Table VII. Logarithms of the Rate Constants for Hg^{2+}, Br_2, and I_2 with Various Pentaaquoorganochromium(III) Ions ($(H_2O)_5CrR^{2+}$)

R	log (k_E/M^{-1} s^{-1})		
	Hg^{2+} [a]	Br_2	I_2
CH_3	7.0	6.32	4.93
CH_2CH_3	5.15	5.69	
$CH_2CH_2CH_3$	4.54	5.99	
CH_2Ph	4.69	5.92	3.62[c]
$CH(CH_3)_2$	0.19	4.25	
c-C_5H_9	0.033	4.11	0.91

[a] References: c-C_5H_9, this work; all other alkyls, ref 3a. [b] References: c-C_5H_9 and $CH(CH_3)_2$, this work; all other alkyls, ref 3b. [c] Reference 24.

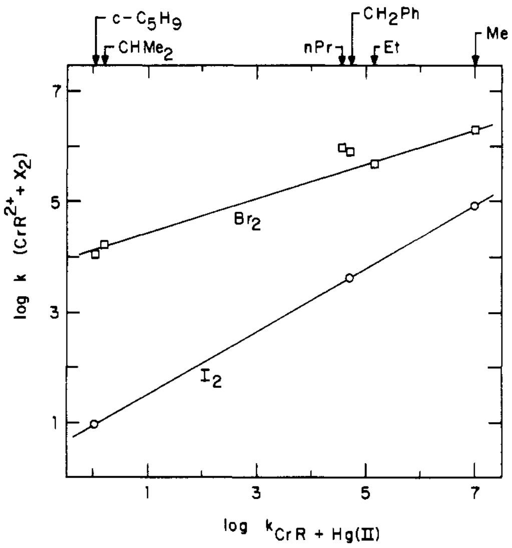

Figure 2. Correlation of the rate constant for reactions of various CrR^{2+} complexes with Br_2 and I_2, as compared to that for the reactions with Hg^{2+}. The coordinates for each point are (log $k^R_{Hg^{2+}}$, log $k^R_{X_2}$).

against attack of an external water molecule.

The rate constants reported here permit calculation of the equilibrium constant for the reversible homolytic dissociation equilibrium:

$$(H_2O)_5Cr\text{-}c\text{-}C_5H_9^{2+} + H_2O \underset{k_7}{\overset{k_H}{\rightleftharpoons}} Cr(H_2O)_6^{2+} + \cdot C_5H_9 \quad (19)$$

The kinetically determined value is $K_{eq} = k_H/k_7 = (1.3 \pm 0.2) \times 10^{-12}$ M at 25 °C, corresponding to $\Delta G°_{298} = 67.8$ kJ mol^{-1}. The value of $\Delta H°$, given by $H° = \Delta H^{\ddagger}_H - \Delta H^{\ddagger}_7$, can be calculated only if we estimate $\Delta H^{\ddagger}_7 \approx 0$. In that case $\Delta H° \approx 126$ kJ mol^{-1}, which may be taken (with suitable caution[11]) as an approximate measure of the chromium–carbon bond dissociation enthalpy.

Electrophilic Cleavage Reactions. Data are now available giving the rate constants for the three electrophiles Br_2, I_2, and Hg^{2+} reacting with various $(H_2O)_5CrR^{2+}$ complexes, from this and previous work,[3a,b,24] as summarized in Table VII. A linear free energy diagram, Figure 2, constructed from these data show a good correlation of the bromine and iodine electrophiles to the Hg^{2+} electrophile. The slopes of the lines (0.31 and 0.57, respectively) are a measure of the steric demand of the given electrophile relative to that of Hg^{2+}. Both bromine and iodine show a smaller steric deceleration than mercuric ion; as expected from the size of the molecules, the bromine's steric requirement is smaller than iodine's.

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Registry No. Cyclopentylpentaaquachromium(III) ion, 84559-49-9; chromium(II) perchlorate, 13931-95-8; hydrogen peroxide, 7722-84-1; cyclopentane, 287-92-3; copper(2+), 15158-11-9; iron(3+), 20074-52-6; pentaamminefluorocobalt(2+), 15392-06-0; bromine, 7726-95-6; iodine, 7553-56-2; mercury(2+), 14302-87-5; pentaaqua(1-methylethyl)chromium(2+), 60764-48-9; pentaamminechlorocobalt(2+), 14970-14-0; pentaamminebromocobalt(2+), 14970-15-1; deuterium, 7782-39-0; pentaaquamethylchromium(2+), 32108-96-6.

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Base Hydrolysis of $[Co(NH_3)_5X]^{n+}$—Capture of the Oxygen and Nitrogen of the Nitrite Ion

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Nitrite ion competition has been measured for the base hydrolysis reaction of a series of $[(NH_3)_5CoX]^{n+}$ ions (X = $CF_3SO_3^-$, $CH_3SO_3^-$, NO_3^-, $(CH_3)_2SO$, $OP(OCH_3)_3$, $OC(NH_2)_2$, and $OC(NH_2)N(CH_3)_2$) in 1.00 M $NaNO_2$. Contrary to previous reports, both O- and N-bonded $[(NH_3)_5Co(NO_2)]^{2+}$ are formed. A constant O-isomer/N-isomer ratio (67 ± 3% $CoONO^{2+}$, 33 ± 3% $CoNO_2^{2+}$) pertains for both anionic and neutral X. The total NO_2^- capture shows a slight dependence on the overall charge of the complex (7.0 ± 0.5% for 2+ cations, 8.3 ± 0.5% for 3+) but is less dependent on the nature of X. The results are consistent with a common, reactive intermediate of reduced coordination number, $[(NH_3)_4(NH_2)Co]^{2+}$, in the base hydrolysis process, provided the intermediate is considered to capture the environment of its precursor.

Introduction

The linkage isomerization of the oxygen-bonded nitrite complex $[(NH_3)_5CoONO]^{2+}$ to the nitrogen bound form $[(NH_3)_5CoNO_2]^{2+}$ has been reexamined recently, particularly in relation to a base-catalyzed path for the rearrangement.[2-4] The base hydrolysis reactions of $[(NH_3)_5CoX]^{n+}$ ions in the

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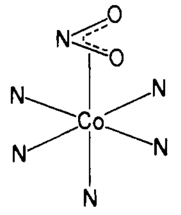
presence of excess Y^{m-} lead to the production of some $[(NH_3)_5CoY]^{(n-m)+}$ along with $[(NH_3)_5CoOH]^{2+}$. For $Y^{m-} = NO_2^-$, it seemed reasonable that the reduced coordination number intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ postulated for the base hydrolysis reaction could capture NO_2^- to produce initially both the O- and the N-bonded linkage isomers of $[(NH_3)_5Co(NO_2)]^{2+}$. Also, it occurred to us that this reaction might proceed via a similar, if not the same, π intermediate[2a,5]



as the base-catalyzed rearrangement of the nitrito isomer. This can be tested experimentally by characterizing the intermediate through its collapse to a mixture of O- and N-bonded NO_2^- complexes. It can be readily shown that this O-isomer/N-isomer ratio should match the relative rates of the O scrambling[4,5] and O to N linkage isomerization processes for the nitrito isomer reacting by the base-catalyzed pathway.

Another facet of the NO_2^- capture experiments is of special interest. In the past several lines of evidence for the reactive five-coordinate intermediate species $[(NH_3)_4NH_2Co]^{2+}$ in the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ ions have accumulated.[6] One line was the leaving-group independence of the anion competition, measured as $[CoY^{(n-m)+}]/[CoX^{n+}][Y^{m-}]$ (=R). Subsequently it was found that R is not strictly leaving-group independent but appears to show a small dependence on the formal charge of the reactant. This result has been intepreted in two ways—a reactive intermediate that inherits the ion atmosphere of the precursor aminato complex $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$, a function of n, or direct anion entry into the $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$ complex without the intervention of a reduced coordination number intermediate. A useful way to distinguish these two possibilities is to exploit a property free from the complication of ion pairing and hence the inherited ion atmosphere. While total NO_2^- capture could depend upon the nature of the leaving group, the O-isomer/N-isomer ratio should not if an independent although very reactive five-coordinate intermediate is involved. Both donor atoms could be captured from a common ion atmosphere. In this article, we report NO_2^- competition data for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ using several neutral and 1− leaving groups.

Experimental Section

Electronic spectra were measured at 25.0 °C with a Cary 210 spectrophotometer. ^1H NMR spectra were obtained on a Varian T60 spectrometer at 35 °C using $Me_2SO\text{-}d_6$ as solvent and a tetramethylsilane reference. Sephadex SP-C25 (Na^+ form) resin was employed as the ion-exchange medium. Columns were ice jacketed at 2 °C with water circulated from a Lauda thermostat bath.

The complex salts $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$,[7] $[(NH_3)_5CoO_3SCH_3](ClO_4)_2$,[7,8] $[(NH_3)_5CoI](ClO_4)_2$,[10,11] $[(NH_3)_5CoONO_2](ClO_4)_2$,[10] $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3\cdot H_2O$,[6] $[(NH_3)_5CoOP(OCH_3)_3](ClO_4)_3\cdot H_2O$,[6] $[(NH_3)_5CoOC(NH_2)_2](S_2O_6)_{3/2}\cdot 1.5H_2O$,[6] $[(NH_3)_5Co(OC(NH_2)N(CH_3)_2)](S_2O_6)_{3/2}\cdot 1.5H_2O$,[9] $[(NH_3)_5CoONO](ClO_4)_2$,[2] and $[(NH_3)_5CoNO_2](ClO_4)_2\cdot H_2O$[2] were synthesized by standard methods. The nitrito complex was stored under a dry atmosphere at −15 °C in the absence of light to prevent isomerization to the nitro isomer and was always used within 24 h of its synthesis. The urea-*O* and the dimethylurea-*O* salts were freshly prepared; they slowly accumulate aquapentaammine impurity on storage. The other complexes were air-dried and stored in the dark until required, except the sulfonate derivatives (stored in P_2O_5 under vacuum) and the hydrated trimethyl phosphate and Me_2SO complexes (air-dried and used freshly). All the complexes gave satisfactory analyses for C, H, N, and, where appropriate, I, F, P, and Cl. Ion-exchange chromatography (Sephadex) and ^1H NMR spectroscopy[6,8] were used to establish the absence of trace impurities, particularly $[(NH_3)_5CoOH_2]^{3+}$.

The NO_2^- competition experiments were peformed with use of a standardized technique to enable a reliable comparison of the results. To solid reactant (~200 mg) was added 1.00 M $NaNO_2$ (25 mL, 0.10 M in NaOH) at 25 °C with vigorous stirring. It dissolved quickly and reacted ($\geq 10t_{1/2}$ in each case). After 1.0 min, NH_4Cl (1.0 g) was added to quench the reaction (pH ~9). The product mixture was diluted to 300 mL with ice water and quickly sorbed on Sephadex in a 15 × 5 cm column jacketed at 2 °C. After it was washed with water (2 × 400 mL, 0 °C) followed by 0.01 M acetic acid (250 mL), the column was eluted with 0.5 M NaCl (AR, pH ~3.5, 0.01 M acetic acid). The $[(NH_3)_5CoONO]^{2+}$ and $[(NH_3)_5CoNO_2]^{2+}$ ions were quickly eluted together, followed by and well separated from $[(NH_3)_5CoOH_2]^{3+}$. The eluates were quickly warmed to 25 °C and their volumes and visible spectra promptly recorded. The spectra of the nitrito/nitro bands were repetitively scanned and extrapolated to zero time to correct for some nitrito to nitro isomerization, which is slight but significant at 25 °C ($t_{1/2}$ 167 min).[2a] Subsequently samples of this band were heated to 60–70 °C for 30 min (in the absence of light) and cooled, and their visible and UV spectra were recorded to enable the determination of the total [Co] in the nitrito/nitro mixture (as $[(NH_3)_5CoNO_2]^{2+}$). In separate experiments, it was shown that authentic $[(NH_3)_5CoONO]^{2+}$ isomerizes quantitatively to $[(NH_3)_5CoNO_2]^{2+}$ in 0.5 M NaCl (pH 3.5) under these conditions, with no competitive aquation to $[(NH_3)_5CoOH_2]^{3+}$, as found previously.[2]

The base hydrolysis of the urea-*O* type complexes produces, along with O- and N-bonded $[(NH_3)_5Co(NO_2)]^{2+}$ and $[(NH_3)_5CoOH]^{2+}$, the N-bound complexes $[(NH_3)_5Co(NHCoNH_2)]^{2+}$ (7%) or $[(NH_3)_5Co(NHCON(CH_3)_2)]^{2+}$ (3%).[12] With use of the authentic urea-*N* complexes mixed with the nitro and nitrito complexes, it was shown in separate experiments that these ions elute well behind the $[(NH_3)_5Co(NO_2)]^{2+}$ complexes and together with $[(NH_3)_5CoOH_2]^{3+}$, provided the eluent is sufficiently acidic (but not too acidic, since the nitrito complex is destroyed in strong H^+[2]—hence the use of 10^{-2} M acetic acid). Indeed, the N-bonded isomers ($pK_a \approx 2.5$) protonate and isomerize ($t_{1/2} \approx 1$ min) to their urea-*O* forms (3+ ions) in the time ($\lesssim 2$ h) required for the chromatography and spectrophotometric measurements, and their presence as such in the aqua bands was corrected for by using the known extinction coefficients.[9,12]

The following molar extinction coefficients were used to determine [Co] in the eluates: $[(NH_3)_5CoONO]^{2+}$, $\epsilon_{325} = 151$; $[(NH_3)_5CoNO_2]^{2+}$, $\epsilon_{457}{}^{max}$ 95.6, $\epsilon_{325}{}^{max} = 1730$;[2] $[(NH_3)_5CoOH_2]^{3+}$, $\epsilon_{490}{}^{max} = 47.7$.[10] One of the several isosbestic points in the spectra of the nitrito and nitro isomers (ϵ_{484} 66.6) was used to check on the total [Co] in isomeric mixtures.

Results and Discussion

The nitrito complex $[(NH_3)_5CoONO]^{2+}$ is known to isomerize slowly ($t_{1/2} = 167$ min, 25 °C) but completely to the nitro form $[(NH_3)_5CoNO_2]^{2+}$ in aqueous solution.[2a] Recently we noted that this reaction has a base-catalyzed path ($k_{OH} = 5.9 \times 10^{-3}$ M^{-1} s^{-1}, 25 °C, $\mu = 1.0$ M),[2] and it seems likely that in previous attempts[10,13] to measure NO_2^- competition for the

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Table I. Comparison of Present and Previous Results for the Capture of NO_2^- during the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.00 M $NaNO_2$/0.1 M OH^- at 25 °C

leaving group, X	% total nitrite capture[a]		
	lit.[b]	revised[c]	present[d]
Cl^-	4.2		
Br^-	5.0		
I^-	4.5		
SCN^-	5.5 (4.0)[e]		
NO_3^-	5.1	6.4, 6.0, 6.8, 6.4 (av 6.4 ± 0.4)	7.5 ± 0.4
$OS(CH_3)_2$	7.8 ± 1.0	8.1, 8.2, 8.5 (av 8.3 ± 0.2)	8.8 ± 0.4
$CH_3SO_3^-$		6.6, 6.6 (av 6.6 ± 0.4)	6.6 ± 0.4
$CF_3SO_3^-$		5.6, 6.2 (av 5.9 ± 0.4)	7.0 ± 0.4

[a] $\Sigma(CoNO_2^{2+} + CoONO^{2+})$; other product is $CoOH^{2+}$. [b] Reported to be only $CoNO_2^{2+}$.[10,13,14] [c] Jackson, W. G., previous unpublished data. $\Sigma(CoNO_2^{2+} + CoONO^{2+})$ was measured as $CoNO_2^{2+}$ at 457 nm (ϵ 95.6) by allowing all the $CoONO^{2+}$ in the eluates (pH 4) to spontaneously isomerize to $CoNO_2^{2+}$ (24 h in the dark, 25 °C, $>8t_{1/2}$; $t_{1/2} = 167$ min). [d] Mean values, from Table II. The "present" values are considered much more accurate than the "revised" numbers because $CoNO_2^{2+}$ was estimated with use of ϵ_{325} 1730 rather than ϵ_{457} 95.6; i.e., the latter absorbance data are more accurate. [e] Uncorrected value. The other reaction pathway (24%), $CoSCN^{2+} \rightarrow CoNCS^{2+}$, does not involve a net substitution reaction.[14]

base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in OH^-/NO_2^- media, some of the O isomer initially formed would have isomerized to the N isomer. It is also known that the O (but not the N) isomer is readily cleaved by acid to give $[(NH_3)_5CoOH_2]^{3+}$ and HNO_2 (by N–O rather than Co–O bond rupture);[2] hence, any strong acid used in the elution of the complexes from cation-exchange resin would prevent the detection of the nitrito isomer. Finally, depending upon the time elapsed between the absorption of the product mixture on columns and measurement of the spectra of the eluates, much of any nitrito isomer formed would have isomerized to the nitro form by the spontaneous pathway, particularly in experiments conducted at ~25 °C. It is therefore not surprising that only the nitro form of $[(NH_3)_5Co(NO_2)]^{2+}$ has been reported[10,13] as the product of NO_2^- competition in base hydrolysis. Despite these difficulties, the results for *total* NO_2^- capture (O plus N isomer) presented previously and in this work (Table I) do not differ substantially, presumably because in the earlier work there was little loss of nitrito complex through the use of acid, and some of the ONO complex had isomerized to the N form. Where they do differ, the previous numbers are lower; the nitrito isomer is less strongly absorbing at the wavelength employed to measure the nitro isomer (457 nm, a maximum for $[(NH_3)_5CoNO_2)]^{2+}$).

In the present study, NO_2^- competition was determined for $[(NH_3)_5CoX]^{n+}$ reacted for a standard time (1.0 min, 25 °C) in 1.00 M $NaNO_2$/0.1 M NaOH. Seven different leaving groups were used, and the complexes were chosen such that they were all completely hydrolyzed ($>10t_{1/2}$) under the conditions. Subsequent base-catalyzed oxygen to nitrogen linkage isomerization was slight (~3.5% of total initial NO_2^--*O* capture) and was readily corrected for. We were unable to separate the isomers by ion-exchange chromatography, but the isomer ratio for the single 2+ band from Sephadex was defined accurately with use of the absorption at 325 nm (ϵ_{ONO} 151, ϵ_{NO_2} 1730). The total [Co] in the band was determined with use of ϵ 1730 and the absorption of the

Table II. Product Distributions for the Capture of the Oxygen and Nitrogen of NO_2^- in the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.00 M $NaNO_2$/0.1 M NaOH at 25 °C

X	O/N ratio[a]	% ONO	% NO_2	$\Sigma(NO_2)$[b]	av values[c]	
					% ONO	% NO_2
$CF_3SO_3^-$	1.8	4.2	2.4	6.6	66 ± 3	34 ± 3
	1.9	4.6	2.4	7.0		
	2.0	4.7	2.4	7.1		
	2.0	4.9	2.4	7.3		
av	1.9_3			7.0 ± 0.4[d]		
$CH_3SO_3^-$	1.8	4.2	2.4	6.6	67 ± 3	33 ± 3
	1.7	4.1	2.4	6.5		
av	1.7_5			6.6 ± 0.4		
NO_3^-	2.0	5.0	2.6	7.6	67 ± 3	33 ± 3
	2.0	4.9	2.5	7.4		
av	2.0			7.5 ± 0.4		
$(CH_3)_2SO$	1.6	5.4	3.5	8.9	63 ± 3	37 ± 3
	1.8	5.6	3.1	8.7		
av	1.7			8.8 ± 0.4		
$PO(OCH_3)_3$	1.4	4.3	3.1	7.4	61 ± 3	39 ± 3
	1.8	5.0	2.8	7.8		
	1.5	4.9	3.3	8.2		
	1.5	5.0	3.3	8.3		
av	1.5_5			7.9 ± 0.4		
$OC(NH_2)_2$[e]	2.0	5.5 (5.0)	2.8 (2.5)	8.3 (7.5)	66 ± 3	34 ± 3
	1.8	5.2 (4.7)	2.9 (2.6)	8.1 (7.3)		
av	1.9			8.2 ± 0.4		
$OC(NH_2)N(CH_3)_2$[e]	1.8	5.1 (5.0)	2.8 (2.7)	7.9 (7.7)	64 ± 3	36 ± 3
	1.8	5.4 (5.2)	2.9 (2.9)	8.3 (8.1)		
av	1.8			8.1 ± 0.4		
mean	1.8 ± 0.2				64.5 ± 2.5	35.5 ± 2.5
cor[f]	2.0 ± 0.2				66.7 ± 2.5	33.3 ± 2.5

[a] Initial ratio of $CoONO^{2+}/CoNO_2^{2+}$; after 1.0-min reaction in 0.1 M OH^-/(μ = 1.1 M, 25 °C). [b] % $CoONO^{2+}$ + % $CoNO_2^{2+}$; other product is $CoOH^{2+}$. [c] Percent of total $CoONO^{2+} + CoNO_2^{2+}$. [d] Estimated error. [e] Values in parentheses are those observed; they required correction correction for some O to N linkage isomerization of the urea complexes (7% for urea, 3% for Me_2urea) and some C–O cleavage (2.5%, in the case of the unsubstituted urea). The corrected values then are appropriate to the metal substitution (Co–O cleavage) path. [f] The $CoONO^{2+}$ and $CoNO_2^{2+}$ proportions are corrected for the small amount of $CoONO^{2+} \rightarrow CoNO_2^{2+}$ rearrangement (3.5%) that occurs in the (common) 1.0-min reaction time by the base-catalyzed route[2a] ($k_{OH} = 5.9 \times 10^{-3}$ M^{-1} s^{-1} for $[OH^-] = 0.1$ M, $\mu = 1.1$ M, 25 °C, $k_{obsd} = 5.9 \times 10^{-4}$ s^{-1} and $t_{1/2} = 19.6$ min).

same sample following complete isomerization to the nitro form (60 °C, 30 min).

The results are presented in Table II. The most striking fact is that the unstable O rather than the stable N isomer is the major product in each case ($O/N \approx 2.0/1$). This result parallels that found for the NCS^- system, where the preferred competitor is the S atom, which yields the thermodynamically unstable thiocyanato linkage isomer ($S/N \approx 3/1$).[6,14] The general trend in the competition process is that the best competitors are those least solvated by the solvent.[6,7] For example, the strong bases OH^-, F^-, and NH_3 are poor competitors, while NO_3^-, which is a very weak base, is a good competitor.[11] The rate-determining step in the collapse of the $[(NH_3)_4(NH_2)Co]^{2+}$ five-coordinate intermediate can still be argued as the abstraction of the competing anion from the solvation sheath for the bulk of the anions. However, the nitrite competition data (Table II) are atypical since in HNO_2 the proton is known to reside on oxygen. There are other anomalies among the competitors. Azide ion, for example, is a much stronger base than chloride ion and is nonetheless a better competitor. The nature of the donor atom clearly exerts some effect, and in the case of NO_2^- this would also seem to be the case. Also the O center although more basic would be preferred on statistical grounds alone (2/1), which implies that the O and N atoms are equally effective in capturing the intermediate.

The second feature of the results (Table II) is the consistently higher competition afforded by the 3+ substrates, i.e. neutral leaving groups (8.3 ± 0.5 (4)%), as opposed to the 2+ ions (7.0 ± 0.5 (3)%), albeit the differences are not pronounced. This trend parallels that found for other competitors ($Y^{m-} = S_2O_3^{2-}$,[15] SO_4^{2-}, $O_2CCH_3^-$, SCN^-, and N_3^-) with a range of 2+ and 3+ substrates (and one 1+ reactant, $Y^{m-} = N_3^-$).[6] It is discussed in detail elsewhere, and it suffices to note here that the result is consistent with a reactive five-coordinate intermediate, $[(NH_3)_4(NH_2)Co]^{2+}$, which does not survive for a time sufficient to *completely* equlibrate with the bulk environment and establish its own ion atomsphere, i.e., one appropriate to a 2+ ion. It reacts with an inherited ion atmosphere, and therefore there is a *slight* but definite dependence of the degree of anion competition on the charge of the complex ion. It cannot be asserted that the competition numbers are different for different leaving groups within each set of complexes of contant formal charge (2+ or 3+) since they agree within experimental error.

The most significant feature of the results is the very constant O-isomer/N-isomer ratio (67 ± 3% O, 33 ± 3% N). This is independent of the nature of the leaving group, even where it involves a variation in charge and the *total* NO_2^- competition varies. The result is expected of a reaction where the product-determining step is the collapse of a reactive intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ and where the O- and N-bonded isomers of NO_2^- are captured from the *same* ion atmosphere. Indeed, the NO_2^- competition data strongly support the case for such an intermediate, since the leaving groups of varying size, charge, and bonding geometry exert no effect and must be presumed absent at the product-determining step. There is now a need to test the generality of this result with use of other ambidentate competitors. Results for $S_2O_3^{2-}$, where S- and O-bonded isomers are captured, will be communicated shortly,[15] and we are presently looking at S and N capture of SCN^- for a wider variety of substrates. The present (limited) data indicate a difference in S/N product ratios for 2+ and 3+ substrates,[6,14] and this warrants a closer investigation.

Registry No. NO_2^-, 14797-65-0; $[(NH_3)_5CoO_3SCF_3](ClO_4)_2$, 76024-69-6; $[(NH_3)_5CoO_3SCH_3](ClO_4)_2$, 76024-71-0; $[(NH_3)_5CoONO_2](ClO_4)_2$, 15156-24-8; $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(NH_3)_5CoOP(OCH_3)_3](ClO_4)_3$, 15041-41-5; $[(NH_3)_5CoOC(NH_2)_2](S_2O_6)_{3/2}$, 75522-61-1; $[(NH_3)_5Co(OC(NH_2)N(CH_3)_2](S_2O_6)_{3/2}$, 84623-22-3.

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