Synthesis and Reactivity of the Linkage Isomers of Pentaammine(glycinamide)cobalt(III)

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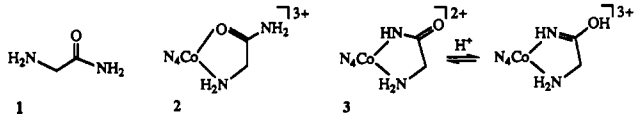
*Received April 15, 1993**

The three monodentate pentaamminecobalt(III) linkage isomers of glycinamide have been synthesized and characterized by visible and ^1H and ^{13}C NMR spectroscopy and microanalysis. A nitrile-bonded ammonioacetonitrile complex was synthesized, it reacts in liquid ammonia to produce the amidine-bonded aminoacetamidine complex while in aqueous base it hydrolyzes to the amido-N-bonded glycinamide ion. Both $[(NH_3)_5CoNHCOCH_2NH_2]^{2+}$ and $[(NH_3)_5CoNHC(OH)CH_2NH_3]^{4+}$ have been isolated. The diprotonated species, a strong acid (pK_a <0.5), rearranges readily to form the oxygen-bonded linkage isomer in acid solution (water or Me_2SO) with parallel solvolysis. The rate of the amide N to O rearrangement has been measured in Me_2SO at 25 °C: $k_{NO} = 3.2 \times 10^{-3}$ s^{-1}. The oxygen-bonded glycinamide complex, $[(NH_3)_5CoOC(NH_2)CH_2NH_3]^{4+}$, was synthesized directly from $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ and the amine-protonated ligand while the thermodynamically more stable amine-bonded complex, $[(NH_3)_5CoNH_2CH_2CONH_2]^{3+}$, was prepared by using the same reactants but by warming them with a noncoordinating base in sulfolane. $[(NH_3)_5CoOC(NH_2)CH_2NH_3]^{4+}$ solvolyzes rapidly in aqueous acid ($k_H = 2.8 \times 10^{-3}$ s^{-1}, 25 °C, 0.1 M $HClO_4$). When the pH is just high enough so that the remote amine group is not protonated (pH 6–10), there is a spontaneous rearrangement of the oxygen- to the amine-bonded linkage isomer ($k_{ON} = 2.6 \times 10^{-4}$ s^{-1}) and competitive solvolysis ($k_{solv} = 5.4 \times 10^{-4}$ s^{-1}); capture of the amide nitrogen is not competitive. At higher pH $[(NH_3)_5CoOC(NH_2)CH_2NH_2]^{3+}$ (amide pK_a 10.75, I = 1.00 M, $NaClO_4$, 25 °C) undergoes base-catalyzed solvolysis ($k_2K_2 = 25$ M^{-1} s^{-1}, I = 1.00 M ($NaClO_4$), 25 °C) and there is no detectable amide hydrolysis. However a trace is detected if the reaction is carried out at 2 °C. There is no detectable OH^--catalyzed linkage isomerization. The reactivity of the monodentate glycinamide complexes is compared with that of the corresponding chelates.

Introduction

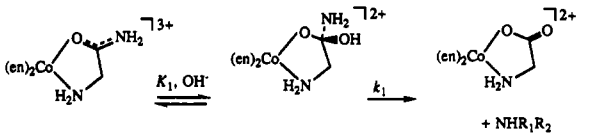
Glycinamide (**1**) is a simple model for the N-terminus of peptides,[1] and it can coordinate metal ions through its amide and amine functional groups. It can also form chelate complexes through the amine nitrogen and amide oxygen (**2**) and through the amine and amide nitrogen atoms (**3**).



1 **2** **3**

The effects of chelation on the properties of coordinated amides and esters have been the subject of conjecture for some time. The chelated ester in (ethyl glycinate)bis(ethanediamine)cobalt(III) is hydrolyzed in base to chelated glycinate,[2] but the monodentate ester complex (methyl acetate)pentaamminecobalt(III) reacts in aqueous base, largely by cobalt–oxygen bond cleavage, to form the hydroxo pentaammine complex and the unhydrolyzed ester.[3] It has been suggested that the difference in reactivity arises from the decrease in the rate of release of the ester ligand in the chelated species as compared with the rate of release in the monodentate form.[3]

Complexes have been prepared with glycinamide, *N*-methylglycinamide, and *N,N*-dimethylglycinamide chelated through N and O to $(en)_2Co^{III}$. In aqueous base, all these complexes hydrolyzed solely to chelated glycinate:[4]



Subsequent work has shown that this reaction proceeds by attack of external hydroxide ion on the chelate ring and not by base-catalyzed Co–O ring opening and subsequent intramolecular hydrolysis.[5,6]

The rate of base hydrolysis of the *N,N*-dimethylglycinamide chelate is comparable with the rate of amide hydrolysis in the oxygen-bonded monodentate amide complex (dimethylformamide)pentaamminecobalt(III). It was concluded from these data that chelation did not play a significant role in determining the reactivity of the oxygen-coordinated amide group.[7] The acidity of the bis(ethanediamine) glycinamide-*N,O* complex (pK_a 11.2)[4] is comparable with those of the monodentate (acetamide-*O*)-(pK_a 11.6) and (formamide-*O*)pentaamminecobalt(III) complexes (pK_a 11.9).[8] However recent studies of (amide-*O*)pentaamminecobalt(III) complexes have shown that, while formamide com-

* Abstract published in *Advance ACS Abstracts*, October 1, 1993.

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(8) Angus, P. M.; Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 450–459.

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Table I. ^{1}H NMR Spectral Data (δ, ppm) for Aminoacetonitrile and Its Derivatives and Their Pentaamminecobalt(III) Complexes in Me_2SO-d_6 at 20 °C

	cis and *trans* NH_3		$-CH_2-$	others	
$NCCH_2NH_2 \cdot HClO_4$			3.99	8.52	$-NH_3^+$
$[(NH_3)_5CoNCCH_2NH_3]^{4+}$	3.79	3.37	4.48	7.90	$-NH_3^+$
$[(NH_3)_5CoNHCNH_2CH_2NH_2]^{3+}$		3.28[a]	3.30	5.78	$-NH_2$
				6.80	$-NHC(NH_2)-$
$H_2NCOCH_2NH_2 \cdot HClO_4$			3.59	7.42, 7.64	$-NH_2$ (amide)
				7.84	$-NH_3^+$
$[(NH_3)_5CoNH_2CH_2CONH_2]^{3+}$	3.38	3.28	2.93	4.28	$-NH_2-$ (amine)
				7.45, 7.62	$-NH_2$ (amide)
$[(NH_3)_5CoNHCOCH_2NH_2]^{2+}$	3.24	3.16	3.32	4.19	$-NH-$ (amide)
				5.68	$-NH_2$
$[(NH_3)_5CoNHC(OH)CH_2NH_3]^{4+}$	3.18	3.10	3.48	7.35	$=NH-$ (amide)
				7.72	$-NH_3^+$
$[(NH_3)_5CoOC(NH_2)CH_2NH_3]^{4+}$	4.00	2.72	3.48	7.89, 9.35	$-NH_2$ (amide)
				7.88	$-NH_3^+$
$^+H_3NCH_2COOH$			3.54	8.00	$-NH_3^+$
$[(NH_3)_5CoOCOCH_2NH_3]^{3+}$	3.68	2.61	3.25	7.54	$-NH_3^+$

[a] *cis* and *trans* ammine signals not resolved.

plexes ($HCONR_1R_2$) react largely by amide hydrolysis and the rate constants are comparable with those of glycinamide chelates, C-substituted amides ($R_3CONR_1R_2$) react largely by Co–O rupture.[8] This variation in the reactivity of monodentate amide-*O* complexes means that the effects of chelation on the reactivity of the coordinated amide group can only be determined reliably by comparing monodentate glycinamide-*O* with *N,O*-chelated glycinamide.

In amido-bonded complexes of cobalt(III) no similarity in chemical properties has been observed between the glycinamide chelates and the monodentate amide complexes. The pK_a of the acetamide-*N* pentaammine complex is 3.02,[9] whereas that of the glycinamide-*N,N'* tetraammine complex is only ~0.4[10] and that of the corresponding bis(ethanediamine) complex is 1.2.[11] A comparable difference has been found in the analogous complexes of Ru(III),[12] and it has been suggested that this difference is due, at least in part, to the effects of the formation of a chelate ring.[13]

It is difficult to perceive why chelation should have little effect on the acidity of oxygen-bonded amide complexes but a substantial effect on the acidity of those bonded through nitrogen. Perhaps chelation is not the factor which causes the greater acidity of glycinamide-*N,N'* tetraamine complexes compared with the acetamide-*N* pentaammine complex. Recent studies on the reactivity of N-bonded amide complexes have shown that the acidity of the amide group is affected by the nature of the substituent on the amide carbon. Those complexes with electron-withdrawing substituents are more acidic and rearrange to their oxygen-bonded forms more rapidly than those with electron-releasing substituents.[14,15] Glycinamide (*amino*acetamide) has an amine substituent, and this could be the dominant influence in the reactivity of its complexes.

We have prepared for the first time the three monodentate pentaamminecobalt(III) complexes of glycinamide in order to compare their reactivity with that of the complexes containing chelated glycinamide. In addition, we wished to determine if the rate of base hydrolysis of the oxygen-bonded amide group (C–N cleavage) was enhanced by the presence of a remote amine group in the pentaammincobalt(III) glycinamide-*O* ion. The reaction takes place via the formation of a tetrahedral intermediate when hydroxide ion adds to the amide carbon, and proton transfer from the hydroxide oxygen to the amide nitrogen is required before the intermediate can rupture to form coordinated carboxylate and free amine. This proton-transfer process could be aided by the intramolecular amine group in the tetrahedral intermediate, and if so, the rate of base hydrolysis should be significantly faster for this complex than for comparable monofunctional amide-*O* complexes.

Table II. ^{13}C NMR Spectral Data (δ, ppm) for Aminoacetonitrile and Its Derivatives and Their Pentaamminecobalt(III) Complexes in Me_2SO-d_6 at 20 °C

	$-CH_2-$	other	
$NCCH_2NH_2 \cdot HClO_4$	27.6	115.7	$-C\equiv N$
$[(NH_3)_5CoNCCH_2NH_3]^{4+}$	28.7	126.8	$-C\equiv N$
$[(NH_3)_5CoNHCNH_2CH_2NH_2]^{3+}$	43.7	175.2	$-NHC(NH_2)^-$
$^+H_3NCH_2CONH_2$	40.3	168.0	$-CONH_2$
$[(NH_3)_5CoNHCOCH_2NH_2]^{2+}$	43.7	178.5	$-CONH_2$
$[(NH_3)_5CoNH_2CH_2CONH_2]^{3+}$	42.9	170.0	$-CONH_2$
$^+H_3NCH_2COOH$	40.2	169.5	$-COOH$
$[(NH_3)_5CoOCOCH_2NH_3]^{3+}$	41.5	174.8	$-COO-$

Results

Syntheses. Attempts to prepare the amido-*N* glycinamide complex directly from glycinamide using $[(NH_3)_5Co(Me_2SO)]^{3+}$ and a noncoordinating base in dimethyl sulfoxide[16] were unsuccessful, and the synthesis was achieved through base hydrolysis of the precursor nitrile complex.[9] The ammonioacetonitrile pentaammine complex **5** was prepared by warming aminoacetonitrile hydroperchlorate with the pentaammine(trifluoromethanesulfonato)cobalt(III) (triflato) complex in acidified sulfolane. The nitrile signals of the product in the ^{13}C NMR (Table II) and infrared spectra are at a higher frequency than those for the free ligand, and this implies coordination through the nitrile group, while in the ^{1}H NMR spectrum (Table I) the *cis* and *trans* ammine signals are consistent with a nitrile-bonded complex.[15] The latter spectrum also shows a remote protonated amine group. This complex reacts with liquid ammonia to form a pale orange species whose ^{1}H and ^{13}C NMR spectra are consistent with a coordinated amidine structure, the ammonioacetamidine complex **6**. This is clear evidence that the reactant is coordinated through the nitrile group.[17]

In aqueous base, the ammonioacetonitrile complex reacts rapidly, with minimal decomposition, to form an orange complex whose visible and NMR spectra imply that it is the amido-N-bonded glycinamido complex **7**. In acid solution, the latter,

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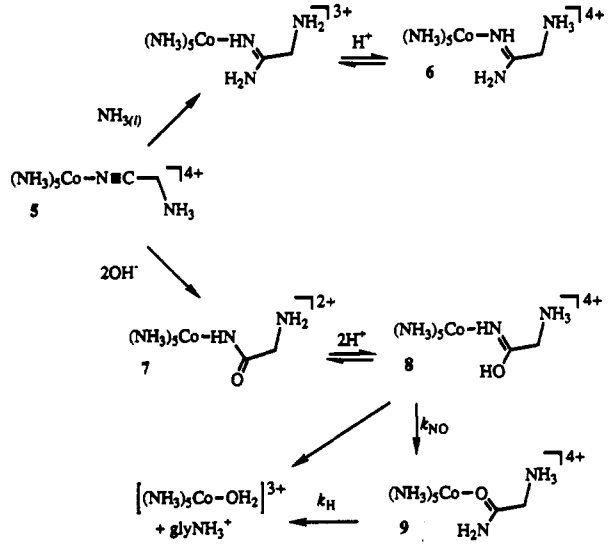
(16) Fairlie, D. P.; Jackson, W. G. *Inorg. Chim. Acta* **1990**, *175*, 203–207.
(17) Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.* **1990**, *29*, 140–143.

Scheme I



protonated on both the amine and amide group (**8**), was crystallized at 2 °C. The reactions of the ammonioacetonitrile complex are summarized in Scheme I.

The oxygen-bonded glycinamide complex **9** was formed in a kinetically controlled synthesis by reacting glycinamide hydroperchlorate with the triflato complex in acetone. It was crystallized as the dithionate salt of the amine-protonated species. The thermodynamically most stable linkage isomer, the amine-bonded glycinamide complex **10**, was synthesized by heating glycinamide hydroperchlorate in sulfolane with the triflato complex and a noncoordinating base. The ^{1}H NMR spectrum clearly shows the signal for the coordinated amine group (2H) at 4.25 ppm and the two peaks for the remote amide group at 7.41 (1H) and 7.58 (1H) ppm. This complex was unreactive in dilute acid, but it decomposed slowly in basic solution; the products were largely fusco salts and a trace of the hexaammine complex.

An anticipated product of the base hydrolysis of the glycinamide-*O* complex was the glycinato-*O* complex **11**. The latter complex was synthesized from the aquapentammine complex and glycine[18] and was characterized in its acidic form, $[(NH_3)_5CoOCOCH_2NH_3](ClO_4)_3$.

Reactivity of $[(NH_3)_5CoOC(NH_2)CH_2NH_3]^{4+}$. In acid solution the title complex solvolyzed rapidly to form the aquapentaammine complex and free ligand. The rate of solvolysis is the highest of all the known amide-*O* complexes, $k_H = 2.8 \times 10^{-3}$ s^{-1}; *cf.* 1.3×10^{-3} s^{-1} for the fluoroacetamide-*O* complex.[8] It is the only one of the amide-*O* complexes studied which has a positively charged leaving group. In basic solution, the remote amine group is not protonated; the complex was crystallized in this form as the dithionate salt, but it was very insoluble in both water and Me_2SO. It is assumed that the pK_a of the remote amine group in this complex is not significantly different from that of the free ligand (glycinamide pK_a 8.06).[19] Base hydrolysis at 25 °C of the glycinamide-*O* complex in 0.1 M NaOH, I = 1.0 M ($NaClO_4$), yields the hydroxo pentaammine complex; no glycinato complex was detected. At lower pH (8–10) a second species was found, an orange 3+ complex whose ^{1}H and ^{13}C NMR spectra were identical with those of the amine-bonded glycinamide complex. A trace of glycinato complex was observed in the products of the reaction at 2 °C. It is concluded that the glycinamide-*O* complex undergoes a spontaneous rearrangement if the remote amine group is not protonated and the product is the thermodynamically more stable amine-bonded linkage isomer. Contributions from the protonated-amine solvolysis and the base-catalyzed solvolysis are negligible at pH 7, where the glycinamide-*O* complex undergoes oxygen- to amine-bonded rearrangement (32%) and competitive solvolysis; no amide-*N* product was detected. The reactions of the glycinamide-*O* complex are summarized in Scheme II.

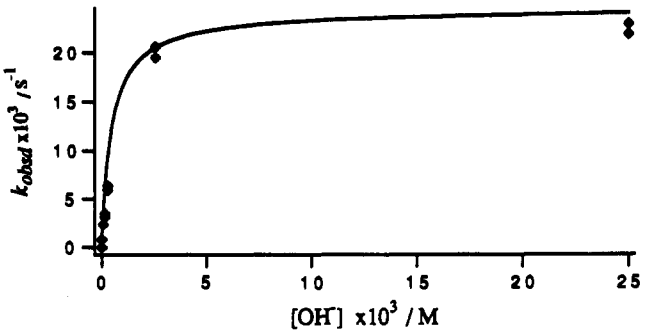
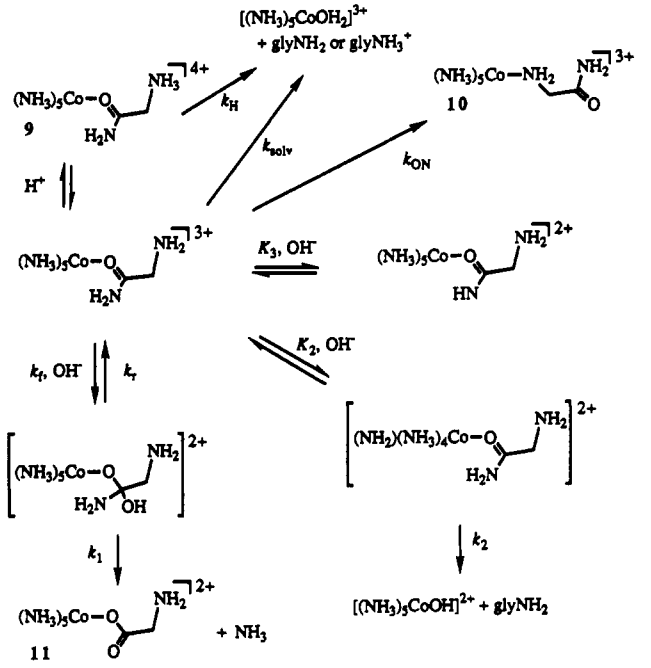


Figure 1. Graph showing the variation of the observed rate constant with [OH$^-$] for the base hydrolysis of the glycinamide-*O* complex (I = 1.00 ($NaClO_4$), 25 °C): points, measured; line, calculated.

Scheme II



The kinetics of the reactions in aqueous base have been measured and the rate law is

$$k_{obsd} = \frac{k_{ON} + k_{solv} + k_{OH}[OH^-]}{1 + K_3[OH^-]}$$

where k_{OH} = 25 M^{-1} s^{-1}, $k_{ON} = 2.6 \times 10^{-4}$ s^{-1}, and $k_{solv} = 5.4 \times 10^{-4}$ s^{-1}. The pK_a of the coordinated amide group is 10.8 from the kinetic data, and it was determined spectrophotometrically as 10.7. This is consistent with the reactions shown in Scheme II. The variation of the observed rate constant with [OH$^-$] is shown in Figure 1. The term k_{OH} is the sum of the k_2K_2 and k_1^* terms where $k^* = k_f/(k_r + k_1)$. Since no glycinato complex was detected at 25 °C, the metal–oxygen cleavage pathway (k_2K_2 = 25 M^{-1} s^{-1}) substantially exceeds the amide hydrolysis pathway ($k_1k^* \sim 0.1$ M^{-1} s^{-1}). The latter path is gauged reasonably, since some glycinato complex was detected during base hydrolysis at 2 °C. The rate constant for the hydrolysis of free glycinamide is reported as 2.9×10^{-3} M^{-1} s^{-1},[19] while in chelated glycinamide there is no metal–oxygen cleavage reaction and the rate constant for amide hydrolysis is 25 M^{-1} s^{-1}.[4]

Reactivity of $[(NH_3)_5CoNHCOCH_2NH_2]^{2+}$ and $(NH_3)_5CoNHCOCH_2NH_3]^{4+}$. The 2+ complex decomposed slowly in

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aqueous base, producing fusco salts. In aqueous acid it is protonated on both the amine and amide groups and this species is quite reactive. The coordinated amide is a strong acid: To crystallize a pure sample of the protonated species, it was necessary to keep the solution at or near to 0 °C. The product of the reaction in aqueous acid was the aquapentaammine complex. The amide-*N* complex was reacted in acidified Me_2SO-d_6 and the course of the reaction monitored by ^1H NMR spectroscopy. Inspection of the spectra showed that the complex reacted by amide N to O rearrangement and direct solvolysis; the products, the Me_2SO–pentaammine and glycinamide-*O* complexes, were readily identified. The reaction was relatively rapid, being complete within 45 min. As with previous amide N to O rearrangements,[14] the oxygen-bonded complex was not detected in aqueous solution, presumably because it solvolyzed much faster than it was formed. It is concluded that the reaction is essentially the same in both solvents. The rate of amide N to O rearrangements in acidified Me_2SO was monitored at 556 nm, an isosbestic point for the glycinamide-*O* and Me_2SO complexes, and the specific rate constant (k_{NO}) was determined as 3.2×10^{-4} s^{-1} (25 °C, [CF_3SO_3H] = 1.0 M). It is assumed that the acidity of the remote amine group is not significantly greater than that of the free ligand (glycinamide pK_a 8.06).[19] The reactions of the amido-N-bonded glycinamide complexes are summarized in Scheme I.

Discussion

In the reactions of the linkage isomers of the pentaammine(glycinamide)cobalt(III) ion, two rearrangements, amide-*N* to amide-*O* and amide-*O* to amine-bonded glycinamide, have been identified under different conditions.

The amide-*O* to amine-bonded glycinamide rearrangement occurs in the pH range where the amine group is not protonated in aqueous solution, and there is accompanying solvolysis. This rearrangement must be intramolecular, as the free ligand does not compete with solvent water for the metal site under these conditions. Capture of a remote group has not been observed previously in the rearrangement of a monodentate ligand in aqueous media. Amines generally are not good competitors for cobalt(III),[20,21] but this rearrangement is not a result of competition by external nucleophiles, since it occurs before ligand loss. In the monodentate ethanediamine complex *cis*-$[Co(en)_2(NH_2CH_2CH_2NH_3)Cl]^{3+}$, the remote amine group competes poorly during base hydrolysis for the coordination site previously occupied by the chloride ion; $[Co(en)_3]^{3+}$ constituted less than 5% of the reaction products.[22] While the latter reaction involves the formation of a chelate ring rather than linkage isomerization, the two systems have certain similarities. Especially notable is that both remote amine groups would be solvated and hydrogen-bonded to the same degree. The obvious difference is that glycinamide can only adopt bent conformations, since rotation about the amide bond is restricted, whereas ethanediamine is free to assume extended conformations. It could be that the enforced proximity of the amine group to the metal ion in the glycinamide complex promotes its capture during base hydrolysis.

An N- to O-bonded amide rearrangement in acidic solution is not new, and clearly in the glycinamide case the amine is not captured competitively because it is protonated. The reaction was not examined in detail in the intermediate-pH region, where the reactant is half-protonated as $[(NH_3)_5CoNHCOCH_2NH_3]^{3+}$ (in equilibrium with $[(NH_3)_5CoNH(COH)CH_2NH_2]^{3+}$); competitive amine capture is a distinct possibility via the latter tautomer, but it is likely to be 10^5 times less abundant, given the probable pK_a's for the two functional groups (estimated to be ca. 8 and 1, respectively); in any event, the 3+ ion was observed to be quite unreactive.

Although no hydrolysis of the coordinated amide group was detected during the base hydrolysis of the glycinamide-*O* complex at 25 °C, some was at 2 °C. The reactivity of this complex is comparable with that of other C-substituted primary amide complexes (acetamide-*O* and benzamide-*O*), where there is little or no amide hydrolysis also, and the rates of Co–O cleavage and the acidities are very similar.[8] The only disparity is that the rate constant for amide hydrolysis (ca. 0.1 M^{-1} s^{-1}) for the glycinamide-*O* complex is less than expected. In simple amide-*O* complexes, the difference in rate between the coordinated and the free amide, where it could be detected, is 10^3–10^4,[7,8] but here it is only ca. 10^2.

By contrast chelated glycinamide, $[(en)_2Co(glyNH_2\text{–}N,O)]^{3+}$ (pK_a 11.2), does not undergo base-catalyzed solvolysis but reacts only by amide hydrolysis, producing chelated glycinate. The rate constant for amide hydrolysis is 25 M^{-1} s^{-1}. It is unlikely that the difference in the amine ligands (NH_3; *cf.* en) is significant; $[trienCo(glyNHCH_3)]^{3+}$ and $[(en)_2Co(glyNHCH_3)]^{3+}$ all hydrolyze to chelated glycinate at very similar rates, and the pK_a's of the amide groups are the same.[4] The difference in the acidities of the chelate and the monodentate complex is not significant (ΔpK 0.4); this indicates that the degree of polarization of the ligand by the metal ion varies little between the two. Hence, their susceptibility to nucleophilic attack was expected to be similar. The two sets of kinetic data show that the lack of amide hydrolysis in the monodentate complex cannot be attributed simply to faster base-catalyzed solvolysis. If glycinamide hydrolysis proceeded at the same rate in the monodentate and chelate complexes, then the reaction in the former complex would be competitive with base-catalyzed solvolysis, as the reactions happen to have very similar rates. Therefore the difference in reactivity would seem to lie in the greater rate of amide hydrolysis in the chelate. The explanation for the disparity may be that, in the chelate, the amine group is coordinated to the metal ion; this produces a strongly electron-withdrawing functional group bonded to the amide carbon, which enhances the rate of amide hydrolysis. The amine group in the monodentate complex is not activated in this way; in fact, if anything, it is electron-donating to the reaction center inductively.

It is clear from the results that proton transfer during the decay of the tetrahedral intermediate, thereby assisting ammonia loss, is not effected by the remote amine group even though it would seem to be well placed to act in this way. Chelated glycinamide-*N*,*O* is base-hydrolyzed more rapidly than the corresponding monodentate complex, despite the fact that the amine group is bonded to the metal ion and therefore unavailable for the proton-transfer process.

The amide-N-bonded complexes, monodentate and chelates, are strong acids. In a comparison of their acidities, there is a charge difference to take into account, 3+ for the chelates compared with 4+ for the monodentate species. However, it appears that bonding the amine group to a proton or to the metal ion has similar effects on the acidity of the N-bonded amide group in the glycinamide ligand, even though the proton is considered to be more polarizing than a metal ion.[23]

The monodentate complex rearranges rapidly in acid solution (water or dimethyl sulfoxide) to form the oxygen-bonded isomer, with parallel solvolysis. This reaction has been observed in monofunctional amide complexes of cobalt(III)[14,15] and in the Cu(II), Ni(II),[1] Ru(II), and Ru(III)[13] chelates of glycinamide but not in the Co(III) chelates.[10,11] Cu(II) and Ni(II) are labile metal ions, and the rearrangement in those species could take place off the metal ion. However, this is not the case with the ruthenium complexes. Even with these species, the chemistry is atypical: rearrangement is facile with Ru(II), but with the Ru(III) chelate, catalysis by Ru(II) is required.[13]

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Experimental Section

Spectra. UV–visible spectra were obtained with a Cary 210 spectrophotometer using quartz cells. IR spectra were recorded with a JASCO A-100 spectrophotometer in Nujol mulls with NaCl windows. ^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. The central peak of the solvent signal was used as the internal reference (^1H 2.49 ppm and ^{13}C 39.4 ppm downfield from $SiMe_4$).

Syntheses. All complexes analyzed satisfactorily for H, C, and N. ***Caution: Perchlorate salts are potentially explosive.***

$NCCH_2NH_2$·$HClO_4$. $NCCH_2NH_2$·HCl (Aldrich, 10 g) was dissolved in a minimum amount of water and concentrated $HClO_4$ added until crystallization commenced. The mixture was chilled and the white solid filtered off, washed copiously with ether, and dried over P_2O_5 under vacuum (12 g, 79%). Infrared spectrum: nitrile stretching frequency 2270 cm^{-1}. ^1H NMR (δ, Me_2SO-d_6): 3.99, $-CH_2-$; 8.52, $-NH_3^+$. ^{13}C NMR (δ, Me_2SO-d_6): 27.6, $-CH_2-$; 115.7, $-C\equiv N$.

$H_2NCOCH_2NH_2$·$HClO_4$. $H_2NCOCH_2NH_2$·HCl (Sigma, 10 g) was dissolved in a minimum amount of water, and concentrated $HClO_4$ (10 mL) was added.[10] The solution was chilled and the white solid filtered off, washed copiously with ether, and dried over P_2O_5 under vacuum (12 g, 84%). ^1H NMR (δ, Me_2SO-d_6): 3.59, $-CH_2-$; 7.42, 7.64, $-NH_2$; 7.84, NH_3^+. ^{13}C NMR (δ, Me_2SO-d_6): 40.3, $-CH_2-$; 168.0, $CONH_2$.

$[(NH_3)_5CoNCCH_2NH_3](ClO_4)_4$·$H_2O$. $NCCH_2NH_2$·$HClO_4$ (4.0 g) was dissolved in sulfolane (20 mL) with CF_3SO_3H (0.5 mL), and *finally* $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$[24] (3.0 g) was added. The solution was heated in a sealed flask for 3 h at 60 °C. The yellow product was precipitated in ether, taken up in acidified water (pH 4, CH_3COOH), crystallized by adding 6 M $HClO_4$, recrystallized from acidified water with concentrated $NaClO_4$ solution, washed with ethanol and ether, and air-dried (1.0 g, 33%). Infrared spectrum: nitrile stretching frequency 2340 cm^{-1} (shoulder). Visible spectrum (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{473} 67.0, ϵ_{337} 72.0. ^1H NMR (δ, Me_2SO-d_6): 3.37, *trans* NH_3; 3.79, *cis* NH_3; 4.48, $-CH_2-$; 7.90, $-NH_3^+$. ^{13}C NMR (δ, Me_2SO-d_6): 28.7, $-CH_2-$; 126.8, $-C\equiv N$.

$[(NH_3)_5CoNHC(NH_2)CH_2NH_2](ClO_4)_3$·$H_2O$. $[(NH_3)_5CoNCCH_2NH_3](ClO_4)_4$·$H_2O$ (0.30 g) was dissolved in liquid ammonia (30 mL) in an open beaker, and the solvent was allowed to evaporate. The orange residue was dissolved in water and recrystallized with concentrated $NaClO_4$ solution, washed with ethanol and ether, and air-dried (0.17 g, 55%). Visible spectrum (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{481} 84, ϵ_{343} 110. ^1H NMR (δ, Me_2SO-d_6): 3.28, *cis* and *trans* NH_3; 3.30, $-CH_2-$; 5.78, $-NH_2$; 6.80, $-NHC(NH_2)-$. ^{13}C NMR (δ, Me_2SO-d_6): 43.7, $-CH_2-$; 175.2, $-NHC(NH_2)-$.

$[(NH_3)_5CoNHCOCH_2NH_2](ClO_4)_2$·$H_2O$. $[(NH_3)_5CoNCCH_2NH_3](ClO_4)_4$·$H_2O$ (1.0 g) was dissolved in 0.5 M NaOH (50 mL), and the solution was stirred for 1 h and then filtered. The filtrate was chromatographed on Sephadex, and an orange 2+ band was eluted with 0.50 M $NaClO_4$ (pH 8). The amido-*N* complex was crystallized from the eluate after rotary evaporation of most of the solvent and was recrystallized from aqueous Tris with cold concentrated $NaClO_4$ solution, washed with ethanol and ether, and air-dried (0.20 g, 33%). Visible spectrum (0.1 M Tris, M^{-1} cm^{-1}): ϵ_{477} 84.0. ^1H NMR (δ, Me_2SO-d_6): 3.16, *trans* NH_3; 3.24, *cis* NH_3; 3.32, $-CH_2-$; 4.19, $-NHCO-$; 5.68, $-NH_2$. ^{13}C NMR (δ, Me_2SO-d_6): 43.7, $-CH_2-$; 178.5, $-CONH-$.

$[(NH_3)_5CoNHC(OH)CH_2NH_3](ClO_4)_4$·$H_2O$. A concentrated solution of $[(NH_3)_5CoNHCOCH_2NH_2](ClO_4)_2$·$H_2O$ was chilled, and then an equal volume of chilled 6 M $HClO_4$ was added. The solution was kept in freezer for 1 h, after which pale yellow crystals were filtered off, washed with ether, and air-dried. The complex reacts too quickly in aqueous acid to record the visible spectrum accurately and also too quickly in Me_2SO to record the ^{13}C NMR spectrum. ^1H NMR (δ, Me_2SO-d_6): 3.10, *trans* NH_3; 3.18, *cis* NH_3; 3.48, $-CH_2-$; 7.35, $=NH-$; 7.72, $-NH_3^+$.

$[(NH_3)_5CoOC(NH_2)CH_2NH_3](S_2O_6)_2$·$2H_2O$. $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (3.0 g) and $H_2NCOCH_2NH_2$·$HClO_4$ (4.0 g) were stirred in acetone (30 mL) for 1 h. The products were oiled out in ether (250 mL), taken up in acetone, and precipitated again with ether. The red oil was taken up in cold concentrated $Na_2S_2O_6$ solution and the bright pink complex crystallized by rapidly adding methanol. The crude product was filtered off, purified by washing with aqueous edta, which had been half-neutralized with LiOH,[8] ethanol, and ether, and air-dried (0.40 g, 14%). Visible spectrum (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{515} 70, ϵ_{345} 65 (adjusted for aquation during preparation). The complex solvolyzes too quickly to record the ^{13}C NMR spectrum. ^1H NMR (δ, Me_2SO-d_6): 2.72, *trans* NH_3; 4.00, *cis* NH_3; 3.48, $-CH_2-$; 7.88, $-NH_3^+$; 7.89, 9.35, $CONH_2$.

$[(NH_3)_5CoNH_2CH_2CONH_2](ClO_4)_3$·$H_2O$. $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (3.0 g), lutidine (0.5 g), and $H_2NCOCH_2NH_2$·$HClO_4$ (4.0 g) were heated in sulfolane (30 mL) for 1 h at 50 °C. The products were oiled out in ether, taken up in aqueous Tris, and crystallized with $NaClO_4$ solution and ethanol. The pale orange complex was recrystallized from Tris in the same way (0.71 g, 24%). Visible spectrum (M^{-1} cm^{-1}, water): ϵ_{482} 69.5, ϵ_{332} 91.0 (sh). ^1H NMR (δ, Me_2SO-d_6): 3.28, *trans* NH_3; 3.38, *cis* NH_3; 2.93, $-CH_2-$; 4.28, $-NH_2-$; 7.45, 7.62, $CONH_2$. ^{13}C NMR (δ, Me_2SO-d_6): 42.9, $-CH_2-$; 170.0, $-CONH_2$.

$[(NH_3)_5CoOCOCH_2NH_3](ClO_4)_3$·$H_2O$. This complex was prepared from glycine (Ajax, 3.0 g) and the aqua pentaammine complex (3.0 g) in aqueous solution.[18] Small amounts of bright pink byproducts (*cis*- and *trans*-bis(glycinato-*O*) tetraammine complexes) were fractionally crystallized with $NaClO_4$ and filtered off. The filtrate was reduced by rotary evaporation until crystallization commenced, and the pink complex was recrystallized from water with 6 M $HClO_4$. Visible spectrum (0.1 M $HClO_4$, M^{-1} cm^{-1}): ϵ_{500} 68.0, ϵ_{349} 55.0; *cf.* ϵ_{500} 69.2, ϵ_{342} 55.0.[18] ^1H NMR (δ, Me_2SO-d_6): 2.61, *trans* NH_3; 3.68, *cis* NH_3; 3.25, $-CH_2-$; 7.54, $-NH_3^+$. ^{13}C NMR (δ, Me_2SO-d_6): 41.5, $-CH_2-$; 174.8, $-COO$.

Kinetic Studies. Pseudo-first order rate constants were obtained by measuring the changes in absorbance over time of solutions formed by dissolving samples of the solid complex in solvent pre-equilibrated at 25.0 ± 0.05 °C. In acid hydrolysis studies, the solvent was 0.1 M $HClO_4$ and the reactions were monitored at 510 nm. The rate of base hydrolysis was studied at 290 nm in buffer solutions made up respectively from triethanolamine, diethanolamine, and ethanolamine which had been partially neutralized with $HClO_4$, using $NaClO_4$·H_2O as the supporting electrolyte (I = 1.00 M) (see supplementary material). The pH of the buffer solutions was determined as previously described.[25]

The changes in the visible spectrum during the solvolysis of the glycinamide-*O* complex in acidified Me_2SO were monitored over the wavelength range 600–350 nm, and an isosbestic point was identified at 556 nm. The kinetics of the amide N to O rearrangement of the amide-*N* complex were measured at this wavelength by directly dissolving samples of that complex in preequilibrated (25 °C) Me_2SO which was 0.50 or 1.0 M in triflic acid and then measuring the absorbance changes over time.

Product Analyses. For acid hydrolysis, the complex (~0.5 g) was dissolved in 0.10 M $HClO_4$, and the solution was stored in a sealed container at 22 °C overnight, after which it was diluted with distilled water and chromatographed on Sephadex. The white background of this resin allows small amounts of complexes to be easily seen. The resin was eluted first with 0.5 M $NaClO_4$ (pH 5, NaH_2PO_4) to remove any 2^+ ions which may have been present (none were found) and finally with 0.75 M NaCl (pH 7, NaH_2PO_4/Na_2HPO_4) which removes the aquapentaammine complex. The volumes of the eluates were measured with "A" grade measuring cylinders, and the concentrations were determined spectrophotometrically using 10-cm quartz cells (ϵ_{492} 50.5 M^{-1} cm^{-1} [26]).

For base hydrolysis, pH >9, the complex (~0.5 g, accurately weighed) was dissolved in 0.10 M NaOH/1.00 M $NaClO_4$ solution (50 mL, 22 °C). After 15 min, the solution was acidified with 6 M $HClO_4$, and the resulting solution, diluted with distilled water, was chromatographed on Sephadex resin; the columns were eluted as above. Under these conditions, any glycinato complex formed by ligand hydrolysis will not be significantly decomposed during the experiment. Attempts to measure the rate of base hydrolysis of the glycinato pentaammine complex were foiled by decomposition of the complex, but in the time comparable to that allowed for the amide hydrolysis experiment, no significant change in the absorbance of the glycinato complex solution was observed. The concentration of the product was determined as above.

For the reactions in dilute base, $[(NH_3)_5CoOCNH_2CH_2NH_3](S_2O_6)_2$·$2H_2O$ (0.5 g) was added to 0.1 M Tris (50 mL) at 2 °C and the initial suspension was left to stir for 3 days at that temperature in a sealed flask. The products, diluted with water (2 L), were chromatographed on Sephadex. The resin was eluted with 0.5 M $NaClO_4$ (pH 10), which removed the hydroxo complex, and then with 1.0 M $NaClO_4$ (pH 3), which removed an orange 3+ ion, leaving only cobalt oxides on the column and a trace of the hexaammine complex. Eluting after the hydroxo

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complex was a trace of a red cation, dipositive at pH 10 and tripositive at pH 3. The second eluate was taken to dryness by rotary evaporation of the solvent, and an orange complex was isolated by washing the residue with ethanol to remove the excess $NaClO_4$. The complex was recrystallized from water with concentrated $NaClO_4$ solution and its NMR spectra recorded.

For the reactions at near-neutral pH, $[(NH_3)_5CoOCNH_2CH_2NH_3](S_2O_6)_2 \cdot 2H_2O$ (0.5 g) was dissolved in morpholinoethanesulfonate buffer, $I = 1.00$ M ($NaClO_4$), 25 °C; after the reaction was complete, the products were diluted with water and the resulting solutions was chromatographed on Sephadex. The column was eluted with 1.0 M NaCl (pH 7 phosphate buffer), and the amounts of aquapentaammine (ϵ_{492} 50.5 M^{-1} cm^{-1}) and amine-bonded glycinamide complexes (ϵ_{482} 69.5 M^{-1} cm^{-1}) were determined spectrophotometrically as described above.

Acknowledgment. We gratefully acknowledge the ANU Microanalytical Service for elemental analyses. This work was supported by the Australian Research Council.

Supplementary Material Available: Tables of kinetic and spectrophotometric data (1 page). Ordering information is given on any current masthead page.