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Reactions of Pentaammineruthenium Complexes of Glycinamide, Glycylglycine, and Derivatives in Acidic Solution

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In weakly acidic solutions (pH 3), pentaammineruthenium(III) complexes of glycinamide, *N'*-ethylglycinamide, glycylglycine, glycylglycinamide, and ethyl glycylglycinate undergo reaction leading to (N,O)-bound tetraammineruthenium(III) chelates, ammonia being released into solution. At higher acidities (up to 0.1 M H^+), the chelation is accompanied by an aquation reaction producing $[Ru(NH_3)_5H_2O]^{3+}$ and the free ligand. The rate of consumption of the reactants is given by $k = k' + k''[H^+]$. In this rate law, the first term corresponds to chelate ring closure and the second to aquation. In the presence of Ru(II), the rate of aquation (and thus the aquation yield) is increased, but the rate of formation of the chelate is not affected. In the pH regime in which the (N,N') chelate is stable with respect to the (N,O), addition of Ru(II) leads to rapid isomerization to the (N,N') form. A similar reaction is not observed for (ethyl glycinate)pentaammineruthenium(III); here N-bound to O-bound linkage isomerization, followed by the parallel reactions aquation to free ester and hydrolysis of the ester, occurs instead. When glycylglycine is the ligand, a single chelate product is observed at pH 3, but an additional chelate product is obtained at pH 1. These are very similar chemically but have different UV and NMR spectra. These species are assigned as isomers of the (N,O)-bound chelate. It is suggested that, in the C-N peptide bond of the product formed at the higher pH, the hydrogen is trans to the oxygen. In this configuration, a hydrogen bond can be formed between the carboxylate and an adjacent ammonia ligand; in the second isomer, where the hydrogen is cis to the oxygen, such a hydrogen bond cannot be formed. This interpretation of the differences in the products implies that the barrier to rotation about the C-N peptide bond is greatly increased when a metal ion is attached to the carbonyl oxygen of the peptide.

Linkage isomerization of glycine and its esters from the N-bound to the O-bound state has been shown to be facile in pentaammineruthenium(III) complexes,[1,2] and in a slight extension of this kind of study,[3] it was found that α-alanine, but not β-alanine, readily undergoes a similar reaction. More recently, the linkage isomerization of the tetraammineruthenium(III) chelates of glycinamide, *N'*-ethylglycinamide, and glycylglycine, as catalyzed by Ru(II) was studied.[4] By exploiting the lability of the Ru(II) complexes and the facile electrochemical conversion to ruthenium(III), it was possible to determine the relative stabilities of the isomeric forms of both the Ru(III) and the Ru(II) species as a function of acidity.

The studies referred to above illustrate two of the special opportunities that the ruthenium ammines offer in comparison to the analogous cobalt systems, the study of which have been so productive of important mechanistic conclusions.[5] Linkage isomerization in cases thus far studied takes place much more readily than for Co(III), a result which was unexpected in view of the fact that simple substitution on Ru(III) is only slightly more rapid than on Co(III). Secondly, there is an advantage in having available an adjacent, more labile oxidation state to provide a mechanism for equilibration of the less labile state. Many advantages of substitution inertia are retained however because NH_3 is replaced relatively slowly even from Ru(II).

In this paper we describe a third feature of the Ru(III) system that sets it apart from other substitution-inert centers that have been most studied. The dominant path for reaction of pentaammineruthenium(III) complexes of glycinamide, glycylglycine, and their derivatives in weakly acidic solution is ring closure leading to a tetraammineruthenium(III) with the ring closing on the carbonyl of the amide function (the (N,O) form; the designation (N,N') is used for the form in which the chelate closes on the nitrogen of the amide group). This ring closure is very much more rapid than for Co(III) (where it has not yet been reported[5]), and though rapid enough to take place under mild conditions, it is slow enough so that the process can be followed readily. In a sense, Ru(III) combines the virtues of a substitution-labile center, where the stages of substitution follow rapidly on each other, with those of a substitution-inert one, and the study of the substitution on Ru(III) of yet more complex ligands of biological interest should provide insight into the course of substitution when the reaction center is labile.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared according to the method of Vogt et al.[6] and was purified by recrystallization from 0.1 M HCl.

Glycinamide hydrochloride (Aldrich Chemical Co.), glycylglycinamide hydrochloride (Sigma Chemical Co.), and glycylglycine and ethyl glycylglycinate hydrochloride (Vega), were used without further purification. *N'*-Ethylglycinamide was prepared as described before.[4]

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 the Nanopure ultrafiltration system of Barnstead was used throughout.

Argon, rendered free of oxygen by passing it through a bubbling tower containing Cr^{2+}, was used as a blanketing gas and, as needed, for transfer of liquids.

Preparation of Complexes. Pentaammineruthenium(II) complexes of glycinamide ($NH_2CH_2CONH_2$), *N'*-ethylglycinamide ($NH_2CH_2CONHC_2H_5$), glycylglycine ($NH_2CH_2CONHCH_2COOH$), glycylglycinamide ($NH_2CH_2CONHCH_2CONH_2$), and ethyl glycylglycinate ($NH_2CH_2CONHCH_2COOC_2H_5$) were prepared by a method similar to that described.[2] A 75-mg sample of silver oxide was suspended in 2 mL of hot water, concentrated trifluoroacetic acid was added dropwise until the solids were dissolved, and 100 mg of $[Ru(NH_3)_5Cl]Cl_2$ was then added, with stirring to facilitate dissolution. The silver chloride that formed was filtered off, and the residue was washed with 3 mL of water. The solution, which included the washings, was reduced over zinc amalgam under an argon atmosphere for ~20 min, in a Zwickel flask.[7] At this point, the solid ligand was added in a 6-10-fold excess over $[Ru(NH_3)_5OH_2]^{2+}$, and the pH was raised to ~8.2 with 4 M NaOH. The reaction was allowed to proceed for ~20 min, and then the pH was adjusted to ~1 with concentrated trifluoroacetic acid. The solution was transferred under gas pressure to a bubbling flask attached to the end of the Zwickel flask and containing an argon-saturated solution of ~1 g of NH_4PF_6 or $NaPF_6$

(1) Diamond, S. E.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5921.
(2) Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1980**, *102*, 4725.
(3) Scott, N. S.; Taube, H., unpublished results.
(4) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655.
(5) Buckingham, D. A. In "Biological Aspects of Inorganic Chemistry"; Addison, A. W., Cullen, W. R., Dolphin, D., James, B. R., Eds.; Wiley: New York, 1977; p 141.
(6) Vogt, L. H.; Katz, J. L.; Wiberly, S. E. *Inorg. Chem.* **1965**, *4*, 1157.
(7) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689.

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Table I. Microanalyses of $[(NH_3)_5Ru^{II}NH_2CH_2CONHR](PF_6)_2$ Complexes

R		calcd	found[a]	found[b]	calcd for A% complex + B% NH_4PF_6			calcd for A% complex + B% $NaPF_6$		
						A	B		A	B
H	%C	4.36	4.06		4.05	93	7			
	%H	3.82	3.83		3.72					
	%N	17.82	17.11		17.17					
CH_2CH_3	%C	8.30	7.87	7.76	7.89	95	5	7.80	94	6
	%H	4.33	4.20	4.17	4.24			4.07		
	%N	16.96	16.53	15.97	16.54			15.94		
CH_2COOH	%C	7.89	7.75		7.73	98	2			
	%H	3.78	3.70		3.75					
	%N	16.12	15.80		15.97					
CH_2CONH_2	%C	7.91	7.37		7.36	93	7			
	%H	3.95	4.02		3.85					
	%N	18.45	16.80		17.76					
$CH_2COOCH_2CH_3$	%C	11.32	9.70	10.70	9.62	85	15	10.75	95	5
	%H	4.24	3.85	3.97	3.97			4.03		
	%N	15.41	14.50	14.82	14.39			14.64		

[a] Precipitated with NH_4PF_6. [b] Precipitated with $NaPF_6$.

in a minimum amount of water. The yellow solid that formed was collected and washed with ethanol and ether. The yields ranged from 70 to 80%. The analyses are given in Table I; they indicate that the complexes were contaminated with small amounts of the precipitating salt. Recrystallization attempts were unsuccessful because of the high solubility of these complexes. Reprecipitation required addition of PF_6^- ions, and coprecipitation occurred again. Cyclic voltammograms showed only one electroactive species.

Tetraammine(glycinamide)ruthenium(II) hexafluorophosphate, $[(NH_3)_4\overline{RuNH_2CH_2CONH_2}](PF_6)_2$, was prepared as described before.[4]

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

Analyses for NH_4^+ were done after separating the complex on a column of Sephadex SP-C25-120 strongly acidic cation-exchange resin (Sigma Chemical Co.). Ammonium ion was eluted with either 0.1 M $HClO_4$ or 0.1 M $LiClO_4$ at pH 3 ($HClO_4$), elution being continued until no more came off the column. The determination was performed with use of Nessler's reagent[8] against a calibration curve based on NH_4PF_6 solutions in $HClO_4$ and $LiClO_4$.

NMR spectra were obtained on a Varian XL-100 spectrometer, with a Nicolet Model TT100 computer system and pulser. Chemical shifts were referenced to Me_4Si as an external standard, by using a capillary within the NMR tube.

High-pressure liquid chromatography was performed with a Waters, Inc., instrument equipped with a variable-wavelength UV detector. The column used was a Beckman Ultrasphere (octadecylsilane, 5-μm particles) 4.6 mm × 250 mm column. The complexes were eluted from the column with use of water–methanol mixtures.

Electrochemical Measurements. Cyclovoltammograms were recorded with a PAR Model 173 potentiostat and Model 175 universal programmer system and an Omnigraph 2000 X-Y recorder. The electrochemical cell was a conventional two-compartment cell in which the reference electrode was isolated from the test solution by 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 0.1 M (CF_3COOH, $HClO_4$, or $HClO_4$ + $LiClO_4$). Potentials were converted to the normal hydrogen electrode scale by adding 240 mV.

Spectra of Ru(II) Complexes. Solutions were prepared in a Zwickel flask. In some cases, solid samples of the Ru(II) complexes were used; in these cases, allowance was made for inert salt contamination in calculating extinction coefficients. When Ru(II) was obtained from a Ru(III) complex that had been produced in situ, freshly prepared Eu^{2+} solution in 5–10% excess was used as reducing agent. This solution of known concentration ($\sim 1 \times 10^{-3}$ M) was prepared by dissolving Eu_2O_3 in 0.15 M CF_3CO_2H or CF_3SO_3H and reducing it over Zn/Hg for at least 20 min. Spectra were measured by transferring part of the solution to a spectrophotometer cell attached to the Zwickel flask by an adapter,[9] with use of gas pressure.

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

Reactions of the pentaammineruthenium(III) complexes were initiated with $S_2O_8^{2-}$ to oxidize the freshly prepared Ru(II) solutions.

Reactions with 4-$CNpyH^+$ were initiated by transferring a solution of the Ru(II) complexes to a second Zwickel flask containing the 4-$CNpyH^+$ solution in an equal concentration of CF_3SO_3H, by argon pressure. After a few seconds of bubbling argon in the mixture, part of the solution was transferred to a spectrophotometer cell as described. The reactions were monitored in the 520–570-nm range, the wavelength chosen being dependent on the concentration of the complex. The final pH of the solution was 1.2. First-order or pseudo-first-order rate constants were obtained from the slopes of the linear-squares fit of log $(A_\infty - A_t)$ vs. time plots.

Results

Pentaammineruthenium Complexes. All the Ru(II) complexes, the analyses of which are shown in Table I, have similar absorption spectra in the UV as measured in 0.1 M CF_3COOH. Each features a maximum at 265 ± 1 nm, with an extinction coefficient of 750 ± 50 M^{-1} cm^{-1}. These spectra are similar to that reported for (ethyl glycinate)pentaammineruthenium(II) (λ_{max} at 266 nm, $\epsilon = 7.2 \times 10^2$ M^{-1} cm^{-1}).[2]

Immediately following the oxidation of the Ru(II) complexes in acidic solutions (pH 1–3.5, μ = 0.1, CF_3CO_2H + CF_3CO_2Na, $HClO_4$ + $LiClO_4$, or CF_3SO_3H + CF_3SO_3Na), an absorption band with a maximum at 275 ± 2 nm, with an extinction coefficient of 550 ± 30 M^{-1} cm^{-1}, appeared. This band is similar to that of hexaammineruthenium(III)[9] and to that reported for (ethyl glycinate)pentaammineruthenium(III) ($[(NH_3)_5RuNH_2CH_2COOC_2H_5]^{3+}$).[2]

Cyclovoltammetry showed couples with $E_{1/2}$ = +185, +160, and +135 mV vs. NHE in 0.1 M CF_3COOH for the *N'*-ethylglycinamide, glycylglycine, and ethyl glycylglycinate complexes, respectively. These can be compared with $E_{1/2}$ = +160 mV for the pentaammine(glycine)ruthenium complex,[1] $E_{1/2}$ = +165 mV in 0.1 M HCl for the ethyl glycinate com-

(8) Bassett, J.; Denney, R. C.; Jefferey, G. H.; Mendham, J. "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed.; Longmans, Green and Co.: New York, 1978; p 730.

(9) Armor, J. N. Ph.D. Thesis, Stanford University, 1970.

Table II. Spectral Features and pK_a Values of the Products of $[(NH_3)_5Ru^{III}NH_2CH_2CONHR]^{3+}$ Reaction at pH 3.0[a]

R	λ_{max}[b] ($10^{-3}\epsilon$[c]) pH 3	pH 7.5	pK_a[d]
H	296 (1.5), 229 (2.3)	302 (2.2)	5.0
CH_2CH_3	317 (1.4), 225 (2.3)	304 (1.9)	6.2
CH_2COO^-	316 (1.0), 225 (2.4)	300 (1.8)	6.2
CH_2CONH_2	309 (1.2), 226 (2.1)	303 (1.9)	5.4
$CH_2COOC_2H_5$	307 (1.6), 225 (2.7)	303 (2.1)	5.2

[a] Conditions: $\mu = 0.1$ ($LiClO_4$ + $HClO_4$ or CF_3COONa + CF_3COOH); 25 °C. [b] ±1 nm. [c] M^{-1} cm^{-1}, ±5%. [d] ±0.2.

plex,[10] and $E_{1/2}$ = +185 mV in 0.1 M LiCl (pH 2) for the methyl sarcosinate complex $[(NH_3)_5RuNH(CH_3)CH_2COOCH_3]^{3+/2+}$.[10]

Products of the Reaction after Complete Oxidation of the Pentaammineruthenium(II) Complexes. Immediately after the initial change in absorption attributable to the oxidation of the Ru(II), another, much slower absorption change begins, the maximum shifting to longer wavelengths, as shown in Figure 1. The final absorption of the reaction mixture depends on the specific ligand and on pH.

At pH 3 (μ = 0.1, $LiClO_4$ + $HClO_4$), the spectra were identical, within experimental error, with the spectra of the respective (N,O) tetraammineruthenium(III) chelates.[4] These spectral features are shown in Table II. When the pH of the product solution was increased, rapid (and reversible) spectral changes took place, from which the pK_a values given in Table II were calculated. For the glycinamide, *N'*-ethylglycinamide, and glycylglycine complexes, they are identical with those of the (N,O) tetraammineruthenium(III) chelates of these ligands, as are also the absorption changes that occur upon increasing the pH.[4] When the pH of the product solution after oxidation of the glycylglycine complex was decreased, another reversible change in absorption was observed—the peak shifted to 306 nm ($\epsilon = 1.1 \times 10^3$ M^{-1} cm^{-1}), with a pK_a of 2.2 ± 0.2. This again is identical with the change that occurs in a solution of the (N,O) (glycylglycine)tetraammineruthenium(III) chelate ($[(NH_3)_4\overline{RuNH_2CH_2CONHCH_2COOH}]^{3+}$).

When oxidation of the pentaammineruthenium(II) complexes of *N'*-ethylglycinamide, glycylglycinamide, and ethyl glycylglycinate was effected at pH 1 ($HClO_4$, CF_3SO_3H), spectral shifts similar to those observed at pH 3 were also observed, but the final absorption was lower than that observed at the higher pH, and a shoulder appeared near 270 nm (Figure 1). When the pH of the product solutions was increased above 3, the absorption maxima shifted to shorter wavelengths and an absorption increase was registered. The absorption changes in the pH range 3–4 cannot be accounted for by the deprotonation of the amido nitrogen of the (N,O) chelates, since this has a pK_a of 5.2 or higher (Table II). We infer that the spectral changes in the pH range 3–4 range and the lower yield of the (N,O) chelates are the result of the formation of pentaammineaquoruthenium(III), by an aquation process which occurs in parallel to the formation of the chelate. $[Ru(NH_3)_5OH]^{2+}$ has a peak at 295 nm ($\epsilon \approx 2.1 \times 10^3$ M^{-1} cm^{-1})[11] and a pK_a of 4.2.[7] Our inference is further supported by evidence which will be introduced below.

The final spectrum after oxidation of (glycinamide)pentaammineruthenium(II) at pH 1 (0.1 M $HClO_4$ or CF_3COOH) showed a peak at 268 nm with an extinction coefficient of 740 ± 30 M^{-1} cm^{-1}. This peak shifted reversibly to 297 nm ($\epsilon = 2.1 \times 10^3$ M^{-1} cm^{-1}) at higher pH (it was taken to 7.5). It appears that, under these experimental conditions for this complex, the aquation path takes over completely, and $[Ru(NH_3)_5H_2O]^{3+}$ is the only significant Ru(III) product.

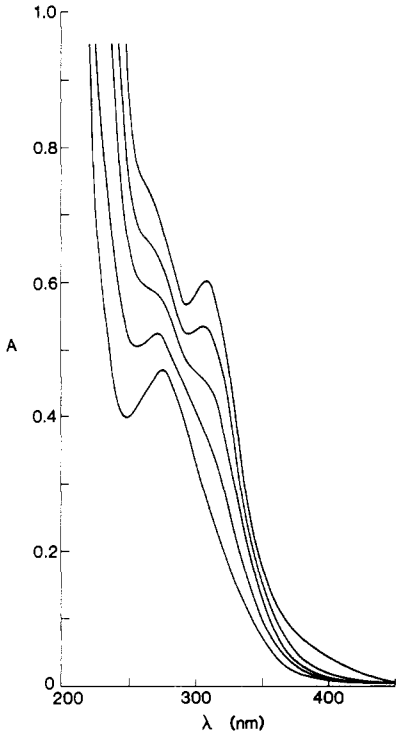


Figure 1. Ultraviolet spectrum of $[(NH_3)_5Ru^{III}NH_2CH_2CONHCH_2COOC_2H_5]^{3+}$ in 0.1 M CF_3SO_3H, immediately after oxidation by an 8% excess of $Na_2S_2O_8$, and the spectra of this solution 9, 19, 33, and 113 min after oxidation (25 °C). The spectrum is changing from that of the initial $[(NH_3)_5RuNH_2CH_2CONHCH_2COOC_2H_5]^{3+}$ ion (lowest spectrum) to a superposition of 75% $[(NH_3)_5\overline{RuNH_2CH_2CONHCH_2COOC_2H_5}]^{3+}$ and 25% $[(NH_3)_5RuOH_2]^{3+}$ (uppermost spectrum).

The final spectrum after oxidation of (glycylglycine)pentaammineruthenium(II) at pH 1 (0.1 M $HClO_4$ or CF_3SO_3H) showed a peak at 300 nm. This peak shifted to 295 nm and decreased 10% at pH 3. From the reversible change of the spectrum as a function of pH, a pK_a of 2.2 ± 0.2 was calculated. When the pH was increased further, the absorption also increased, and at pH 8, the final absorption peak had shifted to 300 nm. The absorption changes upon increase of the pH are a superposition of the changes caused by deprotonation of $[Ru(NH_3)_5H_2O]^{3+}$ and of another product, and they can be accommodated by a pK_a of 4.2 for $[Ru(NH_3)_5H_2O]^{3+}$ and 6.2 for the other product.

Oxidation of the *N'*-ethylglycinamide, glycylglycine, glycylglycinamide, and ethyl glycylglycinate complexes in 0.1 M CF_3COOH solutions produced a final absorption spectrum that was somewhat different from the spectra observed when the solutions contained $HClO_4$ or CF_3SO_3H instead of CF_3COOH. These differences can be accounted for by assuming that $[Ru(NH_3)_5O_2CCF_3]^{2+}$ is one of the reaction products. This complex has an absorption maximum at 285 nm ($\epsilon = 1.19 \times 10^3$ M^{-1} cm^{-1}).[12]

The spectra of the product solutions after oxidation of the Ru(II) complexes in perchlorate or in trifluoromethanesulfonate media were stable for at least a few hours, but on an extended time scale changes were observed, the absorption shifting to shorter wavelengths, reaching 260–265 nm in a few days. These changes were faster at pH 1 than at lower acidities. The product of the *N'*-ethylglycinamide complex is more stable than the others, and its absorption did not change significantly for several days. The spectral changes

(10) Yeh, A.; Taube, H. *Inorg. Chem.* **1980**, *19*, 3750.
(11) Eliades, T.; Harris, R. O.; Reinsalu, P. *Can. J. Chem.* **1969**, *47*, 3824.
(12) Stritar, J. A.; Taube, H. *Inorg. Chem.* **1969**, *8*, 2281.

Table III. Spectral Features of the Products of $[(NH_3)_5Ru^{II}NH_2CH_2CONHR]^{2+}$ Oxidation after Partial Reduction by Eu^{2+} [a]

R	λ_{max}, nm	R	λ_{max}, nm
H	360, 252	CH_2COOH [c]	387, 255
CH_2CH_3	406, 263	CH_2CONH_2	390, 255
CH_2COO^- [b]	406, 262	$CH_2COOC_2H_5$	385, 255

[a] Conditions: $\mu = 0.1$ ($CF_3SO_3H + CF_3SO_3Na$); pH 1.3; 25 °C. [b] pH 8.5. [c] pH 2.2.

were much faster in 0.1 M CF_3COOH and could be observed within a few hours.

On partial (10%) reduction of the product solutions of each of these complexes with Eu^{2+}, spectral changes ensued which were completed within a few minutes, the final spectra having the features shown in Table III. For all of the complexes studied, except the *N'*-ethylglycinamide, the change could be observed at pH 1.2, but to observe similar changes in the product solutions of the latter, the pH had to be raised above 2. The spectra obtained after partial reduction of the product solutions of glycinamide, *N'*-ethylglycinamide, and glycylglycine complexes are identical with those of the (N,N') tetraammineruthenium(III) chelates of these ligands. This is true also of the changes in absorption in ~8 M $HClO_4$, where the absorption shifts to shorter wavelengths and decreases, and the change in the absorption of the glycylglycine complex product solution, which shows a pK_a of 3.2.[4]

The solutions of the products of the *N'*-ethylglycinamide and of the glycylglycine complexes were analyzed for NH_4^+, about 3 h after oxidation. In both cases, these results agree with an assignment of the products at pH 3 as tetraammine chelates and, at pH 1, as a mixtures of ~60% tetraammine chelates and ~40% $[Ru(NH_3)_5H_2O]^{3+}$.

In one experiment with the product solution of *N'*-ethylglycinamide, at 0.1 M $HClO_4$, $[Ru(NH_3)_5H_2O]^{3+}$ was eluted from the column with 1 M $LiClO_4$ at pH 2 ($HClO_4$), followed by the elution of the tetraammine chelate with the same eluent. The yield of $[Ru(NH_3)_5H_2O]^{3+}$ was determined, by the spectrum with $\epsilon_{268} = 7.5 \times 10^2$ M^{-1} cm^{-1},[9] as 44 ± 5% and that of the chelate, with $\epsilon_{317} = 1.4 \times 10^3$ M^{-1} cm^{-1}, as 59 ± 5%.

Reaction of the Reduced Products with 4-CNpyH$^+$. The oxidation products of the glycylglycine complex were reduced with Eu^{2+} about 2.5 h after oxidation, and the reactions of the reduced products with 4-$CNpyH^+$ were followed. The products formed at pH 3 showed a monophasic pseudo-first-order reaction, the rate of which was proportional to the 4-$CNpyH^+$ concentration in the range 0.07–0.3 M. The specific rate at 25 °C is 0.018 ± 0.002 M^{-1} s^{-1} and is close to that measured[4] for reaction of the (N,O) form of (glycylglycine)tetraammineruthenium(II) with 4-$CNpyH^+$ (0.020 ± 0.002 M^{-1} s^{-1}). The product solution formed at pH 1, which had been treated in the same manner, showed a biphasic reaction. Both phases were pseudo first order and became faster as the 4-$CNpyH^+$ concentration was increased. The kinetic analysis was done by first analyzing the slower phase and using the extrapolated initial value of the absorption of this phase as the final value of the absorption of the faster phase. This analysis indicated that 56 ± 5% of the absorption change occurred in the slower phase and 44 ± 5% in the faster. The specific rate constants calculated are 0.015 ± 0.002 M^{-1} s^{-1} for the slower phase and 0.13 M^{-1} s^{-1} for the faster. The rate of the faster phase is comparable to the rate of $[Ru(NH_3)_5H_2O]^{2+}$ with 4-$CNpyH^+$ under similar experimental conditions—0.11 M^{-1} s^{-1}.[4]

Rates of Reactions after Oxidation of the Pentaammineruthenium(II) Complexes. Rates were measured as a function of H^+ concentration in the range 0.001–0.1 M, at a constant ionic strength of 0.1 M, with $LiClO_4 + HClO_4$. Throughout this pH range, the kinetic results were unchanged when $CF_3SO_3H + CF_3COONa$, or $CF_3COOH + CF_3COONa$, was used, even though the spectral results with the last pair were different at low pH, as noted above.

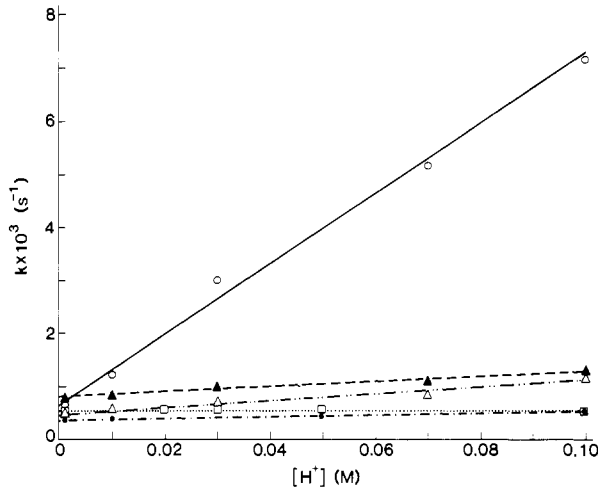


Figure 2. Rate constants of the reactions of $[(NH_3)_5Ru^{III}NH_2CH_2CONHR]^{3+}$ as a function of pH (μ = 0.1 ($HClO_4 + LiClO_4$), 25 °C): (○) R = H (—); (▲) R = CH_2CH_3 (- - -); (□) R = CH_2COOH (···); (●) R = $CH_2COOC_2H_5$ (-·-·); (△) R = CH_2CONH_2 (-··-··).

Table IV. Rates of the pH-Independent (k') and pH-Dependent (k'') Paths for the Reactions of $[(NH_3)_5Ru^{III}NH_2CH_2CONHR]^{3+}$ [a]

R	$10^4k'$, s^{-1}	$10^3k''$, M^{-1} s^{-1}	R	$10^4k'$, s^{-1}	$10^3k''$, M^{-1} s^{-1}
H	6.4	66	CH_2CONH_2	4.5	6.8
CH_2CH_3	8.0	4.9	CH_2COOH	5.5	<0.3
$CH_2COOC_2H_5$	4.1	1.4			

[a] Conditions: $\mu = 0.1$ ($HClO_4 + LiClO_4$); 25 °C.

The reactions are first order in [Ru(III)], as was shown by following the course of reaction in each experiment as well as by varying the concentration of the pentaammine complexes over the range 2×10^{-4}–5×10^{-3} M. In Figure 2, the values of k_{obsd}, where k_{obsd} is the pseudo-first-order rate constant as determined for each experiment, are shown as a function of $[H^+]$. The rates can be expressed as

$$k_{obsd} = k' + k''[H^+]$$

Table IV gives the values of k' and k'' for the various ligands, as calculated from the intercept and slope of Figure 2.

Reactions after Partial Oxidation of the Pentaammineruthenium(II) Complexes. Both rate and stoichiometry are affected when the oxidation of the Ru(II) complexes is incomplete. The reaction was initiated by dissolving the solid Ru(II) complexes in an argon-saturated solution that contained all other solutes, including the oxidant $S_2O_8^{2-}$. The ionic strength was kept at 0.1 M ($CF_3SO_3H + CF_3SO_3Na$), in the pH range 1–3. Immediately after dissolution of the complex, part of the solution was transferred into a spectrophotometer cell attached to the Zwickel flask by an adapter, and the spectrum was recorded as a function of time. The Ru(II) concentration left after the oxidation by $Na_2S_2O_8$ was ~8×10^{-4} M, and this represented half of the total ruthenium.

The effect of Ru(II) both on the yield of the tetraammine products and on the rate of their formation is shown in Table V.

In one case, that of the ethyl glycylglycinate complex, the concentration of Ru(II) was varied over the practical range. The data accumulated in this series of experiments are summarized in Table VI. When k_{obsd} is plotted against [Ru(II)],

Table V. Rates and Yields of Formation of the Tetraammine Chelates after Partial Oxidation of $[Ru^{II}(NH_3)_5NH_2CH_2CONHR]^{2+}$ As Compared to Results after Full Oxidation[a]

		no Ru(II)			~8×10^{-4} M Ru(II)	
		% tetraammine[b]				
R	pH	obsd	calcd[d]	k_{obsd}, s^{-1}	% tetraammine[c]	k_{obsd}, s^{-1}
H	1	<10	9	7.2×10^{-3}		
	2	~40	48	1.2×10^{-3}		
	3	~95	90	6.4×10^{-4}	~15	3.5×10^{-3}
CH_2CH_3	1	60	62	1.3×10^{-3}	~30	2.5×10^{-3}
	2	~90	94	8.2×10^{-4}	~90	8.0×10^{-4}
	3	100	99	7.9×10^{-4}	100	7.6×10^{-4}
$CH_2COOC_2H_5$	1	77	75	5.4×10^{-4}	~35	1.3×10^{-3}
	2	85	97	4.4×10^{-4}		
	3	100	100	3.8×10^{-4}	100	3.1×10^{-4}
CH_2CONH_2	1	48	43	1.2×10^{-3}	25	2.1×10^{-3}
	2	85	86	5.7×10^{-4}		
	3	100	98	4.1×10^{-4}		
CH_2COOH	1	60		5.4×10^{-4}	~45	1.2×10^{-3}
	2	~90		5.5×10^{-4}		
	3	100		5.7×10^{-4}		

[a] Conditions: $\mu = 0.1$ ($HClO_4$ + $LiClO_4$ or CF_3SO_3H + CF_3SO_3Na); $[Ru]_{total} = 1.6 \times 10^{-3}$ M; 25 °C. [b] (N,O) chelate. [c] Sum of (N,O) and (N,N′) chelates. [d] Calculated as $k'/(k' + k''[H^+])$ thus on the assumption that only the k' path produces tetraammine.

Table VI. Rates and Yields of Formation of the Tetraammine Chelates after Partial Oxidation of $[(NH_3)_5RuNH_2CH_2CONHCH_2COOC_2H_5]^{2+}$ by $S_2O_8^{2-}$, as a Function of Ru(II) Concentration[a]

10^4[Ru(II)], M[b]	10^4k, s^{-1}	% tetraammine yield	
		exptl[c]	calcd[d]
0	5.4	77	76
2.0	7.5	50	55
4.8	9.8	40	42
9.8	13	30	32
17	16	25	26

[a] Conditions: pH 1.0 (CF_3SO_3H); 25 °C. [b] Calculated from $[Ru]_{total} - 2[S_2O_8^{2-}]$. [c] ±5%. [d] Calculated from k'/k_{obsd}, where $k' = 4.1 \times 10^{-4}$ s^{-1} (Table IV).

Table VII. NMR Spectral Features of the Reaction Products of $[(NH_3)_5Ru^{II}NH_2CH_2CONHR]^{2+}$, after Oxidation[a]

R = CH_2COOH		R = $CH_2COOC_2H_5$		
product at pD = 1	product at pD = 3	product at pD = 1	product at pD = 3	R = H[b]
+41.0				
+30.9	+31.0	+31.4	+31.0	
−1.0		+2.6[c]	+2.6[c]	
		+2.0[c]	+2.0[c]	
−11.0	−10.9	−10.6	−10.8	−11.8

[a] Conditions: solvent D_2O; all spectra recorded at pD = 1 ($DClO_4$); $\mu = 0.1$ ($DClO_4$ + $LiClO_4$); [Ru(III)] ≈ 5×10^{-3} M; chemical shifts in ppm vs. an external standard of Me_4Si. [b] Produced by direct synthesis by way of *cis*-$Ru(NH_3)_4(H_2O)_2^{2+}$ and ligand. [c] Sharp peaks.

the linear dependence is not maintained over the range of concentrations investigated. Rather there is rate saturation, which is qualitatively like that observed for the rate of linkage isomerization of the ethyl glycinate complex as a function of pH, but a plot of $1/k_{obsd}$ vs. 1/[Ru(II)] also does not yield a straight line.

In all cases, except that of the *N*′-ethylglycinamide complex, the products as determined from the spectra were $[Ru(NH_3)_5H_2O]^{3+}$ and the (N,N′) tetraammine chelates over the pH range covered. In the case of the *N*′-ethylglycinamide complex, the spectrum of the final solution at pH 1 showed it to be comprised of a mixture of $[Ru(NH_3)_5H_2O]^{3+}$ and the (N,O) form of the (*N*′-ethylglycinamide)tetraammineruthenium(III) complex; at pH 2, the spectrum showed that the (N,N′) species was also eventually formed; at pH 3, the spectrum indicated that the initial product was almost solely the (N,O) chelate, which then isomerized to the (N,N′) chelate.

Products of the (Glycylglycine)pentaammineruthenium(III) Complex. In a comparison of the absorption spectrum of the tetraammine chelate species produced from (glycylglycine)-pentaammineruthenium(III) at pH 3 to that of the species produced at pH 1, after they have been adjusted to the same pH and allowance has been made for the formation of some $Ru(NH_3)_5H_2O^{3+}$ at the lower pH, significant differences are noted. These differences are greater when the comparison is made at pH 3 than at pH 1. The spectrum of the species produced at pH 1 can be transformed into that produced at pH 3, by full reduction of the products (Eu^{2+}), followed by full oxidation ($S_2O_8^{2-}$). The solution obtained this way showed spectral changes as a function of pH, which were the same as those characteristic of the solution produced at pH 3. This method was not effective in the other direction: when a solution of the oxidation product at pH 3 was fully reduced and then fully oxidized, the spectrum and its behavior as a function of pH were the same as before the redox cycle.

Differences are noted also in the NMR spectra. These were measured in product solutions prepared in D_2O, both at pD = 3 and pD = 1, ca. $2^1/_2$ h after oxidation, the solutions having been adjusted to common conditions (pD = 1 ($DClO_4$), μ = 0.1 ($DClO_4$ + $LiClO_4$)). Since Ru(III) is paramagnetic, the peaks are broadened, and to obtain useful spectra, data from 1×10^3 to 10×10^3 scans were accumulated. The results are summarized in Table VII. The table contains also the NMR data for the (N,O) form of (glycinamide)tetraammineruthenium(III) in 0.1 M $DClO_4$. The solution was prepared by dissolving the solid Ru(II) chelate in a solution containing an ~10% excess of $Na_2S_2O_8$ in 0.1 M $DClO_4$. The results enable us to assign to peak near −11 ppm to the methylene group which is near the amino end of the ligand in the chelate ring.

The NMR spectra of the product solutions of the reaction of (ethyl glycylglycinate)pentaammineruthenium(III) in $DClO_4/D_2O$ solutions at pD = 1 and at pD = 3 were also recorded, after the pD was adjusted to 1. These results are also shown in Table VII. All the peaks, except those at 2.0 and at 2.6 ppm in the spectrum of the ethyl glycylglycinate complex, were broad. We assign these two sharp peaks to the ethyl group of the ester.

Despite the differences in the UV absorption and NMR spectra, the products of the oxidation at pH 3 and pH 1 show several very similar properties: (a) both have pK_a's of 2.2 and 6.2; (b) both show similar cyclovoltammograms with $E_{1/2}$ = 130 mV vs. NHE in 0.1 M $HClO_4$, as does also the (N,O) (glycylglycine)ruthenium(III) chelate;[4] (c) both are tetraammines; (d) the rates of reaction of the reduced forms of both with 4-CNpyH$^+$ are similar; (e) both have the same retention time and could not be separated on a reversed-phase octadecylsilane column, with 10–20% aqueous methanol (pH 2, CF_3COOH) as the eluent. Under these conditions, $[Ru(NH_3)_5H_2O]^{3+}$ could easily be separated from the other products.

Discussion

Aquation of $Ru(NH_3)_6^{3+}$ is a very slow process, the half-time at 25 °C in aqueous acidic solution for conversion to the pentaammine aquo complex being ~2 years.[13] When an ammonia is replaced by the amine function of glycine or of a glycine ester, in acidic solution, rapid rearrangement to a pentaammine carboxylato complex occurs.[1,2] Both kinds of behavior are in marked contrast to that observed when the sixth ligand is an amido derivative of an amino acid, where, as we have observed, the dominant product at pH 3, on a time scale not much slower than that of linkage isomerization for glycine or its ester, is the (N,O) tetraammine chelate. The quantitative difference between the rate of ring closure to produce a tetraammine for the glycine ester and *N'*-ethylglycinamide is quite large. From the results of analysis for NH_4^+ and the total reaction rate,[14] the upper limit for the specific rate of ring closure in the former system is calculated as 2×10^{-7} s^{-1}; for ring closure in the latter case it is 8×10^{-4} s^{-1}. The enhanced rate for the amide is in harmony with there being more negative charge on the "carbonyl" oxygen in the case of the amide than of the ester and with the proposition to be commented on further below, that, in substitution on Ru(III), bond making in the activated complex is important.

The discrimination in favor of ring closure on oxygen of the amide group rather than nitrogen is remarkable. Is it a consequence of the fact that for the former a σ lone pair is available but for the latter only a π lone pair? That ring closure, as we have asserted, takes place on oxygen rather than nitrogen is as certain as the structural assignment we have made, based on what we believe to be a direct synthesis of the (N,N') species, as well as of an independent route to the (N,O) species that involves the oxidation of the Ru(II) tetraammine chelate.[4] The properties of the products of ring closure are in accord in all particulars—the UV spectra and their changes with Ph as well as after partial reduction—with those of the species previously identified as (N,O) chelates. Attempts in our present investigations to isolate the products as solids were unsuccessful. This failure is partly attributable to the fact that the product solutions were rather dilute—~1×10^{-3} M—in Ru(III). At higher concentrations, 1×10^{-2} M or higher, new features appear in the spectra, indicating that processes second order in reactant play a role, but those have not been investigated.

The rate law governing the consumption of the pentaammineruthenium(III) reactant as a function of acidity has been shown to take the form $k_{obsd} = k' + k''[H^+]$. Columns three and four of Table V give the observed and calculated yields of the tetraammine products in the absence of Ru(II) (calculated yield of tetraammine $k'/(k' + k''[H^+])$). Comparison of the data in these two columns shows that the first term in the rate law corresponds to the production of the tetraammine and the second to the production of $Ru(NH_3)_5OH_2^{3+}$. The two terms represent independent processes; in particular they do not involve a common intermediate. (The glycylglycine system, which is complicated by the protonation equilibrium of the hetero ligand, is an exception—its rate of reaction is independent of pH (see below).)

On this basis, the rate of formation of the tetraammine is independent of pH in the acidity range that was investigated, while the rate of aquation is first order in $[H^+]$ in the same range. It is likely that the latter reaction involves the same mechanism as does linkage isomerization for the glycine ester complex. This mechanism, as adapted to the present systems, is

$$[(NH_3)_5Ru^{III}NH_2CH_2CONHR]^{3+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(NH_3)_5Ru^{III}O{=}C(NHR)(CH_2NH_2)]^{3+} \quad (1)$$

$$[(NH_3)_5Ru^{III}O{=}C(NHR)(CH_2NH_2)]^{3+} + H^+ \overset{K_H}{\rightleftharpoons} [(NH_3)_5Ru^{III}O{=}C(NHR)(CH_2NH_3)]^{4+} \quad (2)$$

$$[(NH_3)_5Ru^{III}O{=}C(NHR)(CH_2NH_3)]^{4+} \xrightarrow{k_2} [(NH_3)_5Ru^{III}OH_2]^{3+} + NH_3CH_2CONHR^+ \quad (3)$$

It leads to the rate law

$$\frac{d[(NH_3)_5RuOH_2^{3+}]}{dt} = \frac{k_1k_2K_H[H^+]}{k_{-1} + k_2K_H[H^+]}[(NH_3)_5Ru^{III}NH_2CH_2CONHR^{3+}]$$

so that

$$k'' = \frac{k_1k_2K_H[H^+]}{k_{-1} + k_2K_H[H^+]}$$

The rate will be linear in $[H^+]$, as reported, if $k_2K_H[H^+] << k_{-1}$. For the ethyl glycinate system[2] in the same range of $[H^+]$, the two terms are much more nearly alike and rate saturation in 0.1 M H^+ is substantial. The values of K_H for the two different systems are expected to be almost equal, so that the difference between them resides in the ratio of k_2/k_{-1}. But because a greater negative charge on the carbonyl oxygen of the amide compared to that on the ester, as discussed above, will decrease both k_{-1} and k_2, the net effect could not have been predicted.

Bond breaking is usually considered to be much more important than bond making in substitution in octahedral metal ion complexes.[15] The systems under study provide an exception to this. The rate of the pH-independent path by which

(13) Armor, J. N.; Scheidegger, H. A.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 5928.

(14) Yeh et al.[2] set a limit of 2% production of tetraammine in the reaction of the ethyl glycinate complex of pentaammineruthenium(III) in 1 M $HClO_4$; we repeated the determination of NH_4^+ production in the same system at pH 3 and found a similar upper limit. At higher pH, k for the disappearance of the Ru(III) complex is ~1×10^{-5} s^{-1}.

(15) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions-A Study of Metal Complexes in Solution", 2nd ed.; Wiley: New York, 1967; Chapter 3.

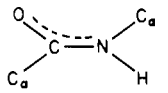
the tetraammine chelates are formed is, as already noted, much less for the ethyl glycinato complex[2,14] than for the amide derivatives, and this implies a crucial role for the ligand in determining the reaction path. α-Alaninate, which can form a five-membered ring with a metal center, with its amine nitrogen and carboxylato oxygen attached to the metal, readily undergoes linkage isomerization on $Ru(NH_3)_5^{3+}$; in contrast, β-alaninate, which would lead to a six-membered ring including the metal centr, reacts much less readily.[3] A recent study of substitutions of Cl^-, H_2O, and $CF_3SO_3^-$ on $[Ru(NH_3)_6]^{3+}$ suggests bond making to be more important than bond breaking in this system as well, with H_2O being the preferred nucleophile.[16]

The observations made with Ru(II) in the reaction system are in accord with the analysis that has been made. Ru(II) is expected to react with the pentaammine carbonyl-bound intermediate, thus in effect increasing the rate of the k_2 step: $k_2' = k_{Ru(II)}[Ru(II)]$. Were we in the concentration regime with respect to H^+ in which the rate of aquo formation is independent of acidity, Ru(II) could not affect the stoichiometry or the rate; it affects both. A detailed kinetic analysis of the effect of Ru(II) on the system was not attempted, because it is quite complicated. Among the complications are these: (a) The efficiency of Ru(II) will depend on acidity and will reach a maximum short of the regime in which $k_2K_H[H^+] >> k_{-1}$, where it becomes independent of acidity; it decreases in efficiency at low acidity because then less of the Ru(III) at the steady state is present as the carbonyl-bound intermediate. (b) Ru(II) also catalyzes the redistribution of the Ru(III) product between the (N,O) and (N,N′) forms. An effort was made in one case, that of the ethyl glycylglycinate complex, to arrive at an estimate of the specific rate of linkage isomerization (k_1) by raising the concentration of Ru(II). The values of k_{obsd} (Table VI), when plotted against [Ru(II)], show that though there is evidence of rate saturation at high [Ru(II)], a limiting rate is not attained. A plot of $1/(k_{obsd} - k')$ vs. $1/[Ru(II)]$ is not linear, because the k_2 step is now composed of two parallel paths: $k_2' = k_2 + k_{Ru(II)}[Ru(II)]$. Without a more complete study, it is impossible to extract an accurate value of k_1 from the data. It exceeds $k_{obsd} - k'$, or 1.0×10^{-3} s^{-1}; from the leveling off observed at high [Ru(II)] we think that it is unlikely to be in excess of 2×10^{-3} s^{-1}. Thus, k_1 is not much greater than that observed for ethyl glycinate. The data of Table V, however, show that k_1 is very sensitive to the nature of the group R on the amide function. For the glycinamide complex, there is no evidence of rate saturation at the highest acidity, and in this case k_1 is likely to be at least 5-fold greater than $k_{obsd} - k'$, or 300×10^{-3} s^{-1}. A comparison with ethyl glycinate ($k_1 = 1.14 \times 10^{-3}$ s^{-1}) is appropriate, because in neither case is there a complication by bulky groups. The enhanced rate for the amide is in line with the greater negative charge on the carbonyl of the amide. The facility of the k_1 process for the glycinamide is really quite remarkable; both for it and for the formation of the tetraammine, a Ru(III)–N bond must be severed. That in which the carbonyl replaces a nitrogen of the same molecule is at least 500 times more rapid than that in which a cis ammonia is replaced.

In concluding the discussion of the effect of Ru(II), we draw attention to the fact that the product yields calculated, assuming that the k' path yields tetraammine only and the remaining paths aquo only (see Table V), confirm this assumption.

The glycylglycine complex behaves differently from the other systems, because although the specific rate of reaction is almost independent of acidity, the Ru(III) product distribution is strongly affected by it. In an analysis of the data the protonation equilibrium must be taken into account. Even allowing for this, we have been unable to fit the data by assuming parallel reaction paths. The behavior suggests the formation of an intermediate, the reactions of which depend on acidity. The glycylglycine complex differs also in another respect, as featuring two products which resemble each other in certain chemical properties but which exhibit different absorption and NMR spectra.

The fact that, of all the compounds studied, only the glycylglycine complex, which is the only one having a free carboxylate, gives two tetraammine products suggests that these two products, which are both (N,O) tetraammine chelates, differ in some interaction of the carboxylate group. A study of the three-dimensional model of this chelate shows that two isomers of the molecule are possible, differing in the configuration around the peptide C–N bond:



The peptide configuration is known to be planar.[17] Rotation around the C–N bond is restricted,[18] and when the oxygen is bound to a metal center, the rotational barrier about the C–N bond is expected to increase because the double-bond character increases. In one configuration the oxygen is trans to the hydrogen bound to the nitrogen, whereas in the second configuration, the oxygen is cis to this hydrogen. The trans configuration is the more stable in free peptides.[17]

When the (N,O) chelate is in the trans configuration, the carboxylate oxygen can approach a hydrogen of an ammonia ligand within a hydrogen bond distance. In the second isomer, which has the cis configuration, such a hydrogen bond is impossible.

In the higher pH range of this study, only one tetraammine product is observed. We infer that this is the isomer in which a hydrogen bond is formed, namely the trans isomer. This assignment is consistent with the species showing carboxylate ion-to-metal charge-transfer absorption at lower energy. The two peaks observed in the NMR spectrum of this product can be assigned to the two methylene groups present in the molecule. At lower pH, when the carboxylate is at least partially protonated, both isomers are produced, as shown by the NMR spectrum.

The equilibration from the cis form to the more stable trans by Ru(II) is expected from the fact that on Ru(II) the (N,O) and (N,N′) isomers are in labile equilibrium.[4] The state in which the chelate is opened thus appears to be readily accessible in the Ru(II) complexes.

To our knowledge, the evidence we cite for an increase in the C–N rotational barrier when a metal ion is coordinated to the oxygen of the amide is the first of its kind. However, the interaction between the carboxylate of a ligand and a hydrogen of an adjacent amino ligand of the kind we suggest has been observed in several systems.[19-21] When L-glutamic acid reacts with racemic (carbonato)bis(ethylenediamine)cobalt(III), the D enantiomer of the diaquobis(ethylenediamine)cobalt(III) ion reacts much more rapidly than the L enantiomer, and the salt containing the D isomer is much less soluble in water. Crystallographic data show that in the D isomer the free carboxylate forms a hydrogen bond with an

(16) Lay, P. A.; Taube, H., manuscript in preparation.

(17) Marsh, R. E.; Donohue, J. *Adv. Protein Chem.* **1967**, *22*, 235.
(18) Robin, M. B.; Bovey, F. A.; Basch, H. In "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; Chapter 1.
(19) Dunlop, J. H.; Gillard, R. D.; Payne, N. C.; Robertson, G. B. *Chem. Commun.* **1966**, 874.
(20) Job, R.; Kelleher, P. J.; Stallings, W. C., Jr.; Monti, C. T.; Glusker, J. P. *Inorg. Chem.* **1982**, *21*, 3760.
(21) Keyes, W. E.; Legg, J. I. *J. Am. Chem. Soc.* **1973**, *95*, 3431.

N-H group of an ethylenediamine chelate ring. Such an interaction is impossible in the L enantiomer.[19] X-ray crystallography of the complex (citrato)(triethylenetetramine)cobalt(III) shows a three-point attachment of the citrato ligand. It is coordinated via the hydroxyl group and one of the oxygen atoms of the central carboxyl group, and in addition, an internal hydrogen bond between one of the terminal carboxyl groups, and the tetraamine ligand is formed.[20] Hydrogen bond formation between the side chain carboxylate of aspartic acid chelated in (aspartato)bis(ethylenediamine)cobalt(III) and one of the amino ligands was invoked to explain the asymmetric deuteration of the α-carbon of the amino acid ligand.[21]

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Registry No. $[(NH_3)_5Ru^{II}NH_2CH_2CONH_2](PF_6)_2$, 86885-72-5; $[(NH_3)_5Ru^{II}NH_2CH_2CONHCH_2CH_3](PF_6)_2$, 86885-74-7; $[(NH_3)_5Ru^{II}NH_2CH_2CONHCH_2COOH](PF_6)_2$, 86885-77-0; $[(NH_3)_5Ru^{II}NH_2CH_2CONHCH_2CONH_2](PF_6)_2$, 86885-79-2; $[(NH_3)_5Ru^{II}NH_2CH_2CONHCH_2COOCH_2CH_3](PF_6)_2$, 86885-81-6; $[(NH_3)_5Ru^{III}NH_2CH_2CONH_2]^{3+}$, 86885-82-7; $[(NH_3)_5Ru^{III}NH_2CH_2CONHCH_2CH_3]^{3+}$, 86885-83-8; $[(NH_3)_5Ru^{III}NH_2CH_2CONHCH_2COO^-]^{2+}$, 86885-84-9; $[(NH_3)_5Ru^{III}NH_2CH_2CONHCH_2CONH_2]^{3+}$, 86885-85-0; $[(NH_3)_5Ru^{III}NH_2CH_2CONHCH_2COOC_2H_5]^{3+}$, 86885-86-1; (glycinamide-*N*,*O*)tetraammineruthenium(III), 85320-45-2; (*N'*-ethylglycinamide-*N*,*O*)tetraammineruthenium(III), 85320-46-3; (glycylglycinato-*N*,*O*)tetraammineruthenium(III), 85320-47-4; (glycylglycinamide-*N*,*O*)tetraammineruthenium(III), 86885-87-2; (ethyl glycylglycinate-*N*,*O*)-tetraammineruthenium(III), 86885-88-3; (glycinamide-*N*,*N'*)tetraammineruthenium(III), 86885-89-4; (glycylglycinato-*N*,*N'*)tetraammineruthenium(III), 86885-90-7; (glycylglycinamide-*N*,*N'*)-tetraammineruthenium(III), 86885-91-8; (ethyl glycylglycinate-*N*,*N'*)tetraammineruthenium(III), 86885-92-9.

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A New μ-Peroxo Cobalt(III) Complex: Kinetics and Mechanism of the Oxygenation of the Bis(*o*-phenylenediamine)cobalt(II) Ion

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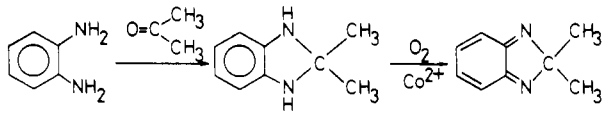
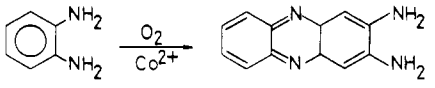
Methanol solutions of cobalt(II) salts containing a large excess of *o*-phenylenediamine (OPD) absorb 0.5 mol of dioxygen/mol of cobalt, leading to the formation of the purple (μ-peroxo)bis[bis(*o*-phenylenediamine)cobalt(III)] ion. Subsequent slower O_2 uptake is accompanied by ligand oxidation. Stopped-flow kinetic results are consistent with a two-step oxygenation mechanism of the bis(*o*-phenylenediamine)cobalt(II) ion, the only reactive species in the $Co(OPD)_n^{2+}$ system (n = 1-6). The rate constant for the reversible first step, k_1, is 47.0 ± 7.0 mol^{-1} dm^3 s^{-1}, and k_{-1}/k_2 = (8.0 ± 2.0) × 10^{-6} mol dm^{-3}. Kinetic analysis also provides the first two stability constants K_1 = 14.0 ± 3.0 and K_2 = 4.5 ± 1.3 mol^{-1} dm^3, not available from other sources.

Introduction

We have recently reported that *o*-phenylenediamine (OPD) can be catalytically oxidized by molecular O_2 in the presence of Co^{2+} salts. The product of oxidation depends on the type of solvent used.[2] In acetone, 2,2-dimethyl-2*H*-benzimidazole is formed via 2,2-dimethyl-2,3-dihydrobenzimidazole with good selectivity.



In nonreactive solvents, 2,3-diaminophenazine (DAP) is the only product.



We have found that the initial stages of these catalytic reactions consist of the oxygenation of the OPD/cobalt(II) system. In this paper, we report on the nature of oxygen complexes formed and describe the kinetics and mechanism of the dioxygen absorption process.

Results and Discussion

Stoichiometry of Oxygenation. Under anaerobic conditions, various cobalt(II) salts have been reported to form a series of OPD complexes of the formula $Co(ODP)_nX_2$, where n = 1, 2, ..., 6 and X is a univalent anion.[3-6] No data are available for the stabilities of these complexes. Their sensitivity to dioxygen has been noted, but there is no information concerning their reactions with O_2.

Addition of cobalt(II) perchlorate to a solution of OPD in MeOH saturated with dioxygen leads to immediate appearance of an intense purple color. Successive UV-vis spectra of the system are shown in Figure 1. Initially, up to spectrum 4, the absorbance increases monotonically, reflecting the progress of a single reaction. The color is due either to a single species or to a set of products in a constant ratio, which follows from the constant ratio of absorbances at any selected wavelength. After the solution is allowed to stand, a new band appears at 440 nm, indicating the formation of DAP, the product of catalytic OPD oxidation. The spectra exhibiting the 440-nm band (e.g., spectrum 5 in Figure 1) are superpositions of spectrum 4 and of the spectrum of DAP, up to at least 50% conversion of OPD to DAP.

The final spectrum 4, preceding the noticeable start of OPD oxidation, is independent of the cobalt(II) salt used (X may be NO_3^- or Cl^-, too) and of the type of solvent employed (MeOH, THF, acetone). Beer's law was found to be valid in the 400-800-nm range at various initial CoX_2 concentrations.

The absorbance of the OPD/Co^{2+} system under O_2-free N_2 was found to be negligible compared with the spectra shown in Figure 1.

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(2) Németh, S.; Simándi, L. I. *J. Mol. Catal.* **1982**, *14*, 241-246.
(3) Duff, E. J. *J. Chem. Soc. A* **1968**, 434-437, 836-837.
(4) Marks, D. R.; Philips, D. J.; Redfern, J. P. *J. Chem. Soc. A*, **1967**, 1464-1469; *Ibid.* **1968**, 2013-2017.
(5) Duff, E. J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2106-2107.
(6) Kakazai, B. J. A.; Melson, G. A. *Inorg. Chim. Acta* **1970**, *4*, 360-364.

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