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A Comparison of the Isomeric Changes in the Induced and Spontaneous Aquation of Ions of the Type $Co^{III}(en)_2YX$

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The isomeric changes during the mercuric ion assisted aquation of ions of the series $Co^{III}(en)_2YX$ have been determined and are compared with those for the aquations of the azido complexes induced by nitrous acid and for the spontaneous reactions. In all the cases studied, the stereochemical courses of the two kinds of induced reactions agree, but in most cases differ from those of the spontaneous aquation reactions. The results are consistent with the view that the induced reactions, involving as they do "good" leaving groups, do proceed by common intermediates and show that the spontaneous reactions in most instances do not involve the same intermediate.

Introduction

The recent chemical literature gives evidence of the continuing concern with the fundamental aspects of the mechanism of substitution on Co(III).[1] For aquation in the series $Co^{III}(en)_2YX^{+n} \rightarrow Co^{III}(en)_2YH_2O^{+(n+1)}$, the stereochemistry as well as the rates have been studied, and Ingold, Nyholm, and Tobe have formulated a set of rules designed to predict how the rates, the mechanisms, and the steric course of the reactions will be affected by the properties of the group Y.[2] The extent of bond breaking in the transition state is recognized as an important feature of the mechanisms, but there is evidence as well that the reactions are solvent assisted.[3]

The reaction of HONO with coordinated azide ion has been suggested as a method of generating a pentacoordinated intermediate in the supposition that N_2 as a good leaving group is formed by the reaction

$$[\text{-NNN}]^- + H^+ + HONO \longrightarrow [\text{-NN}] + N_2O + H_2O$$

The agreement between the competition ratios in the formation of rival products for the spontaneous aquation and the nitrosation of azide led Haim and Taube[1a] to conclude that the two types of reactions involve a common intermediate. This conclusion has, however, been set aside by the observations of Pearson and Moore which show that the competition ratios Haim and Taube calculated do not account for the product distributions in other reactions depending on spontaneous aquation as a means of generating the presumed pentacoordinated intermediate. Haim and Taube[1a] were led to an incorrect conclusion by a fortuitous coincidence in part made possible because of the limited accuracy of some of the values of competition ratios. The general approach which depends on searching for common kinetic properties for presumed reaction intermediates is, of course, not disqualified by the particular misapplication. It should further be noted that while Pearson and Moore's[1b] results prove that the spontaneous aquations and the nitrosation reactions in the pentaammine series do not involve a common intermediate, the possibility remains that the nitrosation reaction does proceed by way of a genuine pentacoordinated intermediate.

We here describe further applications of the comparison method, but now using the competition in the formation of various isomers as a possible means of demonstrating common intermediates. It is known that in some cases the nitrous acid induced aquation of azide from ions of the type $Co^{III}(en)_2YN_3$ produces isomers different from those produced in the spontaneous displacement by water of halide ion in corresponding complexes. In searching for a method alternative to the nitrosation of coordinate azide as a possible means of generating a pentacoordinated intermediate, we turned to the removal of halide ion assisted[4] by Hg^{2+}.

Experimental Section

Materials.—*trans*-$[Co(en)_2(N_3)_2]ClO_4$ was prepared as previously described[5] and repeatedly recrystallized to remove traces of the *cis* isomer until a constant absorption spectrum was obtained. *Anal.* Calcd for *trans*-$[Co(en)_2(N_3)_2]ClO_4$: C, 13.25; N, 38.63; H, 4.68; Co, 16.25. Found: C, 13.51; N, 38.33; H, 4.66; Co, 16.31.

cis-$[Co(en)_2(N_3)_2]ClO_4$ was also prepared as described by Staples and Tobe.[5]

Anal. Found: C, 13.52; N, 38.44; H, 4.68; Co, 16.22.

trans-**$[Co(en)_2ClN_3]ClO_4$**.—The crude complex was prepared either by the method of Staples and Tobe[5] or by warming *trans*-$[Co(en)_2(N_3)_2]ClO_4$ (3.65 g) in concentrated hydrochloric acid (15 ml) until a blue-green solution was obtained. Solid sodium perchlorate (5 g) was added to the solution, which was cooled rapidly in crushed ice. The beaker was scratched to induce crystallization and after 5 min the crude product was filtered off and washed with a small volume of cold ethanol and ether. This entire procedure should be carried out in the hood and care must be taken to avoid breathing the toxic HN_3 vapors which are generated.

The crude product was extracted on the filter with cool (~10–15°) water until only bright green *trans*-$[Co(en)_2Cl_2]ClO_4$ remained. A large excess of solid $NaClO_4$ was added to the filtrate and the solution cooled in ice, again inducing crystallization of the product by scratching the beaker. To remove

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[1] (a) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963); (b) R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964); (c) S. C. Chan, *J. Chem. Soc.*, 2375 (1964); (d) C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965); (e) D. Loeliger and H. Taube, *ibid.*, **4**, 1032 (1965).

[2] C. Ingold, R. S. Nyholm, and M. Tobe, *Nature*, **187**, 477 (1960).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

[4] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

[5] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

residual *trans*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ the once-recrystallized product was extracted with acetone at room temperature. The *trans*-$[\mathrm{Co(en)_2ClN_3}]\mathrm{ClO_4}$ dissolved and was freed from the *trans*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ contaminant by filtration. The filtrate was maintained at ~20° while the solvent was removed under vacuum. A final recrystallization removed the last traces of contaminants.

Anal. Calcd for *trans*-$[\mathrm{Co(en)_2ClN_3}]\mathrm{ClO_4}$: C, 13.49; N, 27.54; H, 4.53; Cl, 19.92. Found: C, 12.8; N, 27.4; H, 4.4; Cl, 18.7.

***trans*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{SO_4}$.**—The procedure of Meisenheimer[6] was followed in preparing *trans*-$[\mathrm{Co(en)_2ClOH}]\mathrm{Cl}$. The hydroxo complex was converted to the aquo by dissolving it in a small excess of 1 *M* sulfuric acid. A moderate amount of ethanol was added to the solution to precipitate the *cis*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{SO_4}$ present, and this contaminant was removed by filtration. The filtrate was diluted with a large volume of ethanol to precipitate *trans*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{SO_4}$. The product was recrystallized to constant spectrum by adding ethanol to aqueous solutions of the complex. It was filtered, washed with ether, and air dried.

Anal. Calcd for *trans*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{SO_4}$: C, 14.62; N, 17.05; H, 5.52. Found: C, 14.48; N, 17.07; H, 5.51.

cis-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{Cl_2}$ was prepared using Werner's method[7] and recrystallized from aqueous solution by adding small amounts of ethanol. This procedure was repeated until the filtrate no longer had the green color of the *trans* isomer. The sulfate was converted to the chloride salt by grinding it in ice-cold concentrated hydrochloric acid. The precipitate was washed with large amounts of ethanol and ether and air dried.

Anal. Calcd for *cis*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{Cl_2}$: C, 15.83; N, 18.46; H, 5.98. Found: C, 15.52; N, 18.73; H, 6.00.

***l-cis*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{Br_2 \cdot H_2O}$** was obtained from the racemic chloride salt using published procedures.[8]

***cis*-$[\mathrm{Co(en)_2BrH_2O}]\mathrm{Br_2}$** was prepared from $[\mathrm{Co(en)_2CO_3}]\mathrm{Br}$ using Werner's method[9] and recrystallized to constant spectrum by adding NaBr to aqueous solutions of the complex.

Anal. Calcd for *cis*-$[\mathrm{Co(en)_2BrH_2O}]\mathrm{Br_2}$: C, 11.00; N, 12.82; H, 4.15. Found: C, 10.8; N, 12.7; H, 4.2.

***cis*-$[\mathrm{Co(en)_2(H_2O)_2}]\mathrm{Br_3 \cdot 2H_2O}$** and ***trans*-$[\mathrm{Co(en)_2(H_2O)_2}]\mathrm{Br_3}$** were prepared using published methods,[10] and the spectra were found to agree with those reported.[11]

Mercuric perchlorate solutions were prepared by dissolving weighed samples of reagent grade mercuric oxide in standardized perchloric acid. Hydrolysis of the mercuric ion was suppressed with excess acid.

Kinetic and Isomerization Studies

Kinetic and isomerization studies were carried out spectrophotometrically using a Cary Model 14 recording spectrophotometer. The kinetic data were obtained at 25.0 ± 0.1° and the isomerization data were obtained at ambient temperature, 22 ± 2°. Optical activity was measured with a Zeiss polarimeter at 22 ± 2°.

The mercuric ion assisted aquations were studied by dissolving weighed samples of the complex in a small amount of water in a volumetric flask. A known excess of mercuric perchlorate–perchloric acid solution was pipetted into the flasks and volume deficiences were made up with water. The samples were then transferred to the spectrophotometer and observed at a wavelength chosen to give a large change in optical density for the reaction under investigation. When no further change of optical density was noticeable (8–10 half-lives), the spectrum of the solution was recorded. For the mercuric ion assisted aquations of *trans*-diazido and *trans*-chloroazido, the product was observed to undergo a slow isomerization. The large difference in rates for the aquation and isomerization made feasible correcting the optical densities to eliminate the changes due to isomerization of the product.

The isomeric compositions of the reaction products were determined by comparing the spectra to those of the corresponding pure *cis* and *trans* isomers.

Results

***cis*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{Cl_2}$.**—The half-life for the aquation of ~0.01 *M* complex by 0.22 *M* mercuric ion in 0.89 *M* acid at 23° is 60 ± 10 sec. After 10 min the spectrum of the product was recorded from 400 to 600 mμ. Table I contains the results, which indicate the reaction proceeds with 100 ± 2% retention of *cis* configuration.

TABLE I

PRODUCT DISTRIBUTION FOR THE *cis*-$[\mathrm{Co(en)_2ClH_2O}]^{2+}$–$\mathrm{Hg^{2+}}$ REACTION

(complex) ≈ 0.01 *M*, $(\mathrm{Hg^{2+}}) = 0.22\ M$, $(\mathrm{H^+}) = 0.89\ M$, $T = 23 \pm 1°$

	% *cis*-$[\mathrm{Co(en)_2(H_2O)_2}]^{3+}$ product	
λ, mμ	Expt I	Expt II
400	100	
420	97	100
460	103	101
470	102	102
490	101	100
510	99	99
530	97	97
570	...	98
590	102	98
Av	100 ± 2	99 ± 2

***l-cis*-$[\mathrm{Co(en)_2ClH_2O}]\mathrm{Br_2 \cdot H_2O}$.**—A weighed sample of the *levo* isomer was treated with excess mercuric ion. After 10 half-lives for the aquation an excess of sodium bicarbonate was added to the solution to convert the diaquo to chelated carbonato; 30 min later the mercuric oxide–carbonate precipitate was removed by filtration and washed with water to remove adhering cobalt complex. The filtrate and washings were combined and diluted to a known volume, and the rotation was measured at the sodium D line. The molar rotation observed in this manner was compared to the rotation observed for the chelated carbonato complex prepared by the direct reaction of bicarbonate ion with *l-cis*-$[\mathrm{Co(en)_2ClH_2O}]^{2+}$. The reaction of bicarbonate with either the diaquo or chloroaquo complex proceeds with complete retention of configuration to give the stable chelated carbonato complex, which has a much higher specific rotation than the diaquo.[12] In this manner the mercuric assisted aquation was observed to occur with the

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[6] J. Meisenheimer, *Liebigs Ann.*, **438**, 254 (1924).

[7] A. Werner, *ibid.*, **386**, 123 (1912).

[8] A. Werner, J. E. Schwyzer, and W. Karrer, *Helv. Chim. Acta*, **4**, 113 (1921).

[9] A. Werner, *Liebigs Ann.*, **386**, 127 (1912).

[10] A. Werner, *Ber.*, **40**, 267 (1907).

[11] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

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

formation of 94.6 ± 2.5% *l-cis*-$[Co(en)_2(H_2O)_2]^{3+}$. The remaining 5.4 ± 2.5% can be attributed either to the racemic product or to complex lost by adsorption on the copious mercuric oxide–carbonate precipitate.

cis-**$[Co(en)_2BrH_2O]Br_2 \cdot H_2O$.**—When the mercuric ion assisted aquation of the *cis*-bromoaquo complex is carried out under the same conditions as for the *cis*-chloroaquo complex the reaction is complete in less than 45 sec. Reducing the mercuric and hydrogen ion concentrations by a factor of five still leads to complete reaction in less than 60 sec. Table II indicates the reaction proceeds with 99 ± 2% retention of *cis* configuration under both sets of conditions.

TABLE II

PRODUCT DISTRIBUTION FOR THE *cis*-$[Co(en)_2BrH_2O]^{2+}$–Hg^{2+} REACTION

λ, mμ	% *cis*-$[Co(en)_2(H_2O)_2]^{3+}$	
	Expt I[a]	Expt II[b]
400	98	103
420	96	101
460	98	98
470	98	100
490	98	97
510	97	97
530	99	99
570	103	101
590	99	94
Av	98 ± 2%	99 ± 2%

[a] (complex) = 6.2 × 10^{-3} *M*; (Hg^{2+}) = 0.22 *M*; (H^+) = 0.90 *M*. [b] (complex) = 4.8 × 10^{-3} *M*; (Hg^{2+}) = 4.5 × 10^{-2} *M*; (H^+) = 0.18 *M*.

trans-**$[Co(en)_2ClH_2O]SO_4$.**—Observations at 490 mμ indicate that the mercuric assisted aquation of *trans*-$[Co(en)_2ClH_2O]^{2+}$ is slower than for the *cis* isomer under the same conditions. In order to reduce *cis–trans* isomerization of the chloroaquo complex to a minimum, the assisted aquation was conducted with ~0.4 *M* Hg^{2+} and ~1.6 *M* H^+. At these concentrations the half-life at 23° is about 60 sec. Table III indicates that the spectrum of the product corresponds to 40 ± 5% *cis*-diaquo in the product.

trans-**$[Co(en)_2ClN_3]ClO_4$.**—Samples of the complex were weighed and transferred to a volumetric flask. The flasks were half-filled with water and swirled to dissolve the complex. As soon as dissolution was complete an excess of mercuric perchlorate–perchloric acid solution was added and any volume deficiency made up with water. Visually the assisted aquation of the chloride ion was observed to be complete on mixing. The spectrum from 400 to 600 mμ was recorded immediately. The complete spectra of *cis*- and *trans*-$[Co(en_2)N_3H_2O]^{2+}$ are not known accurately, but it is known that at 500 mμ the *trans* and *cis* isomers have extinction coefficients of 110 ± 10 and 241 cm^{-1} M^{-1}, respectively. The observed value at 500 mμ for the Hg^{2+} assisted aquation of *trans*-$[Co(en_2)ClN_3]^+$ was 106 ± 3 cm^{-1} M^{-1}. Thus within the limits with which the extinction coefficient of the *trans* isomer is known the Hg^{2+} induced aquation leads to retention of configuration.

TABLE III

PRODUCT DISTRIBUTION FOR THE *trans*-$[Co(en)_2ClH_2O]^{2+}$–Hg^{2+} REACTION

λ, mμ	% *cis*-$[Co(en)_2(H_2O)_2]^{3+}$		
	Expt I	Expt II	Expt III
400		47	44
420		39	38
460	41	35	36
470	39	36	40
490	40	35	36
510	39	34	36
530	39	32	34
570	53	49	42
590	48	50	36
Av	43 ± 4%	40 ± 5%	38 ± 3%

trans-**$[Co(en)_2(N_3)_2]ClO_4$.**—The rate of the mercuric assisted release of an azide ligand from the *trans*-diazido complex was determined at 537 mμ, the isosbestic point of the aquoazido isomers. At 25° with 0.22 *M* mercuric ion, 0.89 *M* perchloric acid, and 5 × 10^{-3} *M* complex a half-life of 85 sec is observed for the loss of the first azide ligand. The loss of the second azide ligand is so slow that the slow *trans–cis* isomerization of the aquoazido complex can be observed for over 100 min without complications due to the formation of the diaquo complex.

In order to determine the steric course of the reaction a recording of optical density *vs.* time was made at 500 mμ under the same reaction conditions as were used to determine the rate of aquation. Using the rate of loss of diazido complex, its extinction coefficient under the reaction conditions, and the observed optical densities, the extinction coefficient of the product was calculated throughout the course of its formation. For the first 100 sec of the reaction less than 1% *trans–cis* isomerization takes place and the extinction coefficient is observed to be 114 ± 5 cm^{-1} M^{-1}. Again within the limits with which the extinction coefficient is known this corresponds to full retention of *trans* configuration.

cis-**$[Co(en)_2(N_3)_2]ClO_4$.**—The attempts to induce the aquation of an azide group from the *cis*-diazido complex by the addition of excess mercuric ion led to the immediate production of a color change. The spectrum of this solution could not be attributed to a mixture of the various aquo and azido complexes that might be produced. Possibly a binuclear complex is formed in which azide ion acts as a bidentate bridging group between cobalt(III) and mercury(II).

Table IV summarizes the data available where direct comparisons can be made of the steric course of spontaneous and proton, Hg^{2+}, or nitrous acid assisted aquations.

Discussion

The rates of spontaneous (noninduced) isomerization of and the rates of spontaneous (noninduced) aquation of azide or halide ligands from *trans*-diazido, *trans*-chloroazido, *cis*- and *trans*-chloroaquo, and *cis*-bromoaquo are either known and reported or can be

TABLE IV

SUMMARY OF STERIC COURSE OF AQUATIONS

Starting complex	Method of aquation	Product	% *cis* product	Ref
D-*cis*-$[Co(en)_2(N_3)_2]^+$	HONO	$[Co(en)_2N_3H_2O]^{2+}$	76 ± 3 D	1e
cis-$[Co(en)_2(N_3)_2]^+$	H^+	$[Co(en)_2N_3H_2O]^{2+}$	>95	*b*
cis-$[Co(en)_2N_3Cl]^+$	Spontaneous	$[Co(en)_2N_3H_2O]^{2+}$	100	*c*
trans-$[Co(en)_2(N_3)_2]^+$	HONO	$[Co(en)_2N_3H_2O]^{2+}$	0 ± 5	1e
trans-$[Co(en)_2(N_3)_2]^+$	Hg^{2+}	$[Co(en)_2N_3H_2O]^{2+}$	Little	*b*
trans-$[Co(en)_2(N_3)_2]^+$	H^+	$[Co(en)_2N_3H_2O]^{2+}$	0 ± 5	
trans-$[Co(en)_2N_3Cl]^+$	Hg^{2+}	$[Co(en)_2N_3H_2O]^{2+}$	0 ± 5	
trans-$[Co(en)_2N_3Cl]^+$	Spontaneous	$[Co(en)_2N_3H_2O]^{2+}$	20	*c*
D-*cis*-$[Co(en)_2Cl_2]^+$	Hg^{2+}	$[Co(en)_2ClH_2O]^{2+}$	70 D	*d*
D-*cis*-$[Co(en)_2Cl_2]^+$	Spontaneous	$[Co(en)_2ClH_2O]^{2+}$	100 D	*e*
cis-$[Co(en)_2ClBr]^+$	Spontaneous	$[Co(en)_2ClH_2O]^{2+}$	>95	*f*
trans-$[Co(en)_2ClN_3]^+$	HONO	$[Co(en)_2ClH_2O]^{2+}$	27 ± 3	1e
trans-$[Co(en)_2Cl_2]^+$	Hg^{2+}	$[Co(en)_2ClH_2O]^{2+}$	28	*d*
trans-$[Co(en)_2ClBr]^+$	Spontaneous	$[Co(en)_2ClH_2O]^{2+}$	35	*g*
trans-$[Co(en)_2ClBr]^+$	Spontaneous	$[Co(en)_2ClH_2O]^{2+}$	20 ± 5	*f*
D-*cis*-$[Co(en)_2(H_2O)N_3]$	HONO	$[Co(en)_2(H_2O)_2]^{3+}$	100 ± 5 D	1e
D-*cis*-$[Co(en)_2(H_2O)Cl]^{2+}$	Hg^{2+}	$[Co(en)_2(H_2O)_2]^{3+}$	100 ± 5 D	
cis-$[Co(en)_2(H_2O)Br]^{2+}$	Hg^{2+}	$[Co(en)_2(H_2O)_2]^{3+}$	98 ± 3	
cis-$[Co(en)_2(H_2O)Cl]^{2+}$	Spontaneous	$[Co(en)_2(H_2O)_2]^{3+}$	90–100	*h*
trans-$[Co(en)_2(H_2O)N_3]^{2+}$	HONO	$[Co(en)_2(H_2O)_2]^{3+}$	40 ± 5	1e
trans-$[Co(en)_2(H_2O)Cl]^{2+}$	Hg^{2+}	$[Co(en)_2(H_2O)_2]^{3+}$	40 ± 5	
trans-$[Co(en)_2(H_2O)Cl]^{2+}$	Spontaneous	$[Co(en)_2(H_2O)_2]^{3+}$	0–50	*h*
trans-$[Co(en)_2(H_2O)_2]^{3+}$	*a*	$[Co(en)_2(H_2O)_2]^{3+}$	38	*a*

[a] Calculated from the rates of exchange and isomerization: W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961). The calculations are made on the assumption that the total rate of oxygen exchange measures the rate of formation of the presumed intermediate $Co(en)_2OH_2^{3+}$; the intermediate can react with water, restoring the original form, but with oxygen exchange, or can rearrange and then react with water. [b] P. J. Staples, *J. Chem. Soc.*, 745 (1964). [c] P. J. Staples and M. L. Tobe, *ibid.*, 4803 (1960). [d] A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964). [e] J. P. Mathieu, *Bull. Soc. Chim. France*, [5] **4**, 687 (1937). [f] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963). [g] M. L. Tobe, S. C. Chan, and M. E. Baldwin, *ibid.*, 4637 (1961). [h] S. C. Chan, *ibid.*, 5137 (1963).

estimated.[13] Comparison of these known rates with the rate of induced loss of ligand precludes significant spontaneous alteration of the complexes prior to reaction.

Furthermore any Hg^{2+} induced isomerization of the starting material prior to the aquations can also be ruled out. Sargeson[14] observed that neither the rate of isomerization nor the equilibrium ratio of the chloroaquo complexes is affected by dilute mercuric ion. The full retention of *trans* configuration during the induced aquations of the *trans*-diazido and *trans*-chloroazido complexes indicates that there is either no isomerization prior to aquation or the *cis* isomer of the starting material aquates to give only the *trans* isomer of the product. This latter alternative can be excluded since the product spectrum for the mercuric ion–*trans*-diazido reaction did not show any indication of the relatively stable species formed when mercuric ion and *cis*-diazido are mixed. Furthermore, the Hg^{2+} induced aquation of crude samples of *cis*-chloroazido[5] indicated that the product was not exclusively the *trans*-aquoazido isomer.

With regard to the products, Bjerrum and Rasmussen[11] have shown that spontaneous interconversion of *cis*- and *trans*-diaquo is slow at the hydrogen ion concentrations employed in these experiments. As stable solutions of the products are obtained with *cis* to *trans* isomer ratios of about 1 and >50 there can be no mercuric ion induced isomerization of the diaquo complexes.

Finally, although the aquoazido complexes were not stable with respect to isomerization, corrections are made for changes in product composition caused by this reaction.

Therefore there is little doubt that the observed product distribution is the direct result of the induced aquations and not the result of some spontaneous or induced isomerization of the products or starting materials.

Definite conclusions on the question of formation of a pentacoordinated intermediate cannot be drawn from the data presented in Table IV. However, the data exhibit enough of a pattern to warrant some discussion and to support some inferences.

Firstly, other evidence, based on chemical and isotopic competition data, is consistent with the conclusion that the nitrous acid and mercuric ion assisted aquations of acido cobalt(III) pentaammine systems proceed with the production of an intermediate.[1a,4] Examination of the data of Table IV shows that in every case where a direct comparison can be made between the two modes of aquation the same stereochemistry is observed. The strongest support for the formation of a common intermediate is given by the results for the *trans*-$[Co(en)_2ClX]^+$ and *trans*-$[Co(en)_2H_2OX]^{2+}$ systems. For these systems the ratio of the stereoisomers of the product is neither extremely large nor extremely small so that any factor

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(13) (a) S. C. Chan, *J. Chem. Soc.*, 5137 (1963); (b) P. V. Stables and M. L. Tobe, *ibid.*, 4803 (1960); (c) S. C. Chan and M. L. Tobe, *ibid.*, 5700 (1963); (d) P. J. Staple, *ibid.*, 745 (1964).

(14) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

which alters the ratio of product isomers should be readily detectable. If the leaving group is present in the transition state just prior to the addition of water the charge and/or size difference between N_2 ($+N_2O$) and HgX^+ would be expected to manifest itself in affecting the product ratio. The data in fact do show that the product ratio is sensitive to the nature of the process—note, for example, that some of the spontaneous aquations do show differences from the assisted processes. The fact that the alternate modes of inducing aquation lead to the same product ratio indicates that the leaving group has little or no participation in the transition state for the induced reactions. In other words, the data seem to indicate that the same intermediate is formed by mercuric ion or nitrous acid induced aquations.

As has already been pointed out, the stereochemistry of the induced reactions does not agree with that observed for the spontaneous. These differences are most marked for the *cis*-$[Co(en)_2N_3X]^+$, *trans*-$[Co(en)_2N_3X]^+$, and *cis*-$[Co(en)_2ClX]^+$ systems. In each case the ratio of the product isomers is different by a factor of at least three from that observed for the corresponding induced reaction, indicating that the mechanisms of the two types of reaction do differ. The stereochemistry observed for the aquation of *trans*-$[Co(en)_2ClX]^+$ provides a further indication that the leaving group in spontaneous aquations participates in the transition state observed. If the literature values are accurate the *cis*:*trans* product ratio changes from 1:2 to 1:4 with the change of Cl^- to Br^- for leaving group.

Using the "linear free energy relationship" to analyze the influence of the leaving group and a Hammond analysis to determine the importance of the entering group, Langford[1d] has concluded that at best both entering and leaving groups are only weakly bonded in the transition state for the aquation of $Co^{III}(NH_3)_5X$. The present evidence for the series $Co^{III}(en)_2YX$ shows that the spontaneous aquation in most cases does not involve an intermediate of the type occurring in the induced reactions, but the evidence also suggests that the induced reactions (which involve better leaving groups) do take place by a common intermediate. According to the present study the activated complexes for the reactions appear to be in the general range of bond making–bond breaking character described by Langford.

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Complexes of Cobalt(III) and Rhodium(III) with a Cyclic Tetradentate Secondary Amine

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The following complex cations of cobalt(III) and rhodium(III) containing 1,4,7,10-tetraazacyclododecane (cyclen) have been prepared and characterized: $[Co(cyclen)Cl_2]^+$, $[Co(cyclen)Br_2]^+$, $[Co(cyclen)CO_3]^+$, $[Co(cyclen)C_2O_4]^+$, $[Co(cyclen)(NO_2)_2]^+$, and $[Rh(cyclen)Cl_2]^+$. Comparison of the visible absorption spectra of these cyclen complexes with the spectra of corresponding tetraammine, bis(ethylenediamine), triethylenetetramine, and 4-(2-aminoethyl)diethylenetriamine complexes strongly suggests that the cyclen ligand in these complexes adopts a configuration such that the remaining two coordination positions are *cis*. The significantly higher molar absorptivities of the cyclen complexes are discussed in terms of steric constraint and distortion of the octahedral field.

Introduction

Selective N-terminal hydrolyses of simple peptides[2] have been carried out using "pseudo-enzymatic" cationic chelates such as *cis*-β-$[Co(trien)(OH)(OH_2)]^{2+}$ and *cis*-$[Co(tren)(OH)(OH_2)]^{2+}$.[3] In the course of evaluating the scope, mechanism, and utilization of this peptide-cleavage reaction, we decided to investigate other *cis* cobalt(III) complexes containing tetradentate ligands. Two *cis*-coordinated water molecules are necessary to effect peptide hydrolysis. Concurrent mechanism studies using *cis*-β-$[Co(trien)(OH)(OH_2)]^{2+}$ and *cis*-$[Co(tren)(OH)(OH_2)]^{2+}$ have been complicated by the nonequivalence of the reactive *cis* positions. Furthermore, two isomeric amino acid complexes can arise from each case.[4] This difficulty would be

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[2] J. P. Collman and D. A. Buckingham, *J. Am. Chem. Soc.*, **85**, 3039 (1963).

[3] The following abbreviations are used in this article: cyclen for 1,4,7,10-tetraazacyclododecane; cyclam for 1,4,8,11-tetraazacyclotetradecane; en for ethylenediamine; trien for triethylenetetramine; tren for 4-(2-aminoethyl)diethylenetriamine; tetramine for any four nitrogen atoms attached to cobalt(III) or rhodium(III); tetraammine for four ammonia molecules in complexes of cobalt(III).

[4] L. G. Marzilli, honors paper in chemistry, Brown University, Providence, R. I., 1965.