7 is a plot of chemical shift *vs.* σ constant for the N-methylpyridinium compounds.

Table III lists slopes and intercepts calculated by a least-squares fit of the dependence of the chemical shift on Hammett's σ constants. The electronic effect of the pyridine ring substituent upon the chemical shift of the methyl group is reduced from a slope of −0.245 to a slope of −0.155 or −0.171 upon interposition of a cobalt(III) ion. Therefore, about two-thirds of the electronic effect is transmitted through the cobalt to the methyl group. This ratio is surprisingly high. It can be compared with a corresponding value for an sp^3 carbon, commonly one-third but with estimates as high as half.[19] Since the electronic effect must depend on the overlap between the methyl and cobalt orbitals, we expected to find a larger conduction in the more negatively charged (and hence more extended orbitals) dimethylglyoximato complexes than in the diacetyl monoxime iminopropanato complexes, but this appears not to be true. The total charge is larger on the dimethylglyoximato complex but there are two oxygens to carry the charge compared to only one in the diacetyl monoxime iminopropanato complexes.

TABLE III

CORRELATION OF CHEMICAL SHIFTS WITH HAMMETT'S σ CONSTANTS BY A LEAST-SQUARES FIT TO A STRAIGHT LINE

Ordinate	Intercept	Slope	Correlation coefficient	Per cent conduction
$\tau(CH_3\text{–Co})^a$	9.32	−0.155	−1.00	63
$\tau(CH_3\text{–Co})^b$	9.47	−0.171	−0.98	70
$\tau(CH_3\text{–Co})^c$	9.21	−0.166	−0.95	68
$\tau(CH_3\text{–N}^+)^d$	5.65	−0.245	−0.94	100

[a] For $CH_3Co(DH)_2py$-4-X in CH_2Cl_2. [b] For $CH_3Co(DH)_2py$-4-X in DMSO-d_6. [c] For $[CH_3Co[(DOH)(DO)pn]pyX]^-$ in DMSO-d_6. [d] For CH_3py^+ in D_2O.

Clearly, the trans effect is large. The conduction through the cobalt atom is highly efficient. These results do not answer the question of what orbitals are responsible for the trans effect, σ or π orbitals.

Acknowledgments.—This study was supported by U. S. Public Health Service Grant GM 8285.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK, STONY BROOK, NEW YORK 11790

Aquation of Nitritopentaamminecobalt(III) Catalyzed by Hydrogen, Halide, and Thiocyanate Ions[1]

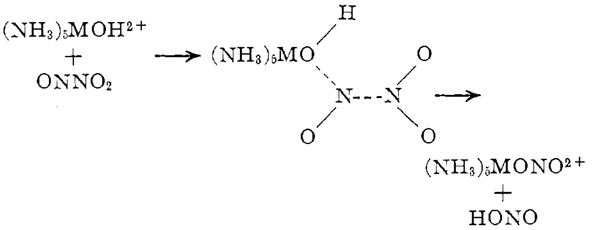
BY DANIEL E. KLIMEK, BERNARD GROSSMAN, AND ALBERT HAIM*

Received March 2, 1972

The reaction $Co(NH_3)_5ONO^{2+} + H_2O + H^+ = Co(NH_3)_5OH_2^{3+} + HNO_2$ has been studied kinetically at 25° and $\mu = 1.00$ M. With $HClO_4$–$LiClO_4$ mixtures to adjust μ, the rate law is $d \ln [Co(NH_3)_5ONO^{2+}]/dt = k_1[H^+] + k_2[H^+]^2$, where $k_1 = 1.32 \times 10^{-3}\ M^{-1}\ sec^{-1}$ and $k_2 = 1.37 \times 10^{-3}\ M^{-2}\ sec^{-1}$. Halide and thiocyanate ions catalyze the reaction, and the dominant additional terms in the above rate law are $k_3^X[H^+][X^-]$ where k_3^X has the values 8.47×10^{-2}, 1.04, 15.8, and 6.53 $M^{-2}\ sec^{-1}$ for chloride, bromide, iodide, and thiocyanate, respectively. The mechanistic implications of these results are discussed in the context of possible linear free energy relationships. It is concluded that nitrosation reactions implicated in the coordination chemistry of O-bonded nitrite involve, in addition to the previously established species N_2O_3 and NO^+, the participation of species XNO, where $X^- = Cl^-, Br^-, I^-$, and SCN^-.

Introduction

Kinetic and mechanistic studies of diazotization and deamination reactions[2] have uncovered three pathways for nitrosation, namely nitrosation *via* N_2O_3, NO^+ (or H_2ONO^+), and XNO ($X^- = Cl^-, Br^-, I^-, SCN^-$). In the coordination chemistry of nitrite ion, the N_2O_3 path has been detected in the formation reactions of nitritopentaammine complexes of cobalt(III),[3] chromium(III), rhodium(III), iridium(III), and platinum(IV)[4] from the corresponding aquo complexes. These types of reactions have been shown to proceed without metal–oxygen bond breaking[5] according to the rate law $k[HNO_2]^2[M(NH_3)_5OH^{2+}]$.[3,4] The kinetic and tracer results have been interpreted on the basis of O-nitrosation by N_2O_3 as depicted in eq 1. More



(1)

recently, the NO^+ path has been uncovered in the acid-catalyzed aquations of nitrito complexes of chromium(III),[6-8] cobalt(III), rhodium(III), and iridium(III).[9]

---

[1] (a) This work was supported by Grant GP-9669 from the National Science Foundation. (b) Abstracted in part from the B.S. thesis of D. E. Klimek, State University of New York at Stony Brook, May 1970.

[2] J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961).

[3] R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Amer. Chem. Soc.*, **76**, 5920 (1954).

[4] F. Basolo and G. S. Hammaker, *Inorg. Chem.*, **1**, 1 (1962).

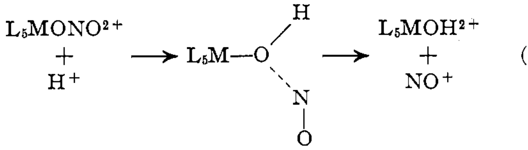
[5] R. K. Murmann and H. Taube, *J. Amer. Chem. Soc.*, **78**, 4886 (1956).

[6] T. C. Matts and P. Moore, *J. Chem. Soc. A*, 219 (1969).

[7] T. C. Matts and P. Moore, *ibid.*, 1997 (1969).

[8] W. W. Fee, J. N. M. Harrowfield, and C. S. Garner, *Inorg. Chem.*, **10**, 290 (1971).

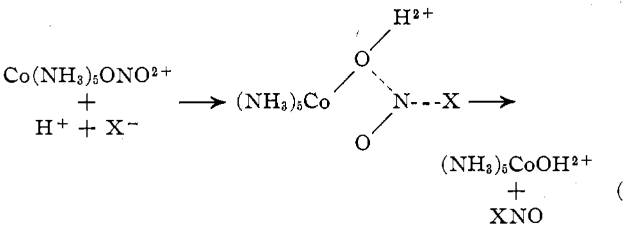
[9] B. E. Crossland and P. J. Staples, *J. Chem. Soc. A*, 2853 (1971).



(2)

According to microscopic reversibility considerations, these reactions correspond to O-nitrosation on L_5MOH^{2+} *via* NO^+.

Since nitrosation reactions by means of XNO ($X^- = Cl^-, Br^-, I^-, SCN^-$) provide such well established pathways for diazotization in organic chemistry, it is perhaps somewhat astonishing that these paths have not been observed in the coordination chemistry of nitrite ion. In the present work, we report the results of the halide- and thiocyanate-catalyzed aquations of $Co(NH_3)_5ONO^{2+}$.



(3)

These reactions, when examined in the context of microscopic reversibility, provide evidence for O-nitrosation on $(NH_3)_5CoOH^{2+}$ *via* XNO.

Experimental Section

Materials.—Aquopentaamminecobalt(III) perchlorate was prepared by the reaction of carbonatopentaamminecobalt(III) nitrate[10] with perchloric acid. Recrystallization was accomplished by dissolution in water followed by addition of 70% perchloric acid. Nitritopentaamminecobalt(III) perchlorate was prepared and recrystallized (twice) by the procedure of Linhard, Siebert, and Weigel.[11] The absorption spectrum of $[Co(NH_3)_5ONO](ClO_4)_2$ in water exhibited maxima at 491 and 361 nm with extinction coefficients 69.9 and 263 M^{-1} cm^{-1}, respectively. In order to retard the linkage isomerization of nitrito- to nitropentaamminecobalt(III), the crystals of $[Co(NH_3)_5ONO](ClO_4)_2$ were stored at $-12°$. According to Balzani and coworkers,[12] the nitrito complex can be stored for several months at this temperature without appreciable isomerization. However, in order to minimize the amount of nitro complex in the samples of the nitrito complex used for kinetic and stoichiometric measurements, the complex was prepared monthly during the course of the present work.

Lithium perchlorate used as a background electrolyte in the acid-catalyzed kinetic measurements and in the stoichiometric measurements was obtained as a solid from solutions obtained by dissolution of lithium carbonate in perchloric acid. The solid was recrystallized twice from water. The lithium perchlorate used in the halide and thiocyanate studies was prepared in solution by the dissolution of lithium carbonate in perchloric acid.

The water used for the preparation of all the solutions was obtained by passing distilled water through a Barnstead ion-exchange demineralizer, and then distilling the effluent in a Corning Model AG-1b all-glass apparatus. All other chemicals were reagent grade.

The sodium bromide, sodium iodide, and sodium thiocyanate were standardized by titration with silver nitrate solutions. The lithium chloride solutions were standardized acidimetrically by an ion-exchange procedure.

Kinetic Measurements.—All kinetic measurements were carried out spectrophotometrically at 25° in a Cary 14 recording spectrophotometer equipped with a thermostated cell compartment and cell holder. The technique used to study the relatively slow acid-catalyzed aquation consisted of adding the $HClO_4$–$LiClO_4$ solution at 25° to the solid $[Co(NH_3)_5ONO](ClO_4)_2$. Following the dissolution of the complex, a portion of the solution was transferred to a spectrophotometric cell, and a recording of absorbance *vs.* time was obtained. For the faster anion-catalyzed reactions, the desired amounts of $HClO_4$, $LiClO_4$, and the appropriate salt of the anion were placed in a spectrophotometric cell. After temperature equilibration to 25° in the cell compartment, the desired amount of freshly prepared $Co(NH_3)_5ONO^{2+}$ solution at 25° was rapidly added by means of a syringe, and a recording of absorbance *vs.* time was obtained. Reactions were followed for 4–5 half-lives, and pseudo-first-order rate constants were obtained by nonlinear least-squares fitting of absorbance to time according to the equation $(A - A_\infty) = (A_0 - A_\infty) \exp(-k_{obsd}t)$. The wavelengths for the measurements were chosen to obtain large (*e.g.*, 0.5–1.0) absorbance changes on reaction, and depended on the particular system studied. The acid-catalyzed aquation with $[H^+] > 0.40$ M and the reactions assisted by Br^- and Cl^- were studied at 275 nm. Measurements of the acid-catalyzed reaction with $[H^+] < 0.40$ M and of the isomerizations to the nitro complex were carried out at 325 nm. The reaction in the presence of iodide ion produces iodine, and therefore the rate of appearance of I_3^- was followed at 420 nm. The reaction induced by SCN^- was followed at 290 nm since nitrosyl thiocyanate absorbs strongly below 280 nm.

Stoichiometric Measurements.—The relative amounts of aquation and isomerization were measured by a spectrophotometric method. The desired amounts of $\sim$2 M $HClO_4$, $\sim$2 M $LiClO_4$, and 25 ml of water were placed in a 100-ml volumetric flask immersed in a 25° bath. The desired amount of $[Co(NH_3)_5ONO](ClO_4)_2$ was dissolved in water and then transferred to the volumetric flask, which was then made up to volume. The flask was covered with aluminum foil and left in the constant temperature bath for 24 hr to ensure complete reaction. The visible spectrum was measured in a 10-cm cell, and the absorbance at 458 nm, an absorption maximum for $Co(NH_3)_5NO_2^{2+}$, was especially useful in determining the yields of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5NO_2^{2+}$.

Results

Linkage Isomerization and Acid-Catalyzed Aquation of $Co(NH_3)_5ONO^{2+}$.—Weakly acidic solutions of $Co(NH_3)_5ONO^{2+}$ are known to be unstable with respect to isomerization to $Co(NH_3)_5NO_2^{2+}$, and quantitative measurements of the rate of this rearrangement have been published previously.[3,13] The earlier measurements were carried out either at low ionic strength[13] or with sodium salts as background electrolytes.[3] In measuring the acid-catalyzed aquation of $Co(NH_3)_5ONO^{2+}$, we have used $LiClO_4$ to adjust the ionic strength in an attempt to minimize medium effects caused by replacing H^+ by an equivalent amount of a unipositive ion. Therefore, we have also measured the isomerization in the presence of 1.0 M Li^+, and the results, together with those from previous investigations, are presented in Table I. It will be seen that the rate constant for isomerization depends on the nature and concentration of negative and positive ions in solution, a rather surprising result for a reaction which proceeds by an intramolecular rearrangement mechanism.[3,5] Thus, the rate of isomerization is *ca.* 30% faster in 1.00 M LiCl than in 1.00 M $LiClO_4$, with 1.00 M $NaNO_2$ giving an intermediate rate. It is not known whether these variations in rate are medium effects or manifestations of chemical pathways. However, the changes in rates are rather small, especially when compared with the substantial effect that chloride ion has on the rate of aquation of $Co(NH_3)_5ONO^{2+}$ (*vide infra*).

We have confirmed that, at low hydrogen ion concentrations, $Co(NH_3)_5ONO^{2+}$ rearranges quantitatively

---

(10) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

(11) M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allg. Chem.*, **278**, 287 (1955).

(12) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

(13) B. Adell, *Sv. Kem. Tidskr.*, **56**, 318 (1944); **57**, 260 (1945).

TABLE I

ISOMERIZATION OF $Co(NH_3)_5ONO^{2+}$ TO $Co(NH_3)_5NO_2^{2+\,a}$

Conditions	10^5k, $sec^{-1\,b}$	Ref
$[Co(III)] = 4.11 \times 10^{-4}$ *M*, 1.00 *M* $LiClO_4$	6.2	*c*
$[Co(III)] = 4.63 \times 10^{-4}$ *M*, 1.00 *M* LiCl	8.2	*c*
$[NO_2^-] = 5 \times 10^{-2}$ *M*, $[HNO_2] = 6 \times 10^{-3}$ *M*, $\mu = 1.125$ adjusted with $NaClO_4$	4.2	*d*
$[NO_2^-] = 1.0$ *M*, $[HNO_2] = 0.125$ *M*, $\mu = 1.125$ adjusted with $NaClO_4$	7.7	*d*
$[Co(III)] = 2.5 \times 10^{-3}$ *M*, $[Cl^-] = 5.0 \times 10^{-3}$ *M*, no other substances added	3.5	*e*
$[Co(III)] = 2.5 \times 10^{-3}$ *M*, $[Cl^-] = 5.0 \times 10^{-3}$ *M*	3.5	*e*
$[NaCH_3COO] = 0.013$ *M*, $[CH_3COOH] = 0.013$ *M*		

[a] Measurements in aqueous solution at 25°. [b] First-order rate constant defined by $-d \ln [Co(NH_3)_5ONO^{2+}]/dt = k$. [c] This work. [d] Reference 3. [e] Interpolated from data at 20 and 30° from ref 13.

to $Co(NH_3)_5NO_2^{2+}$. Thus, a solution 1.01×10^{-3} *M* in $Co(NH_3)_5ONO^{2+}$, 9.83×10^{-4} *M* in $HClO_4$, and 1.00 *M* in $LiClO_4$ displayed, after 24 hr at 25°, an absorption maximum at 458 nm with a calculated extinction coefficient of 96, in perfect agreement with values previously reported[14] for an authentic sample of $Co(NH_3)_5NO_2^{2+}$.

The rate of disappearance of $Co(NH_3)_5ONO^{2+}$ increases with increasing acidity, with increasing amounts of $Co(NH_3)_5OH_2^{3+}$ being produced in addition to $Co(NH_3)_5NO_2^{2+}$.[15] Stoichiometric and kinetic measurements were performed as a function of the hydrogen ion concentration, and the pertinent results are summarized in Tables II and III. In column three of Table II we list the values of $k_{cor}/[H^+]$, where k_{cor} $(= k_{obsd} - k_{iso})$ is the pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$ corrected for the spontaneous isomerization.[16] It will be seen that $k_{obsd}/[H^+]$ increases with increasing $[H^+]$, and therefore, as previously observed for the analogous reactions of $Cr(OH_2)_5ONO^{2+}$ and $Cr(NH_3)_5ONO^{2+}$,[6,7] the acid-catalyzed aquation of $Co(NH_3)_5ONO^{2+}$ is higher than first order in $[H^+]$. Using the previously suggested[6,7] functional dependence

TABLE II

KINETICS OF THE ACID-CATALYZED AQUATION OF $Co(NH_3)_5ONO^{2+\,a}$

$[H^+]$, *M*	10^4k_{obsd}, $sec^{-1\,b}$	$10^3k_{cor}/[H^+]$, $M^{-1}\,sec^{-1\,c}$	10^4k_{calcd}, $sec^{-1\,d}$
0.0786	1.65,[e] 1.69[e]	1.31, 1.36	1.74
0.197	3.73,[e] 3.97[e]	1.58, 1.70	3.76
0.394	8.13, 8.19	1.91, 1.92	7.96
0.591	13.3, 13.8	2.15, 2.23	13.2
0.789	19.3, 19.4, 19.5[e]	2.37, 2.38, 2.39	19.6
0.983	26.1, 26.7	2.59, 2.65	26.9

[a] Measurements at 25° and $\mu = 1.00$ *M* adjusted with $LiClO_4$. $[Co(III)] = (8–10) \times 10^{-4}$ *M*. Wavelength of observation 275 nm, except where indicated. [b] Pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$. [c] $k_{cor} = k_{obsd} - k_{iso}$, where $k_{iso} = 6.2 \times 10^{-5}\ sec^{-1}$. [d] Calculated from $k_{calcd} = k_{iso} + k_1[H^+] + k_2[H^+]^2$, where $k_{iso} = 6.2 \times 10^{-5}\ sec^{-1}$, $k_1 = 1.32 \times 10^{-3}\ M^{-1}\ sec^{-1}$, and $k_2 = 1.37 \times 10^{-3}\ M^{-2}\ sec^{-1}$. [e] Measurement at 325 nm.

TABLE III

PRODUCTS OF THE REACTION OF $Co(NH_3)_5ONO^{2+}$ IN ACIDIC SOLUTION[a]

$[H^+]$, *M*	[Co(III)], *M*	A^b	$f_{nitro}{}^c$	$f_{calcd}{}^d$
0.0786	0.984, 1.01	0.558, 0.587	0.34, 0.37	0.37
0.197	1.01, 1.01	0.460, 0.468	0.15, 0.17	0.16
0.591	1.01	0.398	0.050	0.046
0.983	0.984, 1.01	0.378, 0.384	0.028, 0.032	0.023

[a] At 25° and ionic strength 1.00 adjusted with $LiClO_4$. [b] Measured absorbance at 458 nm in a 10-cm cell. [c] Fraction of $Co(NH_3)_5NO_2^{2+}$ produced in the reaction (see eq 5). [d] Calculated from $k_{iso}/(k_{iso} + k_1[H^+] + k_2[H^+]^2)$.

$$k_{cor} = k_1[H^+] + k_2[H^+]^2 \qquad (4)$$

the values of k_1 and k_2 obtained by a nonlinear least-squares treatment of the data are $(1.32 \pm 0.04) \times 10^{-3}$ $M^{-1}\ sec^{-1}$ and $(1.37 \pm 0.07) \times 10^{-3}$ $M^{-2}\ sec^{-1}$, respectively. These two parameters adequately reproduce the observed behavior since there is good agreement between the values of k_{calcd} $(= k_{iso} + k_1[H^+] + k_2[H^+]^2)$ in column four and the values of k_{obsd} in column two.

As already indicated, the disappearance of $Co(NH_3)_5ONO^{2+}$ at low $([H^+] \leq 1 \times 10^{-3}$ *M*) acidities results in the quantitative formation of $Co(NH_3)_5NO_2^{2+}$. At higher acidities, however, mixtures of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5NO_2^{2+}$ are produced. The values of f_{nitro} (the fraction of $Co(NH_3)_5NO_2^{2+}$ produced in the reaction) listed in column four of Table III were calculated from the expression

$$f_{nitro} = \frac{(A/l[Co(III)]) - \epsilon_{aquo}}{\epsilon_{nitro} - \epsilon_{aquo}} \qquad (5)$$

where *A* is the measured absorbance at 458 nm at the completion of the reaction, *l* is the path length, [Co(III)] is the initial concentration of $Co(NH_3)_5ONO^{2+}$, and ϵ_{nitro} and ϵ_{aquo} are the extinction coefficients at 458 nm of $Co(NH_3)_5NO_2^{2+}$ (96) and $Co(NH_3)_5OH_2^{3+}$ (36.4), respectively. If it is assumed that the rate of isomerization is acid independent and that the $[H^+]$-dependent paths k_1 and k_2 result in the formation of $Co(NH_3)_5OH_2^{3+}$, then the fraction of $Co(NH_3)_5NO_2^{2+}$ produced at any given acidity can be calculated from the expression $f_{calcd} = k_{iso}/(k_{iso} + k_1[H^+] + k_2[H^+]^2)$. Values of f_{calcd} obtained in this manner are listed in column five of Table III. The excellent agreement between the calculated values f_{calcd} and the observed values f_{nitro} provides strong support for the assumption that the nitrito–nitro rearrangement is acid independent, whereas the aquation of $Co(NH_3)_5ONO^{2+}$ proceeds *via* parallel first- and second-order paths in $[H^+]$.

Anion-Catalyzed Aquations of $Co(NH_3)_5ONO^{2+}$.—The addition of small quantities of halide or thiocyanate ions in acidic solution dramatically increases the rate of disappearance of $Co(NH_3)_5ONO^{2+}$. Thus, the half-life for disappearance of $Co(NH_3)_5ONO^{2+}$ when $[HClO_4] = 0.10$ *M* and $[LiClO_4] = 0.90$ *M* is *ca.* 1 hr. With the same $HClO_4$ but with $[LiCl] = 0.90$ *M*, the

---

(14) D. A. Buckingham, I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88**, 5443 (1966).

(15) Adell[13] reported a *retardation* of the rate of isomerization with increasing acid concentration. However, it must be noted that Adell studied the reaction at 436 nm where the values of the extinction coefficients for $Co(NH_3)_5ONO^{2+}$, $Co(NH_3)_5NO_2^{2+}$, and $Co(NH_3)_5OH_2^{3+}$ are 37, 74, and 22.[12] Any aquation therefore results in a smaller increase in absorbance than that accompanying quantitative isomerization. We believe this to be the reason for Adell's conclusion regarding the effect of acid. For example, for the disappearance of $Co(NH_3)_5ONO^{2+}$ *via* 71% aquation and 29% isomerization, no change in absorbance would occur at 436 nm, and this result could be taken as an indication of the absence of any reaction.

(16) In applying this type of correction, it is implicitely assumed that the rate of isomerization of $Co(NH_3)_5ONO^{2+}$ is acid-independent. The adequacy of this assumption is confirmed by the results of the stoichiometric measurements in Table III.

half-life decreases by a factor of 40 to *ca.* 1.5 min. An extensive series of measurements, summarized in Table IV, was performed in order to determine the rate law for the chloride-catalyzed aquation. It must be admitted that after completing 66 independent kinetic runs, the exact form of the rate law is not firmly established. Undoubtedly, the dominant term in the rate law is a term first order in $[H^+]$ and first order in $[Cl^-]$, but a single-term rate law of the form $k_{cor} = k_{HCl}[H^+]\cdot[Cl^-]$ gives an unsatisfactory fit of the data (nonlinear least-squares value of k_{HCl} is 0.094 M^{-2} sec^{-1}, average deviation 7.9%). A somewhat better fit (average deviation 4.2%) can be obtained by using the functional dependence given by eq 6. For X = Cl, the nonlinear

$$k_{cor} = k_3^{X}[H^+][X^-] + k_4^{X}[H^+]^2[X^-] \qquad (6)$$

least-squares values of k_3^{Cl} and k_4^{Cl} are $(8.47 \pm 0.11) \times 10^{-2}$ M^{-2} sec^{-1} and $(2.6 \pm 0.2) \times 10^{-2}$ M^{-3} sec^{-1}, respectively. The values of k_{calcd} using eq 6 with the above parameters and the contributions of the acid-catalyzed path and the spontaneous isomerization are listed in column five of Table IV. Except for the experiments with $[H^+][Cl^-] > 0.4$ M^2, the agreement between experimental and calculated values is relatively good. The reason for the discrepancies at the higher $[H^+]$ and $[Cl^-]$ values is not clear, but at the higher concentrations medium effects, associated with the replacement of both ClO_4^- and Li^+ by Cl^- and H^+, might come into play.

TABLE IV

KINETICS OF THE AQUATION OF $Co(NH_3)_5ONO^{2+}$ CATALYZED BY CHLORIDE ION[a]

$10[H^+]$, M	$10[Cl^-]$, M	10^3k_{obsd}, sec^{-1}	$10k_{cor}/[H^+][Cl^-]$,[b] M^{-2} sec^{-1}	10^3k_{calcd},[c] sec^{-1}
1.00	1.00	1.04, 1.07	0.84, 0.86	1.07
3.00	1.00	3.55, 3.62, 3.78	0.98, 1.01, 1.07	3.38
5.00	1.00	6.02, 6.28	0.99, 1.04	5.97
6.00	1.00	7.30, 7.33	0.99, 1.00	7.37
7.00	1.00	9.32, 9.52	1.09, 1.12	8.85
8.00	1.00	11.0, 11.1	1.11, 1.12	10.4
9.00	1.00	11.3, 12.0, 12.3, 12.4	1.00, 1.07, 1.11, 1.12	12.0
10.00	1.00	13.2, 13.5, 13.8, 14.1	1.05, 1.08, 1.11, 1.14	13.8
1.00	2.00	2.03, 2.12	1.02, 1.06	1.94
2.00	2.00	4.27, 4.28	1.07, 1.07	3.98
5.00	2.00	11.2, 11.7	1.02, 1.07	10.8
5.00	3.00	15.8, 15.9	0.99, 1.00	15.7
1.00	4.00	3.50, 3.58	0.81, 0.84	3.71
5.00	4.00	20.7, 21.3	0.98, 1.02	20.6
1.00	5.00	4.83, 4.87	0.92, 0.93	4.56
5.00	5.00	25.3,[d] 26.0,[d] 26.3,[e] 26.8[e]	0.97, 1.00, 1.01, 1.03	25.4
1.00	6.00	5.05, 5.22	0.81, 0.83	5.44
5.00	6.00	28.8, 31.7	0.93, 1.02	30.3
1.00	7.00	6.28, 6.38	0.90, 0.91	6.31
5.00	7.00	34.0	0.97	35.2
7.00	7.00	48.5, 49.7	0.99, 1.01	52.0
1.00	8.00	7.03, 7.18	0.85, 0.87	7.19
5.00	8.00	36.8, 38.3	0.89, 0.93	40.1
1.00	9.00	7.90, 7.93, 7.93, 7.95, 8.10, 8.12	0.85, 0.86, 0.86, 0.86, 0.91, 0.91	8.05
5.00	9.00	41.8, 42.3	0.91, 0.94	45.0
1.00	10.0	8.67, 8.70, 8.75, 8.80	0.87, 0.87, 0.88, 0.88	8.93
5.00	10.0	45.8, 47.2	0.92, 0.94	49.9

[a] At 25° and ionic strength 1.00 M adjusted with $LiClO_4$. $[Co(III)] = (3.0\text{–}4.0) \times 10^{-4}$ M. [b] $k_{cor} = k_{obsd} - k'$, where k' is the pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$ at the same $[H^+]$, but in the absence of Cl^-. [c] Calculated from $k_{calcd} = k' + k_3^{Cl}[H^+][Cl^-] + k_4^{Cl}[H^+]^2[Cl^-]$, with $k_3^{Cl} = 8.47 \times 10^{-2}$ M^{-2} sec^{-1} and $k_4^{Cl} = 2.6 \times 10^{-2}$ M^{-3} sec^{-1}. [d] Solutions made using standard solutions of HCl and $LiClO_4$. [e] Solutions made using standard solutions of LiCl and $HClO_4$.

Less extensive measurements were carried out for the aquations catalyzed by Br^-, I^-, and SCN^-. The results are summarized in Tables V–VII. The functional dependence given by eq 6 describes the bromide data quite accurately with $k_3^{Br} = 1.04 \pm 0.02$ M^{-2}

TABLE V

KINETICS OF THE AQUATION OF $Co(NH_3)_5ONO^{2+}$ CATALYZED BY BROMIDE ION[a]

$10[H^+]$, M	$10[Br^-]$, M	10^2k_{obsd}, sec^{-1}	$k_{cor}/[H^+][Br^-]$,[b] M^{-2} sec^{-1}	10^2k_{calcd},[c] sec^{-1}
1.00	1.00	1.07, 1.08	1.06, 1.07	1.08
1.00	2.00	2.13, 2.17	1.06, 1.08	2.14
1.00	3.00	3.23, 3.27	1.07, 1.08	3.22
3.00	1.00	3.42, 3.45	1.12, 1.13	3.45
5.00	1.00	5.92, 5.98	1.16, 1.18	6.06
6.00	1.00	6.98, 7.82, 7.98	1.14, 1.28, 1.31	7.46
7.00	1.00	8.38, 9.12	1.17, 1.28	9.03
8.00	1.00	10.5, 10.7	1.26, 1.31	10.5
9.00	1.00	12.0, 12.3	1.31, 1.33	12.0

[a] At 25° and ionic strength 1.00 M adjusted with $LiClO_4$. $[Co(III)] = (3.2\text{–}3.6) \times 10^{-4}$ M. [b] $k_{cor} = k_{obsd} - k'$, where k' is the pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$ at the same $[H^+]$, but in the absence of Br^-. [c] Calculated from $k_{calcd} = k' + k_3^{Br}[H^+][Br^-] + k_4^{Br}[H^+]^2\cdot[Br^-]$, with $k_3^{Br} = 1.04$ M^{-2} sec^{-1} and $k_4^{Br} = 0.31$ M^{-3} sec^{-1}.

TABLE VI

KINETICS OF THE AQUATION OF $Co(NH_3)_5ONO^{2+}$ CATALYZED BY IODIDE ION[a]

$10[H^+]$, M	$10^2[I^-]$, M	10^2k_{obsd}, sec^{-1}	$k_{cor}/[H^+][I^-]$,[b] M^{-2} sec^{-1}	10^2k_{calcd},[c] sec^{-1}
1.00	1.00	1.66, 1.68	16.5, 16.7	1.59
1.00	2.00	2.90, 3.35	14.4, 16.7	3.17
1.00	3.00	4.45, 4.48	14.7, 14.9	4.75
5.00	1.00	7.80, 7.88	15.4, 15.6	7.99
7.00	1.00	11.5, 11.6	16.1, 16.3	11.2
8.00	1.00	13.5, 14.0	16.6, 17.2	12.8
9.00	1.00	14.0, 14.2	15.3, 15.4	14.4

[a] At 25° and ionic strength 1.00 M adjusted with $LiClO_4$. $[Co(III)] = (3.2\text{–}3.3) \times 10^{-4}$ M. [b] $k_{cor} = k_{obsd} - k'$, where k' is the pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$ at the same $[H^+]$, but in the absence of I^-. [c] Calculated from $k_{calcd} = k' + k_3^{I}[H^+][I^-]$, with $k_3^{I} = 15.8$ M^{-2} sec^{-1}.

TABLE VII

KINETICS OF THE AQUATION OF $Co(NH_3)_5ONO^{2+}$ CATALYZED BY THIOCYANATE ION[a]

$10[H^+]$, M	$10^2 \times [SCN^-]$, M	10^2k_{obsd}, sec^{-1}	$k_{cor}/[H^+][SCN^-]$,[b] M^{-2} sec^{-1}	10^2k_{calcd},[c] sec^{-1}
1.00	1.00	0.658, 0.658	6.38, 6.38	0.673
1.00	2.00	1.35, 1.36	6.65, 6.70	1.33
1.00	3.00	1.92, 1.93	6.33, 6.40	1.98
3.00	1.00	1.98, 2.08	6.44, 6.77	2.01
5.00	1.00	3.53, 3.77	6.88, 7.34	3.35
6.00	1.00	4.03, 4.08	6.50, 6.58	4.05
7.00	1.00	4.77, 4.85	6.58, 6.70	4.71
8.00	1.00	5.25, 5.43	6.33, 6.55	5.41
9.00	1.00	5.78, 5.82	6.18, 6.21	6.10

[a] At 25° and ionic strength 1.00 M adjusted with $LiClO_4$. $[Co(III)] = (3.2\text{–}3.6) \times 10^{-4}$ M. [b] $k_{cor} = k_{obsd} - k'$, where k' is the pseudo-first-order rate constant for disappearance of $Co(NH_3)_5ONO^{2+}$ at the same $[H^+]$, but in the absence of SCN^-. [c] Calculated from $k_{calcd} = k' + k_3^{SCN}[H^+][SCN^-]$, with $k_3^{SCN} = 6.53$ M^{-2} sec^{-1}.

sec^{-1} and $k_4^{Br} = 0.31 \pm 0.03\ M^{-3}\ sec^{-1}$. Only the k_3^X terms are necessary in the case of I^- and SCN^-. The values of k_3^X are $15.8 \pm 0.2\ M^{-2}\ sec^{-1}$ and $6.53 \pm 0.06\ M^{-2}\ sec^{-1}$ for I^- and SCN^-, respectively.

Discussion

The results of the kinetic measurements on the aquation of $Co(NH_3)_5ONO^{2+}$ catalyzed by H^+ and by halide and thiocyanate ions show that the compositions of the dominant transition states for the reactions are $Co(NH_3)_5ONOH^{3+}$ and $Co(NH_3)_5ONOHX^{2+}$ ($X^- = Cl^-, Br^-, I^-, SCN^-$), respectively. Moreover, the rapidity of these reactions strongly suggests to us that they proceed by O–N rather than Co–O bond cleavage. The proposed[6–8] mechanism for the acid-catalyzed aquation of nitritochromium(III) complexes involves a rapid preequilibrium protonation of the coordinated nitrite ligand, followed by slow N–O bond bond breaking to produce NO^+, and we adopt the same mechanism for the path first order in H^+ (eq 7 and 8). Although

$$Co(NH_3)_5ONO^{2+} + H^+ \rightleftharpoons Co(NH_3)_5\overset{H}{O}NO^{3+} \quad \text{rapid, } Q \qquad (7)$$

$$Co(NH_3)_5\overset{H}{O}NO^{3+} \longrightarrow Co(NH_3)_5OH^{2+} + NO^+ \quad \text{slow, } k_8 \qquad (8)$$

the site of protonation is not known, the most reasonable formulation places the proton on the adjacent oxygen atom, since protonation of the nitrogen or remote oxygen atoms followed by O–N bond breaking would result in the formation of the highly unstable species $Co(NH_3)_5O^+$ and HNO^+ or NOH^+.

The halide and thiocyanate catalyzed paths can be viewed as anion-assisted removal of NO^+ from the protonated species, and the proposed mechanism involves the rapid preequilibrium represented by eq 7 followed by the slow step represented by eq 9. The

$$Co(NH_3)_5\overset{H}{O}NO^{3+} + X^- \longrightarrow Co(NH_3)_5OH^{2+} + XNO \quad k_9^X \quad (9)$$

question arises as to the extent of assistance offered by the anion X^- in removing NO^+. Two extreme situations can be envisioned: (1) an associative mechanism whereby N–X bond making plays a most important role in the activation process; (2) a dissociative mechanism whereby O–N bond breaking is the dominant feature, and there is little or no assistance by the incoming anion. Some information about the extent of bond making and bond breaking in the transition state for eq 9 can be obtained by considering the variation of rates with the nature of the anion in the context of possible free-energy relationships.[17] However, before considering the reactions of the cobalt complex, it is instructive to examine the kinetic and thermodynamic information regarding the formation of nitrosyl halides and nitrosyl thiocyanate. The pertinent information is summarized in Table VIII. It will be seen that in going from Cl^- to SCN^- the equilibrium constant increases by *ca.* 10^5 but the rate constant increases by less than a factor of 2. Moreover, the rates of formation of the XNO compounds are quite similar to the rate of formation of NO^+. These reactivity trends are entirely analogous to those observed previously for the anation reactions of aquopentaamminecobalt(III).[17] In particular, the strong equilibrium discrimination displayed by the nitrogen center toward the various anions, contrasted with the insensitivity of the rate constants to the identity of the incoming anion suggests, at most, a very weak bond between nitrogen and the anion in the transition state. This conclusion is depicted quantitatively in Figure 1, where a log *k vs.* log *Q* plot has been constructed. Assuming that the free-energy relationship is linear, we obtain a value of ~0.04 for the slope, a value indicative of extremely weak bonding of the incoming anion in the transition state.

TABLE VIII

RATE AND EQUILIBRIUM CONSTANTS AT 0°

$$HONO + H^+ + X^- \rightleftharpoons H_2O + XNO$$

X^-	10^2k, $M^{-2}\ sec^{-1}$	Q, M^{-2}	Ref
	6.2	2×10^{-7}	*a, b*
Cl^-	9.8	5.6×10^{-4}	*c, d*
Br^-	11.7	2.2×10^{-2}	*e, d*
I^-	13.7		*e*
SCN^-	14.6	46	*c, f*

[a] D. J. Benton and P. Moore, *J. Chem. Soc. A*, 3179 (1970). [b] T. A. Turney and G. A. Wright, *ibid.*, 2415 (1958); value of *Q* at 20°. [c] G. Stedman, *ibid.*, 2949 (1959). [d] H. Schmid and E. Hallaba, *Monatsh. Chem.*, **87**, 568 (1956). [e] E. D. Hughes, C. K. Ingold, and J. H. Ridd, *J. Chem. Soc.*, 88 (1958). [f] G. Stedman and P. A. E. Whincup, *ibid.*, 5796 (1963).

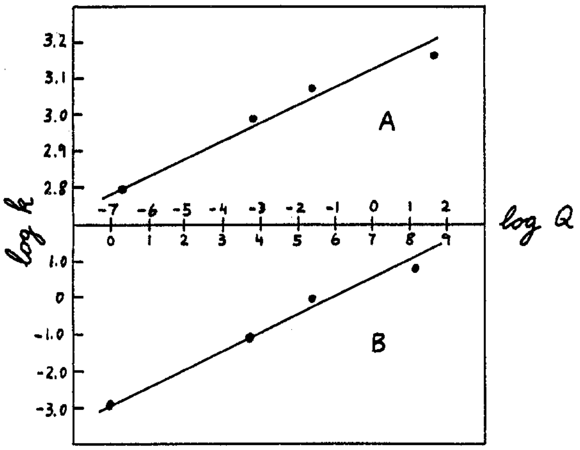


Figure 1.—Log *k vs.* log *Q* plots for the reactions (A) $HNO_2 + X^- + H^+ = H_2O + XNO$ and (B) $Co(NH_3)_5ONO^{2+} + X^- + H^+ = Co(NH_3)_5OH^{2+} + XNO$. From left to right the points correspond to no added anion, chloride, bromide, thiocyanate.

Similar considerations applied to the anion-assisted aquation of $Co(NH_3)_5ONO^{2+}$ lead to the conclusion that both O–N bond breaking and N–X bond making are important in the activation process that leads to the formation of $Co(NH_3)_5OH^{2+}$ and XNO from $Co(NH_3)_5ONO^{2+}$, H^+, and X^-. The pertinent kinetic and equilibrium data are summarized in Table IX. It will be seen that the range of kinetic discrimination toward the incoming anion, although appreciably smaller than

TABLE IX

RATE AND EQUILIBRIUM CONSTANTS AT 25°

$$Co(NH_3)_5ONO^{2+} + H^+ + X^- \rightleftharpoons Co(NH_3)_5OH^{2+} + XNO$$

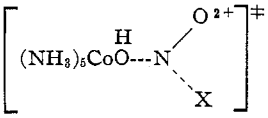
X^-	k, $M^{-2}\ sec^{-1}$	Q,[a] M^{-1}	Ref
	1.3×10^{-3}	1	*b*
Cl^-	8.5×10^{-2}	5.5×10^3	*b, c*
Br^-	1.04	2.6×10^5	*b, d*
I^-	15.8		*b*
SCN^-	6.5	1.5×10^8	*b, e*

[a] Equilibrium quotient relative to a value of 1.0 for $Co(NH_3)_5ONO^{2+} + H^+ \rightleftharpoons Co(NH_3)_5OH^{2+} + NO^+$. [b] This work. [c] A. Maschka, *Monatsh. Chem.*, **85**, 853 (1953). [d] H. Schmid, *ibid.*, **85**, 424 (1954). [e] Footnote *f* of Table VIII.

---

(17) A. Haim, *Inorg. Chem.*, **9**, 426 (1970).

the range of thermodynamic discrimination, covers four orders of magnitude. This is in contrast with the reactivity patterns for the reactions of HONO where the rate constants for the formation of XNO are practically independent of the nature of X^-. In the case of HNO_2 it was concluded that no N–X bond making obtains in the transition state. Therefore, in the case of $Co(NH_3)_5ONO^{2+}$, there must be some N–X bond making in the transition state. A "quantitative" measure of the amount of bond breaking and bond making that obtains in the transition state can be estimated from the log *k* *vs.* log *Q* plot presented in Figure 1. Assuming a linear free energy relationship, we obtain a slope of ~0.5, a value which suggests approximately "equal" contributions of bond making and bond breaking in the transition state for the reaction.



Finally, it is noteworthy that the catalysis of aquation of $Co(NH_3)_5ONO^{2+}$ by halides and thiocyanate ions, when combined with microscopic reversibility considerations, indicates that, provided the equilibrium is favorable, O-nitrosation on $Co(NH_3)_5OH^{2+}$ would be accomplished by XNO. Thus, the range of reagents involved in nitrosation in inorganic chemistry has been extended from the early studies with N_2O_3[3,5] to the more recent studies implicating NO^+[6-9] and to the present studies which show the importance of reaction paths involving nitrosyl halides and nitrosyl thiocyanate. We are planning to extend the studies of the effects of halides and pseudohalides to other metal complexes containing coordinated nitrite and coordinated nitrosyl.

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, PARKVILLE, VICTORIA 3052, AUSTRALIA

The Single-Crystal Electronic Spectrum of Bromotetrakis(2-methylimidazole)nickel(II) Bromide and an Interpretation of the Energy Levels of Some Tetragonally Distorted Nickel Complexes Using the Angular Overlap Model

BY M. A. HITCHMAN*

Received February 24, 1972

The single-crystal polarized electronic spectrum of the five-coordinate complex bromotetrakis(2-methylimidazole)nickel(II) bromide is reported. A general method for the analysis of the excited-state energies observed in the "d–d" electronic spectra of nickel halide complexes with D_{4h} or C_{4v} symmetry is described and used to derive the angular overlap σ- and π-bonding parameters of the ligands in several nickel halide complexes of known crystal structure.

Introduction

There has been considerable interest recently both in the electronic spectra of five-coordinate nickel complexes[1] and in the interpretation of the energy levels of tetragonally distorted compounds using ligand-field bonding parameters.[2] The single-crystal spectrum of bromotetrakis(2-methylimidazole)nickel(II) bromide, [Ni(2-meim)$_4$Br]Br, is therefore interesting both because it is a representative example of the spectrum of a square-pyramidal nickel complex and because it allows the ligand σ- and π-bonding parameters of a five-coordinate complex to be compared with those of similar six-coordinate compounds.

Single-Crystal Spectrum of [Ni(2-meim)$_4$Br]Br

The complex crystallizes in the tetragonal space group *P*4*nc*, $Z = 2$, with the faces (010), (100), etc. well developed. Although the refinement of the structure is not yet complete ($R \approx 9\%$) and the bond lengths are only approximate, the overall molecular geometry is quite clear.[3] The nickel ion is bonded to four imidazole nitrogen atoms, with a fifth bond to a bromide ion (Ni–Br $\approx$ 2.53 Å) and each NNiBr angle ~99°. The second bromide is trans to the first, but at the much longer distance of ~3.6 Å. The nickel ion is thus effectively five-coordinate and the molecular symmetry is C_{4v}. Each Ni–Br bond lies along the *c* crystal axis. The electronic spectra of three crystals were measured at room temperature with the electric vector parallel (||) and perpendicular (⊥) to the *c* axis (which is also the molecular *z* axis) using a microspectrophotometer[4] and a Glan–Thomson polarizing prism. A typical spectrum is shown in Figure 1A. The extinction coefficients of the bands were obtained by measuring the crystal thicknesses using a microscope with a graduated eyepiece.

Low-Temperature Mull Spectra of [Ni(2-meim)$_4$Br]Br and [Ni(2-meim)$_4$Cl]Cl.—As low-temperature spectra could not be obtained using the microspectrophotometer, the spectra of [Ni(2-meim)$_4$Br]Br and [Ni(2-meim)$_4$Cl]Cl, which is isomorphous with the bromide complex,[3] were measured as Nujol mulls at ~80°K (Figure 1B) using a Unicam SP 700 spectrophotometer.

---

* Address correspondence to the University of Tasmania, Hobart, Tasmania, 7005, Australia.

[1] C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968), and references therein.

[2] A. B. P. Lever, *ibid.*, **3**, 119 (1968).

[3] D. M. L. Goodgame and A. Skapski, private communication.

[4] The microspectrophotometer and its method of use are described by P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).