of the specific activity of the free thiocyanate ion also present. The system of rate equations then becomes, for short times

Aquation: (first-order regardless of mechanism)

$$\underset{a}{\mathrm{MA_5X^{++}}} + \mathrm{H_2O} \xrightarrow{k_1} \mathrm{MA_5(H_2O)^{+++}} + \underset{b}{\mathrm{X^-}}$$

$$\underset{x}{\mathrm{MA_5X^{*++}}} + \mathrm{H_2O} \xrightarrow{k_1} \mathrm{MA_5(H_2O)^{+++}} + \underset{y}{\mathrm{X^{*-}}}$$

Exchange:

$$\underset{x}{\mathrm{MA_5X^{*++}}} + \underset{b}{\mathrm{X^-}} \overset{k_2}{\rightleftharpoons} \underset{a}{\mathrm{MA_5X^{++}}} + \underset{y}{\mathrm{X^{*-}}}$$

where x, y and a, b are the moles per liter of radiothiocyanate and of total thiocyanate in the two forms. Also $x^0 = x + y$, $c^0 = a^0 + b^0 = a + b$, where the superscript denotes the initial value, and $S_x = x/a$, $S_x{}^0 = x^0/a^0$. The resulting rate equations are

$$\mathrm{d}x/\mathrm{d}t = -k_1x - k_2xb + k_2ay$$
$$\mathrm{d}S_x/\mathrm{d}t = -k(c^0S_x - a^0S_x{}^0)$$

and

$$S_x/S_x{}^0 = \frac{1}{c^0}[a^0 + b^0 \exp\,(c^0\ k_2t)]$$

which reduces to the McKay equation if $k_1 = 0$. If P is the increase in concentration of free thiocyanate that would correspond to the observed increase in S_y (*i.e.* assuming no exchange), then

$$P = S_yb^0/(S_x{}^0 - S_y) \qquad (1)$$

and if F be defined as the fraction of such apparent aquation, $F = P/a^0$, then

$$\mathrm{d}F/\mathrm{d}t = k_{\mathrm{app}} = k_1 + b^0k_2 \text{ (at short times)} \qquad (2)$$

Thus any direct exchange should appear as a dependence of k_{app} on the free thiocyanate concentration.

Aquation and Exchange of Cr(NH$_3$)$_5$(SCN)$^{++}$.—The results are summarized in Fig. 3 in which are plotted as a function of time both the apparent aquation in the presence of added thiocyanate and the true aquation as measured spectrophotometrically with no free thiocyanate initially present. Considering first the data of 50°, it is seen that the radiochemically determined values of F for b^0 = 0 agree well with the spectrophotometric ones, confirming the accuracy of the two techniques. However, for b^0 = 0.02 M at 50° and 0.2 M at 70°, no change in k_{app} was detectable. Thus b^0k_2 was less than a few per cent. of k_1; at 70°, k_2 in hr.$^{-1}M^{-1}$ was less than 0.015.

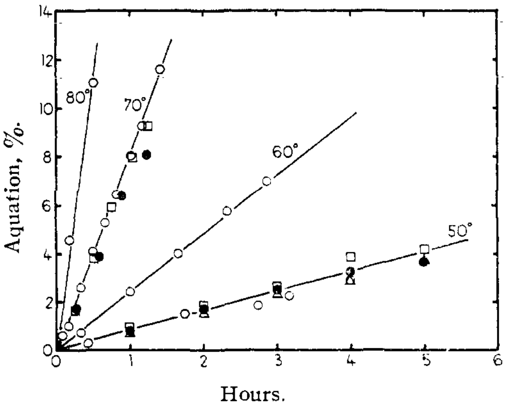

Fig. 3.—Aquation and exchange of [Cr(NH$_3$)$_5$(SC*N)]-(ClO$_4^-$)$_2$, A^*, at pH 2.5: 80°: ◑, A = 0.01 M; 70°: ○, A = 0.02 M; □, A = 0.02 M and (SCN$^-$) = 0.055 M; ●, A = 0.2 M and (SCN$^-$) = 0.4 M (no ClO$_4^-$); 60°: ○, A = 0.01 M; 50°: ○△, A = 0.01 M; ●, A = 0.01 M; □, A = 0.01 M, (SCN$^-$) = 0.02 M.

Aquation and Exchange of [Co(NH$_3$)$_5$(SCN)]$^{++}$.—These results are given in Figs. 4 and 5. It is seen that at 90°, the apparent aquation rate increased several fold in the presence of up to 0.5 M added thiocyanate ion. Although concordant values of k_2 result from the application of equation 2 to the data, the possibility remained that the aquation rate itself, *i.e.*, k_1, was varying. Thus Garrick[8c] found that the aquation rate of Co(NH$_3$)$_5$Cl^{++}

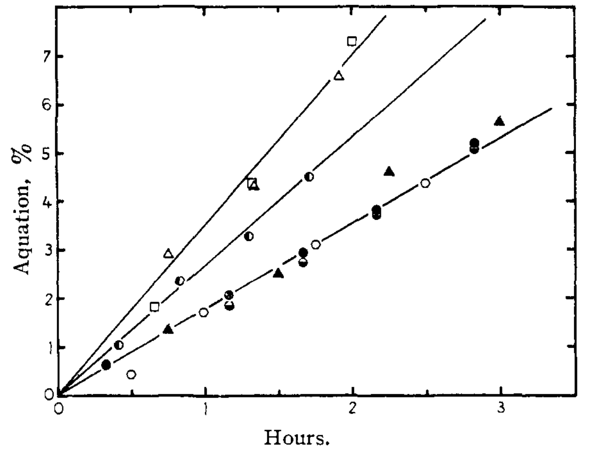

Fig. 4.—Aquation and exchange of $[Co(NH_3)_5(SC^*N)](ClO_4)_2$, A^*, at 90°, pH 2.5. Spectrophotometric: ○ ◒, $A = 0.02$ M; C^{14} labeled complex: ●, $A^* = 0.02$ M; △, $A = 0.07$ M and $(SCN^-) = 0.54$ M (no ClO_4^-); ◐, $A = 0.167$ M and $(SCN^-) = 0.33$ M (no ClO_4^-); Co^{60} labeled complex: □, $A = 0.07$ M and $(SCN^-) = 0.55$ M (no ClO_4^-); △, $A = 0.02$ M.

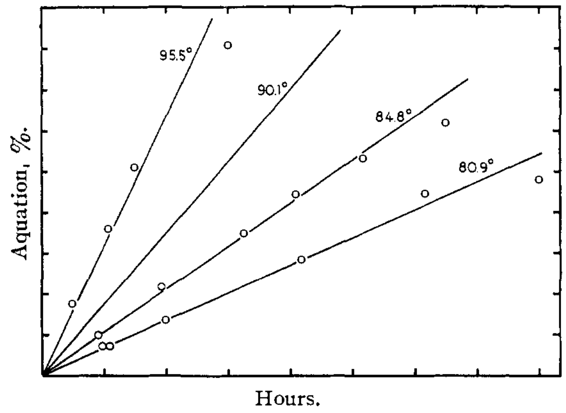

Fig. 5.—Aquation rates for $[Co(NH_3)_5(SCN)](ClO_4)_2$; (complex) = 0.02 M, pH 2.5.

varied with the nature of the anion, and Taube and Posey[8e] likewise for $Co(NH_3)_5(SCN)^+$. Since such an effect, if any, occurred in the present work only at high free thiocyanato to complex ratios, the spectrophotometric method was insufficiently accurate. The procedure finally adopted was that of employing Co^{60} labeled $Co(NH_3)_5(SCN)^{++}$ and determining the rate of production of radioactive aquo complex, as described under Experimental. Because of the elaborate procedure, the results suffered in precision but, as shown in Fig. 5, clearly demonstrated that the aquation rate increased with free thiocyanate concentration to the same degree as did the apparent aquation rates previously determined. This anion effect on the aquation rate may be represented by the equation $k_1(\text{hr.}^{-1}) = 0.019 + 0.029(SCN^-)$, at 90°.

Aquation and Exchange of *trans*-Co $en_2(SCN)_2^+$.—The results are given in Fig. 6. This system was studied in less detail because of the curvature in the rate plots even at short times, presumably due to a *trans* to *cis* isomerization. Again, however, the apparent aquation rate with $b^0 = 0.05$ M was the same as the spectrophotometric value, although an increase was found in the presence of 0.5 M chloride ion.

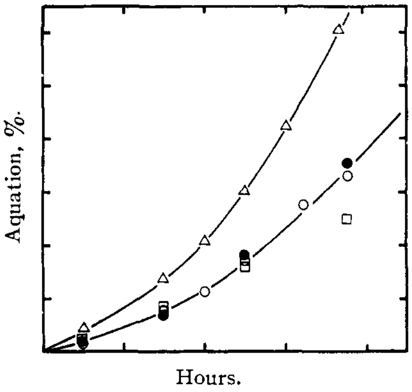

Fig. 6.—Aquation and exchange of *trans*-$[Co\ en_2(SC^*N)_2](ClO_4)$, A^*, at 80°, pH 6.5: ○, $A = 0.05$ M; ●, $A^* = 0.05$ M; □, $A^* = 0.05$ M, $(SCN^-) = 0.05$ M; $A = 0.05$ M, $Cl^- = 0.05$ M.

Summary of Aquation Data.—The temperature dependence of the aquation rate constants for $Cr(NH_3)_5(SCN)^{++}$ and $Co(NH_3)_5(SCN)^{++}$ is shown in Fig. 7, and data are summarized in Table I, with results for other pentammine complexes included for purposes of comparison.

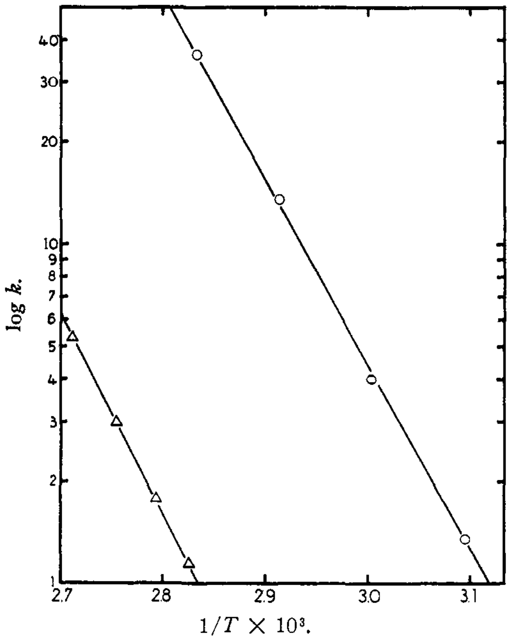

Fig. 7.—Temperature dependence of the aquation rates: ○, $[Cr(NH_3)_5(SCN)](ClO_4)_2$; △, $[Co(NH_3)_5(SCN)](ClO_4)_2$ (k in min.$^{-1}$).

It is seen that for the pentamine complexes the order of increasing aquation rate is SCN, Cl, Br, I, and that the cobalt(III) complexes aquate more slowly than do the corresponding Cr(III) ones. These effects stem primarily from activation energy differences. Interestingly, while thiocyanate ion catalyzed the aquation of $Co(NH_3)_5(SCN)^{++}$, it did not catalyze that of $Cr(NH_3)_5(SCN)^{++}$, yet in the studies of water exchange, the exchange of

TABLE I

AQUATION OF ACIDOPENTAMMINE COMPLEXES AT 25°[a]

Complex	k^b, min.$^{-1}$	$\Delta H\ddagger$	$\Delta S\ddagger^c$
$Co(NH_3)_5(SCN)^{++}$	1.7×10^{-7}	26.8	−8.4
(Cl)	1.0×10^{-4}	23.7	−1.6
(NO_3)	1.6×10^{-4}	26.0	7.1
(Br)	3.8×10^{-4}	24.0	−2.4
$Cr(NH_3)_5(SCN)^{++}$	5.6×10^{-6}	24.9	−7.8
(Cl)	4.8×10^{-4}	21.8	−8.8
(Br)	3×10^{-3}	22	−5
(I)	10^{-2}(0°)		

[a] Values for other than the thiocyanato complexes from references 8a, 8b. [b] Calculated values. [c] Calculated on the basis of a frequency factor of 10^{13} sec.$^{-1}$.

H_2O^{18} with $Cr(H_2O)_6^{+++}$ was first order in anion[8g] while the exchange with $Co(NH_3)_5(H_2O)^{+++}$ was unaffected or slightly retarded by sulfate ion.[9]

Ion Pair Formation.—In view of the anion effects found here, the absorption spectra of the various complexes were determined with and without the presence of added thiocyanate ion. Evans and Nancollas[19] found that with $Co(NH_3)_6^{+++}$ ion pair formation occurred with halide and with azide ions, with considerable shifts in the extinction coefficient of the complex in the wave length region 200–300 mμ. Although as complete a study was not made here, it is apparent from Fig. 8 that the spectra of $Co(NH_3)_5(H_2O)^{+++}$ and $Cr(NH_3)_5(H_2O)^{+++}$ are drastically shifted in this wave length region. Those of the thiocyanato complexes were unaffected. Presumably, the ion pair formation is extensive between SCN^- and $M(NH_3)_5H_2O^{+++}$, but not between SCN^- and $M(NH_3)_5(SCN)^{++}$.

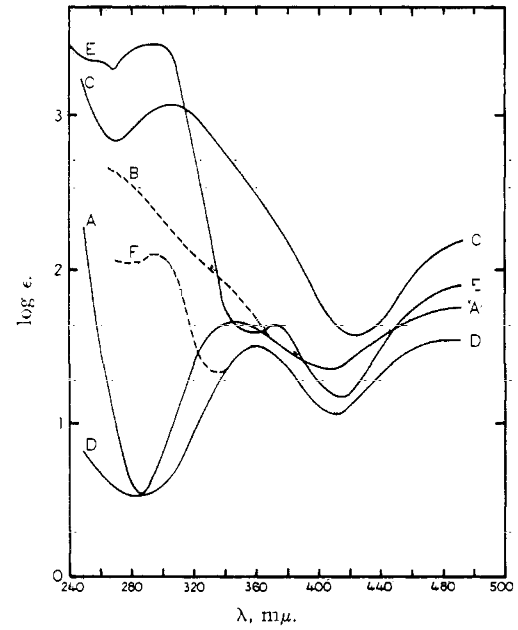

Fig. 8.—Absorption spectra: AA, $[Co(NH_3)_5(H_2O)](ClO_4)_3$; B, same as AA but with 0.3 *M* added SCN^-; CC, $[Co(NH_3)_5(SCN)](ClO_4)_2$ (no effect with added SCN^-); DD, $[Cr(NH_3)_5(H_2O)](ClO_4)_3$; F, same as DD, but with 0.3 *M* added SCN^-; EE, $[Cr(NH_3)_5(SCN)](ClO_4)_2$ (no effect with added SCN^-). The concentrations of complex were chosen so that in the various wave length regions, optical densities at *ca.* unity were obtained with 1-cm. cells. (Some of the spectra were obtained by Mr. K. Vorres.)

Discussion

The present results and those cited in the introduction have indicated that with hexacoördinated complex ions the bimolecular or S_N2 replacement of ligands does not occur except insofar as it contributes to the aquation process. There remains the question of whether the specific anion effects observed in the aquation and water exchange reactions with positively charged complex ions permit reasonable inference.

In view of the results of Evans and Nancollas[19] as well as those of Olson and Simonson[8b] it seems reasonable to treat the specific anion effects as arising from ion pair formation, modifying either the reactants, or, in the case of an S_N1 mechanism, the pentacoördinated intermediate as well. Considering this last possibility first, the mechanism could then be particularized as

$$M(NH_3)_5X^{++} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [M(NH_3)_5]^{+++}X^- \text{ (ion pair)}$$

$$[M(NH_3)_5]^{+++}X^- = M(NH_3)_5^{+++} + X^- \quad \text{(rapid equilibrium)}$$

$$M(NH_3)_5^{+++} + H_2O \xrightarrow{k_2} M(NH_3)_5(H_2O)^{+++}$$

$$[M(NH_3)_5]^{+++}X^- + H_2O \xrightarrow{k_3} [M(NH_3)_5(H_2O)]^{+++}X^-$$

$$[M(NH_3)_5(H_2O)]^{+++}X^- \overset{K}{=} M(NH_3)_5(H_2O)^{+++} + X^- \quad \text{(rapid equilibrium)}$$

Assuming a stationary state restriction on the sum of the species $M(NH_3)_5^{+++}$ and $[M(NH_3)_5]^{+++}X^-$, the rate law becomes

$$R = \frac{k_1[M(NH_3)_5X^{++}]}{1 + k_{-1}/[k_3 + k_2K/(X^-)]}$$

However, as (X^-) increases, R *decreases* from the upper limit $k_1[M(NH_3)_5X^{++}]$ to the lower limit $k_1[M(NH_3)_5X^{++}]/(1 + k_{-1}/k_3)$, which is the opposite of the observed effect.

It thus appears that the specific anion effects must result from ion pair formation with the reactant species, regardless of mechanism. Therefore, the fact that essentially opposite effects are found for the chromium and the cobalt complexes, both in the case of aquation and in that of water exchange, strongly suggests that different mechanisms are important in the two cases. It might be supposed that the S_N1 mechanism should be about equally available to both chromium and cobalt complexes, but that the chromium ones should, in addition, have a lower energy path for reaction through the S_N2 process. This would explain qualitatively the greater lability of the chromium complexes, as evidenced by their aquation rates, and would be in agreement with the observation of Brown, *et al.*,[10] that the second-order ligand replacements in Co $en_2Cl_2^+$ in methanol were faster than these proceeding by first-order kinetics, if one accepts their conclusion that the former represented an S_N2 and the latter an S_N1 process.

A reasonably consistent explanation of the various anion effects can be made with this assumption

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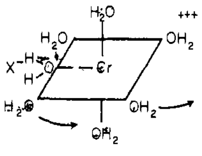
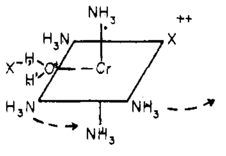
[19] M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

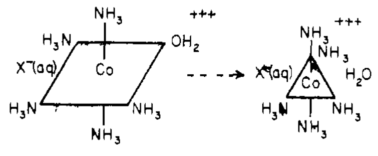
that the trivalent chromium complexes do react primarily through the S_N2 mechanism and those of cobalt through the S_N1 mechanism. Accepting the edge displacement hypothesis of Brown, *et al.*, as applying to S_N2 processes, then the exchange of water with $Cr(H_2O)_6^{+++}$ involves the displacement of identical groups. The strong ion pairing that would be present might favor the displacement process through orienting effect of the anion on the outer sphere waters as was suggested by Taube, *et al.*[9g] For $Cr(NH_3)_5X^{++}$, not only would ion pairing be much weaker, but since the ion paired anion would tend to be on a side away from the bound anion, it could not influence edge displacement leading to aquation. For the cobalt complexes, assuming an S_N1 mechanism, the transition state leads to a pentacoördinated intermediate, and the edge displacement picture does not apply. Since the rate-determining step here appears to be the formation of the intermediate, the rate of substitution processes would be affected by ion pairing in the reactant only through general attraction or repulsion effects. Thus, for the water exchange with $Co(NH_3)_5(H_2O)^{+++}$, although strong ion pairing would occur, no particular effect on the rate of dissociation of a neutral water molecule would be expected, nor is observed. Rutenberg and Taube[9] commented that the slight retardation in this exchange, in the presence of sulfate ion, constituted strong evidence for an S_N1 mechanism. On the other hand, the aquation of $Co(NH_3)_5X^{++}$ might well be anion influenced since some ion pairing would be expected even with a divalent ion, and the charge repulsion between the inner and outer X groups should favor the dissociation of the inner group. The above representations are (the actual geometry of the pentacoördinated intermediate is not known, and the one chosen is for illustrative purposes)



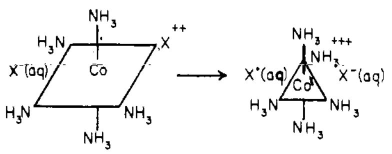
H_2O exchange catalyzed by X^-



Aquation not catalyzed by X^-



H_2O exchange not catalyzed by X^-



Aquation catalyzed by X^-

Brown, *et al.*,[10] consider that the second-order kinetics of the hydrolysis of $Co(NH_3)_5Br^{++}$[8a,b] and of the substitution in methanol solution of Cl^- in $Co\,en_2Cl_2^+$ by nucleophilic ions such as methoxide[10] to be evidence for an S_N2 mechanism in these cases. While this may be correct, it is noteworthy that the preceding discussion of ion pair effects accounts for anion dependencies in some cases strong enough to give rates first order in anion or second order over-all. Thus the SCN^- effect on the aquation rate of $Co(NH_3)_5(SCN)^{++}$ was expressible by the rate law $k_1 = 0.019 + 0.029(SCN)^-$. Had the anion effect been somewhat stronger, a simple second-order rate expression would have been found. It is thus possible that the second-order kinetics of hydrolysis is in this category, with the anion adding to a pentacoördinated S_N1 intermediate as well as catalyzing its formation. Although Brown, *et al.*, dealt with 1–1 electrolytes, in methanol solution some ion pairing would still be expected, and ionic strength effects were in fact noted in the first-order rate constants computed for the displacement by halide and thiocyanate ions. In order to evaluate the possibility that the second-order displacement kinetics observed with methoxide, azide and nitrite ions might correspond to a higher degree of ion pair catalysis, rather than to a change in mechanism, studies on ion pair formation in this solvent would be necessary.

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