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Nitrogen- and Oxygen-Bonded Urethane: Hydrolysis and Linkage Isomerization of $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$ and $[(NH_3)_5CoOC(NH_2)OCH_2CH_3]^{3+}$

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Coordination of ethyl carbamate via N rather than O to the pentaamminecobalt(III) moiety results in activation toward ligand hydrolysis. The carbonyl oxygen of the carbamate anion and of its ethyl ester (urethane) are preferentially coordinated in kinetically controlled syntheses. Noncoordinating bases facilitate the thermal rearrangement of the O-bound urethane complex in solution to the N-bonded linkage isomer, which has been isolated as its unreactive deprotonated form $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$. Similarly, the N-bound carbamate complex, previously believed to be an intermediate in the acid-induced conversion of $[(NH_3)_5CoNCO]^{2+}$ to $[(NH_3)_6Co]^{3+}$ and CO_2, has been detected for the first time in this reaction by quenching with strong base and chromatographic isolation as the unreactive ion $[(NH_3)_5CoNHCO_2]^+$. In acid solution, the N-coordinated ethyl carbamate complex protonates, giving the reactive entity $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$. Its acidity constant ($pK'_a = 0.38$, 25 °C, $I = 1.0$ M, $NaClO_4$) has been determined kinetically, and this value and the specific rate of decay ($k(\text{obsd}) = 1.21 \times 10^{-2}\ s^{-1}$, 25 °C, H_2O) are very similar to the corresponding numbers for the N-bonded carbamate species. The product distribution for the reaction of the $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$ ion in water is acid-independent (0.1–1.2 M H^+; $I = 1.0$ M, $NaClO_4$, 25 °C), consistent with a single reactive species. The products are $[(NH_3)_6Co]^{3+}$ (40%), $[(NH_3)_5CoOC(NH_2)OCH_2CH_3]^{3+}$ (36%), and $[(NH_3)_5CoOH_2]^{3+}$ (24%). These products arise through three parallel reactions: ligand degradation (CoN–C cleavage, $k_{deg} = 4.84 \times 10^{-3}\ s^{-1}$), intramolecular linkage isomerization ($k_{NO} = 4.36 \times 10^{-3}\ s^{-1}$), and normal aquation (Co–O cleavage, $k_{aq} = 2.90 \times 10^{-3}\ s^{-1}$). No O-bonded carbamate complex $[(NH_3)_5CoOC(NH_2)O]^{2+}$ was detected as a product, even for larger scale product distribution experiments. This observation excludes an elimination pathway to the N-bonded cyanate complex, and it also excludes a primary hydrolysis path of the N-bonded ester complex to the corresponding N-bonded acid or acidate, $[(NH_3)_5CoNH_2CO_2H]^{3+}/[(NH_3)_5CoNH_2CO_2]^{2+}$, since the product distribution for reaction of the latter is acid-dependent, and it results in 2% O-bonded carbamate product at 1 M $HClO_4$. Thus, the ester complex $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$ would appear to decay directly to $[(NH_3)_6Co]^{3+}$, CO_2, and ethanol, and the rate is many orders of magnitude greater than that for reaction of the free urethane ligand. The O-bonded ethyl carbamate complex forms only $[(NH_3)_5CoOH]^{2+}$ in aqueous base and $[(NH_3)_5CoOH_2]^{3+}$ in aqueous acid ($pH < 4$; $k_s = 5.95 \times 10^{-5}\ s^{-1}$, 1 M $HClO_4$, 25 °C). However, at pH values above the pK'_a of the N-bonded species but not so high as to induce base-catalyzed reaction, some O- to N-linkage isomerization (2%) is detectable ($pH = 6.3$, 0.1 M NaMES buffer, $I = 1.0$ M, $NaClO_4$). In dimethyl sulfoxide, only solvolysis is observable. The N-bonded/O-bonded isomer equilibrium is pH-dependent owing to the different acidities of the N- and O-bonded ethyl carbamate complexes. Coordination through the carbonyl oxygen is preferred in aqueous acid ($K'_{NO} = 3570$) and in nonaqueous solution, where the proton of the N-bonded isomer is not dissociated. The N-bonded isomer becomes substantially more stable when coordinated as an anionic ligand ($pH = 6.3$, $K'_{NO}(\text{obsd}) = K'_{NO}[H^+]/([H^+] + K'_a) = 0.004$).

Introduction

Recent interest in the enzymic hydrolysis of urea by the nickel(II)-containing[1] urease has focused on carbamate as a probable intermediate in the reaction[2,3]

$$H_2NCONH_2 + H_2O \rightarrow \{H_2NCO_2H + NH_3\} \rightarrow CO_2 + 2NH_3$$

The precise role of the metal is still unclear, but studies on substrate specificity and inhibition implicate direct coordination of urea to one or two nickel ions and are consistent with an O-bonded intermediate carbamate complex.[2,3]

Neither N- nor O-bonded urea complexes of pentaamminemetal(III) (metal = Co,[4] Rh,[5] Cr,[6] Ru,[7] Os[8]) hydrolyze directly to carbamate complexes, but facile elimination for some urea-*N* complexes was observed:[4d,5,8]

$$[(NH_3)_5M\text{-}NH_2CONHR]^{3+} \rightarrow [(NH_3)_5M\text{-}NCO]^{2+} + NH_3R^+$$

The resulting N-bound cyanate product (M = Co^{III},[9] Rh^{III},[10] Ru^{III}[10]) decomposes rapidly in aqueous acid to hexaamminemetal(III) and CO_2

$$M\text{-}NCO^{2+} + H^+ \rightarrow M\text{-}NCOH^{3+} \xrightarrow{H_2O} M\text{-}NH_2CO_2H^{3+} \rightarrow M\text{-}NH_3^{3+} + CO_2$$

probably via a N-bonded carbamate complex.[11] No well-characterized complexes containing an N-coordinated carbamate ligand have previously been reported. However (carbamate-*O*)pentaamminecobalt(III) was obtained from $[(NH_3)_5CoNCO]^{2+}$ in very strong aqueous acid and this was believed to arise through intramolecular linkage isomerization of a reactive (carbamate-*N*)pentaamminecobalt(III) intermediate complex.[11]

We now report the syntheses and reactivities of the first isolated linkage isomeric metal complexes containing a carbamate ligand. We further report on the intramolecular interconversion of the linkage isomers, factors that determine the mode of coordination of carbamates to the metal ion, and the reactivities of particular tautomers.

Results

Syntheses and Isomer Characterization. The labile complex $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$[12] reacts with excess ethyl carbamate in poorly coordinating solvents (e.g. acetone, sulfolane), forming exclusively the pink O-coordinated linkage isomer $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. It is readily crystallized from water as its dithionate salt. Its visible absorption spectrum (ϵ_{509}^{max} 68.0, ϵ_{343}^{max} 62.5 $M^{-1}\ cm^{-1}$; 0.1 M $HClO_4$) is similar to that for the known O-bonded carbamate complex $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$ (ϵ_{508}^{max} 77.5, ϵ_{356}^{max} 60.8 $M^{-1}\ cm^{-1}$; H_2O),[11] as well

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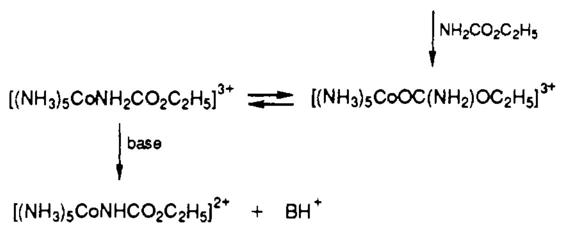
Table I. ^1H NMR Chemical Shifts for Carbamate Complexes and Potential Reaction Products (Me_2SO-d_6 at 35 °C)

	δ, ppm[a]				
substance	cis-NH_3	trans-NH_3	NH/NH_2	CH_2[b]	CH_3[c]
$[(NH_3)_5CoNHC(O)OC_2H_5]^{2+}$	3.27	3.27[d]	2.37	3.93 (4.03[e])	1.13 (1.20[e])
$[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$	4.10	2.75	7.53	4.13 (4.32[e])	1.18 (1.42[e])
$[(NH_3)_5CoO_2C(NH_2)]^{2+}$	3.78	2.65	5.22		
$[(NH_3)_5CoNCO]^{2+}$	3.52	2.97			
$[Co(NH_3)_6]^{3+}$	3.22	3.22			
$NH_2C(O)OCH_2CH_3$			6.32	4.00 (4.13[e])	1.17 (1.23[e])
C_2H_5OH				3.52 (3.70[e])	1.08 (1.18[e])

[a] Relative to TMS. [b] Quartets; all have J_{H-H} = 7 Hz. [c] Triplets; all have J_{H-H} = 7 Hz. [d] Masked by the cis-NH_3 resonance. [e] Solvent D_2O; reference NaTPS.

as the O-bound acetamide[13] and urea-*O*[4a] analogues, all of which have the common CoN_5O chromophore.

In nonaqueous solvents such as dimethyl sulfoxide, dimethylformamide, or trialkylphosphates, noncoordinating bases (NEt_3, 2,2,6,6-tetramethylpiperidine) facilitate thermal rearrangement of the O-bonded ethyl carbamate complex to the deprotonated form of the N-bonded linkage isomer $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ in good yield. This synthesis



$$\begin{tikzcd}
{[(NH_3)_5CoOSO_2CF_3]^{2+}} \arrow[r, "\text{solvent}"] & {[(NH_3)_5Co(solvent)]^{3+}} \arrow[d, "NH_2CO_2C_2H_5"] \\
{[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}} \arrow[d, "\text{base}"] & {[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}} \arrow[l, shift left] \\
{[(NH_3)_5CoNHCO_2C_2H_5]^{2+} + BH^+} &
\end{tikzcd}$$

works equally well when a 10-fold excess of ethyl carbamate is reacted with either $[(NH_3)_5Co(solvent)](ClO_4)_3$ or $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ under similar conditions. The method relies on the greater thermodynamic stability and chemical inertness of $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ over $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. Under the forcing experimental conditions the reaction is driven to the left; small amounts of $[Co(NH_3)_6]^{3+}$ and $[(NH_3)_4Co(NHCO_2C_2H_5)_2]^+$ were also present in the product mixture.

The orange $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ complex has an absorption spectrum (ϵ_{495}^{max} 80.8, ϵ_{353}^{max} 105.1 M^{-1} cm^{-1}) similar to those of the related complexes $[(NH_3)_5CoNHCONH_2](ClO_4)_2$ (ϵ_{498}^{max} 90.4, ϵ_{350}^{max} 125 M^{-1} cm^{-1})[4c] and $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$ (ϵ_{484}^{max} 73.9, ϵ_{344}^{max} 87.3 M^{-1} cm^{-1})[13] in aqueous 0.1 M Tris. As a 2+ ion, it can also be identified by its order of elution from SP-Sephadex C-25 cation-exchange resin ($[Co(NH_3)_6]^{3+}$ < $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ < $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ < $[(NH_3)_5Co(OH_2)]^{3+}$ < $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ < $[(NH_3)_5CoNCO]^{2+}$ < $[(NH_3)_4Co(NHCO_2C_2H_5)_2]^+$) using 0.23 M Na^+ (pH 7, 0.2 M Cl^-, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}) aqueous eluant.

The ^1H NMR data (Table I) distinguish the N- and O-bound ethyl carbamate complexes from each other and their potential impurities. Complexes[4c,14] with a CoN_5O coordination environment have well-separated resonances for the ammines cis (12 H) and trans (3 H) to the sixth ligand, whereas CoN_6 complexes often show coincident signals for these protons. The location (δ 2.37 ppm) of the Co–NH proton of $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ is similar to that for $[(NH_3)_5CoNHCONRR']^{2+}$ (NRR' = NH_2, NHMe, NMe_2, NHPh; δ 1–2 ppm)[4c] and upfield of the corresponding signal for the amide analogues $[(NH_3)_5CoNHCOR]^{2+}$ (R = H, alkyl, aryl; δ 3.5–6 ppm).[13]

The exo-NH_2 protons for $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ appear as a singlet (δ 7.53) in the ^1H NMR spectrum (Me_2SO-d_6) at 60 MHz (35 °C) but are resolved[15] at 300 MHz (18 °C) into two 1 H singlets (δ 7.05, 7.95) either side of the 2 H singlet. Clearly at the lower field strength and higher temperature these protons have coalesced, and we are observing a restricted rotation phenomenon. [A similar observation has been reported recently for the amidine complex $[(NH_3)_5CoNHC(NH_2)CH_3]^{3+}$.[16]] Interestingly, the free ligand shows only a singlet for the NH_2 protons (δ 6.42) even at 300 MHz and 18 °C. These observations parallel those reported for amides and ureas and their O-bonded pentaamminecobalt(III) complexes and are consistent with an increase in the C–N bond order on coordination.[17] Urethane appears to lie between amides and ureas in terms of ease of rotation about the C=N bond.

The ^{13}C NMR chemical shifts for $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ (δ 162.15 pm, C=O; 58.89, CH_2; 14.96, CH_3) are quite distinct from $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ (162.38, C=O; 63.65, CH_2; 13.93, CH_3), $[(NH_3)_5CoO_2CNH_2]^{2+}$ (166.19, C=O), $[(NH_3)_5CoNCO]^{2+}$ (127.34, C=O), and free ligand $NH_2CO_2C_2H_5$ (156.84, C=O; 59.28, CH_2; 14.65, CH_3) in Me_2SO-d_6.

The large difference in acidities of the complexes containing neutral ethyl carbamate as a N-donor (pK'_a ~ 0.4) and an O-donor (pK'_a ~ 13) ligand is a property consistent with analogous complexes of amides,[13] ureas,[4-8] sulfamate,[18] sulfinamides,[13] and sulfonamides.[13] This pK'_a difference was usefully exploited in product analysis experiments detailed ahead.

Reactivity of Ethyl Carbamate-*N* Isomer. Expectations of obtaining $[(NH_3)_5CoNHCO_2]^{2+}$ through ester hydrolysis of the deprotonated N-bound ethyl carbamate complex $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ in aqueous base were not realized. No reaction was detected in 0.1 M NaOD, and the ethyl carbamate complex appears to be indefinitely stable in D_2O or Me_2SO-d_6 at ambient temperature. Prolonged heating (>4 h, 80–90 °C) of $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ in dimethyl sulfoxide containing a sterically hindered base did produce, however, a small quantity of $[(NH_3)_5CoNCO]^{2+}$. This reaction, elimination of ethanol, parallels the synthesis of $[(NH_3)_5CoNCO]^{2+}$ from $[(NH_3)_5CoOH_2]^{3+}$ and urea under forcing conditions.[9,11]

In aqueous $HClO_4$, $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ reacts rapidly to form $[Co(NH_3)_6]^{3+}$, $[(NH_3)_5CoOH_2]^{3+}$, and $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ (Table II). After reaction for 10 min (25 °C) in 1.17 M $HClO_4$, four cationic species were observed following ion-exchange chromatography on Sephadex cation-exchange resin. Two of the products were identified, following separation, by visible absorption spectra as $[Co(NH_3)_6]^{3+}$ (33%) and $[(NH_3)_5CoOH_2]^{3+}$ (21%); there was also some unreacted $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ (14%). The other product was pink (λ_{max} 504, 341 nm), and it eluted as a 3+ ion well behind $[(NH_3)_5CoOH_2]^{3+}$ but just ahead of $[Co(NH_3)_6]^{3+}$, as indicated in Table II.

The reaction was also monitored by ^1H NMR spectroscopy in acidic D_2O. Three sets of matching methyl and methylene proton resonances were observed, and the identities of two of these ethyl-containing products were established as free ethyl carbamate and ethanol by addition of authentic compounds to the NMR tube

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Table II. Product Distribution Data for Reactions of $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2{\cdot}H_2O$ in Acid Media at 25.0 °C

		distribution, %[a]				
		$HClO_4$			Me_2SO	
products	R_f[b]	0.117 M[c]	0.17 M	1.17 M	CH_3SO_3H[d]	CF_3SO_3H[d]
$[Co(NH_3)_6]^{3+}$	2.8	39.5	39.9	38.6	9.9	8.8
$[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$	3.5	36.2	34.8	39.4		
$[(NH_3)_5CoOS(CH_3)_2]^{3+}$	4.0				72.2	91.2
$[(NH_3)_5CoOH_2]^{3+}$	5.5	24.3	25.3	22.0		
$[(NH_3)_5CoOSO_2CH_3]^{2+}$	10.0				17.9	

[a] Data normalized for 100% reaction (see Experimental Section). [b] Relative distances travelled by ions on SP-Sephadex C-25 resin; eluant = 0.23 M Na^+ (pH 6.88; 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-). [c] I = 1.17 M ($NaClO_4$). [d] [Acid] = 5 × [Co]; the hexaammine product arises from hydration by the lattice water.

Table IV. Product Analysis[a] and Solvolysis Rate Constants for Reactions of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ at 25.0 °C

reagent	% CoN^{2+}[e]	% $Co(OH_2)^{3+}$[e]	10^5k(obsd), s^{-1}[b]
0.1 M NaOH[c]	0	100	
0.1 M NaMES[c,d]	2.0	98.0	6.14 (±0.08)
0.1 M $HClO_4$[c]	0	100	5.47 (±0.06)
1.0 M $HClO_4$[c]	0	100	5.95 (±0.08)
Me_2SO	0	100[f]	

[a] Data normalized for 100% reaction. [b] Determined at 520 nm; mean of ≥3 determinations (standard deviations ≤±3%). [c] I = 1.17 M ($NaClO_4$). [d] pH 6.3 (half-neutralized with NaOH). [e] CoN^{2+} is $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$; $Co(OH_2)^{3+}$ is $[(NH_3)_5Co(OH_2)]^{3+}$. [f] Product here is $[(NH_3)_5CoOS(CH_3)_2]^{3+}$.

at the end of the experiment. The third set of resonances was established by the same method to be attributable to $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. These slowly diminished over 1 h (35 °C), consistent with the rate of aquation of the O-bonded isomer reported ahead (Table IV). Commensurate with their demise, resonances due to ethyl carbamate (but not ethanol) increased in intensity. These observations support the chromatographic evidence for formation of an O-bonded ethyl carbamate complex $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ from the N-bonded isomer in aqueous acid and indicate that it hydrolyses via simple Co–O cleavage; there was no detectable hydrolysis of the ligand.

The visible absorption spectrum of $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ in 1.17 M $HClO_4$ changes rapidly with time. There was an initial fast reaction with large absorbance decreases around 300 nm, followed by a much slower reaction involving an absorbance decrease in the 450–550-nm region. The specific rate for the second stage corresponded with that independently determined for the O-bonded urethane complex (vide infra). The O-bonded urethane species is the only first formed product that reacts further, a significant observation that excludes the formation of appreciable N-bonded cyanate or N-bonded carbamate complexes, which under the conditions react at rates comparable to that of the N-bonded urethane complex and which could have appeared in the kinetics as a detectable consecutive reaction. Chromatography of the products at long reaction times for the N-bonded isomer (60 min, $>10t_{1/2}$) revealed the three products and no residual reactant.

Product distribution data for reactions of $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ in acidic water and dimethyl sulfoxide are summarized in Table II. The product distributions are very similar for 0.117 M H^+ and 1.17 M H^+ (I = 1.17 M, $NaClO_4$), consistent with a single reactive species, i.e., the protonated N-bonded urethane complex. In acidic dimethyl sulfoxide, some $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ is initially formed from the N-bonded isomer, as established by ^1H NMR spectroscopy, but subsequent solvolysis rapidly leads to $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ and free ethyl carbamate; therefore the precise amount is not known. When the acid was $MeSO_3H$, a considerable amount of a 2+ ion (λ_{max} 499 nm) was also detected in the product distribution (Table II). It was identified as $[(NH_3)_5CoO_3SCH_3]^{2+}$ by its rate of solvolysis[12] and its absence in identical experiments using CF_3SO_3H instead of CH_3SO_3H. This result highlights the greater coordinating property of $CH_3SO_3^-$ relative to $CF_3SO_3^-$.[12] No $[(NH_3)_5CoNCO]^{2+}$ was detected in these experiments, yet this ion is stable[4d] in dry acidic Me_2SO. In a large scale experiment (>1 g), $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ when reacted in Me_2SO/CF_3SO_3H still failed to yield any detectable 2+ ion, thereby limiting the amount of $[(NH_3)_5CoNCO]^{2+}$ formed to <0.05%.

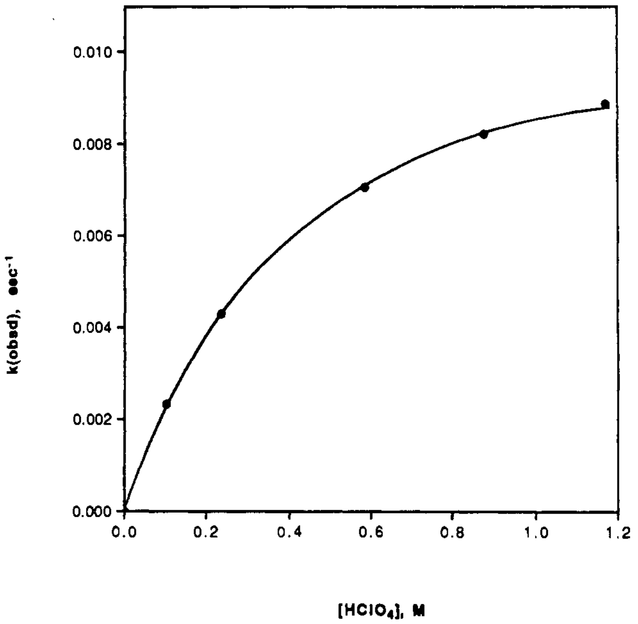
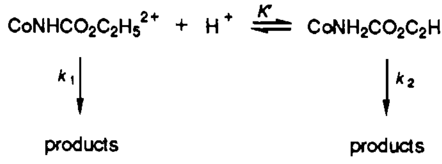


Figure 1. Plot of k(obsd) against $[H^+]$ for the reaction of $[(NH_3)_5CoNHC(O)OC_2H_5]^{2+}$ in $HClO_4$ at 25 °C, I = 1.2 M ($NaClO_4$).

A kinetic study of the fast primary reaction of the urethane-*N* complex (0.1–1.17 M $HClO_4$, I = 1.0 M, $NaClO_4$, 25.0 °C) using absorbance data collected at 300 nm produced excellent first-order rate fits, k(obsd) ± 1% (Table III, supplementary material). A plot of k(obsd) versus $[H^+]$ clearly indicates that protonation does occur, but it is incomplete even in 1.17 M $HClO_4$ (Figure 1). From k(obsd) vs $[H^+]$ data the parameters for the rate law $k(\mathrm{obsd}) = (k_1 + k_2K'[H^+])/(1 + k'[H^+])$ appropriate to the reaction scheme



were obtained by using a nonlinear least-squares analysis. Since k_1 is negligible (the deprotonated N-bonded isomer is essentially inert), the rate law simplifies to $k(\mathrm{obsd}) = k_2k'[H^+]/(1 + k'[H^+])$ or $k(\mathrm{obsd})^{-1} = (k'k_2)^{-1}[H^+]^{-1} + 1/k_2$. The linearity of the plot of $k(\mathrm{obsd})^{-1}$ versus $[H^+]^{-1}$ (Figure 2) indicates that the fit is good and the mechanistic model reasonable, and of course this is also reflected in the standard deviations obtained by the (better) weighted nonlinear regression analysis. From the double reciprocal plot, $1/k'k_2 = 34.9$ and $1/k_2 = 82.2$. Thus, $k_2 = 1.22 \times 10^{-2}\ s^{-1}$ and $K' = 2.35$; $K'_a = 1/K' = 0.425$, and $pK'_a = 0.37$. From the weighted nonlinear regression analysis, $k_2 = (1.21 \pm 0.01) \times 10^{-2}$

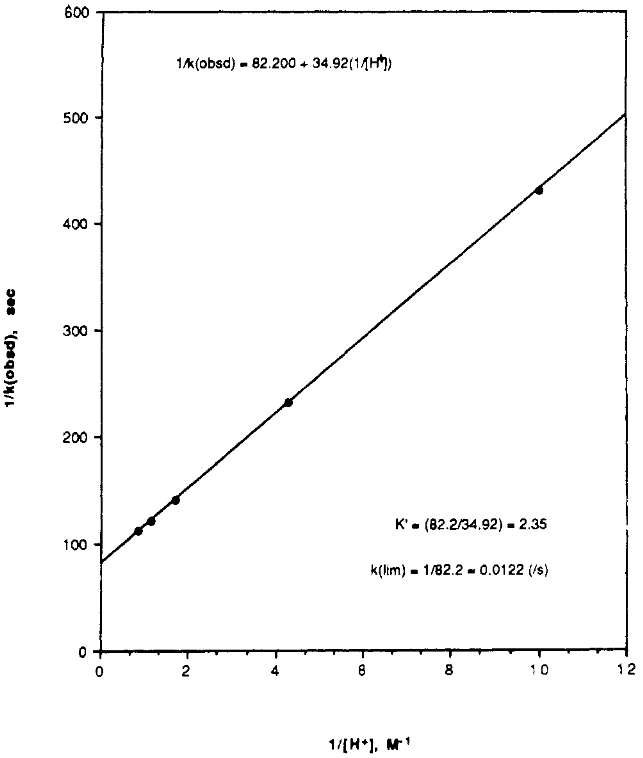


Figure 2. Double reciprocal plot of the data shown in Figure 1 used to evaluate the acidity constant and limiting specific rate for $[(NH_3)_5CoNH_2C(O)OC_2H_5]^{3+}$.

s^{-1} and $K' = 2.37 \pm 0.035$; thus, $K'_a = 0.42$ ($pK'_a = 0.38$).

Reactivity of Ethyl Carbamate-*O* Isomer. Chromatographic analysis of solutions of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ in aqueous $HClO_4$ (0.1 M, 1.0 M) indicates that the O-bonded isomer reacts entirely to give $[(NH_3)_5CoOH_2]^{3+}$. This process has a half-life of ~3 h (25 °C), similar to the rate of aquation of $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ under identical conditions.[4a,c] Note that in view of its acidity and reactivity in aqueous acid, the N-bound linkage isomer (if formed from the O-bonded isomer) would decompose in aqueous $HClO_4$ to give the stable hexaamine complex. However, no $[Co(NH_3)_6]^{3+}$ was detected, so O- to N-bonded rearrangement clearly does not occur at low pH. Similarly in dimethyl sulfoxide, only $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ is formed from $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ (sharp isosbestic points at 562 and 402 nm), but solvolysis appeared to be faster ($t_{1/2} \sim 4$ min, 25 °C; ca. 40-fold) than in water (Table IV). This acceleration parallels that observed[4d] for $[(NH_3)_5CoOC(NH_2)NHC_6H_5]^{3+}$ although it is much more dramatic in the present case. The analogous urea[4c] and amide[13] complexes show a much smaller and reverse trend in solvolysis rates for H_2O and Me_2SO. Steric bulk is insufficient to account for these solvolyses anomalies, since the analogous O-bonded benzamide complex[13] does not exhibit this behavior. Possibly the phenyl substituent in $[(NH_3)_5CoOC(NH_2)NHC_6H_5]^{3+}$ may be twisted out of the plane of the carbamate/urea ligand thereby contributing more effectively to solvent destructuring.

It should be noted that the slow aqueous acid rate and fast Me_2SO rate for the urethane-*O* complex were perchance reproducible for two samples of the dithionate salt prepared six years apart, yet conversion to the perchlorate salt in the presence of edta (to trap any Co(II) gave a material that solvolyzed substantially slower in Me_2SO. This curious phenomenon, catalyzed substitution in one solvent and not another, is often a problem in these systems and has been traced to Co(II) catalysis. Care need be exercised in identifying it, since the kinetics are often still simple first-order and can be reproducible.

In 0.1 M NaOH (I = 1.0 M) only $[(NH_3)_5CoOH]^{2+}$ was detected from the base hydrolysis of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. Under these conditions, $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ is stable and would have been detectable if formed in >0.5% yield through O- to N-linkage isomerization isomerization. At pH 6.3 (0.1 M NaMES buffer, I = 1.0 M), some (2%) O- to N-linkage isomerization did compete with aquation (98%) (Table IV). Since the same sample of O-bonded isomer was used for all product analyses, it is clear that the observed $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ was not a low-level impurity in the O-bonded isomer.

Preparation and Reactivity of Isomeric Complexes of the Carbamate Anion. The O-bonded carbamate complex $[(NH_3)_5CoO_2CNH_2]^{2+}$ is available via several synthetic routes and is quite stable in neutral or basic aqueous solution. In strongly acidic solutions the complex slowly aquates ($k = 1.98 \times 10^{-5}\ s^{-1}$, 1 M $HClO_4$, 25 °C)[19] due to partial protonation ($pK'_a \sim 1$).[20] The remote nitrogen atom of the O-bound carbamate ligand appears to be the more basic site, a conclusion supported by results[20] from this laboratory.

$$[(NH_3)_5CoO_2CNH_2]^{2+} + H^+ \overset{K}{\rightleftharpoons} [(NH_3)_5CoO_2CNH_3]^{3+} + H^+ \xrightarrow[H_2O]{k} [(NH_3)_5CoOH_2]^{2+}$$

By contrast free carbamic acid (HO_2CNH_2) protonates on the carbonyl oxygen atom (−60 °C, $FSO_3H/SbF_5/SO_2$).[21]

The N-bonded carbamate isomer has been observed but not isolated. Attempts to capture the N terminus of the carbamate anion in the base-catalyzed reaction of $[(NH_3)_5CoOSO_2CF_3](ClO_4)_2$ in aqueous 0.1 M Tris/1.0 M $NH_4^+NH_2CO_2^-$ (15–30 s, 25 °C) were unsuccessful. The reaction mixture was quenched (to pH < 2) with strong HCl and left for sufficient time (5 min) to ensure complete conversion to any N-bonded carbamate complex to the inert $[Co(NH_3)_6]^{3+}$. None (>0.5%) was detected. The reproducible result was ~2% $[(NH_3)_5CoO_2CNH_2]^{2+}$ (a stable ion under these conditions) and 98% $[(NH_3)_5CoOH_2]^{3+}$. Similar experiments with NO_2^- and SCN^- give ~7% capture as a mixture of linkage isomers.[22] Clearly the carbamate anion is a poorer competitor for pentaamminecobalt(III) via the base-catalyzed route, and it resembles I^-, Cl^-, Br^-, and $CH_3CO_2^-$ (2–3% capture) in this regard.[22] Moreover, the O-terminus of $NH_2CO_2^-$, which is more basic toward H^+ than the N-terminus, is also the more nucleophilic atom toward pentaamminecobalt(III), the nitrogen terminus resembling NH_3 (and OH^-, F^-, CO_3^{2-}, and others) in this regard.

Noting that the $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ ion was unreactive in basic and even neutral solution, we reasoned that the intermediate N-bonded carbamate complex formed in the acid-catalyzed conversion[11]

$$[(NH_3)_5CoNCO]^{2+} \xrightarrow{k_a} [(NH_3)_5CoNH_2CO_2H]^{3+} \xrightarrow{k_b} [(NH_3)_5CoNH_3]^{3+}$$

could be stabilized by double deprotonation as the $[(NH_3)_5CoNHCO_2]^+$ ion. Moreover, its rate of formation was much faster than its rate of consumption in strong aqueous acid ($k_a/k_b = 22$ (3 M $HClO_4$), 53 (3 M HNO_3), 66 (3 M HCl). Consequently, $[(NH_3)_5CoNCO]^{2+}$ was briefly reacted in strong aqueous acid (<10 s) before quenching with strong base. Ion-exchange chromatography of the products revealed the formation of a pink 1+ ion (15% total cobalt), along with unreacted red $[(NH_3)_5CoNCO]^{2+}$ (50%) and yellow $[Co(NH_3)_6]^{3+}$ (35%). Moreover, the 1+ ion transformed quantitatively to $[Co(NH_3)_6]^{3+}$ in acidic aqueous solution, thereby establishing its identity as the N-bonded carbamate and also affording a means of determining its concentration. The $[(NH_3)_5CoNHCO_2]^+$ ion was characterized by a visible absorption spectrum ($\epsilon_{507}^{max} \sim 99$, $\epsilon_{358}^{max} \sim 185$) typical of $[(NH_3)_5CoNHCOR]^{2+}$ ions. Attempts to isolate crystals of the pure product have so far been thwarted by the high

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(19) Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027.

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(21) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 405.

(22) Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; p 273.

solubility in water of the ClO_4^- salt as well as the relatively fast ensuing decarboxylation to $[Co(NH_3)_6]^{3+}$ in neutral to acidic solution.

Discussion

We have reported selective syntheses for both N- and O-bonded ethyl carbamate complexes of pentaamminecobalt(III), and these are elaborated elsewhere[13] in connection with preparations of amide, urea, sulfinamide, sulfonamide, and sulfamate analogues. The linkage isomers have been readily distinguished on the basis of their electronic absorption spectra, NMR (^1H, ^{13}C) chemical shifts, ion-exchange properties, acidities, and reactivities.

A fundamentally important distinction between the isomers lies in their widely differing acidities

$$CoNH_2CO_2C_2H_5 \xrightleftharpoons{K'_N} CoNHCO_2C_2H_5 + H^+$$

$$CoOC(NH_2)OC_2H_5 \xrightleftharpoons{K'_O} CoOC(NH^-)OC_2H_5 + H^+$$

Electron density is more effectively removed from the ^-NH-$C(:O)OC_2H_5$ ligand when it is N- rather than O-bonded to the acidic metal ion, and thus ethyl carbamate is appreciably more acidic when N-coordinated ($pK'_N \sim 0.38$) rather than O-bonded (pK'_O(estd) ~ 13) to $(NH_3)_5Co^{III}$. This distinction is common to other ambident molecules[4-8,11-14,18] bound to highly charged metal ions and is not simply attributed to differing proximities of the acidic proton to the electron-withdrawing metal center. It should be noted that it is not always the proton on the bound atom that is the more acidic; $[(NH_3)_5Co(NH_2C(O)R)]^{3+}$ (R = alkyl) for example exists as $[(NH_3)_5CoNHC(OH)R]^{3+}$ rather than $[(NH_3)_5CoNH_2C(O)R]^{3+}$ in acid solution, whereas for R = NH_2 the converse is true.[4c,13a]

This effect dramatically influences the position of the linkage isomer equilibrium:

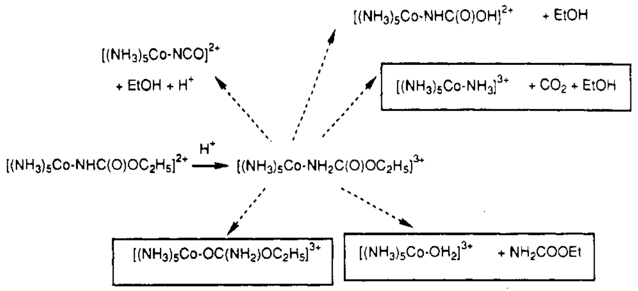
$$\begin{tikzcd}
CoNH_2CO_2C_2H_5^{3+} \arrow[r, shift left, "k_{NO}"] \arrow[d, shift left] & CoOC(NH_2)O_2C_2H_5^{3+} \arrow[l, shift left, "k_{ON}"] & K_{NO} = k_{NO}/k_{ON} \\
CoNHCO_2C_2H_5^{2+} + H^+ \arrow[u, shift left, "K'_a"]
\end{tikzcd}$$

The observed isomer distribution varies with pH as

$$K'_{NO}(\text{obsd}) = [\text{O-bonded isomer}]/[\text{total N-bonded isomer}] = K'_{NO}[H^+]/(K'_a + [H^+])$$

We sought to determine K'_{NO} by measuring the specific rates k_{NO} and k_{ON}, noting that ethyl carbamate is an uncharged ligand only in strong aqueous acid. From the analysis of the data in Table III (supplementary material), the limiting rate constant for reaction of $[(NH_3)_5CoNH_2C(O)OC_2H_5]^{3+}$ in aqueous $HClO_4$ is 1.21×10^{-2} s^{-1} (25 °C), and by use of the known product distribution (Table II), the specific rate of N- to O-linkage isomerization k_{NO} was determined as $0.36 \times 1.21 \times 10^{-2} = 4.36 \times 10^{-3}$ s^{-1}. In strong acid solution no O- to N-bonded isomerization of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ is observed because of the unfavorable equilibrium position (vide infra), but by use of the product distribution and specific rate for its reaction at pH 6.3 (Table IV) where isomerization and aquation do compete, and by assumption of negligible base-catalyzed reaction of the O-bonded isomer at this pH, k_{ON} can be evaluated as $0.020 \times 6.1 \times 10^{-5} = 1.22 \times 10^{-6}$ s^{-1}, as discussed previously.[4c] Thus, the equilibrium constant ($K'_{NO} = k_{NO}/k_{ON} = 3570 \pm 300$) indicates that, under conditions where ethyl carbamate is uncharged as either an N- or O-bound ligand on $(NH_3)_5Co^{III}$, the O-coordinated linkage isomer is the thermodynamically more stable form by 20.3 kJ mol^{-1} at 25 °C ($\Delta G° = -RT \ln K'_{NO}$). This preference, expected on the basis of the high charge/size ratio or "hard" nature of this metal ion, would normally preclude observation of the energetically unfavorable O- to N-linkage isomerization were it not for the selective higher acidity of the N-bonded isomer. Thus, the N-bonded isomer assumes thermodynamic stability over the O-bonded isomer in the weakly acidic, neutral, or alkaline region (e.g. pH 6.3, $K'_{NO}(\text{obsd}) = (3570 \times 5.01 \times 10^{-7})/(5.01 \times 10^{-7} + 0.42) = 4.25 \times 10^{-3}$).

Scheme I



The O- to N-bonding rearrangement is undoubtedly base catalyzed as observed[4c] for linkage isomerization of $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ and likely obeys the same rate law: $k(\text{obsd}) = k_s + k_{OH}[OH^-]$. However, we were unable to detect this process in aqueous 0.1 M NaOH, thus setting an upper limit of about 0.2% $[(NH_3)_5CoNHC(O)OC_2H_5]^{2+}$ by this route. This result, which is attributed to greater base catalysis of the aquation route than the isomerization path, is consistent with observations made for the reactions of $[(NH_3)_5CoOC(NH_2)R]^{3+}$ (R = NH_2, NHMe, NMe_2, NHC_6H_5)[4c] and other complexes[13,23] where linkage isomerization competes significantly better with aquation at neutral than at high pH. An account has been offered.[4c]

The reactivity of (ethyl carbamate-*N*)pentaamminecobalt(III) in water (0.1 M < $[H^+]$ < 1.2 M) can be described by Scheme I. The unreactive form $[(NH_3)_5CoNHC(O)OC_2H_5]^{2+}$ protonates in strongly acidic solution to give the labile conjugate acid $[(NH_3)_5CoNH_2C(O)OC_2H_5]^{3+}$. We have no direct evidence for the site of protonation because first we cannot protonate it fully and second it is too reactive to readily observe by NMR spectroscopy.

By analogy with the known reactions of other $[(NH_3)_5CoNHC(O)R]^{2+}$ complexes, the possibilities for reaction of the protonated N-bonded isomer $[(NH_3)_5CoNH_2C(O)OC_2H_5]^{3+}$ are shown in Scheme I. The products actually observed (chromatography and NMR) are shown boxed, and it remains to consider the possibility that one or more of the other paths are transient routes. [Note that the ethyl esters of carbonic acid are not stable species in water.]

The N-bonded cyanate complex was sought by separately carrying out reactions with dilute aqueous acetic acid and with acidic dimethyl sulfoxide. In Me_2SO this ion is trapped, since water is required for its subsequent hydration, while in dilute acid its subsequent reaction is slowed to the point where it can be observed (note that the rate of the generating reaction is also slowed). Such experiments, which were successful[4d] in identifying $[(NH_3)_5CoNCO]^{2+}$ as an intermediate in the facile degradation of $[(NH_3)_5CoNH_2CONHC_6H_5]^{3+}$ to $[Co(NH_3)_6]^{3+}$, failed to reveal any N-bonded cyanate species, and we are therefore confident that it is not formed here.

The other possibility, prior ester hydrolysis to give $[(NH_3)_5CoNH_2CO_2H]^{3+}$ and C_2H_5OH, was more difficult to dismiss as a route through to $[(NH_3)_5CoNH_3]^{3+}$, CO_2, and C_2H_5OH. First, the rates of reaction of $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$ (primary) and $[(NH_3)_5CoNH_2CO_2H]^{3+}$ (secondary) under the conditions would be comparable, and hence consecutive reactions should be observed in the kinetics. None were observed, although we are mindful of the pitfalls in this argument. Far more compelling however is the conclusion drawn from careful chromatographic product analyses. The reaction of $[(NH_3)_5CoNH_2CO_2H]^{3+}$ involves three parallel paths,[11] the main one giving $[(NH_3)_6Co]^{3+}$ but the minor ones yielding $[(NH_3)_5CoOC(O)NH_2]^{2+}$ and $[(NH_3)_5CoOH_2]^{3+}$. Furthermore, the product ratio distribution is both pH- and medium-dependent, especially the latter. The pH dependence

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arises because $[(NH_3)_5CoNHCO_2H]^{2+}$, unlike the urethane analogue, is reactive and contributes to the products, and $[(NH_3)_5CoNHCO_2H]^{2+}$ and its protonated form $[(NH_3)_5CoNH_2CO_2H]^{3+}$ give different product distributions. The most significant difference however is the appearance of the 2+ ion $[(NH_3)_5CoOCONH_2]^{2+}$ among the products for the N-bonded carbamate species, especially in strong $HClO_4$, whereas the corresponding product in the urethane system is the 3+ O-bonded ion $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$ (which ultimately hydrolyses, but without ester hydrolysis, and hence it does not form $[(NH_3)_5CoOCONH_2]^{2+}$). Thus, any prior ester hydrolysis would quickly lead to some O-bonded carbamate complex. In larger scale experiments designed to detect the 2+ ion, none (<0.05%) was observed; hence, any significant reaction pathway via an initial ester hydrolysis reaction yielding $[(NH_3)_5CoNH_2COOH]^{3+}$/ $[(NH_3)_5CoNHCOOH]^{2+}$ can be discounted. The result confirms that an elimination path producing $[(NH_3)_5CoNCO]^{2+}$ is absent also, since this ion reacts via the N-bonded carbamate through to an identical product distribution that includes the 2+ O-bonded carbamate species.

In hindsight, this is not an especially surprising result because even the O-bonded urethane complex, much less reactive than the N-bonded form, provides no detectable ester hydrolysis path in competition with the slow aquation reaction, and the activated carbonyl center in question is the same number of bonds removed from the polarizing metal ion.

Some comment on the vastly different reactivities of $[(NH_3)_5CoNHC(O)OH]^{2+}$[11] and $[(NH_3)_5CoNHC(O)OC_2H_5]^{2+}$ is appropriate. The former can adopt the tautomeric $[(NH_3)_5CoNH_2COO]^{2+}$ form whereas the latter cannot, and clearly this species is better disposed toward the ready elimination of CO_2 to yield the hexaammine complex. In contrast, the analogy for the 3+ ions is very close, with respect to both the acidity ($pK'_a = 0.38$ for urethane, 0.37 inferred for carbamate[11]) and rate of reaction (25 °C, $k = 1.2 \times 10^{-2}\ s^{-1}$ for urethane, 0.8×10^{-2} for carbamate[11]). However, in the study of the N-bonded carbamate system,[11] it was deduced from the $[H^+]$-dependent (and/or medium-dependent) product distribution that $[(NH_3)_5CoNH_2CO_2H]^{3+}$ reacted only via linkage isomerization and direct aquation, while the conjugate base $[(NH_3)_5CoNHCO_2H]^{2+}$ (or its tautomer $[(NH_3)_5CoNH_2CO_2]^{2+}$, as we have argued) was believed solely responsible for rapid decarboxylation ($k \sim 3.8 \times 10^{-1}\ s^{-1}$) to CO_2 and $[Co(NH_3)_6]^{3+}$. In the light of the results for the urethane system, it would seem probable that $[(NH_3)_5CoNH_2CO_2H]^{3+}$ like $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$ also gives some hexaammine complex, and this aspect of the original work could merit reexamination.

While free urethane survives for hours in strong acid and base, free carbamic acid NH_2COOH is relatively unstable, suggesting the zwitterion $^+NH_3CO_2^-$ as the reactive entity. A similar configuration is achieved for urethane ($^+NH_3C(O)OC_2H_5$) by protonation, and the reactive N-bonded urethane complex is analogous to this. Clearly, metal ion coordination through the N-center has substantially activated the molecule. In contrast, urethane is not *detectably* activated through O-coordination, since we did not observe ester hydrolysis in competition with Co–O cleavage in either acid- or base-catalyzed hydrolysis.

The ligands phenylurea[4d] and the carbamate ion itself resemble urethane in that ligand activation is via N-coordination rather than O-coordination, and in this respect they should be contrasted with molecules such as amides, where O-coordination provides the demonstrable ligand activation.[13,24] The point to the gleaned is that both bonding modes can be effective, and what appears to be the more effective bonding mode could simply be the result of the inability to observe the desired reaction while a competitive side reaction dominates.

Finally, the ligand hydrolysis reaction of the N-bonded urethane complex may be contrasted with elimination of anilinium ion[4d] from $[(NH_3)_5CoNH_2CONHC_6H_5]^{3+}$. While both are facile reactions for Co(III) complexes, it is evident that the R substituent in $[(NH_3)_5CoNHCOR]^{2+}$ has a profound effect on the course of reaction of the conjugate acid.[4c,d,11,13]

Experimental Section

NMR spectra were recorded on complexes in anhydrous $Me_2SO\text{-}d_6$ (internal reference TMS) or D_2O (internal reference NaTPS) on a Jeol 90FXQ Fourier transform spectrometer with quadriture detection or Varian T60 continuous-wave instrument (probe temperature 35 °C). Visible absorption spectra were measured on Cary 118C and 210 spectrophotometers.

Kinetic measurements were obtained by rapidly dissolving the solid complexes (10^{-4}–10^{-5} M) in solutions that had been thermally preequilibrated (25.0 ± 0.1 °C) in the cell compartment of the spectrophotometer, and full spectra or absorbance–time traces (300, 520, 540 nm) were recorded without delay. Cell temperatures were measured with a miniprobe accurate to ±0.02 °C and calibrated against a Hewlett-Packard quartz-crystal thermometer. The spectrophotometer cell block was thermostated by a Lauda bath (25 ± 0.05 °C).

$[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3\cdot 3H_2O$. Ethyl carbamate (2 g, 22 mmol) and $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (2 g, 3.4 mmol) were reacted in sulfolane (5 mL) for 10 min at 20 °C. Portions of diethyl ether were added and decanted repeatedly until a solid pink precipitate had formed. This product was dissolved in a minimum volume of ice water and filtered through a fine-porosity frit into a cold saturated aqueous solution of $Li_2S_2O_6$. Pink crystals, which separated from the orange supernatant, were recrystallized from cold H_2O/acetone, collected by vacuum filtration, and washed successively with ice water (3 × 5 mL), cold absolute ethanol (5 mL), and diethyl ether (15 mL). Yield: 0.8 g.

Alternatively ethyl carbamate (5 g, 56 mmol) and $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$ (5 g, 8.5 mmol) were reacted in acetone (10 min, 20 °C). The acetone was removed by rotary evaporation, and the red oil was treated with ice-cold aqueous $Na_2S_2O_6$ causing precipitation of pink crystals, which were washed as above to remove traces of the more water-soluble orange $[Co(NH_3)_5OH_2]_2(S_2O_6)_3$. Yield: 2.15 g (51%). Electronic spectrum: ϵ_{509}^{max} 68.0, ϵ_{343}^{max} 62.5 (0.1 M $HClO_4$). ^{13}C NMR (δ, ppm downfield of TMS in $Me_2SO\text{-}d_6$): 162.38 (C=O), 63.65 (CH_2), 13.93 (CH_3).

The perchlorate salt was made from the dithionate by triturating a thin paste of the finely ground dithionate salt with cold 5 M $HClO_4$. After 10 min, the product was collected, washed with ethanol and ether, dried, and recrystallized from water containing Na_2edta (0.01 M) by using aqueous $NaClO_4$ (5 M) as the precipitant.

$[(NH_3)_5CoNHCOOC_2H_5](ClO_4)_2$. Ethyl carbamate (15.5 g, 174 mmol) and $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3\cdot H_2O$ (10 g, 18.5 mmol) were reacted in Me_2SO (25 mL) with $N(C_2H_5)_3$ (80 mmol) for 4 h (70–80 °C). Addition of butan-2-ol (30 mL) and diethyl ether (1 L) to the cooled reaction mixture precipitated quantitatively the cobalt complexes. They were dissolved in water, the solution was sorbed on SP-Sephadex C-25 cation-exchange resin, and the fractions were separted with 0.23 M Na^+ (0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-, pH 6.88) eluant. $[(NH_3)_5CoNHCOOC_2H_5]^{2+}$, which eluted as an orange 2+ ion behind a trace of a lilac 1+ ion and adhead of $[Co(NH_3)_6]^{3+}$, was removed from the column with 0.5 M $NaClO_4$ and isolated as the perchlorate salt following evaporation of water at reduced pressure. ^1H NMR spectroscopy indicated that the complex was the monohydrate. Storage in vacuo over P_2O_5 resulted in the anhydrous salt. Yield: 5.6 g (70%). Anal. Calcd: C, 8.35; H, 4.87; N, 19.49; Cl, 16.47. Found: C, 8.28; H, 4.92; N, 19.23, Cl, 16.31. Electronic spectrum: ϵ_{495}^{max} 80.8, ϵ_{353}^{max} 105.1 (0.1 M Tris). ^{13}C NMR (δ, ppm downfield of TMS in $Me_2SO\text{-}d_6$): 162.15 (C=O), 58.89 (CH_2), 14.96 (CH_3).

$[(NH_3)_5CoNHCO_2]^+$. A solution of $[(NH_3)_5CoNCO](ClO_4)_2$ (1.0 g, 2.6 mmol) in water (50 mL) was mixed with 2 M $HClO_4$ (50 mL, 100 mmol) in a U-tube for 6–7 s (25 °C) before pouring the solution into ice-cold aqueous NaOH (6.4 g, 160 mmol). The basic solution was sorbed onto Dowex 50Wx2 cation-exchange resin and eluted with 0.1 M NaCl (pH 10). $[Co(NH_3)_6]^{3+}$ and unreacted $[(NH_3)_5CoNCO]^{2+}$, which were identified by elution rate and their absorption spectra, eluted behind a pink 1+ ion. Molar absorptivities for the latter ion (ϵ_{507}^{max} 99, ϵ_{358}^{max} 185) were determined by measuring its absorption spectrum before and after acidification with HCl to a final $[H^+] = 0.1$ M. The final absorption spectrum was identical with that of $[Co(NH_3)_6y^{3+}$, for which the extinction coefficient is known: ϵ_{476}^{max} 57.6.

Product Analyses. The following details are representative.

Anion Capture Experiments. $[(NH_3)_5CoOSO_2CF_3](ClO_4)_2$ (0.258 g, 5.25×10^{-4} mol) was reacted with aqueous 0.1 M Tris/1 M NH_4^+-$NH_2CO_2^-$ (100 mL) for 15 s (25 °C) before quenching to pH 1.5 with 1 M HCl. This procedure ensures conversion of product $[(NH_3)_5CoNCO]^{2+}$ to $[Co(NH_3)_6]^{3+}$. After 25 min (25 °C) the product

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[24] Buckingham, D. A.; Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726.

mixture was diluted with ice water (1.5 L), sorbed on SP-Sephadex C-2k cation-exchange resin, and eluted with 1 M NaCl (pH ca. 3). The two cations that separated were identified by their visible absorption spectra as $[(NH_3)_5CoO_2CNH_2]^{2+}$ (ϵ_{508}^{max} 77.5; 2.2%) and $[(NH_3)_5CoOH_2]^{3+}$ (ϵ_{492}^{max} 47.7; 97.8%). Triplicate experiments gave 2.5, 2.1, and 1.9% $[(NH_3)_5CoO_2CNH_2]^{2+}$ (Co recoveries = 100 ± 1.5%).

Reactions of $[(NH_3)_5CoNH_2CO_2C_2H_5]^{3+}$. $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.290 g, 6.4×10^{-4} mol) was reacted with aqueous 1.17 M $HClO_4$ (25.0 mL, 10^{-2} M H^+) for 20 min (25 °C) before quenching with ice and diluting the solution 20-fold with ice water. The mixture was sorbed on SP-Sephadex C-25 resin and chilled in a jacketed column to 2 °C. Elution commenced with 0.23 M Na^+ (pH 6.9, 0.2 M Cl^-, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}) eluant, and later elution proceeded with eluant twice this concentration. The product distribution (Table II) was determined by measuring visible absorption spectra for the separated complexes and using the following molar absorptivities: $[(NH_3)_5CoOH_2]^{3+}$, ϵ_{492}^{max} 50.3; $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$, ϵ_{495}^{max} 80.8; $[Co(NH_3)_6]^{3+}$, ϵ_{476}^{max} 57.6; $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$, ϵ_{509}^{max} 68.

$[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.187 g, 4.15×10^{-4} mol) was reacted with 0.117 M $HClO_4$ (50 mL, $I = 1.17$ M ($NaClO_4$)) for 60 min (25 °C) before quenching with ice and assaying as above. This experiment was repeated on the 2.0-g scale; no 2+ ion (>0.05%) was detected.

$[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (0.993 g, 2.055×10^{-3} mol) was reacted on dimethyl sulfoxide containing methanesulfonic acid (>5 equiv) for 60 min (25 °C) before cooling, diluting with water, and chromatographing as described above. A pink 2+ ion ($\lambda_{max} = 512$, 358 nm) was detected and observed to transform to $[(NH_3)_5CoOH_2]^{3+}$ (see Table II). This 2+ ion was absent when CF_3SO_3H was substituted for CH_3SO_3H. To test for $[(NH_3)_5CoNCO]^{2+}$, $[(NH_3)_5CoNHCO_2C_2H_5](ClO_4)_2$ (1.175 g, 2.62×10^{-3} mol) was reacted for $10t_{1/2}$ in dimethyl sulfoxide containing $\sim 3 \times 10^{-2}$ mol of CF_3SO_3H. Chromatographic analysis showed only $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ eluting ahead of $[Co(NH_3)_6]^{3+}$. No 2+ ion (>0.5%) was detected.

Reactions of $[(NH_3)_5CoOC(NH_2)OC_2H_5]^{3+}$. $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3 \cdot 3H_2O$ (1.034 g, 2.069×10^{-3} mol) was reacted with aqueous 0.1 M NaMES buffer (pH 6.3, 50 mL, $I = 1.0$ M ($NaClO_4$)) for $5t_{1/2}$ (16 h, 25 °C). The product solution was diluted (10x) with water and sorbed on SP-Sephadex C-25 resin, and elution with 0.46 M Na^+ (0.4 M Cl^-, 0.02 M $H_2PO_4^-$, 0.02 M HPO_4^{2-}, pH 6.9) eluant separated two products that were identified by visible spectra as 2.0 ± 0.2% $[(NH_3)_5CoNHCO_2C_2H_5]^{2+}$ (ϵ_{495}^{max} 80.8) and 98.0% $[(NH_3)_5CoOH_2]^{3+}$ (ϵ_{492}^{max} 50.3); average Co recovery = 101.1%.

When $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3 \cdot 3H_2O$ (0.486 g, 9.7×10^{-4} mol) was reacted with 0.1 M NaOH (25 mL, $I = 1.0$ M ($NaClO_4$)) for 60 s before quenching to pH 5 and assaying as above, only the $[(NH_3)_5CoOH_2]^{3+}$ ion was chromatographically detected (≥99% [Co]).

Acknowledgment. This work was supported by a grant from the Australian Research Grants Scheme.

Registry No. $[(NH_3)_5CoOC(NH_2)OC_2H_5]_2(S_2O_6)_3$, 128444-74-6; $[(NH_3)_5CoNHCOOC_2H_5](ClO_4)_2$, 128444-76-8; $[(NH_3)_5CoNHCO_2]^+$, 128444-77-9; $[Co(NH_3)_5O_3SCF_3](CF_3SO_3)_2$, 75522-50-8; $[Co(NH_3)_5OS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(NH_3)_5CoNCO](ClO_4)_2$, 27427-52-7; $[(NH_3)_5CoO_2C(NH_2)]^{2+}$, 19173-65-0; $[Co(NH_3)_6]^{3+}$, 14695-95-5; $NH_2C(O)OCH_2CH_3$, 51-79-6.

Supplementary Material Available: Table III, containing rate constants (1 page). Ordering information is given on any current masthead page.

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Linkage Isomeric Pentaamminecobalt(III) Complexes of Methanesulfinamide

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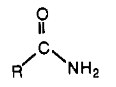
The selective syntheses and reactivities of the linkage isomeric pentaamminecobalt(III) complexes containing N- and O-bound methanesulfinamide ($MeSONH_2$) are described. The N-bonded isomer is isolated as the deprotonated form $[(NH_3)_5Co–NHSOCH_3]^{2+}$, which is stable above pH ca. 4. It protonates in more acidic media, forming the reactive intermediate $[(NH_3)_5Co–NH_2SOCH_3]^{3+}$. The acidity constant was determined both kinetically ($pK'_a = 2.91 \pm 0.03$, 1.0 M KCl; $pK'_a = 2.44 \pm 0.06$, 1.0 M $NaClO_4$, 25 °C) and spectrophotometrically ($pK'_a = 2.83 \pm 0.04$, 1.0 M KCl, 25 °C). The site of protonation was established by ^1H NMR spectra in Me_2SO-d_6; the NH_2 protons are diastereotopic and appear as two separate signals because of the presence of the chiral sulfur center, and neither is in rapid exchange with free H^+. This protonated N-bonded isomer rearranges rapidly in solution, yielding $[(NH_3)_5Co–OS(NH_2)CH_3]^{3+}$ (95%) and $[(NH_3)_5Co–OH_2]^{3+}$ (5%); $k(obsd) = (1.30 \pm 0.03) \times 10^{-2}$ s^{-1}, $I = 1.0$ M (KCl), 25 °C. The rearrangement rate is comparable in Me_2SO; $k(obsd) = (1.47 \pm 0.02) \times 10^{-2}$ s^{-1}, 25 °C. The O-bonded isomer is less reactive, undergoing complete but slow solvolysis (25 °C, $k_s = 1.0 \times 10^{-5}$ s^{-1}, 0.1–2.0 M $HClO_4$, $I = 1$ or 2 M) to $[(NH_3)_5Co(solvent)]^{3+}$ (and free NH_2SOCH_3). The disappearance of the O-bonded sulfinamide complex is appreciably acid catalyzed but only in the presence of Cl^-, and here the reaction is mainly ligand hydrolysis, producing NH_4^+ and the O-bonded sulfinate complex $[(NH_3)_5CoOS(CH_3)O]^{2+}$, which has been synthesized independently. The sulfinamide NH_2 group on the O-bonded isomer is rapidly nitrosated (NO^+) under milder acidic conditions to give the O-bonded sulfinate complex. In aqueous solution above pH ca. 3 an O- to N-linkage isomerization competes with hydrolysis; this competition is more effective via the spontaneous (pH 6.2; 24% isomerization, 76% aquation) compared with the base-catalyzed route (0.1 M OH^-, 8.5% isomerization). From these data k_{ON} could be obtained, and k_{ON} coupled with k_{NO} enabled the calculation of the isomeric equilibrium constant K'_{NO} ($= k_{NO}/k_{ON} = 4450$). This result indicates the greater stability of the O-bonded form over the (protonated) N-bound form in aqueous acid, consistent with results for analogous $[(NH_3)_5Co(NH_2COR)]^{3+}$ systems (e.g., R = OH, H, aryl, alkyl, NR′R″, OR′); however, in neutral to basic solution, the calculated relative stability constant shows that the N-bound form is more stable, and this is because it is selectively deprotonated.

Introduction

Carboxylic acid amides (I, R = H, alkyl, aryl)[1-3] and related molecules (I, R = NH_2,[4] NMe_2,[5] OH,[6] OEt[7]) interact with transition-metal ions through either the carbonyl oxygen or nitrogen atoms, and the synthesis and interconversion of the linkage



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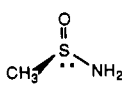

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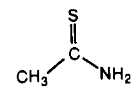
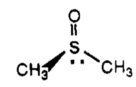


III



IV

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