contains XeF_2^- but not XeO_2^- or XeO_2F^-. These observations are consistent with the greater electronegativity of fluorine.

If the spectra of oxide fluoride molecules containing a certain number of fluorine atoms are compared, it can be seen that an increase in the number of oxygen atoms tends to increase the number of oxygen-containing fragments and their intensities relative to fragments containing only xenon and fluorine. This can be seen from the spectra of XeO_4 and XeO_2F_4.

Pictures of the negative-ion spectra of xenon oxide tetrafluoride[19] and xenon dioxide difluoride[3] have previously been published.

Base Hydrolysis of Pentaamminecobalt(III) Complexes of Urea, Dimethyl Sulfoxide, and Trimethyl Phosphate

NICHOLAS E. DIXON,[1a] W. GREGORY JACKSON,[1b] WERNER MARTY,[1a] and ALAN M. SARGESON*[1a]

The base hydrolysis of the $[(NH_3)_5CoL]^{3+}$ ions (where L is $(NH_2)_2C{=}O$, $(CH_3)_2S{=}O$, and $(CH_3O)_3P{=}O$) and the $[(NH_3)_5CoOSO_3]^+$ ion has been studied over a range of conditions. Trace studies (with $^{18}OH_2$) show that the three 3+ ions cleave very largely (>97%) by Co–O bond rupture with rate laws of the form $-d[(NH_3)_5CoL^{3+}]/dt = k[(NH_3)_5CoL^{3+}][OH^-]$. In the presence of azide ion, both $[(NH_3)_5CoOH]^{2+}$ and $[(NH_3)_5CoN_3]^{2+}$ are produced. The ratio of these products is constant among the 3+ substrates but differs from that observed with the $[(NH_3)_5CoOSO_3]^+$ ion and with complexes of the type $[(NH_3)_5CoX]^{2+}$, where X includes a variety of anions. The results support the conjugate base dissociative (S_N1cB) mechanism where the short-lived intermediate five-coordinate species captures the atmosphere of its immediate precursor. Some results obtained with the neutral competitor methanol are reported, and the evidence for the mechanism is reviewed.

Introduction

Studies on a variety of $[Co(NH_3)_5X]^{2+}$ complexes have accumulated evidence in support of a conjugate base dissociative (S_N1cB) mechanism for hydrolysis under basic conditions.[2-4] The evidence derives from kinetic studies,[5] competition studies using the isotopes of water[6] and anions,[7] stereochemical studies,[4,8] and the examination of sterically crowded molecules,[9] all of which indicate the existence of an intermediate of reduced coordination number. In many cases it has been demonstrated that deprotonation at a coordinated amine center precedes hydrolysis of the cobalt–ligand bond. In most of the anion competition studies, the leaving group has been anionic, usually with unit charge. This paper explores the competition properties further for the neutral leaving groups urea, dimethyl sulfoxide, and trimethyl phosphate, with selected anionic (azide, acetate, and thiocyanate ions) and neutral (methanol) competitors. In order to determine the dependence of anion competition (with N_3^-) on the charge of the substrate, we have also examined the base hydrolysis of the $[Co(NH_3)_5OSO_3]^+$ ion, where the leaving group is a dianion.

For each of the 3+ complexes, the possibility existed that O-coordination to Co(III) might enhance the susceptibility of the ligand to nucleophilic attack by hydroxide ion and that this pathway might be competitive with cobalt–oxygen bond fission. Hydroxide ion dependent hydrolysis of the $[(NH_3)_5CoOCH\cdot NMe_2]^{3+}$ ion has been observed to give $[(NH_3)_5CoOOCH]^{2+}$ and $NHMe_2$. It occurs at a rate $\sim 10^4$-fold faster than the hydrolysis of the uncoordinated ligand.[10] A similar reaction of hydroxide ion with the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion would, for example, produce either NH_3 and $[(NH_3)_5CoO_2CNH_2]^{2+}$ or free urea and $[(NH_3)_5CoOH]^{2+}$, in which the oxygen atom derived from urea, depending on the leaving group from the tetrahedral (at carbon) intermediate. If ammonia were the leaving group, the reaction could model the chemistry of jack bean urease, the nickel metalloenzyme[11] which produces ammonium carbamate as the initial product of the hydrolysis of urea.[12] The $[(NH_3)_5CoO_2P(OMe)_2]^{2+}$ ion could be produced from $[(NH_3)_5CoOP(OMe)_3]^{3+}$ by an analogous route. Oxygen-18 tracer studies have been used to determine the positions of bond cleavage, and the kinetics of base hydrolysis of the complexes are described.

Experimental Section

Visible spectra were recorded with Cary 14 or Cary 118C spectrophotometers. ^1H NMR spectra were measured with JEOL Minimar (100MHz) or Varian T60 spectrometers using Me_2SO-d_6

(1) (a) The Australian National University. (b) University of New South Wales.
(2) Tobe, M. L. *Acc. Chem. Res.* **1970,** *3,* 377 and references therein.
(3) Sargeson, A. M. *Pure Appl. Chem.* **1973,** *33,* 527 and references therein.
(4) Jackson, W. G.; Sargeson, A. M. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed; Academic Press: New York, 1980; Vol. 2, pp 321–335 and references therein.
(5) Ahmed, E.; Tucker, M. L.; Tobe, M. L. *Inorg. Chem.* **1975,** *14,* 1 and references therein.
(6) Green, M.; Taube, H. *Inorg. Chem.* **1963,** *2,* 948.
(7) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966,** *88,* 5443.
(8) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967,** *89,* 5129.
(9) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M. *Inorg. Chem.* **1970,** *9,* 1790.

(10) Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974,** *96,* 1726.
(11) Dixon, N. E.; Gazzola, C.; Blakely, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975,** *97,* 4131. Dixon, N. E.; Blakely, R. L.; Zerner, B. *Can. J. Biochem.* **1980,** *58,* 469. Dixon, N. E.; Gazzola, C.; Asher, C. J.; Lee, D. S. W.; Blakely, R. L.; Zerner, B. *Ibid.* **1980,** *58,* 474; **1980,** *58,* 481.
(12) Blakely, R. L.; Hinds, J. A.; Kunze, H. E.; Webb, E. C.; Zerner, B. *Biochemistry* **1969,** *8,* 1991. Dixon, N. E.; Riddles, P. W.; Gazzola, C.; Blakely, R. L.; Zerner, B. *Can. J. Biochem.* **1980,** *58,* 1335.

as solvent and Me$_4$Si as internal reference unless otherwise stated. All evaporations were carried out with Büchi rotary evaporators under reduced pressure ($\sim$20 mmHg) so that the temperature of the solutions did not exceed 25 °C.

[Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$, [Co(NH$_3$)$_5$Br](ClO$_4$)$_2$, and [Co(NH$_3$)$_5$-I](ClO$_4$)$_2$ were prepared as described;[7] their purity was established by ^{1}H NMR (Me$_2$SO-d_6) and visible (0.01 M HClO$_4$) spectra and elemental analysis.

[Co(NH$_3$)$_5$OC(NH$_2$)$_2$](S$_2$O$_6$)$_{3/2}$·1.5H$_2$O. The O-bonded urea complex was prepared as described.[13] Anal. Calcd: C, 2.55; H, 4.70; N, 20.80; S, 20.41; Co, 12.50. Found: C, 2.7; H, 4.7; N, 20.8; S, 20.7; Co, 12.6. The perchlorate salt was obtained by dropwise addition of 70% HClO$_4$ ($\sim$3 mL) to an ice-cold stirred suspension of the dithionate salt (1 g) in water (10 mL) and recrystallized from a saturated aqueous solution on cooling and addition of 70% HClO$_4$ (0.2 volumes). Pink plates were obtained on cooling overnight (5 °C). ^{1}H NMR (Me$_2$SO-d_6): δ 6.62 (4 H, urea NH$_2$), 3.90 (12 H, cis-NH$_3$), 2.50 (3 H, trans-NH$_3$). The visible spectra of freshly prepared solutions of the dithionate and perchlorate salts in water were identical: ϵ^{max}_{517} 79.0, $\epsilon^{max}_{351.5}$ 59.7 M^{-1} cm^{-1}. The O-bonding of the urea complex has been established.[13] The salts were shown to be free of [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ and the N-bonded linkage isomer by chromatography on SP-Sephadex C-25 (Na$^+$ form) using 0.25 M NaCl in 0.05 M phosphate buffer (pH 6.9) as eluant.[14]

The other complexes described below were routinely checked for [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ and other impurities by ^{1}H NMR spectrometry and chromatography on SP-Sephadex as above.

[Co(NH$_3$)$_5$OP(OMe)$_3$](BF$_4$)$_3$·OP(OMe)$_3$, [Co(NH$_3$)$_5$OP-(OMe)$_3$](CF$_3$SO$_3$)$_3$, and [Co(NH$_3$)$_5$OP(OMe)$_3$](ClO$_4$)$_3$·xH$_2$O (x = 0, 1). The [Co(NH$_3$)$_5$OP(OMe)$_3$]$^{3+}$ ion was generated by nitrosation of [Co(NH$_3$)$_5$N$_3$]$^{2+}$ in PO(OMe)$_3$.[15,16] Trimethyl phosphate was dried over 4-Å molecular sieves at 30 °C (24 h) and then freshly distilled at reduced pressure. [Co(NH$_3$)$_5$N$_3$](BF$_4$)$_2$ (3.0 g) in PO-(OMe)$_3$ (20 mL) was stirred vigorously as excess NOBF$_4$ (1.0 g) was added (5 min). Excess solvent was removed by trituration with anhydrous ether (10 × 30 mL portions) in a stream of dry N$_2$. The purple-red residue was dried in vacuo. Anal. Calcd for [Co-(NH$_3$)$_5$OP(OCH$_3$)$_3$](BF$_4$)$_3$·PO(OCH$_3$)$_3$: C, 10.53; H, 4.86; N, 10.23; Co, 8.61. Found: C, 10.6; H, 4.8; N, 10.7; Co, 8.6. ^{1}H NMR (Me$_2$SO-d_6): two doublets of equal intensity centred at δ 3.66 (J_{PH} = 11 Hz) and 3.75 (J_{PH} = 11 Hz) (free and coordinated PO(OCH$_3$)$_3$, respectively). [Co(NH$_3$)$_5$OP(OMe)$_3$](CF$_3$SO$_3$)$_3$ was prepared similarly from [Co(NH$_3$)$_5$N$_3$](CF$_3$SO$_3$)$_2$ and NO·OSO$_2$CF$_3$. It was recrystallized by extracting the solid on a filter quickly with water and filtering into a cold concentrated solution of NaClO$_4$, HClO$_4$ (70%)/ice, or 5 M CF$_3$SO$_3$H. The shiny pink plates which deposited readily on scratching were collected, washed with ethanol and ether, and dried in air. The perchlorate salt thus isolated as its monohydrate effloresced in vacuo over P$_2$O$_5$. Anal. Calcd for [Co(NH$_3$)$_5$OP-(OCH$_3$)$_3$](ClO$_4$)$_3$: C, 6.19; H, 4.15; N, 12.02; P, 5.32; Cl, 18.26; Co, 10.12. Found: C, 6.3; H, 4.3; N, 12.2; P, 5.1; Cl, 18.6; Co, 10.0. Calcd for [Co(NH$_3$)$_5$OP(OCH$_3$)$_3$](ClO$_4$)$_3$·H$_2$O: C, 6.00; H, 4.36; N, 11.66; P, 5.16; Cl, 17.71. Found: C, 6.1; H, 4.3; N, 11.5; P, 5.0; Cl, 17.9. Calcd for [Co(NH$_3$)$_5$OP(OCH$_3$)$_3$](CF$_3$SO$_3$)$_3$: C, 9.85; H, 3.31; N, 9.58; F, 23.38; S, 13.15; Co, 8.06. Found: C, 10.2; H, 3.5; N, 9.9; F, 24.5; S, 13.4; Co, 7.9. All of the [Co(NH$_3$)$_5$OP(OMe)$_3$]$^{3+}$ salts had identical visible spectra in H$_2$O: ϵ^{max}_{518} 49.3, ϵ^{max}_{347} 39.6. ^{1}H NMR (ClO$_4$$^-$ salt) (Me$_2$SO-d_6): δ 4.04 (12 H, cis-NH$_3$), 2.59 (3 H, trans-NH$_3$), 3.75 (9 H, d, J_{PH} = 11 Hz). Lattice water in the monohydrate was observed at δ 3.37 (2 H).

Salts of the PO(OMe)$_3$ complex prepared from [Co(NH$_3$)$_5$N$_3$]$^{2+}$ all contained a trace of an impurity which was not removed by repeated recrystallization. A sample was hydrolyzed in 0.05 M NaOH (4 min, 25 °C, quenched to pH 3 with HClO$_4$) and sorbed on SP-Sephadex. A pink 2+ band eluted with 0.2 M NaClO$_4$ (pH 3). This material, identified as [Co(NH$_3$)$_5$O$_2$P(OMe)$_2$]$^{2+}$ from its visible spectrum (λ_{max} 514 nm, by comparison with the spectrum of an authentic sample[17])

was also observed in similar proportion ($\sim$2.5%) on chromatography of a fresh aqueous solution of the PO(OMe)$_3$ complex.

[Co(NH$_3$)$_5$OSMe$_2$](ClO$_4$)$_3$·Me$_2$SO, [Co(NH$_3$)$_5$OSMe$_2$]Br$_3$·3H$_2$O, [Co(NH$_3$)$_5$OSMe$_2$](CF$_3$SO$_3$)$_3$, and [Co(NH$_3$)$_5$OSMe$_2$](ClO$_4$)$_3$·xH$_2$O (x = 1, 2). The Me$_2$SO complex was prepared initially as the Me$_2$SO solvate[18] from [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ in dimethyl sulfoxide (80 °C, 8 h) or from [Co(NH$_3$)$_5$Cl](ClO$_4$)$_3$ and AgClO$_4$ (1.1 equiv) in dimethyl sulfoxide (60 °C, 20 min). The product was recrystallized from water/NaClO$_4$ as pink plates of the dihydrate or needles of the monohydrate. The exact conditions under which each were formed were not determined; the dihydrate effloresced to a pink powder (monohydrate) on washing with ethanol followed by ether. The triflate salt was crystallized from H$_2$O/NaCF$_3$SO$_3$, collected, washed with 50% ethanol/ether and then ether, and dried in vacuo over P$_2$O$_5$. Anal. Calcd for [Co(NH$_3$)$_5$OS(CH$_3$)$_2$](ClO$_4$)$_3$·H$_2$O: C, 4.46; H, 4.30; N, 13.00; Cl, 19.75; Co, 10.94. Found: C, 4.6; H, 4.3; N, 12.8; Cl, 19.7; Co, 10.6. Calcd for [Co(NH$_3$)$_5$OS(CH$_3$)$_2$](CF$_3$SO$_3$)$_3$: C, 8.97; H, 3.16; N, 10.46; F, 25.54; S, 19.16; Co, 8.80. Found: C, 9.1; H, 3.2; N, 10.5; F, 25.4; S, 19.0; Co, 8.5. A saturated solution of the perchlorate salt in water was treated with a concentrated aqueous solution of LiBr and cooled in an ice bath (10 min). The crystals were collected, washed with methanol and ether, and dried in air. The product was twice recrystallized in the same manner immediately before use. Anal. Calcd for [Co(NH$_3$)$_5$OS(CH$_3$)$_2$]Br$_3$·3H$_2$O: C, 4.97; H, 5.62; N, 14.47; Co, 12.17; Br, 49.54. Found: C, 5.1; H, 4.9; N, 14.6; Co, 12.3; Br, 50.0. All of the salts of the Me$_2$SO complex had identical visible spectra in H$_2$O: ϵ^{max}_{515} 61.3, ϵ^{max}_{351} 63.7. ^{1}H NMR (ClO$_4$$^-$ salt) (Me$_2$SO-d_6): δ 3.87 (12 H, cis-NH$_3$), 2.64 (3 H, trans-NH$_3$), 2.72 (6 H, Me). Lattice water for the monohydrate was observed at δ 3.38 (2 H).

We discovered subsequently that both the PO(OMe)$_3$ and Me$_2$SO complexes were prepared more conveniently from [Co(NH$_3$)$_5$OS-O$_2$CF$_3$](CF$_3$SO$_3$)$_2$.[13] The PO(OMe)$_3$ complex thus prepared contained no [Co(NH$_3$)$_5$O$_2$P(OMe)$_2$]$^{2+}$ impurity.

[Co(NH$_3$)$_5$OSO$_3$]ClO$_4$ was prepared as described.[19] The crude product was chromatographed on SP-Sephadex C-25 (Na$^+$ form, 0.92 M NaClO$_4$ eluant) to remove an appreciable amount of [Co-(NH$_3$)$_5$OH$_2$]$^{3+}$. On concentration at reduced pressure, the eluate containing the first and major pink band deposited crystals, which were recrystallized from dilute tris buffer (pH $\sim$8)/NaClO$_4$. Anal. Calcd for [Co(NH$_3$)$_5$OSO$_3$]ClO$_4$·H$_2$O: H, 4.79; N, 19.58; S, 8.97; Cl, 9.91; Co, 16.48. Found: H, 4.8; N, 19.8; S, 8.9; Cl, 10.0; Co, 16.6. ^{1}H NMR (Me$_2$SO-d_6): δ 3.88 (12 H, cis-NH$_3$); 2.58 (3 H, trans-NH$_3$). Visible spectrum: ϵ^{max}_{516} 63.9, ϵ^{max}_{355} 51.0 in water.

Methyl Proton Exchange. A weighed sample of [Co-(NH$_3$)$_5$OSMe$_2$](ClO$_4$)$_3$ was dissolved in D$_2$O containing Na$_2$CO$_3$ (2 M, pD 11.3); sodium 2-dimethyl-2-silapentane-5-sulfonate was used as internal reference, and sodium acetate was included as a proton integration standard. The decrease of the [Co(NH$_3$)$_5$OSMe$_2$]$^{3+}$ (methyl) peak (δ 2.72) with time was coincident with the increase in the free Me$_2$SO peak (δ 2.58). A similar experiment was performed in D$_2$O with no added base. In both experiments the sum of the integrations of the bound and free Me$_2$SO signals remained constant over at least 10 $t_{1/2}$ and corresponded to 6.0 protons. Measurements were made with a Varian HA-100 spectrometer.

Product Distributions. The base hydrolysis reactions of [Co-(NH$_3$)$_5$OC(NH$_2$)$_2$]$^{3+}$, [Co(NH$_3$)$_5$OSMe$_2$]$^{3+}$, and [Co(NH$_3$)$_5$OP-(OMe)$_3$]$^{3+}$ were allowed to proceed for 10 $t_{1/2}$ in 0.01 M NaOH at 25 °C, and the major product (>99%) in each case was identified as [Co(NH$_3$)$_5$OH]$^{2+}$ by its visible spectrum in base and following acidification (HClO$_4$, to pH 1; as [Co(NH$_3$)$_5$OH$_2$]$^{3+}$, ϵ^{max}_{492} 47.2). Similarly, reactions under acidic conditions (10 $t_{1/2}$, 0.01 M HClO$_4$, 25 °C) gave ϵ^{max}_{492} 47.5 $\pm$ 0.5 for the product. Closer attention was paid to the reactions of the urea and PO(OMe)$_3$ complexes where reactions of the ligand under basic conditions were anticipated.

[Co(NH$_3$)$_5$OC(NH$_2$)$_2$](S$_2$O$_6$)$_{3/2}$·1.5H$_2$O. Weighed samples of complex ($\sim$0.5 g) were reacted to completion at 25 °C in aqueous buffers or NaOH solutions (50 mL); the reactions were quenched with acetic acid (to pH $\sim$4.8). After dilution (to 0.3 L), the mixtures were quantitatively sorbed on columns (2 × 10 cm) of Dowex 50W × 2 (Na$^+$ form) cation-exchange resin. Elution with 1 M NaClO$_4$ (pH $\sim$5) removed a trace of a red 2+ cation. Further elution with

(13) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.

(14) Mixtures of authentic [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ and [Co(NH$_3$)$_5$OC(NH$_2$)$_2$]$^{3+}$ separate readily under these conditions. [Co(NH$_3$)$_5$NHCONMe$_2$]$^{2+}$ is known and separates readily from [Co(NH$_3$)$_5$OC(NH$_2$)(NMe$_2$)]$^{3+}$ under these conditions (Jackson, W. G., unpublished work).

(15) Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60.

(16) Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1091.

(17) Schmidt, W.; Taube, H. *Inorg. Chem.* **1963**, *2*, 698.

(18) Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2165.

(19) Po, L. L.; Jordan, R. B. *Inorg. Chem.* **1968**, *7*, 526.

1 M NaClO$_4$ (pH ~11) removed the red [Co(NH$_3$)$_5$OH]$^{2+}$ product, which was identified spectrophotometrically following acidification (HClO$_4$, pH 3) as the orange-red [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ ion ($\epsilon^{max}_{492}/\epsilon^{max}_{346}$ ≈ 1.05) and quantified with ϵ_{492} = 47.9 M^{-1} cm^{-1}. In one experiment (2 M NaOH), this product was isolated essentially quantitatively by concentration of the (acidified) eluate at reduced pressure. Anal. Calcd for [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$: H, 3.72; N, 15.21; Cl, 23.10; Co, 12.80. Found: H, 3.6; N, 15.3; Cl, 23.2; Co, 12.6. Visible spectrum: ϵ^{max}_{492} 48.1, ϵ^{max}_{346} 45.1 in H$_2$O. The minor red 2+ product (<1%) was isolated from a larger scale (5 g) reaction in 1 M NaOH (200 mL) at 25 °C by quenching with acetic acid (0.4 mol) after 30 s and chromatographing the products as above. The first band was rechromatographed twice on smaller columns of the same resin using first 2 M NaClO$_4$ and finally 2 M LiNO$_3$ as eluants. The cooled eluate deposited red crystals (~20 mg) which were collected, washed with ethanol and ether, and dried in air. It was identified as [Co(NH$_3$)$_5$O$_2$CCH$_3$](NO$_3$)$_2$ by elemental analysis and by comparison of its visible (λ_{max} 352, 502 nm) and infrared (KBr disk) spectra with those of an authentic sample.[13] Anal. Calcd: C, 7.34; H, 5.55; N, 29.97. Found: C, 7.6; H, 5.4; N, 29.2. Its concentration in the eluates from chromatography were determined by atomic absorption spectrometry.

[Co(NH$_3$)$_5$OP(OMe)$_3$](ClO$_4$)$_3$. Reactions under acidic and basic conditions were followed by ^{1}H NMR spectrometry as described above for the Me$_2$SO complex. Signals due to coordinated PO(OMe)$_3$ (δ 3.88, d, J_{PH} = 10 Hz) were depleted with the simultaneous production of the doublet (δ 3.70, J_{PH} = 10 Hz) due to the free ligand. Methyl resonances attributable to the PO$_2$(OMe)$_2^-$ complex (δ 3.75, d, J_{PH} = 12 Hz) or free methanol (δ 3.32) were not observed (<5%).

Competition for Methanol. Competition between methanol and water during the base hydrolysis of [Co(NH$_3$)$_5$Cl](ClO$_4$)$_2$, [Co(NH$_3$)$_5$I](ClO$_4$)$_2$, and [Co(NH$_3$)$_5$OSMe$_2$](ClO$_4$)$_3$ was examined with MeOH/H$_2$O mixtures of known composition (0.2–0.6 mol fraction MeOH, prepared by weight). Experiments were carried out at least in duplicate as follows. The complex (~0.5 mmol) was dissolved in MeOH/H$_2$O mixture (100 g), to which was added 0.1 M LiOH in a similar solvent mixture (10 g). After 15 min, NaHCO$_3$ was added (to pH ~10) and the mixture was taken to dryness at reduced pressure (<30 °C). The residue was dissolved in D$_2$O (5 mL), which was removed under vacuum (twice), and then finally dissolved in D$_2$O containing anhydrous sodium acetate (0.1 M). The ^{1}H NMR spectrum (1–3 ppm downfield from Me$_4$Si, Varian HA-100 spectrometer) of this solution was recorded. The peak areas of the singlets at δ 3.0 ([Co(NH$_3$)$_5$OMe]$^{2+}$) and 2.3 (MeCO$_2^-$) were determined by cutting and weighing the chart paper, from which the proportions of the products [Co(NH$_3$)$_5$OMe]$^{2+}$ and [Co(NH$_3$)$_5$OH]$^{2+}$ were deduced. Control experiments using mixtures of authentic samples of these products showed them to be unaffected by the analytical procedures and the results therefore to be reliable.

Competition for Anions. The incorporation of anions into complexes during base hydrolysis was investigated for the [Co(NH$_3$)$_5$OC(NH$_2$)$_2$]$^{3+}$ (with N$_3^-$), [Co(NH$_3$)$_5$OP(OMe)$_3$]$^{3+}$ (with N$_3^-$, MeCO$_2^-$), [Co(NH$_3$)$_5$OSMe$_2$]$^{3+}$ (with N$_3^-$, MeCO$_2^-$, NCS$^-$), and [Co(NH$_3$)$_5$OSO$_3$]$^+$ (with N$_3^-$) ions. Competition by azide ion was determined at 25 °C under each of two sets of conditions (for the 3+ complexes); the results did not differ significantly. Weighed samples (0.4–0.5 g) of complex were dissolved either directly in 1.00 M NaN$_3$ (50 mL, 0.1 M in NaOH) or first (over ~10 s) in 1.00 M NaN$_3$ (25 mL) before the addition of 0.2 M NaOH in 1.00 M NaN$_3$ (25 mL). The reactions were quenched at 40 s (~27 $t_{1/2}$) for the urea complex by addition of acetic acid (0.3 g) or, for the other complexes, at ≥10 $t_{1/2}$ (2–3 min) with NH$_4$ClO$_4$ (1 g). The solutions were diluted with water (0.3–0.5 L) and then sorbed on, washed, and eluted from columns of Dowex 50W × 2 (H$^+$ form, 200–400 mesh) cation-exchange resin. The 2+ cationic products were eluted with 1 M NaClO$_4$ (pH 3, HClO$_4$) and [Co(NH$_3$)$_5$OH$_2$]$^{3+}$ was eluted with 2 M H$_2$SO$_4$ or 3 M HCl. The reactions of the Me$_2$SO and PO(OMe)$_3$ complexes were similarly studied in 1.00 M sodium acetate and in azide media over a range of [NaN$_3$] (0.2–1.0 M). Light was rigidly excluded throughout all of these experiments.

Concentrations of the product complexes in the eluate fractions of measured volume were determined spectrophotometrically with the following molar absorption coefficients: [Co(NH$_3$)$_5$O$_2$CMe]$^{2+}$, ϵ^{max}_{502} 75.2; [Co(NH$_3$)$_5$N$_3$]$^{2+}$, ϵ^{max}_{518} 272; [Co(NH$_3$)$_5$OH$_2$]$^{3+}$, ϵ^{max}_{492} 47.7 (3 M HCl), 48.7 (2 M H$_2$SO$_4$). In early experiments with the impure PO(OMe)$_3$ complex, a small correction was applied to allow

for the presence of 2.5% [Co(NH$_3$)$_5$O$_2$P(OMe)$_2$]$^{2+}$ in the 2+ cationic competition product. In later experiments with the pure complex,[13] no correction was necessary, and the final results were equivalent.

Competition by thiocyanate in the base hydrolysis of [Co(NH$_3$)$_5$OSMe$_2$]$^{3+}$ was examined as described above (with 1.0 M NaNCS, 0.1 M in NaOH), except that sufficient time was allowed prior to chromatography (10 $t_{1/2}$, k_{OH} = 0.15 M^{-1} s^{-1}, μ = 1 M, 25 °C) for the initially formed [Co(NH$_3$)$_5$SCN]$^{2+}$ ion to decay completely to [Co(NH$_3$)$_5$NCS]$^{2+}$ (26%) and [Co(NH$_3$)$_5$OH]$^{2+}$ (74%).[20] The proportions of the S- and N-bonded isomers formed initially were determined as follows. Samples of [Co(NH$_3$)$_5$OSMe$_2$](ClO$_4$)$_3$ (~0.5 g) were hydrolyzed in 1.00 M NaNCS at pH 9.98 ± 0.01 (8 $t_{1/2}$, 25 °C, pH stat), and then the pH was adjusted to ~2 (5 M HClO$_4$). The 2+ and 3+ cationic products were separated by chromatography as above. The total cobalt concentration in the 2+ band (containing both isomers) was determined by atomic absorption spectrometry or spectrophotometrically at one of the [Co(NH$_3$)$_5$SCN]$^{2+}$/[Co(NH$_3$)$_5$NCS]$^{2+}$ isosbestic points.[20] The proportions of the two isomers were determined from the absorbance at 300 nm, at which wavelength their molar absorptivities differ by a factor of ~10.[20] Although isomerization of the thiocyanato to the isothiocyanato complex is insignificant during chromatography ($t_{1/2}$ ≈ 9 days at 25 °C under acidic conditions), a small correction was applied to allow for rearrangement during the hydrolysis of the Me$_2$SO complex at pH 10.[20] The rate constant for hydrolysis of [Co(NH$_3$)$_5$OSMe$_2$]$^{3+}$ is ~50 times that for isomerization of [Co(NH$_3$)$_5$SCN]$^{3+}$ under these conditions.

[Co(NH$_3$)$_5$OSO$_3$]$^+$ hydrolyzes slowly in base (k_{OH} = 0.049 M^{-1} s^{-1}, μ = 1 M, 25 °C)[19] but reacts to an extent in 0.1 M NaOH (20–25 min) sufficient to allow competition with 1.00 M NaN$_3$ to be examined as described above. Unreacted [Co(NH$_3$)$_5$OSO$_3$]$^+$ separated readily from the hydrolysis products on chromatography and was determined spectrophotometrically (ϵ^{max}_{515} = 61, in 1 M NaClO$_4$).[7]

All competition experiments were performed at least in duplicate. In all cases, the total recoveries of cobalt from chromatography were >97%.

Kinetic Measurements. Buffers were prepared from reagent grade components and 1.00 N NaOH (Volucon) or standardized 1.02 N HClO$_4$ and were made up to μ = 1.0 M with NaClO$_4$. Measurements of pH were made at 25 °C using a Radiometer PHM26 meter fitted with a G202B glass electrode and K4112 calomel electrode in contact with the solution through a salt bridge containing 1.6 M NH$_4$NO$_3$ and 0.2 M NaNO$_3$ (pH 7). The system was standardized at two pH values as described by Bates.[21]

The kinetics of hydrolysis of the [Co(NH$_3$)$_5$OC(NH$_2$)$_2$]$^{3+}$ ion at 25.0 ± 0.1 °C was followed spectrophotometrically at 540 nm with either a Cary 16K or Cary 118C spectrophotometer. Equal volumes of solutions of complex (~4 mM) in 1 M NaClO$_4$ and buffer at twice the final concentration (μ = 1.0 M, NaClO$_4$) were mixed in a temperature-equilibrated stopped-flow reactor[22] fitted to a flow cell in the thermostated sample compartment of the spectrophotometer. The ensuing absorbance decrease was monitored until no further change was observed (runs at pH >10) or for longer than 4 half-lives (pH <10). For the fastest runs (dilute NaOH), the absorbance change was monitored at 540 nm with a Durrum-Gibson stopped-flow reactor (25.0 °C); data were collected by a Biomation 805 waveform recorder. All runs obeyed strictly a first-order rate law. Rate constants were computed in the usual ways; reported values are the mean of three or more determinations.

The kinetics of hydrolysis of the [Co(NH$_3$)$_5$OP(OMe)$_3$]$^{3+}$ ion was studied at pH values in the range 6.9–10.9, at 1, 15, or 25 °C. Weighed samples of complex (~0.1 mmol) were dissolved in thermostated 1.0 M NaClO$_4$ (25 or 50 mL) which had been adjusted to the required [OH$^-$] with NaOH. Consumption of NaOH (0.1–0.5 M, μ = 1.0, NaClO$_4$) was followed by pH-stat titration using a Mettler pH-stat assembly (DV 11 digital burette, DK 14 414 electrode potential amplifier, DK 11 control unit, DK 31 A/D converter, GA 13 recorder). The reacting solution was stirred under an atmosphere of N$_2$. The potential, measured with a combination glass electrode, remained constant during runs to within ±1 mV. The glass electrode

(20) Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655.

(21) Bates, R. G. "Determination of pH. Theory and Practice", Wiley: New York, 1964.

(22) A device similar to that described by: Inoue, Y.; Perrin, D. D. *J. Phys. Chem.* **1962**, *66*, 1689, modified to include thermostated reservoirs.

Table I. Product Distribution in the Hydrolysis of the
$[(NH_3)_5CoOC(NH_2)_2]^{3+}$ Ion at 25 °C

medium	react time	% 2+ ion[a]	% $[(NH_3)_5CoOH_2]^{3+\ a,b}$
2.0 M NaOH	20 s	0.6	99.4
0.5 M NaOH[c]	20 s	0.4	99.6
0.2 M Et₃N·HClO₄, pH 11.49[c,d]	3.0 min	0.1	99.9
0.2 M Na·Mes, pH 6.29[c,d]	48.0 h	0.7	99.3

[a] Normalized to 100% recovery. The actual recovery on chromatography was 96–98% of the applied complex. [b] After adjustment to pH ~4.8 (acetic acid). [c] $\mu = 1.0$ M (NaClO₄). [d] Abbreviation used: Mes, 2-(N-morpholino)ethanesulfonic acid.

was calibrated (vs. [OH⁻]) by titration of standard HNO₃ solutions with the NaOH used in the experiments. The consumption of base (finally 85–102% of theory) obeyed first-order kinetics for at least 2 half-lives.

The base hydrolysis of the [Co(NH₃)₅OSMe₂]³⁺ ion was followed at 325 and 400 nm (Cary 16K spectrophotometer) in glycine/NaOH buffers (pH 9.2–10.1) and in 0.1 and 0.5 M NaOH at 25 °C and $\mu = 1.0$ M (NaClO₄) as described above for the urea complex.

Oxygen-18 Tracer Studies. Samples (~1 mmol) of [Co(NH₃)₅OC(NH₂)₂](S₂O₆)₃/₂·1.5H₂O, [Co(NH₃)₅OP(OCH₃)₃](ClO₄)₃, or [Co(NH₃)₅OSMe₂](ClO₄)₃·H₂O were dissolved in ¹⁸OH₂ (~1.5 atom %, Biorad, 10 mL) containing NaOH (~0.1 M). Some experiments were carried out with the OP(OMe)₃ complex hydrolyzed similarly at 0 °C (5 min) and with the urea complex hydrolyzed at two different [OH⁻] (0.22 and 0.38 M, at 25 °C). The reactions were quenched after 2–3 min by cooling to 5 °C and adding ice-cold HBr (60% w/v) dropwise. The ¹⁸O enrichments of the reaction solutions and of the isolated [Co(NH₃)₅¹⁸OH₂]Br₃ were determined exactly as described previously.[23] The ¹⁸O in the isolated CO₂ (and hence the reaction medium or product complex) was measured as m/e 46/(45 + 44) (=R) on a ratio recording mass spectrometer (Atlas GD 150 or Micromass 602D); enrichments of ¹⁸O were calculated with the relation atom % ¹⁸O = $10^2 R/(2 + R)$. These values were corrected for the natural abundance of ¹⁸O to give atom % enrichments. Samples of carefully purified [Co(NH₃)₅Cl]Cl₂ were treated identically and concurrently with the other complexes. The [Co(NH₃)₅¹⁸OH₂]Br₃ thus obtained was used as an internal calibrant to compensate for isotopic dilution inherent in the methods used to convert ¹⁸OH₂ to labeled CO₂.[24]

Since reported results[17] of a ¹⁸O-tracer study of the acid hydrolysis of the [Co(NH₃)₅OP(OMe)₃]³⁺ ion were significantly different from our results for the base hydrolysis (vide infra), we reexamined this reaction as follows. The complex (0.4 g) was reacted for 40 min (~1 $t_{1/2}$) with ~0.02 M HCl in ¹⁸OH₂ (10 mL). The [Co(NH₃)₅¹⁸OH₂]Br₃ complex was crystallized (free of unreacted substrate) with cold HBr (60%) and recrystallized from cold H₂O/HBr, under which conditions no ¹⁸O exchange occurs.[23] Ion-exchange chromatography showed only [Co(NH₃)₅OH₂]³⁺. Analyses for ¹⁸O were carried out as above.

Results

Hydrolysis of the [(Urea)pentaamminecobalt(III)](3+) Ion. The major product (>99%) of the spontaneous or base-catalyzed hydrolysis of the [(NH₃)₅CoOC(NH₂)₂]³⁺ ion was [(NH₃)₅CoOH]²⁺ (Table I), which was identified by its elution behavior during ion-exchange chromatography, by its visible spectrum under acidic conditions, and by isolation and elemental analysis as the protonated form, [(NH₃)₅CoOH₂]-

(23) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 904.
(24) Buckingham, D. A.; Cresswell, P. J.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 1647. The systematic error reported by these workers has since been traced to an impurity of N₂O produced on pyrolysis of H₂O with Hg(CN)₂/HgCl₂ at 400 °C. It does not separate from CO₂ on our gas chromatograph and is not resolved from CO₂ by low-resolution mass spectrometry. It is readily identified in high-resolution mass spectra in amounts which are sufficient to account for the error and which are absolutely constant in samples pyrolyzed concurrently.
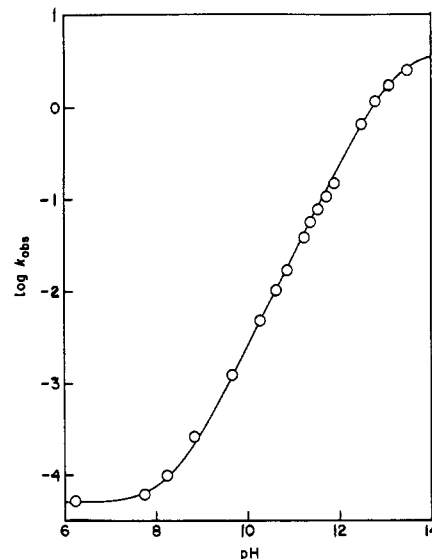

Figure 1. pH–Rate profile for the hydrolysis of the [(NH₃)₅CoOC-(NH₂)₂]³⁺ ion. The solid line was calculated from eq 1, with $k_s = 5.1 \times 10^{-5}$ s⁻¹, $k_{OH} = 15.26$ M⁻¹ s⁻¹, $K_w' = 1.70 \times 10^{-14}$, and $K_a' = 6.5 \times 10^{-14}$ ($\mu = 1.00$ M (NaClO₄); 25.0 °C). Buffers used were 0.10 M sodium 2-(N-morpholino)ethanesulfonate (pH 6.25), 0.10 M sodium N-(2-hydroxyethyl)-N'-piperazine-2-ethanesulfonate (pH 7.75), 0.10 M tris(hydroxymethyl)aminomethane–perchloric acid (pH 8.23), 0.10 M diethanolamine–perchloric acid (pH 8.84, 9.66), 0.10 M triethylamine–perchloric acid HClO₄ (pH 10.28, 10.62, 10.86, 11.21, 11.37, 11.52, 11.70, 11.89), and 0.05, 0.10, 0.20, and 0.50 M NaOH.

(ClO₄)₃. A trace (<1%) of a red 2+ product observed in the product distribution (Table I) was identified as the [(NH₃)₅CoO₂CCH₃]²⁺ ion by its visible and infrared spectra and by isolation and elemental analysis as [(NH₃)₅CoO₂CCH₃](NO₃)₂. It was undoubtedly formed by anation of the initial product [(NH₃)₅CoOH₂]³⁺ in the reaction mixtures after quenching to pH ~4.8 with acetic acid. The known [(NH₃)₅CoO₂CNH₂]²⁺ ion[25] was not detected as a product of the hydrolytic reaction.

Values of the observed first-order rate constants (k_{obsd}) for hydrolysis of the [(NH₃)₅CoOC(NH₂)₂]³⁺ ion are given in Table II,[26] and are plotted as a function of pH in Figure 1. They are independent of pH at pH values less than 7; log k_{obsd} rises linearly with pH to pH ~11, after which curvature of the plot becomes apparent. A plot (not shown) of k_{obsd} vs. [OH⁻] for [OH⁻] in the range 0–0.5 M shows pronounced curvature. All data obey a two-term rate law (eq 1), with k_s

$$k_{obsd} = k_s + K_w k_{OH}/(K_a' + [H^+]) \qquad (1)$$

= 5.1 × 10⁻⁵ s⁻¹, $k_{OH} = 15.26$ M⁻¹ s⁻¹, and $pK_a' = 13.19$ (Figure 1), where $K_w' = [H^+][OH^-] = 1.70 \times 10^{-14}$ (at 25.0 °C, $\mu = 1.0$ M), and pH = $-\log [H^+]$. This rate law is consistent with the mechanism described below, where k_s is the first-order rate constant for spontaneous aquation (eq 2),

$$(NH_3)_5CoOC(NH_2)_2^{3+} \xrightarrow{k_s} (NH_3)_5CoOH_2^{3+} + \text{urea} \qquad (2)$$
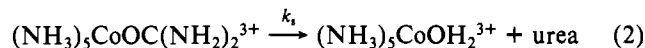
k_{OH} is the second-order rate constant describing the base-catalyzed hydrolysis of the urea complex (eq 3), and K_a' is the

$$(NH_3)_5CoOC(NH_2)_2^{3+} \xrightarrow{k_{OH}[OH^-]} (NH_3)_5CoOH^{2+} + \text{urea} \qquad (3)$$
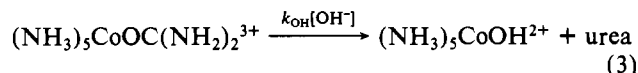
acid dissociation constant of the coordinated urea (eq 4). The data do not cover a sufficient range of pH above pH 12 to

(25) Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1094: (carbamato-O)pentaamminecobalt(III) is stable under the basic conditions on the time scales of these experiments.
(26) Supplementary material.

$$(NH_3)_5CoOC(NH_2)_2{}^{3+} \underset{\longleftarrow}{\overset{K_s'}{\rightleftharpoons}}$$
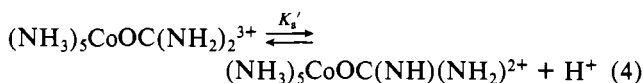
$$(NH_3)_5CoOC(NH)(NH_2)^{2+} + H^+ \quad (4)$$

comment on the rates of the spontaneous (k_s'[OH$^-$]) or base-catalyzed hydrolysis (k_{OH}'[OH$^-$]^2) of the conjugate base of the coordinated urea [(NH$_3$)$_5$CoOC(NH)(NH$_2$)]$^{2+}$, but the fit of the data to eq 1 (Figure 1) demands that k_{OH}'[OH$^-$] $\ll$ k_{OH}. The constancy of k_{obsd} for the conditions in 0.1 M and 0.4 M Et$_3$N·HClO$_4$ buffers (μ = 1.0 M, pH 10.28 and 10.26, respectively; k_{obsd} = 0.00481 and 0.00480 s^{-1}, respectively; Table II[26]) indicates an absence of significant buffer (general-base) catalysis of the hydrolytic reaction.

When [(NH$_3$)$_5$CoOC(NH$_2$)$_2$](S$_2$O$_6$)$_{3/2}$·1.5H$_2$O and [(NH$_3$)$_5$CoCl]Cl$_2$ were hydrolyzed in ^{18}OH$_2$ containing 0.22 M NaOH, the enrichments of ^{18}O in the product [(NH$_3$)$_5$CoO-H$_2$]Br$_3$ (after normalization to account for the small differences in measured values of the isotopic enrichment of the reaction media) were 1.225 and 1.260 atom % ^{18}O, respectively. In an independent experiment using 0.38 M NaOH, the corresponding values were 1.197 and 1.232 atom % ^{18}O. The enrichment in the product of reaction of the urea complex was therefore 97.2% of that derived from [(NH$_3$)$_5$CoCl]$^{2+}$, independently of [OH$^-$].

These results indicate that 97% of the reaction proceeds with rupture of the Co–O bond (producing labeled [(NH$_3$)$_5$CoOH]$^{2+}$), while the remaining 3% involves carbon–oxygen bond cleavage (producing labeled urea; see Discussion). The lack of dependence of the proportion of C–O bond cleavage on [OH$^-$] suggests that the nonlinear dependence of k_{obsd} on [OH$^-$] at pH >11 (Figure 1) is not due to a change in the mechanism of hydrolysis. It further indicates that the pathway which accounts for the retention of ^{16}O in the product complex (i.e., C–O cleavage) also shows a first-order dependence on [OH$^-$]. Although a dependence of this minor pathway on [OH$^-$]^2 would not be apparent in the rate law, it would be evident in the results of the tracer studies.

Hydrolysis of the [(Dimethyl sulfoxide)pentaammine-cobalt(III)](3+) Ion. The Me$_2$SO complex is well established as the O-bonded isomer.[27,28] The exclusive products of base hydrolysis (pH 9.2–13) were [(NH$_3$)$_5$CoOH]$^{2+}$ and Me$_2$SO, as shown by ^{1}H NMR spectrometry and by chromatography of the products. First-order rate constants (k_{obsd}) for the hydrolysis reaction showed a linear dependence on [OH$^-$] (Table III), with k_{obsd}/[OH$^-$] = 5.4 M^{-1} s^{-1}. Since the spontaneous aquation makes no contribution in the range of pH studied (k_s = 1.8 × 10^{-5} s^{-1}; ref 18), this ratio is a direct measure of the second-order rate constant for the base-catalyzed hydrolysis (k_{OH}).[3]

Although Me$_2$SO is a very weak acid, it can be deprotonated by strong bases in nonaqueous media to produce the corresponding sulfinyl methide anion.[29] Its acidity is enhanced by O-alkylation and presumably by coordination to Co(III). The expectation for extensive deprotonation at a methyl group would be a departure of k_{obsd} from a first-order dependence on [OH$^-$] at high [OH$^-$], as observed for the urea complex. Such was not observed (up to 0.1 M OH$^-$) for the Me$_2$SO complex (Table III), indicating a pK_a' > 14 for the [(NH$_3$)$_5$CoOSMe$_2$]$^{3+}$ ion. This was confirmed by ^{1}H NMR experiments which showed negligible H–D exchange at the methyl groups on the time scale of the base hydrolysis. Thus, Me$_2$SO leaves the Co(III) center as a neutral species during base hydrolysis.

Duplicate experiments involving hydrolysis of [(NH$_3$)$_5$CoOSMe$_2$](ClO$_4$)$_3$·H$_2$O in ^{18}O-enriched water con-

(27) Piriz MacColl, C. R.; Beyer, L. *Inorg. Chem.* **1973**, *12*, 7.
(28) Harrowfield, J. MacB.; Sargeson, A. M.; Singh, B.; Sullivan, J. C. *Inorg. Chem.* **1975**, *14*, 2864.
(29) Ledwith, A.; McFarlane, N. *Proc. Chem. Soc., London* **1964**, 108.

Table III. Rate Constants for the Hydrolysis of the [(NH$_3$)$_5$CoOSMe$_2$]$^{3+}$ Ion at 25 °C, μ = 1.0 M (NaClO$_4$)^a

NaOH Solution		
[OH$^-$], M	k_{obsd}, s^{-1}	k_{OH}, M^{-1} s^{-1}
0.10	0.53	5.3
0.05	0.28	5.6
0.1 M Glycine Buffer		
pH	10^4k_{obsd}, s^{-1}	k_{OH},^{b} M^{-1} s^{-1}
9.27	1.71	5.4
9.80	5.57	5.2
10.08	10.97	5.4

^{a} [Co] = 5 × 10^{-3} M. ^{b} Calculated with pK_w' = 13.77.

taining NaOH gave values of atom % ^{18}O of 1.385 for the [(NH$_3$)$_5$Co^{18}OH$_2$]Br$_3$ product, 1.366 for the solvent, and 0.194 for normal CO$_2$. The results correspond to 100 (±2)% incorporation of label from the solvent into the product.

Hydrolysis of the [(Trimethyl phosphate)pentaammine-cobalt(III)](3+) Ion. Most of our early experiments employed the phosphate triester complex obtained by nitrosation of [(NH$_3$)$_5$CoN$_3$]$^{2+}$ in PO(OMe)$_3$.[15,16] A small amount of [(NH$_3$)$_5$CoO$_2$P(OMe)$_2$]$^{2+}$ ion ($\sim$2.5%) was found in the products of hydrolysis in H$_2$O and in dilute NaOH. Chromatography of fresh aqueous solutions under conditions where the extent of hydrolysis was small revealed the same impurity present to the same extent. No 2+ ion (<0.5%) was found in either acid- or base-hydrolyzed solutions (after acidification) of the pure complex prepared[13] by a milder procedure, and no methanol (<2%) was observed by ^{1}H NMR spectrometry. Under the conditions of the experiments, the dimethyl phosphate complex was stable. The sole products of the hydrolysis of the [(NH$_3$)$_5$CoOP(OMe)$_3$]$^{3+}$ ion are therefore [(NH$_3$)$_5$CoOH]$^{2+}$ (or [(NH$_3$)$_5$CoOH$_2$]$^{3+}$) and free trimethyl phosphate.

The percentage of ^{18}O from ^{18}OH$_2$ incorporated into the [(NH$_3$)$_5$CoOH$_2$]$^{3+}$ product was found to be 99 ± 1% for base hydrolysis (0.1 M NaOH) and 100 ± 2% for acid hydrolysis (10^{-3} M HCl). This latter value is considerably higher than that reported previously (80%)[17] where isotopic dilution may have arisen from the presence of some [(NH$_3$)$_5$CoOH$_2$]$^{3+}$ ion in the sample of the OP(OMe)$_2$ complex.

The rate of hydrolysis of the [(NH$_3$)$_5$CoOP(OMe)$_3$]$^{3+}$ ion was studied by pH-stat titration. The observed first-order rate constants (k_{obsd}) over a range of [OH$^-$] at each of three temperatures are given in Table IV[26] and are plotted in Figure 2. The data are consistent with the usual rate law, k_{obsd} = k_s + k_{OH}[OH$^-$] up to 1.2 × 10^{-3} M OH$^-$ (μ = 1.0 M, NaClO$_4$). At higher [OH$^-$], plots (not shown) of log k_{obsd} vs. log [OH$^-$] were linear with slopes of 0.96 (25 °C), 0.97 (15 °C), and 0.99 (1 °C). Values of k_{OH} and k_s deduced from these data are given in Figure 2. A plot of ln k_{OH} vs. 1/T was strictly linear, giving ΔH^* = 30 ± 2 kcal mol^{-1} and ΔS^* = 13 ± 2 cal deg^{-1} mol^{-1} at 25 °C (μ = 1 M), at which temperature k_{OH} = 79 M^{-1} s^{-1} and $k_s \approx$ 1.4 × 10^{-4} s^{-1}. The data for the k_s path are less accurate since it was the smaller contributor to k_{obsd} over the pH range studied. Values of k_s obtained at 25 °C at different ionic strength have been reported previously (2.5 × 10^{-4}, 2.45 × 10^{-4} s^{-1}).[15,17]

Anion Competition. The results for MeCO$_2^-$, N$_3^-$, and SCN$^-$ competition in the hydrolysis of three complexes with neutral leaving groups are summarized in Table V. While these studies were in progress, Reynolds et al.[30,31] reported anion

(30) Reynolds, W. L.; Hafezi, S. *Inorg. Chem.* **1978**, *17*, 1819.
(31) Biruš, M.; Reynolds, W. L.; Pribanić, M.; Ašperger, S. *Croat. Chem. Acta* **1975**, *47*, 561.
(32) Jackson, W. G.; Begbie, C. M. *Inorg. Chem.*, in press.

Table V. Percent [(NH$_3$)$_5$CoY]$^{2+}$ Produced on Hydrolysis of [(NH$_3$)$_5$CoX]$^{n+}$ in 0.1 M NaOH, 1 M in Anion (Y$^-$) at 25 °C^a

X	N$_3^-$	MeCO$_2^-$	SO$_4^{2-}$	SCN^{-b} N$_\infty$	S + N	S	N
Me$_2$SO	12.3 ± 0.2 (4)	2.2 ± 0.3 (2)		9.2 ± 0.2 (2)	22.1	19.3	2.8
	12.8[31],[30]	1.8[31]	3.7[31]	9.9[31]			
OP(OMe)$_3$	12.5 ± 0.3 (3)	2.0 ± 0.3 (2)					
OC(NH$_2$)$_2$	12.0 ± 0.1 (4)^c						
I$^-$	10.0[7]	4.8[7]	5.0,^{d} 8.2[7]	6.3[7]	16[20]	13[20]	3[20]
Br$^-$	8.7[7]			6.1[7]			
	8.8[30]						
Cl$^-$	8.5[7]			5.5[7]			
	8.5[30]						
NO$_3^-$	10.4[7]			7.1[7]	17[20]	13[20]	4[20]
	10.6[30]						
CH$_3$SO$_3^-$	10.0[24]						
CF$_3$SO$_3^-$	9.7[24]		4.7^d				
FSO$_3^-$	9.4^e						
ClO$_4^-$	10.3[24]						
SCN$^-$	10.0[20],^{f}						

^{a} Cobalt recoveries were 98–102%. Results were normalized to 100%. Numbers of determinations are given in parentheses. ^{b} S = [(NH$_3$)$_5$CoSCN]$^{2+}$, N = [(NH$_3$)$_5$CoNCS]$^{2+}$, N$_\infty$ = total [(NH$_3$)$_5$CoNCS]$^{2+}$ following subsequent reactions of initially formed S in base (see the text). ^{c} Corrected for the C–O cleavage pathway. ^{d} W. G. Jackson, M. L. Randall, and A. M. Sargeson. ^{g} Reference 20. ^{h} Reference 24. ^{e} Reference 32. Corrected for the competitive path producing [(NH$_3$)$_5$CoF]$^{2+}$. ^{f} Corrected for the competitive isomerization to [(NH$_3$)$_5$CoNCS]$^{2+}$.
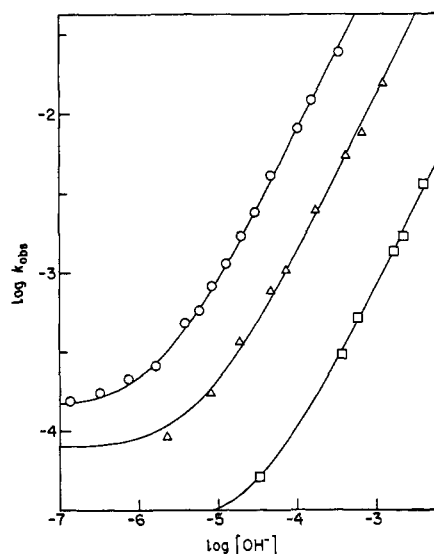
Figure 2. Dependence of k_{obsd} on [OH$^-$] for the hydrolysis of the [(NH$_3$)$_5$CoOP(OMe)$_3$]$^{3+}$ ion at 1.0 (□), 15.0 (▲), and 25.0 °C (○), μ = 1.00 M (NaClO$_4$), determined by pH stat titration. The solid lines were calculated from the equation $k_{obsd} = k_s + k_{OH}$[OH$^-$], with k_s = 1.4 × 10^{-4} s^{-1}, k_{OH} = 79 M^{-1} s^{-1} at 25.0 °C, k_s = 7.8 × 10^{-5} s^{-1}, k_{OH} = 13.5 M^{-1} s^{-1} at 15.0 °C, and k_s = 2.4 × 10^{-5} s^{-1}, k_{OH} = 0.84 M^{-1} s^{-1} at 1.0 °C.

competition data for the Me$_2$SO complex. Their data, together with results for anionic (1–) leaving groups are included in Table V for comparison. The competition for the urea complex has been corrected for the path (3%) not involving cobalt–oxygen bond cleavage (vide infra). All others, where there is ambiguity, are now known to hydrolyze exclusively with cobalt–oxygen cleavage.[6] Competition data for the base-catalyzed hydrolysis of the [(NH$_3$)$_5$CoOSO$_3$]$^+$ ion in 1 M NaN$_3$ (0.1 M in NaOH) are given in Table VI. Although the data for competitors other than azide ion are not extensive, it is clear that the extents of competition observed with the various substrates fall into definite ranges which appear to correlate with the overall charge on the reactant complex (Tables V and VI). In 1 M NaN$_3$, base hydrolysis of the three 3+ complexes produces 12.0–12.5% [(NH$_3$)$_5$CoN$_3$]$^{2+}$ ion, while hydrolysis of the nine 2+ substrates gives 8.5–10.4% competition. [with the 1+ substrate [(NH$_3$)$_5$CoOSO$_3$]$^+$, only 5.8% of the azido complex is produced. When sulfate or

Table VI. Product Analysis for the Base Hydrolysis of the [(NH$_3$)$_5$CoOSO$_3$]$^+$ Ion in 1.00 M NaN$_3$ (0.1 M NaOH), 25 °C^a

react time, min^b	% CoOSO$_3^{+c}$	% CoN$_3^{2+}$	% CoOH^{2+}	calcd % CoN$_3^{2+d}$
15	2.7	5.4	91.9	5.6
20	1.7	5.4	92.9	5.5
	2.5	5.8	91.7	5.9
	1.4	6.0	92.6	6.1
40	0.0	5.8	(103)^e	5.8
av				5.8 ± 0.3

^{a} Cobalt recoveries were 97–101%. Results were normalized to 100%. ^{b} Given k_{OH} = 0.049 M^{-1} s^{-1}, $t_{1/2} \approx$ 2.4 min. ^{c} Recovered substrate. Values are higher than predicted because the complex was slow to dissolve. ^{d} Corrected for incomplete reaction. ^{e} Decomposition of [(NH$_3$)$_5$CoOH]$^{2+}$ but not [(NH$_3$)$_5$CoN$_3$]$^{2+}$ under the conditions.

acetate ion (1 M) is the competitor, the trend is reversed, and the 3+ ions generate less of the acido competition product than does the [(NH$_3$)$_5$CoI]$^{2+}$ ion. Although two 2+ substrates appear to behave similarly with SCN$^-$ as the competitor, the [(NH$_3$)$_5$CoOSMe$_2$]$^{3+}$ ion gives greater overall N + S competition. In this case, the discrimination seems to reside largely in the pathway involving capture through sulfur to produce the [(NH$_3$)$_5$CoSCN]$^{2+}$ isomer (Table V).

As has been observed previously with 2+ substrates,[7] the amount of competition observed with the three 3+ substrates in azide media at constant ionic strength is linearly dependent on the concentration of the competitor (Figure 3).

Methanol Competition. Methanol was chosen as a neutral competitor because the competition product [(NH$_3$)$_5$CoOMe]$^{2+}$ is relatively stable in base. Competition in H$_2$O/MeOH mixtures was measured by ^{1}H NMR spectrometry, since the products (as [(NH$_3$)$_5$CoOH$_2$]$^{3+}$ and [(NH$_3$)$_5$CoOHMe]$^{3+}$, or as [(NH$_3$)$_5$CoOH]$^{2+}$ and [(NH$_3$)$_5$CoOMe]$^{2+}$) could not be separated chromatographically.[33] The standard deviation from duplicate experiments was 10%. Although the results (Figure 4) are clearly not as accurate as the anion competition data, it is apparent that the

(33) This separation has since been achieved by selectively reacting the [(NH$_3$)$_5$CoOH]$^{2+}$ product with HNO$_2$ (pH 5) or CO$_2$ (pH 7) to give the nitrito (2+) or carbonato (1+) complexes, respectively. Either ion is then readily separated from [(NH$_3$)$_5$CoOHMe]$^{3+}$ by ion-exchange chromatography at pH ∼5.

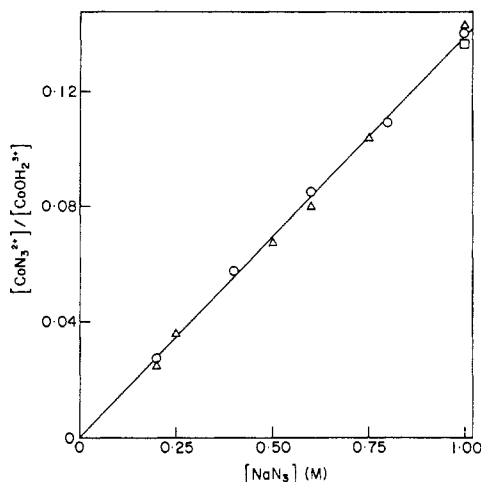**Figure 3.** Dependence of the competition ratio $[(NH_3)_5CoN_3^{2+}]/$ $[(NH_3)_5CoOH^{2+}]$ on $[N_3^-]$ for competition by azide ion in the base hydrolysis of the $[(NH_3)_5CoOSMe_2]^{3+}$ (O), $[(NH_3)_5CoOP(OMe)_3]^{3+}$, ($\triangle$), and $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ($\square$) ions; 25 °C, 0.1 M NaOH, $\mu = 1.1$ M (NaClO$_4$).

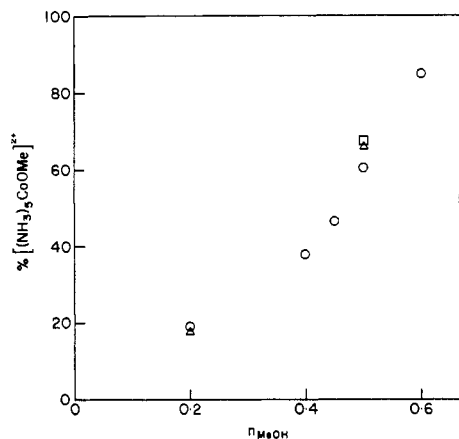**Figure 4.** Dependence on the mole fraction of methanol (n_{MeOH}) of the $\%[(NH_3)_5CoOMe]^{2+}$ produced in base hydrolysis of the $[(NH_3)_5CoCl]^{2+}$ (O), $[(NH_3)_5CoI]^{2+}$ ($\triangle$), and $[(NH_3)_5CoOSMe_2]^{3+}$ ($\square$) ions in methanol/water mixtures; [LiOH] = 0.1 M, 25 °C.

dependence of competition on the mole fraction of methanol is similar for the three substrates examined and that it is not strictly linear.

Discussion

Hydrolysis of the [(Urea)pentaamminecobalt(III)](3+) Ion. Taken together, the kinetic data, product distributions, and ^{18}O tracer experiments are consistent with the mechanisms of alkaline hydrolysis of the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion described by Scheme I. Under basic conditions, two prototropic forms of the urea complex exist; their relative concentrations are governed by an acid dissociation constant of 6.5 $\times 10^{-14}$ (at 25 °C, $\mu = 1.0$ M). As expected, the conjugate base of the urea complex is relatively unreactive. The acid form hydrolyzes by two distinct pathways to produce $[(NH_3)_5CoOH]^{2+}$ and the free ligand. Path A (Scheme I) involves a unimolecular conjugate base mechanism (S_N1CB, vide infra) leading to the production of an intermediate species of reduced coordination number which is captured by $^{18}OH_2$ to produce $[(NH_3)_5Co^{18}OH]^{2+}$ or may be trapped by an added nucleophile (such as N_3^-, producing $[(NH_3)_5CoN_3]^{2+}$). Path B (Scheme I) involves nucleophile attack by hydroxide ion on the carbonyl carbon atom of the coordinated urea to produce a tetrahedral (at carbon) intermediate which collapses to produce urea and $[(NH_3)_5CoOH]^{2+}$. The $[(NH_3)_5CoOH]^{2+}$
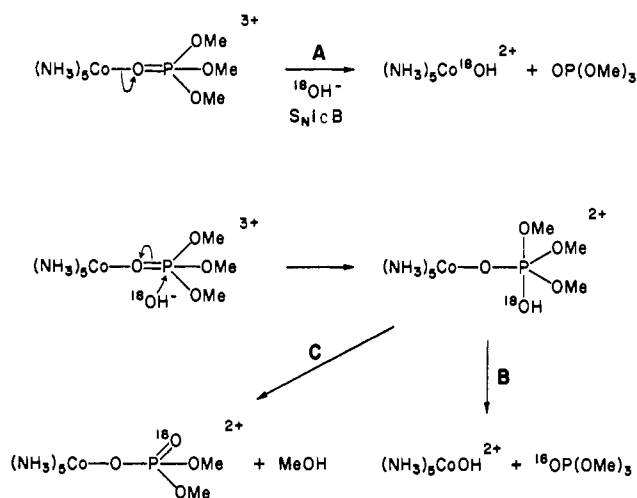
Scheme I
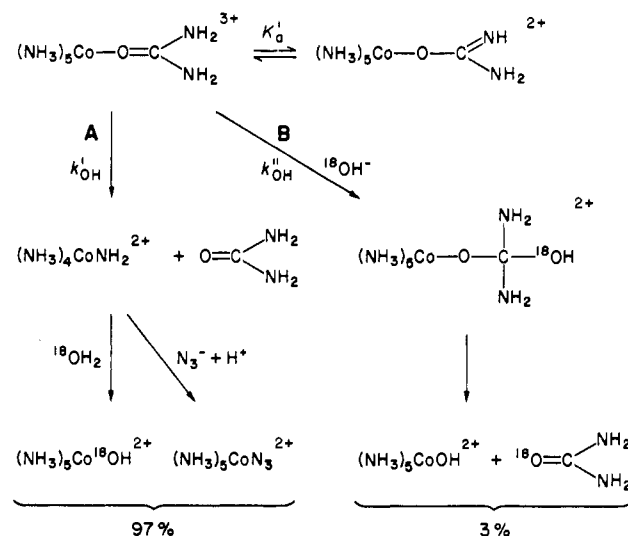
cation is apparently a better leaving group from the intermediate than is NH_3 since no $[(NH_3)_5CoO_2CNH_2]^{2+}$ ion is produced. The oxygen atom of the original ligand remains coordinated to Co(III) since the $[(NH_3)_5CoOH]^{2+}$ produced by this pathway when the hydrolysis is carried out in $^{18}OH_2$ is not labeled.[34] The results of the tracer studies indicate that 97.2% of hydrolysis occurs via path A (Scheme I, $k_{OH}' = 14.8$ M^{-1} s^{-1}) and the remaining 2.8% occurs via path B (Scheme I, $k_{OH}'' = 0.44$ M^{-1} s^{-1}).

The kinetically determined value of the pK_a' of the urea complex (13.2) may be compared with reported values for the pK_a' of the uncoordinated ligand (13.7 to 14.3) and of its conjugate acid (0.1–0.2).[35] Such a small lowering in pK_a' on coordiation is remarkably in comparison with those of amphoteric ligands which are protonated at the donor atom in a complex of Co(III).[36] It cannot be ascribed solely to the increased distance between the site of deprotonation and the cationic center since the pK_a' of glycineamide is lowered to 11.2 (25 °C, $\mu = 1.0$ M) by chelation to Co(III) through its amino nitrogen and carbonyl oxygen atoms.[37] Nevertheless, the Co(III)–urea complex studied here could model an O-coordinated Ni(II)–urea complex at the active site of urease. The unperturbed pK_a' of the urease–urea complex would also be expected to be $\sim$13 or greater.

In the proposed mechanism for the enzyme,[12] O-coordination of urea to an active-site nickel ion produces a complex whose pK_a' is decreased and whose reactivity toward an intramolecular nucleophile is markedly increased as a result of the ability of functional groups at the active site to induce charge separation in the coordinated substrate.[12] The reactivity of amides such as dimethylformamide[10] and glycineamide[37] toward nucleophile attack by OH$^-$ is increased from 10^4- to 10^6-fold by coordination to Co(III) through their carbonyl oxgyen atoms. A similar increase in reactivity ought to be observed with urea similarly coordinated. Because the nonenzymatic *hydrolysis* of urea has never been observed[38] it is

(34) The possibility cannot be rigorously excluded that some of the tetrahedral intermediate might collapse by cleavage of the Co–O bond with elimination of $^{18}OH^-$ and production of a $[Co(NH_3)_5]^{3+}$ intermediate similar to that produced by path A. If this reaction were to be significant, it could not be promoted by base (e.g., by an S_N1CB mechanism) since there is no evidence of a term second order in [OH$^-$] in the rate law (see Results).

(35) Summarized by: Woolley, E. M.; Hepler, L. G. *Anal. Chem.* **1974**, *44*, 1520.

(36) Harrowfield, J. MacB.; Norris, V.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7282.

(37) Buckingham, D. A.; Davis, C. E.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 5571.

Scheme II

$(NH_3)_5Co-O=P(OMe)_3^{3+}$ $\xrightarrow[^{18}OH^-]{A}$ $(NH_3)_5Co^{18}OH^{2+}$ + $OP(OMe)_3$
S_N1cB

$(NH_3)_5Co-O=P(OMe)_3^{3+}$ with $^{18}OH^-$ $\longrightarrow$ $(NH_3)_5Co-O-P(OMe)_3^{2+}$ with ^{18}OH

C

B

$(NH_3)_5Co-O-P(=^{18}O)(OMe)_2^{2+}$ + MeOH $(NH_3)_5CoOH^{2+}$ + $^{18}OP(OMe)_3$

clear that a more substantial activation of urea would be necessary were a reaction leading to the production of $[(NH_3)_5CoO_2CNH_2]^{2+}$ in the present system to compete with the cobalt–oxygen bond cleavage reactions we have observed.

Hydrolysis of the [(Dimethyl sulfoxide)pentaamminecobalt(III)](3+) Ion. As with the urea complex, the Me₂SO complex might conceivably hydrolyze by separate pathways, involving cobalt–oxygen or sulfur–oxygen bond cleavage. Experience with other pentaamminecobalt(III) sulfur systems[24] suggested that the latter route was unlikely. In the present system, the ^{18}O tracer studies indicated that hydrolysis occurs exclusively with Co–O bond rupture. Hydroxide ion attack at the sulfur atom with elimination of $[(NH_3)_5CoOH]^{2+}$ is therefore not competitive with base hydrolysis by the usual cobalt–oxygen cleavage route.

Hydrolysis of the [(Trimethyl phosphate)pentaamminecobalt(III)](3+) Ion. A number of alternative reactions of the $[(NH_3)_5CoOP(OMe)_3]^{3+}$ ion in basic media were anticipated (Scheme II). $[(NH_3)_5CoOH]^{2+}$ could be produced as a result of cobalt–oxygen cleavage as an S_N1cB mechanism (path A) or by the collapse of an oxyphosphorane intermediate with phosphorus–oxygen cleavge and elimination of $[(NH_3)_5CoOH]^{2+}$ (path B). Alternatively, methanol could leave from this intermediate, producing $[(NH_3)_5CoO_2P(OMe)_2]^{2+}$ (path C). Since no 2+ product was observed on chromatography of the (acidified) reaction mixtures (of the pure complex), path C is not competitive with the other paths. As with the Me₂SO complex, ^{18}O tracer studies establish that P–O cleavage (path B, producing unlabeled product) is also insignificant (<1%) during base (and acid) hydrolysis. A similar result (98 ± 1% incorporation of ^{18}O into product) was obtained for base hydrolysis at 0 °C. Therefore, a single pathway obtains in the range 0–25 °C, consistent with the linear Arrhenius plot for k_{OH}.

The three complexes studied here share the property of hydrolysis under basic and acidic conditions with elimination of a neutral leaving group. They are intermediate among pentaamminecobalt(III) complexes in terms of reactivity. Rate constants for the hydrolysis at 25 °C of the Me₂SO ($k_s = 1.8 \times 10^{-5}$ s⁻¹,[18] $k_{OH} = 5.4$ M⁻¹ s⁻¹) and urea ($k_s = 5 \times 10^{-5}$ s⁻¹, $k_{OH} = 15.3$ M⁻¹ s⁻¹) complexes are comparable with those for $[(NH_3)_5CoI]^{2+}$ ($k_s = 8.3 \times 10^{-6}$ s⁻¹, $k_{OH} = 3.3$ M⁻¹ s⁻¹) and $[(NH_3)_5CoONO_2]^{2+}$ ($k_s = 2.4 \times 10^{-5}$ s⁻¹, $k_{OH} = 5.7$ M⁻¹ s⁻¹).[39]

(38) Werner, E. A. "The Chemistry of Urea"; Longmans, Green & Co.: London, 1923; pp 31–48. Warner, R. C. *J. Biol. Chem.* **1942**, *142*, 705. Shaw, W. H. R.; Bordeaux, J. J. *J. Am. Chem. Soc.* **1955**, *77*, 4729.
(39) Data for the I⁻ and NO₃⁻ complexes are taken from a compilation by: Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

The PO(OMe)₃ complex is a little more reactive ($k_s = 2.5 \times 10^{-4}$ s⁻¹,[15] $k_{OH} = 79$ M⁻¹ s⁻¹) and is comparable with $[(NH_3)_5CoOSO_2Me]^{2+}$ ($k_s = 2.0 \times 10^{-4}$ s⁻¹, $k_{OH} = 55$ M⁻¹ s⁻¹)[24] under the same conditions. More rapid hydrolysis has been observed in complexes of the better leaving groups ClO₄⁻, CF₃SO₃⁻, and FSO₃⁻.[13]

Anion Competition. Cobalt(III) pentaammine complexes hydrolyze in base in the presence of competing anions (Y⁻) to give largely $[(NH_3)_5CoOH]^{2+}$, together with some $[(NH_3)_5CoY]^{n+}$.[3,7] The amounts of the latter products are generally small (2–10%). Although they depend slightly on the nature of the anion, the product ratios $[(NH_3)_5CoY^{n+}]/[(NH_3)_5CoOH^{2+}][Y^-]$ are very much less dependent on the nature of the leaving group (Table V). These results have been taken collectively to indicate a common reactive intermediate of reduced coordination number, $[(NH_3)_4CoNH_2]^{2+}$. Although the complexes studied previously have varied in reactivity ($k_{OH} = 10^{-1}-10^6$ M⁻¹ s⁻¹) and in size, electronic properties, and bonding geometry of the leaving groups, they all hydrolyze with elimination of an anionc (1–) leaving group. We sought to examine further the case for such an intermediate by examining the dependence of the competition properties on the charge of the substrate complex.
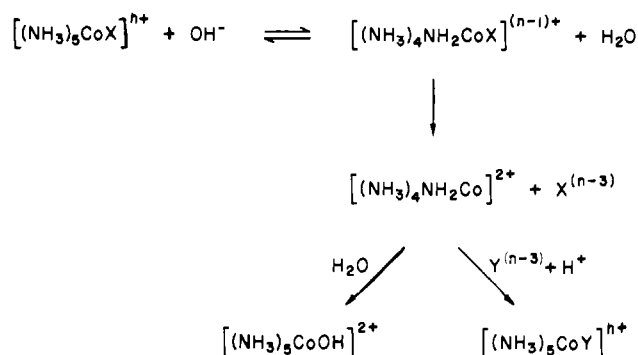
We noted with some of these compounds some years ago that the extent of competition in azide media with the 3+ substrates was measurably greater than with the 2+ ions. This property has also been observed with the Me₂SO complex by Reynolds et al.,[30,31] and, where they overlap, the two sets of data agree (Table V). It is apparent (Table V) that the urea and OP(OMe)₃ complexes behave similarly. Competition results for the OP(OMe)₃ and Me₂SO complexes over a range of [N₃⁻] (Figure 3) show their equivalence at all concentrations of the competitor and the usual[7] linear dependence. All three complexes with neutral leaving groups give essentially the same results, but the values for competition with N₃⁻ are substantially higher, and those for competition with SO₄²⁻ and MeCO₂⁻ are substantially lower than the values obtained with 2+ cations. Superficially it would seem that constant competition obtains for a set of complexes of the same formal charge. Furthermore, the competition data for the Me₂SO complex in SCN⁻ media are different from those for the two 2+ cations for which it has been measured. Both the thiocyanato and the isothiocyanato complexes are formed (Table V). The thiocyanato isomer rearranges in base subsequently to the base hydrolysis reaction to give 26% $[(NH_3)_5CoNCS]^{2+}$ and 74% $[(NH_3)_5CoOH]^{2+}$.[20] After sufficient time in base for this rearrangement to occur, the amount of $[(NH_3)_5CoNCS]^{2+}$ found in the competition experiments (9.2%) is similar to that reported for total NCS⁻ competition by Reynolds et al. (9.9%)[31] The amounts of the two isomers formed initially, determined here by analysis of reaction mixtures quenched at short times, is consistent with this value (i.e., since 26% of the initially formed $[(NH_3)_5CoSCN]^{2+}$ rearranges to $[(NH_3)_5CoNCS]^{2+}$, the expected final proportion of $[(NH_3)_5CoNCS]^{2+}$ (Table V) is (0.26 × 19.3) + 2.8 = 7.8%). Apparently, the initially formed S-bound isomer had largely rearranged under the conditions of the experiment of Reynolds et al.[31]

The view of the apparent dependence of the competition ratios on the formal charge of the complex (2+ or 3+), it was of interest to examine a 1+ complex. Of the known complexes in this category, only the sulfato complex reacted sufficiently rapidly in base ($k_{OH} = 0.049$ M⁻¹ s⁻¹)[19] to allow competition with N₃⁻ to be evaluated (Table VI). Unreacted $[(NH_3)_5CoOSO_3]^+$ was easily separated from the other products (2+ and 3+ ions) and determined spectrophotometrically. The observed extent of competition (5.8% $[(NH_3)_5CoN_3]^{2+}$ in 1 M NaN₃) is about half that found for

Scheme III

$$[(NH_3)_5CoX]^{n+} + OH^- \rightleftharpoons [(NH_3)_4NH_2CoX]^{(n-1)+} + H_2O$$

$$[(NH_3)_4NH_2Co]^{2+} + X^{(n-3)}$$

$$[(NH_3)_5CoOH]^{2+} \qquad [(NH_3)_5CoY]^{n+}$$

$$H_2O \qquad\qquad Y^{(n-3)} + H^+$$

the 2+ or 3+ substrates and clearly demonstrates the leaving group dependence of the anion competition.

Methanol Competition. A plot of % $[(NH_3)_5CoOMe]^{2+}$ produced an hydrolysis of $[(NH_3)_5CoX]^{n+}$ (x = Cl, I, Me$_2$SO) ions in MeOH/H$_2$O mixtures vs. the mole fraction of methanol (n_{MeOH}) shows a linear dependence up to $n_{MoH} \approx 0.4$ and a greater increase at higher n_{MeOH} (Figure 4). The two 2+ substrates $[(NH_3)_5CoCl]^{2+}$ and $[(NH_3)_5CoI]^{2+}$ gave identical results (within experimental error). In contrast with the anion competition results, the Me$_2$SO (3+) complex displayed the same competition properties for MeOH as the 2+ cationic substrates. While this may be anticipated at first sight, it does not necessarily follow. When n_{MeOH} is high, it is conceivable that complex ions of different charge could show different degrees of selective solvation. If this were the case, then the competition ratios could vary with the charge. These effects should become more apparent as the solvent composition becomes more distant from water.

Mechanism of Base Hydrolysis. The dissociative aspect of the conjugate base mechanism (S_N1cB) for hydrolysis of pentaamminecobalt(III) complexes has recently been challenged,[30,40] and it is timely to recapitulate the evidence for the existence of intermediates of reduced coordination number. The mechanism is formulated in Scheme III. Frequently a preequilibrium involving deprotonation of the reactant is established, although rate-determining deprotonation can occur. The deprotonated reactant then undergoes a unimolecular dissociation of the ligand (X) to give an intermediate of reduced coordination number which captures nucleophiles (H$_2$O or Y) from solution.[3] Evidence for the mechanism has accumulated from several sources: the rate laws,[3,5] proton exchange studies,[2,3,5] competition studies for ^{18}OH$_2$ and ^{16}OH$_2$ vs. ^{18}OH$^-$ and ^{16}OH$^-$,[6] competition studies for anions,[7] stereochemical studies,[4,8] and the increased reactivity of sterically crowded molecules.[9] The isotope experiments showed that solvent OH$_2$ is captured in preference to OH$^-$. This preference was also indicated by the lack of dependence of the anion competition properties on [OH$^-$]. The enhanced reactivity of the sterically crowded molecules appears to exclude the possibility of a competitor entering while the leaving group remains attached to the metal ion.

A compelling facet of the competition results was their apparent consistency for the same entering group despite a range of sizes, geometries and electronic properties of the leaving groups. However, all of the systems studied originally were 2+ cations with anionic leaving groups. More recent studies, including this one, indicate that the ratios for anion competition vary with the charge on the cation and that there are some anomalies even among reactants with the same charge.[41] In the latter cases, the small deviations from

"normal" behavior occur with those substrates containing poor leaving groups (Table V).

It was noted in the original study[7] that although different nucleophiles in solution had different competition capabilities, the variation was not large (a factor of 5 at most). There was an implication that they did not have an opportunity to exert their nucleophile capacity because the lifetime of the intermediate was not long and that the rate-controlling step was probably their abstraction from the solvent sheath surrounding the reactants. It further implied a lifetime for the five-coordinate species shorter than or comparable to the time of relaxation of the atmosphere about the reactants. The current results therefore are largely consistent with this proposal. There would be an expectation that the concentration of anions about the cationic reagent would increase with the increasing charge on the latter. This can be viewed as an atmosphere in the Debye–Hückel sense rather than as ion pairing. Clearly, the distinction is not easily defined; we have adopted a pragmatic approach to the problem in the sense that an ion pair is prescribed only if it appears in the rate law. The fate of the species of reduced coordination number can thus be viewed as inheritance of its solvent sheath which appears to be related to that of its immediate precursor.

The leaving group dependence of anion competition has recently been interpreted in terms of an alternative mechanism.[30] It was held that intermediates are not involved and that the mechanism of base hydrolysis is a dissociative interchange where both entering and leaving groups are weakly bonded.[42] Since the rate of reaction of the $[(NH_3)_4NH_2CoX]^{(n-1)+}$ complex with nucleophiles in solution is well below the diffusion-controlled limit,[3] competition by the dissociative interchange mechanism amounts to capture of the anion in preference to water from a solvated ion pair (or encounter complex). In principle, therefore, the experimental distinction between the two mechanisms is straightforward. If the $[(NH_3)_4NH_2Co]^{2+}$ ion exists, then anion entry occurs following, rather than concurrently, with the rate-determining step. The rate constants ought to be independent of added anion and unrelated to the proportions of products. For the alternative dissociative interchange mechanism, the rates and product distributions are necessarily related, and there should be a term in [anion] in the rate law. The rate equation for the base hydrolysis of $[(NH_3)_5CoX]^{2+}$ (X = Cl$^-$, Br$^-$, I$^-$, NO$_3^-$) shows no dependence on [anion] (Y$^-$ = ClO$_4^-$, NCS$^-$, NO$_2^-$, N$_3^-$) up to 1 M.[20] It follows that either ion association is unimportant or that the free ion and ion pair have identical reactivities. The latter would be a remarkable coincidence and an argument difficult to sustain for every anionic competitor. It would require a significant extent of ion association to account for the degree of competition observed. For example, 12% $[(NH_3)_5CoN_3]^{2+}$ arising in 1 M NaN$_3$ would require at least 12% ion pairing and more if each ion pair gives less than 100% azido complex. In this circumstance, saturation effects would be evident in the dependence of the competition ratios on [anion]; no such effects have been observed (e.g., see Figure 3 and ref 30). These considerations lead to the conclusion that ion pairing as described above is unimportant and that anion entry occurs subsequently to the rate-determining step; that is, an intermediate is involved.

A second deficiency of the ion pair mechanism is the lack of correlation of the observed extents of competition with the ion pair association constants. For example, several mo-

(40) Buckingham, D. A.; Edwards, J. D.; Lewis, T. W.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1978**, 892.

(41) The competition differences observed cannot be ascribed to decomposition of $[(NH_3)_5CoN_3]^{2+}$ in the basic media. Stability studies with this ion in the presence of 0.1 M OH$^-$, 1 M N$_3^-$, and 0.1 M OH$^-$, 1 M N$_3^-$, 10^{-3} M $[(NH_3)_5CoOH]^{2+}$ over 5 min at 25 °C indicated no decay of $[(NH_3)_5CoN_3]^{2+}$ (Jackson, W. G.; Randall, M. L., unpublished work).

(42) Langford, C. H.; Gray, H. B. "Ligand Substitution Processes"; W. A. Benjamin: New York, 1965; p 9.

noanions are better competitors than SO_4^{2-31} (Table V). The $[(NH_3)_5CoF]^{2+}$ ion appears to behave anomalously both in its competition properties with anions[32] and with the isotopes of water[6] and is the sole exception to this generalization. Furthermore, NCS⁻ can be captured either through nitrogen or through sulfur; S capture increases with increasing charge on the reactant while N capture appears to remain essentially constant (Table V). Finally, $[(NH_3)_5CoOSO_3]^+$ produces the amido precursor complex $[(NH_3)_4NH_2CoOSO_3]$ of zero charge, yet anion competition in 1 M NaN₃ occurs to an appreciable extent (Table VI). These observations are difficult to reconcile with an ion pair mechanism.

There is still, therefore, a considerable degree of consistency in the evidence in favor of an S_N1cB mechanism which generates a reactive five-coordinate intermediate on a time scale comparable with, or shorter than, that for the relaxation of its precursor's ionic atmosphere. The atmosphere appears to be at least partly controlled by the overall charge and largely independent of the leaving group. There is no correlation with the size, geometry, or electronic properties of the leaving group. Nor is there a general correlation with the ion-pairing ability of competitors. Moreover, it appears that ion-paired species do not always capture the paired ion effectively and that ion pairing may even inhibit the competition properties of the generated intermediate at least toward anions.

The evidence for discrete intermediates is compelling not only in this instance but also in related systems. Notable examples are the base hydrolyses of the (*R*)- and (*S*)-α,β-[(nitrato)(tetraethylenepentamine)cobalt(III)](2+) and β_2-(*RR,SS*)-[Co(trien)((gly)OR)Cl]²⁺ (R = H, C₂H₅) ions, which require intermediates to account for rearrangement after loss of the leaving group and before the entering group is captured.[43,44]

Although, for the pentaamminecobalt(III) complexes, the intermediate $[(NH_3)_4CoNH_2]^{2+}$ appears to be common to all of the systems, the data require it to be generated in different environments. The evidence indicates that it is a short-lived species which does not equilibrate with the total system. Yet it lives long enough to undergo rearrangements.[8]

There is still a need for more competition data, especially for low-charged, zero-charged, and anionic complexes, and we are currently exploring these aspects. The situation is akin to that of the "hot" carbonium ion in organic chemistry, and we can presume a variety of "solvent cage" phenomena will be observed in systems where the lifetimes of the intermediates are too short to allow their equilibration with the whole medium.

(43) Foxman, B. M.; Herlt, A. J.; Marzilli, P. A.; Sargeson, A. M., to be submitted for publication. A preliminary account is given in ref 4, p 328.
(44) Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Helv. Chim. Acta* **1978,** *61,* 2223.

Contribution from the Department of Chemistry,
State University of New York, Stony Brook, New York 11794

Electron-Transfer Reactions of Ion Pairs: Reductions of Various Substituted (Pyridine)pentaamminecobalt(III) Complexes by Hexacyanoferrate(II)[1]

ALTONY J. MIRALLES, ALEK P. SZECSY, and ALBERT HAIM*

The reductions of a series of substituted (pyridine)pentaamminecobalt(III) complexes by hexacyanoferrate(II) proceed via formation of an ion pair $Co(NH_3)_5L^{n+} + Fe(CN)_6^{4-} \rightleftharpoons Co(NH_3)_5L^{n+}|Fe(CN)_6^{4-}$, Q_{IP}, followed by internal electron transfer within the ion pair $Co(NH_3)_5L^{n+}[Fe(CN)_6^{4-} \rightarrow Co(NH_3)_5L^{(n-1)+}|Fe(CN)_6^{3-}$, k_{et}. Values of Q_{IP} (in M⁻¹) and k_{et} (in s⁻¹) at 25.0 °C, ionic strength 0.10 M, and pH 5.0 are as follows: nicotinamide, $(2.5 \pm 0.4) \times 10^3$, $(5.04 \pm 0.18) \times 10^{-2}$; isonicotinamide, $(5.3 \pm 2.3) \times 10^3$, $(3.58 \pm 0.25) \times 10^{-2}$; 4,4'-bipyridine (bpy), $(2.3 \pm 0.2) \times 10^3$, $(2.40 \pm 0.05) \times 10^{-2}$; 1,2-bis(4-pyridyl)ethane, $(2.8 \pm 0.4) \times 10^3$, $(1.01 \pm 0.03) \times 10^{-2}$; *N*-methyl-4,4'-bipyridinium (*N*-Mebpy), $(3.2 \pm 0.4) \times 10^3$, $(4.74 \pm 0.17) \times 10^{-2}$; pyridine-bonded 3-cyanopyridine, $(1.3 \pm 0.2) \times 10^3$, $(34.6 \bullet 2.4) \times 10^{-2}$; pyridine-bonded 4-cyanopyridine, $(2.5 \pm 0.2) \times 10^3$, $(15.1 \pm 0.3) \times 10^{-2}$; nitrile-bonded 3-cyanopyridine, $(1.5 \pm 0.2) \times 10^3$, $(76 \pm 4) \times 10^{-2}$. The ion pairs $Co(NH_3)_5py^{3+}|Fe(CN)_6^{4-}$ and $Co(NH_3)_5(N\text{-Mebpy})^{4+}|Fe(CN)_6^{4-}$ exhibit charge-transfer bands at 445 (molar absorbance 160 M⁻¹ cm⁻¹) and 470 nm (molar absorbance 240 M⁻¹ cm⁻¹). It is postulated that the ion pairs feature approach of $Fe(CN)_6^{4-}$ on the ammonia side of the cobalt(III) complexes. The electron-transfer process is assumed to be adiabatic and the variations in rate are associated with changes in the reduction potentials and/or rate constants for self-exchange of the cobalt(III) complexes.

Introduction

The importance of measuring rates of electron-transfer reactions in the intramolecular mode has been emphasized repeatedly.[2] In previous publications, we have reported rate constants for intramolecular electron transfer in binuclear complexes containing iron(II) and cobalt(III) bridged by various pyridines.[3-6] For inner-sphere reactions, the geometries of the binuclear complexes are well established, and, therefore, structure-reactivity relationships can be studied. For

(1) Abstracted in part from the Ph.D. Dissertation of A.J.M., State University of New York at Stony Brook, July 1974.
(2) Haim, A. *Acc. Chem. Res.* **1975,** *8,* 264.
(3) Gaswick, D.; Haim, A. *J. Am. Chem. Soc.* **1974,** *96,* 7845.
(4) Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976,** *98,* 1172.
(5) Jwo, J. J.; Gaus, P. L.; Haim, A. *J. Am. Chem. Soc.* **1979,** *101,* 6189.
(6) Szecsy, A. P.; Haim, A. *J. Am. Chem. Soc.* **1981,** *103,* 1679.