The inverse $[H^+]$ dependence for Co^{3+} undoubtedly signals $(H_2O)_5CoOH^{2+}$ to be the kinetically active form. This *might*, as suggested earlier, be because the labilizing effect of coordinated OH^- accelerates the rate of alcohol penetration of the coordination sphere of the low-spin d^6 Co(III) complex. On the other hand, it might instead imply a more definite chemical role of the OH group in the mechanism, possibly through a hydrogen atom transfer mechanism. Such a possibility is then, by the microscopic reversibility, the effective reverse of one of the mechanisms suggested for $V(H_2O)_6^{2+}$ (eq 10). It further suggests that there may be differences between the mechanisms for Co^{3+} and Mn^{3+} that should not be overlooked.

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Registry No. $V(H_2O)_6^{2+}$, 15696-18-1; $\cdot C(CH_3)_2OH$, 7277-18-1; $\cdot CH(CH_3)OEt$, 2229-06-3; deuterium, 7782-39-0.

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Isomeric Forms of the Complexes of Tetraammineruthenium(III) and -(II) with Glycinamide and Derivatives

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When *cis*-diaquopentaammineruthenium(III) at a pH such that one of the coordinated water molecules is deprotonated reacts with any of the three amides featured in this work, glycylglycine, glycinamide, and *N'*-ethylglycinamide, in the resulting tetraammine the chelate ring closes on the nitrogen of the amide group (the (N,N') form). The uncatalyzed transformation of these chelates to the (N,O) forms is extremely slow, but the latter can be produced by reducing ruthenium to the 2+ state in acidic solution and reoxidizing. The two forms are distinguished by the differences in pK_a—these are ~ -1 and 5.0 ± 0.2, respectively, for the (N,N') and (N,O) forms of the glycinamide chelates—and by the differences in the ligand to metal charge-transfer absorptions, which at a pH of 1 lie at much lower energies for the (N,N') chelates. By taking advantage of the lability of the Ru(II) chelates and the labilization of the Ru(III) species by Ru(II), and by applying electrochemical and other equilibrium measurements, it has been possible to measure the equilibrium quotients governing the distribution of the species between the (N,N') and (N,O) forms. For glycinamide as the ligand, the equilibrium ratio $Ru^{II}(N,N')/Ru^{II}(N,O)$ at 25 °C when both species are protonated is 1.6×10^{-4}, but as the pH is raised, the (N,N') chelate becomes stable relative to the (N,O) because it is the more acidic ($pK_{a(N,N')}^{II} = 4.3 \pm 0.2$). For the same ligand, the equilibrium ratio $[Ru^{III}(N,O)]/[Ru^{III}(N,N')][H^+]$ is 16. As the pH is raised, the (N,N') chelate becomes more stable: $Ru^{III}(N,O)/Ru^{III}(N,N')$ when both species are deprotonated is 1.6×10^{-5}. Kinetic studies on substitution in $Ru^{II}(N,O)$ in acidic solution indicate that the chelate ring is in fact closed. The (N,N') form in acidic solution is short-lived: $t_{1/2}$ for transformation to the (N,O) form is ~ 0.2 s.

Studies with the substitution-inert center Co(III) have contributed much to improve our understanding of the way in which amino acids and related more complex biological molecules interact with metal ions.[1] The advantages of working with substitution-inert rather than labile centers are as follows: (a) the site and mode of binding of the ligand to the metal ion can be determined with greater certainty (if necessary a determination of the crystal structure can be made, and in most instances the structure is preserved in passing from the solution to the solid phase); (b) where there is a multistep interaction, the intermediate states can be characterized with much greater ease and confidence.

Little systematic work has been done with other substitution-inert centers which favor coordination number 6. A beginning has been made with Ru(III), and even the small amount of work that has been done suffices to show that the behavior of the Ru(III) complexes can be strikingly different from those of Co(III). Whereas (ethylglycinato)pentaamminecobalt(III) in acidic solution at room temperature changes little over a period of 1 month, the corresponding ruthenium(III) complex undergoes a facile linkage isomerization from the N- to the O-bound form, followed by the parallel processes of hydrolysis and aquation.[2] A similar linkage isomerization was first reported for N-bound pentaammine(glycine)ruthenium(III).[3a]

Differences such as those noted alone justify the extension of studies of the kind done with Co(III) to Ru(III). The ruthenium systems offer an additional opportunity that is not available for Co(III). The complexes of Ru(II) are readily obtained from those of Ru(III) by reduction, and the Ru(II) complexes are also substitution inert. The preferred interaction of Ru(II) with the ligand can be quite different from that of Ru(III)—this difference has in fact been exploited in a system studied earlier[3b]—and thus the interaction of ligand and metal center can be controlled by simple electron transfer. We have taken advantage of this particular feature of the ruthenium ammine system in the studies we have performed on the interaction of the tetraammines with glycinamide, *N'*-ethylglycinamide, and glycylglycine and which are described herein. For each oxidation state the ligands are bound as chelates by the amino nitrogen, the ring being closed either by the amide nitrogen (the (N,N') form) or the carbonyl oxygen ((N,O) form). The special properties of the ruthenium system have made it possible to evaluate the standard free energy difference between the two isomeric forms for each oxidation state. To our knowledge, this energy difference has not been determined for any other metal ion.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared by the method of Vogt et al.[4] and was purified by recrystallization from 0.1 M HCl. *cis*-Diaquotetraammine-

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(2) Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4725.
(3) (a) Diamond, S. E.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5921. (b) Diamond, S. E.; Taube, H. *J. Chem. Soc., Chem. Commun.* **1974**, 622.
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0020-1669/83/1322-1655$01.50/0

ruthenium(III) trifluoromethanesulfonate was prepared from chloropentaammineruthenium(III) chloride, converting it to the cis-oxalate complex and dissolving this in 6 M trifluoromethanesulfonic acid, as described by Diamond.[5]

Glycine ethyl ester hydrochloride and glycinamide hydrochloride (Aldrich Chemical Co.) and glycylglycine (Vega) were used without further purification.

N'-Ethylglycinamide hydrochloride was prepared by treating 8 g of *N*-carbobenzoxyglycine *p*-nitrophenyl ester (Sigma Chemical Co.) with 20 mL of 70% aqueous solution of ethylamine at room temperature for 3 hr.[6] The crystals of *N*-(carbobenzoxy)-*N'*-ethylglycinamide were washed thoroughly with ether and suspended in 20 mL of concentrated HCl.[7] The suspension was warmed to 55–60 °C on a water bath for 45 min, which produced an almost clear solution with floating oil drops. The solution was then cooled and diluted with 130 mL of water, and the benzylic products were extracted with ether. The aqueous phase was evaporated almost to dryness, and crystallization of white crystals of the final product was effected by rubbing in ethanol. Anal. Calcd: C, 34.66; N, 20.22; H, 7.94. Found: C, 34.55; N, 19.83; H, 7.83. 4-Cyanopyridine (4-CNpy, Aldrich Chemical Co.) was purified by recrystallization from ethanol, the solution having been treated with decolorizing carbon.

All other chemicals were reagent grade and were used as received.

Deionized water purified by a Barnstead Nanopure ultrafiltration system was used throughout.

Preparation of Complexes. The ruthenium amide complexes described have not been prepared heretofore; in naming them, we anticipate conclusions that are reached on the basis of evidence introduced later in the paper.

(Glycylglycine-*N,N'*)tetraammineruthenium(III) diamminetetrakis(thiocyanato)chromate(III) was prepared by one of the following methods: (1) *cis*-Tetraamminediaquoruthenium(III) trifluoromethanesulfonate (200 mg) was dissolved in 4 mL of argon-saturated water, 400 mg of glycylglycine was added, and the pH was raised to about 8.2 with 4 M NaOH. The solution, which was continuously bubbled with argon, was warmed on a water bath to 40–45 °C for 1 h; it was then cooled to room temperature and the pH adjusted to ~6 with 99% CF_3COOH. Two milliliters of a saturated solution of $NH_4[Cr(NH_3)_2(SCN)_4]$ was added, and the solution was cooled with ice. The orange-brown precipitate was filtered and washed with ethanol and ether. The yield was 55 mg (29%). Anal. Calcd: C, 15.56; N, 27.23; H, 3.89. Found: C, 15.48; N, 25.71; H, 3.81. (2) The former method was modified by adding a piece of zinc amalgam to the solution at pH 8.2 and room temperature and removing it after 1 min and then bubbling argon at room temperature for about 1 h. The yield was 80 mg (42%).

The chelate complex, which is monopositive at pH 6, did not precipitate with any of the common anions; of those tried only Reinecke's anion, $[Cr(NH_3)_2(SCN)_4]^-$, yielded a precipitate, and at that, it was much less effective at lower pH, where the cation has a 2+ charge.

(Glycinamide-*N,N'*)tetraammineruthenium(III) hexafluorophosphate and (*N'*-ethylglycinamide-*N,N'*)tetraammineruthenium(III) hexafluorophosphate were prepared by much the same methods as for the complex described above. To avoid the formation of chloro complexes, the chloride ion introduced as ligand hydrochlorides was removed with use of a freshly prepared solution of silver trifluoroacetate. The ruthenium complexes were precipitated by adding a saturated solution of NH_4PF_6, to form $[(NH_3)_4RuNH_2CH_2CONH](PF_6)_2$ (yellow crystals) in 48% yield (Anal. Calcd: C, 4.51; N, 15.79; H, 3.20. Found: C, 4.63; N, 14.61; H, 3.23) or $[(NH_3)_4RuNH_2CH_2CONCH_2CH_3](PF_6)_2$ (orange crystals) in 37% yield (Anal. Calcd: C, 8.57; N, 15.00; H, 3.75. Found: C, 8.79; N, 14.67; H, 3.76).

(Glycinamide-*N,O*)- and (*N'*-ethylglycinamide-*N,O*)tetraammineruthenium(II) hexafluorophosphates were prepared by reducing solutions of the N,N'-bound chelates, which were prepared as described, by reaction with zinc amalgam in a Zwickel flask,[8] under argon, for about 20 min at pH ~1 (CF_3COOH). The solutions were then transferred to a bubbling flask containing 1.7 g of NH_4PF_6, with argon under pressure, and cooled in an ice bath for about 30 min with continued bubbling of argon. The precipitates that formed were yellow. They were filtered, washed with ethanol and ether, and kept in a vacuum desiccator to avoid oxidation (50% yield). Anal. Calcd for the glycinamide chelate: C, 4.50; N, 15.76; H, 3.38. Found: C, 4.65; N, 15.03; H, 3.35. Calcd for the *N'*-ethylglycinamide chelate: C, 8.56; N, 14.97; H, 3.92. Found: C, 8.69; N, 14.65; H, 3.77.

(Glycylglycine-*N,O*)tetraammineruthenium(II) was prepared by the same method and was precipitated by transferring the reaction mixture into 1 mL of a saturated solution of $NH_4[Cr(NH_3)_2(SCN)_4]$, saturated with argon. A purple precipitate of $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH][Cr(NH_3)_2(SCN)_4]_2$ forms: this was filtered and washed with ethanol and ether. The yield was 35%. Anal. Calcd: C, 15.37; N, 26.89; H, 3.42. Found: C, 15.13; N, 24.54; H, 3.44.

Tetraammine(glycinato)ruthenium(III) hexafluorophosphate was prepared by the method used for the other Ru(III) complexes. To avoid the high pH required to deprotonate the ammine nitrogen of the ligand (pK_a = 9.6 for glycinate[9]), the ethyl ester (pK_a = 7.7[9]) was used. The ester undergoes rapid hydrolysis when bound to the ruthenium(III) tetraammine complex, and the final product is the glycinate chelate. The yield was 35%. Anal. Calcd for $[(NH_3)_4RuNH_2CH_2COO](PF_6)_2 \cdot {}^1/_2H_2O$: C, 4.43; N, 12.92; H, 3.14. Found: C, 4.47; N, 12.97; H, 3.14.

Analytical Methods. Visible and UV spectra were measured on a Beckman Acta MVII recording spectrophotometer; the pH was measured with a Brinkman Instruments pH-101 Metrohm digital pH meter. The microanalyses were performed by the Stanford Microanalytical Laboratory.

Electrochemical Measurements. Cyclovoltammograms were recorded with a PAR Model 173 potentiostat, a Model 175 universal programmer system, and either an Omnigraph 2000 X-Y recorder or a Tektronix 5103N oscilloscope. Normal pulse voltammetry measurements were performed with a PAR Model 174A polarographic analyzer and a Hewlett-Packard Model 7045A X-Y recorder.

The electrochemical cell was of the conventional two-compartment design, in which the reference electrode was isolated from the test solution by means of a glass frit. A carbon-paste working electrode, platinum wire auxiliary electrode, and saturated calomel reference electrode were used. All experiments were performed in argon-saturated solutions. The concentrations of complexes were $(1–2) \times 10^{-3}$ M, and the ionic strength was kept at 0.1–0.2 (CF_3COOH + CF_3COONa, $HClO_4$ + $LiClO_4$, phosphate buffer, or tris(hydroxymethyl)aminomethane–HCl buffer).

Potentials were converted to the normal hydrogen electrode scale by adding 240 mV.

Reduction of Complexes. Solutions of the oxidized complexes were prepared in a Zwickel reaction flask and were reduced with a 5–10% excess of freshly prepared Eu^{2+} solution (prepared by reducing a 1×10^{-3} M Eu_2O_3 solution in 0.15 M CF_3COOH or CF_3SO_3H, over zinc amalgam under argon, for at least 20 min). The Eu^{2+} solution was transferred by a syringe. Spectra of these solutions were measured by transferring part of the solution into a spectrophotometer cell attached to the Zwickel flask by an adaptor[10] with use of a positive argon pressure.

Kinetic Measurements. Kinetics were followed spectrophotometrically. The temperature was kept at 25 ± 0.5 °C by a Haake FK2 temperature bath.

For the investigation of rates of substitution on Ru(II), solutions of the reduced complexes were prepared as described and transferred to a second Zwickel flask containing the 4-$CNpyH^+$ solution with CF_3CO_2H at equal concentration by argon under pressure. After a few seconds of bubbling argon into the mixture, part of the solution was transferred to a spectrophotometer cell as described. The reactions were monitored at a wavelength in the 520–575-nm range, the choice depending on the concentration of the complex. The final pH of the solution was 1.3.

The reactions with mixtures of acetonitrile and 4-$CNpyH^+$ were designed to be rapid, and they were too rapid to be followed in the same manner. They were followed on a Cary 15 spectrophotometer, using a rapid-mixing device.[11] This consisted of a small, hand-operated Teflon stopped-flow mixer, which introduced the solution into a Helma

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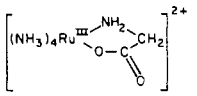
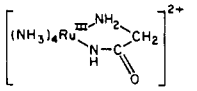
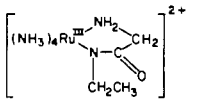
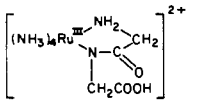
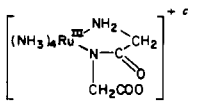
(7) White, J. *J. Biol. Chem.* **1934**, *106*, 141.
(8) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.
(9) Hay, R. W.; Morris, P. J. *Met. Ions Biol. Syst.* **1976**, *5*, 173.
(10) Armor, J. N. Ph.D. Thesis, Stanford University, 1970.
(11) This was supplied by courtesy of Prof. A. M. Sargeson of the Australian National University, Canberra, Australia.

Table I. Spectral Features of Tetraammineruthenium(III) Chelates of Glycine and of N,N′-Bound Glycinamide Derivatives[a]

complex	λ_{max} (ϵ)[b]
	288 (1.9 × 10³), 215 (sh)
	360 (3.9 × 10³), 252 (1.8 × 10³)
	406 (3.8 × 10³), 263 (1.5 × 10³)
	387 (3.7 × 10³), 255 (1.6 × 10³)
	407 (3.6 × 10³), 261 (1.8 × 10³)

[a] At 25 °C in 0.1 M $HClO_4$. [b] In nm and M^{-1} cm^{-1}, respectively; ±5% uncertainty in the extinction coefficient. [c] At pH 8.3; pK_a for carboxylate deprotonation 3.2.

quartz flow-through cell (1.00 cm) via two Teflon syringes (delivery volume 5 mL each). The reservoirs, syringes, cell, and mixing chamber were maintained at 25 °C. The Ru^{III} glycylglycine-*N,O* chelate was reduced over zinc amalgam for ~30 min under argon and was mixed with an argon-saturated solution of acetonitrile and 4-CNpyH$^+$ in trifluoromethanesulfonic acid. The final pH was 1.4; the concentration of 4-CNpyH$^+$ was in the range 0.15–0.3 M and that of CH_3CN in the range 0.5–2 M. The kinetics were followed at 520–570 nm, where the complex of Ru(II) with 4-CNpyH$^+$ absorbs strongly.

The pseudo-first-order rate constants (entering ligand in excess) were obtained from the slopes of the linear least-squares fits of log $(A_\infty - A_t)$ vs. time plots.

Kinetics of the Ru(II)-catalyzed transformation from the N,O-bound to the N,N′-bound chelates were followed by transferring some of the partially reduced solution from the Zwickel flask to the spectrophotometer cell, as described. Plots of $\Delta t/\Delta A$ vs. $1/(A_\infty - A_t)$ yielded straight lines.

Results

UV–Visible Spectra. The salient features of the spectra of tetraammine(glycinato)ruthenium(III), where only the N,O-bound form is in question, and of the N,N′-bound amide chelates are summarized in Table I. For the glycinato complex, a peak at 290 nm (ϵ = 1.8 × 10³ M^{-1} cm^{-1}) has been reported,[5] while for the O-bound pentaammineglycinate complex there are recorded the features λ_{max} = 288 nm (ϵ = 1.46 × 10³ M^{-1} cm^{-1})[2] and λ_{max} = 288 nm (ϵ = 1.43 × 10³ M^{-1} cm^{-1}).[3] These values are similar to those found for other carboxylate complexes of pentaammineruthenium(III).[12] The spectra of the N,N′-bound chelates of the glycinamide derivatives are similar both in maxima and in intensities to the spectra of N-bound amido complexes of pentaammineruthenium(III) (Table II).[13,14] It is partly on the basis of the spectrophotometric evidence cited that we believe that where we designate the tetraammineruthenium(III) complexes as (N,N′) on the one hand, or (N,O) on the other, we have made the correct assignment. These conclusions are amply borne out by other evidence, to be introduced in due course.

The band maximum for the glycylglycine chelate shifts to lower energy as the pH is increased; a pK_a of 3.2 ± 0.2 is indicated, which we attribute to the carboxylate group.

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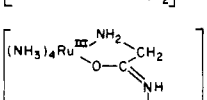
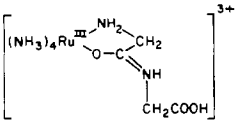
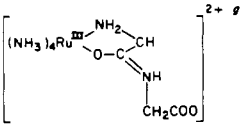
Table II. Spectral Features and pK_a's of Amido Nitrogen Bound Pentaammineruthenium(III) Complexes

complex	λ_{max}[a]	$10^{-3}\epsilon$[b]	pK_a	ref
$[(NH_3)_5Ru^{III}NHCOCH_3]^{2+}$	283	3.46	2.00	13
	249	2.31		
$[(NH_3)_5Ru^{III}NH_2COCH_3]^{3+}$	322	1.55		13
$[(NH_3)_5Ru^{III}NHCOC_6H_5]^{2+}$	393	4.08	0.90	13
	314	3.68		
	270	2.68 (sh)		
	219	9.45		
$[(NH_3)_5Ru^{III}NH_2COC_6H_5]^{3+}$	385	1.47		13
	320	3.45		
	270	3.78 (sh)		
	228	9.40		
$[(NH_3)_5Ru^{III}NHSO_3]^{+}$	398	4.15	2.6	14
$[(NH_3)_5Ru^{III}NH_2SO_3]^{2+}$	280	5.1		14

[a] In nm. [b] In M^{-1} cm^{-1}.

Table III. Spectral Features and pK_a's of the Tetraammineruthenium(III) (N,O) Chelates of Glycinamide Derivatives[a]

complex	λ_{max} ($10^{-3}\epsilon$)[b,c]	λ_{max} ($10^{-3}\epsilon$)[b,d]	pK_a[e]
	296 (1.5), 229 (2.3)	302 (1.9)	5.0 ± 0.2
	317 (1.4),	304 (1.9)	6.2 ± 0.1
	306 (1.1), 225 (sh)		(2.2 ± 0.2)[f]
	316 (1.0), 225 (sh)	300 (1.8)	6.2 ± 0.2

[a] N,N′-bound chelates were dissolved in 0.1 M CF_3COOH, reduced by Eu^{2+}, and oxidized by $Na_2S_2O_8$; The final pH was 1.1–1.3. [b] In nm (M^{-1} cm^{-1} ±5% uncertainty in extinction coefficient). [c] Protonated amide, pH ~1.2. [d] Deprotonated amide, pH 7.8. [e] For protonation of the amido group. [f] For protonation of the carboxylate. [g] pH 3.6.

The spectra of the (N,N′) chelates are unchanged on increasing the acidity to 2 M $HClO_4$. At still higher concentrations of perchloric acid, spectral changes are evident—the peaks shift to higher energies and decrease in intensity, and these shifts are reversible upon increasing the pH. The changes are only partial in 4 M $HClO_4$ but are virtually complete in 10 M $HClO_4$ (λ_{max} = 340 nm), and thus a value of p$K_a \approx -1$ is indicated. Table II shows that the absorption peaks of pentaammineruthenium(III) amido complexes also shift to higher energy and decrease in intensity upon protonation of the amido group.[13,14]

The spectra of the (N,N′) amido complexes were quite stable over a period of 2–3 weeks, only 5–10% of the absorption being lost after the solutions were kept at room temperature in 0.1 M $HClO_4$.

Reactions Following Changes in Oxidation State. Upon reduction with a 5–10% excess of Eu^{2+} solution at pH 1–1.5, the solutions of the complexes showed a broad band around 300 nm. The reduced glycinato complex showed a broad band with a peak at 275 nm. These spectra were unchanged after 12 h.

When the solutions of the reduced amido complexes were reoxidized with a slight excess (5–10% over Eu^{2+}) of $Na_2S_2O_8$

solution, the original spectra of the oxidized complexes were not regained. Instead, new spectra were observed with maxima in the 295–320-nm region, as shown in Table III. An upper limit of 0.5% can be set for the amount of the absorption that can be attributed to the original (N,N′) chelates. The spectra of the reoxidized glycinamide and *N*′-ethylglycinamide chelates change upon increasing the pH above 4, and peaks with higher intensities are formed at 302 nm and at 304 nm. The changes are governed by pK_a values of 5.0 ± 0.2 and 6.2 ± 0.2, respectively (Table III). In the case of the glycylglycine complex, two pK_a's are observed: 2.2 ± 0.2 and 6.2 ± 0.2 (Table III).

We infer that the complexes formed by a cycle of full reduction followed by full oxidation of the (N,N′) chelates are the (N,O) forms in which the ligands are bound by the amine nitrogen and the carbonyl oxygen. On this basis, the pK_a's at 5.0 and 6.2 are assigned to the amido nitrogens and that of 2.2 in the glycylglycine chelate is assigned to the carboxylate group.

The absorptions of the (N,O) chelates of glycinamide and glycylglycine at pH 1.0 changed over a period of a few days to give a final spectrum similar to that of the tetraammine-diaquoruthenium(III) ion. This change was much smaller for the (N,O) form of the *N*′-ethylglycinamide complex, where about 90% of the original absorption was left after 3 weeks in 0.1 M CF_3COOH.

Kinetics after Partial Reduction of the N,O-Bound Chelates. When Ru(II) is present in deaerated acidic (pH 1.2–1.9) solutions of the Ru(III) (N,O) chelates of glycylglycine and glycinamide, the (N,N′) chelates are formed within a few minutes. Under similar conditions the (N,N′) Ru(III) *N*′-ethylglycinamide chelate is not produced in significant amount (<3%) from the (N,O) form, but at higher pH (6.8, 0.05 M phosphate buffer), the (N,N′) chelate spectrum appears in a few minutes, and it accounts for an almost quantitative transformation of the Ru(III) (N,O) chelate to the Ru(III) (N,N′) chelate.

In an appropriate pH range, equilibrium between the (N,N′) deprotonated and the (N,O) protonated chelates of Ru(III) can be measured directly with Ru(II) as catalyst. This was done for the glycinamide complex by partially reducing solutions of the (N,N′) deprotonated chelate with Eu^{2+} solutions under argon, in the acidity range of 0.2–1.0 M (HTFMS). The ratio of the (N,N′) deprotonated species to the (N,O) protonated species at equilibrium was calculated from the final spectra, and from this ratio and the known H^+ concentration, the equilibrium quotient for the reaction of H^+ with deprotonated (N,N′) to form protonated (N,O) was calculated as 8 ± 2 (mean of four measurements).

Some experiments on the kinetics of the isomerization were done, enough to settle some issues, but the study is incomplete. It is difficult to fix the concentration of Ru(II) accurately by the preparative method we adopted, which was to produce Ru^{III}(N,O) from the Ru(II) state by adding a known excess of $S_2O_8^{2-}$ and then initiate the reaction by adding a known amount of Eu^{2+}. Apart from this, there is the additional problem that, following the rather rapid major change, there is a slow unexplained change in the absorption, which made it difficult to fix the "final" absorbance appropriate to the first stage. It is unlikely that the slow following reaction is intrinsic to the system, and we ascribe it to trace impurities in the original preparation of the ruthenium chelate.

The reactions were carried out in acidic solution (pH 1.7–1.9) at a wavelength chosen in the 400–425-nm range according to the concentration of Ru(III). First-order plots showed curvature, the slope increasing with time. This change is intrinsic and is not simply a result of the slow following reaction referred to above. A plot of $\Delta t/\Delta A$ vs. $1/(A_\infty - A_t)$, where ΔA is the absorption change in a time interval Δt, A_t is the absorption at the beginning of Δt, and A_∞ is the "final" absorption, is shown in Figure 1. The straight line is the linear least-squares fit to the experimental points. Similar plots were obtained for the other experiments, the results (slopes and intercepts) of which are summarized in Table IV.

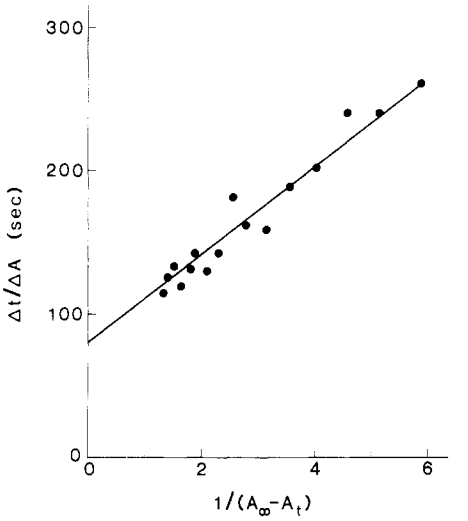


Figure 1. $\Delta t/\Delta A$ vs. $1/(A_\infty - A_t)$, after partial reduction of the glycylglycine-*N,O* chelate by Eu^{2+} ([Ru(II)] = 1.6 × 10^{-4} M, pH 1.75, 25.5 °C).

Table IV. Kinetic Results for the Isomerization of the (N,O) Glycylglycine Chelate to the (N,N′) Chelate in the Presence of Ru(II)[a]

[Ru(II)], M	pH	slope, s	intercept, s	k_4, M^{-1} s^{-1}	k_1, s^{-1}	k_{-1},[b] s^{-1}
7.3×10^{-5}	1.9	260	57.0	8.4×10^4	0.17	280
1.6×10^{-4}	1.75	25.3	85.1	4.2×10^5	0.049	82
1.7×10^{-4}	1.8	24.7	63.8	4.0×10^5	0.042	70
2.3×10^{-4}	1.65	32.1	50.5	2.3×10^5	0.057	95

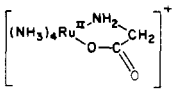
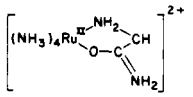
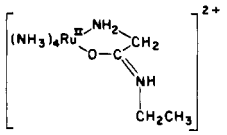
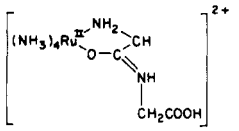
[a] Derived from Figure 1 and similar plots. [b] Calculated by using k_1 and $K_1 = 6 \times 10^{-4}$.

Substitution in the Ru(II) Chelates by CH_3CN and 4-CNpyH$^+$. The rate of reaction of 4-CNpyH$^+$ with [Ru$(NH_3)_5H_2O]^{2+}$ was measured by Allen and Ford,[15] and k was found to be 0.23 M^{-1} s^{-1} in 1.0 M ionic strength. Our experiments were performed in lower ionic strength, 0.1–0.3 M, and it was necessary to determine the rate of the reaction under our experimental conditions. [Ru$(NH_3)_5Cl]Cl_2$ was dissolved in 0.1 M CF_3COOH and reduced as described. The reaction with 4-CNpyH$^+$ was followed at 515 nm in a 0.1 M solution of 4-CNpy at pH 1.3, and the second-order rate constant was determined as 0.11 ± 0.01 M^{-1} s^{-1}. The pK_a of 4-CNpyH$^+$ is 1.90,[16] and at a pH of 1.3, 20% of the 4-cyanopyridine is deprotonated. The neutral ligand reacts with [Ru$(NH_3)_5H_2O]^{2+}$ at a rate similar to that of the protonated form (k = 0.26 M^{-1} s^{-1})[15] in 50% aqueous methanol. The rate for the neutral ligand is expected to be independent of ionic strength, and if we assume that the rate for it in the mixed solvent is that in aqueous solution, the specific rate of the reaction of 4-CNpyH$^+$ with [Ru$(NH_3)_5H_2O]^{2+}$ under our experimental conditions is calculated as 0.073 ± 0.01 M^{-1} s^{-1}. This rate is about one-third that at 1 M ionic strength, in accord with both reactants being positively charged.

The absorption spectrum that we measured for the (4-cyanopyridinium)pentaammineruthenium(II) ion under our experimental conditions (0.1 M CF_3COOH, 0.1 M total 4-CNpy concentration) has a peak at 527 nm with an extinction

(15) Allen, R. J.; Ford, P. C. *Inorg. Chem.* **1972**, *11*, 679.
(16) Clarke, R. E.; Ford, P. C. *inorg. Chem.* **1970**, *9*, 495.

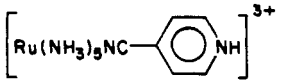
Table V. Second-Order Rate Constants for the Reaction of 4-Cyanopyridine with Tetraammineruthenium(II) Chelates of Glycine and Glycinamide Derivatives and Absorption Maxima of the Products of This Reaction[a]

complex	10^3k,[b] M^{-1} s^{-1}	λ_{max}, nm
	48 ± 4 1.8 ± 0.2[c]	521 421, 515 (sh)[c]
	9.8 ± 0.5	523
	10 ± 0.5	524
	20 ± 2	521

[a] Conditions: 25 °C, pH 1.3, μ = 0.1–0.3. [b] For $(NH_3)_5RuH_2O^{2+}$, $k = (110 \pm 10) \times 10^{-3}$ M^{-1} s^{-1} and λ_{max} = 527 nm. [c] pH 3.6.

coefficient of 1.4×10^4 M^{-1} cm^{-1}, as compared to λ_{max} = 532 nm and $\epsilon = 8.2 \times 10^3$ in 1 M HCl, as reported by Clarke and Ford.[16] Kuehn and Taube[8] reported λ_{max} = 530 nm and $\epsilon = 1.63 \times 10^4$ at 0.1 M HCl, values that are close to ours.

The second-order rate constants, $k_{4\text{-CNpyH}^+}$, for the reaction of the Ru(II) chelates with 4-cyanopyridine, at pH 1.3 (calculated by dividing the observed pseudo-first-order rate constants by the overall concentration of 4-cyanopyridine ([4-CNpy] + [4-CNpyH$^+$]) are presented in Table V. They were found to be independent of ligand concentration over a fourfold range. The rates are 5–10 times slower than the rate of reaction of $[Ru(NH_3)_5H_2O]^{2+}$ under similar conditions. The absorption maxima (Table V) of the tetraammine products are slightly different from that of



The rate of reaction of 4-CNpyH$^+$ with the glycinato chelate is slower than its rate with $[Ru(NH_3)_5H_2O]^{2+}$ by only a factor of 2 at pH 1.2 but becomes much slower at pH 3.6 (Table V). The pK_a of 4-CNpyH$^+$ bound to ruthenium(II) pentaaamine is 2.72,[16] and on deprotonation the absorption maximum shifts to 425 nm. Our reaction product at pH 3.6 has a maximum at 421, and a shoulder around 515 nm, which corresponds to the small amount of the protonated complex (~11%) still left at this pH.

In an effort to detect rate saturation at high ligand concentration, we resorted to using a mixture of 4-CNpyH$^+$ and CH_3CN. The mixed-ligand system makes it possible to increase the rate of substitution in $Ru^{II}(N,O)$ without increasing the ionic strength, simply by increasing the concentration of CH_3CN. The reaction was monitored by following the formation of the 4-CNpyH$^+$ complex. The results are summarized in Table VI. The observed specific rate is the sum $k_{CH_3CN}[CH_3CN] + k_{4\text{-CNpyH}^+}$[4-CNpyH$^+$]. Since the concentrations of both ligands and the rate of reaction of 4-CNpyH$^+$ with $Ru^{II}(N,O)$ are known, the rate of reaction with CH_3CN can be calculated (see Table VI). No evidence of rate saturation is found; the specific rate for CH_3CN reacting with the glycylglycine chelate is 10-fold less than for its reaction with $[Ru^{II}(NH_3)_5H_2O]^{2+}$ [17] and is similar to the rate of 4-CNpyH$^+$ with the Ru(II) chelate of glycylglycine.

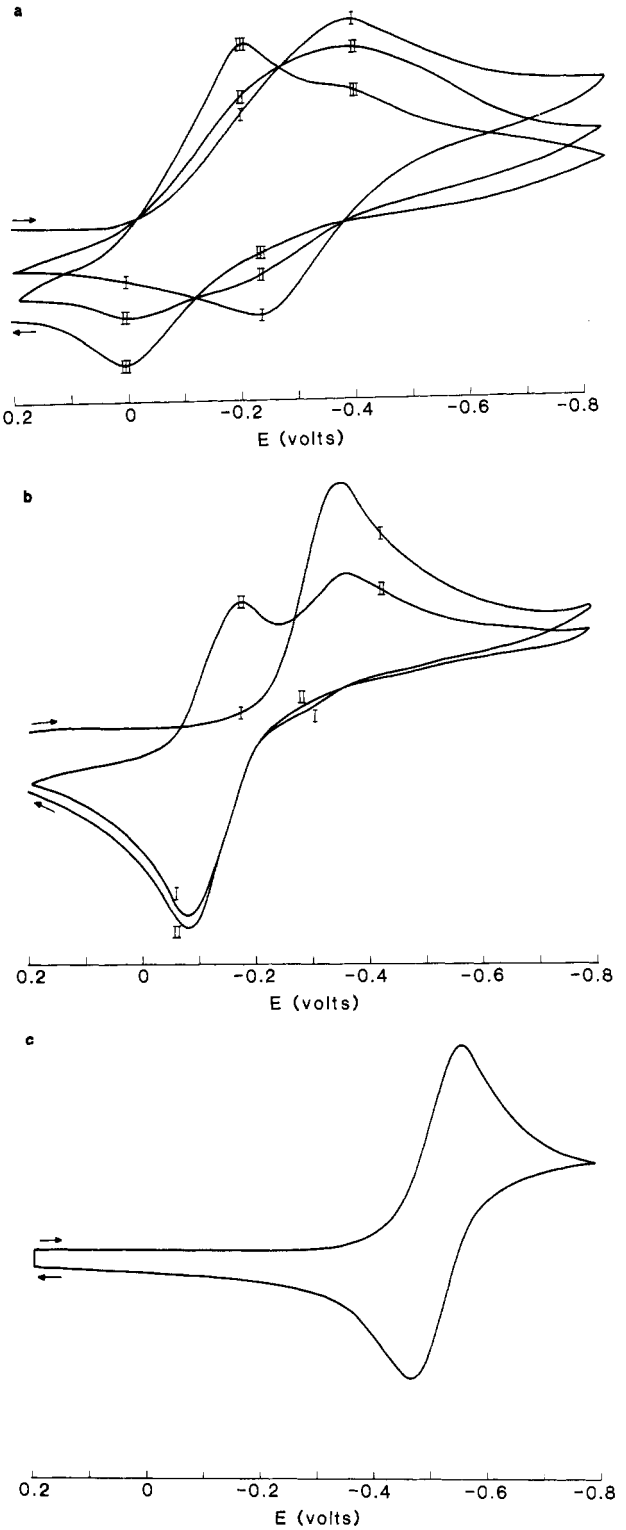


Figure 2. Cyclic voltammograms of the (N,N′) chelate of glycinamide. (a) 0.1 M CF_3COOH, sweep rate 10 V s^{-1}: (I) 1st scan; (II) 5th scan; (III) 30th scan. (b) 0.1 M CF_3COOH, sweep rate 0.05 V s^{-1}: (I) 1st scan; (II) 2nd scan. (c) 0.1 M $LiClO_4$, pH 7.1, sweep rate 0.02 V s^{-1}.

Electrochemical Experiments. All three (N,N′) complexes showed irreversible cyclic voltammograms in 0.1 M CF_3COOH. The cyclic voltammetric behavior of the glycinamide complex is illustrated in Figure 2. In the first scan at a sweep rate of 10 V s^{-1}, starting at positive potential, a pair of broad peaks appeared with a separation of ~140 mV, with a mean

(17) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392.

Table VI. Kinetic Results for the Reaction of the Ru(II) Glycylglycine Chelate with Mixtures of Acetonitrile and 4-CNpyH$^+$ [a]

	2 M CH_3CN + 0.15 M 4-CNpyH$^+$	1 M CH_3CN + 0.3 M 4-CNpyH$^+$	0.5 M CH_3CN + 0.3 M 4-CNpyH$^+$
k_{obsd}, [b] s^{-1}	0.048	0.030	0.017
$k_{obsd} - k_{4\text{-CNpyH}^+}$[4-CNpyH$^+$], s^{-1}	0.045	0.024	0.014
k_{CH_3CN}, M^{-1} s^{-1}	0.023	0.024	0.028

[a] Conditions: pH 1.4, 25 °C, μ = 0.15–0.3. [b] $k_{obsd} = k_{4\text{-CNpyH}^+}$[4-CNpyH$^+$] + k_{CH_3CN}[CH_3CN].

potential ($E_{1/2}$) of −60 mV vs. NHE. On continuation of the same scan, another peak appeared in the anodic current at a more positive potential. In the second scan a new peak appeared in the cathodic current pairing with the more positive peak of the anodic current. On repetitive scans, the more negative pair decreased in amplitude, parallel to an increase in the more positive pair of peaks, until a steady state was reached (Figure 2a). In a scan at a sweep rate of 0.05 V s^{-1}, only two peaks appeared in the first scan—one in the cathodic current and one in the anodic current, the latter featuring a slight shoulder corresponding to the match of the cathodic current peak. A second scan showed a new cathodic peak, which paired with the anodic peak. The separation of these peaks was 95 mV, with $E_{1/2}$ = +135 mV vs. NHE (Figure 2b). This behavior is typical of an irreversible chemical reaction coupled between two reversible charge transfers—an $E_rC_iE_r$ scheme as described by Nicholson and Shain.[18,19]

We infer that the more negative potential belongs to the (N,N′) chelates and the more positive to the (N,O) chelates, which are formed very rapidly from the (N,N′) chelates in the Ru(II) state. The specific rate of conversion from the (N,N′) to the (N,O) forms of Ru(II) can be estimated from our results as being in the range 2–10 s^{-1}.

At higher pH (7.1–8.3), only two peaks are observed in the first scan, as well as in repetitive scans. These peaks are separated by 85 mV in a 0.02 V s^{-1} scan, and $E_{1/2}$ ranges from −265 to −230 mV vs. NHE (Table VII, Figure 2c) for the different species.

At pH 6.7, a small peak of the (N,O) chelates appears in the first scan, and its partner peak grows in on repetitive scans. This pair of peaks becomes larger as the pH is decreased, parallel to a shift in $E_{1/2}$ of both the (N,N′) and the (N,O) chelates to lower values.

A plot of $E_{1/2}$ for the (N,N′) chelates of glycinamide and *N′*-ethylglycinamide vs. pH is shown in Figure 3. $E_{1/2}$ is constant at high pH, within the experimental error; at lower pH it changes linearly with a slope of −0.060 and −0.053 mV/pH unit for the glycinamide and the *N′*-ethylglycinamide chelates, respectively, in reasonable agreement with the theoretical slope at 20 °C of −0.058 mV/pH unit. From the intersection of the two straight lines, values of 4.3 and 5.0 are extracted for the pK_a's of the (N,N′) Ru(II) chelates of glycinamide and *N′*-ethylglycinamide, respectively (Table VII). These values agree with an estimated value of 4.5 ± 0.5, which can be derived from the change of the amplitudes of the waves of the (N,O) and (N,N′) chelates as a function of pH.

Figure 4 shows the variation with pH of the cathodic peak potential ($E_{p,c}$) registered in the cyclic voltammograms of the glycylglycine (N,N′) chelate. The isomerization from the (N,N′) to the (N,O) chelate after reduction at low pH is somewhat faster in this case ($k \approx 10$ s^{-1}), and values of $E_{1/2}$ are not as reliable as for the other two chelates. The dependence of $E_{p,c}$ on pH at constant sweep rate is expected to be

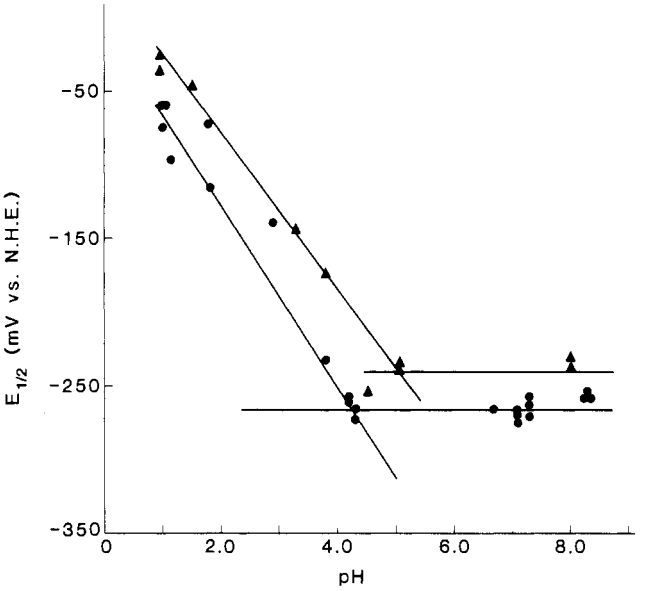


Figure 3. Formal potentials of the glycinamide-*N,N′* (●) and *N′*-ethylglycinamide (▲) chelates as a function of pH (0.1 M $LiClO_4$, titrated with $HClO_4$).

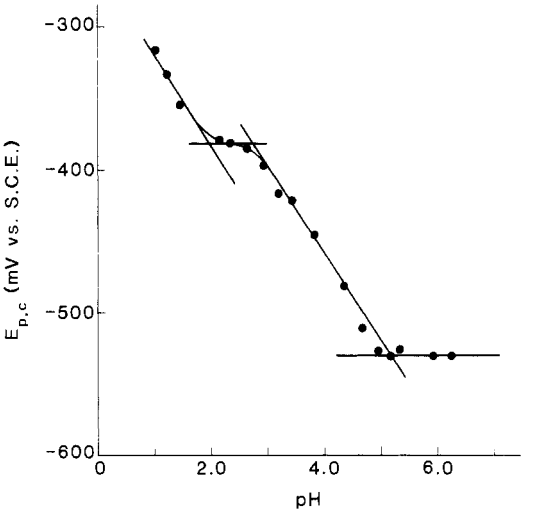


Figure 4. Cathodic peak potential ($E_{p,c}$) of the glycylglycine-*N,N′* chelate as a function of pH (0.1 M $LiClO_4$, titrated with $HClO_4$). The potential is in mV vs. SCE.

the same as that of $E_{1/2}$. The behavior at pH >3 is similar to that observed for the other two chelates, with a slightly higher slope (62.7 mV/pH unit); a pK_a of 5.2 ± 0.2 can be calculated from the intersection of the two straight lines. In the pH range 2–3, a break occurs, and at pH >2, the dependence is again linear with a slope similar to that observed at pH >3. The latter behavior is explained by the protonation equilibria of the carboxylate. The pK_a for the proton equilibrium of the carboxylate of the Ru(III) form is known to be 3.2; if the Ru(II) complex, which must be remembered to be protonated on the amide nitrogen, has a lower pK_a for the protonated carboxyl group, the profile of $E_{1/2}$ vs. pH below pH 3.2 will tend to zero slope, and accordingly we assign the break at still lower pH to protonation of the carboxyl group of the Ru(II) form, the pK_a being ~2. We do not understand why the value of pK_a for the Ru(III) form, ~2.7, indicated by the electrochemical data differs from that gotten by spectrophotometry, and we believe the latter (3.2) to be closer to the true value.

Another set of electrochemical experiments was performed starting with the (N,O) Ru(II) chelates, with scanning from negative to positive potentials. The cyclic voltammograms at

(18) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.
(19) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 190.

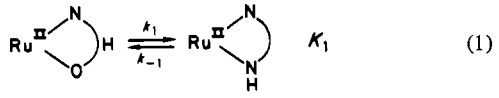
Table VII. Equilibrium Constants and Formal Potentials[a] for Ru(II) and Ru(III) (N,N′) and (N,O) Tetraammine Glycinamide Derivatives

derivative	E_f(N,N′) deprotonated	E_f(N,O) protonated	$K_1{}^{II}K_{a(N,N')}$	$p^{II}K_{a(N,N')}$	$p^{III}K_{a(N,N')}$	$p^{III}K_{a(N,O)}$	pK_1[d]	K_3[e]
glycylglycine	−265 ± 10	+140 ± 10	8.4 ± 0.3[b]	5.2 ± 0.2[b]	~−1[c]	6.2 ± 0.2[c]	3.2 ± 0.5	33
N′-ethylglycinamide	−230 ± 10	+130 ± 10	8.4 ± 0.2[b]	5.1 ± 0.2[b]	~−1[c]	6.2 ± 0.2[c]	3.3 ± 0.4	2.1×10^2
glycinamide	−265 ± 10	+140 ± 10	8.1 ± 0.2[b]	4.3 ± 0.2[b]	~−1[c]	5.0 ± 0.2[b,c]	3.8 ± 0.2	16

[a] In mV vs. NHE; sweep rate 10 V s^{-1}. [b] From electrochemical experiments. [c] From spectrophotometric experiments. [d] Calculated by $K_1{}^{II}K_{a(N,N')}/{}^{II}K_{a(N,N')}$, both species protonated. K_1 is the equilibrium ratio $Ru^{II}(N,N')/Ru^{II}(N,O)$, with both forms protonated. [e] K_3 is the equilibrium quotient $[Ru^{III}(N,O)]/([Ru^{III}(N,N')][H^+])$ as calculated from the potentials and the values of $K_1{}^{II}K_{a(N,N')}$.

pH 1.0 (CF_3COOH) showed one pair of waves in a scan of 0.02 V s^{-1}, with $E_{1/2}$ as shown in Table VII. The peak separation was 75 mV. In faster scans the peaks broadened and became more separated with unchanged $E_{1/2}$, and no new waves appeared.

At pH 6.8 (0.05 M phosphate buffer), the cyclic voltammograms showed a pair of broad peaks with $E_{1/2}$ = 30–40 mV vs. NHE and peak separation of ~150 mV in a scan of 0.05 V s^{-1} and another pair of much smaller amplitudes with $E_{1/2}$ ≈ −240 to −270 mV vs. NHE with peak separation of 95 mV. This pair was unequal in amplitude, the anodic peak (recorded at the beginning of the scan) being smaller than the cathodic peak (recorded at the end of the scan). We infer that the following reactions are occurring:



(1)

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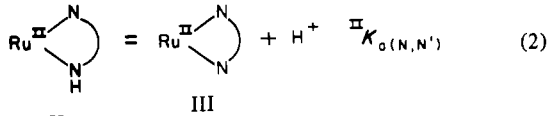


(2)

II III

Protonation–deprotonation is rapid so that species II and III are in equilibrium at all times. With use of the values of K_1 (they range from 1.5×10^{-4} to 6×10^{-4}; see Table VII) and k_{-1} as measured at low pH as about 2 s^{-1} for the glycinamide and the *N*′-ethylglycinamide chelates and ~10 s^{-1} for the glycylglycine chelate, the values of k_1 are estimated as 3×10^{-4}, 1×10^{-3}, and 6×10^{-3} s^{-1} for the chelates—the rate of conversion of the (N,O) to the (N,N′) chelate is slow on the cyclic voltammetry time scale.

The cathodic peak of the (N,N′) chelate is somewhat larger than the anodic because some of the (N,O) chelate is transformed to the (N,N′) form, catalyzed by Ru(II), as in a partially reduced solution of the (N,O) chelates. When the scan is stopped for about 30 s at a potential so that part of the (N,O) chelate is reduced, the cathodic wave of the (N,N′) chelate increases further.

Cyclic voltammetry at pH 7.6 (0.05 M phosphate buffer) showed two anodic current peaks with more of the (N,N′) chelate peak than at pH 6.8. The cathodic current behavior was more complex and showed three peaks. One peak was the cathodic one of the (N,N′) chelate. One broad peak that appeared in a scan at 0.5 V s^{-1} resolved into two peaks in a scan at 0.2 V s^{-1}. In a 0.05 V s^{-1} scan, the more negative peak grew at the expense of the more positive one, which appeared as a shoulder. This behavior indicates that a further, still unidentified chemical reaction is taking place in the Ru(III) state. A further increase in pH showed very complex behavior, which we did not attempt to analyze.

Normal pulse voltammetry experiments showed two distinct waves in the pH range 6.8–8.7, with amplitude ratios that depended on pH and on the ligand. These two waves monitor the protonated (N,O) and the deprotonated (N,N′) chelates. During the potential pulse (57 ms), redistribution between (N,O) and (N,N′) forms is negligible, but the protonation equilibrium is maintained so that the (N,N′) chelate is monitored as the deprotonated chelate. The period in which the potential is positive enough to oxidize the chelates is so short that no appreciable side reactions occur in the Ru(III) state.

The p*K* of the overall equilibrium of reactions 1 and 2 can be calculated by using

$$pK = pH - \log \frac{i_{(N,N)}}{i_{(N,O)}}$$

where $i_{(N,N)}/i_{(N,O)}$ is the ratio of currents measured for the (N,N′) and (N,O) chelates. The calculated values are given in Table VII. ${}^{II}K_{a(N,N)}$ was calculated from the dependence of the potential on pH (Table VII), and thus K_1 can be calculated as well.

From $E_{1/2}$ measured for the (N,O) chelate of glycinamide at pH 1.0 and at pH 6.8, the pK_a of the (N,O) Ru(III) chelate can be calculated by using

$$E_{1/2}{}^{obsd} = E_{1/2}{}^{H} + \frac{RT}{nF} \ln \frac{1 + {}^{II}K_{a(N,O)}/[H^+]}{1 + {}^{III}K_{a(N,O)}/[H^+]}$$

where $E_{1/2}{}^{obsd}$ is the $E_{1/2}$ measured at each pH, $E_{1/2}{}^{H}$ is $E_{1/2}$ measured at a pH where both Ru(II) and Ru(III) complexes are protonated, and ${}^{II}K_{a(N,O)}$ and ${}^{III}K_{a(N,O)}$ are the acid dissociation constants of the reduced and oxidized (N,O) chelates. On the assumption that the (N,O) forms of the Ru(II) chelates are protonated at both pH values (${}^{II}K_{a(N,O)} << 10^{-6.8}$) and that at pH 1.0 both Ru(II) and Ru(III) are protonated ($E_{1/2}{}^{obsd}$ at pH 1 is $E_{1/2}{}^{H}$), the calculation gives pK_a = 5.1 for the glycinamide chelate, in good agreement with the value of 5.2 obtained from spectrophotometric experiments (Table III).

Discussion

Relative Stabilities of the (N,N′) and (N,O) Forms. The conclusions about the type of linkage isomerization featured by each of the species we have dealt with were developed in the preceding section. They rest on spectrophotometric evidence, combined with the determinations of pK_a values and the electrochemical properties, and they seem to us to be secure. Of particular interest are the relative stabilities of the linkage isomers for each of the ruthenium oxidation states, taken also as a function of the state of protonation of the ligands. The relevant equilibrium quotients can be calculated from the data in Table VII, and the results are outlined here for glycinamide as a ligand.

For the reaction

$$Ru^{II}(N,N') = Ru^{II}(N,O)$$

K_{eq} is 6×10^3 when both isomers are protonated. The pK_a for $Ru^{II}(N,N')$ is known (4.3 ± 0.2), but for $Ru^{II}(N,O)$ we have only an estimate ($pK_a \approx 13$).[20] This leads to a value

(20) The values of pK_a for amide ligands of the kind we are dealing with are in the range of 13–15.[21] The effect of Ru(II) acting through two intervening atoms in enhancing the acidity is expected to be very small and can amount to at most a factor of 10.

for the equilibrium ratio of $Ru^{II}(N,O)/Ru^{II}(N,N')$, when both species are deprotonated, of $\sim 1 \times 10^{-5}$. The change in the relative stability of the isomeric forms on deprotonation of course simply reflects the differences in the basicities of the two deprotonated forms of the ligand, and the change is in the expected direction (the imide nitrogen on Ru(II) is expected to be less basic than is the imide remote from the metal ion). By the introduction of the appropriate redox potentials (Table VII) and $p^{III}K_{a(N,O)} = 5.0 \pm 0.2$, the equilibrium ratio $Ru^{III}(N,O)/Ru^{III}(N,N')$ when both ligands are deprotonated is calculated as 1.6×10^{-4}. The value of $p^{III}K_{a(N,N')}$ is known only approximately, but a value of -1 is likely within one unit of the true value at $\mu = 0.1$. When this value of pK_a is used together with pK_a for $Ru^{III}(N,O)$, the equilibrium ratio $Ru^{III}(N,O)/Ru^{III}(N,N')$, where now the ligands are protonated, is calculated as 1.6×10^{2}.

These being the only estimates of the relative stabilities of the linkage isomers for these ligands, it is of interest to consider their relevance to other systems. Those for Ru(III) can be taken as a guide to what can be expected for Cr(III), Co(III), or Rh(III), but with differences of at least a factor of 10 to be expected, such differences arising in part from the greater effect of stabilization by charge transfer for Ru(III) compared to that for the other tripositive ions. The comparison with the N-bound monodentate forms as dealt with by Zanella and Ford[13] in their studies of the amide complexes of pentaammineruthenium(III) suggests that the relative stabilities are strongly affected by chelation. The authors found no evidence for isomerization to the O-bound forms even for the neutral ligands. In the face of so many examples of facile linkage isomerization on Ru(III), which include the migration of $Ru(NH_3)_5$ from a ring to an exocyclic nitrogen of adenosine,[22] it is hardly credible that linkage isomerization for the monodentate forms would be slow.

It should be noted that the experimental data in the first three columns of Table VII combine to yield the equilibrium quotient for the reaction

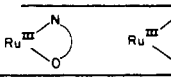
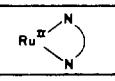
$$Ru^{III}(N,N') + H^+ = Ru^{III}(N,O) \qquad (3)$$

and the values calculated are entered in the last column of the table. It is evident that, in 1 M H^+, $Ru^{III}(N,O)$ is stable with respect to the dominant form of $Ru^{III}(N,N')$, which is the deprotonated complex. The failure to observe significant isomerization of $Ru^{III}(N,O)$ to $Ru^{III}(N,N')$ for *N'*-ethylglycinamide at pH 1.2 is ascribable to the stability of the (N,O) form. In one case, that of glycylamide, the calculated value was checked by direct measurement: 8 ± 2 observed vs. 16 calculated. The agreement is satisfactory, considering the limits of error on the values of $E_{1/2}$ and of $K_1^{II}K_{a(N,N')}$.

Properties. Some comparisons of the spectra for related Ru(III) complexes were introduced in the Results section, and they provide major evidence for the structural assignments we have made. The O-bound isomers for Ru(III) have not been characterized heretofore, and it is of interest that the absorptions are at higher energy than for the N-bound forms. The comparison is understandable only if a proton transfers from the amide nitrogen to the carbonyl oxygen when the amide coordinates to Ru(III).[13,23,24]

Somewhat astonishing is the result that the charge-transfer absorption in the near-UV region is at higher energy for the chelated carboxyl (288 nm), which carries a negative charge, than it is for the (N,O) form of the neutral amide. The result suggests that the work of removing an electron from an amide group is no greater than it is for a carboxylate ion.

Table VIII. pK_a's of the Carboxylate Group of Glycylglycine As Affected by Coordination to Ru(III) and Ru(II)

chelate			
			free ligand
2.2	3.2	2–2.5[a]	3.06[b]

[a] Estimated from Figure 4. [b] Reference 28.

It is to be noted that chelation, with the ring closing on the amide nitrogen, enhances the acidity of the amide group by about 3 orders of magnitude over that observed for the N-bound monodentate amide.[13] A similar effect has been reported for the Co(III) complexes: pK_a for (acetamide)pentaamminecobalt(III) is 3.02 as compared to ~ 0.4 for the (N,N') form of the chelate.[23] The greater acidity of the Ru(III) complex as compared to that of Co(III) is in line with a number of other observations and reflects the importance of ligand to metal charge transfer for the Ru(III) species.

The enhancement in the acidity of the amide brought about by Ru(II), when the ligand is chelated in the (N,N') form, is ca. 10^8–10^9; the acidity of H_2O coordinated to Ru(II) is enhanced by a factor of only 10^2–10^3.[8] Water as a ligand provides a measure of the purely inductive effect exerted by Ru(II), and this fails to account for the large enhancement by Ru(II) of the acidity of the N-amide ligand. Part of the increase is ascribable to chelation, as has been documented for Ru(III) and Co(III). Is there possibly also a contribution from back-bonding to the very large effect exerted by Ru(II)? For a back-bonding interaction to stabilize the deprotonated form more than it does the neutral ligand, it is required that, in the latter species, both protons are on the coordinated nitrogen, thus virtually eliminating a back-bonding interaction. Because the inductive effect of Ru(II) is so small, the implied structure for the neutral (N,N') form on Ru(II) is not unreasonable.

The value of pK_a for the free amide ligand is given as about 10^{14}.[20] The values of pK_a for the N,O-bound bis(ethylenediamine)cobalt(III) complexes of glycinamide, *N'*-methylglycinamide, and glycylglycine are 11.4, 11.3, and 12.5, respectively.[26] Quite astonishing in this context then is the enhancement of acidity produced by Ru(III) in the N,O-bound form, where for these complexes pK_a is measured as ranging from 6.2 to 5.0. The effect observed for Co(III) can be regarded as purely inductive. In acting on H_2O, $Co(NH_3)_5^{3+}$ enhances the acidity by a factor of about 10^{10},[27] and an inductive effect of this kind commonly attenuates by a factor of about 10^3 for every atom that intervenes between the acid-promoting center and the site of deprotonation. The severe attenuation with the length of the linkage, however, is not expected to obtain if there is charge transfer from ligand to metal and if the charge is taken from an orbital that embraces both the atom linked to the metal and the site of deprotonation. Even so, it is difficult to understand why Ru(III) in promoting acidity is so much more effective relative to Co(III) in the case of amide than it is for water.

Even on the face of it, the enhancement of the acidity of the N-bound amide by Ru(III), a factor of 10^{15} over that of the free ligand,[20] is abnormally high, at least compared to the

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effect of Ru(III) on H_2O, which is a factor of 10^{12}.[25] If, as we believe, the site of deprotonation is the carbonyl oxygen, the factor of 10^{15} must be multiplied by the equilibrium ratio of $Ru^{III}NHC(OH)R/Ru^{III}NH_2COR$ to make the comparison with the simple case of H_2O valid.

In Table VIII are summarized the data on the acidity of the carboxyl function of glycylglycine for the ligand in different states of bonding. In an appraisal of the data it must be borne in mind that for $Ru^{III}(N,N')$ in the pH range in question the ligand has lost a proton, while in the Ru^{II} form, the ligand is neutral. This explains what otherwise would appear to be an anomalous effect on the pK_a of reducing the oxidation state.

Preparations. The direct reaction of the amide ligands with *cis*-hydroxoaquotetraammineruthenium(III) yields the (N,N') form, behavior which contrasts with that of the analogous Co(III) system, where the (N,O) form is produced with eventual hydrolysis to the glycinato chelate.[1,9] Ruthenium(II) has been shown to catalyze the interconversions of the Ru(III) chelates, and at high pH the (N,N') form is more stable. Thus, the possibility must be considered that the putative direct reaction also involves catalysis by Ru(II). Ruthenium(II) can in principle arise by disproportionation of Ru(III),[29] a process that would be favored by the high pH and the relative ease of deprotonation of coordinated water. It was found, however, that the reaction course is not altered when the preparation is done in air, rather than, as in the usual case, under an inert atmosphere. The difference in the behavior of Co(III) and Ru(III) is likely an intrinsic difference in the substitution properties of the centers, namely, that bond making in the activated complex is relatively more important for the latter center. This difference is reflected in the much greater lability of Ru(III) to linkage isomerization.[2,3a]

The preparation of $Ru^{III}(N,N')$ from the diaquo tetraammine complex proceeds under much milder conditions when Ru(II) is present, and the procedure exploiting electron-transfer catalysis is in fact preferred because side reactions are minimized.

In producing $Ru^{III}(N,O)$ by oxidizing the Ru(II) complex, we take advantage of the fact that in acidic solution $Ru^{II}(N,O)$ is much more abundant than $Ru^{II}(N,N')$ and that redistribution between the forms can be intercepted by rapid oxidation. It is remarkable that $Ru^{III}(N,O)$ is also produced by ring closure from, for example, $[(NH_3)_5RuNH_2CH_2CONH_2]^{3+}$ and that this chelation is a facile process. The details of these reactions will be the subject of a separate communication.[30]

Catalysis by Ru(II) of the Transformation of $Ru^{III}(N,O)$ to $Ru^{III}(N,N')$. The principles that govern electron-transfer catalysis of substitution reactions are well understood: it is required that the catalyst center be more labile than the substrate and that electron transfer between substrate and catalyst be facile. These conditions are often met by Ru(II) acting as a catalyst for substitution on Ru(III)[31] and are met in the system under present study.

The simplest mechanism that incorporates these principles is

$$Ru^{II}(N,O) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{II}(N,N') \qquad (1)$$

$$Ru^{II}(N,N') + Ru^{III}(N,O) \xrightarrow{k_4} Ru^{III}(N,N') + Ru^{II}(N,O) \qquad (4)$$

In the above, the possible dependence of the specific rates on $[H^+]$ is neglected because in our experiments this variable was kept virtually constant.

This mechanism leads to the rate law

$$d[Ru^{III}(N,N')]/dt = \frac{k_1k_4[Ru^{II}(N,O)][Ru^{III}(N,O)]}{k_1 + k_4[Ru^{III}(N,O)]}$$

In acidic solution, the (N,O) form of Ru(II) is much more stable than the (N,N') form and thus $[Ru^{II}(N,O)]$ is essentially equal to [Ru(II)]. The rate law leads to the expression

$$\Delta t/\Delta A = \frac{1}{K_1k_4[Ru^{II}(N,O)]}\frac{1}{A_\infty - A_t} + \frac{1}{k_1[Ru^{II}(N,O)]\epsilon}$$

which is compatible with a plot such as shown in Figure 1. Neither $Ru^{II}(N,O)$ nor $Ru^{III}(N,O)$ absorb significantly at the monitoring wavelength, and ϵ is the extinction coefficient of the product. It and the value of $[Ru^{II}(N,O)]$ are known for each run, and K_1 being known (6×10^{-4} for the glycylglycine chelate), k_1 and k_4 can be evaluated from a plot such as that shown in Figure 1. The values of k_1 (5×10^{-2} s^{-1} even with omission of the highest value shown in Table IV) are found to be much higher than those that were determined more directly from the cyclic voltammetric results: for the Ru(II) glycylglycine, this was calculated as 6×10^{-3}. The discrepancy, a factor of 8, we consider to be outside that attributable to the inherent accuracies in our measurements.

We have also considered an alternative mechanism in which electron transfer occurs between $Ru^{III}(N,N')$ and a Ru(II) complex in which the chelate has been opened. Such a mechanism is compatible with the plot shown in Figure 1, and it fixes the specific rate of chelate ring opening as about 5×10^{-2} s^{-1}. This sets a limit on the rate at which substitution on $Ru^{II}(N,O)$ can take place but only if an S_N1 process operates. The data on substitution will be considered in the next section; it is appropriate to note here that the rates of substitution at high ligand concentration exceed that set by the limit $(5 \times 10^{-2})[Ru(II)]$.

Substitution in the $Ru^{II}(N,O)$ Species. The rates of reaction of the Ru(II) chelates with 4-$CNpyH^+$ and with CH_3CN at pH ~1.3 are 5–10 times slower than the rates with the same ligands observed for $[Ru(NH_3)_5H_2O]^{2+}$ (cf. Tables V and VI). This indicates that the Ru(II) species are in fact chelated but does not rule out a mechanism involving an open intermediate:

$$Ru^{II}(N,O) \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Ru^{II}—N—O \qquad (5)$$

$$Ru^{II}—N—O + L \longrightarrow Ru^{II}\begin{matrix}L\\ \diagdown\\ N—O\end{matrix} \qquad (6)$$

from which the rate law

$$\frac{-d[Ru^{II}(N,O)]}{dt} = \frac{k_5[Ru^{II}(N,O)][L]}{k_{-5}/k_6 + [L]}$$

follows.

If this mechanism is obeyed, k_{obsd} cannot exceed k_5, and when k_{obsd} approaches k_5, there should be strong evidence of rate saturation. If Ru^{II}–N–O is taken as the species that undergoes electron transfer with $Ru^{III}(N,N')$ (see the previous section), k_5 is calculated at $\sim 5 \times 10^{-2}$ s^{-1}. Although k_{obsd} for substitution as recorded in Table VI is this large, there is no evidence of rate saturation. We must conclude that either (a) the particular mechanism for the catalyzed linkage isomerization of Ru(III) involving electron transfer between Ru^{II}–N–O and the Ru(III) chelate is invalid or (b) substitution by the entering groups does not wait on ring opening and bond making in the activated complex by the entering group is important. Neither alternative is palatable: with alternative a we are left with no mechanism, even in general terms, for the catalysis of substitution on Ru(III) by Ru(II) in our system, and this mechanism is unlikely to involve anything exotic; alternative b runs counter to so much other evidence bearing on substitution in $Ru(NH_3)_5H_2O^{2+}$, which indicates

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that there is little, if any, assistance by the entering group on the activated complex for substitution.[32]

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Registry No. $[(NH_3)_4RuNH_2CH_2CONCH_2COOH][Cr(NH_3)_2(SCN)_4]_2$, 85320-34-9; $[(NH_3)_4RuNH_2CH_2CONH](PF_6)_2$, 85320-36-1; $[(NH_3)_4RuNH_2CH_2CONCH_2CH_3](PF_6)_2$, 85320-38-3; $[(NH_3)_4RuNH_2CH_2CONH_2](PF_6)_2$, 85320-40-7; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3](PF_6)_2$, 85320-42-9; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH][Cr(NH_3)_2(SCN)_4]_2$, 85335-31-5; $[(NH_3)_4RuNH_2CH_2COO](PF_6)_2$, 85335-32-6; $[(NH_3)_4RuNH_2CH_2COO]^{2+}$, 85320-43-0; $[(NH_3)_4RuNH_2CH_2CONH]^{2+}$, 85320-35-0; $[(NH_3)_4RuNH_2CH_2CONCH_2CH_3]^{2+}$, 85320-37-2; $[(NH_3)_4RuNH_2CH_2CONCH_2COOH]^{2+}$, 85320-44-1; $[(NH_3)_4RuNH_2CH_2CONCH_2COO]^{+}$, 85320-33-8; $[(NH_3)_4RuNH_2CH_2CONH_2]^{3+}$, 85320-45-2; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3]^{3+}$, 85320-46-3; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH]^{3+}$, 85335-33-7; $[(NH_3)_4RuNH_2CH_2CONHCH_2COO]^{2+}$, 85320-47-4; $[(NH_3)_4RuNH_2CH_2COO]^{+}$, 85320-48-5; $[(NH_3)_4RuNH_2CH_2CONH_2]^{2+}$, 85320-39-4; $[(NH_3)_4RuNH_2CH_2CONHCH_2CH_3]^{2+}$, 85320-41-8; $[(NH_3)_4RuNH_2CH_2CONHCH_2COOH]^{2+}$, 85320-49-6; $[(NH_3)_5Ru^{III}NHCOCH_3]^{2+}$, 52843-03-5; $[(NH_3)_5Ru^{III}NHCOC_6H_5]^{2+}$, 52843-05-7; $[(NH_3)_5Ru^{III}NH_2COC_6H_5]^{3+}$, 52843-10-4; 4-CNpy, 100-48-1; bis(4-cyanopyridine)tetraammineruthenium(II), 85320-50-9; *cis*-tetraamminediaquoruthenium(III) trifluoromethanesulfonate, 74468-24-9; acetonitrile, 75-05-8.

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Structural and Mechanistic Studies of Coordination Compounds. 35. Steric Effects and the Dissociative Mechanisms for Simple Ligand Substitution Reactions and Base Hydrolysis of Some Ruthenium(III) Amine Complexes

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Kinetics of substitution reactions of *trans*-$[Ru(teta)Cl_2]^+$ by bromide and of *trans*-$[Ru(L)Br_2]^+$ (L = teta or tetb) by chloride have been studied over a range of temperatures. The observed steric acceleration of k_1(tetb) > k_1(teta) > k_1(cyclam) for the release of the first coordinated halide from analogous dihalogen complexes supports a dissociative mechanism for these reactions. A similar trend of steric acceleration has also been found to support the S_N1cB mechanism for the base hydrolysis of *trans*-$[Ru(L)ACl]^+$ (L = tetb, teta, or cyclam; A = Cl or OH).

Introduction

Ligand substitution reactions of ruthenium(III) amine complexes have received much attention in recent years.[1-11] Conflicting arguments have been advanced to support either a dissociative or an associative mechanism under different experimental conditions. The first systematic study[2] on the *cis*-tetraammineruthenium(III) series of complexes showed that charge had little effect on the aquation rates, and an associative mechanism was invoked. However, Ohyoshi et al.[5] have demonstrated the existence of a linear free energy relationship with unit slope, though over only one logarithmic unit, for the aquation of $[Ru(NH_3)_5X]^{2+}$ complexes (X = some halogen-substituted carboxylate ligands). This indicated a dissociative mechanism. A dissociative mechanism was also supported by the aquation study of $[Ru(NH_3)_5Cl]^{2+}$ and *cis*-$[Ru(en)_2Cl_2]^+$ in a variety of water–organic solvent mixtures[7] and by the observation[9] that the aquation rates of *trans*-$[Ru(L)Cl_2]^+$ decreased with increasing chelation of L: $(NH_3)_4 \approx (en)_2$ > (*R*,*S*)-2,3,2-tet > cyclam, where en, 2,3,2-tet, and cyclam represent ethylenediamine, 3,7-diazanonane-1,9-diamine and 1,4,8,11-tetraazacyclotetradecane, respectively. Recently, Fairhurst and Swaddle[11] have examined the effect of pressure on both the forward aquation and the reverse anation of $[Ru(NH_3)_5Cl]^{2+}$. The observed negative volumes of activation for both processes were taken to support an associative mechanism. The aim of this investigation is to examine the steric effects on rates in order to resolve this mechanistic ambiguity.

The structure of *trans*-$[Ru(teta)X_2]^+$ (X = Cl or Br) is known from the crystallographic work[12] on *trans*-$[Ru(teta)Br_2]_2[ZnBr_4]$ to possess the same skeleton as *trans*-$[Ru(cyclam)Cl_2]^+$ (structure I),[13] where teta represents *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. The structure of *trans*-$[Ru(tetb)X_2]^+$ (X = Cl or Br) is not known, where tetb is the racemic isomer of teta. However, it is most likely that these tetb complexes possess structure II by reference to that of $[Ni(tetb)]^{2+}$,[14] in which the steric environments above and below the RuN_4 plane are different. The studies of the relative rates of release of these halide ions from corresponding tetb, teta, and cyclam complexes would yield important information about the influence of steric effects on ruthenium(III) substitution reactions. Work has also been extended to investigate steric effects on the base hydrolysis

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