complexes are generated from the oxidation of excess ligand by Cr(VI). However, the isolation of these complexes as pure solids still remains a difficult problem.

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Contribution from the Department of Chemistry, University College, University of New South Wales, Australian Defence Force Academy, Campbell, ACT 2600, Australia

Factors Influencing the Nitrogen vs Oxygen Bonding Mode of Amides Bound to Pentaamminecobalt(III) and the Kinetics and Mechanism of Rearrangement

David P. Fairlie, Patricia M. Angus, M. David Fenn, and W. Gregory Jackson*

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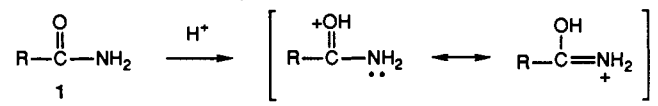
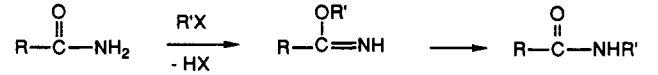
The preparation, characterization, properties, and rearrangements of a series of pentaamminecobalt(III) complexes of amides, $RCONH_2$, are described (R = H, CH_3, CF_3, CH_2Cl, CH_2F, $CH{=}CH_2$, C_6H_5, C_6H_4-4-F, C_6H_4-2-NO_2). Some of the nitrogen-bonded amide complexes were synthesized by base-catalyzed hydration of $[(NH_3)_5CoN{\equiv}CR]^{3+}$; others, including those inaccessible by this route, were synthesized by linkage isomerization of the oxygen-bonded amide complexes, $[(NH_3)_5CoOC(NH_2)R]^{3+}$, in coordinating but aprotic solvents containing noncoordinating base. The N-bonded amide products were isolated pure in both basic and acidic forms, $[(NH_3)_5CoNHCOR]^{2+}$ and $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$. The former are thermodynamically stable, while the latter (pK'_a <4), although kinetically robust, are thermodynamically unstable with respect to the corresponding O-bonded linkage isomer and rearrange slowly in solution ($t_{1/2}$ hours, 25 °C). The isomer equilibrium for amides as O- or N-bonding *neutral* ligands lies at least 100:1 to the side of the O-bonded isomer in sulfolane, in which neither ligand deprotonation nor solvolysis of either isomer could be detected. In coordinating solvents, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ also solvolyzes, at a rate comparable to that for competing N to O isomerization. For Me_2SO these reactions have been identified by ^1H NMR measurements. The results require the isomer interconversion to be intramolecular. All the N-bonded amide complexes $[(NH_3)_5CoNHCOR]^{2+}$ protonate at oxygen (in Me_2SO-d_6), producing $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$; the sole exception is the case R = CF_3, which does not detectably protonate. The rate of N to O isomerization in sulfolane is dependent on the substituent R, but the rates span a range of only a factor of about 20. When the substituent can donate an electron pair (R = NH_2, $NHCH_3$, $N(CH_3)_2$, NHC_6H_5, OC_2H_5, OH), N to O isomerization is several orders of magnitude faster ($t_{1/2}$ seconds). The rate distinction between these two classes of isomerizing compounds is attributed to the different positions of the tautomeric equilibrium between N- and O-protonated forms of $[(NH_3)_5CoNHCOR]^{2+}$ and the differences in reactivity between the tautomers. The solution structures for these tautomers in Me_2SO are established by the ^1H NMR spectra. The O to N linkage isomerization was not observed in neutral aqueous solution because competing hydrolysis is faster. However the reaction can be forced in aprotic solvents in the presence of a noncoordinating base, and the propensity for this reaction is related to the ability of the O-coordinated neutral amide to dissociate a proton from the remote nitrogen (pK'_a ca. 11, H_2O, formamide-*O*, and acetamide-*O*). The mechanism is discussed and analogies are drawn with the Chapman rearrangement, which involves O to N migration of substituents on organic amides and imino esters. Factors that influence the interconversion of linkage isomers, including the site of protonation, isomer acidity, solvent, temperature, and amide substituents, are discussed and compared with related linkage isomeric complexes of pentaamminecobalt(III).

Introduction

Carboxylic acid amides **1** are very weak bases and also poor nucleophiles for electrophilic reagents. The oxygen is both more



basic and more nucleophilic than the nitrogen atom.[1] However, while good electrophiles *initially* alkylate the O-terminus of amides, these compounds often rearrange upon heating to the N-substituted products:[2]



This result indicates that the carbonyl oxygen is the preferred nucleophile whereas the N-alkylated amide is the thermodynamically more stable compound. This (Chapman[3]) rearrangement is carried out typically at about 180 °C, or as low as 100 °C in the presence of excess alkylating agent. The mechanism is intramolecular for *O*-aryl imidates although at least partly intermolecular for *O*-alkyl compounds.[4]

Amides are ambidentate ligands for metal ions,[5a] and by analogy with the above, one might expect kinetically controlled syntheses to lead to the O-metalated complex, while the N-bonded form would be favored under equilibrium conditions. Amides, for which formamide and acetamide have been the prototypes,[5a,12,13] have a tendency to coordinate via oxygen to "hard" metal complexes[5] but via nitrogen to "soft" metals,[6] consistent with the greater basicity of the amide oxygen. Thus the "hard" labile complex[7] $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ reacts with **1** in poorly coordinating solvents (acetone, sulfolane), yielding exclusively[8] the

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Table I. Rate Data for the Isomerization and Aquation Reactions of Urea-*N* and Amide-*N* Complexes $[(NH_3)_5CoY]^{3+}$

Y	k_{NO}, s^{-1} [a]	k_{aq}, s^{-1} [b]	ref
$-NH_2CONH_2$	3.15×10^{-3}	3.4×10^{-4}	14
$-NH_2CON(CH_3)_2$	1.7×10^{-2}	9.0×10^{-4}	14
$-NH_2CO_2C_2H_5$	4.4×10^{-3}	2.9×10^{-3}	15
$-NH{=}C(OH)H$	0.75×10^{-5} [c]	0.84×10^{-5} [c]	13
	(3.7×10^{-5}) [d]	(3.3×10^{-5}) [d]	13
$-NH{=}C(OH)CH_3$	(11.7×10^{-5}) [d]	(3.1×10^{-5}) [d]	21

[a] Specific rate constant for N to O isomerization in H_2O at 25 °C (0.1 M $HClO_4$). [b] Specific rate constant for spontaneous aquation. [c] 35 °C. [d] Data for Me_2SO/H^+ as solvent, 35 °C.

oxygen-bonded isomer $[(NH_3)_5CoOC(NH_2)R]^{3+}$. This rearranges to the deprotonated N-bonded form in aprotic solvents containing base,[9] but this reaction is not observed in the absence of base, nor in neutral or basic aqueous solution because of faster and irreversible hydrolysis to $[(NH_3)_5CoOH]^{2+}$.[13]

The N-bonded isomers can in most cases be obtained quantitatively through base hydrolysis of the corresponding nitrile precursors:[10-12]

$$[(NH_3)_5Co{-}NCR]^{3+} + OH^- \rightarrow \underset{\mathbf{2}}{[(NH_3)_5Co{-}NHCOR]^{2+}}$$

The red-orange product **2** is a weak base, protonating only below pH 4 to give its yellow conjugate acid:[13]

$$\underset{\mathbf{2}}{[(NH_3)_5CoNHCOR]^{2+}} + H^+ \rightleftharpoons \begin{cases} \underset{\mathbf{4}}{[(NH_3)_5CoNH{=}C(OH)R]^{3+}} \\ \underset{\mathbf{3}}{[(NH_3)_5CoNH_2COR]^{3+}} \end{cases}$$

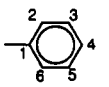
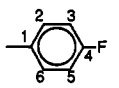
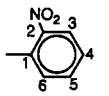
For formamide-*N* and acetamide-*N*, **4** rather than **3** is the predominant tautomer, and we have suggested that the site of protonation may be important in determining the reactivity of the N-bonded isomer.[13,14] We have identified **3**, rather than **4**, for the analogous urea complexes (R = NH_2, $NHCH_3$),[14] which undergo fast Co–NH_2COR cleavage in solution and in the solid state ($t_{1/2}$ seconds–minutes, 25 °C):

$$[(NH_3)_5CoNH_2COR]^{3+} \rightarrow \begin{cases} [(NH_3)_5CoOC(NH_2)R]^{3+} \quad >90\% \\ [(NH_3)_5Co(solvent)]^{3+} + RCONH_2 \quad <10\% \end{cases}$$

The linkage isomerization (N to O) is intramolecular (the amide never leaves the metal). For ureas and the related urethane-*N* complex, it occurs 1 order of magnitude more quickly than competing dissociative solvolysis and 3 orders of magnitude more rapidly than isomerization of the two amide-*N* complexes (R = H, CH_3).[13] For the latter two amides, solvolysis now occurs at a rate similar to that for N to O rearrangement.[13] Table I summarizes these data.

In view of these differences, we have now examined a series of amides to determine whether the substituent (R) affects the site of protonation, the rate of isomerization, or the position of the isomer equilibrium. We envisaged that all of these features may be influenced by electronic and steric changes to the amide.

Table IV. ^1H NMR Spectral Data (δ, ppm) for N-Bonded Amide Complexes $[(NH_3)_5CoHCOR]^{2+}$ in Me_2SO-D_6 at 20 °C[a]

R	cis NH_3	trans NH_3	CoNH	other	assgnt
$-H$	3.22	3.14	3.86	8.06	H–C[b]
$-CH_3$	3.21	3.12	3.79	1.94	CH_3
$-CH_2Cl$	3.30	3.16	4.34	4.06	CH_2Cl
$-CH_2F$	3.30	3.15	4.28	4.62[c]	CH_2F
$-CF_3$	3.31	3.19	5.15		
$-CH{=}CH_2$	3.28	3.22	4.22	5.29[d]	$=CH_{trans}$
				5.78[d]	$=CH_{cis}$
				6.28[d]	$=CH_{gem}$
	3.30	3.16	4.59	7.40[e]	H-3, H-5, H-4
				7.77[e]	H-2, H-6
	3.38	3.25	4.63	7.23[f]	H-3, H-5
				8.06[g]	H-2, H-6
	3.30	3.23	4.95	7.60[e]	H-6
				7.72[e]	H-4, H-5
				7.87[e]	H-3

[a] Shifts downfield from TMS. [b] Doublet, J = 4 Hz. [c] Doublet, J_{H-F} = 48 Hz. [d] Quartet, ABX spectrum. [e] Center of multiplets. [f] Approximately triplet. [g] Approximately quartet.

Electron-withdrawing substituents, for example, should facilitate Co–N(amide) bond scission, accelerating N to O isomerization or competing solvolysis of the N-bonded amides or both.

In contrast to the chemistry of coordinated ureas and carbamates,[14,15] the N to O isomerization of amides is difficult to observe because it occurs more slowly than subsequent solvolysis of intermediate O-bonded isomer product. Therefore in order to compare reactivities for a wider range of amide-*N* complexes, it was useful to examine the isomerization process in a noncoordinating solvent to avoid this complicating feature, and for this purpose sulfolane proved suitable. We also report some results for Me_2SO as solvent.

Results and Discussion

Synthesis and Characterization. The synthesis and characterization of a wide range of (pink) oxygen-bonded amide complexes have been detailed elsewhere.[8] The ^1H and ^{13}C NMR and visible absorption spectra, chromatographic behavior, and acid–base properties permit the distinction between linkage isomers as indicated below.

A convenient and high-yield synthesis of the N-bonded isomer utilizes the nitrile precursors.[12] While alternative syntheses of nitrile complexes exist,[7,16] the reaction of $[(NH_3)_5CoOSO_3CF_3](CF_3SO_3)_2$ with the appropriate nitrile either in pure form[7] or in solution[17] is a fast, convenient, and efficient method. The nitrile complexes so obtained were characterized by NMR (^1H, ^{13}C) spectroscopy (Tables II and III, supplementary material) and assayed for purity by cation-exchange chromatography. They each show the diagnostic nitrile sp carbons in their ^{13}C NMR spectra as well as the signals attributable to the substituent R. When R = alkyl and aryl, the ^{13}C resonance for the nitrile carbon shifts substantially (ca. 15 ppm) to lower field upon coordination, and this appears to be characteristic.[18]

The nitrile complexes are rapidly and quantitatively converted to the N-bonded amide complexes by base hydrolysis:[10a]

$$[(NH_3)_5Co{-}NCR]^{3+} + OH^- \rightarrow [(NH_3)_5Co{-}NHCOR]^{2+}$$

For the nitriles considered here, these reactions are about 6 orders

(9) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1990**, *175*, 203.
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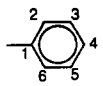
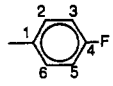
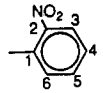
Table V. Carbon-13 NMR Spectral Data (δ, ppm) for Amides ($RCONH_2$) and Deprotonated N-Bonded Amide Complexes $[(NH_3)_5CoNHCOR]^{2+}$ in Me_2SO-d_6 at 20 °C[a]

R	C=O free	C=O coord	other carbons free	other carbons coord	assgnt
-H	164.0	173.5			
$-CH_3$	172.4	180.6	22.6	27.2	CH_3
$-CH_2Cl$	168.6	176.3	42.8	44.2	CH_2Cl
$-CH_2F$	169.9[b]	177.2[b]	79.9[c]	80.5[c]	CH_2F
$-CF_3$	158.5[d]	165.0[d]	116.2[e]	114.1[e]	CF_3
$-CH=CH_2$	166.7	176.0	125.8	120.2	=CH
			132.0	135.3	$=CH_2$
	168.2	176.9	127.6	126.7	C-3, C-5
			128.3	127.9	C-2, C-6
			131.3	129.8	C-4
			134.3	138.1	C-1
	166.8	175.8	115.1[f]	114.4[f]	C-3, C-5
			130.1[g]	128.9[g]	C-2, C-6
			130.7[h]	134.5[h]	C-1
			163.9[i]	162.1[i]	C-4
	167.4	175.5	124.1	123.5	C-3
			128.9	128.8	C-1
			130.8	129.5	C-6
			132.7	133.0	C-4
			133.5	135.1	C-5
			147.3	148.5	C-2

[a] Shifts downfield from TMS, internal reference *p*-dioxane (δ 66.26). [b] Doublet, J_{C-F} = 18 Hz. [c] Doublet, J_{C-F} = 180 Hz. [d] Quartet, J_{C-F} = 25 Hz. [e] Quartet, J_{C-F} = 290 Hz. [f] Doublet, J_{C-F} = 21 Hz. [g] Doublet, J_{C-F} = 9 Hz. [h] Doublet, J_{C-F} = 3 Hz. [i] Doublet, J_{C-F} = 250 Hz.

of magnitude faster when the nitrile is anchored to cobalt(III) than when uncoordinated.[10,12] The deprotonated form of the amide-*N* product is inert under the basic preparative conditions (but it becomes much more reactive upon protonation—vide infra). The stable deprotonated amide-*N* complex can also be synthesized in greater than 60% yield directly from the amide. This synthesis is valuable when the appropriate nitrile precursor is unavailable or nonexistent, and we have used it successfully for the R = H, CF_3, and FCH_2 derivatives.

Table IV reports the ^1H NMR data for the deprotonated N-bonded isomers, $[(NH_3)_5CoNHCOR]^{2+}$. Unlike the spectra for the N- and O-bonded complexes of neutral amides (vide infra), the signals for cis (12 H) and trans (3 H) NH_3 groups are only slightly separated (<0.2 ppm); these are positioned ca. 3.2–3.3 ppm downfield of TMS. The location of the proton resonance for the CoNH of the coordinated amide (3.7–5.2 ppm) is diagnostic of these complexes; it occurs *downfield* of the NH_3 signals. This contrasts with the analogous peak of $[(NH_3)_5CoNHCOR]^{2+}$ for ureas and carbamates, which appears markedly *upfield*, at 1–3 ppm.[14,15] We have ascribed this difference to the greater degree of CoNH= character versus $CoNH_2$— in the amide complexes relative to the urea and carbamate complexes.[14] Electron-withdrawing substituents shift this resonance to lower field as expected. The other ^1H resonances derived from the amide substituent (R) aid in "fingerprinting" each compound.

The ^{13}C NMR chemical shifts for the free amides and the basic forms of the N-bonded isomers are given in Table V. In all cases the carbonyl resonance is 5–10 ppm downfield from the corresponding signal of the free amide. All of the complexes show the C resonance for C=O between 175 and 180 ppm (except, inexplicably, for formamide and trifluoroacetamide). In general, the C=O signal, while identifying the mode of amide coordination (N or O), does not distinguish the protonated from the deprotonated amide-*N* forms. (The position of the Co–NH_3 resonances in the ^1H NMR spectra do however provide this distinction, as noted earlier.) Indeed, the ^{13}C spectra for the protonated and deprotonated amide-*N* species are almost superimposable, a surprising observation, given that protonation occurs on the remote oxygen; the shielding effect of a change in C–O bonding is closely compensated by the change in the C–N bond electron distribution.

The aromatic carbons for the 4-fluorobenzamido-*N* complex were assigned on the basis of the magnitude of the coupling constants for carbons ortho, meta, and para to the fluorine.

Table VI. Molar Absorptivities (ϵ, M^{-1} cm^{-1}, at λ_{max}, nm) for $[(NH_3)_5CoNHCOR](ClO_4)_2$ in Aqueous Base and Acid

R	0.1 M Tris λ_{max}	0.1 M Tris ϵ	0.1 M Tris λ_{max}	0.1 M Tris ϵ	0.1 M CF_3SO_3H λ_{max}	0.1 M CF_3SO_3H ϵ	λ_{max}	ϵ
-H	483	68.6	346	80.5	478	62.0	348	64.1
$-CH_3$	484	72.4	349	86.5	475	64.1	340	60.8
$-CH_2Cl$	481	74.3	342	95.4	481	74.3	345	84.4
$-CH_2F$	480	70.7	345	88.3	480	68.1	345	86.4
$-CF_3$	480	68.4	345	73.4	480	70.9	345	75.0
$-CH=CH_2$	484	82.8	346	107.4	477	76.4	342	88.9
$-C_6H_5$	486	88.9	347	118.2	478	82.9	343	98.8
$-C_6H_4$-4-F	485	88.8	346	117.3	481	84.0	343	102.2
$-C_6H_4$-2-NO_2	484	83.7			481	86.1		

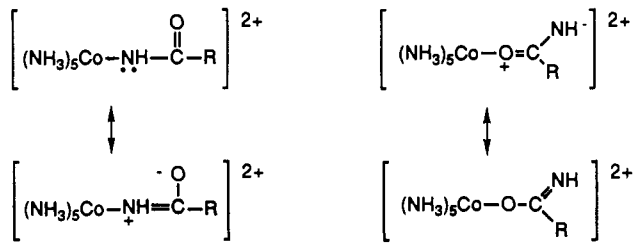
Table VII. Kinetic Data[a] for the Rearrangement of $[(NH_3)_5CoNH=C(OH)R](ClO_4)_3$ in Sulfolane at 35 °C[b]

R	10^5k_{obs}, s^{-1}	R	10^5k_{obs}, s^{-1}
-H	3.46	$-CH=CH_2$	41.6
$-CH_3$	4.68	$-C_6H_5$	49.5
$-CH_2Cl$	12.4	$-C_6H_4$-4-F	68.3
$-CH_2F$	7.6	$-C_6H_4$-2-NO_2	59.5

[a] Determined from absorbance changes at 520 nm. [b] No added acid.

The colors and associated visible absorption spectra are a useful guide to the coordination mode of the amide ligand. Whereas the pink oxygen-bonded isomers, $[(NH_3)_5CoOC(NH_2)R]^{3+}$, show absorbance maxima at 505–515 nm,[8] the orange-red deprotonated N-bonded complexes $[(NH_3)_5CoNHCOR]^{2+}$ have maxima ca. 480–486 nm (Table VI), consistent with the stronger ligand field expected for coordination as an anion. The yellow acidic forms, $[(NH_3)_5CoNH=C(OH)R]^{3+}$, have maxima at even higher energy (477–481 nm) for reasons outlined elsewhere[12,13] for the case of R = CH_3.

Acid–Base Properties and Site of Acidic Proton. An important distinction between the linkage isomers concerns their relative acidities. The amide-*N* complexes (pK'_a <4) are at least 7 orders of magnitude more acidic than their amide-*O* isomeric counterparts (pK'_a ca. 11).[8] This difference originates in the different resonance stabilizations of the conjugate bases $[(NH_3)_5CoNHCOR]^{2+}$ and $[(NH_3)_5CoOC(NH)R]^{2+}$:



the former is more effectively stabilized. This striking difference in acidity causes the marked pH dependence of the position of the isomeric equilibrium and can be vitally important in detecting linkage isomerization reactions, as explained for the case of O- to N-bonded urea rearrangements.[14]

^1H NMR evidence unequivocally established O- rather than N-protonation of $[(NH_3)_5CoNHCOCH_3]^{2+}$ in Me_2SO, and this result is also expected in water.[13] The structure of the formamide analogue was likewise identified as $[(NH_3)_5CoNH=C(OH)H]^{3+}$ through ^1H NMR spectra. Because NMR studies[14] showed that the analogous urea complexes protonate on nitrogen rather than oxygen, yielding $[(NH_3)_5CoNH_2COR]^{3+}$, we examined closely the ^1H NMR spectra for all our amide complexes.

The CoNH proton of $[(NH_3)_5CoNHCOC_6H_5]^{2+}$ resonates at 4.60 ppm in Me_2SO-d_6 and at 5.97 ppm for the crystallized protonated species $[(NH_3)_5CoNH=C(OH)C_6H_5](ClO_4)_3$ dissolved in Me_2SO-d_6 containing no excess acid. However for the latter the chemical shift was concentration dependent, and clearly the complex partly dissociates in Me_2SO, in accord with its anticipated strong acidity. However the fact that this signal still integrates for only one rather than two protons establishes the

Table VIII. Selected ^{1}H NMR Spectral Data (δ, ppm) for Amide-*N*[a] and Amide-*O*[b] Complexes and Uncoordinated Amides Suitable for Monitoring Linkage Isomerization in Me_2SO-d_6 at 20 °C[c]

	cis NH_3	trans NH_3	NH/NH_2
$[(NH_3)_5CoNHC(OH)CH_2Cl]^{3+}$	3.31	3.17	7.67
$[(NH_3)_5CoOC(NH_2)CH_2Cl]^{3+}$	3.95	2.68	8.22, 9.40
$CH_2ClCONH_2$			7.38, 7.62
$[(NH_3)_5CoNHC(OH)CH_2F]^{3+}$	3.39	3.26	6.72
$[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$	4.10	2.76	8.11, 9.22
CH_2FCONH_2			7.49, 7.59
$[(NH_3)_5CoNHC(OH)CH{=}CH_2]^{3+}$	3.42	3.32	7.50
$[(NH_3)_5CoOC(NH_2)CH{=}CH_2]^{3+}$	3.99	2.78	7.56, 9.19
$CH_2{=}CHCONH_2$			7.14, 7.55
$[(NH_3)_5CoNHC(OH)C_6H_5]^{3+}$	3.40	3.26	6.45
$[(NH_3)_5CoOC(NH_2)C_6H_5]^{3+}$	4.08	2.84	7.90,[d] 9.51
$C_6H_5CONH_2$			6.84,[d] 7.00
$[(NH_3)_5CoNHC(OH)C_6H_4\text{-}2\text{-}NO_2]^{3+}$	3.37	3.24	6.28
$2\text{-}NO_2C_6H_4CONH_2$			7.70, 8.16
$[(NH_3)_5CoNHC(OH)C_6H_4\text{-}4\text{-}F]^{3+}$	3.42	3.33	[e]
$4\text{-}FC_6H_4CONH_2$			7.41, 8.01

[a] Spectra recorded in Me_2SO with a trace of CF_3COOH or CF_3SO_3H to ensure complex remains protonated in solution. [b] Synthesized directly by published methods.[8] [c] Downfield from TMS. [d] Identified by proton decoupling. [e] No signal observed.

CoNH–, rather than the $CoNH_2$–, entity for the coordinated amide. [In the presence of added acid (CF_3SO_3H, CF_3CO_2H) the signal shifts downfield to 7.6 ppm but no further, and there is still no alteration in its area.] In addition to the aromatic resonances, a separate signal detected further downfield (8.5 ppm) is attributed to the OH proton, and this continues to move and increase in area on addition of more acid to greater than 12 ppm, consistent with exchange of the acidic oxygen proton with H^+ and trace water. Note that the alternative form of the acid complex, $[(NH_3)_5CoNH_2COC_6H_5]^{3+}$, would give rise to a single NH_2 resonance rather than two because of the acid-exchange phenomenon. The ^{1}H NMR data for all the protonated amide complexes are summarized in Table VIII.

Supporting evidence for protonation at oxygen was obtained by monitoring the changes with time of the location of the most downfield (OH) resonance in the absence of added acid but with a trace of water present. The acidic benzamide-*N* complex (pK'_a 1.65) slowly linkage-isomerizes to the nonacidic benzamide-*O* complex (pK'_a ca. 11), and as the reaction proceeds, the low-field resonance progressively moves upfield until it finally reaches the position of free H_2O (3.6 ppm). Throughout this reaction the separate signal at 5.97 ppm diminishes in intensity but its position is invariant. This behavior is consistent with the protonated form possessing one acidic proton that is always in rapid (NMR time scale) exchange with H_2O present and one ligand proton that is not in exchange.

The ^{1}H NMR spectra of several other protonated amide-*N* complexes were also monitored with time. In *all* cases, the above behavior was reproduced: one low-field signal one proton in magnitude and invariant in position with $[H^+]$ and time and another signal further downfield with a strong chemical shift dependence on $[H^+]$ and time. We conclude that all these amide-*N* complexes protonate on the carbonyl oxygen atom.

The location of the lowest energy ligand field absorption maximum in the visible spectra of the deprotonated amide-*N* complexes occurs in the fairly narrow range 480–486 nm (Table VI). Upon protonation of the complexes, this band moves up to 8 nm to lower wavelength, an observation consistent with the increased ligand field expected for the protonated amide ligand. The magnitude of this shift and the positions of this first absorption maximum for the protonated amide complexes and their conjugate bases is a feature we have argued as characteistic of O-protonation.[13,14] The slight difference in energy between the absorption maximum for the deprotonated and protonated complexes is consistent with the minor change in electron distribution near cobalt upon protonation of the remote oxygen of $[(NH_3)_5CoNHCOR]^{2+}$, whereas protonation at the bound nitrogen would be expected to more significantly alter the electron environment around the metal.

Acidity constants for some amide-*N* species have been determined previously. The 20-fold difference in acidity for the complexes R = H (pK'_a 2.16)[5a] and R = CH_3 (pK'_a 3.02)[12] can be attributed to the electron-releasing (base-strengthening) property of the methyl substituent vis-à-vis the formyl proton. The even greater acidity (pK'_a 1.65)[10a] of the benzamide-*N* complex can be attributed to the electron-attracting power of the aromatic ring, which enhances delocalization of the negative charge of the amide ligand in $[(NH_3)_5CoNHCOC_6H_5]^{2+}$. This electron-withdrawing effect is even more striking in the trifluoroacetamido-*N* complex. It does not detectably protonate in either water or Me_2SO solution containing CF_3SO_3H (1 M). This fact and the lack of detectable acid catalysis for loss of the amide would suggest a pK'_a significantly less than zero, consistent with, for example, the relative acidities of CH_3CO_2H and CF_3CO_2H.

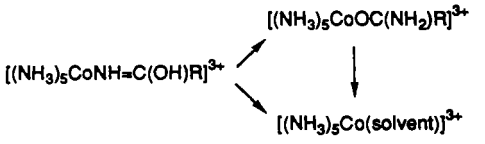
N to O Linkage Isomerization: Noncoordinating Solvents. To avoid complications caused by solvolysis of either N- or O-bonded linkage isomers, we examined the kinetics of isomer rearrangement in the poorly coordinating solvent tetramethylene sulfone (sulfolane). In this solvent, even the strongly acidic $HClO_4$ is known to be undissociated (pK'_a 2.7).[19] Thus the much less acidic N-bonded isomer must be undissociated, provided the solvent is dry. In sulfolane the yellow protonated N-bonded amide complexes rearrange slowly but completely to their pink O-bonded isomers. We have established that neither proton dissociation nor ligand dissociation (solvolysis) of N- and O-bonded amide isomers occurs in sulfolane; only linkage isomerization is observed:

$$[(NH_3)_5CoNH{=}C(OH)R]^{3+} \rightarrow [(NH_3)_5CoOC(NH_2)R]^{3+}$$

Chromatographic product analyses for these reactions confirmed the formation of the O-bonded isomers exclusively. Experiments with large (>1 g) quantities of the reactant N- and O-bonded isomers demonstrated, first, that the O-bonded isomers do not rearrange to N-bonded isomers (<1%) and, second, that all the N-bonded isomers listed in Table VII transform quantitatively (>98%) to the O-bonded isomers. Thus the equilibrium lies well to the side of the O-bonded isomer in every case ($K_{NO} = k_{NO}/k_{ON} \geq 100$). These results imply that the O-bonded isomers are at least 10 kJ mol^{-1} more stable thermodynamically ($\Delta G° = -RT \ln K_{NO}$) than the respective N-bonded isomers.

Table VII lists the observed first-order rate constants for this rearrangement at 35 °C as a function of the alkyl or aryl substituent (R) of the amide. The substituent clearly influences the rate of linkage isomerization, although the rates span only about a factor of 20. The N-bonded formamide complex is the slowest ($t_{1/2}$ = 5.6 h, 35 °C) while the N-bonded *p*-fluorobenzamide is the fastest ($t_{1/2}$ = 17 min, 35 °C). Note that the sulfolane work does not distinguish between inter- and intramolecular rearrangements, but in coordinating solvents the isomerization is intramolecular (vide infra). Also the N to O isomerization occurs very slowly in the solid state on heating (formamide-*N*, 80 °C, $k = 1.8 \times 10^{-4}$ s^{-1}),[20] and this process also is likely to be intramolecular. (Note however that the analogous S to N thiocyanate isomerization in the solid state is evidently intermolecular.[21])

N to O Linkage Isomerization: Coordinating Solvents. To observe the N to O rearrangement in coordinating solvents was more difficult. The problem arises because not only does direct solvolysis compete with N to O isomerization, but also the O-bonded amide products solvolyze at comparable rates. The concentration of O-bonded isomer therefore rises and falls with time, according to the sequence of reactions



and if the rate of disappearance of the O-bonded isomer is much

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(20) Balahura, R. J.; Lewis, N. A. *Coord. Chem. Rev.* **1976**, *20*, 109–153.
(21) Snow, M. R.; Boomsma, R. F. *Acta Crystallogr.* **1972**, *B28*, 1908.

greater than its rate of formation, the O-bonded isomer will be difficult to detect. The point is highlighted elsewhere[13] in a detailed kinetic study of solvent effect on the rearrangement of the formamide-*N* and acetamide-*N* complexes.

The rate of solvolysis of the formamide-*O* complex of pentaamminecobalt(III) is 2.5 times *slower* in Me_2SO than in water.[13] Moreover the specific rate of rearrangement of formamide-*N* is 5–6 times *faster* in Me_2SO. Similar solvent effects appear to apply to the acetamide analogues. Thus these two solvent effects each enhance the prospect of observing the consecutive reactions commencing with the protonated amide-*N* isomer, by slowing the second and accelerating the first, and explain why linkage isomerization can be observed for acetamide-*N* in Me_2SO but not in water.[13] Thus, by confining the present work to Me_2SO, we have now detected linkage isomerization reactions of eight amide-*N* complexes (acetamide, formamide, chloroacetamide, fluoroacetamide, benzamide, 4-fluorobenzamide, 2-nitrobenzamide, and acrylamide). Nonetheless, most systems conform to a slow–fast sequence of reactions, making the quantification of even the relative rates of the various pathways difficult. They have therefore been examined only qualitatively, by using ^1H NMR spectroscopy, as now described.

^1H NMR data are recorded in Table VIII for the protonated amide-*N* complexes, their product amide-*O* isomers, and free amides in Me_2SO-d_6. The magnitude and location of the intense resonance for the cis NH_3 (12 H) is usually the best indicator of the linkage isomerization reaction. The chemical shift for these protons is quite different for the O- and N-bonded isomers. Although the cis NH_3 signals for the O-bonded isomers and $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ have similar chemical shifts, the two are resolved.

The ^1H NMR spectra for the chloroacetamide complexes reveal single sharp resonances diagnostic of uncoordinated, O-, or N-coordinated chloroacetamide (Table VIII). Immediately following dissolution of the complex $[(NH_3)_5CoNH{=}C(OH)CH_2Cl](ClO_4)_3$ in Me_2SO-d_6 (at 35 °C), consecutive spectra were recorded, and a group of resonances appeared in the region 3.95–4.10 ppm, corresponding to the sharp methylene singlets of authentic O-bonded isomer (246 Hz) and free chloroacetamide (241 Hz) riding on a broad signal for the combined cis NH_3 resonances of $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and $[(NH_3)_5CoOC(NH_2)CH_2Cl]^{3+}$ (235 Hz). The latter signal ultimately split into a doublet, and the specific resonances for each of the latter products were distinguished (234 and 237 Hz, respectively). Further support for the formation of the O-bonded isomer was the early observation of the two low-field signals for the chemically distinguishable NH_2 protons of the O-bonded chloroacetamide ligand (the inequivalence is due to restricted rotation about the partial C=N bond and is characteristic of the amide-*O* species). All of the signals assigned to the N- and O-bonded isomers had vanished within 40 min (35 °C) of dissolution, leaving only those for $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and uncoordinated chloroacetamide. The estimated half-life for the primary (but slower) process (parallel isomerization and direct solvolysis of the N-bonded isomer) was 10–15 min at 35 °C.

The methylene signals for the corresponding fluoroacetamide complexes were doublets rather than singlets due to coupling with ^{19}F, but otherwise the N-bonded isomer behaved like the chloro analogue, with relatively rapid isomerization observed concurrently with solvolysis.

A similar N to O linkage isomerization reaction was identified for the benzamide complex in Me_2SO-d_6. The reactant was half-depleted within 40 min (35 °C), during which time separate signals could be detected for the cis NH_3 protons of the benzamide-*O* (240 Hz) and the Me_2SO complexes (230 Hz). One of the separate proton resonances for the inequivalent NH_2 protons of the benzamide-*O* product complex was also detected. The signals attributable to the benzamide-*O* isomer were always larger than the corresponding ones of the Me_2SO complex up until this time, and in the same ratio, and hence it can be concluded that N to O rearrangement and solvolysis reactions occur in parallel but the rearrangement is faster. The O-bonded isomer could not be detected beyond 3 h after dissolution of the N-bonded isomer, and the final spectrum was identical with that of a mixture of authentic samples of $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and free benzamide.

These results conflict with a previous report[10a] in which it was suggested that the O-bonded benzamide complex (which had not been isolated until this study) had been detected from the reaction of the N-bonded isomer in Me_2SO-d_6 after 24 h at room temperature. In view of the above results, it is now certain that only $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and free benzamide were observed.

Evidence for linkage isomerization of the acrylamide-*N* complex is similar to that reported above. Resonances for the cis NH_3 protons of each of $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ and $[(NH_3)_5CoOC(NH_2)CH{=}CH_2]^{3+}$ were detected during the first hour at 35 °C, indicative of their parallel formation. The inequivalent NH_2 protons of the O-bonded isomer were also detected during this time. They initially increased in intensity before subsequently diminishing, commensurate with growth of the separate resonances for the NH_2 protons of free acrylamide.

The isomerization of the 4-fluorobenzamide-*N* complex in Me_2SO was identified on the basis of the formation of separate resonances for the cis NH_3 protons of the O-bonded isomer and $[(NH_3)_5CoOS(CD_3)_2]^{3+}$. The resonance for the latter was initially less intense than the former, but eventually became the larger of the two signals. After 40 min at 35 °C, only signals for free amide and $[(NH_3)_5CoOS(CD_3)_2]^{3+}$ were apparent.

The 2-nitrobenzamide-*N* complex underwent only slow reaction in Me_2SO-d_6/CF_3CO_2H ($t_{1/2}$ = 2 h, 35 °C), and linkage isomerization could not be detected by ^1H NMR spectroscopy; only solvolysis of the N-bonded isomer was observed.

In summary (i) the N to O isomerization is generally 1–2 orders of magnitude faster in Me_2SO than in sulfolane, (ii) competing solvolysis of the N-bonded isomers is more prevalent in H_2O than in Me_2SO, and (iii) the isomerization path becomes more favorable than solvolysis of N-bonded isomer at higher temperatures for both water and Me_2SO solvents.

Conclusions

Consistent with O-alkylation of carboxamides, at ambient temperatures the electrophilic pentaamminecobalt(III) entity first binds the more electronegative/basic O-terminus of $RCONH_2$, and it binds selectively. Subsequently this O-bonded species can rearrange to the N-bonded form in a noncoordinating solvent when forced by deprotonation; it is the more thermodynamically stable. In this regard, it resembles the organic chemistry if the ROC(R)=NH and $[(NH_3)_5CoOC(R){=}NH]^{2+}$ species are considered analogous.

The inductive effect of the substituent in $[(NH_3)_5CoNHCOR]^{2+}$ did not alter the preferred site of protonation to any observable extent. However, in the face of the results for ureas and carbamates,[14,15] the tautomeric equilibrium concerning N- versus O-protonation of the amide-*N* isomer appears to be responsible for the observed low reactivity of the amide-*N* complexes.

$$CoNH{=}C(OH)R^{3+} \underset{}{\overset{K_T}{\rightleftharpoons}} CoNH_2COR^{3+}$$

Thus K_T is greater than (e.g.) 20 for the *very reactive* urea[14] and carbamate[15] complexes where only the $CoNH_2$– form is observed, whereas K_T is less than (e.g.) 20 for these *unreactive* alkyl and aryl amide-*N* complexes since only the other CoNH= tautomer is observed. This corresponds to a shift in K_T of at least a factor of 400. For analogous Ru(III) complexes, the more electropositive metal appears to make K_T even smaller for amides and ureas, and the site of protonation even for the urea complex is argued to be on oxygen.[22]

Experimental Section

UV–visible absorption spectra were monitored with a Cary 210 or 118C spectrophotometer. ^1H NMR spectra were measured on a Varian 60-MHz spectrometer at 35 °C to monitor the rearrangements. ^{13}C NMR and other ^1H spectra used to characterize complexes were recorded

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with a Varian 300 XL instrument at 20 °C. All ^1H chemical shifts are reported as positive downfield from TMS, while ^{13}C spectra were obtained relative to 1,4-dioxane (66.26 ppm in Me_2SO-d_6) but are reported relative to TMS. All chemicals were AR grade. Known complexes were characterized by comparison of their spectroscopic properties (NMR and UV–vis) with literature values. Where unreported, analytical data were satisfactory for complexes used in this work. The cation-exchange resin SP-Sephadex C25 (Pharmacia) was used routinely for separation of complexes.

Syntheses. *Caution*! Perchlorate salts are potentially explosive!

$[(NH_3)_5CoN{\equiv}CR](ClO_4)_3$ (R = CH_3, CH_2Cl, $CH{=}CH_2$, C_6H_5, C_6H_4-2-NO_2, C_6H_4-4-F). These complexes were synthesized from $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ and the appropriate nitrile and recrystallized as perchlorate salts according to published methods.[7,17]

$[(NH_3)_5CoNHCOR](ClO_4)_2$. A. From $[(NH_3)_5CoN{\equiv}CR]^{3+}$ (R = CH_3, CH_2Cl, $CH{=}CH_2$, C_6H_5, C_6H_4-2-NO_2, C_6H_4-4-F). $[(NH_3)_5Co{\equiv}CR](ClO_4)_3$ was reacted briefly in water with 1 stoichiometric equiv of NaOH as reported elsewhere,[12] and solid $NaClO_4$ was added to precipitate the title complexes as monohydrates. Recrystallization from warm aqueous Tris (pH 9.5) and concentrated $NaClO_4$ solution yielded pure complexes, which were washed with absolute ethanol and then diethyl ether and dried over P_2O_5 under vacuum. Analytical calculated (found) values for $[(NH_3)_5CoNHCOR](ClO_4)_2$ are as follows. R = CH_3: 5.98 (5.96); H, 4.74 (4.75); N, 20.94 (20.62); Cl, 17.71 (17.68). R = CH_2Cl: C, 5.51 (5.69); H, 4.13 (4.50); N, 19.29 (19.48); Cl, 24.43 (24.24). R = $CH{=}CH_2$: C, 8.72 (8.93); H, 4.60 (4.53); N, 20.34 (20.30); Cl, 17.19 (17.44). R = C_6H_5: C, 18.14 (18.21); H, 4.54 (4.63); N, 18.14 (18.81); Cl, 15.33 (15.42). R = C_6H_4-2-NO_2: C, 16.54 (16.36); H, 3.94 (4.21); N, 19.29 (19.07). R = C_6H_4-4-F: C, 17.46 (17.52); H, 4.16 (4.17); N, 17.46 (17.13).

B. From $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ (R = H, CH_3, CH_2F, CF_3). $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$ (5 g, 0.012 mol) are free amide (0.08 mol) were dissolved in a minimum volume of Me_2SO (30 mL) containing the sterically hindered base 2,2,6,6-tetramethylpiperidine (0.02 mol), and the quickfit flask was stoppered. The reaction mixture was heated (60–80 °C, 2 h) and subsequently cooled, and the cobalt complexes were quantitatively precipitated by addition of an equal volume of 2-butanol and excess diethyl ether. The resultant oily residue was taken up in water and sorbed onto Sephadex. Elution with 0.5 M NaCl or $NaClO_4$ (pH 9.5, Tris) yielded in order a trace of pink 1+ ion and the desired $[(NH_3)_5CoNHCOR]^{2+}$ just ahead of $[(NH_3)_5CoOH]^{2+}$ and well in front of any unreacted $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ followed by $[Co(NH_3)_6]^{3+}$. No amide-*O* complex survives the experimental conditions. The solution of $[(NH_3)_5CoNHCOR]^{2+}$ was rechromatographed and the pH of the eluant was reduced (acetic acid, pH ca. 4) to ensure that the desired complex was eluted as $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$, which easily separates from any contaminating $[(NH_3)_5CoOCOR]^{2+}$. The complex was deprotonated by adding Tris and isolated by rotary evaporation of the eluate and addition of sodium perchlorate. The perchlorate salts of the fluoroacetamido-*N* and especially trifluoroacetamido-*N* complexes were less water-soluble than those of other amide-*N* complexes. The crude complexes were recrystallized as in paragraph A above. Anal. Calc (found) for $[(NH_3)_5CoNHCHO](ClO_4)_2$: C, 3.10 (3.17); H, 4.39 (4.37); N, 21.71 (21.49); Cl, 18.35 (18.15).

$[(NH_3)_5CoNH{=}C(OH)R](ClO_4)_3$ (R = CH_2Cl, CH_2F, $CH{=}CH_2$, C_6H_5, C_6H_4-2-NO_2, C_6H_4-4-F). All complexes were prepared by adding 6 M $HClO_4$ dropwise to aqueous solutions of $[(NH_3)_5CoNHCOR](ClO_4)_2$. The solutions turned bright yellow, and the desired complexes subsequently precipitated in the presence of excess acid. They were washed copiously with diethyl ether (no alcohol) and dried under vacuum over P_2O_5. Note that all previous workers washed their products with alcohols and so obtained a mixture of acidic and basic forms. Analyses were satisfactory for fully protonated species in all cases.

Product Analyses. Chromatography on Sephadex proved to be an effective method of verifying both purity and the charge of $[(NH_3)_5CoN{\equiv}CR]^{3+}$, $[(NH_3)_5CoNHCOR]^{2+}$, $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$, and $[(NH_3)_5CoOC(NH_2)R]^{3+}$. Following kinetic studies, products from the reactions of $[(NH_3)_5CoNH{=}C(OH)R]^{3+}$ in sulfolane were assayed by ion-exchange techniques. They were sorbed onto jacketed columns of Sephadex resin (2 °C) and eluted with phosphate-buffered NaCl (Cl^-:total phosphate = 9:1; HPO_4^{2-}, $H_2PO_4^-$, pH ca. 7). No N-bonded isomer was detected, even though under these conditions it elutes as a 2+ ion well ahead of $[(NH_3)_5CoOH_2]^{3+}$.

Kinetic Studies. General techniques for monitoring the reactions and determining specific rates are described elsewhere;[11,14] standard deviations in rate constants were less than 3% for at least triplicate measurements. All kinetic experiments were monitored with a Cary 210 spectrophotometer fitted with a computer-controlled five-cell turret assembly and a cell compartment thermostated by water circulating from a Lauda bath with temperature control to ±0.1 °C. The specific rates reported were measured under the same conditions, and since five runs could be conducted simultaneously, the results accurately relate to one another. Due to the slow rate of dissolution of $[(NH_3)_5CoNH{=}C(OH)R](ClO_4)_3$ complexes in sulfolane at temperatures (e.g. 35 °C) just above its melting point (28 °C), complexes were usually added to the dried solvent and the mixtures were shaken and quickly filtered through finely sintered glass by using dry-N_2 blanketed Schlenck equipment before equilibrating to 35 °C in stoppered spectrophotometer cells.

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Registry No. $[(NH_3)_5CoNHCOCH_3](ClO_4)_2$, 43067-18-1; $[(NH_3)_5CoNHCOCH_2Cl](ClO_4)_2$, 132374-37-9; $[(NH_3)_5CoNHCOCH{=}CH_2](ClO_4)_2$, 132373-85-4; $[(NH_3)_5CoNHCOC_6H_5](ClO_4)_2$, 54832-58-5; $[(NH_3)_5CoNHCOC_6H_4$-2-$NO_2](ClO_4)_2$, 132344-26-4; $[(NH_3)_5CoNHCOC_6H_4$-4-F$](ClO_4)_2$, 132344-28-6; $[(NH_3)_5CoOC(NH_2)CH_2Cl]^{3+}$, 132344-29-7; $[(NH_3)_5CoN{\equiv}CCH_3](ClO_4)_3$, 15663-50-0; $[(NH_3)_5CoN{\equiv}CCH_2Cl](ClO_4)_3$, 88157-88-4; $[(NH_3)_5CoN{\equiv}CCH{=}CH_2](ClO_4)_3$, 15648-92-7; $[(NH_3)_5CoN{\equiv}CC_6H_5](ClO_4)_3$, 38363-82-5; $[(NH_3)_5CoN{\equiv}CC_6H_4$-2-$NO_2](ClO_4)_3$, 132344-31-1; $[(NH_3)_5CoN{\equiv}CC_6H_4$-4-F$](ClO_4)_3$, 123881-65-2; $[(NH_3)_5CoOC(NH_2)CH{=}CH_2]^{3+}$, 132344-32-2; $[(NH_3)_5CoOC(NH_2)C_6H_5]^{3+}$, 132344-33-3; $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(NH_3)_5CoNHCOH](ClO_4)_2$, 26729-10-2; $[(NH_3)_5CoNHCOCH_2F](ClO_4)_2$, 132316-07-5; $[(NH_3)_5CoNHCOCF_3](ClO_4)_2$, 132316-09-7; $[(NH_3)_5CoNH{=}C(OH)CH_2Cl](ClO_4)_3$, 132344-36-6; $[(NH_3)_5CoNH{=}C(OH)CH_2F](ClO_4)_3$, 132344-38-8; $[(NH_3)_5CoNH{=}C(OH)CH{=}CH_2](ClO_4)_3$, 132344-40-2; $[(NH_3)_5CoNH{=}C(OH)C_6H_5](ClO_4)_3$, 132344-42-4; $[(NH_3)_5CoNH{=}C(OH)C_6H_4$-2-$NO_2](ClO_4)_3$, 132408-17-4; $[(NH_3)_5CoNH{=}C(OH)C_6H_4$-4-F$](ClO_4)_3$, 132344-44-6; $[(NH_3)_5CoOC(NH_2)CH_2F]^{3+}$, 107440-55-1; $[(NH_3)_5CoNH{=}C(OH)H](ClO_4)_3$, 132344-46-8; $[(NH_3)_5CoNH{=}C(OH)CH_3](ClO_4)_3$, 132344-47-9; $N{\equiv}CCH_2Cl$, 107-14-2; $N{\equiv}CCH{=}CH_2$, 107-13-1; $N{\equiv}CC_6H_5$, 100-47-0; $N{\equiv}CC_6H_4$-2-NO_2, 612-24-8; $N{\equiv}CC_6H_4$-4-F, 1194-02-1; $N{\equiv}CCH_3$, 75-05-8; $ClCH_2CONH^-$, 132344-21-9; $H_2C{=}CHCONH^-$, 132344-22-0; $C_6H_5CONH^-$, 72409-60-0; O_2N-2-$C_6H_4CONH^-$, 132344-23-1; F-4-$C_6H_4CONH^-$, 132344-34-4; FCH_2CONH^-, 132344-24-2; $NHCOCH_3^-$, 63285-19-8; $NHCHO^-$, 67131-48-0.

Supplementary Material Available: Tables II and III, giving ^{13}C and ^1H NMR data for free nitriles and (nitrile)pentaamminecobalt(III) complexes (2 pages). Ordering information is given on any current masthead page.