Wiberg[5,6] reported that his FeH_6 was stable to 300 °C and was completely decomposed by 500 °C. Ray and Sahai[3] reported that the equilibrium dissociation pressure of the hydride FeH_3 was 3.5 cm at 20 °C and that at 60 °C it decomposed to FeH. This author cannot rationalize these last observations with his experience.

Nature of the YCS. There is no physical evidence for the structure or the bonding in the YCS. Attempts to obtain an infrared spectrum and thus establish the presence of an Fe–H bond failed due to decomposition. Kost et al.[8] reported an infrared spectrum for their white hydridic product and stated that there was no evidence for an Fe–H bond but rather an Mg–H bond. Such information serves only to indicate that there may be other hydridic products.

A possible structure is indicated by $Mg_4Br_6O[(C_2H_5)_2O]_4$[25] and similar compounds of beryllium.[26] It is suggested that the fundamental unit of the YCS molecule is a tetrahedron determined by the four magnesium atoms. A bridging hydrogen is on each edge and the iron atom is at the center of the tetrahedron. A halide atom is σ bonded to each magnesium atom. Two compounds consisting of four such tetrahedrally disposed metal atoms and bridging hydrogen atoms are $H_6Re_4(CO)_{12}^{2-}$[27] and $Co_4C_{20}H_{24}$.[28]

Acknowledgment. This work was initiated by the author at the suggestion of Dr. G. N. Tyson while we were both employed by the National Engineering Science Co., Pasadena, Calif., in 1961. All the work reported here except the stoichiometry of preparations 1, 2, and 3 was carried out at the University of Victoria. The author is grateful for financial support from the University and also from the National Research Council of Canada.

Registry No. $FeH_6Mg_4Br_4(THF)_8$, 63688-44-8; $FeH_6Mg_4Cl_4(THF)_8$, 63688-45-9.

References and Notes

(1) A preliminary report was given at the Vth international Conference on Organometallic Chemistry, Moscow, Aug 1971, and at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.
(2) T. Weichselfelder, *Justus Liebigs Ann. Chem.*, **447**, 64 (1926).
(3) R. C. Ray and R. B. N. Sahai, *J. Indian Chem. Soc.*, **23**, 67 (1946).
(4) C. Haenny and E. Levi, *Chimia*, **1/10**, 203 (1947).
(5) B. Sarry, *Z. Anorg. Allg. Chem.*, **288**, 48 (1956).
(6) J. Tullis, Office of Naval Research, London, European Scientific Notes, No. 7, 1953.
(7) Y. Takegami and T. Fujmaki, *Kogyo Kagaku Zasshi*, **64**, 741 (1961).
(8) M. E. Kost, N. N. Mal'tseva, and V. I. Mikheeva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **9**, 576 (1964).
(9) A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Am. Chem. Soc.*, **83**, 4909 (1961).
(10) S. G. Gibbins, *J. Catal.*, **23**, 398 (1971).
(11) S. G. Gibbins, *Anal. Chim. Acta*, **56**, 486 (1971).
(12) S. G. Gibbins, *Anal. Chem.*, **43**, 1349 (1971).
(13) S. G. Gibbins, *Anal. Chem.*, **43**, 621 (1971).
(14) S. G. Gibbins, *Anal. Chim. Acta*, **60**, 242 (1972).
(15) S. G. Gibbins, *Anal. Chem.*, **43**, 295 (1971).
(16) S. G. Gibbins, *Anal. Chem.*, **43**, 1348 (1971).
(17) S. G. Gibbins, to be submitted for publication.
(18) Hydrogen and deuterium as H_2, HD, and D_2.
(19) H. Meerwein, *Angew. Chem.*, **59**, 168 (1947).
(20) I. G. Farbenindustrie A.-G., British Patent 506038 (May 18, 1939); *Chem. Abstr.*, **33**, 93287 (1939).
(21) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).
(22) H. Gilman, A. L. Jacoby, and H. Ludeman, *J. Am. Chem. Soc.*, **60**, 2336 (1938).
(23) B. Sarry, M. Dettke, and H. Grossman, *Z. Anorg. Allg. Chem.*, **329**, 218 (1964).
(24) H. Gilman and M. Lichtenwalter, *J. Am. Chem. Soc.*, **61**, 957 (1939).
(25) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 484 (1964).
(26) C. C. Addison and A. Walker, *J. Chem. Soc.*, 1220 (1963).
(27) H. D. Kaesz et al., *J. Am. Chem. Soc.*, **91**, 1021 (1969).
(28) J. Muller and H. Dorner, *Angew. Chem., Int. Ed. Engl.*, **12**, 843 (1973).

Contribution from the William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1., England

Effect of Steric Constraints on the Rates of Base Hydrolysis of Cobalt(III) Complexes

RICHARD A. HENDERSON and MARTIN L. TOBE*

Received March 11, 1977 AIC70198L

The rate constants for the base hydrolysis of a number of cobalt(III) complexes of the type $[Co(L_4)Cl_2]^{n\pm}$ (L_4 is a linear quadridentate ligand containing two nonterminal secondary nitrogen donors) are reported. The α-cis isomers are some 10^4 times less reactive than the corresponding β-cis and trans species. The various factors contributing to the overall rate constants for base hydrolysis are considered, and it is concluded that the ability of the deprotonated (amido) nitrogen to become planar in the trigonal-bipyramidal intermediate and to orient its plane perpendicular to the trigonal plane of the cobalt is the major cause of this reactivity difference. The α-*cis*-$[Co(trien)Cl_2]^+$ cation (trien = 1,8-diamino-3,6-diazaoctane) is also some 10^4 times less reactive than its β-cis and trans isomers even though it possesses alternative sites for deprotonation. Compounds without nonterminal secondary amine donors do not exhibit this marked reduction of reactivity of the α-cis isomer. The effect of ring size is also discussed and the rules are applied to the reactivity pattern in a very extensive series of chloropentaminecobalt(III) complexes.

Introduction

The base-catalyzed hydrolysis of octahedral acidoaminecobalt(III) complexes has been shown to occur by a mechanism that involves the rapid dissociative solvolysis of the deprotonated amido conjugate base.[1,2] It has been suggested that the considerably enhanced lability of the conjugate base is due to strong π donation from the amido nitrogen to the cobalt in the trigonal-bipyramidal five-coordinate intermediate of the dissociative process[3] and it has been shown that, in the base hydrolysis of *trans*-$[Co(R,R(S,S)\text{-}2,3,2\text{-}tet)Cl_2]^+$ (2,3,2-tet = 1,9-diamino-3,7-diazanonane), the deprotonation is rate determining and takes place at one of the secondary nitrogens;[4] the initial reaction product, *trans*-$[Co(R,S\text{-}2,3,2\text{-}tet)OHCl]^+$, is the same as that obtained from the *R*,*S*- (or meso) trans dichloro isomer.[5] In order to account for these results it was necessary to invoke a common intermediate. The β-*cis*-$[Co(R,R(S,S)\text{-}2,3,2\text{-}tet)Cl_2]^+$ isomer also yields the same product (presumably through the same intermediate) but, in this case, proton transfer is not rate determining.[6] The formation of a common intermediate from these three substrates requires that deprotonation takes place at a nitrogen that is the middle member of a meridional set of three donors and which we shall call "flat" for convenience and further requires that, in the five-coordinate intermediate formed by loss of chloride, (a) the cobalt is trigonal bipyramidal, (b) the amido group is planar, (c) the nitrogen lies in the trigonal plane

Table I. Analytical Data for the Complexes

			% C		% H		% N	
			Found	Calcd	Found	Calcd	Found	Calcd
α-*cis*-$[Co(picen)Cl_2](ClO_4)$	Mauve	$C_{14}H_{18}N_4Cl_3O_4Co$	36.0	35.6	3.70	3.85	11.80	11.88
β-*cis*-$[Co(picpn)Cl_2](ClO_4)$	Mauve-red	$C_{15}H_{20}N_4Cl_3O_4Co$	36.5	37.1	4.20	4.15	11.40	11.54
β-*cis*-$[Co(pictn)Cl_2](ClO_4)$	Mauve	$C_{15}H_{20}N_4Cl_3O_4Co$	36.3	37.1	4.05	4.15	11.20	11.54
K-α-*cis*-$[Co(edda)Cl_2]\cdot 2H_2O$	Turquoise	$C_6H_{14}N_2O_6Cl_2CoK$	18.94	19.01	2.97	3.72	7.41	7.39
K-β-*cis*- $[Co(edda)Cl_2]\cdot 2H_2O$	Turquoise	$C_6H_{14}N_2O_6Cl_2CoK$	18.86	19.01	3.01	3.72	7.27	7.39
H-*trans*-$[Co(tmdda)Cl_2]$	Dark green	$C_7H_{13}N_2O_4Cl_2Co$	26.15	26.35	4.10	4.11	8.55	8.78
α-*cis*-$[Co(trien)Cl_2]Cl\cdot H_2O$	Mauve	$C_6H_{20}N_4Cl_3OCo$	21.85	21.87	6.30	6.12	16.25	17.01
β-*cis*-$[Co(trien)Cl_2]Cl\cdot {}^1/_2H_2O$	Mauve-red	$C_6H_{19}N_4Cl_3O_{1/2}Co$	22.25	22.48	5.87	5.97	16.70	17.48
α-*cis*-$[Co(Me_2trien)Cl_2]ClO_4$	Mauve	$C_8H_{22}N_4Cl_3O_4Co$	23.75	23.81	5.50	5.49	14.00	13.89
β-*cis*-$[Co(Me_2trien)Cl_2]ClO_4$	Mauve-red	$C_8H_{22}N_4Cl_3O_4Co$	23.50	23.81	5.40	5.49	13.85	13.89

of the cobalt, and (d) the chelate rings must have time to equilibrate their conformations. The coordination plane of the nitrogen in the intermediate is more or less perpendicular to the trigonal plane of the cobalt and so the donor orbital on the nitrogen is well oriented to overlap with the acceptor orbital on the cobalt. With a succession of five-membered rings, as in the corresponding 2,2,2-tet complexes, the orientation is almost perfect. We thought that it might be of interest to see how important this π overlap might be in determining the lability of the amido conjugate base and for this reason have studied the kinetics of the base hydrolysis of complexes where the multidentate ligand prevented such an orientation. This restriction is present in the α-cis isomers of complexes containing linear quadridentate ligands, especially when the chelate rings were five-membered. This paper compares the rate constants for the base hydrolysis of pairs of α-cis and β-cis isomers where deprotonation can only take place at the nonterminal donor sites.

Experimental Section

Preparations. 1,6-Bis(2-pyridyl)-2,5-diazahexane (picen), 1,6-bis(2-pyridyl)-3-methyl-2,5-diazahexane (picpn), and 1,7-bis(2-pyridyl)-2,6-diazaheptane (pictn) were prepared by a slight modification of Lions' method.[7] A vigorously stirred mixture of zinc dust (50 g) and the appropriate diamine (1,2-diaminoethane, 1,2-diaminopropane, and 1,3-diaminopropane, respectively) (0.12 mol) and glacial acetic acid (50 mL) in ethanol (250 mL) was heated on a water bath at 70–80 °C. A solution of pyridine-2-carboxaldehyde (27 g, 0.25 mol) in ethanol (125 mL) was gradually added over a period of 90 min. During this time more glacial acetic acid and zinc dust were added in small portions at intervals until a further 100 g of each had been added. The reaction mixture was stirred for a further 4 h at 70–80 °C and then left overnight at room temperature before filtration. The filtrate was evaporated to a thick syrup which was refiltered and made alkaline with pellets of sodium hydroxide and allowed to stand for 2 h before being filtered again. When the syrup was too viscous to filter, it was diluted with acetone which could then be stripped off the filtrate. The syrup was washed with anhydrous ether and dried over anhydrous sodium sulfate. Attempts at vacuum distillation led to "cracking" and the crude oils were therefore used without further purification.

1,3-Diaminopropane-*N*,*N*′-diacetic acid dihydrochloride ($tmddaH_2\cdot 2HCl$) was prepared by the method of Douglas and Igi.[8]

N,*N*′-Dimethyl-1,2-diaminoethane was prepared by the method of Boon[9] and converted to 1,8-diamino-3,6-dimethyl-3,6-diazaoctane tetrahydrochloride ($Me_2trien\cdot 4HCl$) by the method of Searle.[10]

α-*cis*-Dichloro(1,6-bis(2′-pyridyl)-2,5-diazahexane)cobalt(III) perchlorate was prepared by a modification of Bosnich's method.[11] A solution of cobalt(II) chloride hexahydrate (10 g, 0.04 mol) in water (100 mL) was mixed with one of 1,6-bis(2-pyridyl)-2,5-diazahexane (14.5 g, 0.06 mol) in water (270 mL) and a vigorous stream of air passed through the mixture for 6 h. Concentrated hydrochloric acid (10 mL) and concentrated perchloric acid (10 mL) were then added and the solution was concentrated on a steam bath with a stream of air passing over its surface. The color changed from brown to mauve and when crystals started to appear the mixture was set aside to cool and crystallize overnight. The solid was filtered off, washed with methanol and ether, and air-dried. Further crops could be obtained by adding methanol to the filtrate.

β-*cis*-Dichloro(1,6-bis(2′-pyridyl)-3-methyl-2,5-diazahexane)cobalt(III) perchlorate and β-*cis*-dichloro(1,7-bis(2′-pyridyl)-2,6-diazaheptane)cobalt(III) perchlorate were prepared in the same way using the appropriate ligand.

Potassium α-*cis*-dichloro(ethylenediamine-*N*,*N*′-diacetate)cobalt(III)ate and potassium β-*cis*-dichloro(ethylenediamine-*N*,*N*′-diacetate)cobalt(III)ate were prepared from the corresponding α- and β-cis carbonato complexes (kindly supplied by Dr. T. P. Dasgupta) by the method of Garnett and Watts.[12] Hydrogen *trans*-dichloro(1,3-diaminopropane-*N*,*N*′-diacetate)cobalt(III)ate was prepared by the method of Igi and Douglas.[8] α-*cis*-Dichloro(1,8-diamino-3,6-diazaoctane)cobalt(III) chloride hydrate, β-*cis*-dichloro(1,8-diamino-3,6-diazaoctane)cobalt(III) chloride hemihydrate, and *trans*-dichloro(1,8-diamino-3,6-diazaoctane)cobalt(III) chloride were prepared by the method of Sargeson.[13,14]

α-*cis*-Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) perchlorate was a portion of Bosnich's original preparation[15] and was recrystallized from hot water containing sodium perchlorate.

α-*cis*-Dichloro(1,8-diamino-3,6-dimethyl-3,6-diazaoctane)cobalt(III) perchlorate and β-*cis*-dichloro(1,8-diamino-3,6-dimethyl-3,6-diazaoctane)cobalt(III) perchlorate were prepared by the method of Searle.[16]

Analytical data for all complexes are collected in Table I. When comparison could be made, visible, infrared, and ^1H NMR spectra agreed well with literature data.

Kinetics

For reactions with half-lives greater than 10 min a known volume of a solution containing all of the other reagents and previously brought to the reaction temperature was added to a weighed amount of the solid complex in a standard volumetric flask and when all had dissolved the solution was transferred to a silica spectrophotometer cell that was placed in the SP 870 constant-temperature cell housing of a Pye-Unicam SP 800 spectrophotometer. The spectrum between 700 and 315 nm was scanned from time to time. For faster reactions with half-lives between 30 s and 10 min, the solution of reagents other than the complex was brought to the reaction temperature in the spectrophotometer cell and the reaction started by adding a weighed amount of a finely powdered sample of the complex and shaking or stirring the solution until all had dissolved. The change in absorbance at one wavelength was monitored as a function of time. The temperature was held constant by a Unicam SP 875 electrical control unit when working at 60 °C and above and with water circulation at temperatures below this and was measured by a SP 872 thermocouple inserted in the thermostat block. Preliminary experiments showed that the temperature of the block was within 0.05° of that of the solution. The thermocouple potential was measured with a Solartron LM 1604 digital voltmeter and was calibrated against a standard thermometer while the reaction was being followed.

Base hydrolysis reactions with half-lives less than 5 s were followed with a Durrum-Gibson D110 stopped-flow spectrophotometer incorporating a Durrum D131 Photometric log amplifier and a Tektronix storage oscilloscope (Type 564B). For reactions with half-lives greater than 1 s the output from the photonmultiplier was connected to the Y axis of a Servoscribe RE 511-20 potentiometric recorder. For faster reactions, the output was first stored in a Datalab DL905 transient recorder and then transferred to the potentiometric recorder. The complexes were dissolved in 2×10^{-4} M nitric or perchloric acid to minimize the amount of solvolysis that occurred before the reagents were mixed.

Results

All of the complexes examined in this study undergo spectral changes in aqueous solution corresponding to the loss of at least one chloride, possibly accompanied by simultaneous or subsequent stereochemical change. The rate of change of spectrum is sensitive to the pH of the solution and, of course, the nature of the complex. Apart from β-*cis*-[Co(picpn)Cl_2]$^+$, the rate of change is independent of pH in the range 0–2. For the less labile complexes it was possible to scan the spectra of the reacting solutions from time to time. The aquation of α-*cis*-[Co(picen)Cl_2]$^+$ presents a set of spectra with two good isosbestic points at 528 and 442 nm which remain throughout the reaction involving the loss of the first chloride. The aquation of β-*cis*-[Co(pictn)Cl_2]$^+$ is characterized by one apparent isosbestic point at 450 nm but the other crossing point, originally at 548 nm, moves to 522 nm as the reaction proceeds. The aquation of β-*cis*-[Co(picpn)Cl_2]$^+$ is characterized by two crossing points that shift from 522 to 508 nm and 444 to 428 nm. No mention is made of the presence or absence of good isosbestic points in the reports of the aquation of the [Co(trien)Cl_2]$^+$ complexes,[14] the [Co(edda)Cl_2]$^-$ complexes,[12] or the α-*cis*-[Co(Me_2trien)Cl_2]$^+$ species,[16] but on reexamination of the aquation of the last named species we find very good isosbestic points at 530 and 460 nm. The presence of a wandering crossing point is indicative of a subsequent reaction and it is possible that we are observing the isomerization of the originally formed aquo–chloro complex at a rate whose constant is similar to that of the original aquation. Such a situation is quite common in the aquation of complexes of the type [Co(en)$_2$ACl]$^{n+}$ and fortuitous isosbestic points have often been observed in the aquation of *trans*-[Co(L_4)Cl_2]$^+$ when the final product contains substantial amounts of the *cis*-chloroaquo species, e.g., when L_4 = (en)$_2$ or *R*,*R*(*S*,*S*)-2,3,2-tet.[17] Since our interest lies in the base-catalyzed hydrolysis we did not investigate these systems in the depth required to analyze the stereochemistry, and the rate constants estimated from the change in absorbance at the wavelength of maximum variation may well be affected by interference from subsequent reactions. However, the semilogarithmic plots were linear over more than 2 half-lives, and the error is unlikely to be greater than 20%. The labilities of *trans*-[Co(tmdda)Cl_2]$^-$ and β-*cis*-[Co(Me_2trien)Cl_2]$^+$ were too great for the repetitive scanning method to be used and the kinetics were followed at a suitable single wavelength; no information, therefore, was obtained about the presence of absence of isosbestic points. The first-order rate constants are collected in Table II.

As the pH is increased a point is reached where the rate of hydrolysis also increases. This base-catalyzed process was studied, where possible, under pH conditions where the background aquation makes only an insignificant contribution to the rate of reaction. The catalyzed reaction of the α-cis isomers of [Co(picen)Cl_2]$^+$, [Co(edda)Cl_2]$^-$, and [Co(Me_2trien)Cl_2]$^+$ could still be studied by the repetitive scan method and in all cases excellent isosbestic points were observed throughout. The base hydrolysis of α-*cis*-[Co(eee)Cl_2]$^+$, although slow, could not be studied in this way because, like *trans*-[Co(ete)Cl_2]$^+$,[18] the initial product of base hydrolysis undergoes further reaction under these conditions which results in decomposition of the ligand and the formation of a black suspension. The rate of this interfering reaction is not strongly dependent on pH and so does not interfere with the base hydrolysis when the latter is carried out in alkaline solution. The base hydrolysis of the β-cis isomers of [Co(picpn)Cl_2]$^+$, [Co(pictn)Cl_2]$^+$, [Co(edda)$Cl_2$$^-$, and [Co(trien)$Cl_2$]$^+$, as well as *trans*-[Co(trien)Cl_2]$^+$, was followed in buffer solution at a single wavelength by means of stopped-flow spectrophotometry, while the base hydrolyses of α-*cis*-[Co(eee)Cl_2]$^+$ and some of the less reactive α-cis species were followed in NaOH solution by stopped-flow techniques. The two complexes whose aquation lability was too great to allow stopped-flow techniques, *trans*-[Co(tmdda)Cl_2]$^-$ and β-*cis*-[Co(Me_2trien)Cl_2]$^+$, were studied by adding the solids to solutions of the required pH and following the change of absorbance at a single wavelength. It was not possible to work at pH's where the background aquation did not make a major contribution to the overall reaction and it was necessary to make corrections accordingly. In some cases, [OH^-] was varied and, where it was tested, the base hydrolysis rate had a first-order dependence on [OH^-]. The observed first-order rate constants, the corrected values where appropriate, and the derived second-order rate constants are collected in Table III. In some of the studies the buffer concentration was varied while the buffer ratio and the ionic strength were held constant in order to search for general base catalysis. These results are collected in Table IV.

Table II. First-Order Rate Constants for the Aquation of [Co(L_4)Cl_2]$^{n\pm\ a,b}$

Complex	[H^+]/M	Temp/°C	$10^4 k_{obsd}$/ s^{-1}
α-*cis*-[Co(picen)Cl_2]$^+$	0.10	70.0	1.45
	0.010		1.43
β-*cis*-[Co(picpn)Cl_2]$^+$	1.0		4.01
	0.50		5.85
β-*cis*-[Co(pictn)Cl_2]$^+$	1.0	56.0	10.6
	1.0	48.5	6.22
	1.0	42.8	2.53
	0.50		2.84
trans-[Co(tmdda)Cl_2]$^-$	0.10	25.0	223
	0.010		214
α-*cis*-[Co(Me_2trien)Cl_2]$^+$	0.10	43.0	14.8
	0.010		15.0
	0.010	35.9	6.60
	0.10	25.0	1.49
	0.010		1.62
	Various		1.77[c]
β-*cis*-[Co(Me_2trien)Cl_2]$^+$	0.010	34.5	700
	0.10	25.0	315
	0.010		329
	0.010	21.1	212
	0.010	13.6	91

[a] Ionic strength controlled by the added perchloric acid. [b] [Complex] within the range 0.005–0.01 M. [c] Data from ref 16.

Discussion

The rate constants for acid and base hydrolysis are summarized in Table V, which also contains relevant data from the literature for comparison. It is clear that, with the dichloro complexes of linear quadridentate ligands containing two, nonterminal secondary amine groups, there is an extremely large difference in the reactivity toward base hydrolysis of the α-cis and the β-cis isomers, while their aquation labilities are not much different. In the case of [Co(edda)Cl_2]$^-$ it was possible to make direct comparison of the two isomers and it can be seen that, whereas the β-cis isomer is only some 9 times more labile than the α-cis toward aquation at 25 °C, it is some 30 000 times more labile in base hydrolysis. Similar studies show that, in spite of the change in the sign of the charge on the complex, the reactivity pattern for [Co(trien)Cl_2]$^+$ is very similar (k_β/k_α for aquation = 8, k_β/k_α for base hydrolysis = 20 000). Although McKenzie[19] reported the formation of α-cis and β-cis isomers of [Co(picen)Cl_2]$^+$, we were only able to prepare the α-cis species (characterized by a single set of ^{1}H

Table III. Rate Constants for the Base Hydrolysis of $[\mathrm{Co(L_4)Cl_2}]^{n+}$ [a,b]

Complex	pH	$[\mathrm{OH^-}]$/M	$k_{\mathrm{obsd}}/\mathrm{s^{-1}}$	$k_{\mathrm{corr}}/\mathrm{s^{-1}}$	$k_{\mathrm{B}}/\mathrm{M^{-1}\ s^{-1}}$
α-*cis*-$[\mathrm{Co(edda)Cl_2}]^-$		2.50×10^{-3}	3.04	3.04	1.22×10^{3}
		5.00×10^{-3}	5.62	5.62	1.12×10^{3}
		10.00×10^{-3}	10.9	10.9	1.09×10^{3}
β-*cis*-$[\mathrm{Co(edda)Cl_2}]^-$	6.840[c]	1.04×10^{-7}	2.97	2.97	2.86×10^{7}
	6.840[c]	1.04×10^{-7}	3.13	3.13	3.01×10^{7}
	6.505[c]	0.48×10^{-7}	1.46	1.46	3.08×10^{7}
trans-$[\mathrm{Co(tmdda)Cl_2}]^-$	5.500[d]	4.7×10^{-6}	3.03×10^{-2}	8.1×10^{-3}	1.7×10^{6}
	5.500[d]	4.7×10^{-6}	3.14×10^{-2}	9.2×10^{-3}	2.0×10^{6}
	5.240[d]	2.6×10^{-6}	2.66×10^{-2}	4.4×10^{-3}	1.7×10^{6}
α-*cis*-$[\mathrm{Co(trien)Cl_2}]^+$		5.0×10^{-3}	0.336	0.336	6.72×10^{1}
		10.0×10^{-3}	0.696	0.696	6.96×10^{1}
		20.0×10^{-3}	1.363	1.363	6.82×10^{1}
	10.975[e,f]	1.72×10^{-3}	0.115	0.115	6.69×10^{1}
	10.975[e,f]	1.72×10^{-3}	0.112	0.112	6.52×10^{1}
	10.75[e,f]	1.72×10^{-3}	0.113	0.113	6.58×10^{1}
β-*cis*-$[\mathrm{Co(trien)Cl_2}]^+$	6.922[c,e]	1.54×10^{-7}	0.168	0.168	1.09×10^{6}
	6.922[c,e]	1.54×10^{-7}	0.172	0.172	1.12×10^{6}
	6.890[c,e]	1.43×10^{-7}	0.173	0.173	1.21×10^{6}
trans-$[\mathrm{Co(trien)Cl_2}]^+$	6.922[c,e]	1.54×10^{-7}	0.244	0.244	1.59×10^{6}
	6.922[c,e]	1.54×10^{-7}	0.251	0.251	1.63×10^{6}
	6.890[c,e]	1.43×10^{-7}	0.228	0.228	1.60×10^{6}
α-*cis*-$[\mathrm{Co(picen)Cl_2}]^+$	6.922[c,e]	1.54×10^{-7}	1.73×10^{-4}	1.72×10^{-4}	1.12×10^{3}
	6.922[c,e]	1.54×10^{-7}	1.80×10^{-4}	1.79×10^{-4}	1.16×10^{3}
	6.890[c,e]	1.43×10^{-7}	1.53×10^{-4}	1.52×10^{-4}	1.06×10^{3}
β-*cis*-$[\mathrm{Co(picpn)Cl_2}]^+$	6.922[c,e]	1.54×10^{-7}	3.04	3.04	1.98×10^{7}
	6.922[c,e]	1.54×10^{-7}	3.02	3.02	1.96×10^{7}
	6.890[c,e]	1.43×10^{-7}	2.87	2.87	2.01×10^{7}
β-*cis*-$[\mathrm{Co(pictn)Cl_2}]^+$	6.922[c,e]	1.54×10^{-7}	0.322	0.322	2.09×10^{6}
	6.922[c,e]	1.54×10^{-7}	0.320	0.320	2.08×10^{6}
	6.890[c,e]	1.43×10^{-7}	0.304	0.304	2.12×10^{6}
α-*cis*-$[\mathrm{Co(eee)Cl_2}]^+$		2.50×10^{-3}	9.86	9.86	3.94×10^{3}
		5.00×10^{-3}	21.2	21.2	4.24×10^{3}
		10.0×10^{-3}	42.8	42.8	4.28×10^{3}
α-*cis*-$[\mathrm{Co(Me_2trien)Cl_2}]^+$	6.950[c]	1.31×10^{-7}	9.37×10^{-4}	7.76×10^{-4}	5.9×10^{3}
	6.950[c]	1.31×10^{-7}	8.98×10^{-4}	7.37×10^{-4}	5.6×10^{3}
	6.950[c]	1.31×10^{-7}	9.29×10^{-4}	7.68×10^{-4}	5.8×10^{3}
β-*cis*-$[\mathrm{Co(Me_2trien)Cl_2}]^+$	11.120[f]	1.94×10^{-3}	9.60×10^{-2}	6.45×10^{-2}	3.3×10^{1}
	11.120[f]	1.94×10^{-3}	9.52×10^{-2}	6.37×10^{-2}	3.3×10^{1}
	11.120[f]	1.94×10^{-3}	8.87×10^{-2}	5.72×10^{-2}	3.0×10^{1}
	11.120[f]	1.94×10^{-3}	7.60×10^{-2}	4.45×10^{-2}	2.3×10^{1}

[a] At 25.0 °C. [b] $\mu = 0.050$ except where stated. [c] 2,6-Dimethylpyridine–$\mathrm{HClO_4}$ buffer. [d] Pyridine–$\mathrm{HNO_3}$ buffer. [e] $\mu = 0.15$. [f] Diethylamine–$\mathrm{HClO_4}$ buffer.

Table IV. Effect of Buffer Concentration on the Rate Constants for Base Hydrolysis[a–c]

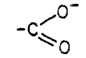
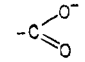
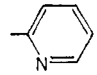
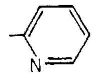
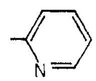
Complex	$[\mathrm{B}] + [\mathrm{BH^+}]$/M	$k_{\mathrm{obsd}}/\mathrm{s^{-1}}$ [d]	$k_{\mathrm{B}}/\mathrm{M^{-1}\ s^{-1}}$
β-*cis*-$[\mathrm{Co(trien)Cl_2}]^+$	0.025	0.172	7.7×10^{5}
	0.200	0.180	8.0×10^{5}
trans-$[\mathrm{Co(trien)Cl_2}]^+$	0.025	0.245	1.09×10^{6}
	0.200	0.235	1.05×10^{6}
α-*cis*-$[\mathrm{Co(picen)Cl_2}]^+$	0.025	0.000178	7.9×10^{2}
	0.200	0.000170	7.6×10^{2}
β-*cis*-$[\mathrm{Co(picpn)Cl_2}]^+$	0.025	2.75	1.23×10^{7}
	0.200	2.74	1.22×10^{7}
β-*cis*-$[\mathrm{Co(pictn)Cl_2}]^+$	0.025	0.297	1.31×10^{6}
	0.200	0.314	1.40×10^{6}

[a] At 25.0 °C. [b] 2,6-Dimethylpyridine–perchloric acid buffer, $[\mathrm{B}]/[\mathrm{BH^+}] = 1.33$, pH 7.040, $[\mathrm{OH^-}] = 2.24 \times 10^{-7}$ M. [c] $\mu = 0.25$. [d] Average value from three independent runs.

NMR signals for the pyridine protons) and we have been forced to compare this complex with the corresponding $[\mathrm{Co(picpn)Cl_2}]^+$ and $[\mathrm{Co(pictn)Cl_2}]^+$ species which are known to have β-cis geometry (characterized by two sets of ^{1}H NMR signals for the pyridine protons). The presence of a *C*-methyl substituent in the middle five-membered ring of picpn is not expected to affect the reactivity to any great extent and the ratio $k_{\beta(\mathrm{picpn})}/k_{\alpha(\mathrm{picen})} = 3$ for aquation and so does not differ greatly from that observed for the other two exact pairs. For base hydrolysis, however, the ratio $k_{\beta(\mathrm{picpn})}/k_{\alpha(\mathrm{picen})} = 20\,000$ and once again reflects the dramatic difference between such pairs of α-cis and β-cis isomers with five-membered chelate rings. It was not possible to compare α-cis and β-cis isomers of complexes with a six-membered central chelate ring owing to the rarity of the α-cis form, but all the β-cis and trans species of this sort examined were very sensitive to base hydrolysis. Where comparison can be made it would appear that β-cis and trans species with the six-membered central chelate ring are considerably less reactive toward base hydrolysis than their five-membered ring analogues. Comparison of *trans*-$[\mathrm{Co(tmdda)Cl_2}]^-$ with β-*cis*-$[\mathrm{Co(edda)Cl_2}]^-$ again demonstrates a similar reduction in reactivity toward base hydrolysis even though the aquation lability of the tmdda complex is markedly greater than that of the edda species.

In discussing the causes of these behavior patterns it is necessary, first of all, to realize that the observed second-order rate constant for base hydrolysis can be, and generally is, a composite quantity of a number of rate constants. In its most general form, $k_{\mathrm{B}} = \sum_i n^i k_1^i k_2^i/(k_{-1}^i + k_2^i)$ where k_1^i is the second-order rate constant for the exchange of the protons in the *i*th group of n_i equivalent protons, k_2^i is the rate constant for the dissociation of the conjugate base formed by the removal of one of this *i*th group of protons, and k_{-1}^i is the rate constant for its reprotonation. When $k_2^i \gg k_{-1}^i$ this reduces to $k_{\mathrm{B}} = \sum_i n^i k_1^i$ and the lability toward base hydrolysis simply reflects the lability of the amine protons. This limiting case has been observed in the base hydrolysis of the meso and racemic *trans*-$[\mathrm{Co(2,3,2\text{-}tet)Cl_2}]^+$ isomers,[4,5,20] *trans*-$[\mathrm{Co(cyclam)Cl_2}]^+$,[22] and other *trans*-diacidocyclam complexes

Table V. Rate Constants for the Aquation and Base Hydrolysis of $[Co(L_4)Cl_2]^{n+}$ at 25 °C ($L_4 = RCH_2R'CH_2R$)

			$10^4k_{aq}/s^{-1}$			$10^{-4}k_B/M^{-1}\ s^{-1}$		
L_4	R	R′	α-Cis	β-Cis	Trans	α-Cis	β-Cis	Trans
edda		$-NH(CH_2)_2NH-$	2.08[a]	17.9[a]		0.114[b]	2980[b]	
tmdda		$-NH(CH_2)_3NH-$			214			180[b]
trien	$-CH_2NH_2$	$-NH(CH_2)_2NH-$ (*RR*)(*SS*)	1.71[c]	14.1[c]	35.3[c]	0.0068[b] 0.0066[d]	114[d]	161[d]
2,3,2-tet	$-CH_2NH_2$	$-NH(CH_2)_3NH-$ (*RR*)(*SS*) $-NH(CH_2)_3NH-$ (*RS*)		11.0[e]	2.9[e] 0.15[e]		1.6[f–h]	5.1[b,f,i] 2.5[b,f,i]
picen		$-NH(CH_2)_2NH-$	1.45[j]			0.111[d]		
picpn		$-NHCH(CH_3)CH_2NH-$		4.01[j]			1980[d]	
pictn		$-NH(CH_2)_3NH-$		46.0[k]			210[d]	
eee	$-CH_2NH_2$	$-S(CH_2)_2S-$	0.120[l]			0.415		
ete	$-CH_2NH_2$	$-S(CH_2)_3S-$			0.041[m]			1.54[b,n]
Me_2trien	$-CH_2NH_2$	$-(H_3C)N(CH_2)_2N(CH_3)-$	1.57	320		0.58[b]	0.0030[b]	

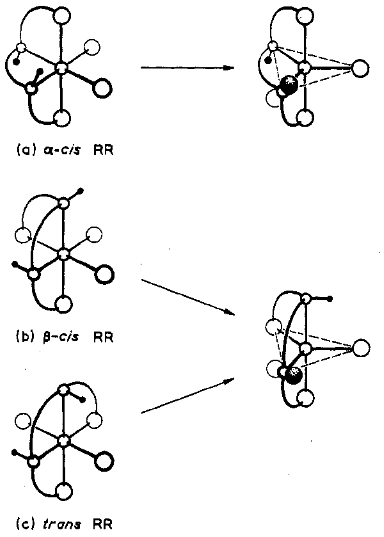
[a] Reference 12. [b] $\mu = 0.05$. [c] Reference 14. [d] $\mu = 0.15$. [e] Reference 17. [f] At 20.0 °C. [g] $\mu = 0.040$. [h] Reference 6. [i] Reference 20. [j] At 70.0 °C. [k] Extrapolated to 70.0 °C. [l] Reference 21. [m] Reference 18. [n] Extrapolated from data in ref 18.

(cyclam = 1,4,8,11-tetraazacyclotetradecane)[23] but is quite unusual. All of the other reactions listed in Table IV (with the possible exception of *trans*-$[Co(tmdda)Cl_2]^-$ which was not tested) fall into the category where $k_{-1}{}^i >> k_2{}^i$ where $k_B = \sum_i n^i k_1{}^i k_2{}^i/k_{-1}{}^i$ and can be characterized by the absence of general base catalysis as in the reactions of β-*cis*-$[Co(trien)Cl_2]^+$, *trans*-$[Co(trien)Cl_2]^+$ (note the change in the rate-determining step on changing from the 2,3,2-tet ligand to trien (2,2,2-tet)), α-*cis*-$[Co(picen)Cl_2]^+$, and β-*cis*-$[Co(picpn)Cl_2]^+$ or by direct measurement of k_B and the various $k_1{}^i$ values as in β-*cis*-$[Co(2,3,2\text{-tet})Cl_2]^+$.[6]

Since k_1 enters into all expressions for k_B it is necessary to see whether variation of k_1 with the geometry of the complex can account for the observations. There is considerable evidence, although systematic studies have yet to be made, that the protons on an amine trans to chloride exchange much more rapidly than those on an amine trans to another amine.[6,24–26] But, while k_1 for the secondary amine D trans to Cl in β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)$Cl_2]^+$ exchanging with H (3×10^6 $M^{-1}\ s^{-1}$ at 20 °C)[6] is some 10^2 times greater than k_1 for the analogous exchange in *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)$Cl_2]^+$ ($2.6 \times 10^4\ M^{-1}\ s^{-1}$ at 20 °C),[20] the value for k_B is some three times smaller. In going from the β-cis to the trans isomer there is also an enormous change in the ratio k_{-1}/k_2 from 180 to 0.05 (or less) and, as it seems unlikely that this is due to a 4000-fold increase in k_2, it must be concluded that k_{-1} is also extremely sensitive to the nature of the trans ligand and its variation can counterbalance, or even reverse, the effect of varying k_1. In any case, while trans effects of this sort might account for differences between cis and trans isomers, they cannot account for differences between α-cis and β-cis species since both possess at least one secondary amine group with a chloride trans to it. A second factor that has a significant effect upon the magnitude of k_1 is whether the nitrogen is "flat" or "angular" in the sense of it being the central member of a meridional or facial set of three linked donors, respectively. While there have been no systematic studies it would appear that the protons on "flat" secondary nitrogens are more labile than those on "angular" ones, all other factors being equal. Thus, the flat secondary nitrogens in $β_2$-*cis*-[Co(*R*,*S*(*S*,*R*)-trien)(glyO)]$^{2+}$ and $β_2$-*cis*-[Co(*R*,*R*(*S*,*S*)-trien)(glyO)]$^{2+}$ exchange in D_2O at rates that are some 50 times greater than those for the exchange of the protons on the "angular" secondary nitrogens. In the $β_2$-cis isomer both secondary nitrogens are trans to $-NH_2$ groups (either from the glycinate or the end of the quadridentate) and so the difference in proton lability cannot be ascribed to a trans effect. It would seem, therefore, that the absence of a "flat" secondary nitrogen in the α-cis isomer might lead to a decrease in k_1 but that this would be small compared to the factor of 10^4 required to account for the large decrease in k_B on going from the β-cis to the α-cis complex.

In the absence of a direct measurement of the acidity of the amine protons it is not possible to calculate values for k_{-1} and to examine whether their variation can be responsible for the change in k_B. If this change were solely the result of a change in the acidity of the complex, i.e., in the ratio k_1/k_{-1}, it would require a pK_a difference of 4 units between the α-cis and β-cis species. This seems unlikely and, from a comparison of the behavior of the β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)$Cl_2]^+$ cation with that of its trans isomer[6] and of trans-[Co(*R*,*R*(*S*,*S*)-trien)$Cl_2]^+$ with *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)$Cl_2]^+$ (see below), there is reason to believe that k_{-1} changes in the same direction as k_1 and that the acidity, and hence k_B, does not parallel the lability of amine protons toward exchange (assuming, of course, that k_1 is not rate determining).

The third contribution toward the reactivity that must be considered is the lability of the conjugate base, as quantified by k_2. This can respond to changes in the stabilization of the ground state and/or changes in the stabilization of the transition state. The difference in the rates of aquation of the α-cis and β-cis amine complexes, where π donation is not implicated, is rarely more than an order of magnitude and even if coupled with the enhanced value of k_1 resulting from the presence of a "flat" nitrogen could not easily account for the 10^4-fold increase in k_B. The five-coordinate intermediate derived from the α-cis complex differs from the other in the sense that a chelate ring links two equatorial positions. In all



(a) α-*cis* RR

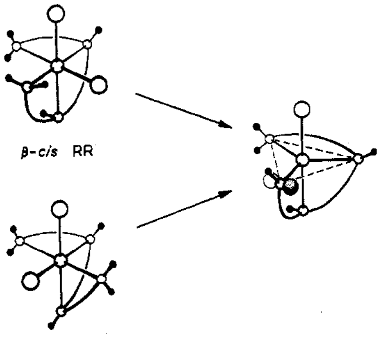
(b) β-*cis* RR

(c) *trans* RR

Figure 1. Trigonal-bipyramidal intermediates with equatorially bound planar amido nitrogen groups showing the restriction to favorable orientation of the donor orbital when the precursor has the α-cis form.

of the cis-α complexes examined this equatorial ring is five-membered and it might be argued that the strain resulting in the opening of the angle at the metal from 90 to 120° is a major cause of the lower reactivity. It is not possible to prepare α-cis complexes with a six-membered middle ring and so a direct study of the effects of ring size is not possible. However, comparison of compound **12** in Figure 3 with compound **13** and comparison of **15** with **16** indicate that the five-membered ring strain cannot account for a rate reduction of more than an order of magnitude or so.

This then leaves the suggestion that the π-donor abilities of the "angular" and "flat" nitrogens, when they are deprotonated and become planar, differ markedly because of the geometric requirements of the quadridentate ligand. Factors that affect the stability of the five-coordinate intermediate must also greatly influence the transition state nearby it and hence the rate of reaction. It can be seen, in Figure 1, that a nonterminal amido nitrogen in a linear quadridentate ligand can become planar without undue strain, even when there is a sequence of three five-membered rings, but its plane cannot become perpendicular (or even parallel) to the trigonal plane of the trigonal-bipyramidal metal when the precursor has an α-cis geometry. On the other hand, the "flat" nitrogen in the β-cis and trans precursors can become planar and orient its plane perpendicular to the trigonal plane of the cobalt; indeed, when it is linking two five-membered rings, molecular models show that the minimum strain conformation has the right orientation for maximum overlap. When the "flat" nitrogen is linking a five- and a six-membered ring or two six-membered rings, the minimum energy conformations lie with the plane on either side of the vertical and the optimum orientation corresponds to a somewhat higher energy conformation. Orientation restrictions would therefore seem to be the explanation for the low k_B for the α-cis complexes and also for the smaller decrease in reactivity when the "flat" nitrogen is linked to one or two six-membered rings. In the α- and β-*cis*-[Co(edda)Cl$_2$]$^-$ anions and the α-*cis*-[Co(picen)Cl$_2$]$^+$, β-*cis*-[Co(picpn)Cl$_2$]$^+$, and β-*cis*-[Co(pictn)Cl$_2$]$^+$ cations there are no terminal sites for amine deprotonation, and the argument is reasonably valid. It is gratifying to note that the effect is absent in the base hydrolysis of the α-*cis*-[Co(eee)Cl$_2$]$^+$ and *trans*-[Co(ete)Cl$_2$]$^+$ cations, and the α-*cis*- and β-*cis*-[Co(Me$_2$trien)Cl$_2$]$^+$ cations, where the amido nitrogens must occupy terminal positions, although the suppressed activity of the last mentioned complex, in spite of its high aquation lability, calls for further comment.



β-*cis* RR

α-*cis* RR

Figure 2. Generation of trigonal-bipyramidal intermediates with an axial chloride.

In spite of the fact that α-*cis*-[Co(trien)Cl$_2$]$^+$ possesses terminal –NH$_2$ groups that can provide a labilizing amide, it is still some 10^4 times less reactive than the β-cis isomer. It would seem that the site of deprotonation is still the secondary nitrogen and the complete retention of configuration in the base hydrolysis of the α- and β-cis complexes[28,29] indicates the absence of a common intermediate and suggests that the intermediates with equatorial chloride depicted in Figure 1 are correct. The alternative intermediate with the chloride in an axial position, Figure 2, allows the terminal amido group to act as an efficient π donor and lie in trigonal plane of the metal with its own plane perpendicular to it, but this should give a mixture of α- and β-cis products on subsequent recombination. It is possible that the pathway to give an α-cis product predominates but, whatever the nature of the intermediate, the low value of k_B (67 M^{-1} s^{-1} at 25 °C) provides an upper limit to the rate constant for reaction by way of the intermediate with axial chloride. In view of the higher reactivity of α-*cis*-[Co(eee)Cl$_2$]$^+$ (k_B = 4.15 × 10^3 M^{-1} s^{-1} at 25 °C) and α-*cis*-[Co(Me$_2$trien)Cl$_2$]$^+$ (k_B = 8.52 × 10^3 M^{-1} s^{-1} at 25 °C) this low reactivity is unexpected. Until such time as the rate constants for proton exchange in α-*cis*-[Co(trien)Cl$_2$]$^+$ have been measured one can only speculate as to the extent to which a very low value for k_1 for the terminal amine protons is the reason for this. It is possible to estimate an upper limit for k_1 for the protons on the –NH$_2$ group trans to NH in β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl$_2$]$^+$. In this complex there is less than 5% exchange of deuterium in this position after 85% of the material has been consumed in base hydrolysis[6] (k_B = 1.6 × 10^4 M^{-1} s^{-1} at 20 °C) which suggests an upper limit of 5 × 10^2 M^{-1} s^{-1} for this exchange, which, if isotope effects and the temperature differences are taken into account, might rise to 10^3 M^{-1} s^{-1} at 25 °C. If k_1 for the terminal amine protons in α-*cis*-[Co(trien)Cl$_2$]$^+$ was of similar magnitude (and having already shown that k_1 can be very sensitive to minor variations in the nature of the complex we recognize the rashness of this assumption) and if k_{-1}/k_2 was much greater than unity, k_B by this pathway might be too small for this route to contribute significantly to the base hydrolysis. There is no a priori reason that the pathway leading to the intermediate with an axial chloride should have a much smaller value of k_2. Such an intermediate has been invoked to account for the presence of 16% of the Λ-*cis*-[Co(en)$_2$OHCl]$^+$ in the product of base hydrolysis of Δ-*cis*-[Co(en)$_2$Cl$_2$]$^+$ [30,31] and some 30–40% of the reaction is thought to go by this route. Clearly more work is called for.

It is possible to compare, directly, two sets of complexes differing only in the size of the middle chelate ring, i.e., β-*cis*-[Co(trien)Cl$_2$]$^+$ with β-*cis*-[Co(2,3,2-tet)Cl$_2$]$^+$ and *trans*-[Co(trien)Cl$_2$]$^+$ with *trans*-Co(2,3,2-tet)Cl$_2$]$^+$, all with the *R*,*R*(*S*,*S*) configuration of the ligand, and one fairly similar pair, namely, β-*cis*-[Co(picpn)Cl$_2$]$^+$ with β-*cis*-[Co(pictn)Cl$_2$]$^+$.

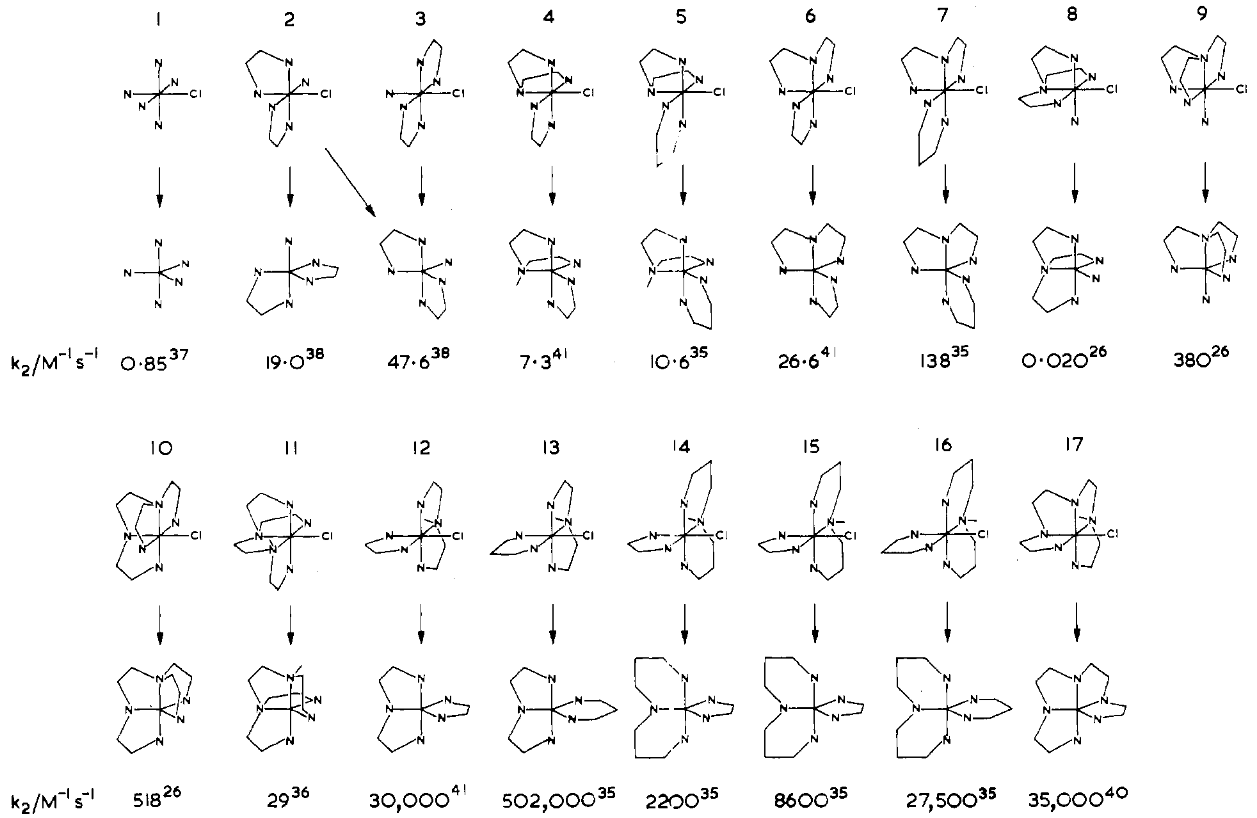


Figure 3. Rate constants for the base hydrolysis of chloropentaminecobalt(III) complexes at 25 °C. The monodentate ammonia appears in **1**, **2**, **3**, **8**, and **9**; the bidentate 1,2-diaminoethane in **2**, **3**, **4**, **6**, **12**, **14**, and **15**; the bidentate 1,3-diaminopropane in **5**, **7**, **13**, and **16**; the terdentate 1,5-diamino-3-azapentane in **4**, **5**, **6**, **7**, **12**, and **13**; the terdentate 1,7-diamino-4-azaheptane in **14**, **15**, and **16**; the quadridentate tris(2-aminoethyl)amine in **8** and **9**; the pentadentate 1,8-diamino-3-(2′-aminoethyl)-3,6-diazaoctane in **10**; the pentadentate 1,8-diamino-3-(2′-aminoethyl)-6-methyl-3,6-diazaoctane in **11**; and the pentadentate 1,11-diamino-3,6,9-triazaundecane in **17**. The five-coordinate intermediates indicated are either those deduced from the known steric courses or else those predicted from the factors discussed in the text.

In all three cases, k_B is significantly greater in the complex with the five-membered central ring. It is tempting to ascribe this to a contribution to k_2 arising from the greater ease of orienting the planar amido nitrogen when it has five-membered rings on either side of it but caution must be exercised since, in the case of *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl$_2$]$^+$ it has been shown that $k_2 >> k_{-1}$ and so does not appear in the expression for k_B.[4] The other complexes behave normally with $k_B = nk_1k_2/k_{-1}$. The change in reactivity pattern on going from *trans*-[Co(*R*,*R*(*S*,*S*)-trien)Cl$_2$]$^+$ with its gauche five-membered ring to *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl$_2$]$^+$ with a skew six-membered central ring[32] is quite dramatic. Not only does k_B decrease by a factor of 30 but the ratio of k_{-1}/k_2 must change from a value that is much greater than unity, since no general acid–base catalysis is observed, to a value that is less than 0.05.[4] For the 2,3,2-tet complex, $k_1 = {}^1/_2k_B = 2.5 \times 10^4$ M^{-1} s^{-1} and for the trien complex k_1 must be considerably greater than k_B. The decrease of k_1 by at least two orders of magnitude on going from the five- to the six-membered central ring species may be the result of a decrease of ring strain or it may be due to the presence of a larger lyophobic group in the region of the secondary amine protons. Neither explanation seems particularly plausible in the light of the close similarity of the values of k_1 for the *R*,*R*(*S*,*S*) and *R*,*S* isomers of the *trans*-[Co(2,3,2-tet)Cl$_2$]$^+$ cation, which differ by no more than a factor of 2. The meso (*R*,*S*) isomer adopts a chair conformation for the six-membered ring which is more strain free than the skew arrangement of the *R*,*R*(*S*,*S*) form and also places the –(CH$_2$)$_3$– grouping well away from the amine protons. In order to cause the ratio of k_{-1}/k_2 to decrease so much, a decrease in k_2 would require an even greater decrease in k_{-1}. It seems most unlikely that k_2 increases and certainly not by the amount required. In the absence of base catalysis the 2–3–2 system is generally less labile than the 2–2–2 system. One must therefore conclude that the decrease in k_1 is accompanied by a similar decrease in k_{-1} so that, once again, we have an example where proton acidity and proton lability are not related. Until the values of k_{-1} and k_2 can be separately evaluated it will not be possible to decide whether ring size has any significant effect on the magnitude of k_2.

The unusual inversion of the reactivity pattern going from acid to base hydrolysis in the α-cis and β-cis isomers of [Co(Me$_2$trien)Cl$_2$]$^+$ has yet to be explained satisfactorily. We fully confirm the assignment of the β-cis-(*R*,*R*(*S*,*S*)) configuration to the solvolytically labile species as made by Searle et al.[16] and, like them, we are unable to find a plausible reason that the β isomer is so much more labile than the α. Both aquate with complete retention of configuration and the greater lability of the β species arises from a much lower activation energy (16.6 ± 0.7 kcal mol^{-1}) only partially compensated by a lower entropy of activation (−10 ± 2 cal K^{-1} mol^{-1}), cf., for α-*cis*-[Co(Me$_2$trien)Cl$_2$]$^+$, $\Delta H^{\ddagger} = 22.9 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = +0.5 \pm 1.3$ cal K^{-1} mol^{-1}. The entropies of activation suggest that the "noninvolved" ligands in the aquation adopt a square-pyramidal geometry.[33] Analysis of the steric course of base hydrolysis shows clearly that the α-cis substrate gives only α-cis product but a similar treatment of the base hydrolysis of the β-cis species is more difficult because of the interference by the noncatalyzed aquation and the subsequent solvolysis of the hydroxochloro product. Nevertheless, the product seems to be mainly β-*cis*-[Co(Me$_2$trien)ClOH]$^+$. Thus, although both α- and β-cis species can form a common intermediate with an axial chloride (Figure 2) it appears that they do not. It is not at all clear why the base hydrolysis of the β-cis species is so slow. If the explanation of Buckingham et al.[34] of the increase in the lability of $Co(NH_2R)_5Cl^{2+}$ toward base hydrolysis as the bulkiness of R increases in terms of relief of strain in the dissociation step (i.e., increase in k_2) is correct, then one might expect the same to apply in this system. However, instead of the β-cis isomer being much more labile than the α-cis toward base hydrolysis it is much less reactive. Furthermore, the behavior of this system contradicts the proposal of Sargeson[26] that an amido group trans to the leaving group is a more effective labilizer than one in the cis position, since the α-cis species does not possess a deprotonatable amine group trans to chloride while the β-cis isomer does. Their observation that the base hydrolysis of the p isomer (chloride trans to a primary amine) of $[Co(tren)(NH_3)Cl]^{2+}$ (compound **9** in Figure 3) (tren = tris(2-aminoethyl)amine) is some 10^4 times faster than that of the t isomer (Cl trans to the tertiary nitrogen, compound **8** in Figure 3) is just as easily explained in terms of the ease of formation of a trigonal-bipyramidal intermediate which, with axial sites occupied by ammonia and the tertiary nitrogen, has a far less strained quadridentate ligand than the one with ammonia and the tertiary nitrogen in the equatorial positions. The latter intermediate would account for the stereochemical change observed in the base hydrolysis of the t isomer.

Having considered the factors that affect the reactivity of complexes of the type $[Co(L_4)Cl_2]^{n+}$, where L_4 is a linear quadridentate ligand, generally but not necessarily containing four nitrogen donors, toward base hydrolysis, we must conclude that a major contribution comes from the ability of the amido group to become planar and orient itself perpendicular to the trigonal plane of the cobalt in the five-coordinate intermediate. Nonterminal amine groups provide the best labilization, especially when they are cis to the leaving group (the Nordmeyer cis effect[34]). It is convenient to list the requirements for high lability toward base hydrolysis as follows: (i) there should be a "flat" secondary nitrogen to form the amido group, (ii) the amido group must be cis to the leaving group, (iii) the plane of the amido group in the intermediate should be able to lie perpendicular to the trigonal plane of the cobalt, (iv) there should be five-membered rings on either size of this group to hold it in position, and (v) there should be monodentate amines or a six-membered chelate occupying the remaining equatorial sites in the intermediate, so that there is minimal strain. Data for a number of chloropentaminecobalt(III) complexes with ammonia, 1,2-diaminoethane, 1,3-diaminopropane, 1,5-diamino-3-azapentane, 1,7-diamino-4-azaheptane, tris(2-aminoethyl)amine, 1,11-diamino-3,6,9-triazaundecane, 1,8-diamino-3-(2′-aminoethyl)-3,6-diazaoctane, and 1,8-diamino-3-(2′-aminoethyl)-6-methyl-3,6-diazaoctane as nitrogen donors are collected in Figure 3 where it will be seen that the rate constants cover some seven orders of magnitudes. The kinetics of proton exchange in compounds **1**,[24,25] **2**,[25] **3**,[25] **8**,[26] **9**,[26] **10**,[25] and **11**[36] have been studied either completely or in part and all meet the requirement that $k_1 >> k_B$ (i.e., $k_{-1} >> k_2$). It would seem unlikely that any of the others, except perhaps the most labile, fell into the category where k_1 was rate determining. Of all the compounds listed, only **13** fulfills all five requirements and is by far the most reactive. Compounds **12** and **17** do not meet condition (v) and **16** does not meet condition (iv). These are just over an order of magnitude less reactive. Compounds **14** and **15** fulfill neither of these conditions and are even less reactive. Compound **10** has a "flat" secondary nitrogen but does not fulfill condition (ii). It is some 10^3 times less reactive than **13** which it resembles, apart from the position of the chlorine with respect to the secondary amine. This is further evidence in favor of the proposal that, in spite of the very large value of k_1 for the exchange of the unique secondary proton in **10** (*sym*-$[Co(trenen)Cl]^{2+}$), the secondary amine nitrogen does not act as the labilizing π donor. All of the other complexes in the figure contain no "flat" secondary nitrogens and are all even less reactive. Two critical predictions that can be made are (i) the unsymmetrical isomer of $[Co(trenen)Cl]^{2+}$ retaining the "flat" nitrogen should be much more labile than the one that has been studied and (ii) of the two isomers of $[Co(dien)(NH_3)_2Cl]^{2+}$ with the meridional configuration, that with the two ammonias cis and chloride trans to ammonia (analogous to **13** in Figure 3) should be very much more labile than the symmetrical isomer with the two ammonias trans and chloride trans to the "flat" secondary nitrogen (analogous to **10** in Figure 3).

Acknowledgment. We thank Mr. C. J. Cooksey for synthesizing 1,8-diamino-3,6-dimethyl-3,6-diazaoctane (Me_2trien) for us and Dr. T. P. Dasgupta for the generous gift of the potassium salts of *α-cis-* and *β-cis*-carbonato(ethylenediaminediacetate)cobalt(III)ate. R.A.H. acknowledges a grant from the Science Research Council.

Registry No. *α-cis*-$[Co(picen)Cl_2](ClO_4)$, 32593-90-1; *β-cis*-$[Co(picpn)Cl_2](ClO_4)$, 36545-11-6; *β-cis*-$[Co(pictn)Cl_2](ClO_4)$, 63492-42-2; *α-cis*-$[Co(picen)Cl_2]^+$, 47100-19-6; *β-cis*-$[Co(picpn)Cl_2]^+$, 47176-30-7; *β-cis*-$[Co(pictn)Cl_2]^+$, 63492-41-1; *trans*-$[Co(tmdda)Cl_2]^-$, 63412-80-6; *α-cis*-$[Co(Me_2trien)Cl_2]^+$, 48145-39-7; *β-cis*-$[Co(Me_2trien)Cl_2]^+$, 49856-57-7; *α-cis*-$[Co(edda)Cl_2]^-$, 26145-35-7; *β-cis*-$[Co(edda)Cl_2]^-$, 26135-76-2; *α-cis*-$[Co(trien)Cl_2]^+$, 63492-43-3; *β-cis*-$[Co(trien)Cl_2]^+$, 63492-44-4; *trans*-$[Co(trien)Cl_2]^+$, 46135-28-8; *α-cis*-$[Co(eee)Cl_2]^+$, 32594-33-5.

References and Notes

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, p 177.
(2) See M. L. Tobe, *Acc. Chem. Res.*, **3**, 337 (1970), for a fairly recent review.
(3) F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4878 (1956).
(4) E. Ahmed and M. L. Tobe, *Inorg. Chem.*, **13**, 2956 (1974).
(5) G. Marangoni, M. Panayotou, and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, 1989 (1973).
(6) E. Ahmed and M. L. Tobe, *Inorg. Chem.*, **15**, 2635 (1976).
(7) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).
(8) K. Igi and B. E. Douglas, *Inorg. Chem.*, **13**, 425 (1974).
(9) W. R. Boon, *J. Chem. Soc.*, 307 (1947).
(10) G. H. Searle, M. Petkovic, and F. R. Keene, *Aust. J. Chem.*, **25**, 2045 (1972).
(11) B. Bosnich and W. R. Kneen, *Inorg. Chem.*, **9**, 2191 (1970).
(12) P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, **8**, 307 (1974).
(13) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).
(14) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).
(15) B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, **8**, 2567 (1969).
(16) G. H. Searle, M. Petkovic, and F. R. Keene, *Inorg. Chem.*, **13**, 399 (1974).
(17) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).
(18) M. L. Tobe and M. L. Tucker, *Inorg. Chem.*, **12**, 2994 (1973).
(19) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. A*, 1666 (1971).
(20) E. Ahmed, M. L. Tucker, and M. L. Tobe, *Inorg. Chem.*, **14**, 1 (1975).
(21) T. A. Jackman and J. H. Worrell, *J. Am. Chem. Soc.*, **93**, 1044 (1971).
(22) C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).
(23) F. W. Mak and C. K. Poon, *Inorg. Chem.*, **15**, 1949 (1976).
(24) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960).
(25) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).
(26) D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, **14**, 1485 (1975).
(27) D. A. Buckingham, M. Dwyer, G. Gainsford, V. Janson Ho, L. G. Marzilli, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *Inorg. Chem.*, **14**, 1739 (1975).
(28) J. C. Bailar, Jr., L. J. Boucher, and E. Kyuno, *J. Am. Chem. Soc.*, **87**, 4458 (1965).
(29) J. C. Bailar, Jr., and E. Kyuno, *J. Am. Chem. Soc.*, **88**, 1120 (1966).
(30) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).
(31) F. Basolo and R. G. Pearson, *Inorg. Chem.*, **4**, 1522 (1965).
(32) H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).
(33) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).
(34) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).
(35) L. S. Dong and D. A. House, *Inorg. Chim. Acta*, **19**, 23 (1976).
(36) D. A. Buckingham, M. Dwyer, A. M. Sargeson, and K. J. Watson, *Acta Chem. Scand.*, **26**, 2813 (1972).
(37) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956).
(38) Extrapolated from data at 0 °C[39] using $\Delta H^* = 23$ kcal mol^{-1}.
(39) S. C. Chan and F. Leh, *J. Chem. Soc. A*, 129 (1966).
(40) T. L. Ni and C. S. Garner, *Inorg. Chem.*, **6**, 1071 (1967).
(41) R. W. Hay and K. B. Nolan, *J. Inorg. Nucl. Chem.*, **38**, 2118 (1976).