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Base Hydrolysis of Anionopentaamminecobalt(III) Complexes: The Role of Ion Association and the Question of a Common Coordinatively Unsaturated Intermediate

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This paper examines critically the relationship between the rate law and product distribution for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in the presence of competing anions Y^{m-}. It is concluded that there is *no* relationship, supporting our previous contention that the product-determining step is not rate determining and implicating a reactive intermediate, five-coordinate $[(NH_3)_4(NH_2)Co]^{2+}$. Rate law studies employing the strongly ion-pairing SO_4^{2-}, CO_3^{2-}, $S_2O_3^{2-}$, and PO_4^{3-} anions reveal a correlation with their ion-pairing capacities. Ion-pair constants have been determined independently for some model $[(NH_3)_5CoX]^{n+}$ ($n = 2, 3$) complexes with CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}. Parallel product distribution studies show no obvious correlation with ion pairing. For example, the strongly ion-pairing PO_4^{3-} and CO_3^{2-} ions are shown to be very poor competitors, SO_4^{2-} is a weak competitor, and $S_2O_3^{2-}$ is a reasonable competitor. Furthermore, the poorly ion-pairing 1– anions N_3^-, SCN^-, $CH_3CO_2^-$, and others range from very weak to good competitors. Nonetheless, anion competition correlates well with the degree of anion hydration, consistent with a product-determining step involving the pentacoordinate $[(NH_3)_4(NH_2)Co]^{2+}$ species and rate-determining anion abstraction from the solvent. Rate constants for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ ($X = Cl^-, I^-, NO_3^-, OSMe_2, SO_4^{2-}$) in $ClO_4^-, N_3^-, CH_3CO_2^-, NCS^-, NO_2^-, NH_2SO_3^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, S_2O_3^{2-}$, and PO_4^{3-} media at 25 °C, $\mu = 1$ or 3 M, are reported. Rate reductions commensurate with the degree of ion pairing of the $[(NH_3)_5CoX]^{n+}$ reactant are observed, the ion pair being ca. 4-fold less reactive. It is shown that the free-ion and ion-paired forms of the conjugate base $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$, the reactive entity in the base hydrolysis reaction, are comparable in reactivity. Thus, the rate reduction rests largely with the diminished acidity of the coordinated ammine in the ion pair $[(NH_3)_5CoX]^{n+}, Y^{m-}$. It is demonstrated that, irrespective of mechanism, the ion pairs with CO_3^{2-} and PO_4^{3-}, and probably also with SO_4^{2-}, must collapse inefficiently; i.e., the product is largely $[(NH_3)_5CoOH]^{2+}$. Further, mixed-anion competition studies using SO_4^{2-}, $S_2O_3^{2-}$, and ClO_4^- with N_3^- demonstrate that selective ion pairing by Y^{2-} or Y^{3-} has no measurable effect on the capture of N_3^-. Both observations provide compelling evidence for the intervention of the $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate.

Introduction

The mechanism of base hydrolysis of Co(III) amine complexes incorporates a conjugate base process.[1] However, there is still controversy over the question of a discrete reduced coordination number intermediate.[2,3] This has arisen from anion competition studies in which $[(NH_3)_5CoX]^{n+}$ is hydrolyzed in the presence of a large excess of a competing anion Y^{m-} to produce $[(NH_3)_5CoY]^{(n-m)+}$ along with $[(NH_3)_5CoOH]^{2+}$. For the earliest competition experiments where the $[(NH_3)_5CoX]^{2+}$ ($X = I^-, NO_3^-, Cl^-, Br^-$) ions were base hydrolyzed in the presence of a wide variety of anions Y^- (up to 1 M), e.g. N_3^-, NO_2^-, and SCN^-, the amount of $[(NH_3)_5CoY]^{2+}$ was found to be independent of the leaving group X.[4] It has been shown that N_3^- competition is detectably higher (10–20%) for the $[(NH_3)_5CoX]^{3+}$ species ($X = Me_2SO, OC(NH_2)_2, OP(OMe)_3$) compared to the $[(NH_3)_5CoX]^{2+}$ ions.[2,3] Recently, this small difference between the 2+ and 3+ ions has been shown to be consistent for the competitors NO_2^-, OAc$^-$, and $S_2O_3^{2-}$.[5–7] It has been argued that this difference arises directly from the ion-paired conjugate base complex, which still contains the leaving group X, through an S_N2CB or an I_dCB process.[3] However, a short-lived reduced coordination number intermediate has been claimed to accommodate the data better.[2,5–8] This paper explores the reactivity of ion pairs and the role of ion association in this conjugate base process where it could be expected that the ion pairing was substantial and readily measurable. We report spectrophotometrically determined outer-sphere association constants for typical 2+ and 3+ $[(NH_3)_5CoX]^{n+}$ complexes with 2– (SO_4^{2-}, CO_3^{2-}) and 3– (PO_4^{3-}) anions. The association constants from these models are then used to interpret new kinetic and competition data for the base hydrolysis of 2+ and 3+ $[(NH_3)_5CoX]^{n+}$ ions in

a variety of Y^{m-} media, including mixed-anion systems (e.g., N_3^-/SO_4^{2-}).

Experimental Section

Visible spectra (ϵ, M^{-1} cm^{-1}; λ, nm) were recorded on Cary 16, Cary 118C and 210 instruments. Matched silica cells were thermostated to 25.0 ± 0.05 °C.[2] Water was deionized and doubly distilled. All chemicals were analytical grade. The cation-exchange resins used were Biorad Dowex 50W-X2 (200–400 mesh; H$^+$ or Na$^+$ form) and SP Sephadex C-25 (Na$^+$ form). ^{1}H NMR spectra were measured with use of a Varian T60 spectrometer (35 °C).

The complexes $[(NH_3)_5CoNCS]Cl_2$,[8,9] $[(NH_3)_6Co](ClO_4)_3$,[10] $[(NH_3)_5CoOH_2](ClO_4)_3$,[10] $[(NH_3)_5CoOCO_2]NO_3 \cdot 0.5H_2O$,[11] $[(NH_3)_5CoOSMe_2](ClO_4)_3 \cdot H_2O$,[2] $[(NH_3)_5CoOC(NH_2)_2](ClO_4)_3 \cdot 2H_2O$,[13] $[(NH_3)_5CoOC(NH_2)_2]_2(S_2O_6)_3 \cdot 3H_2O$,[2,10] $[(NH_3)_5CoOP(OMe)_3](ClO_4)_3 \cdot H_2O$,[10] $[(NH_3)_5CoOC(NH_2)NMe_2]_2(S_2O_6)_3 \cdot 3H_2O$,[14] $[(NH_3)_5CoCl](ClO_4)_2$,[6] $[(NH_3)_5CoI](ClO_4)_2$,[6] $[(NH_3)_5CoO_3SM$-

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e](ClO$_4$)$_2$,[12] [(NH$_3$)$_5$CoO$_3$SCF$_3$](ClO$_4$)$_2$,[10] [(NH$_3$)$_5$CoONO$_2$](ClO$_4$)$_2$,[4] [(NH$_3$)$_5$CoN$_3$](ClO$_4$)$_2$, and [(NH$_3$)$_5$CoN$_3$](CF$_3$SO$_3$)$_2$,[12] were prepared, purified, and characterized (elemental analyses, visible absorption (H$_2$O, pH 3), and ^{1}H NMR spectroscopy (Me$_2$SO-d_6)) by the cited methods. Many of the samples were from freshly prepared and characterized batches used in concurrent work.[5-8]

[(NH$_3$)$_5$CoOSO$_3$]ClO$_4$·H$_2$O. The complex [(NH$_3$)$_5$CoO$_3$SCF$_3$]-(CF$_3$SO$_3$)$_2$[10] (5.0 g, 8.5 mmol) was dissolved in H$_2$SO$_4$ (98%; 20 mL) with stirring and left to react for 30 min ($\sim$22 °C). The resultant pink solution was poured carefully into cold 2-propanol (1.5 L) to precipitate crude [(NH$_3$)$_5$CoOSO$_3$]HSO$_4$. This was collected and washed with 2-propanol (3 × 15 mL) and ether (2 × 50 mL). The air-dried product was recrystallized twice from saturated aqueous solution ($\sim$25 °C) by addition of sodium perchlorate (10 M). Yield: 2.6 g (7.3 mmol, 86%). Anal. Calcd for CoH$_{17}$N$_5$SO$_9$C: H, 4.79; N, 19.59; S, 8.97; Cl, 9.91. Found: H, 4.8; N, 19.8; S, 8.9; Cl, 10.0. The product had an visible spectrum (ϵ_{516}^{max} 63.9, H$_2$O) identical with those of samples obtained by other routes,[2,8] and ion-exchange chromatography and the ^{1}H NMR spectrum[12] (Me$_2$SO-d_6) confirmed the absence of [(NH$_3$)$_5$CoOH$_2$](ClO$_4$)$_3$.

[(NH$_3$)$_5$CoOPO$_3$]·3H$_2$O. The complex [(NH$_3$)$_5$CoO$_3$SCF$_3$](C-F$_3$SO$_3$)$_2$[10] (5.0 g; 8.5 mmol) was dissolved in H$_3$PO$_4$ (100%; 25 mL). To this solution was added Na$_2$HPO$_4$ (2.0 g, 14.1 mmol), and the mixture was stirred for 36 h ($\sim$22 °C). The product solution was added to ethanol (absolute; 1.5 L) to precipitate crude [(NH$_3$)$_5$Co-OPO$_3$]. Following washing with ethanol (3 × 15 mL) and ether (2 × 50 mL) and air-drying, the complex was recrystallized from HClO$_4$ (2 M) by careful neutralization with aqueous NH$_3$ (4 M). The pink needles were washed with ethanol (3 × 15 mL) and ether (2 × 50 mL) and air-dried. Yield: 2.0 g (6.8 mmol, 80%). Anal. Calcd for CoN$_5$H$_{21}$O$_7$P: H, 7.20; N, 23.90; P, 10.57. Found: H, 7.17; N, 23.89; P, 10.83. Visible spectra: ϵ_{523}^{max} 89.7 (H$_2$O), ϵ_{516}^{max} 65.4 (1 M HClO$_4$), ϵ_{517}^{max} 73.5 (1 M KH$_2$PO$_4$). The complex eluted as a single pink band from Dowex resin using a 0.5 M NaH$_2$PO$_4$ eluant, corresponding to the expected 1+ to 2+ ion [[(NH$_3$)$_5$CoO$_3$P(OH)]$^+$/[(NH$_3$)$_5$CoO$_2$P(OH)$_2$]$^{2+}$] distribution.

Outer-Sphere Association (Ion-Pair) Constants. These were determined spectrophotometrically at 25.0 ± 0.05 °C by monitoring the changes in UV absorption accompanying ion association. Measurements were made at several wavelengths in the range 250–315 nm by using 10-cm silica cells and the Cary 16 instrument. For each cation ([NH$_3$)$_5$CoNCS]$^{2+}$, [(NH$_3$)$_6$Co]$^{3+}$), anion Y^{m-} (SO$_4^{2-}$, CO$_3^{2-}$, PO$_4^{3-}$), and wavelength, absorbances were determined for six–eight solutions of varying [Co] and [Y] at fixed ionic strength (NaClO$_4$·H$_2$O or NaCF$_3$SO$_3$·H$_2$O,[10] μ = 1.0 and 3.0 M). Solutions were prepared by mixing appropriate volumes (A-grade burets, V ± 0.1%) of stock NaClO$_4$ (or NaCF$_3$SO$_3$) and Na$_m$Y solutions at the same μ (1.0 or 3.0 M). The cobalt complex was introduced by stirring the solid salt ($\sim$0.2 g) with each solution for 5 min at 25 °C, with Millipore filtration of the excess. Cobalt was determined from the absorbances at the maxima of the low-energy ligand field bands, shown in separate experiments to be insensitive to ion pairing: [(NH$_3$)$_5$CoNCS]$^{2+}$, ϵ_{500}^{max} 177;[8] [(NH$_3$)$_6$Co]$^{3+}$, ϵ_{475}^{max} 56.7.[10] Note that, under all conditions, [Y] >> [Co] and it can be shown therefore that the computed ion-pair constants do not depend upon the *accuracy* of these ϵ values—only, of course, on the precision of the absorbance measurements.

All glassware was carefully cleaned with MeOH/KOH (1:1) mixtures, rinsed thoroughly with distilled water, and dried (100 °C).

The UV ϵ_{obsd},[Y] data were computer fitted by standard nonlinear least-squares procedures to the function describing the ion-pairing phenomenon (eq 1), where ϵ^λ_{obsd} is the observed molar absorption

$$\epsilon^\lambda_{obsd} = (\epsilon^\lambda_1 + \epsilon^\lambda_2 Q[Y])/(1 + Q[Y]) \qquad (1)$$

coefficient at wavelength λ, ϵ^λ_1 and ϵ^λ_2 are those for the free ion and ion pair, and Q is the equilibrium quotient (ion-pair constant). In these data fits, ϵ^λ_1 was held at its measured value (ϵ^λ_{obsd} for [Y] = 0), and ϵ^λ_2 and Q were used as parameters. For each complex and anion, values for Q obtained for the different wavelengths agreed reasonably and were averaged. Moreover, the value of ϵ^λ_2, at each wavelength and for a particular cation and anion, agreed satisfactorily for the μ = 1.0 and 3.0 M data. However, more reliable values of Q (i.e., lower standard deviations) for some systems at μ = 1.0 M were computed by data fitting to eq 1 using ϵ^λ_2 values obtained from the corresponding data at μ = 3.0 M.

Kinetic Measurements. Where possible the perchlorate salts of the [(NH$_3$)$_5$CoX]$^{n+}$ species were added directly into silica cells (1 cm)

containing temperature-equilibrated (15 min) solutions of the various Na$_m$Y salts containing NaOH (Volucon; 0.005, 0.01, 0.02, and/or 0.1 M). Generally, [OH$^-$] >> [Co], and the kinetics were pseudo first order. Wavelengths were chosen to maximize the absorbance change (Cary 118C and 210 instruments); at low [OH$^-$], the UV region was monitored to achieve sufficient absorbance change consistent with the condition [OH$^-$] >> [Co]. But here, competition by anions, e.g. N$_3^-$, NCS$^-$, and S$_2$O$_3^-$, contributed to this change, and it was necessary to further scrutinize the wavelength choice to minimize (or remove) absorbance changes associated with subsequent base-catalyzed hydrolysis and/or linkage isomerization[5,7,8] reactions of the competition products. In some cases, the visible region had to be used to circumvent this problem, and consequently higher [Co] ($\simeq$[OH$^-$]) were employed. Here a bifurcated cell method was employed, involving the rapid mixing of temperature-equilibrated solutions of complex (in H$_2$O, known [Co]) and the Na$_m$Y medium (containing OH$^-$) at a calculated factor above the desired final concentration. The compartments of the bifurcated cell were filled (1:1 to 2:1 by volume) with use of micropipets. Second-order kinetics were observed, and it was necessary to accommodate in the data analysis cases of appreciable anion competition accompanying base hydrolysis, i.e. a path that does not involve the consumption of OH$^-$.

Rate constants (k_{OH}(obsd)) were computed by fitting A,t data to the appropriate function, the integrated form of the rate law, using standard nonlinear least-squares procedures. Good fits were obtained for data covering at least 85% reaction, and the agreement between k_{OH}(obsd) values derived from both pseudo-first-order and second-order kinetic studies at various [OH$^-$], in instances permitting both sets of experiments, was taken as an indication of the reliability of the data; that is, for all complexes the usual first-order dependence of the rate on [OH$^-$] ($\leq$0.1 M) was observed.

Anion Competition. For the Na$_2$SO$_4$, NaN$_3$, NaN$_3$/NaClO$_4$, and NaN$_3$/Na$_2$SO$_4$ systems, solid reactant ($\sim$0.2–0.3 g) was dissolved directly in the appropriate medium (20–80 mL; 0.1 M in NaOH) by rapid stirring and allowed to react at 25 °C for $\geq$10$t_{1/2}$. For [(NH$_3$)$_5$CoCl]$^{2+}$, a 5.0-min reaction time was employed and 30–60 s for all other [(NH$_3$)$_5$CoX]$^{n+}$ ions except [(NH$_3$)$_5$CoO$_3$SCF$_3$]$^{2+}$ (5 s). The reactions were quenched with dilute HClO$_4$ or CH$_3$CO$_2$H (1 M). In some cases NH$_4$ClO$_4$ (1.0 g) was employed as the quenching reagent (to pH $\sim$9), specifically for the urea-O and dimethylurea-O complexes (see below). The product solutions were diluted (H$_2$O) and sorbed on and eluted from Dowex (Na$^+$ form) resin, using 1 M NaClO$_4$ (pH 3) to remove [(NH$_3$)$_5$CoOSO$_3$]$^+$ followed by [(NH$_3$)$_5$CoN$_3$]$^{2+}$ and 3 M HCl to remove [(NH$_3$)$_5$CoOH$_2$]$^{3+}$. Cobalt contents were determined as previously,[2,4,5-8] by using ϵ_{515}^{max} 63.9 for the sulfato complex, ϵ_{515}^{max} 272 for the azido ion, and ϵ_{490}^{max} 47.7 for the aqua complex. All experiments were performed in triplicate (and, for Y^{m-} = N$_3^-$, in subdued light), and cobalt recoveries were routinely 100 ± 1.5%. Some experiments were performed with Sephadex in lieu of Dowex resin, in which case reaction volumes were minimized ($\leq$30 mL, μ = 3.1 M) and product solutions were diluted more ($\sim$50-fold) to retain the 1+ sulfato complex as a narrow band on the resin. The eluants used in these cases were 0.25 M NaClO$_4$ (pH 3) for the 1+ band and 0.5–1.0 M NaClO$_4$ (pH 3) for the 2+ and 3+ bands. The molar absorption coefficient data (above) for these media were the same, as were the product analyses and cobalt recoveries. Authentic samples of the competition product [(NH$_3$)$_5$CoN$_3$]$^{2+}$ were shown to be recovered unchanged under all the conditions given, but the [(NH$_3$)$_5$CoOSO$_3$]$^+$ product was demonstrated in blank experiments to have undergone some subsequent hydrolysis, especially (36%) in the 5.0 min at 25 °C required to completely base hydrolyze the [(NH$_3$)$_5$CoCl]$^{2+}$ ion in 1.0 M SO$_4^{2-}$; all data have been corrected for subsequent reaction of [(NH$_3$)$_5$CoOSO$_3$]$^+$, by using the measured specific rates appropriate to the medium, and known reaction times.

The urea-O complexes base hydrolyze with parallel O- to N-linkage isomerization.[14] The corrections for this reaction pathway were made after determining the amount of urea-N isomer formed, by using two methods[5-8] that gave equivalent results. Product solutions quenched to pH $\leq$3 lead to conversion of the urea-N species to its O-bonded isomer, which elutes with [(NH$_3$)$_5$CoOH$_2$]$^{3+}$ under our conditions. The aqua band was therefore determined by using the ϵ value corrected for presence of the urea-O species (in known amount). Alternatively, the amount of urea-N isomer was directly determined by using NH$_4^+$ to quench the primary base hydrolysis reaction (to pH $\sim$9). The urea-N isomers are stable to linkage isomerization, as their depro-

Table I. Ion-Pair Constants (25.0 °C)[a]

cation	anion	$Q(\mu = 1 \text{ M})$, M^{-1}	$Q(\mu = 3 \text{ M})$, M^{-1}	ref
$[(NH_3)_5CoNCS]^{2+}$	CO_3^{2-}	0.9 ± 0.3	0.5 ± 0.2	this work
$[(NH_3)_5CoNCS]^{2+}$	SO_4^{2-}	0.8 ± 0.3	0.4 ± 0.2	this work
$[(NH_3)_5CoNCS]^{2+}$	PO_4^{3-}	3.3 ± 0.7^d	2.1 ± 0.4^d	this work
$[(NH_3)_6Co]^{3+}$	CO_3^{2-}	6.3 ± 1.3	2.1 ± 0.4	this work
$[(NH_3)_6Co]^{3+}$	SO_4^{2-}	4.5 ± 1.5^e	1.9 ± 0.5^e	this work
$[(NH_3)_5CoOH_2]^{3+}$	SO_4^{2-}	11.2^b		18
$[(en)_3Co]^{3+}$	$S_2O_3^{2-}$		1.3 ± 0.1^c	23
$[(en)_3Co]^{3+}$	SeO_3^{2-}		1.2 ± 0.5^c	23
$[(NH_3)_6Co]^{3+}$	PO_4^{3-}	15.0 ± 3.5^e	4.0 ± 1.8^e	this work
$[(NH_3)_6Co]^{3+}$	SO_4^{2-}	2100^f		18
$[(NH_3)_6Co]^{3+}$	$S_2O_3^{2-}$	1800^f		45
$[(NH_3)_5CoOH_2]^{3+}$	SO_4^{2-}	1888^f		18
$[(NH_3)_6Co]^{3+}$	SO_4^{2-}	138^g		18
$[(en)_3Co]^{3+}$	SO_4^{2-}	33.9 ± 0.8^g		43
$[(NH_3)_5CoOH_2]^{3+}$	SO_4^{2-}	92^g		18

[a] Some data refer to other temperatures (see footnotes *b* and *c*); NaClO$_4$ supporting electrolyte except where noted (see footnote *d*). [b] 24.5 °C. [c] 20.0 °C. [d] NaClO$_4$ or NaCF$_3$SO$_3$ supporting electrolyte. [e] NaCF$_3$SO$_3$. [f] $\mu = 0$ M. [g] $\mu = 0.1$ M.

tonated forms $[(NH_3)_5CoNHCONR_2]^{2+}$ (R = H, Me), at a pH well above their pK'_a (~ 3).[13,14] By using a buffered eluant (1.0 M Na$^+$, ~ 0.9 M Cl$^-$/0.1 M HPO$_4^{2-}$/H$_2$PO$_4^-$ (1:1), pH ~ 7) on Dowex resin, the urea-*N* species were eluted behind the sulfato complex but in front of the 2+ ion (N$_3^-$) competition product and the aqua ion. The cobalt contents of the eluates were determined by using the independently measured[13,14] ϵ_{505}^{max} 114.0 for $[(NH_3)_5CoNHCONMe_2]^{2+}$ and ϵ_{499}^{max} 88.0 for $[(NH_3)_5CoNHCONH_2]^{2+}$ in this medium.

The competition experiments in the presence of Na$_2$CO$_3$ (1.0 M), Na$_3$PO$_4$ (0.5 M), and NaN$_3$/Na$_3$PO$_4$ were carried out as above, except the CO$_3^{2-}$ reactions were not acid quenched but diluted and sorbed directly on Dowex Na$^+$ form resin. The PO$_4^{3-}$ reactions were quenched with HClO$_4$ to pH ~ 2 in order to retain the $[(NH_3)_5CoOPO_3]$ species on the resin in its 1+/2+ protonated form(s). For the CO$_3^{2-}$ reaction products, the resin was washed thoroughly with dilute Na$_2$HPO$_4$ to maintain pH >7 and to remove excess CO$_3^{2-}$, and the converse (0.1 M HClO$_4$) was used for the phosphate reaction products. For CO$_3^{2-}$, this procedure was necessary because the $[(NH_3)_5CoOH_2]^{3+}$ ion reacts rapidly[30] with HCO$_3^-$ around pH 7, yielding $[(NH_3)_5CoOCO_3]^+$. The eluants used in the respective CO$_3^{2-}$ and PO$_4^{3-}$ competition experiments were 1.0 M NaClO$_4$ and 1.0 M NaH$_2$PO$_4$, and 3 M HCl was used for the aqua ion as usual. The cobalt contents of the eluates were determined by using ϵ_{510}^{max} 132.5 for $[(NH_3)_5CoOCO_2]^+$, ϵ_{517}^{max} 73.5 for $[(NH_3)_5CoO_3P(OH)]^+$, and ϵ_{490}^{max} 47.7 for the aqua ion.

The S$_2$O$_3^{2-}$ and S$_2$O$_3^{2-}$/ClO$_4^-$ competition experiments were performed as described.[7] The S$_2$O$_3^{2-}$/N$_3^-$ work followed that given above for SO$_4^{2-}$/N$_3^-$, except longer reaction times were employed, sufficient to react all of the initially formed $[(NH_3)_5CoO_3S_2]^+$. The $[(NH_3)_5CoSSO_3]^+$ ion is stable under the conditions (0.1 M OH$^-$).[7]

Results

Ion-Pair Constants. The values for association of $[(NH_3)_5CoNCS]^{2+}$ and $[(NH_3)_6Co]^{3+}$ with each of the anions CO$_3^{2-}$, SO$_4^{2-}$, and PO$_4^{3-}$ at 25.0 °C, $\mu = 1.0$ and 3.0 M, are recorded in Table I. Average values are given—the full data set illustrating the wavelength independence of Q is available as supplementary material (Table II). For ion-pair constants ≤ 5 (M^{-1}), the errors are necessarily large. Nonetheless, the constants are sufficiently well-defined where $Q \geq 0.5$ to justify the generalizations below. Also included in Table I are some relevant literature data.

The following general points emerge:
(i) The magnitude of Q is strongly ionic strength dependent in the low-μ region (0–0.1 M). The dependence on μ is much less in the range 1.0–3.0 M. There is a consistent reduction in Q going from $\mu = 1.0$ to $\mu = 3.0$ M that amounts to a factor of ~ 2.

(ii) The ion-pair constants for the multivalent ions are independent of the anion component of the supporting electrolyte, ClO$_4^-$ or CF$_3$SO$_3^-$. We interpret this to imply that as-

sociation with ClO$_4^-$ or CF$_3$SO$_3^-$ is small compared to that with Y^{m-} (*m* = 2, 3). Alternatively, the degree of association of ClO$_4^-$ and CF$_3$SO$_3^-$ with a given cation is nearly identical. Both seem likely, and we note that there is no significant change in the ultraviolet spectra of $[(NH_3)_5CoX]^{n+}$ (*n* = 2, 3) when large amounts (up to 3.0 M) of ClO$_4^-$ or CF$_3$SO$_3^-$ are introduced, compared to the correspondingly large effects of Y^{m-} (*m* = 2, 3). Thus, association of ClO$_4^-$ and CF$_3$SO$_3^-$ is presumed small.

(iii) The ion-pair constants show the expected dependence on the charges of the ions involved. At both $\mu = 1$ and $\mu = 3$ M, an increase in the charge of the anion or cation increases Q from 3- to 5-fold. This correlation holds for 2+ or 3+ cations in association with 2- or 3- anions. Association constants are similar for converse charge types, i.e., 2+/3- and 2-/3+.

(iv) In the range $\mu = 1.0$–3.0 M, the association constants appear to be insensitive to the *nature* of the 2- anion.

(v) The literature data suggest some dependence of Q on the nature of the cation, including a variation in X on the $[(NH_3)_5CoX]^{n+}$ moiety (at constant *n*). Up to a factor of 2 is involved.

Some comments on the spectrophotometric method for determining ion-pair constants seem warranted. The observation that the presence of anions in solutions of cationic transition-metal complexes influences the electronic absorption spectra in the UV region[15-18] is invariably interpreted as the formation of outer-sphere complexes, or ion pairs. Small temperature changes can also markedly affect the UV absorption,[18] and its close control is obviously important. It has been pointed out that not only "real" charge-transfer complexes between a donor D and acceptor A but also contact pairs due to the random collision of D and A affect the UV charge-transfer absorption.[19-21] It is claimed that this leads to an overestimation of Q. A value of ~ 0.2 M^{-1} for random-collision contact pairs has been given.[21] However, Q values that include this random-collision component no doubt reflect the situation in the base hydrolysis reaction that is of most interest, namely where [Y] is in close proximity to the metal complex.

Another problem concerning the accuracy and significance of spectrophotometrically determined Q values is the size of the absorbance change accompanying ion association.[22,23] For example, the small spectral change in the case of SO$_4^{2-}$ with 2+ and 3+ cations, due to the small polarizability of this anion, is reflected in the larger errors for Q (Tables I and II). Nonetheless, it is clear that values for SO$_4^{2-}$, despite the uncertainty, are very similar to Q for CO$_3^{2-}$ where the errors are smaller. Also it is necessary to mention that the ion-pair constants are not to be viewed as absolute values but rather constants relative to those for the much more weakly associating anionic component (ClO$_4^-$, CF$_3$SO$_3^-$) of the supporting electrolyte. It has been pointed out[24] that the Q values for the usually neglected ion pairs with perchlorate (and triflate) are not greatly different from those of other mononegative anions. However, our Q values may be regarded as quasi-absolute since the 2- and 3- associations are at least 10-fold greater than the background 1-.

Base Hydrolysis Rates. The dependence of the second-order rate constants k_{OH} on the nature of the supporting electrolyte (Na$_m$Y) is illustrated by the data given in Tables III and IV.

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Table III. Rate Constants for the Base Hydrolysis of $[(NH_3)_5CoCl]^{2+}$ ($\mu = 1.1$ M, 25.0 °C)

Y^- [a]	$k_{OH}(obsd)$,[b] $M^{-1} s^{-1}$	Y^- [a]	$k_{OH}(obsd)$,[b] $M^{-1} s^{-1}$
ClO_4^-	0.22 ± 0.03	$NH_2SO_3^-$	0.19 ± 0.01
$CH_3CO_2^-$	0.24 ± 0.02	NCS^-	0.22 ± 0.02
NO_2^-	0.21 ± 0.01	N_3^-	0.21 ± 0.01
NO_3^-	0.18 ± 0.01		

[a] 1.0 M NaY; 0.01–0.2 M NaOH; generally 0.1 M [OH⁻].
[b] Mean and standard deviations given; three–five determinations for each Y⁻; $k(obsd) = k_{OH}(obsd)[OH^-]$ strictly observed in the range 0.01–0.2 M NaOH.

Several generalities arise from the data:

(i) At constant ionic strength ($\mu = 1.1$ M), the rate constant is independent of the nature of Y^- over a wide range (Table III). Moreover, the k_{OH} value for $Y^- = ClO_4^-$ agrees well with that published.[25] For the 3+ ion $[(NH_3)_5CoOSMe_2]^{3+}$, the rate is reduced somewhat in NCS^- and more so in N_3^- media, relative to ClO_4^- (Table IV).

(ii) An increase in ionic strength, from 1 to 3 M (ClO_4^-), leads to a small rate reduction, ~30%, for 2+ and 3+ cations alike. Such reductions are expected, but they contrast sharply with the very much larger rate reductions that occur in the low-μ region (e.g., 0–0.5 M).[26]

(iii) At constant ionic strength ($\mu = 3.1$ M), the k_{OH} values in Y^{2-} media are much lower (2- to 7-fold) than for Y^- media. The expected further reduction in Y^{3-} (PO_4^{3-}) medium was not observed, and the explanation probably lies in the lower Y^{3-} concentration (0.5 vs. 1.0 M).

(iv) The 3+ cation shows a consistently greater rate reduction than the 2+ ions in the same Y^{2-} medium.

(v) The rate reductions are essentially independent of the nature of the Y^{2-} anion. For the 2+ ions at least, the magnitude of the reduction is cation dependent (~2-fold variation).

(vi) At the higher ionic strength ($\mu = 3.1$ M), the rate data show a dependence on the nature of Y^- not seen at $\mu = 1.1$ M. Moreover, the rates for 3+, 2+, and even 1+ cations are lower than expected from effect ii alone. The effect is, as expected, greater for the 3+ compared to the 2+ cations, consistent with effect iv above, but the dependence of k_{OH}(obsd) on the nature of Y^- for the 2+ cation contrasts with effect i.

The trends and generalities are discussed in some detail ahead.

Anion Competition. Data for SO_4^{2-} competition (1 M; $\mu = 3.1$ M) are given in Table V for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ complexes, involving six different leaving groups and including a variation in formal charge of the reactant. This table also contains the results for CO_3^{2-} and PO_4^{3-} competition (the leaving group range is limited here because competition is negligible and therefore the X dependence indeterminate). Previously published data[7] for $S_2O_3^{2-}$ competition appear for comparison.

The results for mixed-anion competition are recorded in Table VI, for typical 2+ and 3+ cations in N_3^-/Y^{2-} (SO_4^{2-}, $S_2O_3^{2-}$) and N_3^-/Y^{3-} (PO_4^{3-}) media. The thrust of this work was to examine the effect of strongly ion-pairing Y^{m-} ($m = 2, 3$) agents on the readily measured (and significant) competition observed for the N_3^- ion.

The results are summarized as follows:

(i) SO_4^{2-} competition is independent of the variation in leaving group X (Table V), except for the unique urea-O species that exhibits a lower value. The lower competition

value for $[(NH_3)_5Co(urea-O)]^{3+}$ is observed also for SCN^- competition[8] and for N_3^- competition in the presence of multivalent Y^{m-} ($m = 2, 3$). The previous anomaly[4] for SO_4^{2-} vanishes.

(ii) CO_3^{2-} competition is negligible, and PO_4^{3-} competition, which is barely detectable, appears to be independent of X. Again, previous anomalies[4] for PO_4^{3-} competition vanish.

(iii) N_3^- competition, at constant ionic strength, is independent of the nature of the anion in the Na_mY supporting electrolyte ($Y^{m-} = S_2O_3^{2-}$, SO_4^{2-}, PO_4^{3-}, ClO_4^-, N_3^-). This is also true of $S_2O_3^{2-}$ and SO_4^{2-} competition. This is an especially important result.

(iv) Anion competition is consistently greater (~25%) for 3+ over 2+ cations. This fact is obvious only when anion competition is sufficiently great (>10%); otherwise, the error (±0.4%, absolutely) obscures the trend. The present data (Table V) and previously published results (N_3^-, SCN^-, NO_2^-, $S_2O_3^{2-}$) clearly demonstrate this.[2,3,5-8]

The amount of sulfato complex formed in the base hydrolysis reaction of $[(NH_3)_5CoX]^{n+}$ in 1.0 M SO_4^{2-} (5.1 ± 0.4%) is somewhat smaller than that reported earlier[4] (8.2%). However, the result for $[(NH_3)_5CoOSMe_2]^{3+}$ (5.1%) is identical with that obtained in another study.[27] The present results extend the range of leaving groups to seven and include data for both 2+ and 3+ cations. The leaving group independence is consistent with H_2O and SO_4^{2-} competing for the common reactive $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate. The usual[7,8] small increase in anion competition for 3+ over 2+ reactants (effect iv above), and attributed to a memory effect[2] (inherited ion atmosphere), is not clear (4.9 ± 0.2% for 2+; 5.4 ± 0.3% for 3+). The expected difference, ~1.0% absolutely, is little more than the experimental error (±0.4%).

The present data have been corrected for some subsequent base hydrolysis of the $[(NH_3)_5CoOSO_3]^+$ component of the products; approximately 36% of it is lost in the time (5.0 min) required for the decay ($10t_{1/2}$) of the least reactive of the $[(NH_3)_5CoX]^{n+}$ ions in 1.0 M SO_4^{2-}/0.1 M OH^- at 25 °C. The correction was determined from the measured base hydrolysis constant for the sulfato ion in 1.0 M SO_4^{2-} (about half that for 1.0 M $NaClO_4$). This rate reduction, coupled with the larger rate reduction for the 2+ and 3+ $[(NH_3)_5CoX]^{n+}$ reactants in SO_4^{2-} media, accommodate the discrepancies between the present and earlier[4] SO_4^{2-} competition data. The sulfato product of $[(NH_3)_5CoCl]^{2+}$ base hydrolysis has been suggested[4] to be $[(NH_3)_4CoO_2SO_2]^+$ rather than $[(NH_3)_5CoOSO_3]^+$, because of its lower energy ligand field absorption (λ_{max} 535 nm). However, the competition product shows the correct 515-nm absorption for the sulfato pentaammine product when $[(NH_3)_5CoCl]^{2+}$ is reacted for the longer time required in SO_4^{2-} media, and it is likely that $[(NH_3)_5CoOSO_3]^+$ was admixed with some unreacted $[(NH_3)_5CoCl]^{2+}$ (λ_{max} 535 nm) in the earlier study.

The competition for SO_4^{2-} may be compared with that exhibited[7] by the isoelectronic and structurally related $S_2O_3^{2-}$ ion (Table V). The latter is captured through both sulfur and oxygen to give $[(NH_3)_5CoSSO_3]^+$ and $[(NH_3)_5CoOS(S)O_2]^+$, respectively. Preferential capture by the sulfur center, as with SCN^- (S- and N-capture),[2,8,25] is usual, and an account[28] is offered elsewhere. In the present context the interesting feature of the SO_4^{2-} and $S_2O_3^{2-}$ results is the same competition ratio (statistically corrected) for oxygen capture.

Phosphate ion capture has been determined for a 2+ and 3+ cation (Table V). For 0.5 M PO_4^{3-} ($\mu = 3.1$ M), only a trace (~0.25%) of the $[(NH_3)_5CoOPO_3]$ product was detected and therefore a study was not extended to include the full range

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Table IV. Rate Data for the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ (25.0 °C, μ = 1.1 and 3.1 M)

	$[CoCl]^{2+}$		$[CoI]^{2+}$		$[CoONO_2]^{2+}$		$[CoOSMe_2]^{3+}$		$[CoOSO_3]^{+}$	
anion[b]	$\mu = 1.1^c$	$\mu = 3.3$	$\mu = 1.1$	$\mu = 3.1$	$\mu = 1.1$	$\mu = 3.1$	$\mu = 1.1$	$\mu = 3.1$	$\mu = 1.1$	$\mu = 3.1$
ClO_4^-	0.22 (0.23)[d]	0.14	3.0 (3.3)[d]	1.88	(5.6)[d]	3.8	(5.4)[d]	3.6	0.041 (0.049)[d]	...
NCS^-	0.22	...	...	...	...	...	4.2	2.6		
N_3^-	0.21	...	...	...	...	2.5	2.9	1.1		
SO_4^{2-}		0.080		1.0_3		...		0.51	0.015	
CO_3^{2-}		0.072		1.1_1		...		0.53		
$S_2O_3^{2-}$		0.080		0.96		1.0		0.42		
PO_4^{3-}		0.088		...		...		...		

[a] Mean of three or four determinations given; standard deviation generally ±5%. k(obsd) = k_{OH}(obsd)[OH⁻] strictly observed over the [OH⁻] range studied (see footnote b). [b] 0.5 M Na₃PO₄; 1.0 M Na₂Y or 3.0 M NaY; [OH⁻] = 10^{-3} to 0.2 M. [c] Data from Table III. [d] Published values.[25,26,44]

Table V. Sulfate, Carbonate, and Phosphate Ion Competition Data for the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ (25 °C)

	% $[(NH_3)_5CoY]^{(n-m)+}$ product[a]			
reactant	1.0 M $SO_4^{2-\ b}$	0.5 M PO_4^{3-}	1.0 M CO_3^{2-}	1.0 M $S_2O_3^{2-\ d}$
$[(NH_3)_5CoCl]^{2+}$	4.9	0.25	<0.2	...
$[(NH_3)_5CoO_3SCF_3]^{2+}$	4.7			10.8
$[(NH_3)_5CoI]^{2+}$	5.0			11.3
$[(NH_3)_5CoO_3SCH_3]^{2+}$	...			11.1
$[(NH_3)_5CoOSMe_2]^{3+}$	5.1	0.25	<0.2	12.6
$[(NH_3)_5CoOC(NH_2)_2]^{3+}$	3.8 (3.5)[c]			9.1
$[(NH_3)_5CoOP(OMe)_3]^{3+}$	5.4			12.2
$[(NH_3)_5CoOC(NH_2)NMe_2]^{3+}$	5.7 (5.5)[c]			12.2

[a] Average of two or three determinations, generally ±4% relatively; 0.5 or 1.0 M Na$_m$Y (μ = 3.1); [OH⁻] = 0.1 M. [b] ±0.4%; corrected for any subsequent hydrolysis of $[(NH_3)_5CoOSO_3]^+$. [c] Uncorrected result; parallel intramolecular urea-O to urea-N linkage isomerization (3% dimethylurea; 7% urea). [d] Total S- plus O-capture; product S:O isomer ratio is constant (70:30); data from ref 7.

of leaving groups. This result may be contrasted with the variable 0–6.8% found previously.[4] We suspect the apparent difference to lie in the conditions of the analytical technique. We determined the phosphato complex as $[(NH_3)_5CoOP(OH)O_2]^+/[(NH_3)_5CoOP(OH)_2O]^{2+}$ by using a suitably buffered eluant ($H_2PO_4^-$, pH ~4) to retain the neutral complex on the ion-exchange resin as a rapidly equilibrating mixture of its charged protonated forms (1+/2+). It has been noted previously[13,29] that complexes having ionizable protons with pK'_a values around 7 require buffered eluants to avoid band spreading (and even separation) on the ion-exchange column, despite the fact that the polyprotic forms rapidly equilibrate. The aqua complex ($pK'_a \sim 7$) affords a classical example of this unexpected behavior, and it seems likely that under the previous[4] conditions some $[(NH_3)_5CoOH]^{2+}/[(NH_3)_5CoOH_2]^{3+}$ separated from bulk aqua complex on chromatography and was mistakenly identified as $[(NH_3)_5CoOPO_3]^+$ (the absorption spectra are quite similar).

The competition afforded by CO_3^{2-} has not been explored previously. When a pH well above 7 is always maintained, the rapid reaction[30]

$$[(NH_3)_5CoOH_2]^{3+} \xrightleftharpoons[]{HCO_3^-} [(NH_3)_5CoOCO_2]^+ \quad (2)$$
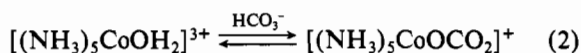
is avoided. Blank experiments demonstrated that both $[(NH_3)_5CoOH_2]^{3+}$ and $[(NH_3)_5CoOCO_2]^+$ could be recovered quantitatively from the ion-exchange column under the conditions employed. In this way, a 2+ and 3+ cation were shown to react in 1 M CO_3^{2-} with no (<0.2%) detectable anion capture.

Discussion

This work was undertaken to examine the relationship, if any, of the degree of ion-pairing (preassociation) between $[(NH_3)_5CoX]^{n+}$ and a competing nucleophile Y^{m-}, to the extent of anion capture in the base hydrolysis reaction.

If the base hydrolysis process is a concerted interchange process (I_d), as some believe,[3] then it can be shown that the amount of $[(NH_3)_5CoY]^{(n-m)+}$ produced must be correlated with the degree of ion association exhibited by its precursor (eq 3). Also, there should be a [Y] term (or terms) in the

$$(3)$$
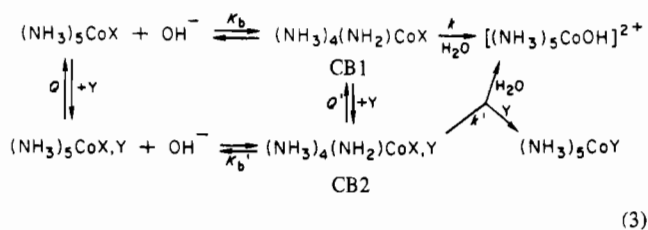
rate law. Alternatively, if a reactive reduced coordination number intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ is involved,[28,31] as the direct precursor of the competition products, then the degree of ion association exhibited by the substrate(s) is unrelated to the product distribution (eq 4).

There *may* be a term in the rate law in [Y], if preassociation is significant, but this is not a requirement. Moreover this [Y] dependence of the rate is independent of the [Y] dependence of the product distribution. Indeed, eq 4 requires the latter to follow the relationship $[(NH_3)_5CoY]/[(NH_3)_5CoOH^{2+}][Y]$ = constant (=R, the competition ratio), and to date this has always been observed.[2–4]

The above distinctions in mechanism represent different aspects of the conjugate base mechanism (S_N1CB) for base hydrolysis.[1,3,28,31] The identity of the reactive species, $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$, and its ion pair is not in dispute;

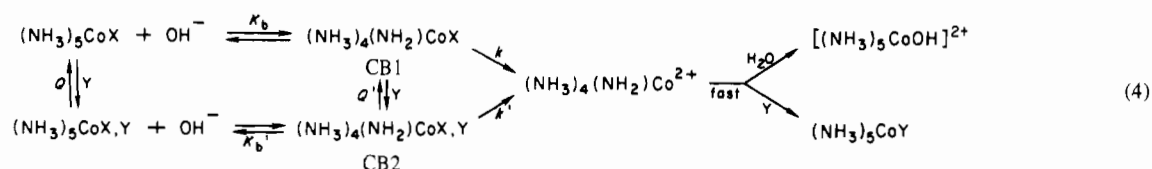(29) Helfferich, F. "Ion-Exchange"; McGraw-Hill: New York, 1962.
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Table VI. Mixed-Anion Competition Data for the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ (25 °C)

substrate	medium[a]	μ, M	% CoN_3^{2+} [b]	R [c]
$[(NH_3)_5CoOSMe_2]^{3+}$	N_3^- (1.0)/PO_4^{3-} (0.33)	3.1	12.7 (~0)	0.145
	N_3^- (1.5)/$S_2O_3^{2-}$ (0.5)		15.0 (4.8)	0.125
	N_3^- (3.0)		27.3	0.125
	N_3^- (1.5)/SO_4^{2-} (0.5)		15.5 (~2)	0.125
	N_3^- (1.0)/ClO_4^- (2.0)		11.8	0.134
	N_3^- (1.5)/ClO_4^- (1.5)		15.1	0.119
$[(NH_3)_5CoO_3SCH_3]^{2+}$	N_3^- (1.5)/$S_2O_3^{2-}$ (0.5)		11.9 (4.3)	0.095
	N_3^- (3.0)		22.9	0.099
	N_3^- (1.5)/ClO_4^- (1.5)		12.7	0.097
$[(NH_3)_5CoO_3SCF_3]^{2+}$	N_3^- (1.0)/ClO_4^- (3.0)	4.1	9.3	0.102
	N_3^- (1.0)/SO_4^{2-} (1.0)		9.3 (~4)	0.107
$[(NH_3)_5CoOSMe_2]^{3+}$	N_3^- (1.0)/ClO_4^- (3.0)		12.4	0.141
	N_3^- (1.0)/SO_4^{2-} (1.0)		12.3 (~4)	0.147

^{a} All Na$^+$ salts. Parenthesized numbers are molarities; [OH$^-$] = 0.1 M. ^{b} ±0.4%. Parenthesized numbers are the percentages for the minor competition product, $[(NH_3)_5CoOSO_3]^+$ or $[(NH_3)_5CoSSO_3]^+$. For $S_2O_3^{2-}$, sufficient time has been allowed for the initial O plus S isomer mixture to convert to the S-bonded form.[7] ^{c} $R = [[CoN_3]^{2+}]/[[CoOH]^{2+}][N_3^-]$; generally ±0.005 (M^{-1}).

$$(NH_3)_5CoX + OH^- \overset{K_b}{\rightleftharpoons} (NH_3)_4(NH_2)CoX \overset{k}{\searrow} \quad (NH_3)_4(NH_2)Co^{2+} \overset{H_2O}{\underset{fast}{\longrightarrow}} \begin{matrix} [(NH_3)_5CoOH]^{2+} \\ \\ (NH_3)_5CoY \end{matrix} \tag{4}$$

CB1

$(NH_3)_5CoX,Y + OH^- \overset{K_b'}{\rightleftharpoons} (NH_3)_4(NH_2)CoX,Y$

CB2

there is overwhelming evidence for a rapid preequilibrium conjugate base formation, giving rise to the [OH$^-$] term in the rate law for the pentaammine complexes.[1,4,28,31,32]

It becomes necessary to consider ion pairing of the conjugate base (CB1, eq 3 and 4) rather than $[(NH_3)_5CoX]^{n+}$, if a decision is to be made about the origin of the $[(NH_3)_5CoY]^{(n-m)+}$ product. For the interchange mechanism the species CB2 (eq 3) is required, whereas for the alternative limiting dissociative process (eq 4), the CB1/CB2 distribution is irrelevant because there it collapses to a common intermediate $[(NH_3)_4(NH_2)Co]^{2+}$.

We have previously[2] argued that the CB2 population of the ion-pair CB1/CB2 equilibrium (eq 3 and 4) was too small, and its reactivity relative to CB1 insufficient, to accommodate the quite significant amounts of $[(NH_3)_5CoY]^{(n-m)+}$ formed, under conditions where ion pairing was apparently weak. This supported the case for the limiting S_N1CB mechanism. It occurred to us that this case could be strengthened by using multivalent ions Y^{m-}, where the effects of ion association on the rate and production distribution were clearly manifest. There have been reports of the effects of ion pairing on base hydrolysis.[33] The multivalent anions SO_4^{2-}, $NaP_3O_9^{2-}$, and $P_3O_9^{3-}$ were shown to profoundly reduce the rate of base hydrolysis of $[(NH_3)_5CoCl]^{2+}$. This study was conducted at low ionic strength (≤0.1 M), where intrinsically ion pairing is greatest. Also, the prospect of anion competition was not considered. Usually higher ionic strengths are required for significant (measurable) anion competition, but at the expense of the extent of ion pairing. Since there is a dearth of reliable ion-pair constant data at 1–3 M, we undertook to measure these for model 2+ and 3+ $[(NH_3)_5CoX]^{n+}$ ions (X = NCS$^-$, NH$_3$), for each of the multivalent ions SO_4^{2-}, CO_3^{2-}, and PO_4^{3-}, and determined the anion concentration dependence of the rates of base hydrolysis and product distributions. These data suffice to answer the key question as to the precise origin of the $[(NH_3)_5CoY]^{(n-m)+}$ competition product.

Ion-Pair Constants. In solution, and especially at high ionic strengths, distribution functions describing the average number of anions surrounding a cation and their average distances of separation may be an appropriate description of anion–cation interactions. Nonetheless, for a cation–anion association of a

considerable degree, we argue ahead that it is reasonable to describe this phenomenon in terms of a simple ion-pair equilibrium, e.g.

$$(NH_3)_5CoX^{n+} + Y^{m-} \overset{Q}{\rightleftharpoons} (NH_3)_5CoX^{n+},Y^{m-} \tag{5}$$
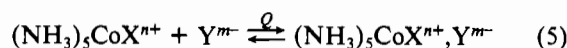
It is recognized that the ion-pair $[(NH_3)_5CoX]^{n+},Y^{m-}$ may comprise several kinds, e.g., direct-contact $[(NH_3)_5CoX]^{n+},Y^{m-}$ and solvent-separated $[(NH_3)_5CoX]^{n+},H_2O,Y^{m-}$ ion pairs. Also, it has been noted that the various techniques adapted to monitor the association indicate only the stoichiometry of the ion-associated species.[22] A priori, the technique cannot distinguish the different types of 1:1 adduct between a cation and Y^{m-}. The measured ion-pair constant is the sum of the individual constants for all ion pairs of the same (1:1) stoichiometry. Perhaps the test of the idea of discrete 1:1 ion pairs in solution, free from overlapping equilibria involving higher aggregates, is the [Y] dependence of the association phenomenon. To test this proposition would seem to require a minimum value for $Q \geq 0.5$, such that ion association over the practical [Y] range can be monitored up to at least 50% ion pairing, in order to be clear on the [Y] dependence. We take strict adherence to

$$Q = [(NH_3)_5CoX^{n+},Y^{m-}]/[(NH_3)_5CoX^{n+}][Y] \tag{6}$$

as indicative of discrete ion-pair formation, i.e. of the direct-contact kind, and perhaps including ion pairs of the one-solvent-layer-separated kind. Clearly there is a gray area, contingent upon how strictly the data conform to eq 6, and the general reliability of solution Q values has been discussed.[34] In the limit $Q \ll 1$, the ion-pair concept collapses to the view of the anion–cation atmosphere distributions in the Debye–Hückel sense. We view apparent Q values much less than 0.5 as difficult to reconcile with discrete close-contact ion pairs of the type recognized for the gas phase and note that this limit $Q \leq 0.5$ is, to some degree, arbitrary.

The ion-pair constant data are given in Table I. It is clear that Q values of >0.5 are involved, and hence it is believed these are real. Within experimental error, the spectrophotometric data follow the [Y] dependence required by eq 6 for a discrete ion-pair equilibrium, and that we interpret to be of the direct-contact type and including perhaps the solvent-

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separated 1:1 ion-pair kind. There appears to be no overlap from secondary ion association, i.e. ion–triplet formation. At the relatively high ionic strengths involved (1 and 3 M), little can be gained from reconciling the data with ion-pair models[35-37] appropriate only to low ionic strength. Nonetheless, in qualitative accord with such models, the results show that (i) Q values are greatest for 3+/3−, 3+/2−, 2+/3−, and 2+/2− interactions, as expected; (ii) the ion-pair constants for 3+/2− associations are similar to those for the conjugate 2+/3− interactions; (iii) Q values, at constant ionic strength, are essentially independent of the *nature* of the anion (CO_3^{2-} or SO_4^{2-}); and (iv) Q values decrease somewhat ($\sim$2- to 3-fold) with an increase in ionic strength (from 1 to 3 M). Note that this decrease is relatively small compared with those that occur at very low ionic strengths,[18] small changes in which that involve at least 1 order of magnitude for Q. The new as well as selected literature data (Table I) testify to all these points.

There is an additional consideration apparent from the literature but not our data. The ion-pair constant is somewhat complex cation dependent. For the ions we are dealing with, the effect spans a factor of ca. 2. This is not an unexpected observation, and it is consistent with the widely held view that there are preferred sites for ion pairing in unsymmetrical cations. A corresponding anion dependence for Q probably does not show up presumably because all involve terminal $O^{\delta-}$–cation interactions.

The use of 2+ and 3+ cations and 2− and 3− anions, despite the high ionic strength (1–3 M), ensured that a significant proportion (up to $\sim$70%) of the $[(NH_3)_5CoX]^{n+}$ complexes were ion paired at the highest [Y] employed (1 M) in the kinetic and anion competition studies. Note that the complexes used in the ion-pair study, for practical reasons, were not identical with those used for the other work, and the results (Table I) indicate that up to a 2-fold variation in Q with varying cation, apart from its charge n, is a possibility that needs to be borne in mind.

Effect of Ion Association on the Rates of Base Hydrolysis. The rate of base hydrolysis of $[(NH_3)_5CoX]^{2+}$ (X = Cl−, I−, SCN−) was shown, in a previous study, to be insensitive to the nature of Y− (ClO_4^-, N_3^-, NO_2^-, NCS−) in the 1 M NaY medium, implying negligible ion association between $[(NH_3)_5CoX]^{2+}$ and Y−.[25] We have extended this work, for the base hydrolysis of $[(NH_3)_5CoCl]^{2+}$, to include ClO_4^-, $CH_3CO_2^-$, NO_2^-, NO_3^-, $NH_2SO_3^-$, NCS−, and N_3^- (Table III). The value for k_{OH}(obsd) is clearly independent of Y; k_{OH} = 0.21 ± 0.02 M^{-1} s^{-1} (μ = 1.1 M, 25 °C) describes the entire data set. The anion competition[4-6,8] varies widely for these conditions (0–18% $[(NH_3)_5CoY]^{2+}$), and it must be concluded that the aniono product does not arise specifically from an ion pair, unless it has a reactivity identical with that of the free ion.

Rate studies using multivalent Y^{m-} shed light on this proviso. These results, coupled with parallel competition and ion-pair measurements, enable some firm conclusions regarding detailed mechanism. In Table IV rate constants for base hydrolysis are recorded for $[(NH_3)_5CoX]^{n+}$ (n = 1–3) in Y^{2-} (SO_4^{2-}, CO_3^{2-}, $S_2O_3^{2-}$) and Y^{3-} (PO_4^{3-}) media, μ = 3.1 M, conditions ranging from moderate to strongly ion pairing. Also given are data for Y− media (ClO_4^-, NCS−, N_3^-), μ = 1.1 and 3.1 M, for both a 2+ and 3+ complex. It is necessary to consider the full reaction scheme (eq 3 and 4), which accommodates ion pairing of both $[(NH_3)_5CoX]^{n+}$ and its conjugate base $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$, in order to derive the rate depen-

dence on [Y].[38] The usual steady-state assumption for the conjugate base and its ion pair leads to the rate law

$$\frac{-d[CoX]}{dt} = \left[\frac{k_{OH} + k_{OH}'Q[Y]}{1 + Q[Y]} \right] [CoX][OH^-]$$

$$= k_{OH}(obsd)[CoX][OH^-] \qquad (7)$$

where k_{OH} ($=kK_b$) is the usual[28,31] second-order rate constant for base hydrolysis for the free ion $[(NH_3)_5CoX]^{n+}$ and k_{OH}' ($=k'K_b'$) is the corresponding constant for the ion pair $[(NH_3)_5CoX]^{n+},Y^{m-}$.

Several important facts emerge from a consideration of eq 7. First, ion pairing is predicted to have no effect on the first-order [OH−] rate dependence, as observed (see Experimental Section). Second, the dependence of k_{OH}(obsd) on [Y] should be detectable if $Q[Y] \geq 0.2$, provided $k_{OH} \neq k_{OH}'$. Third, the curvature of the hyperbolic k_{OH}(obsd) vs. [Y] plot is controlled by Q alone, i.e. by the magnitude of ion pairing of $[(NH_3)_5CoX]^{n+}$, and not that of the reactive conjugate base species. Fourth, the rate should decrease with [Y] if $k_{OH}' < k_{OH}$ (and vice versa). Fifth, the magnitude of this decrease (or increase) is controlled by k_{OH}'/k_{OH} since, for [Y] = 0, k_{OH}(obsd) = k_{OH} and, for large $Q[Y]$, k_{OH}(obsd) = k_{OH}'. Finally, the relative magnitudes of k_{OH} and k_{OH}' are controlled both by the acidity constants and reactivities of the conjugate base forms as we will now show.

We were interested not only in demonstrating the applicability of eq 7 to conditions of strong ion pairing but also especially in evaluating k'/k, which, according to the I_d mechanism (eq 3), also controls the product distribution.

It can be readily shown that

$$k_{OH}'/k_{OH} = (k'/k)(K_b'/K_b) \qquad (8)$$

Thus, if k_{OH}'/k_{OH} could be obtained from the rate data, we could evaluate k'/k provided K_b'/K_b were known or could be measured. Although neither K_b nor K_b' is separately measurable (pK_a > 15),[28] the relationship (9) exists for the cyclic

$$K_b'/K_b = Q'/Q \qquad (9)$$

system of rapid preequilibria shown in eq 3 and 4. Thus, the relative acidities of $[(NH_3)_5CoX]^{n+}$ and its ion pair are directly related to their ion-pair constants, and this information we have (Table I). The ratio of ion-pair constants for 2+/2− and 3+/2− associations, at μ = 1.1 or 3.0 M, is close to 0.25, i.e. $Q':Q$ = 1:4; hence, $K_b \simeq 4K_b'$ (eq 9). This result is consistent with the expectation that $[(NH_3)_5CoX]^{3+}$ should be more acidic than its formally 1+ ion pair $[(NH_3)_5CoX]^{3+},Y^{2-}$. This was noted previously[33,39] but not quantified. While we do not have ion-pair constant data for 1+/2− or 1+/3− systems, clearly they will be less than the corresponding 2+/2− and 2+/3− constants and, hence, $K_b' < K_b$ (probably $\sim$1:4 also). This effect alone implies a rate reduction with increased ion-pairing (eq (8)).

We consider now the observed dependence of k_{OH}(obsd) on Y^{m-} (Table IV). The rate data for the multivalent ions reveal a marked reduction, compared to ClO_4^- media at the same ionic strength (3 M). This reduction is greater for the 3+/2− (6- to 8-fold) than for the 2+/2− systems (2- to 4-fold). Also the effects are independent of the nature of the anion. These

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(38) Note that it is not necessary to know if a *direct* rapid equilibrium exists between the conjugate base free ion CB1 and its ion-pair CB2, although for such six-coordinate species this seems very likely (calculated specific rates of hydrolysis are $\sim$10$^{4-6}$-fold less than those for outer-sphere complex formation). Effective equilibration between CB1 and CB2 is of course achieved in this cyclic system of equilibria via the alternative path (eq 3 and 4).

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results are all consistent with eq 7, where $k_{OH}' < k_{OH}$ and ion pairing is the dominant effect.

It is noted that PO_4^{3-} at 0.5 M leads to about the same rate reduction as Y^{2-} at 1.0 M ($\mu = 3$ M). Again, this is an expectation based on the measured ion-pair constants (Table I); i.e., $[(NH_3)_5CoCl]^{2+}$ is ion paired by 0.5 M PO_4^{3-} and 1.0 M SO_4^{2-} to similar extents ($\sim 30\%$).

Some evidence for ion pairing is provided by the rate data for even the 1– anions (N_3^-, NCS^-), at the 3 M level (Table IV). For $[(NH_3)_5CoOSMe_2]^{3+}$, the base hydrolysis rate in the presence of NCS^- is approximately 70% of the ClO_4^- value, while in N_3^- media the rate reduction is even greater (~ 3-fold). This same trend (k_{OH}(obsd): $ClO_4^- > NCS^- > N_3^-$) is apparent for the 2+ cation $[(NH_3)_5CoONO_2]^{2+}$, but, as expected, it is not so marked. For the 3+ cation, the effect is observed even at $\mu = 1$ M (Table IV), less so than at $\mu = 3$ M, while for the 2+ ion at $\mu = 1$ M (Table III) the effect disappears. All these results are accommodated by weak to moderate ion pairing, 3+ > 2+ and $N_3^- > NCS^- \geq ClO_4^-$, and where the ion pair is less reactive than the free ion.

Implicit in the above rationale is that k'/k (eq 8) is independent of the nature of the electrolyte and that k_{OH}'/k_{OH} is also independent, i.e. the constant ionic strength principle[40] holds. At least for k'/k, this assumption is likely to be valid. Both these constants refer to *aquation* (eq 3 and 4), and reactions between a neutral and a charged species are predicted to be not only independent of the nature of the (aqueous) medium but also independent of ionic strength itself; both are usually observed.[26]

It remains to evaluate k_{OH}'/k_{OH} since this quantity yields k'/k (eq 8). Equation 7 can be restated as

$$k_{OH}(\text{obsd}) = (1 - f)k_{OH} + fk_{OH}' \qquad (10)$$

where f, the fraction of $[(NH_3)_5CoX]^{n+}$ ion paired, equals $Q[Y]/(1 + Q[Y])$. For the 3+ complex in Y^{2-} media, k_{OH}(obsd)$/k_{OH} \simeq 1/7$ (Table IV). From the measured 3+/2– Q (2.0, Table I), $f \simeq 0.7$, leading (eq 10) to the conclusion that $k_{OH}' \sim 0$ (i.e., $k_{OH} \gg k_{OH}'$). The 2+/2– and 2+/3– rate (Table IV) and ion-pair constant data (Table I) lead to a similar conclusion.

In the above calculations, k_{OH} has been taken as k_{OH}(obsd) for ClO_4^- media where ion pairing is assumed negligible. When the details of the calculations are examined, it is apparent that k_{OH}' is actually negative rather than zero (especially for $[(NH_3)_5CoONO_2]^{2+}$ and $[(NH_3)_5CoOSMe_2]^{3+}$ in Y^{2-}). Indeed, if ClO_4^- ion pairing is accommodated, k_{OH}' is even lower. Clearly, a negative rate constant is impossible; hence, either there is a rate reduction additional to the effect of ion-pairing, a difficulty expanded upon below, or the ion-pair constants for the complexes used in the kinetic work are up to 2-fold greater than those for the models (Table I). This latter possibility was noted earlier.

While it seems that $k_{OH}' \ll k_{OH}$, other results indicate that this specific rate difference is not as great as the above results suggest. The specific rates for the 2+ and 3+ cations measured in 3 M N_3^- media, for example, imply ion-pair constants of ~ 0.3 and 0.7 M^{-1}, respectively (from eq 10 and on the assumption that $k_{OH}' = 0$; the calculated ion-pair constants become larger if $k_{OH}' > 0$). Although the relative magnitudes are reasonable, the absolute values seem too large for 2+/1– and 3+/1– associations at $\mu = 3$ M. Furthermore, if the 2+/1– ion-pair constant were correct, then Q should be ~ 0.6 M^{-1} at $\mu = 1$ M (allowing for the demonstrated 2-fold increase on going from $\mu = 3$ to $\mu = 1$ M; Table I). Thus, $[(NH_3)_5CoCl]^{2+}$ in 1 M N_3^- (at $\mu = 1$ M) is calculated to be $\sim 38\%$ ion paired; yet a rate reduction is not observed (Table III). These results suggest that the 3 M data involve, in addition to ion pairing, rate variations with Y attributable to a breakdown in the constant ionic strength principle.[40] The

rates appear to be inherently less in N_3^- and NCS^- compared to ClO_4^- media. While it is not unreasonable to expect some dependence of the mean ionic activity coefficients on the nature of Y (at nominally constant μ), especially when >1 M, we know of no theoretical framework to accommodate the magnitude and sense of the Y dependence. Empirical corrections, admittedly rough, can be made. At $\mu = 3$ M, the rates in N_3^- media need to be inherently 1.5- to 2-fold less than in ClO_4^- to give reasonable Q values. For $Y^{m-} = SO_4^{2-}$, a similar factor is involved, deduced as follows. The effect of ionic strength on rate indicates a value of k_{OH} for $[(NH_3)_5CoOSO_3]^+$ of about $0.7k_{OH}$ ($\mu = 1$ M) = 0.028 M^{-1} s^{-1} in ClO_4^- at $\mu = 3$ M. The value observed for $Y^{m-} = SO_4^{2-}$ at $\mu = 3$ M (0.015 M^{-1} s^{-1}, Table IV) is about half this and cannot reasonably be attributed to the effect of ion pairing. The 1+/2– association constant must be of the order of ≤ 0.1 M^{-1} at $\mu = 3$ M, similar to a conjugate 2+/1– association and essentially negligible (refer to Table III; 2+/1– associations showing the miniscule effect on rate).

The above complication does not alter the general picture $k_{OH}' < k_{OH}$, since ion pairing has the more profound effect. If we use the upper estimate of 2 for the factor attributable to the inherent rate reduction for Y^{m-} ($m = 2, 3$) and N_3^- media, as opposed to ClO_4^-, the conclusion reached is $k_{OH}' \sim (0.1-0.2)k_{OH}$. For the base hydrolysis of $[(NH_3)_5CoONO_2]^{2+}$ in 3 M ClO_4^- and 1 M SO_4^{2-}, for example, the observation k_{OH}(obsd) $\simeq 0.26k_{OH}$ (Table IV) is corrected to k_{OH}(obsd) = $0.52k_{OH}$. With the upper limit $Q = 1.0$ (=$2Q$ for 2+/2–; Table I), the result $k_{OH}' = 0.06k_{OH}$ follows from eq 10. A similar calculation for the 3+ complex/Y^{2-} system yields $k_{OH}' = 0.1k_{OH}$. The other 2+ cations yield a somewhat higher ratio, but in general the k_{OH}'/k_{OH} ratio is in the range 0.1–0.6, given the limits of Q chosen above.

It is calculated from eq 8, knowing reasonable limits for K_b'/K_b and k_{OH}'/k_{OH}, that $k' = (0.5 - 2.0)k$. Thus, the conjugate base free ion and ion pair have similar reactivities, within a factor of 2. Overall our results suggest that the ion pair is slightly less reactive. The essential validity of this analysis is supported by the results of a previous study.[33] At low ionic strength, where the problems we encountered did not arise, the base hydrolysis of $[(NH_3)_5CoCl]^{2+}$ is reduced in Y^{m-} (SO_4^{2-}, $NaP_3O_9^{2-}$, $P_3O_9^{3-}$) media, as we find, and the analysis leads to the conclusion $k' \simeq 2k$. It was important that we establish k'/k at the higher ionic strengths, to adequately interpret the anion competition results for identical conditions, since there was no precedent to suggest the ionic strength independence of this result. We note, however, confirmation of the prediction that k'/k is not especially sensitive to ionic strength.

It is concluded that ion pairing reduces the rate of base hydrolysis significantly, and most of the rate reduction rests with the diminished acidity constant for the $[(NH_3)_5CoX]^{n+},Y^{m-}$ ion pair. The free ion and ion-paired conjugate bases, the reactive entities in base hydrolysis, decay at similar rates. These conditions are consistent with the S_N1CB mechanism.

Anion Competition. The striking collective results for the multivalent ions SO_4^{2-}, $S_2O_3^{2-}$, CO_3^{2-}, and PO_4^{3-} for the capture of oxygen demonstrate how poorly nucleophilic the O-center is. Their capture may be compared with that for

(40) This principle asserts that the ionic activity coefficients of an electrolyte in low but variable concentration are controlled largely by the "swamping" or "inert" electrolyte, in much higher concentration. Provided the latter is not too great, the activity coefficients are also independent of the *nature* of the ions comprising the swamping electrolyte. The breakdown we refer to is this—the activity coefficients appear to become appreciably dependent upon the nature of the anionic component of the supporting electrolyte (the cationic component, Na^+, is constant).

$CH_3CO_2^-$, I^-, Br^-, Cl^-, F^-, OH^-, N_3^-, NO_2^- (O- and N-capture), and SCN^- (S- and N-capture), which ranges from 0 to 19% $[(NH_3)_5CoY]^{2+}$ product in 1 M Y^-.[2-6,8] There is no justification for the suggestion that the anions that ion pair best (CO_3^{2-}, SO_4^{2-}, PO_4^{3-}) are the poorest competitors. The $S_2O_3^{2-}$ ion (>10% total S- and O-capture; Table V) is a good competitor while for the more weakly ion-pairing Y^- anions, OH^-, F^-, NCS^-, and N_3^- for example, the competition results (0–18%) span those found for the Y^{m-} ($m = 2, 3$) ions. Clearly, there is no obvious correlation with ion pairing, a fact strongly militating against the interchange (I_d) base hydrolysis mechanism (eq 3). The kinetic analysis below confirms this.

The poor competition exhibited by the Y^{m-} ions is accommodated by the solvation argument advanced previously.[2,4-7,28] Like F^-, OH^-, and NH_3,[6] each of which is strongly H-bonded to water, the medium to strong bases SO_4^{2-}, PO_4^{3-}, and CO_3^{2-} are undoubtedly also strongly H-bonded in water. Weak competition in the order OH^-, F^-, $CO_3^{2-} \ll PO_4^{3-} < SO_4^{2-}$ is consistent with the idea that the major energy requirement for the rate-determining step, for decay of the very reactive $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate to products (eq 4), is abstraction of the anion from the solvation sheath.

In the previous section it was concluded that the free-ion and ion-paired conjugate base were of comparable reactivity ($k' = (0.5–2.0)k$). For the $[(NH_3)_5CoOSMe_2]^{3+}$ ion in 1.0 M CO_3^{2-} for example, base hydrolysis must proceed via $[(NH_3)_4(NH_2)CoOSMe_2]^{2+}$ (50–80%) and $[(NH_3)_4(NH_2)CoOSMe_2]^{2+},CO_3^{2-}$ (20–50%), by using $Q = 0.5$ for a 2+ complex with CO_3^{2-}, $\mu = 3.0$ M (Table I), and the relationship

$$\% \text{ reaction via ion pair} = 10^2 k'Q[Y]/(k + k'Q[Y]) \quad (11)$$
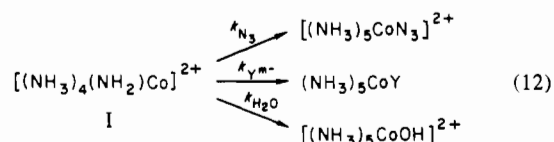
Since no CO_3^{2-} capture is observed, it is clear that collapse of the ion pair to anated product must be inefficient (irrespective of the actual mechanism of the collapse, (eq 3 or 4)). A similar conclusion may be drawn for the reactions of the 2+ cations in CO_3^{2-}, the 2+ and 3+ cations in 0.5 M PO_4^{3-}, and the 3+ ion in 1.0 M SO_4^{2-}. It seems likely that the 2+ complexes, involving a 1+ conjugate base, react via the free ion more so than the ion pair, and since in 1 M SO_4^{2-} ~5% sulfato complex is formed, here the collapse of the ion pair could accommodate the amount of sulfato product. Calculation from eq 12 requires a high efficiency of collapse, if the ion pair is the sole source of the anated product, contrasting sharply with the other results. The degree of ion pairing and efficiency of collapse appear to be irrelevant to product development in the mechanism of base hydrolysis. The data for the base hydrolysis of $[(NH_3)_5CoCl]^{2+}$ and $[(NH_3)_5CoOSMe_2]^{3+}$ in 1.0 M SO_4^{2-} testify to this view. The chloro complex must lead to an ion-paired conjugate base that is about 4-fold less abundant than the analogous Me_2SO complex. Given the fact that $k' \sim k$ in each case, SO_4^{2-} competition should be ~4-fold less. Yet it is essentially the same. It seems unreasonable to argue that the chloro–conjugate base ion pair involves the compensation of more efficient collapse, coincidentally 4-fold better, or that k'/k differ by the same factor.

An equally if not more pursuasive argument is provided by the converse and more usual situation in base hydrolysis—extensive anion competition ($Y^- = NCS^-$, N_3^-) under conditions of insignificant ion pairing. The reaction of $[(NH_3)_5CoOSO_3]^+$ in 1.0 M N_3^- is a good case in point.[2] It involves the neutral conjugate base $(NH_3)_4(NH_2)CoOSO_3$, which must ion pair negligibly; yet N_3^- capture (5.8%) is observed. The base hydrolysis of $[(NH_3)_5CoONO_2]^{2+}$ in 3 M NCS^-, yielding over 30% NCS^- complex, is an even clearer case.[41] The product-determining conjugate base involves a 1+/1- ion-pair equilibrium, and certainly less than 10% of

the conjugate base can exist in the ion-pair form at $[NCS^-] \leq 3$ M. If $[(NH_3)_5Co(SCN)]^{2+}$ arises directly from $[(NH_3)_4(NH_2)CoONO_2]^+,NCS^-$, then this ion pair has to be at least three times as reactive as the free ion and collapse efficiently. Both requirements are contrary to the general trends observed in this work. Moreover, the rate of base hydrolysis would be expected to increase with increasing $[NCS^-]$ (eq 7), whereas in fact it decreases (Table IV).

The inference from all this rationale is that anion capture can arise without prior ion pairing, i.e. the free ion $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$ (eq 3 and 4) can lead to anion capture. But this cannot occur in a single step, since Y^{m-} is not contained in the reactant and therefore cannot be contained in the transition state. As previously,[2] we view the anion-capture process occurring via the reactive reduced coordination number $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate, arising from rate-determining dissociation of X (eq 4).

A further and crucial test for the continued view that base hydrolysis is a limiting dissociative reaction is provided by mixed-anion competition studies. As will be seen, the choice of SO_4^{2-}/N_3^- or PO_4^{3-}/N_3^- is especially convenient—one component strongly ion pairs but poorly competes, the other is the direct converse. Also the problem of the possible involvement of ClO_4^-, the usual anionic component of the supporting electrolyte, is avoided. Capture of the "innocent" ClO_4^- ion has been observed in other reactions.[42] Competition data are presented (Table VI) for the base hydrolysis of 2+ and 3+ complexes in N_3^-/SO_4^{2-}, $N_3^-/S_2O_3^{2-}$, and N_3^-/PO_4^{3-} media. The replacement of N_3^- by ClO_4^-, SO_4^{2-}, $S_2O_3^{2-}$, or PO_4^{3-}, at constant ionic strength, has no detectable effect on the competition ratio for N_3^-. This result is interpreted as highlighting the irrelevance of ion association to the product-determining step in the base hydrolysis reaction. Given the known magnitudes of the relevant ion-pair constants, the more strongly ion-pairing SO_4^{2-}, $S_2O_3^{2-}$, or PO_4^{3-} anions would be expected to reduce N_3^- capture by preferential ion pairing with the conjugate base complex, if this were the direct route to the competition product. The results are undoubtedly more consistent with the product-determining parallel reactions

$$[(NH_3)_4(NH_2)Co]^{2+} \quad \xrightarrow[\substack{k_{N_3} \\ k_{Y^{m-}} \\ k_{H_2O}}]{} \quad \begin{matrix} [(NH_3)_5CoN_3]^{2+} \\ (NH_3)_5CoY \\ [(NH_3)_5CoOH]^{2+} \end{matrix} \quad (12)$$
$$\text{I}$$

Thus, the replacement of N_3^- by another anion, at constant μ, whether it competes or not or whether it strongly ion associates or not has no effect on the N_3^- competition ratio, measured as $R = k_{N_3}[I][N_3^-]/k_{OH_2}[I][OH_2] = (\text{constant})[N_3^-]$.

The interchange mechanism (eq 3) can accommodate the linear dependence of the ratio of competition products on $[N_3^-]$ under special circumstances. It can be shown that the ratios $[(NH_3)_5CoY]/[[(NH_3)_5CoOH_2]^{3+}][Y]$ and $[[(NH_3)_5CoN_3]^{2+}]/[[(NH_3)_5CoOH_2]^{3+}][N_3^-]$ are mutually independent of the ion-pair constants for N_3^- and Y^{m-} associated with $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$, provided *both* ion pairs are efficient with respect to anion capture. However, we have clearly demonstrated the inefficiency of SO_4^{2-} (and PO_4^{3-}) capture from the respective ion pairs and therefore reject this apparent alternative.

In conclusion, anion competition in the base hydrolysis reaction of $[(NH_3)_5CoX]^{n+}$ cannot be reconciled as arising

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directly from preformed ion pairs. However, the previous view[2] of a common five-coordinate intermediate $[(NH_3)_4(NH_2)\text{-}Co]^{2+}$ accommodates the new and more discriminating data reported herein. It needs reemphasis that this intermediate is short-lived to the extent that it does not survive to completely equilibrate with the bulk solution. The small but consistent dependence on leaving group indicates Y^{m-} capture from an inherited ion atmosphere.[2,5–8] The mixed-anion competition experiments suggest that the presence of multicharged ions such as CO_3^{2-} or PO_4^{3-} do not exclude N_3^- from this atmosphere. This difficulty may be overcome if the five-coordinate intermediate is considered to be in free-ion and ion-pair forms where anion capture from the "ion pair" is highly efficient. Support for this view will be presented in a subsequent publication.

Contribution from the Department of Chemistry,
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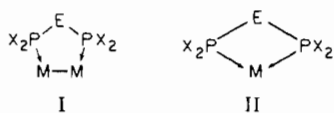# Poly(tertiary phosphines and arsines). 21. Metal Carbonyl Complexes of Bis(dimethylphosphino)methane[1,2]

R. B. KING* and K. S. RAGHUVEER

This paper reports a variety of metal carbonyl complexes of the highly basic small-bite bidentate bis(tertiary phosphine) $(CH_3)_2PCH_2P(CH_3)_2$ (abbreviated as dmpm). Thus, displacement of the coordinated norbornadiene in $C_7H_8M(CO)_4$ (M = Cr, Mo, W) with dmpm gives the corresponding pale yellow mononuclear chelates $(dmpm)M(CO)_4$. Similarly, displacement of the coordinated cycloheptatriene in $C_7H_8M(CO)_3$ (M = Cr, Mo, W) with dmpm gives the corresponding yellow binuclear complexes *fac*-$(dmpm)_3M_2(CO)_6$ shown by their NMR spectra to contain one bridging and two chelating dmpm ligands. The chromium complex *fac*-$(dmpm)_3Cr_2(CO)_6$ is unstable in solution, being converted ultimately to yellow *mer*-$(dmpm)_2Cr(CO)_3$ in which one of the dmpm ligands is monodentate with an uncomplexed $P(CH_3)_2$ unit. The phosphorus-31 NMR spectrum of *mer*-$(dmpm)_2Cr(CO)_3$ is compared with that of *fac*-$(dmpm)_2W(CO)_3$, one of the products obtained by the photolysis of $W(CO)_6$ with dmpm. The acetonitrile complexes *fac*-$(CH_3CN)_3M(CO)_3$ (M = Mo, W) react with dmpm in boiling acetonitrile to give *fac*-$(dmpm)_3M(CO)_3$ containing three monodentate dmpm ligands. Thermal reactions of $M_2(CO)_{10}$ (M = Mn, Re) with dmpm under various conditions give binuclear complexes of the type $(dmpm)_nM_2(CO)_{10-2n}$ (M = Mn, $n = 1$ and 2; M = Re, $n = 2$) containing five-membered bimetallic chelate rings. The orange to red binuclear iron carbonyl complexes $(dmpm)_nFe_2(CO)_{9-2n}$ are obtained from the reaction of dmpm with $Fe_2(CO)_9$ at room temperature ($n = 1$) and by the photolysis of dmpm with $Fe(CO)_5$ ($n = 2$). Reactions of dmpm with the cyclopentadienyl metal carbonyls $C_5H_5Mn(CO)_3$ and $[C_5H_5Fe(CO)_2]_2$ give yellow pyrophoric $(dmpm)Mn(CO)(C_5H_5)$ and green $(dmpm)Fe_2(CO)_2(C_5H_5)_2$, respectively. The nickel carbonyls $Ni(CO)_4$ and $[C_5H_5NiCO]_2$ react with dmpm to give white air-sensitive $(dmpm)Ni(CO)_2$ and yellow relatively air-stable $(dmpm)_3Ni_2(CO)_2$.

Introduction

Small-bite bidentate trivalent phosphorus ligands are of interest because of the possibility of stabilizing binuclear transition-metal complexes through the formation of five-membered chelate rings (I) as well as mononuclear transi-

tion-metal complexes through the formation of four-membered chelate rings (II). Previous work from this laboratory has involved the study of metal carbonyl complexes of the small-bite bidentate ligands $CH_3N(PX_2)_2$ (X = F[3], OCH_3[4])

in which the two donor phosphorus atoms are bridged by a single nitrogen atom. This paper reports a survey of the metal carbonyl coordination chemistry of the small-bite bis(tertiary phosphine) $(CH_3)_2PCH_2P(CH_3)_2$ (abbreviated as dmpm) in which each phosphorus atom is bonded only to carbon atoms. This ligand, which is the simplest possible bis(tertiary phosphine), is also of interest in being highly basic and sterically undemanding and frequently exhibits well-defined proton CH_2 and CH_3 NMR resonances in its metal carbonyl complexes. Also the volatilities of mononuclear metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ are generally sufficient for purification by vacuum sublimation and observation of their mass spectra.

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microanalytical Laboratory, Atlanta, GA, and Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting and decomposition points (Table I) were determined in capillaries and are uncorrected. Infrared spectra (Table II) were taken in the $\nu(CO)$ region in the indicated solvents and recorded on a Perkin-Elmer Model 297 spectrometer. Proton NMR spectra (Table III) were recorded on a Varian EM-390 spectrometer operating at a nominal frequency of 90 MHz. Chemical

(1) Part 20: Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W.; Kim, J. H. *Inorg. Chem.* **1982,** *21,* 3790.
(2) Presented in part at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983; see Abstracts, No. INOR 35.
(3) King, R. B. *Acc. Chem. Res.* **1980,** *13,* 243.
(4) Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W. *Inorg. Chem.* **1982,** *21,* 2139.