ties of the complexes, probably reflects the differing environments of the copper ion in the two cases.

Except for the appearance of an intense band at *ca.* 500 mμ, spectra of the 1:1 copper(II) bromide derivatives are essentially similar to those of the chlorides displaying low magnetic moments. Also, the shoulder at 900 mμ is more pronounced in the case of the bromides. The origin of the 500-mμ band is uncertain, although as seen in Figure 1 spectra of the chlorides do show shoulders of much weaker relative intensity in this region. As with the condensed chloride complexes with high magnetic moments, the spectrum of the 1:1 copper(II) bromide–3-nitro-6-methylquinoline N-oxide derivative is significantly different from those of the corresponding complexes displaying low magnetic moments. As indicated in Table IV, the d–d band is shifted from *ca.* 730 mμ down to 790 mμ in the bromide-bridged species. This again is probably an indication of the different environments of the copper ion in the oxygen-bridged and bromide-bridged species.

The spectra of the 2:1 complexes with copper(II) chlorides show similar features to those of the condensed complexes. The maxima due to transitions within the d shell are shifted to slightly higher energy in the 2:1 derivatives.

Conclusion

The spectral and magnetic properties of the condensed copper(II) halide complexes of substituted quinoline N-oxides indicate that either oxygen-bridged or halogen-bridged derivatives may be formed. The experimental evidence indicates that there must be a critical relationship between such factors as the donor properties and steric requirements of the ligands and the lattice energies of the various compounds in favoring the formation of one species over another.

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The Dissociative Interchange Mechanism for the Formation of Acidopentaamminecobalt(III) Ions[1]

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Abstract: The rates of formation of the complex ions, $Co(NH_3)_5X^{n+}$, are discussed with special attention to the rate of reaction in the outer-sphere complex (or ion pair) $Co(NH_3)_5OH_2^{3+}\cdots X^{(3-n)-}$. (New data are presented for entry of chloride and thiocyanate ions at 45° and unit ionic strength.) It is observed that the rates are similar for all anions studied so far and are a nearly constant fraction (0.2) of the water exchange rate for $Co(NH_3)_5OH_2^{3+}$. These results may be understood in terms of an activation process which is *dissociative*, leading to a *transition state* in which entering and leaving ligands are at most weakly bound *but* in which no intermediate of significant lifetime is formed. The similarity of rates of entry implies weak binding in the transition state. The anion entry rates appear to be related to the water exchange rate through a statistical factor connected with the probability that an anion is to be found in an outer coordination sphere site when a cobalt–water dissociation event occurs.

This paper is concerned with the kinetics and equilibrium of reaction 1, where X is a univalent anionic ligand or sulfate and *n* is 2 or 1, respectively. Two

$$Co(NH_3)_5X^{n+} + H_2O \rightleftharpoons Co(NH_3)_5OH_2^{3+} + X \qquad (1)$$

mechanistic pathways for this process have often been discussed, and neither seems to give an entirely felicitous account of the details. In one case,[2] the process has been regarded as a simple nucleophilic attack of the entering group on the complex, leading to a concerted substitution which is bimolecular and adequately represented by eq 1. The alternative account[3] suggests the participation of five-coordinate intermediate of the pathway represented by

$$\begin{aligned} Co(NH_3)_5X^{n+} &\rightleftharpoons Co(NH_3)_5^{3+} + X \\ Co(NH_3)_5^{3+} + H_2O &\rightleftharpoons Co(NH_3)_5OH_2^{3+} \end{aligned} \qquad (2)$$

The kinetics of eq 2 require the prediction that X and H_2O compete for the intermediate. Strong evidence against eq 2 was presented by Pearson and Moore[4] who were able to show for the case of $X = Br^-$ or NO_3^- that addition of SCN^- to the solution did not lead to any detectable direct production of $Co(NH_3)_5NCS^{2+}$. The experiment is conclusive because sufficient kinetic and equilibrium data are available to predict[3] the rate of capture of the intermediate by SCN^- if the reaction were going by mechanism 2.

The alternative account which focuses attention on the bimolecularity of the substitution is unsatisfactory in the

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(2) (a) S. C. Chan, *J. Chem. Soc.*, 2375 (1964); (b) S. C. Chan and J. Miller, *Rev. Pure Appl. Chem.*, **15**, 11 (1965).

(3) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(4) R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964).

sense that studies of structure variation (*e.g.*, a linear free-energy relationship between rates and equilibria as the leaving group is varied[5]) strongly imply a transition state for the reaction with at most very weak bonds to the participating ligands.

Here, we wish to *explore* the applicability of a mechanistic scheme which assumes that the transition state is reached *dissociatively* but assumes *no* intermediate along the reaction pathway of *sufficient stability to be selective in its reactions.* We assume that the transition state must incorporate a ligand from its immediate solvation shell (outer coordination sphere) so that although activation is dissociative the reaction is "accidentally bimolecular." The entering group must be present in advance of the transition state. Such a scheme is designated "dissociative interchange"[6] (I_d), dissociative to denote the activation process and interchange to indicate that the substitution process is a rearrangement between inner and outer coordination spheres (a process first discussed by Alfred Werner). The I_d mechanism is shown in eq 3 for the complex formation reaction.

$$\begin{gathered} Co(NH_3)_5OH_2^{3+} + X^- \overset{K_a}{\rightleftharpoons} Co(NH_3)_5OH_2^{3+}\cdots X^- \\ Co(NH_3)_5OH_2^{3+}\cdots X^- \xrightarrow{k} Co(NH_3)_5X^{2+}\cdots OH_2 \end{gathered} \tag{3}$$

Note that the degree of ion association characterized by the association constant K_a is quite important and, if the activation process is genuinely dissociative, the rate constant, k, should be independent of the nature of the entering group. There is an additional important prediction from this scheme. In a simple 1:1 outer-sphere complex (ion pair), $s - 1$ of the outer-sphere sites will be occupied by solvent (water) molecules if s is the solvation number of the complex. If the anionic partner occupies outer-sphere sites randomly, dissociation of the coordinated water will not normally occur adjacent to the anion; $(s - 1)/s$ dissociative events will lead to water exchange and only a fraction, $1/s$, will lead to anation. Thus, the I_d mechanism predicts that anations occur at very nearly the *same rate* in 1:1 outer-sphere complexes as the nucleophilicity of the entering group is varied *but* that all anations occur at approximately *1/s times the rate of solvent exchange.*

Experimental Section

Materials. The complexes $[Co(NH_3)_5Cl](ClO_4)_2$, $[Co(NH_3)_5NCS](ClO_4)_2$, and $[Co(NH_3)_5OH_2](ClO_4)_3$ were prepared by well-known methods[7] and characterized spectrophotometrically. Extinction coefficients at wavelengths important to this study are collected in Table I. Reagent grade sodium chloride and sodium thiocyanate were used without further purification. Sodium perchlorate solutions for ionic strength control were prepared by titration of standardized concentrated sodium hydroxide solutions with perchloric acid and dilution to the required volume. Stock solutions of sodium chloride, sodium perchlorate, and water used in preparing reaction mixtures were adjusted to pH 3 by addition of perchloric acid to repress acid dissociation of $Co(NH_3)_5OH_2^{3+}$ (in experiments with thiocyanate, the pH was adjusted to 5).

Table I. Some Features of Visible Spectra of Complexes Used in This Study (Absorption Maxima and Wavelengths Used in Reaction Studies)

Complex	λ_{max}, mμ	ϵ_{max}, M^{-1}	λ, mμ	ϵ, M^{-1}	Ref
$Co(NH_3)_5Cl^{2+}$	532	50.7	555	44.0	This work
	532	51.0	...	...	6b, 10
$Co(NH_3)_5OH_2^{3+}$	491	48.6	555	18.2	This work
	491	47.5	...	...	6b, 10
$Co(NH_3)_5NCS^{2+}$	500	177	500	177	This work
	500	174	...	...	4

Equilibrium Studies. The equilibrium between $[Co(NH_3)_5Ci]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$ was studied at 45.0° as a function of NaCl concentration in a medium maintained at an ionic strength of 1.00 with $NaClO_4$ (pH 3) and in a medium of variable ionic strength (no $NaClO_4$, pH 3). Solutions maintained in constant-temperature baths for more than seven half-lives of the approach to equilibrium reaction were quenched to 25° and examined spectrophotometrically in 5.00-cm cells on a Beckman DU equipped with a Gilford photometer unit or in 1.00-cm cells on a Cary Model 14 equipped with a 0.0–0.2-absorbance unit slidewire. Total cobalt complex concentrations were chosen in the range from 5×10^{-4} to 1.5×10^{-3} M. Sodium chloride concentrations were varied from 0.03 to 0.7 M. The wavelengths examined were 555 and 530 mμ.

Kinetic Studies. The rate at which reaction 1 approaches equilibrium was examined in the case that $X = Cl^-$ in the same media as those employed in the equilibrium studies. The experiments were carried out at 45.0° in the thermostated cell chamber of a Cary 14 spectrophotometer using 1.00-cm cells and a 0.0–0.2-absorbance unit slidewire. Good pseudo-first-order rate plots were obtained over more than two half-lives of the reaction. Rates of the reaction of $[Co(NH_3)_5OH_2]^{3+}$ with thiocyanate (which goes to "completion") were examined under similar conditions except that the pH was 5, the spectrophotometer was a Beckman DU, and the wavelength used was 490 mμ.

Ion-Association Study. The extent of association between $Co(NH_3)_5OH_2^{3+}$ and Cl^- was explored by analysis of the enhancement of ultraviolet absorption by the complex at 230 mμ at 25° (pH 3, $\mu = 1.00$). Data were analyzed by the method of Newton and Arcand as employed by Evans and Nancollas.[8] The concentration of the cobalt complex was 1×10^{-4} M, and the chloride concentration was varied from 0.003 to 0.5 M.

Results

The first column of Table II presents the equilibrium concentration ratio $[Co(NH_3)_5OH_2^{3+}]/[Co(NH_3)_5Cl^{2+}]$ as a function of chloride concentration. Rates of approach to equilibrium are also collected in Table II.

Table II. Equilibrium Concentration Ratios and Rates of Approach to Equilibrium as a Function of Chloride Concentration

	[RCl]/[ROH$_2$]		k, sec^{-1} [a]	
[Cl$^-$], M	μ variable	μ = 1.00	μ variable	μ = 1.00
0.05	0.26	0.14	2.8×10^{-5}	0.7×10^{-5}
0.1	0.44	0.25	3.2×10^{-5}	1.7×10^{-5}
0.2	0.68	0.42	3.7×10^{-5}	2.7×10^{-5}
0.3	0.84	0.52	4.1×10^{-5}	3.2×10^{-5}
0.4	0.92	0.57	4.4×10^{-5}	3.6×10^{-5}
0.5	0.98	0.62	...	3.8×10^{-5}
0.6	...	0.67	...	3.9×10^{-5}

[a] Rate of approach to equilibrium.

Since chloride is in excess, these rates are resolved into pseudo-first-order forward (acid hydrolysis) and reverse (anation) rates with the aid of the equilibrium data and the formalism for opposed first-order reactions.[9] The acid hydrolysis rates are shown in Figure

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[5] C. H. Langford, *Inorg. Chem.*, 4, 265 (1965).

[6] (a) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 1. (b) The term interchange was introduced by H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, 75, 1463 (1953).

[7] (a) F. Basolo and R. K. Murmann, *Inorg. Syn.*, 4, 171 (1953); (b) A. Werner and E. H. Müller, *Z. Anorg. Chem.*, 22, 101 (1900).

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

[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

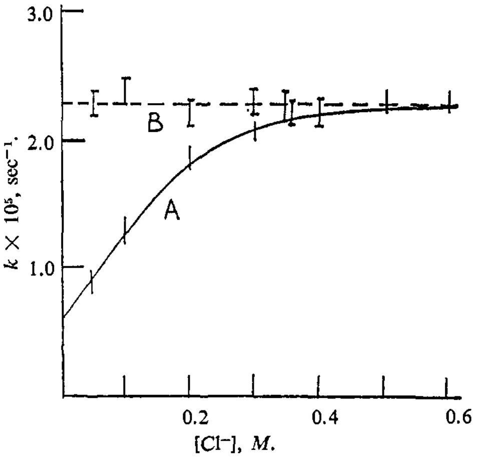

Figure 1. Rates of acid hydrolysis of the chloropentaamminecobalt(III) ion as a function of chloride concentration: (A) constant ionic strength, (B) variable ionic strength (no perchlorate added).

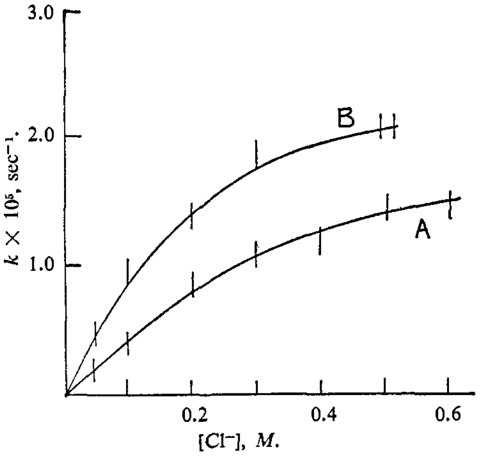

Figure 2. Rates of formation of the chloropentaamminecobalt(III) ion from the corresponding aquo complex as a function of chloride concentration: (A) constant ionic strength, (B) variable ionic strength (no perchlorate added).

1 and the anation rates in Figure 2. Since anation by the thiocyanate ion goes to completion, only anation rates are given. They appear in Figure 3.

According to the dissociative interchange mechanism described in eq 3, the chloride or thiocyanate dependence (X^- dependence) of the observed pseudo-first-order rate constants, k', is given by eq 4, which employs

$$k' = \frac{kK_a[X^-]}{1 + K_a[X^-]} \tag{4}$$

the notation of (3). The distinct *curvature* in Figures 2 and 3 indicate that the term $K_a[X^-]$ is *not small*.

A trial-and-error analysis based on a least-squares criterion was employed to find best choices of the parameters K_a and k, the outer-sphere association constant, and rate constant for interchange, respectively. The values of the parameters with the associated standard deviations are given in Table III along with interchange rate constants from the work of Taube and his collaborators.[6b,10]

The value of K_a for association of chloride with $Co(NH_3)_5OH_2^{3+}$ was not checked independently at 45° because of the relatively rapid formation reaction. However, it was measured at 25° utilizing the effect of chloride on the absorption spectrum of $Co(NH_3)_5OH_2^{3+}$ at 230 mμ. A plot of the function $(A - A_0)/[Cl^-]$ against A, where A is the absorbance at a given $[Cl^-]$ and A_0 is the absorbance in the absence of chloride, should be linear with the slope equal to $-K_a$ and the intercept equal to K_aA_1, where A_1 is the absorbance of the ion pair.[7] This plot is shown in Figure 4. The

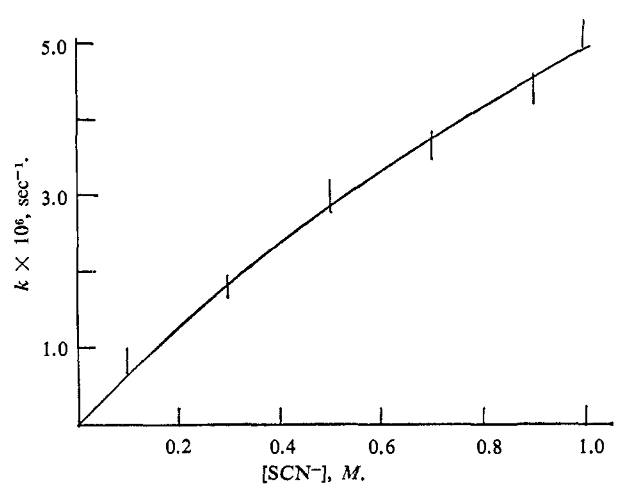

Figure 3. Rates of formation of the thiocyanatopentaamminecobalt(III) ion from the corresponding aquo complex as a function of thiocyanate concentration at constant ionic strength.

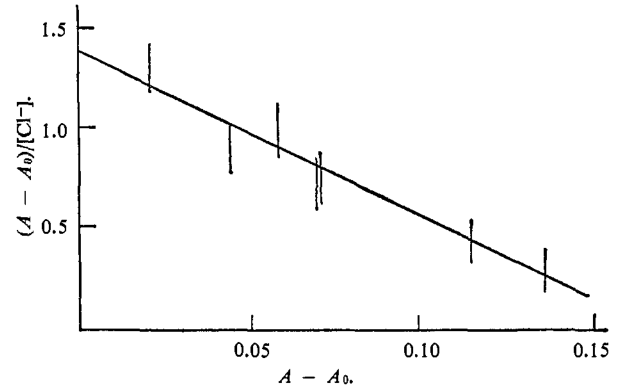

Figure 4. Determination of the outer-sphere association constant of chloride with the aquopentaamminecobalt(III) ion by the method of ref 8. The enhancement of absorbance at 230 mμ ($A - A_0$) is studied as a function of chloride concentration (25.0°, μ = 1.00, and pH 3).

Table III. Conditional Equilibrium Constants for Formation of Outer-Sphere Complexes (K_a) and Rate Constants for Formation of Inner-Sphere Complexes from Outer-Sphere Complexes[a]

X	K_a, M^{-1}	k, sec^{-1}	Std dev	k/k (water exchange)	Ref
SO_4^{2-}	...	2.4×10^{-5}		0.24	6b
Cl^-	3.1	2.1×10^{-5}	0.078×10^{-5}	0.21	This work
SCN^-	0.43	1.6×10^{-5}	0.016×10^{-5}	0.16	This work
$H_2PO_4^-$	...	0.77×10^{-6} [b]		0.13	10a
H_2O	...	1.0×10^{-4}		...	10b
		5.8×10^{-6} [b]			10b

[a] At 45° except where noted. [b] At 25°.

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(10) (a) W. Schmidt and H. Taube, *Inorg. Chem.*, 2, 698 (1963); (b) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, 80, 2642 (1958).

slope yields a value of $K_a = 3.2 \pm 0.3$ in good agreement with the value from analysis of kinetic data and with values obtained at other wavelengths. Note that the results of Evans and Nancollas[8] suggest that the result should be insensitive to temperature, a view which receives direct support from equilibrium studies of the $Co(NH_3)_5OH_2^{3+}$–chloride system reported elsewhere.[11]

Discussion

1. The Importance of Ion Association. Since the extent of ion association between triply charged cobalt ammine complexes and simple anions has been a subject of some controversy,[12] we note that substantial *specific* ion effects are seen in all of the equilibrium and kinetic curves. This would seem to justify the approach adopted here. Additional support is derived from independent spectrophotometric measurement of outer-sphere association between $Co(NH_3)_5OH_2^{3+}$ and Cl^- which gives a value of $K_a = 3.2$ at 25° and unit ionic strength in reasonable agreement with the value in Table III. However, *it must be emphasized that the "constants" reported are in no sense thermodynamic equilibrium constants.* They simply provide a convenient measure of the extent of ion association in these media and indicate anion concentrations at which the equilibrium is "saturated" and a limiting rate for complex formation is reached.

2. The Values of "Limiting" Complex Formation Rates. Compare the first-order rate constants in Table II. The limiting rates for complex formation for the outer-sphere complexes $Co(NH_3)_5OH_2^{3+}\cdots SO_4^{2-}$ and $Co(NH_3)_5OH_2^{3+}\cdots H_2PO_4^-$ are reasonably accurately known since the association constants, K_a, proved large enough to permit fairly unambiguous determinations. They are seen to differ by a factor of about 2, being respectively 0.24 and 0.13 times the water exchange rate. In order to assess the role of the entering group in the transition state for complex formation, it was desirable to obtain similar rate constants for significantly different entering groups. The values have proved more difficult to obtain because of smaller K_a values and are presumably less accurately determined. But, the values for $Co(NH_3)_5OH_2^{3+}\cdots Cl^-$ and $Co(NH_3)_5OH_2^{3+}\cdots NCS^-$ are estimated to be 0.21 and 0.16 times the water exchange rate. Thus, the variation in these first-order rate constants is *less than a factor of 2* for formation of a series of complexes differing in stability by about two powers of ten. That is, with nucleophiles of charge −2 or −1 and donor atoms varying on Cl, O, and N, only very small rate differences are detected. These results lend substantial support to the view that the absence of a five-coordinate intermediate in these reactions does not imply assistance from an entering nucleophile in the activation process. Activation is apparently dissociative (d).

3. Comparison to Water Exchange Rate. The most striking feature of the results is that *all* complex formation rates are *less than* the water exchange rate by a factor near 5. Since anion entry rates are so similar, this might be considered surprising, but it is easily rationalized under the idea of dissociative interchange (I_d). If the transition state is reached by very substantial weakening of the bond to the leaving group but the system does not have access to any reasonably stable five-coordinate state, it must stabilize by adding the immediately available ligand. Since the majority of outer-sphere sites are still occupied by water molecules in the 1:1 outer-sphere complex (ion pair) between $Co(NH_3)_5OH_2^{3+}$ and an anion, the most probable fate of an activated complex is recombination with an outer-sphere water molecule. Except in the study of water exchange (when all outer-sphere sites are occupied by water), water exchange is an undetectable, fruitless process. Thus, anion entry (complex formation) is expected to proceed at a rate less than water exchange and governed by the probability that the anion in the 1:1 outer-sphere complex occupies the site adjacent to the leaving inner-sphere water molecule. The factor of 5 seems reasonable.

Finally, it is important to note that the relationship between interchange complex formation rates and solvent exchange rates discussed for the $Co(NH_3)_5OH_2^{3+}$ system is not an isolated example. Murray and Barraclough observed a sulfate entry rate 0.25 times the water exchange rate for formation of *cis*-$Co(en)_2OH_2SO_4$,[13] and Earley and Duffy[14] observed entry rates for chloride and thiocyanate of about 5% of the water exchange rate in studies of formation of $Cr(NH_3)_5X^{2+}$ ($X = Cl^-, SCN^-$).

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(11) C. H. Langford and W. R. Muir, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9-14, 1967.

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