$\times 10^{-3}$ M) were heated (25–85 °C) in the sample chamber of a UV–visible spectrometer. This temperature-dependent absorption appeared reversibly and was therefore attributed to **4a**. The desired equilibrium constant was estimated by approximating the extinction coefficient of **4a** as 1800 M^{-1} cm^{-1} and calculating its concentration at various temperatures. From van't Hoff plots of three different initial concentrations of **5**, $\Delta H_{diss} = 18$ (1) kcal/mol and $\Delta S = 33$ (3) eu (K_{eq}(25 °C) = $[\mathbf{4a}]^2/[\mathbf{5}] = 7.5 \times 10^{-7}$). Typical ΔH and ΔS values for the dimerization of triarylmethyl radicals are 10 kcal/mol and 20 eu (K_{eq}(25 °C) = 9.2×10^{-4}).[25]

This unique opportunity to spectroscopically observe a reversible C–C bond formation relevant to pinacol coupling is due to three factors: (1) the Ti(III) center in **3** is a potent reductant; (2) the $(silox)_3M$ unit sterically shields the trapped radical; (3) steric factors permit coupling only via the Ph group—loss of its resonance stabilization energy translates into the formation of a weak, reversible C–C bond. Efforts to spectroscopically probe numerous alkoxy and related radicals stabilized by the *tris*-silox coordination sphere are ongoing.

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Articles

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Ion Association and the Reactions of Cobalt(III)–Acido Complexes. 4. Origin of the Products in the Base Hydrolysis of $[Co(NH_3)_5X]^{(3-n)+}$ Complexes

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Reversed-phase high-performance ion-pair chromatography (RP-HPIPC) has been used to accurately determine, or redetermine, under the same experimental conditions (1.0 mol dm^{-3} NaN_3, 25 °C), the amounts of $[Co(NH_3)_5N_3]^{2+}$ (CoN_3^{2+}) formed in the alkaline hydrolysis of a wide range ($k_{OH} = 10^{-2}$ to $>10^6$ dm^3 mol^{-1} s^{-1}) of $[Co(NH_3)_5X]^{(3-n)+}$ ($CoX^{(3-n)+}$) complexes ($X_n^- = SO_4^{2-}$, F^-, $OPO(O^nBu)_2^-$, $OPO(OMe)_2^-$, SCN^-, Cl^-, Br^-, I^-, ONO_2^-, $OSO_2CH_3^-$, $OClO_3^-$, $OSO_2CF_3^-$, $OSMe_2$, $OP(OMe)_3$). For CoX^{2+} there is a trend toward less CoN_3^{2+} production for the more robust systems and a common value for complexes with a rate constant $k_{OH} > 10^2$ dm^3 mol^{-1} s^{-1}. For $CoOSO_3^+$ ~2% less and for CoX^{3+} complexes ~2% more CoN_3^{2+} is formed than with CoX^{2+} systems of similar lability. A similar trend is found for stereochemical change in the $CoOH^{2+}$ products from *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{(3-n)+}$ ($X^{n-} = F^-$, Cl^-, Br^-, ONO_2^-, $OSO_2CF_3^-$, $OSMe_2$, $OP(OMe)_3$). No consistent pattern of stereochemical change is found for the CoN_3^{2+} products. The stereochemistry of $CoOH^{2+}$ and CoN_3^{2+} for a particular leaving group X^- (Br^-) is independent of $[N_3^-]$, but in the absence of N_3^- the stereochemistry of $CoOH^{2+}$ appears to be slightly dependent on the presence, or absence, of other anions (ClO_4^-, $CF_3SO_3^-$, Cl^-, NO_3^-). Hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]^{2+}$ gives no stereochemical change in the $CoNCS^{2+}$ product and some 15% more stereochemical change in $CoOH^{2+}$ compared to CoX^{2+} systems that lose X^- entirely but similar absolute amounts of CoN_3^{2+}. These and other observations suggest that all entering groups, and the leaving group X^{n-}, are present in the various transition states leading to products.

Introduction

The two recent papers by Rotzinger in this journal addressing the questions of the compositions and lifetimes of intermediates in the OH^--catalyzed hydrolysis of pentaamminecobalt(III)–acido complexes,[1,2] and the continuing support by the Jackson and Sargeson groups for a common coordinatively unsaturated intermediate for these reactions,[3] prompt us to report some of our observations on this longstanding problem.[4]

Our first set of results concerns the ability of an external ionic species (and we, like others, have used the N_3^- ion) to compete with H_2O from within the solvent cage for the intermediate formed on departure of X^{n-} as this is varied among different $[Co(NH_3)_5X]^{(3-n)+}$ reactants. There is ample evidence[5] to show that neutral leaving groups (i.e. X = Me_2SO, $(NH_2)_2CO$, $(MeO)_3PO$) result in enhanced N_3^- entry (usually reported as an "*R*" value for the products; $R = [CoN_3^{2+}]/[CoOH_2^{3+}][N_3^-]$, with $R \approx 12\%$ for 3+ complexes) when compared to uninegative leaving groups X^- (*R* = 8.5–10.0%) and to SO_4^{2-} (*R* = 7.2%,[3] 5.8%[5]), but there is also the possibility that variation might also exist among the uninegative leaving groups. Thus, Rotzinger[2] gives the order Cl^-, Br^- < FSO_3^-, $CF_3SO_3^-$ < SCN^-, $CH_3SO_3^-$, I^- < NO_3^-, ClO_4^- on the basis of a summary of experimental data given by Dixon and co-workers,[5] but the authors of this article themselves view the data as being "superficially the same". However, Jackson and Begbie[6] find an acceptable difference with X = F^- (*R* = 5.1%) but support the view that this complex could be "mechanistically different from the rest", while Reynolds and Hafezi[7] see their results of Cl^- < Br^- < NO_3^- as being clearly different. Thus, uncertainty remains, and we have taken the view that the variation or uncertainty in the experimental results from the various sources is large enough, and the difference between them for different X^- groups is small enough, to place considerable doubt on the order

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suggested by Rotzinger; it may indeed be that most X^- leaving groups give the same amount of N_3^- entry, which is less than that for neutral X but greater than that for SO_4^{2-}. In the present study we have obtained an accurate and self-consistent set of product data by the very efficient, and sensitive, reversed-phase high-performance ion-pair chromatographic (RP-HPIPC) analytical method,[8] and a clear order is now established among the 2+ ions.

The second set of results relates to the stereochemistries of the $CoOH_2^{3+}$ and CoN_3^{2+} products formed in such reactions. This has not been looked at in detail since the earliest study[9] with trans-$^{15}NH_3$-labeled reactants and a 60-MHz NMR instrument to follow rearrangement of the $^{15}NH_3$ label in the products. Hydrolysis of three *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$ complexes (*trans*-CoX^{2+}; X = Cl^-, Br^-, NO_3^-) in various NaOH solutions gave ~50% rearrangement to *cis*-$CoOH_2^{3+}$, and this was subsequently modified to ~40% *cis*-$CoOH_2^{3+}$ and ~70% *cis*-CoN_3^{2+} for hydrolysis of *cis*-$CoCl^{2+}$ in an almost saturated NaN_3 solution (100-MHz instrument).[10] The only other stereochemical data are those of Balt and co-workers,[11,12] who report 44%, 48%, 47%, and 0% *cis*-$CoOH_2^{3+}$ on hydrolyzing *trans*-$CoX^{(3-n)+}$ (X = Cl^-, Me_2SO, $CF_3SO_3^-$, and $OCHNMe_2$, respectively) in aqueous solutions (250-MHz instrument). We give here results for the hydrolysis, in both the absence and presence of electrolytes (including N_3^-), of several *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{(3-n)+}$ complexes selected to cover different charged leaving groups X^{n-} (n = 0, 1, 2) and different leaving-group lability for complexes of the same charge (n = 0, 1).

Third, we look in detail at the amounts and stereochemistries of the various products formed on hydrolyzing sulfur-bonded thiocyanate in $[Co(NH_3)_5SCN]^{2+}$, since this complex is known to give relatively large amounts of $CoNCS^{2+}$ (containing N-bound isothiocyanate) as well as $CoOH_2^{3+}$ and CoN_3^{2+} on alkaline hydrolysis; i.e., there is now an additional "internal" competitor present during hydrolysis for this reactant. In the original study[13] the amount of $CoNCS^{2+}$ formed (25–27%, ion-exchange data) was said to be invariant to changing $[OH^-]$ and, more importantly, to the presence or absence of electrolytes, in particular NaN_3. Also, the amount of CoN_3^{2+} (7% in 1 M NaN_3) was taken as being less than that from other CoX^{2+} reactants which lose their X^- group entirely (9–10% in 1 M NaN_3). The two results were interpreted in terms of internal isomerization (to give $CoNCS^{2+}$ from $CoSCN^{2+}$) occurring at an earlier stage than N_3^- or H_2O entry, with the last two groups competing for a subsequent five-coordinate intermediate. The RP-HPIPC data reported here show these competitive processes in greater detail and establish that the two earlier results are inaccurate. In addition, the stereochemical result with *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]^{2+}$ demonstrates an enhanced stereochemical change in the $CoOH_2^{3+}$ product when compared to those from other CoX^{2+} substrates. These new results suggest a somewhat different mechanism for this important reaction.

Experimental Section

Apparatus. Kinetic data were obtained with a Durrum D-110 stopped-flow spectrophotometer interfaced to a Northstar Horizon computer. Data treatment was carried out by using an OLIS data collection package. ^1H NMR spectra were obtained on a Varian VXR 300-MHz spectrometer using a 5-mm thermostated (25.0 °C) probe. Sample solutions were made up with acidified D_2O (CF_3SO_3H) or acidified DMSO-d_6 (D_2SO_4).

RP-HPIPC experiments were carried out with a Varian 5000 HPLC instrument equipped with a Waters U6-K injector and a Varian UV-50 variable-wavelength detector coupled to a Varian 9176 chart recorder and a HP-3390A integrator. Separations were achieved on a μ-Bondapak C_{18} reversed phase column fitted with a C_{18} Guardpak and contained within a Waters Z module. The HPLC pumps were operated at 2 cm^3 min^{-1}. Eluents used were (A) an aqueous solution 25 mM in sodium n-hexanesulfonate and 25 mM in Et_3N adjusted to pH 3.4 (2.0 mol dm^{-3} HCl) and (B) a solution of the same composition as A, adjusted to the same pH, but made up to be 67.5% v/v in methanol. Both eluents were filtered through a Whatman GF/F glass-fiber filter and then through a Nucleopore 0.4-μm membrane filter immediately prior to use.

Preparations. The complexes $[Co(NH_3)_5OSMe_2](ClO_4)_3\cdot H_2O$,[14] $[Co(NH_3)_5OH_2](ClO_4)_3$,[15] $[Co(NH_3)_5F](NO_3)_2$,[16] $[Co(NH_3)_5I]Cl_2$,[16] $[Co(NH_3)_5NCS]Cl_2$,[17] $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$,[18] $[Co(NH_3)_5N_3](ClO_4)_2$,[19] $[Co(NH_3)_5OClO_3](ClO_4)_2$,[20] $[Co(NH_3)_5OSO_2CH_3](ClO_4)_2$,[20] $[Co(NH_3)_5OP(OMe)_3](ClO_4)_3$,[21] and $[Co(NH_3)_5OSO_3]HSO_4\cdot 2H_2O$[22] were prepared by published procedures. $[Co(NH_3)_5Cl]Cl_2$[23] and $[Co(NH_3)_5Br]Br_2$[24] were similarly prepared and were converted to their ClO_4^- salts by passage through ClO_4^--form Amberlite IRA-400 ion-exchange resin. The thiocyanato complex $[Co(NH_3)_5SCN]Br_2$ was prepared in a manner identical with that for *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]Br_2$ as detailed below. These complexes were shown to be homogeneous by RP-HPIPC methods (the exceptions being the triflato and perchlorato complexes, which hydrolyze to $[Co(NH_3)_5OH_2]^{3+}$ in the time scale of the chromatographic procedure).

$[Co(NH_3)_5OP(O)(O^nBu)_2](ClO_4)_2\cdot 2H_2O$. To $HOP(O)(O^nBu)_2$ (3.15 g, 1.5×10^{-2} mol) and Et_3N (1.01 g, 1.0×10^{-2} mol) in dry Me_2SO (20 cm^3) was added $[Co(NH_3)_5OSMe_2](ClO_4)_3$ (1.2 g, 2.3×10^{-3} mol) and the resulting solution stirred at 50 °C for 3 h. Ethanol (150 cm^3) and water (150 cm^3) were then added, and the solution was loaded onto a column of Sephadex SP-C25 ion-exchange resin. The column was washed with water (250 cm^3) and then eluted with pyridinium acetate (0.5–1.0 mol dm^{-3}) and the red-purple 2+ band collected. This fraction was reduced to dryness (rotary evaporator, 50 °C) and the oily residue taken up in H_2O (10 cm^3) and treated with $LiClO_4$ (2 g). The precipitated product was filtered off, dried in air, and crystallized as fine needles from hot 1-butanol. Anal. Calcd for $[Co(NH_3)_5OP(O)(O(CH_2)_3CH_3)_2](ClO_4)_2\cdot 2H_2O$: C, 16.3; H, 6.3; N, 11.9. Found: C, 16.3; H, 5.9; N, 12.0.

$[Co(NH_3)_5OP(O)(OMe)_2](ClO_4)_2$. Solid $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ (2.95 g, 5.0×10^{-2} mol) was added to $NaOP(O)(OMe)_2$ (0.74 g, 5×10^{-3} mol) in MeOH (25 cm^3) and the resultant red solution maintained at 40 °C for 24 h. The solution was poured into dry Et_2O and the mixture stirred until the oil had solidified. The product was filtered off, washed with Et_2O, and dried in air. It was crystallized twice from cold water (10 cm^3) by adding $NaClO_4$ and cooling in ice. The red crystals were recovered, washed with the minimum volume of ice-cold MeOH, and air-dried. Anal. Calcd for $[Co(NH_3)_5OP(O)(OMe)_2](ClO_4)_2$: C, 5.1; H, 4.5; N, 15.0. Found: C, 5.3; H, 4.8; N, 15.1.

Trans-$^{15}NH_3$-Labeled Complexes. The preparation of *trans*-$[Co(NH_3)_4(^{15}NH_3)Br]Br_2$ followed that of the chloro complex as described earlier[9] and as modified by Balt et al.[11] Solid $[Co(NH_3)_4(^{15}NH_3)OSO_2]Cl$ (~5 g) was boiled for 30 min in a LiBr-saturated HBr solution (100 cm^3, 48%) and then cooled in ice. The impure $[Co(NH_3)_4(^{15}NH_3)Br]Br_2$ was recovered and then stirred in 100 cm^3 of water at ambient temperature for ca. 30 min to aquate any $[Co(NH_3)_4Br_2]Br$ impurity and again filtered, washed with MeOH, and air-dried. It was converted to the more soluble $CF_3SO_3^-$ salt by slowly adding 2 mol equiv of $AgOSO_2CF_3$ to a well-stirred aqueous suspension at ambient temperature and rotary evaporating the deep purple solution to low volume. *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ crystallized as deep purple plates. Adding $NaOSO_2CF_3$ and cooling in ice completed the recovery (4.2 g).

Attempts to prepare *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2CF_3](CF_3SO_3)_2$ from $[Co(NH_3)_4(^{15}NH_3)OSO_2](CF_3SO_3)$ as reported previously[12] gave in our hands an impure product. For example, 0.5 g of $[Co(NH_3)_4(^{15}NH_3)OSO_2](CF_3SO_3)$ (prepared from $[Co(NH_3)_4(OH)OSO_2]$ and $^{15}NH_4(CF_3SO_3)$) was added to 10 cm^3 of cold (−15 °C) CF_3SO_3H in a

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stoppered conical flask containing glass beads and the mixture held at this temperature for 20 min with frequent shaking. It was then poured into cold, stirred, dry ether and the crimson gummy solid agitated until it became solid with the use of fresh cold ether to assist solidification. This material was of isomeric purity (9% *cis*-$CoOH_2^{3+}$ on aquation) similar to that reported previously,[12] but its use in the synthesis of *trans*-$CoSCN^{2+}$ (see below) was very wasteful. A more productive triflato complex was prepared as follows. To 0.5 g of HgO (yellow) in a stoppered conical flask containing a magnetic stirrer was added 10 cm^3 of CF_3SO_3H, and the contents were warmed and stirred at 70–80 °C for 4 h, by which time conversion to a white suspension of $Hg(CF_3SO_3)_2$ was complete. $[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ (2 g) dissolved in CF_3SO_3H (10 cm^3) in a large centrifuge tube equipped with a magnetic stirrer was cooled in an ice–salt bath to −15 °C and the $Hg(CF_3SO_3)_2$ suspension added with a Pasteur pipet along with excess CF_3SO_3H (~2 cm^3) to complete the transfer. After ~10 min of stirring at −15 °C the contents were quickly centrifuged, the crimson solution was decanted off, and the remaining white solid of $HgBr_2$ was washed and centrifuged with further cold CF_3SO_3H (2 cm^3). The still cold solution was poured slowly into cold (−15 °C), stirred, dry ether, whence a fine crimson precipitate of the product deposited. This was washed by decantations with dry cold ether and collected and further washed on a glass filter (yield 2.39 g). The solid was stored in an evacuated desiccator.

trans-$[Co(NH_3)_4(^{15}NH_3)SCN]Br_2$ was prepared as follows. To the *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2CF_3](CF_3SO_3)_2$ complex prepared above (2.39 g) was added 24 cm^3 of aqueous LiSCN (a solution of 120 g of LiSCN in 30 cm^3 of warm H_2O that was filtered through Celite and adjusted to pH ≈ 3 with CF_3SO_3H if necessary) and the mixture stirred at ambient temperature for 20 min. The dark red-brown solution (containing solid $CoNCS^{2+}$ complex) was diluted to 2.5 dm^3 with water and loaded onto and eluted from (0.5–2.0 mol dm^3 HCl) cationic ion-exchange resin (Dowex 50W-X2). The purple-red 2+ band (containing both $CoSCN^{2+}$ and $CoNCS^{2+}$) was reduced to low volume (~10 cm^3) at ~30 °C by rotary evaporation, solid *trans*-$[Co(NH_3)_4(^{15}NH_3)NCS]Cl_2$ removed, and the filtrate further reduced to dryness. Dissolution in water (~4 cm^3) and addition of saturated aqueous NaBr (2 drops) precipitated any remaining $CoNCS^{2+}$ complex which was removed), and when further aqueous NaBr was added and the mixture cooled in ice, large deep purple crystals of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]Br_2$ deposited. These were collected, washed with MeOH, and stored in a refrigerator (0.33 g).

trans-$[Co(NH_3)_4(^{15}NH_3)OP(OMe)_3](ClO_4)_3 \cdot H_2O$ was prepared from the above triflato complex by dissolving it (0.5 g) in 5 cm^3 of dry redistilled trimethyl phosphate and after 5 h at room temperature pouring the solution into stirred dry ether. The pink precipitate was collected and dissolved in a small volume of water and the solution immediately filtered onto a mixture of ice, H_2O, and $NaClO_4$. The resultant pink flakes were collected, washed with MeOH, and dried in air. *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_3]ClO_4 \cdot H_2O$ was prepared similarly with use of concentrated H_2SO_4 as described earlier for the unlabeled compound,[3] as was *trans*-$[Co(NH_3)_4(^{15}NH_3)F](CF_3CO_2)_2$ with use of concentrated aqueous HF (Teflon beaker). The latter complex was isolated from considerable $CoOH_2^{3+}$ impurity by ion-exchange separation with SP-C25 cationic ion-exchange resin and elution with 0.2 M CF_3CO_2H followed by rotary evaporation (30 °C) to dryness (δ(trans $^{15}NH_3$) 2.58 ppm, $J(^{15}N)$ = 70.2 Hz, $J(^{19}F)$ = 3.0 Hz).

Kinetic Measurements. Rates of the alkaline hydrolysis of $[Co(NH_3)_5X](ClO_4)_n$ (X = $OP(OMe)_3$, $n = 3$; X = $OP(O)(OMe)_2$, $OP(O)(O^nBu)_2$, $n = 2$) were obtained spectrophotometrically (λ = 370 nm) at 25 °C and I = 1.0 mol dm^{-3} ($NaClO_4$). With $[Co]_T = 2.0 \times 10^{-3}$ mol dm^{-3} and OH^- concentrations of 0.1 or 1.0 mol dm^{-3}, plots of ln $(A_t - A_\infty)$ versus time were linear over $4t_{1/2}$ and derived first-order rate constants were reproducible to ±3%. Second-order rate constants are given in Table I. We note that those for the dimethyl and di-*n*-butyl phosphate complexes are considerably smaller than that recently reported by Norman[25] for the hydrolysis of $[Co(NH_3)_5OP(O)(OEt)_2](CF_3SO_3)_2$, k_{OH} = 9.6 mol^{-1} dm^3 s^{-1} (at 35 °C).

Table I. Second-Order Rate Constants for Alkaline Hydrolysis of $[Co(NH_3)_5X]^{n+}$ Complexes at 25 °C and I = 1.0 ($NaClO_4$) and Competition at $[N_3^-]$ = 1.00 mol dm^{-3}

X	k_{OH}/ mol^{-1} dm^3 s^{-1}	% CoN_3^{2+} [l]	% CoN_3^{2+} [a]
SO_4^{2-}	4.1×10^{-2} [b]	5.8[k]	5.4 (3)
F^-	2.1×10^{-2} [c]	5.1[m]	5.4 (3)
$OPO(O^nBu)_2^-$	3.5×10^{-2} [d]		7.4 (2)
$OPO(OMe)_2^-$	6.7×10^{-2} [d]		8.3 (2)
SCN^-	0.16[e]	7[e]	8.7 (4)
Cl^-	0.25[f]	8.5[n]	8.7 (2)
Br^-	1.4[e]	8.7[n]	9.5 (4)
I^-	3.0[b]	10.2[n]	10.8 (2)
NO_3^-	5.7[g]	10.4[n]	10.3 (3)
$CH_3SO_3^-$	55*k*	10.2[h]	10.6 (2)
ClO_4^-	5×10^4 [i]	10.3[h]	10.1 (4)
$CF_3SO_3^-$	1.0×10^4 [j]	9.8[h]	9.9 (3)
Me_2SO	5.4[k]	12.3[k]	12.6 (4)
$OP(OMe)_3$	78[d]	12.5[k]	12.4 (1)
$(NH_2)_2CO$	15[k]	12.0[k]	

[a] This work; the numbers of determinations are given in parentheses. [b] Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473. [c] Chan, S. C.; Hui, K. Y. *J. Chem. Soc. A* **1968**, 1741 (in 18% EtOH). [d] This work. [e] Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655. [f] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *Inorg. Chem.* **1968**, *7*, 174. [g] Jones, W. E.; Jordan, R. B.; Swaddle, T. W. *Inorg. Chem.* **1984**, *23*, 2473. [h] Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647. [i] Estimated as 5 times faster than for X = $CF_3SO_3^-$. [j] Curtis, N. J.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1986**, *25*, 484. [k] Dixon, N. E.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688. [l] Selected earlier data. [m] Jackson, W. G.; Begbie, C. M. *Inorg. Chem.* **1981**, *20*, 1654. [n] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.

Competition Experiments. To the solid cobalt pentaammine complex (2–8 mg) was added a solution 1.0 mol dm^{-3} in NaN_3 and 0.2 mol dm^{-3} in NaOH (200–400 μL) at 25 °C. The reaction mixture was shielded from the light and stirred to ensure complete dissolution of the reactant complex, and after 10–20 min CF_3SO_3H solution (0.1 mol dm^{-3}, 600 or 1200 μL) was added. The quenched reaction mixtures were immediately analyzed (20–40 μL) for their $[Co(NH_3)_5N_3]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$ content (and for $[Co(NH_3)_5NCS]^{2+}$ in the case of the $[Co(NH_3)_5SCN]^{2+}$ reactant) by RP-HPIPC methods. Estimations were carried out at 230 nm (AUFS = 0.5), except for the reactions of $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5OP(O)(O^nBu)_2]^{2+}$, where the $[Co(NH_3)_5N_3]^{2+}$ product was analyzed at 300 nm (AUFS = 0.1) and the aqua product at 230 nm (AUFS = 0.5). Integrated peak areas were related to concentrations by using appropriate standards.

Products from the Hydrolysis of $[Co(NH_3)_5SCN]Br_2$. Hydrolysis was carried out by injecting 100 μL of the electrolyte (also 0.1 mol dm^{-3} in NaOH) into 100-μL samples of $[Co(NH_3)_5SCN]Br_2$ taken from a freshly made stock solution in H_2O (4–5 mg dissolved in 1000 μL of H_2O). Hydrolysis was allowed to proceed for 30–40 min at 25.0 °C (or for 44 h at 0 °C) before quenching with 400 μL of 0.03 mol dm^{-3} CF_3SO_3H. Products were then determined by RP-HPIPC methods as detailed above. When a ClO_4^- medium was used, the quenched sample was warmed briefly to ~50 °C before cooling and injecting, since crystallization of $[Co(NH_3)_5NCS](ClO_4)_2$ had sometimes occurred. Two sample chromatograms are given in Figure 1 to demonstrate the practicality and resolution obtained by this method of analysis. The $CoNCS^{2+}$ impurity in the reactant (1.44%) was determined at 500 nm, where $\epsilon(CoNCS^{2+})$ = 178 mol^{-1} dm^3 cm^{-1} and $\epsilon(CoSCN^{2+})$ = 71 mol^{-1} dm^3 cm^{-1}.

Results

Reactants and Base Hydrolysis Procedures. The starting complexes used in the stereochemical study, *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ and *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2CF_3](CF_3SO_3)_2$, were prepared from *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2]Cl$ (or its ClO_4^- salt) by published procedures.[9,12] We had some difficulty in obtaining large amounts of pure *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2CF_3](CF_3SO_3)_2$ in this fashion[12] (9% cis impurity) and so prepared it more easily from $[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ with use of $AgOSO_2CF_3$ in neat CF_3SO_3H at −15 °C. The cis impurity in this particular reagent (13%) was determined following its aquation to the aqua complex in 0.01 M $HClO_4$, and it is not yet certain that this process occurs entirely without stereochemical change.[26] The other new

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(25) Norman, P. R. *Inorg. Chim. Acta* **1988**, *145*, 7.

(26) Small, but clearly measurable, stereochemical change occurs in the Hg^{2+}- and Ag^+-catalyzed aquation reactions of $CoBr^{2+}$ (but not for oxidation by Cl_2 to give $CoCl^{2+}$). Some stereochemical change also accompanies water exchange in $CoOH_2^{3+}$: Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. *Inorg. Chem.* **1989**, *28*, 3386.

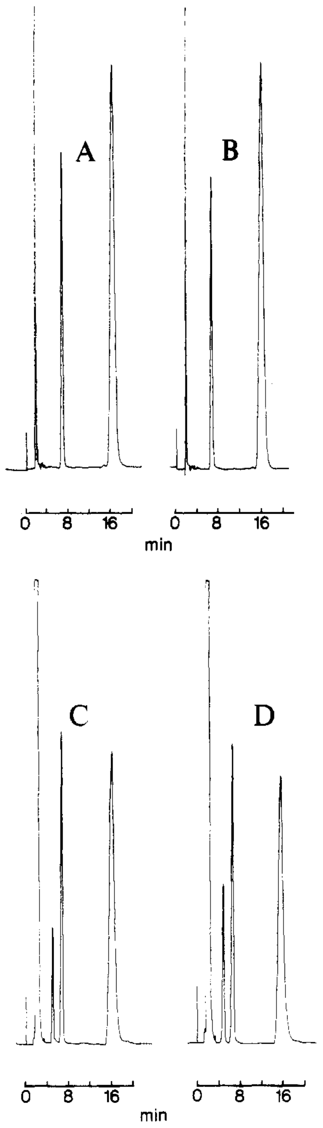

Figure 1. Representative RP-HPIPC chromatograms showing the products resulting from the hydrolysis of $[Co(NH_3)_5SCN]Br_2$ ($\sim 6 \times 10^{-3}$ M) in various electrolytes (all 0.05 M in NaOH): (A) 1.0 M $NaCF_3SO_3$; (B) 1.0 M $NaClO_4$; (C) 1.0 M NaN_3; (D) 2.0 M NaN_3. The eluent was 66.2% aqueous MeOH containing 25 mM sodium hexanesulfonate and 25 mM triethylamine adjusted to pH 3.4 with hydrochloric acid. Analysis was at 230 nm with use of an absorption range of 0.2 and 30-μL injections. The peaks following the solvent front (3 min) represent CoN_3^{2+} (when present, 5.5 min), $CoNCS^{2+}$ (7.1 min), and $CoOH_2^{3+}$ ($\sim$16 min).

trans-$^{15}NH_3$-labeled starting complexes (X = F^-, SO_4^{2-}, Me_2SO, $(MeO)_3PO$, NO_3^-) were prepared as detailed in the Experimental Section, and for some, surprisingly large amounts of stereochemical change had occurred in their synthesis (SO_4^{2-}, $(MeO)_3PO$).

The base hydrolysis experiments were, except for X = F^- and SO_4^{2-}, allowed to go to completion at 25 °C. The F^- and SO_4^{2-} complexes were hydrolyzed in 0.2 M NaOH/0.8 M $NaClO_4$ for 20 min before quenching. For the stereochemical experiments ion-exchange chromatography was used to separate the various products for subsequent ^1H NMR analysis, and for CoN_3^{2+} care was taken to exclude light both during hydrolysis and in its recovery. For X = SCN^- the $CoNCS^{2+}$ product usually crystallized from solution before chromatography, and this material was collected and separately chromatographed. It was shown by varying the time of hydrolysis and recovery, and by repeating the chromatographic recovery procedure on already analyzed (^1H NMR) samples, that no stereochemical change occurred subsequent to base hydrolysis or during chromatographic isolation.

N_3^- Competition. The percentage of CoN_3^{2+} product obtained from the hydrolysis of various $[Co(NH_3)_5X]^{+,2+,3+}$ ions in the presence of 1.0 mol dm^{-3} NaN_3 and 0.2 mol dm^{-3} NaOH are given in Table I. In most cases hydrolysis was complete before the reaction mixture was quenched (10–20 min), and RP-HPIPC analysis at 230 nm under isocratic conditions (i.e. constant eluent composition, =55% solvent B, Experimental Section) allowed direct estimation of the CoN_3^{2+} and $CoOH_2^{3+}$ products (and of $CoNCS^{2+}$ in the case of the $[Co(NH_3)_5SCN]^{2+}$ reactant). Although hydrolysis of $[Co(NH_3)_5OSO_3]^+$ and $[Co(NH_3)_5OP(O)(OMe)_2]^{2+}$ was incomplete under these conditions, this did not interfere with the determinations since both reactants have substantially different retention times compared to those of the products. However, the incomplete reactions of $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5OP(O)(O^nBu)_2]^{2+}$ prevented a straightforward HPLC estimation with a single wavelength, and in these cases the two products were determined from separate injections. CoN_3^{2+} was estimated at 300 nm (maximum) by using a solvent composition of 20% eluent B and $CoOH_2^{3+}$ at 230 nm by using 55% B. Agreement between replicate experiments was on the order of ±2–3% of the percentage of CoN_3^{2+} for all the competition experiments.

Stereochemistry. The % cis_{obs} values for the various products are given in Table II and were found from comparisons of cis-$^{15}NH_3$ and trans-$^{15}NH_3$ ^1H NMR peak areas obtained by cutting out and weighing considerably expanded 300-MHz outputs. Figure 2 gives representative spectra of *trans*-$CoBr^{2+}$, *trans*-$CoOSMe_2^{3+}$, *trans*-$CoOP(OMe)_3^{3+}$, and *trans*-$CoSCN^{2+}$ as well as products derived from these materials. Estimated errors from this procedure were 2–7%, depending on the line shape and background, but agreement between repeat experiments was nearly always better than this and was often the same. The values given in Table II are expected to be accurate to ±2%. Where comparison is possible our data agree with those reported earlier.[9–11] The % cis_{cor} values allow for the *cis*-$CoX^{(3-n)+}$ impurity in the reactant (% cis_r) by using the formula % $cis_{cor} = 100(cis_{obs} - cis_r)/(100 - 1.25cis_r)$.

Hydrolysis of $[Co(NH_3)_5SCN]^{2+}$. Products from the alkaline hydrolysis of $[Co(NH_3)_5SCN]Br_2$ are given in Table III (corrected for the 1.44 % $CoNCS^{2+}$ impurity in the reactant). Although given as the percentage of total recovered product, it is important to note that actual recoveries were excellent (100 ± 1%) and that the absolute areas of the various peaks (cf. Figure 1) showed trends the same as those given in the table; i.e., the presence of electrolyte decreases the absolute amount of $CoNCS^{2+}$ and increases the absolute amount of $CoOH_2^{3+}$. One of the major advantages of the RP-HPIPC method is its speed of analysis, and although the data given here have been averaged over only two injections (with agreement better than 0.4% for each area), experience has shown that if standards are run at the same time very accurate absolute data can be obtained (cf. N_3^- data for variable X^{n-} given above). The two sets of results reported for the 25 °C data were obtained from separate experiments carried out 4 days apart. It is also important to note that the medium at the point of analysis (i.e. the solvent system being analyzed by the spectrophotometer) is exactly the same for each product and for each experiment.

Discussion

Figure 3 gives the percentage of CoN_3^{2+} product (Table I) plotted against log k_{OH} (where k_{OH} is the second-order rate constant for base hydrolysis). The more extensive data for the 2+ ions are given as filled-in circles to distinguish them from those for the 3+ ions, and from that for $CoOSO_3^+$ (open circles). Three general observations can be made.

(1) The 3+ complexes give more CoN_3^{2+} ($\sim$2% more), and $CoOSO_3^+$ gives less CoN_3^{2+} ($\sim$2% less), than comparable 2+ complexes. This trend has been noted several times previously,[3,5,7,27] and comparative data are given in Table I; the agreement is in general excellent.

(2) Among the 2+ complexes there is an increase in the percentage of CoN_3^{2+} as the complex becomes easier to hydrolyze.

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(27) Jackson, W. G.; Begbie, C. M.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7.

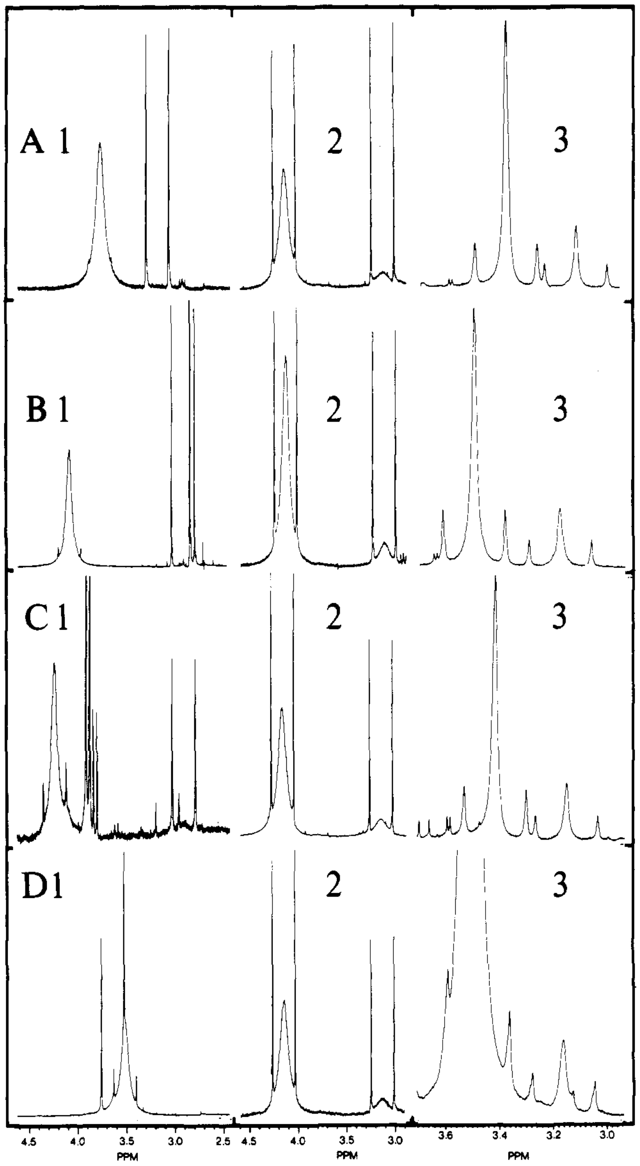

Figure 2. Representative 300-MHz ^1H NMR spectra of various *trans*-$CoX^{2+,3+}$ reactants and products resulting from hydrolysis in 0.05 M NaOH and 1.0 M NaN_3 (25 °C): (A1) *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$ in acidified (CF_3CO_2H) D_2O; (A2) resulting $CoOH_2^{3+}$ product (recovered as the $CF_3CO_2^-$ salt) in acidified D_2O; (A3) CoN_3^{2+} product ($CF_3CO_2^-$ salt) in acidified (D_2SO_4) Me_2SO-d_6; (B1) *trans*-$[Co(NH_3)_4(^{15}NH_3)OSMe_2](ClO_4)_3$ in acidified (CF_3CO_2H) D_2O ($OSMe_2$ adsorption at 2.85 ppm); (B2) resulting $CoOH_2^{3+}$ product in acidified D_2O; (B3) CoN_3^{2+} product in acidified Me_2SO-d_6; (C1) *trans*-$[Co(NH_3)_4(^{15}NH_3)OP(OMe)_3](ClO_4)_3$ in acidified D_2O ($OP(OMe)_3$ doublets centered at 3.88 ppm (coordinated) and 3.82 ppm resulting from a small amount of aquation during sample preparation and measurement; the *trans*-$CoOH_2^{3+}$ product of aquation is seen as the small doublet centered at 3.08 ppm); (C2) $CoOH_2^{3+}$ product in acidified D_2O; (C3) CoN_3^{2+} product in acidified Me_2SO-d_6; (D1) *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]Br_2$ in acidified D_2O (note the trans-$^{15}NH_3$ doublet is now centered at lower field (3.66 ppm) than the cis-$^{15}NH_3$ impurity absorption (3.54 ppm)); (D2) $CoOH_2^{3+}$ product in acidified D_2O; (D3) CoN_3^{2+} product in acidified Me_2SO-d_6. The spectrum of the $CoNCS^{2+}$ product from this reaction is not given, but it showed no rearrangement to the cis geometry.

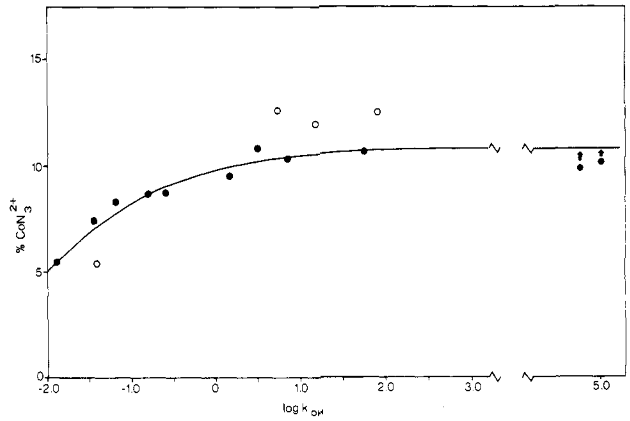

Figure 3. Percentage of CoN_3^{2+} produced in the base hydrolysis of various $[Co(NH_3)_5X]^{n+}$ complexes in 1.0 M NaN_3 (0.05–0.2 M in NaOH, 25 °C) vs log k_{OH} (where k_{OH} is the second-order rate constant for base hydrolysis): (solid circles) $n = 2+$ complexes; (open circles) $CoOSO_3^+$ and the three $n = 3+$ complexes. Individual complexes may be assigned by considering the k_{OH} values given in Table I.

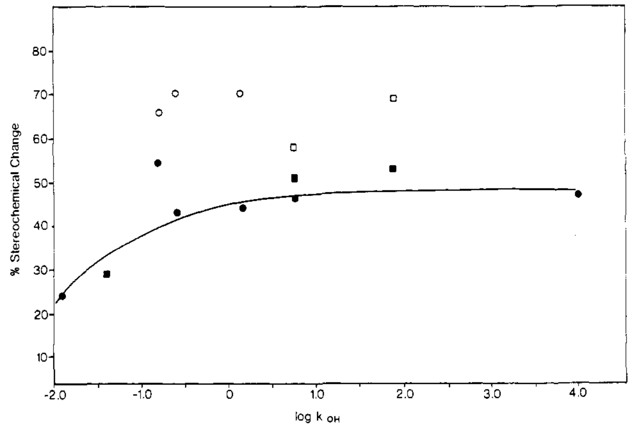

Figure 4. Percent change to the cis geometry vs log k_{OH} (where k_{OH} is the second-order rate constant for base hydrolysis) for the products resulting from the hydrolysis of various *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{n+}$ reactants (Br^-, ClO_4^-, $CF_3CO_2^-$ salts) in 0.05 M NaOH and 1.0 M NaY at 25 °C ($Y = CF_3SO_3^-$ for $X = SCN^-$, NO_3^-, $CF_3SO_3^-$, $OSMe_2$, $OP(OMe)_3$; $Y = OH^-$ for $X = Cl^-$, Br^-; $Y = ClO_4^-$ for $X = SO_4^{2-}$, F^-): (solid circles) $CoOH_2^{3+}$ products from the $n = 2+$ reactants; (solid squares) $CoOH_2^{3+}$ products from $CoOSO_3^+$ and the two $n = 3+$ reactants; (open circles) CoN_3^{2+} products from $n = 2+$ reactants; (open squares) CoN_3^{2+} products from the two $n = 3+$ reactants. Individual complexes may be assigned by considering the k_{OH} values given in Table I.

This trend is most obvious for the more robust complexes ($CoF^{2+} < CoOP(O)(OR)_2^{2+} < CoBr^{2+}$) and appears to approach a limiting value of ~10.5% for the most labile complexes. (The somewhat low values for $CoOClO_3^{2+}$ and $CoOSO_2CF_3^{2+}$ at ~ 10.0% may be due to the presence of some $CoOH_2^{3+}$ impurity in the reactant or they may be real. No experiments were carried out to investigate this.) Again, this trend was suggested by the very earliest results of competition with N_3^- (increasing percentage of CoN_3^{2+} in the order $X^- = Cl^- < I^- < NO_3^-$),[28] and it was noted that "the competition ratio shows little dependence on leaving group". Reynolds and Hafezi[7] confirmed the order for Cl^-, Br^-, and NO_3^-, and we again confirm it here. There is indeed a dependence on X^-.

(3) The percentage of CoN_3^{2+} from $CoSCN^{2+}$ is not low, as was reported earlier,[13] but agrees with the general trend.

Figure 4 gives a similar plot of percentage of *cis*-$CoOH_2^{3+}$ and percentage of *cis*-CoN_3^{2+} (i.e. stereochemical change, Table II) vs log k_{OH} for complexes chosen to cover a wide range of reactivities (~10^6-fold). General observations related to those above are (1) a somewhat larger stereochemical change in the $CoOH_2^{3+}$ product derived from the 3+ reactants (4–5% more), and perhaps a smaller change from $CoOSO_3^+$ (≤5%), compared to that for the 2+ complexes, (2) a similar gradation toward increasing stereochemical change in $CoOH_2^{3+}$ as the complex becomes easier to hydrolyze, with a possible limiting value of ~50% *cis*-$CoOH_2^{3+}$ for the 2+ complexes (and perhaps a higher value for the 3+ complexes), (3) an anomalous result for $CoSCN^{2+}$, with ~15% more *cis*-$CoOH_2^{3+}$ compared to that amount for a 2+ complex

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[28] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443.

Table II. Stereochemical Data for the $CoOH_2^{3+}$, CoN_3^{2+}, and $CoNCS^{2+}$ Products of Alkaline Hydrolysis of Various *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{(3-n)+}$ Complexes (25.0 °C)

X	charge on complex $(3-n)^+$	reacn conditions	% cis_r[a]	% cis_{obs}[b]	% cis_{cor}[c] $CoOH_2^{3+}$ (CoN_3^{2+})
Br^-	2	0.05 M NaOH	1.6	47, 47	46, 46
		1 M NaOH		45	44
		0.5 M NaOH/0.95 M $NaClO_4$		49, 48	48, 47
		0.05 M NaOH/0.95 M NaCl		48	47
		0.05 M NaOH/0.95 M $NaNO_3$		48	47
		0.05 M NaOH/0.95 M (Na(trifl)	2.7, 2.5	47	46
		0.05 M NaOH (45 °C)		45	44
		0.02 M NaOH/0.8 M Na(trifl) (0 °C)		45	44
		0.05 M NaOH/1 M NaN_3	1.6	45, 45	44, 44
				69, 69	69, 69 (CoN_3^{2+})
		0.05 M NaOH/2.5 M NaN_3		44	43
				70	70 (CoN_3^{2+})
		0.05 M NaOH/3 M NaN_3		45, 45	44, 44
				70, 70	70, 70 (CoN_3^{2+})
		0.05 M NaOH/4.36 M NaN_3 (satd)		...	...
				70	70 (CoN_3^{2+})
Cl^-	2	0.05 M NaOH	1.6	47	46
		1 M NaOH		44	43
		0.05 M NaOH/0.95 M $NaClO_4$		47	46
		0.05 M NaOH/1 M NaN_3		44	43
				70	70 (CoN_3^{2+})
NO_3^-	2	0.05 M NaOH	2.3	50	49
		0.05 M NaOH/0.95 M Na(trifl)		47	46
		0.05 M NaOH/1 M NaN_3		47	46
				70	69 (CoN_3^{2+})
$CF_3SO_3^-$	2	0.05 M NaOH	12	52	49
		0.05 M NaOH/0.9 M Na(trifl)		51, 52	48, 49
SCN^-	2	0.05 M NaOH	13	60	56
				14	1 ($CoNCS^{2+}$)
		0.05 M NaOH/0.95 M Na(trifl)		58, 58	54, 54
				14, 14	1, 1 ($CoNCS^{2+}$)
		0.05 M NaOH/0.95 M $NaClO_4$		58	54
				13	2 ($CoNCS^{2+}$)
		0.2 M NaOH/0.8 M Na(trifl) (0 °C)		59	55
		0.05 M NaOH/2.5 M NaN_3		60, 56, 57	56, 52, 53
				68, 67, 72	66, 66, 70 (CoN_3^{2+})
				13, 14, 14	2, 1, 1 ($CoNCS^{2+}$)
		0.05 M NaOH (45 °C)		59	55
				16	3 (CoNCS)
		0.05 M NaOH/2.5 M NaN_3 (45 °C)		58	54
				67	66 (CoN_3^{2+})
F^-	2	0.2 M NaOH/0.8 M $NaClO_4$	12	32	24
SO_4^{2-}	1	0.2 M NaOH/0.8 M $NaClO_4$	27	46	29
		0.2 M NaOH/2.5 M NaN_3	27	45	27
Me_2SO	3	0.05 M NaOH	3.6	52	51
		0.05 M NaOH/0.95 M $NaClO_3$		55	54
		0.05 M NaOH/0.5 M $NaClO_3$/0.5 M NaN_3		52	51
				60	59 (CoN_3^{2+})
		0.05 M NaOH/1 M NaN_3		51	50
		0.05 M NaOH/3 M NaN_3		51	50
				59, 60	58, 59 (CoN_3^{2+})
		0.05 M NaOH/3 M NaN_3		51	50
				62, 621	61, 61 (CoN_3^{2+})
		0.05 M NaOH/4.6 M NaN_3		50	49
				63	62 (CoN_3^{2+})
$(MeO)_3PO$ 3		0.05 M NaOH	17	57	51
		0.05 M NaOH/0.95 M Na(trifl)		59	53
		0.05 M NaOH/2.5 M NaN_3		56	50
				71	69 (CoN_3^{2+})

[a] Cis impurity in trans reactant. [b] Observed percentage of cis species in product. [c] % $cis_{cor} = 100(cis_{obs} - cis_r)/(100 - 1.25cis_r)$.

of similar reactivity which completely loses its trans-acido group (e.g. $CoCl^{2+}$), (4) larger amounts of stereochemical change for the *cis*-CoN_3^{2+} products compared to that for the *cis*-$CoOH_2^{3+}$ products for all the complexes, with that derived from $CoOSMe_2^{3+}$ showing less stereochemical change when compared to the others, and (5) no change in stereochemistry for $CoOH_2^{3+}$ derived from $CoBr^{2+}$ with a change in temperature (0–45 °C).

One generalization can be drawn from these observations; no two complexes behave the same. Either the amounts or stereochemistries, or both, of the products differ for each substrate. Therefore, no common transition state, or intermediate, exists in the base hydrolysis of cobalt(III) pentaammine complexes.[32] The results do not prohibit the formation of a five-coordinate cobalt(III) species in a purely dissociative process, indeed the same five-coordinate species for all substrates, but they require its lifetime to be so short that it captures ligating groups from the immediate environment (solvent cage) before it has had time to adjust to its changed situation.

In such circumstances great care must be taken in devising experiments to answer the question of whether the process is entirely dissociative or is partly concerted, since no assistance is *required* of an entering group in a concerted reaction,[29] although

Table III. Products of the Alkaline Hydrolysis of $[Co(NH_3)_5SCN]Br_2$ (0.05 M NaOH; 25 °C; [Co] = 0.013 M)

electrolyte	% $CoNCS^{2+}$	% $CoOH_2^{3+}$	% CoN_3^{2+}
none	28.7	71.3	
	28.7	71.3	
none (0 °C)	36.3	63.7	
1.0 M $NaOSO_2CF_3$	27.5	72.5	
	27.4	72.7	
1.0 M $NaClO_4$	26.2	73.8	
	26.2	73.8	
1.0 M $NaClO_4$ (0 °C)	31.8	68.2	
1.0 M NaN_3	27.7	63.6	8.7
	27.2	64.2	8.5
1.0 M NaN_3 (0 °C)	32.2	58.9	8.8
2.0 M NaN_3	27.8	57.5	14.7
	27.8	57.5	14.6

this is usually the case. Rotzinger[1] has recently attempted to quantify in absolute terms the effect of ClO_4^- and N_3^- from within the solvation cage on the hydrolysis rate of $CoONO_2^{2+}$, and their influence appears to be quite small. In such cases, especially where multiple preequilibria are involved (associations with OH^- as well as ClO_4^- and N_3^- were considered by Rotzinger[1]), the analysis attempted by Rotzinger is difficult to substantiate. In our view decisions on the stepwise or concerted nature of such reactions can only be made by looking at the products in terms of positions taken up by entering groups in relation to positions they held at the instant of bond rupture; i.e., following rupture of the Co–X bond and before the formation of products, "does stereochemical change occur by bond reorientation about the cobalt(III) center or by the relocation of (subsequent) entering groups within the immediate solvent cage?". If neither can be demonstrated, then for all intents and purposes the process *must* be classified as concerted, even when no activation (effect on the reaction rate) is provided by the entering group or groups. If stereochemical change in this sense can be demonstrated, then a definite lifetime for a five-coordinate cobalt(III) species exists. In our view this question has not been finally settled, and our experiments were designed to probe this.

Although inconclusive in some respects, and possibly conflicting in others, the following observations concerning the stereochemistries of the products (Table II) are pertinent to this question.

(1) Hydrolysis in the presence of 1 M ClO_4^-, $CF_3SO_3^-$, Cl^-, and NO_3^- often gives increased rearrangement in the $CoOH_2^{3+}$ product compared to that found in the absence these ions (i.e. 1 M NaOH) or in the presence of 1 M N_3^-; it is never less. For example, $CoBr^{2+}$ gives 44–45% *cis*-$CoOH_2^{3+}$ with use of 1 M NaOH and 1 M NaN_3 but 47–49% in $CF_3SO_3^-$, NO_3^-, Cl^-, and ClO_4^- media. In particular, the results with 1 M $NaClO_4$ always show slightly more rearrangement (cf. $CoBr^{2+}$, $CoCl^{2+}$, $CoOSMe_2^{3+}$) than when it is absent or when 1 M N_3^- is present. This can be interpreted (if one chooses) as 8–10% ClO_4^- entry to give 70% *cis*-$CoOClO_3^{2+}$, which then hydrolyzes to $CoOH_2^{3+}$ (with 44% rearrangement to cis for $CoBr^{2+}$ and 51% rearrangement to cis for $CoOSMe_2^{3+}$). However, slightly more rearrangement seems to occur in 0.05 M NaOH than in 1 M NaOH ($CoBr^{2+}$, $CoCl^{2+}$), and the above observations largely disappear when the 0.05 M NaOH results are compared with those in 0.05 M NaOH and 0.95 M NaY.

(2) The invariant stereochemistry of $CoOH_2^{3+}$ with increasing N_3^- concentration (cf. from $CoBr^{2+}$, $CoOSMe_2^{3+}$) indicates that the directions of entry of H_2O are not influenced by N_3^-. Likewise, the invariant stereochemistry of CoN_3^{2+} (up to 4.36 M N_3^-) implies that only one associated species leads to this product or that a constant ratio of different ion-paired species (i.e. of various stereochemistries, but with the same K_{IP} value) is involved. For the first alternative, with use of the formalism adopted by Rotzinger,[2] this might suggest that $Co(NH_3)_4(NH_2)$---X,N_3^{n-2} dissociates to $Co(NH_3)_4(NH_2)$---X^{n-1} and N_3^- competitively with azide entry, with H_2O entering the complex from the latter dissociated species only. This is the interpretation given by Rotzinger for the influence of ionic strength on his product results.[2] Alternatively, the stereochemistries of H_2O entry into the two intermediates are the same; i.e. the directions of entry of H_2O are not affected by whether N_3^- is present or absent from the solvent cage.

(3) Hydrolysis of *trans*-$CoOSMe_2^{3+}$ gives increased retention in the CoN_3^{2+} product compared to that from *trans*-$CoBr^{2+}$, for example (40% vs 30%), and a small decrease in retention for the $CoOH_2^{3+}$ product (49% vs 54–56%). Both results could arise from the change from a 1− to a neutral leaving group. The ion-associated species might be expected to have a proportion of N_3^- in the vicinity of a neutral leaving group (leading to retention) larger than that in the vicinity of coordinated Br^-, with correspondingly less about the $^{15}NH_3$ residue. This could also result in the observed increased proportion of *cis*-$CoOH_2^{3+}$ if the ion-paired species also leads to water entry remote from the leaving group. Steric (i.e. solvent-breaking) factors are probably important here, and the return to 69% *cis*-CoN_3^{2+} with the more bulky $OP(OMe)_3$ leaving group could result from such a cause. However, there is no apparent change in the stereochemistry of $CoOH_2^{3+}$ for this latter complex, and an increased amount of cis product would be expected here also if steric factors were solely responsible.

Perhaps the most interesting set of results comes from the base hydrolysis of $[Co(NH_3)_5SCN]^{2+}$. Here there is an internal marker that leads to appreciable $CoNCS^{2+}$ product in addition to $CoOH_2^{3+}$ (and CoN_3^{2+} when the reaction is carried out in the presence of N_3^-). Previously[13] we had taken the amount of $CoNCS^{2+}$ (25–27%) to be the same, independent of the reaction conditions at 25 °C, and this, together with the supposedly low competition figure for CoN_3^{2+} (7% in 1 M N_3^-), led to a mechanistic proposal in which the intramolecular switch $CoSCN^{2+} \rightarrow CoNCS^{2+}$ occurred at an early stage on the reaction coordinate. Complete loss of SCN^- then led to a five-coordinate intermediate which allowed competitive H_2O and N_3^- entry. The new, or revised, facts now discussed make this proposal inappropriate.

First, hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]^{2+}$ results in full retention of the *trans*-$CoNCS^{2+}$ stereochemistry (0–1% *cis*-$CoNCS^{2+}$ in the various experiments; Table II). This, together with the essential lack of exchange (~3%) with solvent $N^{14}CS^-$ found previously,[13] requires either that there be an ion pair which does not have time to dissociate before it reacts to give $CoNCS^{2+}$ (with retention of configuration) or that Co and SCN never separate (i.e. there is no five-coordinate intermediate). Second, the amount of CoN_3^{2+} formed, and the stereochemistry of the $CoOH_2^{3+}$ product, would suggest that entry of N_3^- and H_2O do not occur subsequent to isomerization but at the same time (i.e., they occur in parallel). Just as much CoN_3^{2+} is formed from $CoSCN^{2+}$ as from the other 2+ substrates which completely lose their acido groups (~9%, Figure 3), and a reduced amount (i.e. ~6.3%) would be expected if N_3^- entry occurred subsequently (it seems unreasonable to suggest a larger ion-pair constant with N_3^- for this particular substrate). Also, the increased amount of stereochemical change to give *cis*-$CoOH_2^{3+}$ (54–56% from $CoSCN^{2+}$ vs 46% from $CoBr^{2+}$ at 25 °C) is expected if 27% of the retentive pathway to give a trans product is now blocked to H_2O entry by the isomerization process ($100 \times 46/(46 + (54 - 0.27 \times 54)) = 54\%$). This latter result holds in both the absence and presence of added electrolytes, including N_3^-. However, the stereochemistry of the CoN_3^{2+} product does not show a similar blocking by isomerization. Perhaps this is because most of the N_3^- (i.e. ~70%) enters from a position remote from thiocyanate and, thus, is little influenced by events occurring on the other side of the molecule.

If we turn now to the amount of $CoNCS^{2+}$ product, small but measurable changes occur (Table III), with the presence of electrolytes (e.g. $CF_3SO_3^-$, ClO_4^-, N_3^-) all leading to decreases. At 25 °C these differences are small, but at 0 °C they are much larger with a 4% decrease in $CoNCS^{2+}$ in 1 M N_3^- and a 4.5% decrease in 1 M ClO_4^-. The constant amount of CoN_3^{2+} at the two temperatures (8.7%), compared to the significant increase in $CoNCS^{2+}$ when the temperature is lowered (28.7% to 36.3%), means that the increase in $CoNCS^{2+}$ must arise from a reduced

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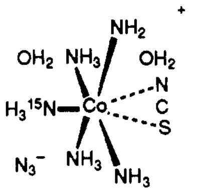
(29) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

H_2O involvement rather than from reduced anion entry (i.e. N_3^-, ClO_4^-, $CF_3SO_3^-$). Clearly the activation energy for the "turnaround" process is higher than that for N_3^- entry, which might suggest different transition states. However, whereas recapture of thiocyanate requires little separation of SCN^- from Co(III) and therefore probably only a minor contribution from the surrounding solvent, the capture of N_3^- contains contributions from both the formation of the ion pair and subsequent coordination to Co. It is likely that K_{IP} increases with decreasing temperature, whereas the release of N_3^- from the ion pair will be made more difficult since this will involve considerable desolvation of the N_3^- ion (breaking of H-bonds). In our view it is these opposing tendencies that lead to the constant incorporation of CoN_3^{2+} at the two temperatures.

In summary, the amount of isomerization $CoSCN^{2+} \rightarrow CoNCS^{2+}$ is only slightly affected by the presence of N_3^- (and other anions) in the immediate solvent cage, and entry of N_3^- from $Co(NH_3)_4(NH_2)$---X^{n-1},N_3^- is little influenced by the presence or absence of isomerization; H_2O is the major entering group when isomerization is absent or when N_3^- entry is reduced. Likewise, only the stereochemistry of H_2O entry is significantly affected by such processes (and then only by isomerization and not by N_3^- entry); the stereochemistry of anion entry (CoN_3^{2+}) is little affected by isomerization ($CoNCS^{2+}$) and the stereochemistry of the isomerized product is not at all affected by the presence of other anions. Also, isomerization is distinguished from N_3^- entry in an energetic sense.

Such facts imply the coupling of H_2O entry with N_3^- and NCS^- entry, but with the last two processes being largely uncoupled. However, all three processes must be competitive in the sense that they happen at the same time; they do not happen in a stepwise fashion with the appearance of a stable intermediate following NCS^- entry and before N_3^- entry. The results would suggest the existence of a number of intermediates, each containing entering groups in stereochemical positions closely related to those adopted in the final product. A relatively important member is



with N_3^- distant in a stereochemical sense from thiocyanate. Whether such intermediates contain truly five-coordinate cobalt(III) species, with complete breaking of the Co–SCN bond before entry of the sixth ligand, remains unknown. If bond breaking is complete, then the lifetime of these intermediates is insufficient to relocate thiocyanate into different stereochemical positions. If relocation of the other ion-paired entering groups or of H_2O from the second coordination sphere is on a similar time scale, then the five-coordinate species do not exist long enough to be observed by the type of experiments outlined here. If this is so in a general sense for all CoX^{n+} reactants (i.e. there is nothing special about the $CoSCN^{2+}$ substrate), then the lifetime of all such five-coordinate species[30] in the base hydrolysis reaction will be insufficient to allow major stereochemical adjustments within the second coordination sphere[31] and this type of experimental distinction between stepwise (e.g. $S_N1(CB)$ or I_d) and concerted ($S_N1(CB)$ or I_a) mechanisms[29] disappears.

Registry No. $[Co(NH_3)_5SO_4]HSO_4$, 49732-36-7; $[Co(NH_3)_5F](NO_3)_2$, 14240-02-9; $[Co(NH_3)_5OPO(O^nBu)_2](ClO_4)_2$, 123812-51-1; $[Co(NH_3)_5OPO(OMe)_2](ClO_4)_2$, 90568-50-6; $[Co(NH_3)_5NCS]Cl_2$, 15244-70-9; $[Co(NH_3)_5Cl]Cl_2$, 13859-51-3; $[Co(NH_3)_5Br]Br_2$, 14283-12-6; $[Co(NH_3)_5I]Cl_2$, 14972-82-8; $[Co(NH_3)_5NO_3]^{2+}$, 15077-44-1; $[Co(NH_3)_5CH_3SO_3](ClO_4)_2$, 76024-71-0; $[Co(NH_3)_5ClO_4](ClO_4)_2$, 18042-14-3; $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$, 75522-50-8; $[Co(NH_3)_5Me_2SO](ClO_4)_3$, 51667-94-8; $[Co(NH_3)_5OP(OMe)_3](ClO_4)_3$, 15041-41-5; $[Co(NH_3)_5SCN]Br_2$, 35672-90-3; CoN_3^{2+}, 14403-83-9; $CoOH_2^{3+}$, 14403-82-8; *trans*-$[Co(NH_3)_4(^{15}NH_3)Br]Br_2$, 123812-52-2; *trans*-$[Co(NH_3)_4(^{15}NH_3)Br](CF_3SO_3)_2$, 123812-54-4; *trans*-$[Co(NH_3)_4(^{15}NH_3)Cl]^{2+}$, 88537-87-5; *trans*-$[Co(NH_3)_4(^{15}NH_3)NO_3]^{2+}$, 123834-34-4; *trans*-$[Co(NH_3)_4(^{15}NH_3)OSO_2CF_3](CF_3SO_3)_2$, 97348-29-3; *trans*-$[Co(NH_3)_4(^{15}NH_3)SCN]Br_2$, 123812-59-9; *trans*-$[Co(NH_3)_4(^{15}NH_3)F](CF_3CO_2)_2$, 123812-56-6; *trans*-$[Co(NH_3)_4(^{15}NH_3)SO_4]ClO_4$, 123812-58-8; *trans*-$[Co(NH_3)_4(^{15}NH_3)Me_2SO](ClO_4)_3$, 88642-41-5; *trans*-$[Co(NH_3)_4(^{15}NH_3)OP(OMe)_3](ClO_4)_3$, 97251-80-4.

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(30) Rotzinger has suggested the existence of a "hexacoordinate cobalt(III) intermediate" following Co–X bond rupture and before entry of adjacent groups.[2] We find it hard to visualize what this might be other than a tight ion pair, but he assures us that he has carried out SCF calculations supporting their existence (private communication). We have no evidence to quantify the lifetime of any intermediate subsequent to breaking the Co–X bond, but the implications from the stereochemical results presented here infer that it must be short relative to major readjustments in the second coordination sphere.

(31) This would require solvent-separated ion pairs to give $CoOH_2^{3+}$, rather than CoN_3^{2+}.

(32) Since a transition state, intermediate, or indeed any configuration is a point on the potential energy surface of a reaction, all contributions to this energy surface, including those from the immediate surroundings, must be taken into consideration.

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Theoretical Study of the Electron Density in Iron(II) Porphyrin Bis(water)

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Ab initio SCF and CI calculations are reported for four different electronic configurations of the high-spin six-coordinate iron(II) porphyrin bis(water) molecule considered as a model for iron(II) tetraphenylporphyrin bis(tetrahydrofuran). The $^5B_{2g}$ and ^5E_g states are the lowest ones in energy and turn out to be nearly degenerate at both levels of theory. The ground-state configuration of iron(II) tetraphenylporphyrin bis(tetrahydrofuran) is assigned as ^5E_g on the basis of a comparison between the theoretical electron deformation density maps and the experimental ones.

Introduction

Recently, Lecomte et al. reported the electron density distribution in iron(II) tetraphenylporphyrin bis(tetrahydrofuran), $FeTPP(THF)_2$, derived from low-temperature X-ray diffraction data, and they attempted to determine the ground state of this high-spin complex.[1] They came to the conclusion that "a further analysis of the electron distribution determined in this study and the corresponding ground-state assignment requires comparison with parallel theoretical calculations. No such calculations are available as yet for $Fe^{II}(THF)_2TPP$." We report here the results obtained from SCF and CI calculations for the different states of the iron(II) porphyrin bis(water) complex $Fe^{II}P(H_2O)_2$ (P = porphine dianion) (Figure 1) considered as a model of the above-mentioned iron(II) porphyrin bis(tetrahydrofuran).[2] In

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(2) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1980**, *102*, 2302.

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