isotropic shifts would be expected to increase with increasing salt concentration and to decrease with temperature. The ratios of isotropic shifts should be essentially independent of these variables. Peak widths should show the same general behavior as the shifts for simple systems.

In chloroform solution the cation protons of $[(C_4H_9)_4N][Co(C_6H_5)_3PI_3]$ systems show resonance shifts which *decrease* with increasing concentration and the shift ratios exhibit a small but definite dependence on concentration.[14] In analogous systems where the anion is $[Co(acac)_3^-]$ the shifts increase with concentration, but the magnitudes of the shifts and their ratios show complicated temperature dependencies[5] indicating that this system is far from ideal. For chloroform solutions of the salt $[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PI_3]$ the shifts generally decrease with increasing salt concentration, and the shift ratios are by no means constant.[14] The above observations may be taken as evidence for ion clustering in these solutions.

In cases where one is interested in ion pairing rather than ion clustering it is important to assess the effect of clustering on the experimental observations. The anions of interest here have only one position at which a cation can approach closely;[2] all other models of approach will be more or less equally favored. A cluster will consist of an ion pair with other cations (and anions) more or less randomly oriented with respect to the principal paramagnetic anion. For such random orientation the dipolar shift averages to zero[2b,3] and this would be expected to decrease the magnitude of the observed isotropic shifts, but not much affect the shift ratios. Preferred orientation within a cluster would, however, tend to modify both the shift magnitude and ratios. Comparison of isotropic shift ratios over a range of concentration is a good experimental test for this effect. The measured line broadening, which depends on $\langle R^{-6}\rangle_{av}$, will, unlike the dipolar shifts, not tend to average to zero. The observed broadenings will represent a weighted average over clusters and pairs and thus estimates of ion-pair interionic distances using this method will be affected by ion aggregation, perhaps to a greater extent than the shift measurements. Because of the limited solubility of $[(C_6H_5)_4As][Co(C_6H_5)_3PI_3]$ in chloroform (<0.01 M), the variation of the shift ratios and line-width ratios with concentration could not be assessed; however, the small concentration of this salt present in solution militates against extensive clustering.

Experimentally, isotropic shifts can be measured more accurately than line widths, particularly in cases where the spectra are complex. Both the shift and peak width methods of estimating interionic distance will be affected by ion clustering, the latter probably more so than the former. To best advantage, both methods should be employed.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA, METCALF RESEARCH LABORATORIES, BROWN UNIVERSITY, PROVIDENCE, RHODE ISLAND, AND THE RESEARCH SCHOOL OF CHEMISTRY, INSTITUTE OF ADVANCED STUDIES, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, A.C.T., AUSTRALIA

The Reaction of the Hydroxoaquobis(ethylenediamine)cobalt(III) Ion with Amino Acids and Dipeptides and Their Esters and Amides

BY DAVID A. BUCKINGHAM AND JAMES P. COLLMAN

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Reactions between *cis*-$[Co(en)_2OH(H_2O)]^{2+}$ and amino acid esters, amino acid amides, and dipeptides have been studied. Amide or ester hydrolysis is usually accompanied by ligand disproportionation leading to mixtures of products which were separated and characterized.

We have recently reported that the β-$[Co(trien)OH(H_2O)]^{2+}$ ion (trien = triethylenetetramine) rapidly hydrolyzes amino acid esters and amides and acts selectively in the N-terminal hydrolysis of small peptide molecules.[1] These reactions have been interpreted on the basis of initial rate-controlling chelate formation by the amino acid derivative followed by rapid hydrolysis.[2]

Earlier attempts made in one of our laboratories to carry out the above hydrolysis reactions using the $[Co(en)_2OH(H_2O)]^{2+}$ ion were less successful, but the results of these experiments are, we feel, of some interest and are reported here.

(1) D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Am. Chem. Soc.*, **89**, 1052 (1967).

(2) (a) E. Kimura and J. P. Collman, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 1967; (b) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 2772 (1967).

Experimental Section

Amino Acids and Peptides.—These materials were obtained from Mann Research Laboratories, Inc., New York, N. Y. Wherever possible they were purchased "chromatographically pure."

Chromatography.—Paper strip and column chromatography were carried out as described in ref 1.

Instrumentation.—Spectrophotometric estimations of the reaction products were obtained on a Cary Model 14 recording spectrophotometer from standardized curves prepared from analytical samples. Infrared spectra were recorded on a Perkin-Elmer "Infracord" or 421 grating spectrophotometer as KBr pellets. Nmr spectra were recorded on a Varian A-60 spectrometer in 99.75% D_2O. Measurements of pH were made on a Beckman Model B pH meter standardized against 0.05 *M* potassium acid phthalate or a 0.025 *M* Na_2HPO_4–0.025 *M* KH_2PO_4 mixture.

$[Co(en)_2CO_3]ClO_4$.—This compound was prepared by the method of Dwyer, Reid, and Sargeson.[3]

$[Co(en)_2OH(H_2O)]^{2+}$.—This was produced *in situ* by treating $[Co(en)_2CO_3]ClO_4$ with 2 moles of $HClO_4$ (or HCl) and after 15 min adding freshly prepared 0.01 *M* NaOH solution to the desired pH.

Hydrolysis Reactions.—$[Co(en)_2OH(H_2O)]^{2+}$ solutions (0.1 *M*) were freshly prepared before each set of experiments and sufficient glycine ethyl ester hydrochloride, glycinamide hydrochloride, dipeptide, or dipeptide ester hydrochloride was added to make the solutions 0.1 *M* with respect to the substrate. Reactions were carried out in the temperature range 60–85°, the pH being checked at frequent time intervals and controlled when necessary (±0.2 pH unit) by adding 0.1 *M* $HClO_4$ or 0.1 *M* NaOH. For the reaction with glycinamide, titration with 1.01 *M* $HClO_4$ was used as a qualitative estimate of the total reaction time. After reaction the solutions were reduced to dryness at pH 7, the residue was dissolved in the minimum amount of water, glacial acetic acid–butanol–pyridine (5:10:1) was added, and the mixture was chromatographed on cellulose columns. The separated bands were reduced to dryness at room temperature, spotted on paper chromatograms against markers to ascertain purity, and rechromatographed where necessary. $[Co(en)_3]^{3+}$, $[Co(en)_2gly]^{2+}$, and $[Co(en)(gly)_2]^+$ were isolated from concentrated aqueous solutions as their complex iodides and characterized by analysis and by infrared and nmr spectra. *Anal.* Calcd for $[Co(en)_3]I_3 \cdot H_2O$: C, 11.30; H, 4.11; N, 13.18. Found: C, 11.41; H, 4.14; N, 13.13. Calcd for $[Co(en)_2gly]I_2 \cdot H_2O$: C, 13.74; H, 4.20; N, 13.38. Found: C, 14.03; H, 4.60; N, 13.49. Calcd for $[Co(en)(gly)_2]I \cdot H_2O$: C, 17.44; H, 4.39; N, 13.57. Found: C, 17.86; H, 4.67; N, 15.28.

Alternatively descending or ascending paper chromatograms were run; the bands were cut out, eluted with water, and made up to a standard volume. Spectrophotometric determinations then gave estimates of the amounts of each species formed. Sample chromatograms of various reactions and their products are given in Figure 1.

In the glycylglycine reaction the more slowly moving bands were combined from three large-scale (10-g) reactions at pH 7.0, and, in order of recovery, $[Co(en)(glygly)(H_2O)]^+$ and $[Co_2(en)_3(glygly)_2]^{2+}$ isolated as their chlorides from aqueous solutions, and $[Co(glygly)_2]^-$ as its potassium salt from water–ethanol. $K[Co(glygly)_2]$ isolated in this manner was similar to that prepared according to the method of Martell, *et al.*[4] $[Co_2(en)_3(glygly)_2]Cl_2 \cdot 3H_2O$ was also obtained in the following manner. $[Co(en)_2CO_3]Cl \cdot H_2O$ (3 g) was converted to $[Co(en)_2OH(H_2O)]^{2+}$ by addition of 2 *N* HCl and a concentrated NaOH solution, glycylglycine (1.36 g) was added, and the whole mixture (100 ml) was heated at 75° at pH 8 for 45 min. The volume was reduced to 40 ml on a steam bath at pH 7 and the $[Co(en)_3]Cl_3$ which separated overnight at 5° was removed (0.3 g). After further standing (48 hr) at 5° a fine pink precipitate was removed and recrystallized three times from hot water by cooling in an ice bath. The pink product was washed with ethanol and acetone and air dried. The gross structures assigned to these dipeptide complexes are based on elemental analyses, infrared spectra, and spectral similarity to known dipeptide complexes of Co(III).[4] *Anal.* Calcd for $[Co_2(en)_3(glygly)_2]Cl_2 \cdot 3H_2O$: C, 24.60; H, 6.49; N, 20.50; Cl, 10.38. Found: C, 24.41; H, 6.55; N, 20.17, 20.30; Cl, 10.68, 10.35. The presence of coordinated glycylglycine was also shown by comparing the infrared spectrum with those of $Na[Co(glygly)_2] \cdot H_2O$ and $[Co(en)(gly)_2]I$.

Figure 1.—Paper chromatograms of the products formed by treating $[Co(en)_2OH(H_2O)]^{2+}$ with (A) glycine methyl ester, (B) glycinamide, (C) glycylglycine methyl ester, (D) glycylphenylalanine ethyl ester, and (E) glycylglycine at pH 7.5 and 85°. In A, B, C, and E the three fastest moving spots are in order of increasing R_f: $[Co(en)(gly)_2]^+$, $[Co(en)_2gly]^{2+}$, and $[Co(en)_3]^{3+}$, respectively.

Reaction with Amino Acids. Glycine.—To $[Co(en)_2CO_3]Cl \cdot H_2O$ (2.5 g) in water (20 ml) was added 6 *N* HCl (2 ml) and after 30 min glycine (0.75 g) in water (20 ml), and the pH was adjusted to 8 with a freshly prepared 10% NaOH solution. After 30 min at 80° the orange solution was reduced to 15 ml on the steam bath and filtered; excess NaI was added to the ice-cold solution. The orange product was removed, washed with 80% ethanol, and twice recrystallized from hot water by adding NaI and cooling. The final orange crystals (2.5 g) were washed with a little ice water and acetone and dried at 100° at 0.5 mm. *Anal.* Calcd for $[Co(en)_2gly]I_2$: C, 14.22; H, 3.98; N, 13.81. Found: C, 14.49; H, 4.16; N, 13.46.

Alaninato, Valinato, Leucinato, Isoleucinato, Serinato, and Phenylalaninato Derivatives.—These compounds were prepared in an identical manner with that described in the preceding paragraph for the glycine complex. *Anal.* Calcd for $[Co(en)_2ala]I_2$: C, 16.12; H, 4.25; N, 13.46. Found: C, 16.30; H, 4.83; N, 13.22. Calcd for $[Co(en)_2val]I_2$: C, 19.70; H, 4.77; N, 12.77. Found: C, 19.99; H, 4.83; N, 12.94. Calcd for $[Co(en)_2leu]I_2$: C, 21.38; H, 5.02; N, 12.45. Found: C, 21.50; H, 5.05; N, 12.62. Calcd for $[Co(en)_2isoleu]I_2$: C, 21.38; H, 5.02; N, 12.45. Found: C, 21.22; H, 5.09; N, 12.60. Calcd for $[Co(en)_2ser]I_2$: C, 15.65; H, 4.13; N, 13.04. Found: C, 15.63; H, 4.25; N, 13.22. Calcd for $[Co(en)_2phe]I_2$: C, 26.15; H, 4.38; N, 11.73. Found: C, 26.33; H, 4.26; N, 11.99.

(3) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

(4) A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).

Results

Amino Acids.—Reaction of *cis*-$[Co(en)_2OH(H_2O)]^{2+}$ ions with glycine, valine, leucine, isoleucine, serine, alanine, and phenylalanine at pH 7.5–8 and 80° gave high yields of the corresponding amino acid complexes. These ions were isolated as their iodides and converted to their chlorides or acetates before chromatography. Attempts to coordinate threonine, proline, or aspartic acid failed, and only $[Co(en)_3]I_3$ was isolated.

With the exception of serine, chromatography and elemental analysis showed the reactions to be essentially free from contamination by $[Co(en)_3]^{3+}$ ions. Ascending or descending paper chromatography or thin layer chromatography on cellulose proved an ideal method for immediate identification. Table I gives R_f values at 28° using 1-butanol–water–acetic acid–pyridine (100:100:20:1) as eluent as well as the R_f values for the parent amino acid, under identical conditions.

TABLE I
R_f VALUES FOR THE $[Co(en)_2AA]^{2+}$ IONS AND AMINO ACIDS AT 28°[a]

Complex ion	R_f	Amino acid	R_f
$[Co(en)_2gly]^{2+}$	0.21	Glycine	0.22
$[Co(en)_2ala]^{2+}$	0.27	Alanine	0.28
$[Co(en)_2val]^{2+}$	0.41	Valine	0.41
$[Co(en)_2isoleu]^{2+}$	0.51	Isoleucine	0.56
$[Co(en)_2phe]^{2+}$	0.52	Phenylalanine	0.58
$[Co(en)_2leu]^{2+}$	0.54	Leucine	0.60
$[Co(en)(gly)_2]^{+}$	0.17		
$[Co(en)_3]^{3+}$	0.26		
$[Co(glygly)_2]^{-}$	~0.05		
$[Co_2(en)_3(glygly)_2]^{2+}$	~0.10		

[a] *n*-C_4H_9OH–H_2O–HOAc–pyridine (100:100:20:1) eluent.

Glycine Ethyl and Methyl Esters and Glycinamide.—Table II lists the reaction conditions and products formed by treating $[Co(en)_2OH(H_2O)]^{2+}$ with glycine methyl ester hydrochloride and glycinamide hydrochloride at 80–85° and pH 7.5. In the case of the glycinamide reaction it was necessary to add 1.01 *M* $HClO_4$ to control the pH; in the other cases the pH remained essentially constant (±0.2 pH unit). The reaction products were separated in quantity by column chromatography on cellulose and estimated spectrophotometrically following elution with *n*-C_4H_9OH–H_2O–HOAc (100:100:20) on descending paper chromatograms. Slight variations in product composition are noted in Table II and result from different reactions. The preparation of $[Co(en)(gly)_2]I$ does not appear to have been previously reported.

Glycylglycine.—Reaction with glycylglycine over the temperature range 60–90° and pH 7–9 gave a complex mixture of products (Table II). Considerable variation in the amounts of the individual complex ions was caused by changing the pH of the reaction. The reaction at pH 7.5 and 85° was studied in detail and column chromatography on cellulose gave six products, these being characterized by paper chromatography against known markers, infrared spectra, and elemental analysis as $[Co(en)_3]^{3+}$ (15–20%), $[Co(en)_2gly]^{2+}$ (30–40%), $[Co(en)(gly)_2]^{+}$ (10–15%), $[Co(en)(glygly)H_2O]^{+}$, $[Co_2(en)_3(glygly)_2]^{2+}$, and $[Co(glygly)_2]^{-}$ in order of their elution. The three most slowly moving bands were collected from three large-scale reactions at pH 7.0 and the center cuts were rechromatographed until pure. That of $[Co_2(en)_3(glygly)_2]^{2+}$ showed signs of further subdivision on using aqueous ethanol as eluent and this may result from the separation of some of the many possible geometrical forms of this compound. At lower pH values, reduced amounts of $[Co(en)_3]^{3+}$, $[Co(en)_2gly]^{2+}$, and $[Co(en)(gly)_2]^{+}$ and proportionally larger amounts of the products containing coordinated glycylglycine were formed.

Glycylglycine Methyl and Ethyl Esters.—Table II lists the product formed by treating $[Co(en)_2OH(H_2O)]^{2+}$ with glycylglycine methyl ester and glycylglycine ethyl ester hydrochlorides at 60–80° and pH 6.5–8.0. Negligible amounts of more slowly moving bands were formed indicating the absence of products containing coordinated glycylglycine. Reaction at pH 6.5 and 60° followed by warming to 80° at pH 7.5 gave the largest amount of $[Co(en)_2gly]^{2+}$.

Glycylphenylalanine Ethyl Ester.—Reaction at 85° and pH 7.5 gave appreciable yields of $[Co(en)_2gly]^{2+}$, little $[Co(en)_3]^{3+}$, and no $[Co(en)_2phe]^{2+}$. A trace of phenylalanine ethyl ester was detected on chromatography and some dibenzyldiketopiperazine was removed from the reaction mixture following evaporation to dryness.

Glycylphenylalaninamide.—Reaction at pH 7.8 and 75° gave similar products to those obtained from glycylglycine (Table II). Also, while $[Co(en)_2gly]^{2+}$ was formed in about 20% yields, no $[Co(en)_2phe]^{2+}$ was detected.

Discussion

The complex ions $[Co(en)_2AA]^{2+}$ were prepared so as to provide convenient markers for the identification of products formed in the more complex ester and dipeptide reactions. Column and paper chromatography proved an easy and rapid method for identifying these ions in the presence of other colored products, and the different amino acid complexes could be easily separated from one another. This may provide a useful method for the analysis of simple amino acid mixtures as the complex ions are orange in color and can be easily detected visually and their amounts estimated spectrophotometrically.

In the hydrolysis experiments the major reacting cobalt(III) species is $[Co(en)_2OH(H_2O)]^{2+}$ over the pH range 7–8.[5] Implicit in this statement is the assumption that the smaller concentrations of $[Co(en)_2(H_2O)_2]^{3+}$ and $[Co(en)_2(OH)_2]^{+}$ also present are not as effective as $[Co(en)_2OH(H_2O)]^{2+}$ in promoting hydrolysis. As the rate-controlling step for ester hydrolysis appears to be initial coordination of the substrate molecule as a monodentate ligand[6,7] and since this is likely to be controlled by the rate of water ex-

(5) M. L. Tobe, *Sci. Progr.* (London), **48**, 483 (1960).
(6) M. D. Alexander and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 1130 (1966).
(7) D. A. Buckingham, D. Foster, and A. M. Sargeson, in preparation.

TABLE II

REACTIONS OF THE $[Co(en)_2OH(H_2O)]^{2+}$ ION (0.1 *M*)

Substrate	Molar concn	Temp, °C	pH	Reaction time, hr[b]	Product	Analytical method[a]
Glycine methyl ester	0.1	85	7.5	2	$[Co(en)_2gly]^{2+}$ (82%), $[Co(en)(gly)_2]^+$ (11%), $[Co(en)_3]^{3+}$ (7%)	I, C
Glycine methyl ester	0.1	80	7.5	2	$[Co(en)_2gly]^{2+}$ (80%), $[Co(en)(gly)_2]^+$ (5%), $[Co(en)_3]^{3+}$ (15%)	C
Glycine methyl ester	0.1	80	7.8	1	$[Co(en)_2gly]^{2+}$ (90%), $[Co(en)(gly)_2]^+$ (5%), $[Co(en)_3]^{3+}$ (trace)	C
Glycinamide[c]	0.1	85	7.5	2	$[Co(en)_2gly]^{2+}$ (78%), $[Co(en)(gly)_2]^+$ (16%), $[Co(en)_3]^{3+}$ (6%)	C
Glycinamide[c]	0.1	85	7.8	1.5	$[Co(en)_2gly]^{2+}$ (83%), $[Co(en)(gly)_2]^+$ (12%), $[Co(en)_3]^{3+}$ (trace)	C
Glycylglycine	0.1	85	7.0	12	$[Co(en)_2gly]^{2+}$ (20%), $[Co(en)(gly)_2]^+$ (10–15%), $[Co(en)_3]^{3+}$ (15–20%), $[Co(en)(glygly)H_2O]^+$, $[Co_2(en)_3(glygly)_2]^{2+}$, $[Co(glygly)_2]^-$	I
Glycylglycine	0.1	85	7.8	4	$[Co(en)_2gly]^{2+}$ (35–40%), $[Co(en)(gly)_2]^+$ (10–15%), $[Co(en)_3]^{3+}$ (30%), others (trace)	C
Glycylglycine	0.2	85	7.5	4	$[Co(en)_2gly]^{2+}$ (30–40%), $[Co(en)(gly)_2]^+$ (10–15%), $[Co(en)_3]^{3+}$ (15–20%), $[Co(en)(glygly)H_2O]^+$, $[Co_2(en)_3(glygly)_2]^{2+}$, $[Co(glygly)_2]^-$	C, I
Glycylglycine methyl ester	0.1	80	7.5	1	$[Co(en)_2gly]^{2+}$ (60%), $[Co(en)(gly)_2]^+$ (10%); $[Co(en)_3]^{3+}$ (5%), others[3]	C
Glycylglycine methyl ester	0.1	60, 80	6.5, 7.5	1, 3	$[Co(en)_2gly]^{2+}$ (80–85%), $[Co(en)(gly)_2]^+$ (10–15%), $[Co(en)_3]^{3+}$ (trace)	I, C
Glycylglycine ethyl ester	0.1	85	7.5	3	$[Co(en)_2gly]^{2+}$ (70%), $[Co(en)(gly)_2]^+$ (20%), $[Co(en)_3]^{3+}$ (trace)	C
Glycylphenylalanine ethyl ester	0.5	85	7.2, 7.5	3	$[Co(en)_2gly]^{2+}$ (30%), $[Co(en)_3]^{3+}$ (trace), phenO-C_2H_5, others	C
Glycylphenylalaninamide	0.3	85	7.5	5	$[Co(en)_2gly]^{2+}$ (10–15%), $[Co(en)_3]^{3+}$ (10–15%), others	C
CBZglycylphenylalaninamide	0.1	80	7.5	6	$[Co(en)_3]^{3+}$ (trace)	C

[a] I = isolation of each species; infrared, nmr, and analytical data obtained. C = identification by chromatography only. [b] Total reaction time; not necessarily minimum time for complete hydrolysis. [c] Hydrolysis completed in about 1 hr.

change which is relatively fast for $[Co(en)_2OH(H_2O)]^{2+}$,[8] we feel the assumption is a reasonable one.

The reaction of $[Co(en)_2(OH)H_2O)]^{2+}$ with glycine esters and glycinamide results in substantial amounts of $[Co(en)_2gly]^{2+}$ being formed. The hydrolysis of the ester and amide bonds at 85° and pH 7.5 is substantially faster than the uncatalyzed reactions and is similar to those carried out in the presence of Cu(II) ions in the region of 40° and pH 5.[9] Cleavage of the peptide bond in glycylglycine and glycylglycine methyl ester is more facile than the Cu(II)-promoted hydrolysis of phenylalanylglycinamide,[10] but a mixture of cobalt(III) complexes is formed. With glycylglycine larger amounts of $[Co(en)_2gly]^{2+}$ are formed at more basic pH values suggesting that under these conditions initial coordination occurs through the terminal amino group of the dipeptide and that $[Co(en)_2gly]^{2+}$ results from subsequent hydrolysis of the N-bound dipeptide. In more acidic solutions where the amino group of glycylglycine is protonated (pK_2 = 8.25) initial coordination probably favors the carboxyl oxygen with subsequent formation of appreciable amounts of coordinated glycylglycine products. This is better demonstrated in the reactions with glycylglycine methyl ester (pK_2 = 7.75) and glycylphenylalanyl ethyl ester (pK_2 = 7.3 estimate) where the ester grouping forces initial coordination through the amino group with subsequent hydrolysis of the peptide bond thus preventing any appreciable tridentate coordination. The amount of $[Co(en)_2gly]^{2+}$ formed is thereby markedly increased over that obtained in the glycylglycine reaction. Similarly, in the reaction with excess glycylphenylalanine ethyl ester 20–30% yields of $[Co(en)_2gly]^{2+}$ are formed as well as some phenylalanine ethyl ester, but no $[Co(en)_2phe]^{2+}$ is detected. When both the amino and carboxyl groups of the dipeptide are blocked, such as in carbobenzoxyglycylphenylalaninamide [CBZglyphenNH$_2$] no coordinated amino acid products, $[Co(en)_2AA]^{2+}$, are formed.

The results of these experiments are in agreement with those obtained using the β-$[Co(trien)OH(H_2O)]^{2+}$ ion,[1] and similar conclusions may be drawn regarding methods of attachment of the substrate and subsequent hydrolysis. It is apparent, however, that $[Co(en)_2OH(H_2O)]^{2+}$ is not nearly so effective as β-$[Co(trien)OH(H_2O)]^{2+}$ at promoting hydrolysis, and a wide diversity of products is formed. This may result from a complication arising out of concurrent *cis* → *trans* isomerization of $[Co(en)_2OH(H_2O)]^{2+}$, from electron transfer catalyzed disproportionation,[11] or from the slower

(8) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

(9) W. A. Conner, M. M. Jones, and D. L. Tuleeu, *Inorg. Chem.*, **4**, 1129 (1965).

(10) L. Meriwether and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 5119 (1956).

(11) D. A. Buckingham, F. P. Dwyer, and A. M. Sargeson, *Australian J. Chem.*, **16**, 921 (1963).

rate of water exchange of $[Co(en)_2OH(H_2O)]^{2+}$ compared to β-$[Co(trien)OH(H_2O)]^{2+}$, or from a combination of these factors.

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The Induced Aquation Reactions of the Resolved Azidochlorobis(ethylenediamine)cobalt(III) Ion

BY D. A. BUCKINGHAM, I. I. OLSEN, AND A. M. SARGESON

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The induced aquation of Cl^- and N_3^- from $(+)_{589}$-$[Co(en)_2ClN_3]^+$ using Hg^{2+} and NO^+, respectively, has been examined. Both reactions give substantial rearrangement to both *cis* and *trans* products whereas the spontaneous aquation of Cl^- gave full retention of the *cis* configuration and activity. The results are compared with the NO^+-assisted aquation of $(+)_{589}$-$[Co(en)_2(N_3)_2]^+$ and the Hg^{2+}-assisted aquation of $(+)_{589}$-$[Co(en)_2Cl_2]^+$ where the same products are produced. A common result was obtained for the two sets of reactions which is interpreted to indicate a common intermediate.

Introduction

The steric courses of aquation of $[Co(en)_2XY]^{n+}$ complexes (where X and Y are a series of substituents such as Cl, Br, NCS, NH_3, OH_2, N_3, NO_2, etc.) have been well studied,[1] and it is still not clear if these reactions proceed by a bimolecular displacement reaction or through an intermediate of reduced coordination number. Attempts have been made to generate the possible five-coordinate intermediates involved,[2-4] to study their properties, and to see if the steric course of the reaction of the supposed intermediate coincides with that of the spontaneous aquation. The methods used have been derived from studies of induced aquations in substituted cobalt(III) pentaammine complexes, namely, the reactions of $[Co(NH_3)_5X]^{2+}$ ions (X = Cl, Br, I) with Hg^{2+}[5] and of $[Co(NH_3)_5N_3]^{2+}$ with NO^+.[6] Evidence has been collected[5-8] to support the existence of a common five-coordinate intermediate in the induced aquations and these reactions have also been used with *cis*- and *trans*-$[Co(en)_2Cl_2]^+$,[2] $[Co(en)_2(N_3)_2]^+$,[3] $[Co(en)_2OH_2N_3]^{2+}$,[3] $[Co(en)_2ClOH_2]^{2+}$,[4] $[Co(en)_2BrOH_2]^{2+}$,[4] $[Co(en)_2ClBr]^+$,[4] and *trans*-$[Co(en)_2ClN_3]^+$[4] ions, to show that the steric courses of the induced aquation and the spontaneous aquations differ. Loeliger and Taube have tabulated data[4] for the Hg^{2+}- and NO^+-induced aquations to show that for the same product a constant ratio of *cis* and *trans* isomers is obtained from different reactants. The authors suggest that the common result indicates the same intermediate is formed in the reactions.

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(2) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).
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The present work is related to this last study and involves primarily the steric course of the Hg^{2+}-assisted aquation of Cl^-, the NO^+-assisted aquation of N_3^-, and the spontaneous aquation of Cl^- in the (+)-$Co(en)_2ClN_3]^+$ ion.

Experimental Section

$(+)_{589}$-*cis*-$[Co(en)(N_3)_2]ClO_4$ was prepared as described.[9] *Anal.* Calcd: C, 13.25; H, 4.45; N, 38.63. Found: C, 13.38; H, 4.55; N, 38.98.

trans-$[Co(en)_2(N_3)_2]ClO_4$ was prepared by the same method as for *cis*-$[Co(en)_2(N_3)_2]ClO_4$ using $Co(ClO_4)_2$ and $HClO_4$ instead of $Co(NO_3)_2$ and HNO_3. A yield of 87% brown *trans*-$[Co(en)_2(N_3)_2]ClO_4$ was obtained. *Anal.* Calcd: C, 13.25; H, 4.45; N, 38.63. Found: C, 13.44; H, 4.50; N, 38.90.

trans-$[Co(en)_2N_3Cl]ClO_4$ was prepared from *trans*-$[Co(en)_2(N_3)_2]ClO_4$ as described.[10]

cis-$[Co(en)_2N_3Cl]Cl$ was prepared by treating *cis*-$[Co(en)_2(N_3)_2]NO_3$ (20 g) with HCl (10 *N*) saturated with LiCl (75 ml) at room temperature until the solution became bluish red (~6 min). The azidochloro complex was then precipitated by pouring the reaction mixture into a large amount of ethanol. It was recrystallized from water at pH 3–4 by adding ethanol until precipitation commenced. The solution was then cooled in an ice bath, yield 5 g.

$(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]ClO_4$.—To *cis*-$[Co(en)_2ClN_3]Cl$ (7.5 g) dissolved in water (80 ml) at pH 3–4 was added $(-)_{589}$-$Na[Co(en)(C_2O_4)_2]\cdot H_2O$ (4.1 g) with stirring. The diastereoisomer (4.4 g) precipitated rapidly and was collected and washed with ice-cold water and methanol. The isomer $(+)_{589}$-*cis*-$[Co(en)_2N_3Cl]I$ (2.4 g) was obtained from the diastereoisomer by grinding an ice-cold suspension of the latter with solid NaI in a mortar. The precipitated iodide was collected and washed with a dilute aqueous solution of NaI and ethanol. The rotation of the iodide was measured, and, in order to ensure that optical purity was obtained, the complex was reresolved. The iodide was converted to the chloride by treating an aqueous suspension (pH 3) with AgCl. After filtration, solid $(-)_{589}$-$Na[Co(en)(C_2O_4)_2]$ (1.83 g) was added to the filtrate and the diastereoisomer collected was converted to the iodide as before. The final rotation of the iodide was the same as that obtained from the first diastereo-

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