Synthesis, Solution Structure, and Reactivity of Oxygen-Bound Amides on Cobalt(III)

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

Department of Chemistry, University College (NSW), Australian Defence Force Academy, Northcott Dr., Campbell, ACT, Australia 2600

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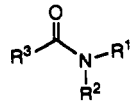
A series of pentaamminecobalt(III) amide complexes containing oxygen-bonded amides are reported. The electronic structure of the amide ligand remains delocalized on coordination to the metal ion, and there is evidence for increased polarization of the amide upon coordination. There is restricted rotation about the carbon–nitrogen bond as shown by separate NMR signals for the amide nitrogen substituents. Also the unsymmetrically substituted formamides ($HCONHCH_3$ and $HCONHC_6H_5$) are in both the *Z* and *E* configurations for both the free and oxygen-coordinated species. In aqueous acid solution and in Me_2SO the complexes slowly producing free amide; the rates of solvolysis have been measured. Complexes of formamides ($HCONR^1R^2$) solvolyze more slowly than those of carbon-substituted amides ($R^3CONR^1R^2$); e.g., 10^6k_H = 5.25 s^{-1} and 118 s^{-1} for formamide-*O* and acetamide-*O*. In both categories electron-releasing substituents ($-CH_3$, $-C_2H_5$) on the amide nitrogen retard solvolysis compared with the primary amide complexes, while electron-withdrawing substituents on the amide nitrogen accelerate it. Complexes with an electron-withdrawing substituent on the amide carbon solvolyze fastest; e.g. for fluoroacetamide-*O*, 10^6k_H = 1300 s^{-1}. In basic solution at 22 °C (0.1 M NaOH, 1.0 M $NaClO_4$) all formamide complexes undergo ligand hydrolysis (*N*,*N*-diethylformamide-*O*, 46%; *N*,*N*-diphenylformamide-*O*, 90%) producing (formato)pentaamminecobalt and free amine; the balance is hydroxopentaamminecobalt(III) complex. Rates of reaction have been measured and are correlated with the nature of the substituent on the formamide nitrogen; k_{OH} = 24.2 M^{-1} s^{-1} for formamide-*O* and 0.32 M^{-1} s^{-1} for *N*,*N*-diethylformamide-*O*, *I* = 1.1 M ($NaClO_4$), 25 °C. The pK_a of the formamide-*O* complex is 11.9, and that for the formanilide-*O* complex, 12.0. In contrast the carbon-substituted amide complexes are less reactive toward ligand hydrolysis, the major product being the hydroxopentaamminecobalt(III) ion. The acetamide-*O* complex yields only 1% (acetato)pentaamminecobalt(III), and the chloroacetamide- and fluoroacetamide-*O* complexes yield 7% and 8% of the relevant carboxylato ions, respectively. However complexes of benzamide, acrylamide, acetanilide, and *N*-methyl-, *N*,*N*-dimethyl-, and *N*,*N*-diethylacetamide yield only the hydroxopentaamminecobalt(III) complex under the same conditions. The rates of these reactions have been measured and acidity constants for some primary and secondary amide complexes have been determined: k_{OH} = 30.2 M^{-1} s^{-1}, pK_a 11.6, acetamide-*O*; k_{OH} = 33 M^{-1} s^{-1}, pK_a 10.6, benzamide-*O*; k_{OH} = 70 M^{-1} s^{-1}, pK_a 9.7, acetanilide-*O*; k_{OH} = 150 M^{-1} s^{-1}, pK_a 9.4, chloroacetamide-*O*; k_{OH} = 55 M^{-1} s^{-1}, pK_a 9.7, fluoroacetamide-*O* [*I* = 1.00 M, $NaClO_4$, 25 °C]. The base hydrolysis of the dimer $[(NH_3)_5CoOCHNHCo(NH_3)_5]^{5+}$ has been investigated. The reaction is slow and proceeds largely by cobalt–oxygen cleavage but with detectable Co–N cleavage. No amide O- to N-bonded linkage isomerization was detected for any of these complexes, and the reactivity of coordinated amides is compared with that of coordinated ureas and cyclic amides.

Introduction

The coordination chemistry of amides **1** is of continuing interest because they serve as simple models for peptides.



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As yet only a few oxygen-bonded, monodentate Co(III) amide complexes have been reported. They are pentaamminecobalt(III) complexes of formamide[13] and of a selection of tertiary amides including *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, *N*,*N*-dimethylbenzamide, and 2-pyridone.[10,14] Coordination of an amide through the nitrogen is considered to be deactivating toward ligand hydrolysis,[8] but a study of the base hydrolysis of *oxygen*-bonded (*N*,*N*-dimethylformamide)pentaamminecobalt(III) has shown that hydrolysis of dimethylformamide was accelerated by 10^4, producing (formato)pentaamminecobalt(III) and dimethylamine.[9] The hydroxopentaamminecobalt(III) complex was a minor product.

Only the chemistry of this dimethylformamide-*O* ion has been studied in detail,[9] and thus this paper reports the synthesis, solution structure, and reactivity of a series of amide-*O* complexes, following on from our work[12,20] on N-bonded amides ($RCONH_2$). Recent advances in synthetic methods have allowed the preparation of these relatively labile complexes using the trifluoromethanesulfonato complex.[15] The amide ligands reported here have been chosen to elucidate the electronic effects of amide substituents on the reactivity of the complexes.

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Table I. Molar Extinction Coefficients (ϵ_{max}, M^{-1} cm^{-1}; λ_{max}, nm) for Oxygen-Bonded Amide Complexes, $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$, at 25 °C

amide ligand	anion	solvent	ϵ_{max}	λ_{max}	ϵ_{max}	λ_{max}
$HCONH_2$[a]	ClO_4^-	0.1 M $HClO_4$	71.5	501	57.5	346
$HCONH(CH_3)$	$S_2O_6^{2-}$	0.1 M $HClO_4$	78.0	501	62.5	345
$HCON(CH_3)_2$[b]	ClO_4^-	0.1 M $HClO_4$	79.5	506	69.0	348
$HCON(C_2H_5)_2$	$CF_3SO_3^-$	0.1 M $HClO_4$	77.0	504	66.0	347
$HCONH(C_6H_5)$	$CF_3SO_3^-$	0.1 M $HClO_4$	80.0	504		
$HCON(C_6H_5)_2$	$CF_3SO_3^-$	0.1 M $HClO_4$	65.5	502		
CH_3CONH_2[a]	ClO_4^-	0.1 M $HClO_4$	80.0	516	60.5	346
$CH_3CONH(CH_3)$	$S_2O_6^{2-}$	0.1 M $HClO_4$	77.0	517	58.0	349
$CH_3CON(CH_3)_2$[b]	$CF_3SO_3^-$	0.1 M $HClO_4$	95.0	524	102	345
$CH_3CON(C_2H_5)_2$	$CF_3SO_3^-$	0.1 M $HClO_4$	90.0	522	94.5	343
CH_2FCONH_2[c]	$S_2O_6^{2-}$	0.01 M LiH_3edta	62	510	49	344
$CH_2ClCONH_2$[c]	$S_2O_6^{2-}$	0.01 M LiH_3edta	65	510	56	346
$C_6H_5CONH_2$[c]	$S_2O_6^{2-}$	0.01 M LiH_3edta	74	510	69	346
CH_2=$CHCONH_2$	$S_2O_6^{2-}$	0.01 M LiH_3edta	81.0	515	60.5	349

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Results

Syntheses and Characterization. The labile $[(NH_3)_5CoOSO_2CF_3]^{2+}$ ion reacts with amides in poorly coordinating solvents (acetone or sulfolane) or in neat amides to form the bright pink complexes of $[(NH_3)_5Co(amide\text{-}O)]^{3+}$. Complexes of the following amides have been synthesized: formamide, *N*-methylformamide, *N*,*N*-dimethylformamide, *N*,*N*-diethylformamide, formanilide, *N*,*N*-diphenylformamide, acetamide, *N*-methylacetamide, *N*,*N*-dimethylacetamide, *N*,*N*-diethylacetamide, acetanilide (exists solely as the *Z* isomer[17]), fluoroacetamide, chloroacetamide, benzamide, and acrylamide. The complexes of all the tertiary amides and also formanilide were easily crystallized from water as trifluoromethanesulfonate (triflate) salts because of their low solubility. They were recrystallized analytically pure, and ^1H NMR spectra show no detectable (<2%) aquapentaamminecobalt(III) complex or other impurity. Triflate salts of the other amide-*O* complexes described here were of solubility similar to that of aquapentaamminecobalt(III). As dithionate salts they were, however, much less soluble than the aqua side product, which was easily removed by washing the crude amide-*O* complex with ice-cold water. To inhibit catalytic solvolysis, observed in many cases, aqueous solutions of $Na_2S_2O_6$ and the iced water wash were made 0.01 M in ethylenediaminetetraacetic acid (edta), which had been neutralized with lithium hydroxide to pH 5 (LiH_3edta solution). We assumed that traces of Co(II) were the cause of the catalytic solvolysis and that it would be sequestered by the edta. This strategy was successful provided subsequent drying was rapid and efficient. ^1H NMR spectra of the complexes confirmed the absence of significant (>2%) amounts of contaminant.

Bonding Mode. The UV-visible (Table I) and ^1H NMR spectra (Tables II and III) of these complexes are characteristic of the CoN_5O chromophore. The ^1H NMR spectra show separate resonances for the $-NR^1R^2$ moiety, and this also is indicative of bonding through oxygen.[9] No nitrogen-bonded amide complexes (<1%) were observed either by ^1H NMR or ion-exchange chromatography; a number of the N-bonded linkage isomers have been synthesized.[13,18-21]

^{13}C NMR spectra for these complexes are listed in Tables IV and V. They demonstrate the presence of the amide ligand in the complexes, and for N-substituted amides they show the inequivalence of the substituents as previously discussed. The chemical shift for the C=O resonance is increased on coordination and is higher than is found in the relevant N-bonded amide complexes. This is evidence that the carbonyl group is polarized by direct coordination to the metal.

The visible spectra (Table I) not only indicate bonding through the amide oxygen but also differentiate formamide complexes from C-substituted amide complexes. The low-energy absorption band for the formamide complexes (near 500 nm) is unaffected by the presence of substituents on the amide nitrogen. By contrast the position of this band for the C-substituted amide complexes is ~10 nm higher in the primary amide complexes and shifted to even higher wavelengths (524 nm for dimethylacetamide-*O*) where the amide nitrogen bears alkyl substituents. In other contexts, the effect has been discussed by Gould[10] and Drago et al.[22]

***Z* and *E* Isomers for Free and O-Bonded Amides.** The electronic structure of the amide bond in **2** does not change dramatically on coordination to cobalt(III). In all the amide-*O* complexes the nitrogen substituents produce two separate ^{13}C and/or ^1H NMR signals, and this is indicative of restricted rotation about the carbon–nitrogen bond caused by electron delocalization. In the benzamide-*O* complex the $NH(R^2)$ resonance is concealed by the aromatic proton envelope but was revealed by spin-decoupling.

Formanilide[23] and *N*-methylformamide[24] can be observed as both *Z* and *E* isomers at ambient temperature:

The *Z*/*E* ratio varies with the concentration of the amide and with the nature of the solvent: At [amide] = ~0.01 M in Me_2SO-d_6 it is 3:1 for formanilide and 10:1 for *N*-methylformamide. The ^{13}C and ^1H NMR spectra of formanilide were recorded from 20 up to 100 °C, and coalescence was observed at the higher temperature. The NMR spectra (Tables II and IV) of the complexes of these ligands showed that they too are a mixture of the geometric isomers in very similar proportions to those in the free ligands. *N*-Methylacetamide also occurs as a *Z*/*E* mixture, 33:1.[16] We detected both these isomers in the NMR spectra of the free ligand (Tables III and V), but only the *Z* rotamer was found in the complex. At such a low concentration however the coordinated *E* isomer would be difficult to detect: Spectra are more complex and resolution is lower due to quadrupolar broadening by ^{59}Co.

Restricted rotation about the C–N bonds is also manifested in the unequal coupling constants of the amide (NH) protons with the formyl (HCO) proton in formamide, *N*-methylformamide, and formanilide. Where there is an amide proton trans to the formyl proton (formamide, *E*-*N*-methylformamide, *E*-formanilide), the coupling constant J = 15 Hz (Table II). The *Z* rotamers of formanilide and *N*-methylformamide have a much smaller coupling constant, $J \leq 3$ Hz. In the formamide-*O* complex the formyl signal is actually a doublet of doublets and cis and trans coupling can be observed. Figure 1 shows the 60-MHz (A) and 300-MHz (B) ^1H NMR spectra of formamide. At the lower resolution ^{14}N decoupling experiments were required to analyze the spectrum,[17] but no such difficulty arises in the 300-MHz spectrum, where the sharp doublet of the formyl proton is clearly seen as are the two broad signals for the NH protons.

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Table II. ^{1}H NMR Spectral Data (δ, ppm) for Formamides ($HCONR^1R^2$) and Their Oxygen-Bonded Pentaamminecobalt(III) Complexes, $[(NH_3)_5CoOCHNR^1R^2]^{3+}$, in Me_2SO-d_6 at 20 °C[a]

ligand	cis-NH_3	trans-NH_3	HCO	R^1	R^2
$HCONH_2$			7.96[b]	7.24 (NH)	7.49 (NH)
	3.91	2.87	7.45[b]	8.98[b]	9.09
Z-$HCONH(CH_3)$			8.07	2.65[c] (N–CH_3)	7.97 (NH)
	3.83	2.71	7.38	2.70[c]	9.73
E-$HCONH(CH_3)$			7.97[b]	7.97[c] (NH)	2.78[c] (N–CH_3)
	3.83	2.71	7.30[b]	9.35 (broad)	2.86[c]
$HCON(CH_3)_2$			7.96	2.73 (N–CH_3)	2.89 (N–CH_3)
	3.86	2.70	7.40	2.88	3.07
$HCON(C_2H_5)_2$			7.98	0.99[d] (NCH_2CH_3)	1.06[d] (NCH_2CH_3)
				3.22[e] (NCH_2CH_3)	3.24[e] (NCH_2CH_3)
	3.84	2.70	7.41	1.01[d] (NCH_2CH_3)	1.15[d] (NCH_2CH_3)
				3.31[e] (NCH_2CH_3)	3.36[e] (NCH_2CH_3)
Z-$HCONH(C_6H_5)$			8.28[f]	7.05[g] (para)	10.20 (NH)
				7.30[g] (meta)	
				7.60[g] (ortho)	
	3.97	2.77	7.55	7.28[g] (para)	11.71 (NH)
				7.46[g] (ortho, meta)	
E-$HCONH(C_6H_5)$			8.79[h]	10.15 (NH)	7.05[g] (para)
					7.19[g] (ortho)
					7.30[g] (meta)
	3.97	2.77	7.99[h]	11.82[h] (NH)	7.28[g] (para)
					7.46[g] (ortho, meta)
$HCON(C_6H_5)_2$			8.65	R^1 and R^2 signals not resolved:	
	3.92	2.75	8.07	7.23, 7.31, 7.42,[g] 7.29, 7.50[g]	

[a] Downfield from TMS. [b] Doublet, J = 15 Hz. [c] Doublet, J = 5 Hz. [d] Triplet, J = 7 Hz. [e] Partly overlapping quartet, J = 7 Hz. [f] Doublet, J = 2 Hz. [g] Center of multiplet. [h] Doublet, J = 11 Hz.

Table III. ^{1}H NMR Spectral Data (δ, ppm) for C-Substituted Amides ($R^3CONR^1R^2$) and Their Oxygen-Bonded Pentaamminecobalt(III) Complexes, $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$, in Me_2SO-d_6 at 20 °C[a]

ligand	cis-NH_3	trans-NH_3	R^3	R^1	R^2
CH_3CONH_2			1.76 (C–CH_3)	6.74 (NH)	7.32 (NH)
	4.01	2.78	1.88	7.50	9.00
Z-$CH_3CONH(CH_3)$			1.66 (C–CH_3)	2.42[b] (N–CH_3)	7.66 (NH)
	4.02	2.75	1.81	2.58[b]	9.20[c]
E-$CH_3CONH(CH_3)$			1.72 (C–CH_3)	n.d. (NH)	2.56 (N–CH_3)
$CH_3CON(CH_3)_2$			1.96 (C–CH_3)	2.79 (N–CH_3)	2.95 (N–CH_3)
	3.99	2.67	1.90	2.83	3.06
$CH_3CON(C_2H_5)_2$			1.94 (C–CH_3)	0.97[d] (NCH_2CH_3)	1.06[d] (NCH_2CH_3)
				3.23[e] (NCH_2CH_3)	3.25[e] (NCH_2CH_3)
	4.05	2.74	1.88	0.95[d] (NCH_2CH_3)	1.06[d] (NCH_2CH_3)
				3.22[e] (NCH_2CH_3)	3.34[e] (NCH_2CH_3)
Z-$CH_3CONH(C_6H_5)$			2.02 (C–CH_3)	7.00[f] (para)	9.92 (NH)
				7.27[f] (ortho)	
				7.58[f] (meta)	10.91
	4.10	2.83	2.07	7.20[f] (para)	
				7.35[f] (meta, ortho)	
$CH_2ClCONH_2$			4.02 (CH_2Cl–)	7.38 (NH)	7.62 (NH)
	3.95	2.68	4.10	8.22	9.40
CH_2FCONH_2			4.72[g] (CH_2F–)	7.49 (NH)	7.59 (NH)
	4.01	2.76	4.84[g]	8.11	9.22
$C_6H_5CONH_2$			6.42[f] (ortho, meta)	6.84[h] (NH)	7.00 (NH)
			6.88[f] (para)		
	4.08	2.84	7.55[f] (ortho, meta)	7.90[h]	9.51
			7.90[f] (para)		
CH_2=$CHCONH_2$			5.57[i] (=CH)	7.14 (NH)	7.55 (NH)
			6.17[i] (=CH)		
			6.60[i] (=CH)		
	3.99	2.78	5.80[i] (=CH)	7.56 (NH)	9.19 (NH)
			6.13[i] (=CH)		
			6.32[i] (=CH)		

[a] Downfield from TMS. [b] Doublet, J = 5 Hz. [c] Quartet, incompletely resolved. [d] Triplet, J = 7.0 Hz. [e] Quartet, J = 7.0 Hz. [f] Center of multiplet. [g] Doublet, J_{H-F} = 50 Hz. [h] Identified by proton decoupling. [i] Quartet, ABX spectrum.

The coupling patterns of the formamide ligands are not affected by coordination to the metal ion, and the same coupling constants are found in the relevant complexes as in the free ligands (Table II). Longer range coupling between protons in the R^3 and R^1 and/or R^2 substituents was not observed in C-substituted amides or their complexes. Both *N*-methylacetamide and *N*-methylformamide show gem coupling patterns, J = 5 Hz, and these are unaffected by coordination (Tables II and III).

These spectroscopic data concerning the electronic structure of the amide complexes are in agreement with the conclusions of studies on the Cr(II) reduction of amide-*O* complexes. Those studies[1,2] found that oxygen-bonded amide complexes were reduced without ligand transfer to chromium as the nitrogen lone pair was delocalized into the amide bond and was unavailable to bond with the chromium ion. A crystal structure of the acetamido-*N* complex[18] suggests that the amide bond remains delocalized when bonded through nitrogen also; the structure shows the characteristic lengthening of the carbon–oxygen bond with concomitant shortening of the carbon–nitrogen bond.

Ligand Conformation in O-Bonded Amides. The orientation

Table IV. ^{13}C NMR Spectral Data (δ, ppm) for Formamides ($HCONR^1R^2$) and Their Oxygen-Bonded Pentaamminecobalt(III) Complexes, $[(NH_3)_5CoOCHNR^1R^2]^{3+}$, in Me_2SO-d_6 at 20 °C[a]

	C=O		others		
ligand	free	coord	free	coord	assgnt
$HCONH_2$	164.0	171.5			
Z-$HCONH(CH_3)$	162.1	168.1	24.2	25.7	N–CH_3
E-$HCONH(CH_3)$	165.6	171.4	27.6	30.1	N–CH_3
$HCON(CH_3)_2$	162.3	167.8	30.6	32.9	N–CH_3 (R^1)
			35.6	38.7	N–CH_3 (R^2)
$HCON(C_2H_5)_2$	162.0	167.4	12.7	12.1	N–CH_2–CH_3 (R^1)
			14.8	13.9	N–CH_2–CH_3 (R^2)
			35.9	38.3	N–CH_2–CH_3 (R^1)
			41.1	11.4	N–CH_2–CH_3 (R^2)
Z-$HCONH(C_6H_5)$	159.7	166.4	119.2	119.5	ortho
			123.7	126.6	para
			128.9	129.8	meta
			138.3	136.2	ipso
E-$HCONH(C_6H_5)$	162.6	170.2	117.6	121.4	ortho
			123.7	126.7	para
			129.5	129.4	meta
			138.4	135.5	ipso
$HCON(C_6H_5)_2$	161.9	169.2	124.7	124.8	ortho (R^1)
			126.7	126.3	ortho (R^2)
			126.7	128.6	para (R^1)
			126.9	128.6	para (R^2)
			129.3	129.7	meta (R^1)
			129.7	130.0	meta (R^2)
			139.8	137.9	ipso (R^1)
			141.7	140.9	ipso (R^2)

[a] Downfield from TMS.

Table V. ^{13}C NMR Spectral Data (δ, ppm) for C-Substituted Amides ($R^3CONR^1R^2$) and Their Oxygen-Bonded Pentaamminecobalt(III) Complexes, $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$, in Me_2SO-d_6 at 20 °C[a]

	C=O		others		
ligand	free	coord	free	coord	assgnt
CH_3CONH_2	172.4	171.5	22.6		CH_3–C
Z-$CH_3CONH(CH_3)$	169.8	176.9	22.4	20.9	CH_3–C
			25.5	27.0	N–CH_3
E-$CH_3CONH(CH_3)$	165.6	172.4	27.6		CH_3–C
			29.1		N–CH_3
$CH_3CON(CH_3)_2$	169.6	176.1	30.6	32.9	CH_3–C
			34.4	36.9	N–CH_3 (R^1)
			37.4	39.1	N–CH_3 (R^2)
$CH_3CON(C_2H_5)_2$	168.4	174.9	21.1	19.2	CH_3–C
			13.0	12.7	N–CH_2–CH_3 (R^1)
			14.0	13.3	N–CH_2–CH_3 (R^2)
			39.1	41.3	N–CH_2–CH_3 (R^1)
			42.1	43.9	N–CH_2–CH_3 (R^2)
Z-$CH_3CONH(C_6H_5)$[b]	168.4		24.1		CH_3–C
			119.2		ortho
			123.1		para
			128.7		meta
			139.5		ipso
CH_2FCONH_2[b]	169.9[c]		79.9[d]		CH_2F–
$CH_2ClCONH_2$[b]	168.6		42.8		CH_2Cl–
$C_6H_5CONH_2$	168.2	175.4	127.6	128.2	meta
			128.3	128.5	ortho
			131.3	131.4	para
			134.3	133.4	ipso
CH_2=$CHCONH_2$	166.7	173.7	125.8	129.5	=CH–
			132.0	131.4	=CH_2

[a] Downfield from TMS. [b] Complex solvolyzes too rapidly to record spectrum. [c] Doublet, J_{C-F} = 19 Hz. [d] Doublet, J_{C-F} = 180 Hz.

of the amide ligand[2] in $[(NH_3)_5CoOCHN(CH_3)_2]^{3+}$ in Me_2SO-d_6 was determined by NOE experiments.[19] Since most of the amide-*O* complexes solvolyze appreciably in that solvent in the time required to perform such an experiment, we chose acetone-d_6 as the solvent and used triflate salts which are soluble in acetone but do not solvolyze in it. Irradiation of the cis NH_3 resonance produced positive NOE enhancements for the trans NH_3 and formyl proton resonances in the DMF-*O* complex, and this confirms the previous work. The same technique in

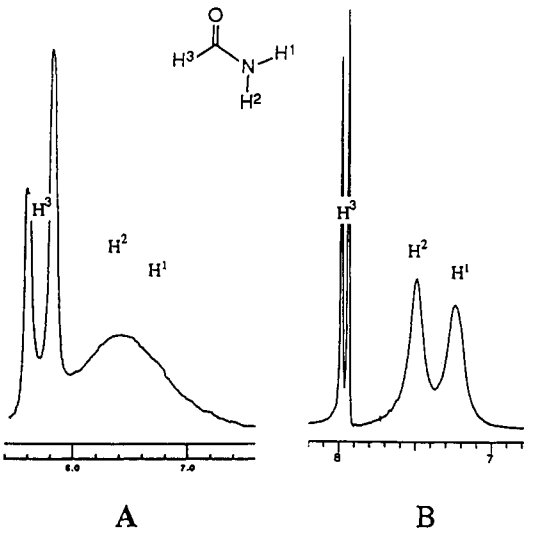
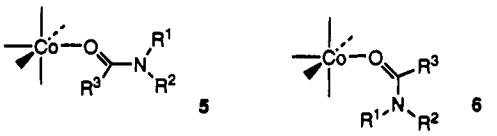


Figure 1. 60-MHz (A) and 300-MHz (B) ^1H NMR spectra of formamide in Me_2SO-d_6 at 20 °C.

dimethylacetamide-*O* and *N*-methylacetamide-*O* complexes produced positive enhancements for the *C*-methyl substituent and for the *N*-methyl substituent cis to the amide oxygen. The results are consistent with those complexes existing as two conformers **5** and **6**, and we note that they must be in rapid equilibrium on the NMR time scale as they cannot be distinguished by NMR spectroscopy.



***Z* and *E* Isomerism in N-Bonded Formamide.** As part of our studies on the structure of amide complexes, we looked for evidence of *Z*/*E* isomerism in the deprotonated formamido-*N* complex. At 20 °C in Me_2SO-d_6, the ^1H and ^{13}C NMR and spectra are consistent with the presence of either one isomer (*Z*) with a coupling constant J = 4 Hz or a mixture of two (*Z* > *E*) which are interconverting rapidly on the NMR time scale. The low-temperature ^1H NMR spectra of the formamido-*N* complex are shown in Figure 2. The peak marked with an asterisk is the aldehyde proton resonance of the solvent. The spectrum at 17 °C is almost identical to that recorded in Me_2SO-d_6 except that the cis and trans NH_3 peaks are not resolved. Spectrum A is assigned as follows (δ, ppm): 3.71 (15H), cis and trans NH_3; 3.78 (2H), lattice water; 4.38 (1H), –NH–; 8.19, J = 4 Hz (1H), HC=O. The *N*-methyl solvent peaks and the TMS peak are not shown in the figure.

At 17 °C the formyl resonance consists of a doublet separated by 4 Hz. This has not changed at –20 °C (B) or –40 °C (C). As the temperature was decreased, the chemical shifts of the peaks changed slightly, but no new signals were detected and the coupling remained the same. As the temperature became less than –40 °C the viscosity of the solvent increased noticeably and the relaxation rates of *both* solute and solvent increased and the lines are broadened. At –60 °C (D) this broadening has caused a loss of resolution and the coupling is lost in the formyl peak. We find no evidence for the presence of two isomers which interconvert sufficiently slowly to be detected by NMR spectroscopy so we cannot account for the spectral data of Balahura and Jordan[1] except to suggest that there may have been some (formato)pentaamminecobalt(III) impurity present in their sample. Studies have found that it is always formed in the synthesis of the formamido-*N* complex and purification requires chromatography.[6]

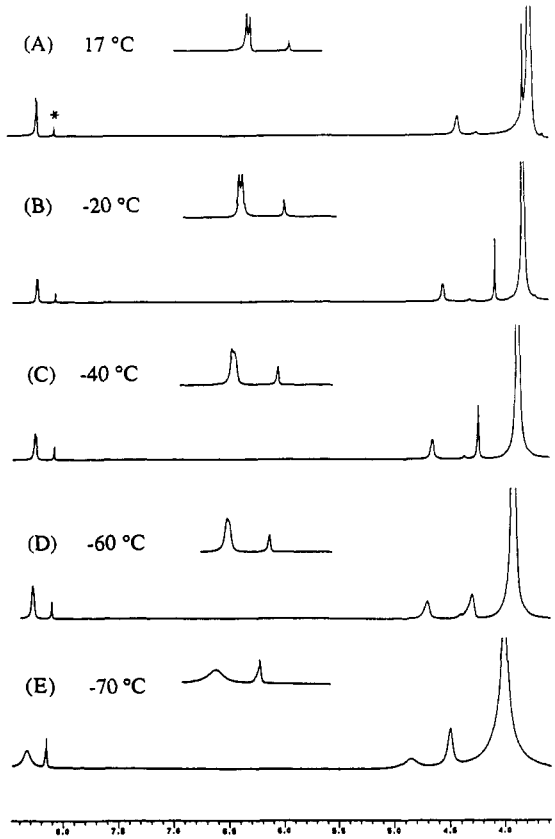


Figure 2. Low-temperature ^1H NMR spectra of the formamido-*N* complex in DMF-d_7.

Table VI. Rates of Aquation of Oxygen-Bonded Amide Complexes, $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$, in 0.10 M $HClO_4$ at 25 °C

ligand	$10^6k_H/s^{-1}$	ligand	$10^6k_H/s^{-1}$
$HCONH_2$	5.25	CH_3CONH_2	118
$HCONH(CH_3)$	2.08	$CH_3CONH(CH_3)$	73
$HCON(CH_3)_2$	1.63	$CH_3CON(CH_3)_2$	81.5
$HCON(C_2H_5)_2$	<1.6	$CH_3CON(C_2H_5)_2$	67.3
$HCONH(C_6H_5)$	170	$CH_3CONH(C_6H_5)$	680
$HCON(C_6H_5)_2$	650		
$C_6H_5CONH_2$	287	CH_2FCONH_2	1300
CH_2=$CHCONH_2$	165	CH_2ClONH_2	900

Acid Hydrolysis of the Amide-O Complexes. Reactions in 0.1 M $HClO_4$ were strictly first order in [amide-*O*] complex. Product analysis showed that the sole cobalt complex produced by this reaction is the aquapentaamminecobalt(III) ion. Some reactions were repeated in 0.01 M $HClO_4$, and the rates were not significantly different; this demonstrates that acid-catalyzed hydrolysis is negligible. The rate constants are listed in Table VI, which shows that as a group the formamide complexes aquate more slowly ($\times10^{-1}$) than do the complexes of C-substituted amides. In each group the rates are affected by the nature of the substituents on the amide nitrogen: electron-releasing groups (methyl or ethyl) retard the reaction, while the electron-withdrawing group (phenyl) accelerates it. In the C-substituted amide complexes those with electron-withdrawing substituents on the amide carbon solvolyze the fastest of all.

This type of reaction has been extensively studied in cobalt(III) complexes,[20] and the accepted mechanism is that of dissociative interchange (I_d) in which there is weak bonding to both the entering and leaving groups in the transition state.[21] The pressure dependence of the aquation reactions of the formamide, *N*-methylformamide, and *N*,*N*-dimethylformamide complexes has been determined,[22] and the results are consistent with an I_d mechanism. The aquation of the DMF-*O* complex has been studied in detail, and mass spectrometry studies have shown that the reaction proceeds by at least 98% Co–O bond cleavage.[23]

Table IX. Product Distribution (mol %) for the Base Hydrolysis of $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$ in 0.10 M NaOH, I = 1.10 M ($NaClO_4$) at 22 °C

ligand	hydroxo-pentaammine-cobalt(III)	(carboxylato)-pentaammine-cobalt(III)
$HCONH_2$	13	87
$HCONH(CH_3)$	23	77
$HCON(CH_3)_2$[a]	16	84
$HCON(C_2H_5)_2$	54	46
$HCONH(C_6H_5)$[b]	25	75
$HCON(C_6H_5)_2$[b]	10	90
CH_3CONH_2	99	1
$CH_3CONH(CH_3)$	100	<0.5
$CH_3CON(CH_3)_2$	100	<0.5
$CH_3CON(C_2H_5)_2$	100	<0.5
$CH_3CONH(C_6H_5)$	100	<0.5
CH_2FCONH_2[c]	93	7
$CH_2ClCONH_2$	92	8
$C_6H_5CONH_2$	100	<0.5
CH_2=$CHCONH_2$	100	<0.5

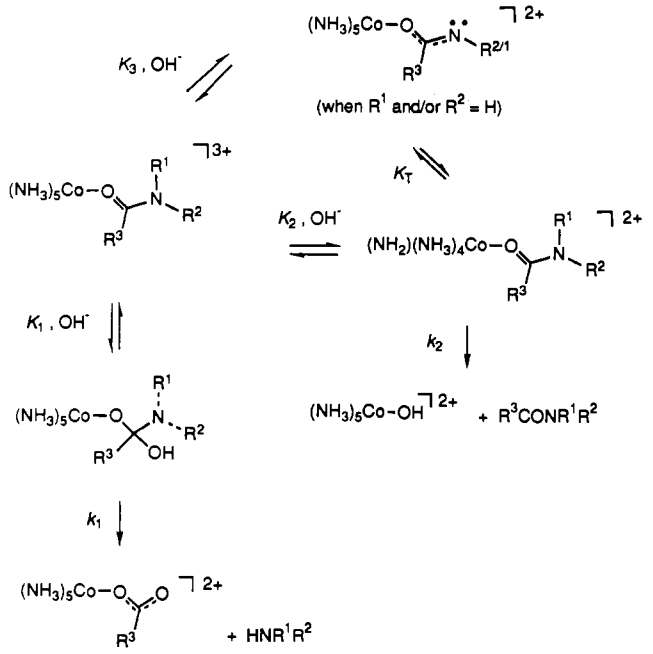
[a] Cf. 88% (formato)pentaamminecobalt(III) from ^1H NMR experiments in: Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726. [b] Cobalt recoveries lower (95–93%) due to accompanying reductive decomposition. [c] Identical result was obtained with 0.20 M NaOH, I = 1.1 M ($NaClO_4$).

Base Hydrolysis. The products from reaction of the complexes in 0.10 M NaOH/1.00 M $NaClO_4$ at 22 °C were isolated by ion-exchange chromatography and analyzed spectrophotometrically. Since ^1H NMR studies with the dimethylformamide complex[5] had shown that the (formato)pentaamminecobalt(III) complex was a major reaction product, we synthesized the relevant (carboxylato)pentaamminecobalt(III) complexes. Comparison of these complexes with any dipositive ions isolated from the acidified reaction solutions confirmed that aquapentaamminecobalt(III) and the relevant (carboxylato)pentaamminecobalt(III) were the only complexes produced by base hydrolysis of oxygen-bonded amides. No O- to N-bonded linkage isomerization was observed under conditions where the N-bonded product would have been detected.

The product distributions for the base hydrolysis reactions are shown in Table IX. All the formamide complexes undergo significant ligand hydrolysis; nucleophilic attack by hydroxide ion at the amide carbon results in the formation of (formato)pentaamminecobalt(III) and liberation of the appropriate amine. The other pathway (S_N1CB) produces the hydroxopentaamminecobalt(III) ion.[5] The reactions are summarized in Scheme I. The relative amounts of the two complexes reflect the ratio of the rate constants of the two reaction pathways and do not vary greatly with the N-substituent. Broadly speaking, the complex with strongly electron-withdrawing substituents on the amide nitrogen (diphenylformamide-*O*) produces the highest percentage (90%) of (formato)pentaamminecobalt(III) and the complex with the most electron-releasing substituents (diethylformamide-*O*) produces the least (46%).

The situation is quite different however for C-substituted amide complexes. The acetamide-*O* complex produces 1% (acetato)pentaamminecobalt(III) on base hydrolysis, but the N-substituted acetamide complexes do not produce any detectable amounts (<0.5%) of that complex at 22 °C. Base hydrolysis of the *N*-methylacetamide and *N*,*N*-dimethylacetamide complexes at 2 °C results in the production of (acetato)pentaamminecobalt(III) in amounts which are small but sufficient to enable quantification (~5%), crystallization, and characterization of the product. This is in accord with the known behavior of the DMF-*O* complex;[5] the C–N cleavage pathway is not very temperature-sensitive, but the Co–O cleavage reaction proceeds

Scheme I



much more slowly at lower temperatures. Consequently base hydrolysis at the lower temperature results in a higher percentage of the C–N cleavage product. It should be noted that these small yields are not due to impurities in the reacting amide-*O* complexes; as was described above, similar amounts of the amide-*O* complexes have been acid hydrolyzed and chromatographed and no 2+ ions were detected. The acetanilide-*O* complex showed no detectable (<0.5%) ligand hydrolysis at either temperature, nor did the benzamide-*O* complex.

Those C-substituted amide complexes with strongly electron-withdrawing substituents at the amide carbon did show higher proportions of ligand hydrolysis; fluoroacetamide-*O* produced 7% (fluoroacetato)pentaamminecobalt(III), and chloroacetamide-*O* gave 8% (chloroacetato)pentaamminecobalt(III). We conclude that these substituents enhance the polarity of the carbon–oxygen bond in the C-substituted amide complexes and render them more susceptible to nucleophilic attack. Base hydrolysis of the fluoroacetamide-*O* complex was repeated in 0.2 M NaOH (I = 1.10 M, $NaClO_4$), and the same product ratio was obtained. This shows that the reactive species is the 2+ ion with a negligible contribution from a doubly deprotonated 1+ ion, unlike the base hydrolysis of more acidic oxygen-bonded succinimide, which proceeds via the 1+ ion.[24]

We also base-hydrolyzed the acetamide-*O* complex in Na_3PO_4 and in Na_3PO_4/Na_2HPO_4 solutions, I = 1.0 M. The former reaction produced 4% (acetato)pentaamminecobalt(III), and the latter, 2%. It has been shown that ion-pairing slows down the rate of Co–O cleavage in base hydrolysis;[25] the higher the concentration of the triply charged PO_4^{3-} anion, the slower the rate of Co–O cleavage and the higher is the ratio of (carboxylato)-pentaamminecobalt(III) to hydroxopentaamminecobalt(III) complexes in the reaction products. Clearly there is no pronounced specific role for HPO_4^{2-} or PO_4^{3-} in these reactions, such as rate-determining H^+ transfer.

In the light of these results we reexamined the benzamide complex, as the phenyl group is also electron-withdrawing. The crystal structure of benzamide[26] shows that the ring is twisted 24° out of plane from the amide group. ^{13}C NMR spectra of the ligand and the complex (Table V) show the ortho and meta carbons of the ring are equivalent; therefore, rotation must be occurring

(25) Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473.
(26) Penfold, B. R.; White, J. C. B. *Acta Crystallogr.* **1959**, *12*, 130.

Table X. Rate Constants (M^{-1} s^{-1}) for the Base Hydrolysis of $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$ in 0.10 M NaOH, I = 1.10 M ($NaClO_4$) at 22 °C

ligand	k_{OH}	k_1K_1	k_2K_2
$HCONH_2$	24.2	20.3	3.9
$HCONH(C_6H_5)$	0.79	0.59	0.20
$HCON(CH_3)_2$	1.3[a]	1.1[b]	0.21
$HCON(C_2H_5)_2$	0.32	0.15	0.17
CH_3CONH_2	30.2	0.3[c]	29.9
$CH_3CONH(C_6H_5)$	70	<0.3	70
$CH_3CON(CH_3)_2$	5.9	<0.03	5.9
$CH_3CON(C_2H_5)_2$	4.6	<0.02	4.6
$C_6H_5CONH_2$	33	<0.2[d]	33
CH_2FCONH_2	55	3.9	51
$CH_2ClCONH_2$	150	10[e]	140

[a] Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 1726. [b] Cf. 1.8 × 10^{-4} M^{-1} s^{-1} for free DMF in: Langlois, S.; Broche, A. *Bull. Soc. Chim. Fr.* **1964**, 812. [c] Cf. 3.75 × 10^{-5} M^{-1} s^{-1} for free acetamide in: Bruylants, A.; Kézdy, F. *Rec. Chem. Prog.* **1960**, *21*, 213. [d] Cf. 1.1 × 10^{-5} M^{-1} s^{-1} for free benzamide in: Shafer, J. A. Directing and Activating Effects of the Amido Group In *The Chemistry of Amides*; Zabicky J., Ed.; Interscience: London, 1970; p 713. [e] Cf. 9.5 × 10^{-3} M^{-1} s^{-1} for the term first-order in hydroxide ion in the rate law for the base hydrolysis of free chloroacetamide in: Kézdy, F.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1960**, *69*, 602.

about the ring–amide bond in solution. These data show that the ring is not conjugated with the amide group so its electronic effect would be somewhat diminished. Separation trials using authentic (benzoato)pentaamminecobalt(III) and aquapentaamminecobalt(III) on Sephadex and Dowex resins showed that the two ions cleanly separate under the conditions described. Consequently, we conclude that the benzamide-*O* complex does not undergo detectable (<0.5%) ligand hydrolysis.

The rates of base hydrolysis of a selection of these complexes were determined. For primary and secondary amide complexes (those of formamide, acetamide, benzamide, fluoroacetamide, chloroacetamide, formanilide, and acetanilide) the variation of k_{obsd} with $[OH^-]$ was not linear. This is consistent with formation of a ligand-deprotonated complex (Scheme I), and the same phenomenon has been observed in oxygen-bonded urea[27] and chelated glycinamides.[28] From the reactions described in Scheme I, the following rate law was derived:

$$k_{obsd} = \frac{[OH^-](k_1K_1 + k_2K_2)}{\{1 + [OH^-](K_1 + K_2 + K_3)\}} \quad (1)$$

For primary and secondary amide complexes the kinetic data fitted the expression

$$k_{obsd} = \frac{[OH^-]k_{OH}}{(1 + K[OH^-])}$$

where $k_{OH} = k_2K_2 + k_1K_1$ and $K = K_3$, and this is consistent with the expected rate law. The values of k_2K_2 and k_1K_1 were determined from k_{OH} and product ratios and are shown in Table X. The k_1K_1 values are compared with the rate constants of free amides where these have been determined.[29-33] The evaluation of K_1 enabled us to determine the pK_a values of these coordinated amides, and they are shown in Table XI along with published pK_a

(27) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.
(28) Buckingham, D. A.; Davis, C. E.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 5571.
(29) Langlois, S.; Broche, A. *Bull. Soc. Chim. Fr.* **1964**, 812.
(30) Bruylants, A.; Kézdy, F. *Rec. Chem. Prog.* **1960**, *21*, 213.
(31) Shafer, J. A. Directing and Activating Effects of the Amido Group. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: London, 1970; p 713 (data recalculated from ref 32).
(32) Bender, M. L.; Ginger, R. D.; Unik, J. P. *J. Am. Chem. Soc.* **1958**, *80*, 1044.
(33) Kézdy, F.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1960**, *69*, 602.

Table XI. pK_a Values of Coordinated Amides, $[(NH_3)_5CoOCR^3NR^1R^2]^{3+}$, I = 1.00 M ($NaClO_4$) at 25 °C Compared with Those Known for Free Amides

ligand	coord amide		free amide
	kinetic	spectrophotometric	
$HCONH_2$	11.9	12.0	17.20[a]
$HCONH(C_6H_5)$	12		15.56[a]
CH_3CONH_2	11.6	11.7	15.1[b]
$CH_3CONH(C_6H_5)$	9.7		17.59[a]
$C_6H_5CONH_2$	10.6	10.8	>19.0[a]
CH_2FCONH_2	9.8		
$CH_2ClCONH_2$	9.4		14.17[c]

[a] Hine, J.; Hine, M. *J. Am. Chem. Soc.* **1952**, *74*, 5266. [b] Branch, G. E. K.; Clayton, J. O. *J. Am. Chem. Soc.* **1928**, *50*, 1680. [c] Kézdy, F.; Bruylants, A. *Bull. Soc. Chim. Belg.* **1960**, *69*, 602.

values of the free amides where available.[33-35] The pK_a values for all the free amides listed except benzamide, acetamide, and chloroacetamide were determined in isopropyl alcohol so the conditions are not identical. However the data show that the acidity of the amides is markedly increased by coordination to cobalt(III).

For the tertiary amide complexes (dimethylformamide,[5] diethylformamide, dimethylacetamide, and diethylacetamide) amide NH deprotonation cannot occur and the variation of k_{obsd} with $[OH^-]$ is linear. This is consistent with the general rate law (1) where $K_3 = 0$ and K_2 is very small:

$$k_{obsd} = [OH^-](k_2K_2 + k_1K_1) \quad (2)$$

The values of the individual rate constants for these complexes are shown in Table X. [The variation of k_{obsd} with $[OH^-]$ for the formanilide-*O* (curved) and *N*,*N*-diethylformamide-*O* (linear) complexes is shown in Figure 3, supplementary material.]

Inspection of the rate constants in Table X shows that for the C-substituted amide complexes the ligand substitution reaction (k_2K_2) is faster than that reaction in the formamide complexes. In the formamide-*O* complex both ligand hydrolysis (k_1K_1) and ligand substitution are noticeably faster (×10) than those for the other formamide complexes. In those complexes where it was detected, ligand hydrolysis is accelerated $\times 10^4$ compared to the same reaction in the free ligand. Derived kinetic and spectrophotometric pK_a data are listed in Table XI; primary data appear in Tables XII–XIV (supplementary material).

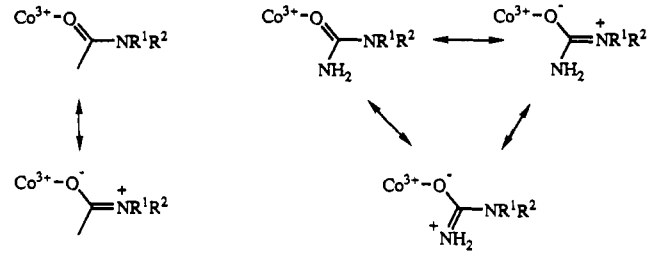
Dinuclear Bridging Formamide Complex. Base hydrolysis of $[(NH_3)_5CoOCHNHCo(NH_3)_5]^{5+}$ proceeds slowly ($t_{1/2}$ = 3 min, $[OH^-]$ = 0.1 M, 25 °C) and is accompanied by some decomposition to cobalt oxide. The product distribution data have been normalized for 100% reaction, and they show two major products in equal amounts, $[(NH_3)_5CoOH]^{2+}$ and $[(NH_3)_5CoNHCHO]^{2+}$, and 2.3% $[(NH_3)_5CoOCHO]^{2+}$. Metal–oxygen bond cleavage is the dominant reaction (95%), but these results also suggest a minor reaction involving carbon–nitrogen bond or cobalt–nitrogen bond cleavage. Since no $[(NH_3)_6Co]^{3+}$ was detected, the minor reaction must involve cobalt–nitrogen cleavage.

Discussion

Bonding Mode. Neutral amides were found to coordinate exclusively through oxygen so the syntheses were regiospecific under ambient conditions. This preference for oxygen-bonding parallels the chemistry of the free amide where oxygen is the most basic site in the molecule.[36] It also complements known chemistry for nitrogen-bonded amide complexes where the neutral N-bonded amide is unstable with respect to the O-bonded form and slowly but completely isomerizes in noncoordinating solvents.[6,7] Monodentate oxygen-bonded amides are weak ligands. In aquation reactions they are poorer leaving groups than sulfonates[37] but (for C-substituted amide complexes) are better leaving groups than ureas.[38]

Polarization of the Amide on O-Coordination. A change in the electronic structure of the amide on O-coordination should be reflected in several ways: the reactivity toward nucleophiles, the acidity, and the barrier to rotation about the C–N bond. Spectroscopic evidence, including the identification of *Z* and *E* geometric isomers, suggests that the electronic structure of the amide group is not greatly changed by coordination to cobalt(III). Nevertheless coordination through the carbonyl oxygen has been found to enhance the reactivity of dimethylformamide toward nucleophiles[5] and the same is true of all the formamide complexes studied here. The outcome of the base-catalyzed reaction does not vary greatly (diphenylformamide-*O*, 90% ligand hydrolysis; diethylformamide-*O*, 46%); this variation correlates well with the electronic properties of the substituents, not with their size. The C-substituted amides do not show this enhancement to the same degree; only complexes with a strongly electron-withdrawing group at the amide carbon show significant ligand hydrolysis (fluoroacetamide-*O*, 7%; chloroacetamide-*O*, 8%) and none at the level shown by the formamides.

In contrast, O-bonded formamide and C-substituted amide complexes do not differ appreciably in their acidities (Table XII). However, the pK_a values of the ligands are reduced by coordination, and this fact in itself is indicative of polarization of the amide on coordination. The reduction is higher than usually observed in complexes where the acidic proton is remote from the coordinated oxygen, e.g. as in the following: $OC(NH_2)_2$ coordinated 13.19,[27] free 13.7–14.3;[39] OCO_2H^- coordinated 8.23, free 9.56.[40] The pK_a values for the primary amide complexes are similar to those determined for chelated glycinamides ($[(en)_2CoglyNH_2]^{3+}$, 11.2; $[(en)_2CoglyNH(CH_3)]^{3+}$, 12.2).[28] There does not seem to be an enhancement in acidity simply through chelation.[41] We attribute the greater acidity of O-coordinated amides compared with ureas to a higher degree of polarization of the electronic structure of the amides by coordination to the metal ion. The ureas have a more delocalized structure:



^1H NMR spectroscopic data do not give any indication of the barrier to rotation about the C–N bond in coordinated primary amides. Amide polarization by the metal ion is expected, and the barrier should be increased as it is for ureas on O-coordination.[42] It would be difficult to determine the barrier to rotation of a coordinated amide because the complexes are not stable at higher temperatures.

The kinetic studies of base hydrolysis also show that the formamide complexes are undoubtedly activated toward nucleophilic attack. For dimethylformamide we can directly compare the rate constants for the coordinated and free amide (Table X),

(34) Hine, J.; Hine, M. *J. Am. Chem. Soc.* **1952**, *74*, 5266.
(35) Branch, G. E. K.; Clayton, J. O. *J. Am. Chem. Soc.* **1928**, *50*, 1680.
(36) Benderley, H.; Rosenheck, K. *J. Chem. Soc., Chem. Commun.* **1972**, 179.
(37) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647.
(38) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1988**, *150*, 81.
(39) Woolley, E. M.; Hepler, L. G. *Anal. Chem.* **1972**, *44*, 1520.
(40) Francis, D. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 5591.
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(42) Fairlie, D. P.; Hounslow, A. M.; Jackson, W. G.; Lincoln, S. F. Results to be published.

and coordination through oxygen has produced an activation of $\sim 10^4$. While data for the other free formamides are not available, it is unlikely that they would differ by more than a factor of 10. The rates of base hydrolysis of benzamide and *N*-methyl- and *N,N*-dimethylbenzamide have been determined[43] and are of the same order of magnitude. So it is concluded that all the formamides show an activation comparable to that of dimethylformamide when coordinated via oxygen.

The formamide-*O* complex base hydrolyzes about 10 times faster than the dimethylformamide complex. This phenomenon has also been observed in the chelated glycinamide series, $[(en)_2CoglyNH_2]^{3+}$, $k' = 25\ M^{-1}\ s^{-1}$; cf. $[(en)_2CoglyN(CH_3)_2]^{3+}$, $k' = 1.1\ M^{-1}\ s^{-1}$.[28] Possibly NH_3 is a more easily solvated leaving group than any of the substituted amines, or the difference could be steric in origin.

Determination of the degree of activation of C-substituted amides toward nucleophiles is complicated by the higher rate of cobalt–oxygen bond cleavage in these complexes. The rate of ligand hydrolysis was determined for coordinated acetamide and chloroacetamide, and they are $\sim 10^4$ greater than the uncomplexed amides; this is approximately the same activation as shown by dimethylformamide.[5] The rate of ligand hydrolysis for acetamide was 10^{-2} times the rate of metal–oxygen cleavage (solvolysis) so it was only just detectable. The other complexes studied except for fluoroacetamide did not show ligand hydrolysis so their rate constants refer solely to the rate of metal–ligand bond cleavage. In the benzamide-*O* complex the rate of solvolysis is $k_2K_2 = 33\ M^{-1}\ s^{-1}$. Since no (benzoato)pentaamminecobalt(III) was detected in the reaction products, its rate of production k_1K_1 must be $<0.2\ M^{-1}\ s^{-1}$. The rate of base hydrolysis of free benzamide is $k_{OH} = 1.1 \times 10^{-5}\ M^{-1}\ s^{-1}$ at 25 °C;[31] now if coordinated benzamide showed the same activation as coordinated dimethylformamide, acetamide, and chloroacetamide, then $k_1K_1 \approx 0.1\ M^{-1}\ s^{-1}$, which would not be detected; the rate of ligand–metal cleavage is simply too fast and undercuts the reaction of interest.

Hydrolysis at the Metal Ion in Relation to Amide Structure. The visible spectral data and the rates of aquation of C-substituted amide complexes suggest that the cobalt–oxygen bond is weaker than in the formamides, possibly because of steric hinderance between the amide substituents and the coordinated ammine ligands.[2,13] The NOE studies confirm this and demonstrate the presence of a conformer where the nitrogen substituent cis to the oxygen is close to the cis ammine ligands. This explains the higher-wavelength shift in the visible spectra of tertiary amide complexes. If the structure of the DMF-*O* complex is representative of all the formamide complexes and the DMA structure of the C-substituted amide complexes, then we can also rationalize the difference between the chemical shifts of the formamide-*O* $-NH_2$ protons (both close to 9 ppm) and those of the other primary amide complexes (7 and 9 ppm). The formamide complexes aquate more slowly and do not show a higher wavelength shift when there are substituents on the amide nitrogen; this is consistent with their demonstrated slower rates of base-catalyzed cobalt–oxygen cleavage. Rhodium and iridium complexes of dimethylformamide do not show metal–oxygen cleavage during base hydrolysis, and this was attributed to the stronger metal–ligand bonding when 2nd and 3rd row transition metal ions are used.[44] It is likely that using these metal ions to complex C-substituted amides would lead to a more definitive assessment of amide activation toward nucleophiles by coordination through oxygen than does complexation by cobalt(III).

O- to N-Bonded Isomerization. The lack of any observed oxygen- to nitrogen-bonded linkage isomerization in the primary amide complexes during base hydrolysis requires explanation. It is known from studies of peptide complexes[4] and from syntheses of N-bonded amides that when the amide ligand is deprotonated, the nitrogen-bonded species is thermodynamically the more stable. Syntheses of amido-*N* complexes under nonaqueous conditions from the parent amide (rather than by base hydrolysis of the coordinated nitrile) are predicted on the assumption that the oxygen-bonded isomer forms first and isomerizes to the stable nitrogen-bonded species with the loss of an amide proton.[1,12] This procedure has been used successfully for a range of primary amides,[6,7] but the isomerization reaction has not been observed directly. N-bonded urea complexes are also synthesized in this manner, and the urea-*O* complex undergoes O to N linkage isomerization in water pH >6, competitive with spontaneous and base-catalyzed solvolysis.[38]

Amide O to N linkage isomerization has been observed in coordinating solvents for a chromium(III) complex of formamide[45] and for the cobalt(III) complexes of the cyclic amides, succinimide,[24] and 2-pyridone;[46] in the latter two it is considered to occur through the ligand-deprotonated oxygen-bonded tautomer. The succinimido-*O* complex isomerizes through both spontaneous and base-catalyzed pathways, but for the 2-pyridonato-*O* complex only spontaneous linkage isomerization ($t_{1/2} = 18$ h) was observed. The cyclic amide complexes are more acidic than those of the primary amides, and in aqueous base they exist as oxygen-bonded, nitrogen-deprotonated complexes, stable species which have been crystallized and characterized. Acyclic amides bonded to cobalt(III) do not exhibit this phenomenon even in strong base, and the explanation can be offered in the following tautomeric equilibrium:

$$[(NH_2)(NH_3)_4CoOCRNH_2]^{2+} \overset{K_T}{\rightleftharpoons} [(NH_3)_5CoOCRNH]^{2+} \quad (3)$$

The concentration of the ammine-deprotonated tautomer, a reactive species, is sufficient in the primary amides to lead to base-catalyzed solvolysis at a rate which is much faster than the rate of spontaneous linkage isomerization so the latter is not observed. In the cyclic amide complexes mentioned above, the amide-deprotonated species is stabilized by delocalization of the negative charge on the nitrogen into the ring, and the tautomeric equilibrium must lie much further to the right in eq 3.

Polarization of Formamide Bonded to Two Metal Ions. The $[(NH_3)_5CoOCHNHCo(NH_3)_5]^{5+}$ ion is relatively inert. Formamide is here coordinated as its anion; nonetheless the dinuclear ion resists protonation. In base, hydrolysis is faster than for the monomeric N-bonded complex but much slower than for the monomeric O-bonded complex.

The site of hydroxide attack in the base hydrolysis of $[(NH_3)_5CoOCHNHCo(NH_3)_5]^{5+}$ was of interest. The production of $[(NH_3)_5CoNHCHO]^{2+}$ (together with $[(NH_3)_5CoOH]^{2+}$) by the major pathway (95%) indicates predominance of Co–O (or C–O) cleavage. The formation of small amounts of the (formato)pentaamminecobalt(III) complex could arise through competing cleavage of the C–N bond in the dimer, but no cobalt(III) hexaammine has been detected and this would be formed in equal amounts (2–3%) if the C–N cleavage mechanism was operating. The alternative mechanism for this minor pathway, cleavage of the cobalt–nitrogen bond and subsequent and much more rapid hydrolysis of the C–N bond in the formamide-*O* complex so formed, must therefore be operative.

Experimental Section

***N,N*-Diethylformamide.** Diethylamine (BDH, 70 g) was stirred over ice, and formic acid (BDH, 40 mL) was added gradually over 15 min. The solution was refluxed for 1 h and then distilled. The fraction distilling at 160–180 °C was reserved and redistilled from molecular sieves with $Ba(OH)_2$: yield 27 g, 28%; bp 175–178 °C.

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Formanilide. Aniline (Ajax, 170 g) was refluxed with formic acid (M&B, 90 g) for 3 h.[47] The excess formic acid was removed by rotary evaporation and the crude amide crystallized when the solution was chilled. It was recrystallized from xylene. Yield: 150 g, 68%.

***N,N*-Diphenylformamide.** Diphenylamine (BDH, 200 g) was refluxed with formic acid (M&B, 100 mL) for 24 h. The solution was extracted with benzene (200 mL), and the benzene fraction was reduced to dryness on a rotary evaporator. The crude product was recrystallized from ethanol (40 g, 17%).

$[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (triflato complex) was prepared by a modification of the original method.[48] Trifluoromethanesulfonic acid (neat, 3M Co., 150 mL) was placed in a large beaker, and crystalline[49] $[(NH_3)_5CoCl]Cl_2$ (45 g) was added gradually with stirring. The beaker was capped with a large petri dish and the mixture left to stir for 3 h at 80 °C. When the mixture no longer gave a positive test for chloride ion, the complex was precipitated by addition to ice-cold AR ether (1 L). The complex was washed repeatedly with ether by decantation and then filtered off and washed well again with ether (90 g, 84%).

All of the following complexes analyzed satisfactorily for at least C, H, and N.

$[(NH_3)_5Co(amide\text{-}O)](CF_3SO_3)_3\cdot H_2O$ [Amide = $HCON(CH_3)_2$ (Ajax), $HCON(C_2H_5)_2$, $HCONHC_6H_5$, $HCON(C_6H_5)_2$, $CH_3CON(CH_3)_2$ (Fluka), and $CH_3CON(C_2H_5)_2$ (Aldrich)]. Triflato complex (3.0 g) and the relevant amide (5.0 g) were stirred for 1 h in AR acetone (30 mL). The products were oiled out in ether (200 mL), dissolved in acetone, and reprecipitated by the gradual addition of ether. The crude product was dissolved in minimal water, recrystallized as the triflate salt by the addition of cold concentrated $NaCF_3SO_3$ solution, washed with ether, and air-dried. Yield: 1.0–1.5 g.

$[(NH_3)_5Co(amide\text{-}O)]_2(S_2O_6)_3\cdot 3H_2O$ [Amide = $HCONH_2$ (Ajax), $HCONH(CH_3)$ (Fluka), CH_3CONH_2 (Ajax), $CH_3CONH(CH_3)$ (Fluka), $C_6H_5CONH_2$ (Hopkin and Williams), and $CH_2{=}CHCONH_2$ (Fluka)]. The crude complexes were prepared as triflate salts as above. They were then dissolved in minimal water and crystallized by the addition of cold, concentrated sodium dithionate solution followed by methanol. The bright pink salts were filtered off, repeatedly washed with LiH_3edta solution, absolute ethanol, and ether, and air-dried. Under vacuum the salts decompose after about 2 weeks. Yield: 1.0–1.5 g.

$[(NH_3)_5CoOC(CH_3)NH(C_6H_5)]_2(S_2O_6)_3\cdot 3H_2O$. Triflato complex (3.0 g) and acetanilide (Ajax, 10 g) were heated at 50 °C in AR acetone (30 mL) for 30 min. The reaction products were oiled out in ether and then chilled. Cold concentrated $Na_2S_2O_6$ solution (10 mL) was added to the oil, and crystallization was induced rapidly by adding methanol. The crude complex was filtered off along with some precipitated acetanilide. The latter was removed by washing the crystals with absolute ethanol (50 mL). The pink salt was washed with LiH_3edta solution (0.01 M, pH 5), absolute ethanol, and ether and then air-dried prior to storage under vacuum. The yield is low and variable; the successful synthesis of this complex is markedly sensitive to impurities in both the triflato complex and in the acetanilide.

The carboxylato complexes of the water-soluble acids (formic, acetic, chloro- and fluoroacetic) were synthesized using the method of Angerman and Jordan,[50] and the (benzoato)pentaamminecobalt(III) complex was prepared by reacting benzoic anhydride and hydroxopentaamminecobalt(III) perchlorate in DMF.[51] Spectroscopic data (^1H and ^{13}C NMR) for these complexes appear in Tables VII and VIII (supplementary material).

$[(NH_3)_5CoO_2CH](ClO_4)_2$. Aquapentaamminecobalt(III) perchlorate (3.0 g), prepared by the action of concentrated perchloric acid on $[(NH_3)_5CoOCO_2]NO_3\cdot 0.5H_2O$,[52] formic acid (Ajax, 5.0 g), and $NaHCO_3$ (0.5 g) were heated in 50 mL of water at 50 °C overnight. The residue was taken up in 20 mL water, and the desired complex was crystallized on the addition of cold concentrated $NaClO_4$ solution and recrystallized from water. The product was washed with ethanol and ether and air-dried (1.3 g, 51%). Visible spectrum (M^{-1} cm^{-1}, 0.1 M $HClO_4$): ϵ_{500} 69.5, ϵ_{350} 55.0; cf. ϵ_{500} 69.4, ϵ_{350} 55.8[53] and ϵ_{500} 69.8, ϵ_{350} 55.6.[5]

$[(NH_3)_5CoO_2CCH_3](ClO_4)_2$. The complex was prepared as for the (formato)pentaamminecobalt(III) complex but with acetic acid (Ajax, 5.0 g). Yield: 1.0 g, 39%. Visible spectrum (M^{-1} cm^{-1}, 0.1 M $HClO_4$): ϵ_{502} 75.5, ϵ_{351} 59.5; cf. ϵ_{502} 75.2, ϵ_{352} 59.1.[8]

$[(NH_3)_5CoO_2CCH_2Cl](ClO_4)_2$. The complex was prepared as for the (formato)pentaamminecobalt(III) complex but with chloroacetic acid (Hopkin and Williams, 5.0 g). The temperature must be controlled carefully during this synthesis otherwise the chloropentaamminecobalt(III) complex is formed from decomposition of the acid. Yield: 1.0 g, 35%. Visible spectrum (M^{-1} cm^{-1}, 0.1 M $HClO_4$): ϵ_{500} 75.0, ϵ_{351} 60.0; cf. ϵ_{502} 74.0, ϵ_{349} 57.5.[54]

$[(NH_3)_5CoO_2CCH_2F](ClO_4)_2$. The aquapentaamminecobalt(III) complex (2.0 g), sodium fluoroacetate (Sigma, 2.0 g), and $NaHCO_3$ (0.5 g) were heated in 50 mL of water overnight at 50 °C. The complex was isolated and purified as for the (formato)pentaamminecobalt(III) complex (1.2 g, 44%). Visible spectrum (M^{-1} cm^{-1}, 0.1 M $HClO_4$): ϵ_{500} 69.0, ϵ_{349} 54.0.

$[(NH_3)_5CoO_2CC_6H_5](ClO_4)_2$. Benzoic anhydride (Aldrich, 1.2 g) was dissolved in DMF (4 mL) and the solution added to a second solution of the aquapentaamminecobalt(III) complex (0.44 g) and tetramethylpiperidine (1.0 g) in DMF (5 mL). The reaction mixture was stirred for 10 min and then diluted with ethanol (10 mL). The crude product was precipitated in ether and crystallized from ethanol/acetone with ether, and dark pink crystals were filtered out, washed with ether, and air-dried (0.17 g, 27%). Visible spectrum (M^{-1} cm^{-1}, 0.1 M $HClO_4$): ϵ_{502} 86.5, ϵ_{350} 75.0.

Spectra. UV–visible spectra were obtained with a Cary 210 spectrophotometer using quartz cells. ^1H and ^{13}C NMR spectra were obtained with a Varian XL 300 spectrometer with a probe temperature of 20 °C using Me_2SO-d_6 (Aldrich) as solvent.

Conformational Studies Using NOE Difference ^1H NMR Spectroscopy. Spectra were recorded with the temperature fixed at 20 °C, and the solvent used was acetone-d_6 (99.5 atom % D, MSD Isotopes). The complexes employed (*N,N*-dimethylacetamide-*O*, and *N*-methylacetamide-*O*) were used as their triflate salts. The solutions were deoxygenated by immersing the tubes in an ultrasonic vibrator for 1 min and then bubbling nitrogen through them. The spectrometer was programmed to record spectra with the decoupler irradiating at the cis NH_3 resonance of each complex and at δ 12 ppm alternately, and the cycle was repeated 64 times. The FIDs were then subtracted and the difference fourier-transformed. The resulting spectrum was plotted to reveal the irradiated cis NH_3 peak and any peaks which demonstrated NOE enhancements.

^1H NMR Spectra of $[(NH_3)_5CoNHCHO](ClO_4)_2$ at Low Temperatures. A sample of $[(NH_3)_5CoNHCHO](ClO_4)_2\cdot H_2O$[6] was analyzed by ^1H and ^{13}C NMR spectroscopy in Me_2SO-d_6. No other substance was detected, especially (formato)pentaamminecobalt(III), which is a common contaminant. A concentrated solution of this sample in DMF-d_7 (99 atom % D, CEA) was prepared and TMS added as an internal reference. DMF is a good solvent for perchlorate salts, and the pure liquid does not freeze until –61 °C. The ^1H spectrum of the solvent had been recorded previously [δ (ppm)]: 2.75, 2.94, ($-N(CH_3)_2$), centers of multiplets; 8.03 (HCO). ^1H spectra of the solution were recorded at 17, –20, –40, –60, and –70 °C; it began to freeze at –75 °C. The temperatures listed were those recorded by the calibrated spectrometer thermocouple of gaseous nitrogen blowing over the sample tube in the probe; they were stable to within ±0.1 °C during the recording of the spectra.

Kinetic Data. Standard techniques were employed.[55] The exception was the acid hydrolysis of the diphenylformamide-*O* complex, which could only be followed spectrophotometrically over 2 half-lives because after that the liberated amide ligand began to precipitate. The reaction was allowed to proceed to completion, the spectrophotometer cuvette was centrifuged, and the final absorbance of the solution was measured accurately without interference from the precipitate.

Acid hydrolysis reactions were monitored at 520 nm. Base hydrolysis reactions of most of the amide-*O* complexes were studied in solutions of NaOH (Con Vol) with $[OH^-]$ = 0.025–0.10 M, I = 1.0 M ($NaClO_4$), and also in buffer solutions made up from triethanolamine, diethanolamine, ethanolamine, and triethylamine which had been partially neutralized with $HClO_4$, using $NaClO_4\cdot H_2O$ as the supporting electrolyte. The pH values of the buffer solutions were determined with an Orion Ross combination pH electrode and a Metrohm 654 pH meter. The electrode was calibrated to read $p[OH^-]$ or $p[H^+]$ by automated titration of 0.010 M NaOH (Con Vol), 1.00 M $NaClO_4$, under a nitrogen atmosphere against standardized 1.00 M $HClO_4$ (pK'_w = 13.77). For the acetamide-*O*

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and formamide-*O* complexes the buffers used were triethylamine solutions partially neutralized with $HClO_4$, I = 1.00 M ($NaClO_4$). As a check on $[OH^-]$ values, the rates of base hydrolysis of two reference complexes, $[(NH_3)_5CoI](ClO_4)_2$ and $[(NH_3)_5CoNCN(CH_3)_2](ClO_4)_3$, were measured in the buffers and the results compared with those obtained in standard NaOH (0.010, 0.015 M, Volucon), I = 1.00 M ($NaClO_4$) solutions and with published results[56,57] with which they were in reasonable agreement.

Rate constants were determined by nonlinear least-squares analysis using the FORTRAN program KINCAL adapted for the Macintosh computer.[55] Rate constant–pH data were fitted to the relevant expressions using weighted nonlinear least-squares analysis by means of the same program.

Acidity Constants. These were determined by two independent methods from the kinetic data as described elsewhere.[58]

Product Distribution Data. For acid hydrolysis the complexes (~0.5 g) were dissolved in 0.10 M $HClO_4$ and stored in a sealed container at 22 °C until reaction was complete. The solutions were diluted with distilled water and chromatographed on SP Sephadex C-25 resin (Pharmacia). The resin was eluted first with 0.5 M $NaClO_4$ (pH 5, NaH_2PO_4) to separate any 2+ ions which might be present (none were found) and finally with 0.75 M NaCl (pH 7, NaH_2PO_4/Na_2HPO_4) which removes the aquapentaamminecobalt(III) complex. The volumes of the eluates were recorded and the concentrations determined spectrophotometrically with 10-cm quartz cells (aquapentaamminecobalt(III), ϵ_{492} 50.5 M^{-1} cm^{-1} [37]). Cobalt recoveries exceeded 98%, and all results are normalized to 100%.

For base hydrolysis reactions the complexes (~0.5 g, accurately weighed) were dissolved in 0.10 M NaOH, 1.00 M $NaClO_4$ solution (50 mL, 22 °C). After 5–10 min the solutions were acidified with 6 M $HClO_4$, diluted with distilled water, and chromatographed and analyzed as above. For those complexes where 2+ ions were detected, the reaction was repeated at 2 °C and the relevant complex crystallized by freeze-drying the eluate and extracting the residue with absolute ethanol to remove $NaClO_4$, and then the residue was recrystallized from water. The (carboxylato)pentaamminecobalt(III) complexes were identified by comparison of their ^1H and ^{13}C NMR spectra (Tables VII and VIII (supplementary material)) with those of authentic carboxylato complexes, and from a knowledge of their molar extinction coefficients (given above) the amounts produced by base hydrolysis at 22 °C were calculated. Each experiment was performed in duplicate. Under these conditions any carboxylato complex formed by ligand hydrolysis will not be significantly decomposed by base during the experiment. The rates of base hydrolysis of some of the relevant carboxylato complexes have been measured at 25 °C: k_{OH} (M^{-1} s^{-1}) = 7.0×10^{-4} for (acetato)pentaamminecobalt(III),[59] 4.2×10^{-3} for (chloroacetato)pentaamminecobalt(III),[59] and 5.8×10^{-4} for (formato)pentaamminecobalt(III).[60] Attempts to measure the rates for (fluoroacetato)- and (benzoato)pentaamminecobalt(III) were foiled by decomposition of the complexes, but in the time comparable to that allowed for the amide hydrolysis experiments no significant change in the absorbance of the carboxylato complex solution was observed.

The binuclear complex $[(NH_3)_5CoOCHNHCo(NH_3)_5](ClO_4)_5$[19] (0.2 g) was reacted in 0.1 M NaOH (I = 0.1 M) for 5 min (25 °C) and then quenched with 0.1 M $HClO_4$ to pH 3. The solution was chromatographed on Sephadex, and the products were analyzed spectrophotometrically as above.

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Supplementary Material Available: Spectral data (Tables VII, VIII, and XIV) and rate data (Tables XII and XIII and Figure 3) (5 pages). Ordering information is given on any current masthead page.

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