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Linkage Isomerization of (Formamide-*N*)- and (Acetamide-*N*)pentaamminecobalt(III) Ions in Water, Dimethyl Sulfoxide, and Sulfolane[1]

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Received December 5, 1988

The orange N-bonded amide complexes $[(NH_3)_5CoNH{=}C(-O)R](ClO_4)_2$ (R = H, CH_3) are protonated in acidic media, forming yellow, kinetically robust $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ ions, which have been isolated as crystalline perchlorate salts. NMR (^1H, ^{13}C) spectroscopy establishes unequivocally (i) in Me_2SO the preferred site of protonation is the carbonyl oxygen, (ii) $[(NH_3)_5CoNH{=}C(OH)H]^{3+}$ exists in two geometrically isomeric forms which are detectable at ambient temperature, and (iii) each protonated N-bonded isomer is thermodynamically unstable and intramolecularly rearranges slowly in solution to yield the O-bound form ($t_{1/2}$ ca. 1.7 h, R = CH_3; 5.2 h, R = H; Me_2SO, 35 °C). The isomerizations have been monitored also by electronic spectroscopy and cation-exchange chromatography, and the reaction kinetics have been investigated for H_2O, Me_2SO, and sulfolane solutions. In the coordinating solvents (H_2O, Me_2SO), the N-bonded isomers react by parallel paths, solvolysis and linkage isomerization, and a consecutive reaction (the solvolysis of the O-bonded isomers) of comparable rate has also been identified. The reverse O- to N-rearrangement (k_{ON}) could not be detected in either coordinating or noncoordinating solvents, and this is attributed to the inherent thermodynamic instability of the protonated N-bonded isomers. For aqueous base, where the N-bonded isomer is selectively deprotonated and thus assumes thermodynamic stability over the O-bonded form, the failure to detect O- to N-isomerization is due to much faster base-catalyzed hydrolysis. In the poorly coordinating solvents sulfolane and acetone, the protonated N-bonded isomers rearrange (k_{NO}) slowly and completely to the O-bound forms without solvent coordination. A lower limit for the equilibrium constants governing the distribution of isomers was determined directly for these solvents by measuring individual isomer concentrations ($K'_{NO} \geq 100$) and indirectly from measured specific isomerization rates ($k_{NO}/k_{ON} \geq 100$) for water and dimethyl sulfoxide. The mechanisms for amide rearrangement in these and other $[(NH_3)_5Co(NH_2COR)]^{3+}$ complexes are discussed.

Introduction

Amides ($RCONH_2$) are potential ambidentate ligands for metal ions. Both N- and O-bonded linkage isomers of (formamide)-pentaamminecobalt(III) are known,[2] but the interconversion of the isomers in solution and the equilibrium position have not been reported. Previous synthetic work[2] was based upon the assumption that the O-bonded isomer forms initially under mild conditions (kinetic control) and subsequently rearranges with release of a proton to give the conjugate base of the N-bonded isomer. This hypothesis has now been tested and verified for a range of amides and has also been found to apply generally to molecules of the type $RCONH_2$ (R = NR'R'', OR'), $RSONH_2$, and RSO_2NH_2 (R = alkyl, aryl).[1b,3]

Although a number of $[(NH_3)_5CoNHCOR]^{2+}$ ions are known and the acidity of their conjugate acids have been determined (pK'_a = 1-3; e.g. R = H,[2] CH_3,[4] C_6H_5,[5] NH_2 and NMe_2[6,7]), crystalline acid forms have not previously been isolated pure. In the present work this problem has been solved. Thus, pure acid and base forms of (formamide-*N*)- and (acetamide-*N*)pentaamminecobalt(III) as well as (formamide-*O*)- and (acetamide-*O*)pentaamminecobalt(III) have been examined and their properties compared with those of analogous ions derived from $[(NH_3)_5CoNHCOR]^{2+}$ (R = alkyl, aryl, NH_2, NMe_2, OH, OC_2H_5, NHC_6H_5) and $[(NH_3)_5Co(L\text{-}L')]^{n+}$ (L-L' = ambidentate ligand), described elsewhere.[3]

Results

Synthesis and Isomer Assignments. In kinetically controlled syntheses, the labile complex $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ was reacted either with neat amide or with amide in poorly coordinating solvents such as sulfolane or acetone to give good yields of the (amide-*O*)pentaamminecobalt(III) ions.[1b,3] The stoichiometry of the products was established by microanalyses, and the isomer selectivity was confirmed by chromatography on cation-exchange resins. No (amide-*N*)pentaamminecobalt(III) ions were detected (<0.2%) under conditions (pH 4-6) where they are known to be deprotonated (2+ ions) and hence elute faster than the much less acidic O-bonded isomers (3+ ions). This distinction between the acidities of the linkage isomers, and their consequent ion-exchange properties, has been exploited in separating mixtures of the isomers as described ahead.

Table I. Molar Absorptivities of Linkage Isomeric Complexes of Formamide and Acetamide

complex	λ, nm (ε, M^{-1} cm^{-1})	solvent
$[(NH_3)_5CoOCHNH_2]^{3+}$	501 (71.7), 346 (57.6)	0.1 M $HClO_4$
	502 (79.4), 343 (66.0)	Me_2SO
$[(NH_3)_5CoNH{=}C(OH)H]^{3+}$	478 (62.0), 348 (64.1)	0.1 M CF_3SO_3H
	477 (71.3), 340 (71.6)	Me_2SO/0.1 M CF_3SO_3H
$[(NH_3)_5CoNHCHO]^{2+}$	483 (68.6), 346 (80.5)	0.1 M Tris
$[(NH_3)_5CoOC(CH_3)NH_2]^{3+}$	516 (80.2), 346 (60.4)	0.1 M $HClO_4$
	510 (78.1), 345 (65.2)	Me_2SO
$[(NH_3)_5CoNH{=}C(OH)\text{-}CH_3]^{3+}$	475 (64.1), 340 (60.8)	0.1 M CF_3SO_3H or $HClO_4$
	476 (73.0), 340 (71.7)	Me_2SO/0.1 M CF_3SO_3H
$[(NH_3)_5CoNHCOCH_3]^{2+}$	484 (72.4), 349 (86.5)	0.1 M Tris

The electronic spectra (Table I) of the complexes allow a distinction between the modes of coordination of the amides. The pink O-bound amide complexes show a long-wavelength absorption maximum (>500 nm) characteristic of a CoN_5O chromophore. The spectrum of the acetamide complex (516 nm) is indicative of (amide-*O*)pentaamminecobalt(III) ions in general;[1b,3] however, the formamide-*O* analogue has a significantly higher energy absorption maximum (501 nm), which may be related to its atypical Co-O bond strength (vide infra). The absorption spectra of the yellow complexes containing the amides N-bound as neutral ligands are typical of a CoN_6 chromophore as represented by $[Co(NH_3)_6]^{3+}$. When the amides are N-bonded as anionic ligands to $Co(NH_3)_5^{3+}$, the complexes are orange-red and the visible absorption maxima are increased somewhat in intensity while the lowest energy maximum is shifted significantly (6-9 nm) to longer wavelength compared to the position for the deprotonated forms.

The ^1H NMR spectra of $[(NH_3)_5CoNHCOR]^{2+}$, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$, and $[(NH_3)_5CoOC(CH_3)NH_2]^{3+}$

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Table II. ^1H and ^{13}C NMR Chemical Shifts for Formamide and Acetamide and Their $(NH_3)_5Co^{3+}$ Complexes in Me_2SO-d_6

	$\delta(^1H)$, ppm				$\delta(^{13}C)$, ppm	
	cis NH_3	trans NH_3	NH/NH_2	CH_n	C=O	CH_3
$HCONH_2$			*a*	*a*	163.18	
$[(H_3N)_5CoOCHNH_2]^{3+}$	3.82	2.72	8.82, 9.12[e]	7.26[e]	170.68	
$[(H_3N)_5CoNHCHO]^{2+}$	3.20	3.20[b]	3.83	8.05[d]	173.53	
$[(H_3N)_5CoNH{=}C(OH)H]^{3+}$	3.28	3.28[b]	*c*	*c*	173.26, 165.94	
$[(H_3N)_5CoO_2CH]^{2+}$	3.73	2.67		7.60	171.95	
$[(H_3N)_5CoOCHNHCo(NH_3)_5]^{5+}$	3.62	2.70				
	3.05	3.22	5.93	7.08	176.91	
CH_3CONH_2			6.66, 7.25	1.77	172.23	22.25
$[(H_3N)_5CoOC(CH_3)NH_2]^{3+}$	3.85	2.63	7.30, 8.83	1.90	180.84	22.98
$[(H_3N)_5CoNHCOCH_3]^{2+}$	3.22	3.22[b]	3.73	1.97	180.96	26.96
$[(H_3N)_5CoNH{=}C(OH)CH_3]^{3+}$	3.28	3.28[b]	7.25 (NH), 10.0 (OH)	2.42	180.62	23.30
$[(H_3N)_5CoO_2CCH_3]^{2+}$	3.73	2.63		1.87	180.81	25.06
$[Co(NH_3)_6]^{3+}$	3.25	*b*				
$[Co(NH_3)_5NCCH_3]^{3+}$	3.72	3.25		2.57	130.81	3.77

[a] Signals evident at 7.18, 7.78, and 7.98 ppm but cannot be directly assigned. [b] Cis- and trans-NH_3 resonances coincident. [c] Part of a complex multiplet; see text. [d] Doublet; J = 4 Hz. [e] Doublet of doublets; J = 13 and 2 Hz.

in anhydrous Me_2SO-d_6 are quite different (R = CH_3, Figure 1). In particular, the locations of, and separation between, resonances for the NH_3 groups cis (12 H) and trans (3 H) to the coordinated amide are sensitive to the mode of amide coordination (N or O),[2,8] as well as to the charge on the amide (neutral or anionic). These observations also apply to a range of linkage isomeric pentaamminecobalt(III) complexes with ambidentate ligands such as $RCONH_2$ (R = H, alkyl, aryl, NH_2, NR′R″, OC_2H_5, OH) and $RSONH_2$ and RSO_2NH_2 (R = NH_2, alkyl, aryl, O^-).[3] In general, the absolute chemical shifts of, and separation between, cis- and trans-NH_3 resonances are almost independent of the substituent (R) but are diagnostic of the nature of the coordinated ambidentate ligand.

Neither ^{13}C NMR (Table II) nor infrared spectra (Figure 2) of $[(NH_3)_5CoOC(R)NH_2]^{3+}$, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$, and $[(NH_3)_5CoNHCOR]^{2+}$ are as informative as to the mode of amide coordination to Co(III), although each spectrum is characteristic of the complex it represents and therefore provides a measure of isomeric purity as well as information relating to the structure of the coordinated amide.

Amide Structure in the Metal Complexes. The solid-state X-ray structure of $[(NH_3)_5CoNHCOCH_3]^{2+}$ has previously established that, as in free acetamide, there is considerable delocalization of π-electron density over the N—C—O bonds in the acetamide ligand.[8] Consistent with retention of this structure in solution is the observed low-field (3.83 ppm) resonance for the Co—NH= group in the ^1H NMR spectrum (Figure 1B)). The location of this resonance can be compared with that for the CoNH proton (1.62 ppm)[6] in $[(NH_3)_5CoNHCONH_2]^{2+}$ and related species and likely signifies greater C=N bond character for the acetamide complex in solution (Me_2SO).[6] The formamide analogue also exhibits a low-field CoNH proton resonance in Me_2SO-d_6 (Table II), as do a range of other amide-*N* complexes (3–5 ppm).[1b,3]

Upon acidification of solutions of $[(NH_3)_5CoNHCOR]^{2+}$ in Me_2SO-d_6, the CoNH proton resonance moves substantially to lower field. Previous observations that the CoNH proton resonance for coordinated acetamide[4] and chelated amides[10] gives an integration for only one proton and that its chemical shift and intensity are independent of excess H^+ suggested that protonation is at the carbonyl oxygen rather than at the coordinated nitrogen of the amide ligand. We have confirmed these observations for the acetamide species, and further evidence for protonation at oxygen is derived from the ^1H NMR spectrum of the *pure* protonated (acetamide-*N*)pentaamminecobalt(III) complex in anhydrous Me_2SO-d_6 (Figure 1A). The observation of separate

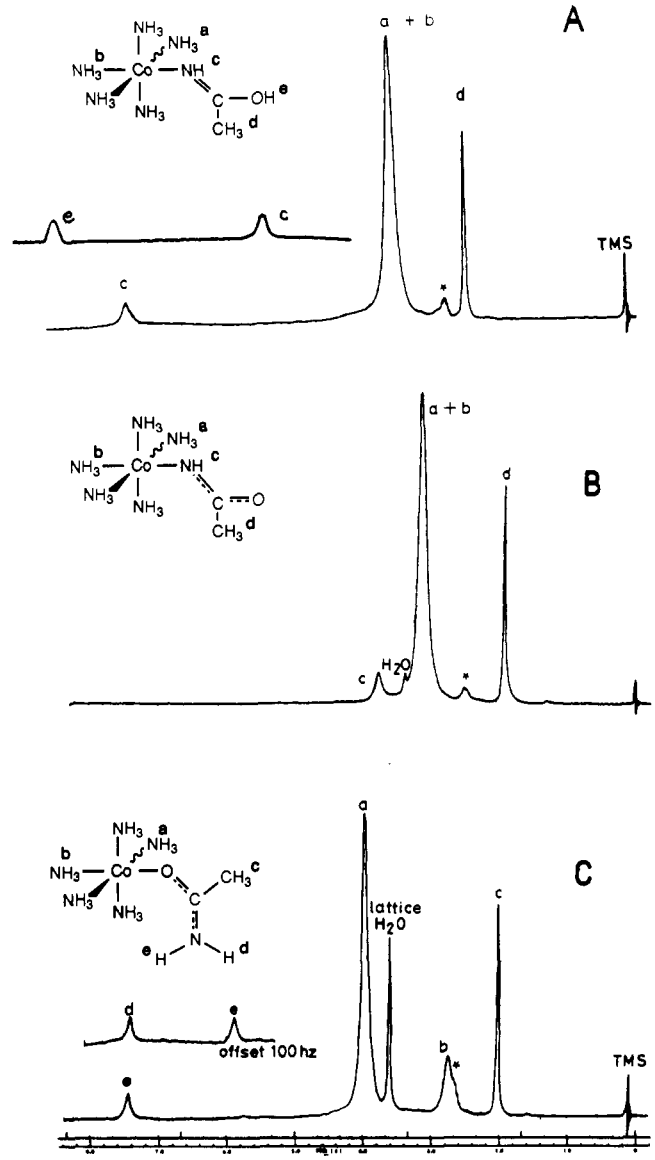

Figure 1. 60-MHz ^1H NMR spectra of linkage isomers of (acetamide)pentaamminecobalt(III) perchlorate in Me_2SO-d_6 (the asterisk denotes the signal for Me_2SO-d_5).

resonances (for the OH and NH protons, respectively) at 10.00 ppm (1 H) and 7.25 ppm (1 H) clearly establishes that $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$, rather than $[(NH_3)_5CoNH_2C(=O)CH_3]^{3+}$, is the dominant tautomer in solution. Note that the lowest field OH signal moves upfield and increases in intensity

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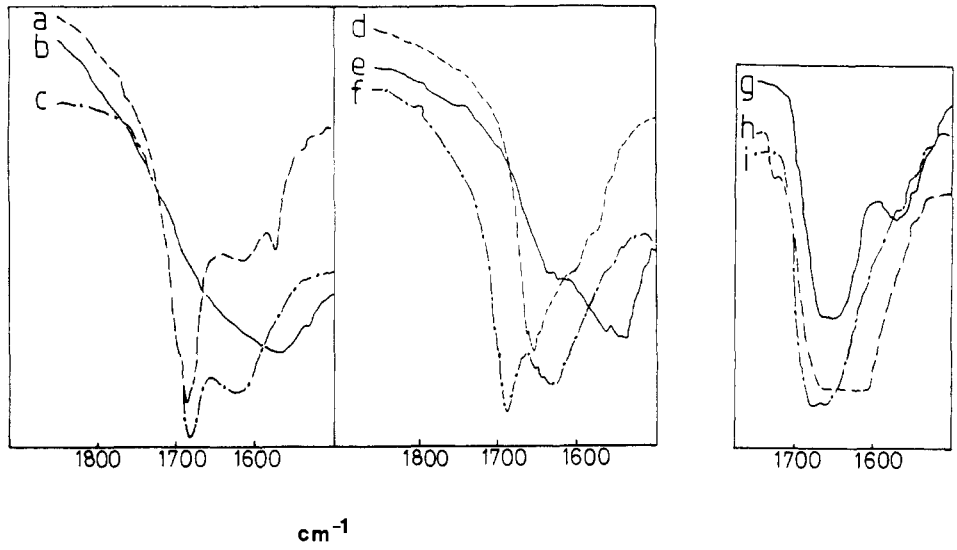


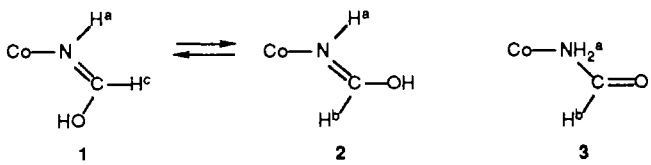
Figure 2. Infrared spectra for $[(NH_3)_5CoX](ClO_4)_n$ complexes: (left) Nujol mulls, X = $-OCHNH_2$ (a), $-NHCHO$ (b), $-NH{=}C(OH)H$ (c), $-OC(CH_3)NH_2$ (d), $-NHCOCH_3$ (e), $-NH{=}C(OH)CH_3$ (f); (right) Me_2SO solvent, X = $-OC(CH_3)NH_2$ (g), $-NHCOCH_3$ (h), $-NH{=}C(OH)CH_3$ (i).

with addition of H_2O, while the same signal moves downfield on introduction of excess H^+; the NH signal is unaffected. These observations are consistent with the acidic OH proton exchanging rapidly with introduced H_2O or H^+ (at 35 °C and at the observation frequency of 60 MHz). Protonation at oxygen in Me_2SO/H^+ for other $[(NH_3)_5CoNHCOR]^{2+}$ ions follows from observations[3] similar to the above.

For the formamide analogue the ^1H NMR spectrum is more complicated (Figure 3). Being more acidic ($pK'_a = 2$)[2] than the acetamide analogue ($pK'_a = 3$)[4] in water, it is not surprising that the isolated $[(NH_3)_5CoNH{=}C(OH)H]^{3+}$ complex is partly deprotonated in Me_2SO-d_6 (Figure 3A), and consequently it displays a weighted-average spectrum for the protonated and deprotonated forms. Addition of CH_3SO_3H causes a shift in the position (but not the intensity) of one of the low-field signals (signal a, Figure 3), and this observation establishes its assignment as the NH proton; a separate resonance (ca. 12 ppm) is observed for $OH/H_2O/H^+$. By analogy with the acetamide-*N* complex, these observations also establish protonation at oxygen.

To simplify the unexpected multiplicity for the low-field proton resonances, the spectrum was recorded for the deuterated complex $[(ND_3)_5CoNDCHO]^{2+}$ in Me_2SO-d_6 containing sufficient D^+ for complete protonation (Figure 3C). *Two* separate aldehyde proton signals (8.23 ppm, 7.47 ppm) were detected, and similarly the ^{13}C NMR spectrum (not shown) for the same solution revealed two separate "aldehyde" carbon resonances (+173.26, +165.94 ppm). The duplication of the signals was not due to partial formation of reaction products and must represent two forms of the protonated (formamide-*N*)pentaamminecobalt(III) ion.

Two geometric isomers (**1** and **2**) of the oxygen-protonated tautomer $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ accommodate the results, or a mixture of oxygen-protonated (**1** or **2**) and nitrogen-protonated (**3**) tautomers. The observed area ratios of signals a, b, and c



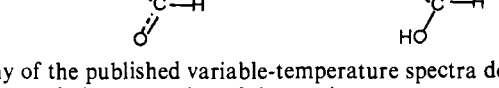
1 **2** **3**

in the spectra for the protonated complex (Figure 3A,B) can be used to decide between the alternatives. Since the positions for the two "aldehydes" protons b and c are known, the area ratios of c:(a + b) = 1:2.6 are consistent with a 55:45 ratio of two O-protonated forms (1:2.64) but inconsistent with a 50:50 mixture of N- and O-protonated forms, which requires a ratio of 1:4. Note, however, that a 1:2 ratio would be expected for the latter situation if the NH_2 protons of **3** were exchanging with free H^+; however, if both the NH_2 proton signals of **3** *and* the OH proton signal of an O-protonated form (**1** or **2**) are exchange-averaged with the H^+ resonance, all these signals for the two species must be exchange-averaged. This is not in accord with observation, and thus the isomeric **1** and **2** oxygen-protonated species are established.

The assignment of the resonances to the particular isomer **1** or **2** is made on the basis of coupling constants. The cis-NH—CHO coupling is generally ca. 3 Hz and is significantly smaller than the trans coupling. In the present case the NH and CH signals for **2** are coincident and, therefore, this larger trans coupling is not observed.

The ^1H and ^{13}C NMR spectra of $[(NH_3)_5CoND{=}C(OD)H]^{3+}$ indicate similar (ca. 60:40) proportions of the geometric isomers **1** and **2** for Me_2SO-d_6, D_2O, Me_2NCDO-d_7, and Me_2CO-d_6 solutions at ambient temperatures. It is not yet possible to definitely assign each NMR signal to its specific geometric isomer, although one of the carbonyl ^{13}C NMR signals (ca. 173 ppm) is similar to that of the deprotonated N-bonded isomer (Table II), whereas the other (ca. 166 ppm) is clearly dissimilar. Since the carbonyl ^{13}C NMR signals of the protonated acetamide-*N* and other analogous amide-*N* complexes are remarkably similar to the corresponding signals of their deprotonated forms, and as they are all (except for N-bonded formamide) likely to exist in only the one conformation **1** (for steric reasons), it seems probable that the lower field ^{13}C resonance arises from the geometric isomer in which the hydroxyl group is trans to the coordinated NH proton, **1**.

Evidence to suggest that the deprotonated formamide complex $[(NH_3)_5CoNHCHO]^{2+}$ also exists as two geometric isomers has been presented,[2] but lower temperatures were required to detect the restricted rotation in the 60-MHz NMR spectra. While these results are consistent with O-protonation shifting π-electron density to the C—N bond, thereby further restricting free rotation about the double bond



scrutiny of the published variable-temperature spectra does not seem to preclude observation of the two isomers even at ambient temperatures if it is accepted that the chemical shifts and isomer ratios are temperature dependent. Furthermore, the cis-NH—CH isomer appears to be more highly populated at the higher temperatures, on the basis of the magnitude of the observed coupling constant (4 Hz).

^1H and ^{13}C NMR data given in Table II for formamide and acetamide, their pentaamminecobalt(III) complexes, and related

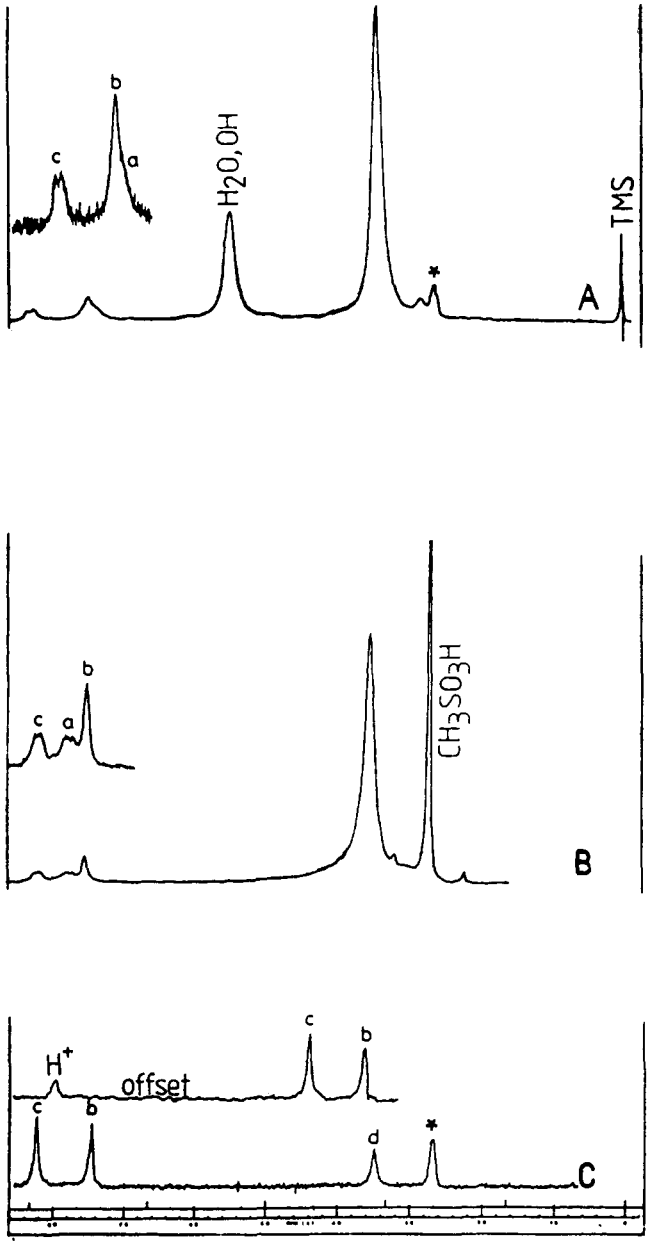


Figure 3. 60-MHz ^{1}H NMR spectra in Me_2SO-d_6: (A) $[(NH_3)_5CoN{=}C(OH)H](ClO_4)_3$; (B) $[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$ in the presence of excess CH_3SO_3H; (C) $[(ND_3)_5CoND{=}C(OD)H](ClO_4)_3$ in the presence of excess D^+. The asterisk denotes the signal for Me_2SO-d_5 and d the signal for residual $Co(NH_3)_5X$ amine protons.

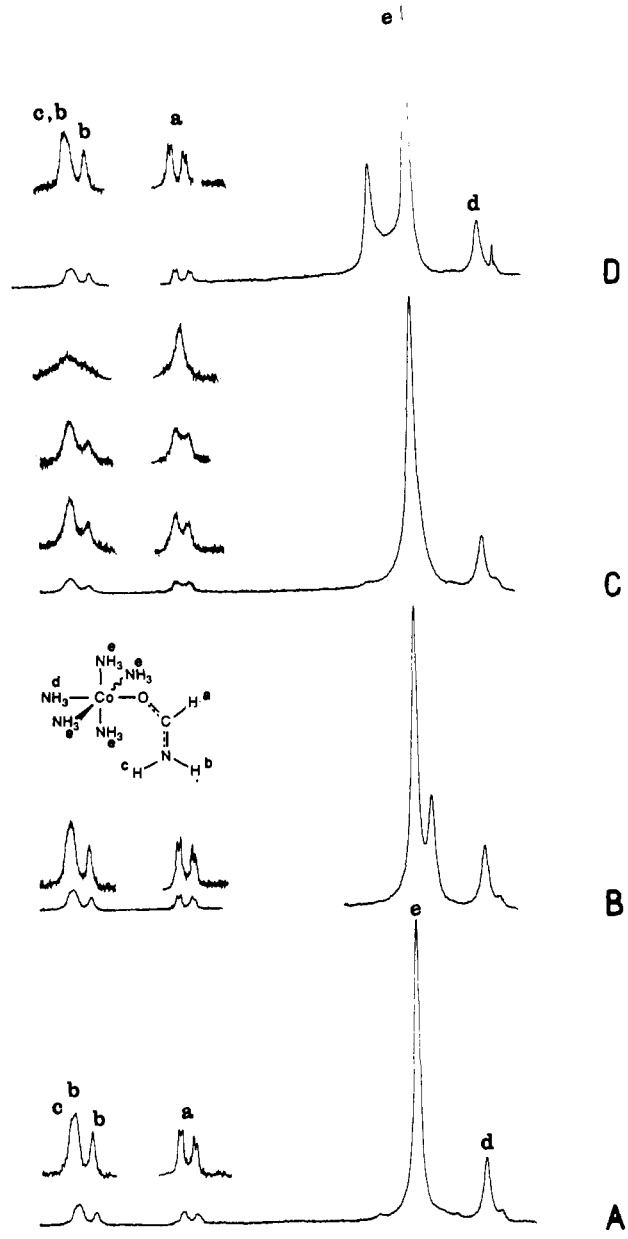


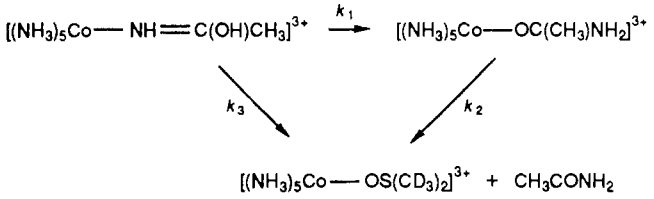
Figure 4. 60-MHz ^{1}H NMR spectra in Me_2SO-d_6 of $[(NH_3)_5CoO{=}C(NH_2)H](ClO_4)_3$: (A) anhydrous salt in dry Me_2SO-d_6; (B) water added; (C) H_2O and Na_2CO_3 added; (D) CF_3CO_2H added to neutralize CO_3^{2-}/HCO_3^- and regenerate spectrum A (or B)).

complexes provide further information concerning the solution structure of the bound amides. It is noted that coordination of the electron-withdrawing $Co(NH_3)_5^{3+}$ ion to the amides causes a substantial downfield shift in both ^{1}H and ^{13}C NMR signals for the coordinated amide. Another feature of the data is that the amide resonances (^{1}H and ^{13}C) are quite different for each complex and thus serve as "fingerprint" identification. Further, the O-bonded amides show separate ^{1}H NMR signals for the diastereotopic $-NH_2$ protons (although the gem-NH coupling is not resolved), consistent with retention of the C=N double bond and the restricted-rotation phenomenon characteristic of free amides. For acetamide, in common with a number of other (amide-*O*)pentaamminecobalt(III) complexes,[3,7] the magnitude of this splitting is enhanced in the coordinated complexes and this could be interpreted as evidence for increased polarization ($^-O{-}C{=}NH_2^+$) of the amide on coordination. Finally, the ^{13}C NMR shifts for carbonyl carbons of acetamide complexes are almost independent of the coordination mode—the differences in the complexes here being more manifest in the remote CH_3 signal.

Although the ^{1}H NMR spectra of the N- and O-bonded formamide complexes have been reported and discussed previously,[2] portions of the spectra were apparently off-scale and therefore missed. Thus, some signals were incorrectly assigned, and N-protonation of the N-bonded isomer was wrongly concluded. The spectrum for the O-bonded complex in Me_2SO-d_6 is shown in Figure 4; proton assignments were confirmed by ^{1}H-decoupling experiments and also by use of the $[(ND_3)_5Co{-}OCHND_2]^{3+}$ complex to positively identify the "aldehyde" proton. The small (cis) and large (trans) H–H couplings (2 and 13 Hz) are observed as expected, but interestingly these may be collapsed by the introduction of H_2O (lattice water in the air-dried ClO_4^- salt) *and* a small amount of base (HCO_3^- or CO_3^{2-}); H_2O alone has no effect. The collapse is due to base-catalyzed H-exchange between H_2O and each of the distinct NH signals; however, this is not sufficiently rapid to completely exchange-average the more widely separated NH signals (and H_2O) into a singlet. We have found that either limiting spectrum may be observed, depending upon the method of isolating the O-bonded complex.

The above results related to the *solution* structure of the amide complexes, but it remains possible that their solid-state structures are different. The carbonyl portions of the solid-state infrared spectra of $[(NH_3)_5CoOC(NH_2)R](ClO_4)_3$, $[(NH_3)_5CoNH{=}C(OH)R](ClO_4)_3$, and $[(NH_3)_5CoNHCOR](ClO_4)_2$ (R = H, CH_3)

Scheme I



are illustrated in Figure 2. Previously,[2] the high stretching frequency shown by the protonated N-bonded isomer was interpreted as support for protonation of the coordinated nitrogen ($[(NH_3)_5CoNH_2COR]^{3+}$) since such protonation localizes π-electron density in the C—O bond. However, the coordinated acetamidine complex $[(NH_3)_5CoNH{=}C(NH_2)CH_3]^{3+}$ exhibits a C—N stretching frequency at ca. 1660 cm^{-1},[1b] and thus the apparently high frequency vibration often interpreted as $\nu_{C=O}$ could equally well be assigned to the C=N stretch of $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$.

Linkage Isomerization. ^1H and ^{13}C NMR Studies. Figure 5 shows the ^1H NMR spectra of $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$ in Me_2SO-d_6 at 35 °C as a function of time. At 5 min (Figure 5A), the resonances are essentially those due to the reactant save for small (new) signals in the methyl (1.77, 1.90 ppm) and Co—NH_3 (3.85 ppm) regions. At 30 min (Figure 5B) these had increased in intensity and are assigned unambiguously to free acetamide, $[(NH_3)_5CoOC(CH_3)NH_2]^{3+}$, and $[(NH_3)_5CoOS(CD_3)_2]^{3+}$. New signals evident at this time can be assigned to the trans NH_3 (2.63 ppm) and one of the exo-NH protons (7.30 ppm) of the O-bonded acetamide complex. By this time all the signals due to the protonated acetamide-*N* complex had decreased concomitantly in intensity.

Further insight into the sequence of events is provided by the relative intensities of the methyl resonances. At 5 and 30 min (Figure 5A,B), the methyl signals due to the acetamide-*O* complex and free acetamide are in the same ratio, with the O-bonded isomer in slight excess over free ligand. Thereafter the methyl resonance for free acetamide grows faster than that for the O-bonded isomer (Figure 5C,D), and eventually it is the dominant and ultimately the only CH_3 signal. Scheme I accommodates these observations. The protonated N-bonded acetamide complex (R = CH_3) reacts by parallel paths (k_1, k_3), yielding the O-bonded isomer, free acetamide, and the solvent complex. There is also a consecutive path (k_2) involving solvolysis of the (intermediate product) O-bonded acetamide complex. The relative rates (by ^1H NMR spectroscopy) for the paths shown in Scheme I are in accord with those measured independently by spectrophotometric means (vide infra).

Figure 6 (supplementary material) shows the time dependence for the ^1H NMR spectra of the protonated N-bonded formamide complex in Me_2SO-d_6. The initial spectrum decays to one that shows signals characteristic[1b,3] of $[(NH_3)_5CoOCHNH_2]^{3+}$ (cis and trans NH_3 and coupling between formamide protons). The spectral changes categorically establish an N to O linkage isomerization in dimethyl sulfoxide. There is also some evidence of free formamide being produced (signal k, Figure 6D), although it is not clear from these spectra whether it arises directly from the N-bonded isomer or via the O-bonded isomer. Resonances for the cis- and trans-NH_3 protons of $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ (signals n and o, Figure 6) are not distinguished from the analogous resonances (signals f and g) of $[(NH_3)_5CoOCHNH_2]^{3+}$. Further, the signal representing the average magnetic environment for free H_2O plus the acidic OH proton moves progressively to higher field. This is consistent with depletion of the acidic N-bonded isomer as it linkage isomerizes to the nonacidic O-bonded isomer, since free H_2O usually resonates at ca. 3.5 ppm.

More direct evidence for the N to O linkage isomerizations was obtained from ^{13}C NMR spectral studies. As shown in Table II, the N- and O-bonded amide complexes may be readily distinguished from each other, as well as from uncoordinated amides, by their characteristic ^{13}C NMR chemical shifts. In Me_2SO-d_6,

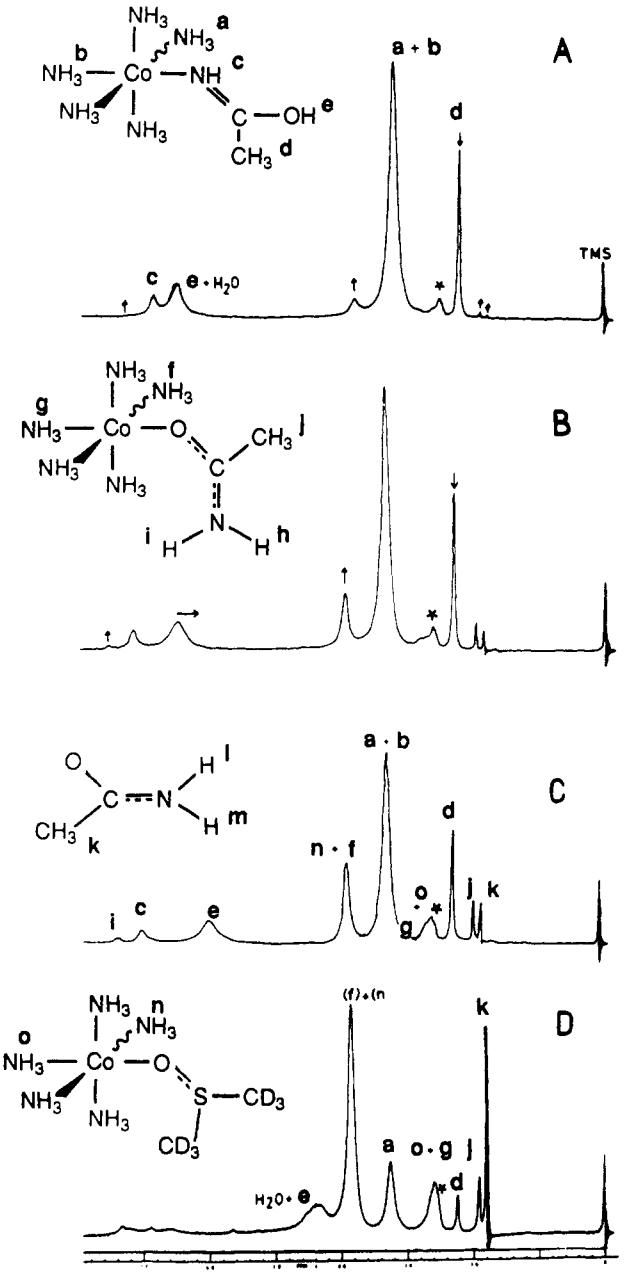


Figure 5. 60-MHz ^1H NMR spectra of $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$ in Me_2SO-d_6 at 35 °C after 5 min (A), 30 min (B), 1.5 h (C), and 6.5 h (D). The asterisk denotes the signal for Me_2SO-d_5.

$[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$ (180.62, 23.36 ppm) in time leads to resonances typical of its O-bonded linkage isomer (180.81, 22.98 ppm) and uncoordinated acetamide (172.22, 22.27 ppm). Similarly, the protonated N-bonded formamide complex (173.26, 165.94 ppm) produces resonances ascribable to its O-bound isomer (170.72 ppm) as well as free formamide (162.93 ppm) within a few hours at 35 °C.

For both $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ ions (R = CH_3, H) it was evident from the ^{13}C NMR observations that the respective O-bonded isomer and free amide were formed concurrently rather than consecutively. This fact is more difficult to quantify in the case of R = CH_3, since the solvolysis of the O-bonded acetamide product is relatively rapid compared with the rate of linkage isomerization, as well as rapid in the absolute sense at the probe temperature (35 °C, $t_{1/2}$ ca. 1 h). In contrast, for R = H the rate of solvolysis of O-bonded formamide is extremely slow ($t_{1/2}$ ca. 100 h, 25 °C; Me_2SO), and hence the *parallel* reactions of $[(NH_3)_5CoNH{=}C(OH)H]^{3+}$ are more clearly observed.

During reactions of the $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ ions (R = H, CH_3), there is also some change in the chemical shifts (R = CH_3, 180.62 and 23.52 ppm; R = H, 173.24 ppm) for the

residual reactants. This can be explained by an increasing dissociation to $[(NH_3)_5CoNHHCOR]^{2+} + H^+$ as the concentration of reactant decreases. Consistent with this account, in each case the direction of change is toward the corresponding deprotonated N-bonded isomer.

Spectrophotometric Equilibrium and Kinetic Studies. The linkage isomerization and solvolysis reactions can be readily detected visually since the linkage isomeric (amide)pentaammine-cobalt(III) complexes differ from one another in color and in their solvolysis products. In the feebly coordinating (or noncoordinating) solvent sulfolane (tetramethylene sulfone) there is no solvolysis of either reactant $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ or product $[(NH_3)_5CoOC(NH_2)R]^{3+}$, and thus the position of equilibrium between the linkage isomers could be easily ascertained by experiments in which each isomer was separately dissolved and equilibrated in sulfolane at 35 °C.

Product analyses by cation-exchange chromatography on Sephadex resin and subsequent spectrophotometric measurements revealed that the N-bonded isomers (R = H, CH_3) reacted completely to give the O-bonded isomers, while the latter did not react over the same period of time ($5t_{1/2}$ and $10t_{1/2}$ for N- to O-rearrangement) and were recovered unchanged. Thus, a lower limit for the equilibrium constant governing the isomer distribution is $K'_{NO} \geq 100$.

The specific rates for the N- to O-rearrangements were determined by following absorption changes in the visible spectrum of the protonated N-bonded amide complexes at 35.0 ± 0.1 °C in dried distilled sulfolane. No competing solvolysis reactions proceed in this solvent, and good linear first-order rate plots of $\ln |A_\infty - A|$ versus time were obtained over $>3t_{1/2}$, consistent with the simple process

$$[(NH_3)_5CoNH{=}C(OH)H]^{3+} \xrightarrow{k(obsd)} [(NH_3)_5CoOC(NH_2)R]^{3+}$$

Values of k(obsd) so obtained (R = H, k(obsd) = 3.46×10^{-5} s^{-1}; R = CH_3, k(obsd) = 4.68×10^{-5} s^{-1}; 35 °C) were independent of wavelength. Note that a possible complication, dissociation of the acidic $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ to the unreactive $[(NH_3)_5CoNHCOR]^{2+}$ resulting in unrealistically small k(obsd) values, can be dismissed since $HClO_4$, a very strong acid in H_2O and Me_2SO, is predominantly undissociated in sulfolane (pK'_a = 2.7), and yet $HClO_4$ is orders of magnitude more acidic than the protonated amide-*N* complexes.[11] This analysis is supported by the linearity of the rate plots, which should curve if dissociation were significant, especially as the reaction progresses and dissociation increases.

The isomer equilibrium for *coordinating solvents* could not be determined by direct measurement because of competitive solvolysis reactions of both linkage isomers. However, estimates could be made, with use of the measured specific rates for the N- to O-rearrangement (k_{NO}) and estimated limiting values (k_{ON}) for the reverse reaction (never observed); the equilibrium constant for the N- to O-rearrangement is $K'_{NO} = k_{NO}/k_{ON}$. This is described later after we deal with the competitive solvolysis/linkage isomerization reactions of the individual N- and O-bonded isomers.

For coordinating solvents, we have seen that the ^1H and ^{13}C NMR analyses show that the N-bonded isomers undergo two parallel reactions, one yielding the O-bonded isomer, which subsequently solvolyzes, and the other leading directly to the solvolysis product (Scheme I). We also showed that the O-bonded isomers solvolyze directly to $[(NH_3)_5Co(solvent)]^{3+}$ and free amide; there was no competitive O- to N-isomerization. This was confirmed by the observation in the visible absorption spectra of sharp isosbestic points in the calculated positions for the solvolysis reactions of the O-bonded isomers; R = CH_3, 575 and 409 nm for DMSO, 425 and 313 nm for acidic H_2O; R = H, 529, 618, and 400 nm for DMSO, 315 and 413 nm for acidic H_2O. These persisted for the complete reaction.

In order to derive the three rate constants (k_1, k_2, k_3) for each system, the solvolysis rates (k_2) of the O-bonded isomers in Me_2SO and 0.1 M $HClO_4$ were first measured independently by following the change in absorbance at suitable wavelengths (500, 520, and 540 nm, 35 and 45 °C). The change in absorbance for each protonated N-bonded isomer at one of the isosbestic point wavelengths for the reaction of the corresponding O-bonded isomer was then monitored for each solvent. Both sets of absorbance changes displayed excellent uniphasic first-order kinetics, the former yielding k_2 and the latter k(obsd) = $k_1 + k_3$ (Scheme I).

Note that the problem of deprotonation, negligible for sulfolane, exists for the acidic $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ ions in H_2O and Me_2SO. The pK'_a values have been determined as 3.02 and 2.16 for the acetamide[4] and formamide[2] complexes in water (25 °C, μ = 1.0 M ($NaClO_4$) and 25.5 °C, μ = 0.92 M ($LiClO_4$), respectively), and we have determined a similar value for the acetamide complex in DMSO (3.6). Thus, deprotonation is considerable (ca. 30%) at cobalt concentrations of 10^{-3} M and significant (ca. 14%) even at 10^{-2} M [Co]. Therefore, all kinetic runs were performed in acidified solvents to eliminate the problem.

A well-defined isosbestic point was observed for the reaction of $[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$ in acidified Me_2SO at 35 °C over early reaction times; similar points, in slightly different positions, were observed for early time data at 45 and 25 °C. The existence of the isosbestic point corresponds to a single product or more than one product formed in constant proportion, and thus its position relates to the ratio of the first formed species in the reaction sequence

$$[(NH_3)_5CoNH{=}C(OH)H]^{3+} \xrightarrow{Me_2SO} \begin{cases} [(NH_3)_5CoOCHNH_2]^{3+} \\ [(NH_3)_5CoOS(CH_3)_2]^{3+} + HCONH_2 \end{cases}$$

The observed molar extinction coefficient for the N-bonded isomer at this isobestic point is equal to the molar extinction coefficient of the two-component product mixture, which is given by $f\epsilon_0 + (1-f)\epsilon_{sol}$, where f is the fraction of the parallel reaction that yields the O-bonded isomer while $1-f$ is the fraction of directly formed $[(NH_3)_5CoOSMe_2]^{3+}$; ϵ_0 is the molar extinction coefficient of the O-bonded isomer, and ϵ_{sol} is the molar extinction coefficient of $[(NH_3)_5CoOSMe_2]^{3+}$ in Me_2SO. Thus, the course of the reaction (f(kin)) was calculated by using this relation and the data contained in Table III.

A similar strategy was employed for the corresponding reactions of N-bonded formamide in 0.1 M $HClO_4$ and also for the reactions of the N-bonded acetamide complex in both solvents (Table III).

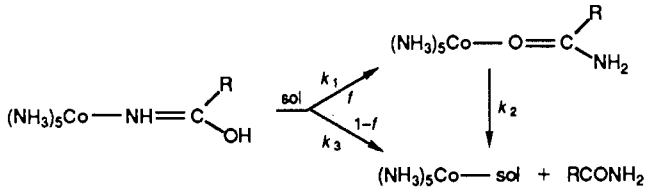
Interestingly, the result for the reaction of the N-bonded acetamide complex in aqueous acid indicates hydrolysis only, i.e. no parallel linkage isomerization. Indeed, three sharp isosbestics were observed (501, 397, 361 nm), and moreover, these persisted for the entire reaction, consistent with the single product $[(NH_3)_5CoOH_2]^{3+}$.

The proportion of the two reaction paths is of course a direct measure of k_1/k_3 ($f = k_1/(k_1 + k_3)$; Scheme I). Thus, with use of the $k_1 + k_3$ values determined from the kinetics and the k_1/k_3 results (Table III), the individual specific rates k_1 and k_3 were obtained. Note that this method for determining k_1/k_3 is subject to sizable error (f ±0.10 to ±0.15) because the extinction coefficients of the alternative products, while different, do not differ greatly at the observed isosbestic point (Table III). Thus, we sought another procedure to confirm the accuracy of the analysis.

The molar extinction coefficient of the initial product mixture at a particular wavelength can be determined by following the absorbance change for the entire reaction at a wavelength where the spectra of the components differ appreciably and carrying out a kinetic analysis that takes the subsequent reaction into account. We have used this procedure with success previously,[9] when the secondary reaction was not overwhelmingly more rapid; this is the case here (Table II). It should be noted that the optimum wavelength is not simply that where ϵ_B and ϵ_C differ most; (ϵ_B –

(11) Benoit, R. L.; Buisson, C.; Choux, G. *Can. J. Chem.* **1970**, *48*, 2353.

Table III. Course of Reaction and Specific Rates for the Reactions of $[(NH_3)_5Co{-}NH{=}C(OH)R]^{3+}$ (R = H, CH_3) in DMSO and Aqueous $HClO_4$



solvent[a]	T, °C	$10^5(k_1 + k_3)$, s^{-1}	10^5k_2, s^{-1}	f(kin)[e]	f(isos)[f]	f(av)	10^5k_1, s^{-1}	10^5k_3, s^{-1}
			Formamide-*N* Reactant					
H_2O[a]	45	5.07	7.76	0.55	0.58	0.57	2.89	2.18
		5.32[b]	7.83[b]	0.59[b]				
	35	1.59	2.59	0.52	0.42	0.47	0.75	0.84
	25				0.46	0.46		
Me_2SO	45	32.5	3.63	0.72	0.66	0.69	22.4	10.1
			3.75[b]					
	35	6.93	0.91	0.53		0.53	3.7	3.3
	25				0.46	0.46		
			Acetamide-*N* Reactant					
H_2O	45	3.40	136.0					
		3.35[b]						
	35	1.41	49.4					
Me_2SO[c]	45	45.5	65.1	0.61	0.58	0.59	26.8	18.7
			67.4[d]					
	35	14.8	19.7					
	25				0.36	0.36		

[a] μ = 1.0 M ($NaClO_4/HClO_4$); $[H^+]$ = 0.1 M. [b] $[H^+]$ = 1.0 M. [c] $[CF_3SO_3H]$ = 0.1 M. [d] No added acid. [e] Obtained kinetically (see text). [f] Obtained from isosbestic point data (see text).

Table IV. Isosbestic Point Data and Product Analysis for the Reactions of $[(NH_3)_5Co{-}NH{=}C(OH)R]^{3+}$ (R = H, CH_3) in Acidic H_2O and DMSO

solvent[a]	T, °C	λ(isos), nm	ϵ_N, M^{-1} cm^{-1}	ϵ_O, M^{-1} cm^{-1}	ϵ_{sol}, M^{-1} cm^{-1}	f(isos)[b]
			Formamide-*N* Reactant			
H_2O	45	486	59.2	67.7	47.5	0.58
	25	489	57.6	69.3	47.6	0.46
DMSO	45	487	68.3	74.9	55.5	0.66
	25	490	65.8	76.4	57.1	0.46
			Acetamide-*N* Reactant			
DMSO	45	491	65.6	71.6	57.4	0.58
	25	493	63.5	72.6	58.4	0.36

[a] 0.1 M $HClO_4$ (H_2O, μ = 1 M; $NaClO_4$) or 0.1 M CF_3SO_3H (DMSO). [b] f = fraction of reaction producing the O-bonded amide; $f = (\epsilon_N - \epsilon_{sol})/(\epsilon_O - \epsilon_{sol})$.

$\epsilon_A)/(\epsilon_C - \epsilon_A)$ and $(k_1 + k_3)/(k_2 - (k_1 + k_3))$ need also differ considerably.

The D, t data were collected at several suitable wavelengths (Table IV) and the parameters D_0, D_∞, D_B, $k_1 + k_3$, and k_2 fitted to the function

$$D = [(D_0 - D_\infty) + (k_1 + k_3)(D_B - D_\infty)/(k_2 - (k_1 + k_3))] \exp(-(k_1 + k_3)t) - [(k_1 + k_3)(D_B - D_\infty)/(k_2 - (k_1 + k_3))] \exp(-k_2t) + D_\infty$$

by weighted nonlinear least-squares analysis; D_B is the absorbance of the first-formed $[(NH_3)_5Co(amide\text{-}O)]^{3+}/[(NH_3)_5Co(solvent)]^{3+}$ mixture. For the purpose of computing the course of the reaction (from D_B, with use of the relations $\epsilon_B = D_B/[Co]$ and $\epsilon_B = f\epsilon_0 + (1 - f)\epsilon_{sol}$, where the symbols have the same meanings as before),[9] more reliable values were obtained by using a reduced parameter fit (four) by constraining k_2 at its independently determined value. The results of these calculations (f(kin)) are given in Table III, where a comparison with the earlier method for obtaining f (f(isos)) is also presented. Within experimental error, the agreement is satisfactory.

The ^1H NMR spectrum for solutions of $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$ in acidified D_2O at 35 °C (Figure 7, supplementary material) showed at all times only a methyl singlet for starting material and/or free acetamide—the likely intermediate $[(NH_3)_5CoOC(NH_2)CH_3]^{3+}$ was never observed. This result is in accord with the spectrophotometric analysis, yet it appears to be at odds both with what was observed for Me_2SO and with the reactions of the formamide analogue in both solvents; in these cases solvolysis and parallel linkage isomerization are comparable in rate. However, the direct formation of some of the O-bonded acetamide isomer (indeterminate amount) can be accommodated if its aquation is much faster than its rate of formation via linkage isomerization; i.e., $k_2 \gg k_1 + k_3$. This is possible (but cannot be proven) since direct measurement of k_2 and $k_1 + k_3$ shows that k_2 is indeed much greater than $k_1 + k_3$. Thus, while the change in solvent from Me_2SO to H_2O results in a much slower N to O linkage isomerization, there is also a much faster solvolysis of the O-bonded isomer.

Discussion

The deprotonated ions $[(NH_3)_5CoNHCOR]^{2+}$ (R = H, CH_3) are quite stable at pH > 4, but on protonation in acidic media they yield the unstable protonated ions. These acidic forms had previously been observed in situ,[2,4] but because of their kinetic inertness, their instability with respect to linkage isomerization in solution had not been detected. We now find that in noncoordinating solvents (e.g. sulfolane) they isomerize completely to the more stable O-bound amides, $[(NH_3)_5CoOC(NH_2)R]^{3+}$ (K'_{NO} = [O-bonded isomer]$_\infty$/[*N*-bonded isomer]$_\infty \geq 100$). In coordinating solvents (H_2O, Me_2SO), N to O linkage isomerization is observed as well but there is considerable (ca. 50%) parallel solvolysis of the reactant N-bonded isomer; eventually, though, the product is totally free amide plus $[(NH_3)_5Co(solvent)]^{3+}$ due to subsequent solvolysis of the O-bonded isomer.

The observation of parallel solvolysis establishes that the N- to O-rearrangement is intramolecular. If the amide were to leave the metal as a direct result of the process of cleaving the Co–N bond, the results indicate that it would not return, and linkage isomerization would not be competitive with solvent entry. The implication therefore is that the rearrangement is concerted and has an element of Co–O bond making in the activation process.

Concerning the identity of the reactive N-bonded isomer, considerable attention has been focused in this work on the solution structures and reactivities of the acid and base forms of (form-

amide-*N*)- and (acetamide-*N*)pentaamminecobalt(III) ions. Previous workers argued (paradoxically) for the respective structures $[(NH_3)_5CoNH_2CHO]^{3+}$ and $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$, on the basis of observations for the acid forms generated in situ.[2,4] For chelating amides on Co(III)[10] and Ru(III)[12] the acidic proton has been regarded as being on the carbonyl oxygen, while for (urea-*N*)pentaamminecobalt(III)[6,7] we have shown that it lies on the coordinated nitrogen atom of the urea, at least in Me_2SO-d_6. On the basis of ^1H NMR evidence for Me_2SO-d_6 solutions, we now conclude that $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ (R = H and CH_3 (Table II), alkyl,[3] aryl[3]) is more abundant (>100:1) than its tautomer $[(NH_3)_5CoNH_2COR]^{3+}$. Moreover, NMR (^1H, ^{13}C) spectra also establish that when R = H, but not when R = CH_3, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ exists in two geometrically isomeric forms, due to restricted rotation about the localized C=N bond, in a range of solvents at 35 °C.

While $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ is certainly more prevalent than its tautomer $[(NH_3)_5CoNH_2COR]^{3+}$, we are unconvinced that the more dominant form is also the reactive entity in the isomerization process. Indeed, circumstantial evidence points to the less abundant form being responsible for the isomerization process. First, in parallel work $[(NH_3)_5CoNHCOR]^{2+}$ (R = NH_2, $NHCH_3$, $N(CH_3)_2$, NHC_6H_5) are known to protonate at the coordinated nitrogen[6] and the resulting ions $[(NH_3)_5CoNH_2COR]^{3+}$ undergo rapid intramolecular linkage isomerization ($t_{1/2}$ 40–400 s, 25 °C, H_2O) to $[(NH_3)_5CoOC(NH_2)R]^{3+}$, without substantial parallel solvolysis of the N-bonded isomer.[3,6,7,13] Second, in comparisons of models of the tautomers it is obvious that the Co···O contact is shorter for the N- compared to the O-protonated forms of the N-bonded isomers. Also, the O-protonated species has the amide in a planar arrangement with Co, a geometry that, as in bound imines $[(NH_3)_5CoNH{=}C<]^{3+}$, enhances stabilization of the complex (i.e. decreased lability). On the other hand, the N-protonated form of the N-bonded amide is expected to be a weak σ-donor ligand due to the presence of the electron-withdrawing carbonyl moiety. Third, a comparison of rates of N- to O-isomerization in H_2O of $[(NH_3)_5CoNH{=}C(OH)CH_3]^{3+}$ with $[(NH_3)_5CoNH_2CON(CH_3)_2]^{3+}$ [7,13] yields a ratio of ca. $1:10^3$. It may be more than coincidence that the ratio of O- to N-protonated forms of the uncomplexed acetamide molecule[14] is also ca. $10^3:1$. In this work it has been estimated that the ratio of O- to N-protonated forms of acetamide N-bound to Co(III) is at least $10^2:1$ and could conceivably be higher. If it were also $10^3:1$, the rates of isomerization would be explained by all of the rearrangement occurring via $[(NH_3)_5CoNH_2COR]^{3+}$. It is notable that for isomerizations of $[(NH_3)_5CoNH_2COR]^{3+}$ ions (R = NH_2,[6] $NHCH_3$,[6] $N(CH_3)_2$,[6,7] NHC_6H_5,[3] OC_2H_5,[3] OH[3,15]) and the related ions $[(NH_3)_5CoNH_2SOCH_3]^{3+}$ and $[(NH_3)_5CoNH_2SO_2R]^{3+}$ (R = alkyl, aryl),[3] all for which the acidic proton is known to reside on the bound nitrogen, their rates cover only the small range 10^{-2}–10^{-3} s^{-1} (25 °C, H_2O).

For all these $[(NH_3)_5CoNH_2SO_nR]^{3+}$ and $[(NH_3)_5CoNH_2COR]^{3+}$ ions, amides excepted, the reverse O to N linkage isomerization has been detected in coordinating solvents (H_2O, Me_2SO, Me_2NCHO)[3,6] under conditions where the product N-bonded isomer is selectively deprotonated. In contrast, no linkage isomerization has been observed for $[(NH_3)_5CoOC(NH_2)R]^{3+}$ (R = H, CH_3) in coordinating (H_2O, Me_2SO) or noncoordinating (sulfolane, acetone) solvents.[3] Even in aqueous base, where the N-bonded isomer selectively deprotonates and hence assumes thermodynamic stability over the O-bonded isomer, there is no detectable O- to N-rearrangement, and this is attributed to much faster competing hydrolysis, which is detailed in a separate publication.[3] In weakly coordinating solvents the absence of the O- to N-isomerization path merely indicates the inherent thermodynamic stability of the O-bonded isomer.

The fact that the acetamide-*N* complex rearranges faster (3–4 times in Me_2SO) than the formamide-*N* ion may be related to the relative populations of the two geometric isomers of $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$. As discussed earlier, the N-bonded acetamide complex exists entirely as the isomer with the hydroxyl substituent adjacent to Co, and this form is predicted to be more reactive toward rearrangement (the other must be unreactive). On the other hand, the N-bonded formamide analogue consists of a 50:50 equilibrium of reactive and unreactive isomers. At most this factor corresponds to only a reactivity difference of 2, and then only if the iminol tautomer is the reactive entity (which we have argued is unlikely). Interestingly, the relative reactivities for the acetamide-*N* and formamide-*N* complexes are reversed for aqueous acid.

For the reactions of the amide-*N* species, higher temperatures consistently favor the linkage isomerization reaction over the direct solvolysis pathway, while a change in solvent from H_2O to DMSO increases both the isomerization rate and N-bonded isomer solvolysis rate but lowers the solvolysis rate for the O-bonded isomer. The product distribution does not seem to be markedly solvent dependent.[1]

From the sulfolane kinetics, the electronic effect of the amide substituent (R) is judged to be small for R = H, CH_3. Nevertheless, there is some contribution since for other amides (R = CH_2Cl, CH_2F, $CH{=}CH_2$, C_6H_5, C_6H_4-*p*-F, C_6H_4-*o*-NO_2) the N- to O-isomerization is faster by up to 2 orders of magnitude for the amides with greater electron-withdrawing substituents.

Experimental Section

All NMR spectra were recorded for samples in anhydrous Me_2SO-d_6 or D_2O with use of TMS or TPPS as internal reference. ^1H NMR spectra were measured at 35 °C with a Varian T60 continuous-wave spectrometer. ^{13}C NMR spectra were obtained with a JEOL 90FXQ instrument, and samples also contained dioxane (+66.26 ppm from TMS) as a second internal reference. Infrared spectra were measured for samples as Nujol mulls between KBr plates (or DMSO solutions in an appropriate cell) on a Jasco IRA-2 instrument. Visible spectra were recorded on Cary 118C or 210 spectrophotometers.

SP-Sephadex C-25 resin was used routinely, and ions separated readily in NaCl (0.2–0.5 M) eluant. A buffered saline solution (pH 6.9, 0.23 M Na^+, 0.2 M Cl^-, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}) was suitable for separating cations with like charges (vide infra). The resin was cleaned by successive washes with traces of aqueous $Na_2S_2O_4$, H_2O, dilute aqueous Br_2, and water.

DMSO and sulfolane were dried over molecular sieves (4 Å) and twice vacuum distilled; the middle cuts were retained for kinetic studies. Triflic acid (3M Co.) was also vacuum distilled immediately prior to use. DMSO/CF_3SO_3H solutions were prepared by adding dropwise a weighed sample of chilled acid to the appropriate volume of DMSO, which was frozen prior to mixing. For kinetic studies corrections were made where appropriate for the large thermal expansion of DMSO ($\gamma = 88.4 \times 10^{-5}$ mL deg^{-1}).

Syntheses. All reagents were analytical grade. $[Co(NH_3)_5Cl]Cl_2$, prepared as described,[16] was recrystallized from hot water/HCl. $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ was prepared by a slight modification[7] of the published method[17] and isolated as the trifluoromethanesulfonate or perchlorate salt. $[(NH_3)_5CoOCHNH_2](ClO_4)_3$ and $[(NH_3)_5CoOC(CH_3)NH_2](ClO_4)_3$ were synthesized from $[(NH_3)_5CoOSO_2CF_3]^{2+}$ according to the method reported elsewhere.[3] The fully N-deuterated formamide-*O* complex $[(ND_3)_5CoOCHND_2]^{2+}$ was obtained by reaction (3 h, 25 °C) in D_2O containing a small amount of NaO_2CCH_3 and monitoring the precipitated material ($NaClO_4$) with ^1H NMR spectroscopy; care must be exercised since C–N cleavage starts to occur at a measurable rate not much above the neutral pH region. The complexes $[(NH_3)_5CoOH_2](ClO_4)_3$ (ϵ_{490} 47.5, ϵ_{342} 44.5, 0.1 M $HClO_4$) and $[(NH_3)_5CoOSMe_2](ClO_4)_3{\cdot}H_2O$ (ϵ_{519} 60.6, ϵ_{348} 63.1, 0.1 M $HClO_4$; ϵ_{518} 65.9, ϵ_{345} 70.5, DMSO) were prepared by reported procedures.

$[(NH_3)_5CoNHCHO](ClO_4)_2$. Formamide (5 g, 0.11 mol) and $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (5 g, 0.009 mol) were heated on a steam bath (70 °C) for 5 h. The mixture was cooled to room temperature,

(12) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655.
(13) Neither the $NH(CH_3)$ nor $N(CH_3)_2$ substituents compete for Co(III) during the linkage isomerization. Further, the latter substituent does not substantially increase the C–$N(CH_3)_2$ bond order as evidenced by the NMR spectra.[7]
(14) Benderley, H.; Rosenheck, K. *J. Chem. Soc., Chem. Commun.* **1972**, 179.
(15) Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630.
(16) Schlessinger, G. G. *Inorg. Synth.* **1967**, *9*, 160.
(17) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.

diluted with an equal volume of propan-2-ol or butan-2-ol, and poured into diethyl ether (200 mL). Decantation of the clear supernatant from the orange oil and two repetitions of the process resulted in an oily residue. This product was dissolved in a minimum volume of water and sorbed onto Biogel-P2 (Bio-Rad) resin. Elution with water resulted in six bands, which were collected successively and identified, following isolation by solvent evaporation, by spectroscopy as Co(II) products (first two bands, 1+ ions), a mixture of $[(NH_3)_5CoOCHO]^{2+}$ and $[(NH_3)_5CoNHCHO]^{2+}$, $[(NH_3)_5CoOCHNH_2]^{3+}$, $[(NH_3)_6Co]^{3+}$, and $[(NH_3)_5CoNHCHOCo(NH_3)_5]^{5+}$. The same elution order was observed on SP-Sephadex C-25 resin (0.5 M $NaClO_4$), but on Dowex resin $[(NH_3)_6Co]^{3+}$ elutes ahead of $[(NH_3)_5CoOCHNH_2]^{3+}$ (1–3 M $NaClO_4$ eluant).

$[(NH_3)_5CoO_2CH]^{2+}$ and $[(NH_3)_5CoNHCHO]^{2+}$ were readily separated on the ion-exchange resins by acidifying the eluant (pH 3–5, CH_3CO_2H), thereby partially protonating the latter ion. Following removal of the former cation, the latter was deprotonated by using aqueous Tris (pH 9.5) and isolated and recrystallized as the orange perchlorate salt from aqueous $NaClO_4$ (pH 9.5); yield 48%. The complex contained one molecule of lattice water, which was removed by drying over P_2O_5 in vacuo. Anal. Calcd for $[(NH_3)_5CoNHCHO](ClO_4)_2$: C, 3.10; H, 4.39; N, 21.71; Cl, 18.35. Found: C, 3.17; H, 4.37; N, 21.49; Cl, 18.15.

$[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$. $[(NH_3)_5CoNHCHO](ClO_4)_2$ was quantitatively converted to its protonated form simply by filtering a saturated aqueous solution into aqueous 5 M $HClO_4$. The yellow granular crystals, which precipitated quickly, were washed copiously with anhydrous diethyl ether (no alcohol) and recrystallized from warm (ca. 30 °C) water/ClO_4^-. While rapid addition of 5 M $HClO_4$ yielded granular crystals, slow crystallization from aqueous $NaClO_4$ (2 M $HClO_4$) on a temperature gradient produced large plates. The products were stored over P_2O_5 in vacuo. Anal. Calcd for $[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$: C, 2.46; H, 3.69; N, 17.23; Cl, 21.85. Found: C, 2.48; H, 3.71; N, 17.10; Cl, 21.73.

$[(NH_3)_5CoNHCOCH_3](ClO_4)_2$ and $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$. $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$ was prepared by the published route[4] involving base-catalyzed hydration of $[(NH_3)_5CoNCCH_3](ClO_4)_3$, except that the latter was synthesized directly from $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ in acetonitrile. A less favorable synthesis of $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$ was achieved by heating $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (5 g, 0.009 mol) with dry acetamide (5 g, 0.08 mol) in acetone (50 mL) on a steam bath (70 °C) for 5 h. The pure product can be isolated by repeated (3×) recrystallization from aqueous $NaClO_4$ or obtained following ion-exchange purification on SP-Sephadex C-25 resin as described for $[(NH_3)_5CoNHCHO]^{2+}$. Anal. Calcd for $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$: C, 5.98; H, 4.74; N, 20.94; Cl, 17.71. Found: C, 5.96; H, 4.75; N, 20.62; Cl, 17.68. The yellow protonated form was obtained as granules or plates as described for $[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$. Anal. Calcd for $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$: C, 4.79; H, 3.99; N, 16.72; Cl, 21.24. Found: C, 4.70; H, 4.13; N, 16.52; Cl, 21.18.

Kinetic Studies. Solid cobalt complexes were rapidly dissolved in solvents that had been preequilibrated in the cell compartment of a Cary 118C or 210 spectrophotometer. Cell temperatures were measured with a glass-housed platinum resistance thermometer, and the cell block was thermostated by a Haake bath with a temperature control better than ±0.1 °C (20–35 °C).

Rates of solvolysis of $[(NH_3)_5CoOC(NH_2)R]^{3+}$ were determined from absorbance changes at 500, 520, and 540 nm, while reactions of $[(NH_3)_5CoNHCOR]^{2+}$ or $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ in acidic solutions (DMSO, H_2O) were followed by scanning the visible spectrum (300–600 nm) and by monitoring absorbance changes at specific wavelengths (R = CH_3, 460, 470, 480, 530 nm; R = H, 460, 470, 480, 340 nm). Three temperatures were investigated, 45 and 35 °C for the kinetics and 25 °C as well for the determination of the course of reaction. For the solvolysis reactions of the O-bonded complexes, and for the reaction of the acetamide-*N* complex in aqueous acid, sharp isosbestic points were observed which persisted for the entire reaction (refer to the Results). The ionic strength was maintained by $NaClO_4$ (μ = 1.0 M). Absorbance/time data were analyzed initially from slopes of semilogarithmic plots by using the Guggenheim method and later by using weighted nonlinear least-squares analysis with the appropriate functional form of the integrated rate equation (simple first order or consecutive first order). All derived rate data were determined at least in triplicate.

pK'_a Determination. The acidity of the acetamide-*N* complex in DMSO at 25 °C was determined spectrophotometrically at 400 nm, where the protonated complex (in the presence of a slight excess of CF_3SO_3H) and deprotonated complex have molar absorptivities of 10.7 and 31.7 M^{-1} cm^{-1}, respectively. The molar absorptivity was then determined for samples of $[(NH_3)_5Co{-}NH{=}C(OH)CH_3](ClO_4)_3$ at various concentrations and the degree of dissociation (and thus K'_a) deduced for each. The consistent result pK'_a = 3.6 was obtained:

10^3[Co], M	ϵ(obsd), M^{-1} cm^{-1}	$10^4K'_a$	pK'_a
0.946	19.0	2.36	3.63
5.10	14.7	2.3	3.6
24.4	12.7	2.3	3.6

Product Analyses. $[(NH_3)_5CoOC(NH_2)R]^{3+}$ ions (R = H, CH_3) were tested for purity by dissolution in water and sorption onto and elution from SP-Sephadex C-25 resin with 0.23 M Na^+ (pH 6.88, 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-) eluant. A single (3+) band was observed in each case, and under these conditions (carboxylato)pentaamminecobalt(III) ions (2+) elute ahead of $[Co(NH_3)_5OH_2]^{3+}$, which elutes ahead of the O-bonded amide complexes. Note that the amide-*N* complex also elutes as a 2+ ion in this medium but may be separated from other 2+ ions as described above in the preparation of $[(NH_3)_5CoNHCHO]^{2+}$. For R = CH_3, the complex was dissolved in ice–water and sorbed onto resin in jacketed columns (ca. 2 °C) to prevent ensuing aquation.

The sulfolane equilibrium was established by separately dissolving $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$ (e.g. 0.496 01 g, 0.989 mmol) and $[(NH_3)_5CoOC(NH_2)CH_3](ClO_4)_3$ (e.g. 0.419 95 g, 0.838 mmol) in dry sulfolane (ca. 30 mL) in stoppered conical flasks and immersing the solutions in a thermostated Laude bath (36.20 ± 0.01 °C) for 21 or 68.5 h. The solutions were then cooled and sorbed as cold aqueous solutions onto jacketed columns (2 °C) of Sephadex resin. Products were separated by using 0.46 M Na^+ (pH ca. 7, 0.02 M $H_2PO_4^-$, 0.02 M HPO_4^{2-}, 0.4 M Cl^-) eluant. Similar experiments were performed for the formamide analogues. No N-bonded isomer was detected from either reaction.

Cobalt recoveries from columns were 100 ± 2%. Product distributions were determined spectrophotometrically for column eluates by using molar absorptivities determined for the appropriate medium; these data appear in the tables or are given elsewhere.[3,6]

Acknowledgment. D.P.F. acknowledges a visiting fellowship to the John Curtin School of Medical Research at the Australian National University. We thank Dr. M. D. Fenn (Medical Chemistry Group, ANU) for assistance in recording some of the ^{13}C NMR spectra. Financial support for this work from the Australian Research Grants Scheme is also gratefully acknowledged.

Registry No. $[(NH_3)_5CoNHCHO](ClO_4)_2$, 26729-10-2; $[(NH_3)_5CoOSO_2CF_3](CF_3O_3S)_2$, 75522-50-8; $[(NH_3)_5CoOCHO]^{2+}$, 19173-64-9; $[(NH_3)_5CoOCHNH_2]^{3+}$, 44819-96-7; $[(NH_3)_6Co]^{3+}$, 14695-95-5; $[(NH_3)_5CoNHCHOCo(NH_3)_5]^{5+}$, 45163-07-3; $[(NH_3)_5Co(NH{=}C(OH)H](ClO_4)_3$, 123752-54-5; $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$, 43067-18-1; $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$, 123752-55-6; $[(NH_3)_5CoOC(NH_2)CH_3]^{3+}$, 123752-56-7; *trans*-$[(H_3N)_5CoNH{=}C(OH)H]^{3+}$, 123808-87-7; $[(H_3N)_5CoO_2CCH_3]^{2+}$, 16632-78-3; $[Co(NH_3)_5NCCH_3]^{3+}$, 44819-13-8; CH_3CONH_2, 60-35-5.

Supplementary Material Available: Figures 6 and 7, giving NMR spectra, and Table V, giving molar absorptivities (3 pages). Ordering information is given on any current masthead page.