Registry No. $\mathrm{I^+ClO_4^-}$, 54713-70-1; $\mathrm{II^+ClO_4^-}$, 54713-72-3; $\mathrm{III^+ClO_4^-}$, 54750-89-9; $\mathrm{I^+I^-}$, 25749-39-7; $\mathrm{II^+I^-}$, 54713-73-4; $\mathrm{III^+I^-}$, 54750-90-2.

References and Notes

(1) V. Kothari and D. H. Busch, *Inorg. Chem.*, **8**, 2276 (1969).
(2) Symbols used for cysteine and related ligands: CyS = $\mathrm{NH_2CH(COO^-)CH_2S^-}$, CySO = $\mathrm{NH_2CH(COO^-)CH_2SO^-}$, and $\mathrm{CySO_2}$ = $\mathrm{NH_2CH(COO^-)CH_2SO_2^-}$.
(3) M. P. Schubert, *J. Am. Chem. Soc.*, **55**, 3336 (1933).
(4) (a) L. S. Dollimore and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, 933 (1973); (b) R. D. Gillard and R. Maskill, *Chem. Commun.*, 160 (1968).
(5) G. Vitzhum and E. Lindner, *Angew. Chem., Int. Ed. Engl.*, **10**, 315 (1971).
(6) A. Wojcicki, *Acc. Chem. Res.*, **4**, 344 (1971).
(7) T. A. George and D. D. Watkins, Jr., *Inorg. Chem.*, **12**, 398 (1973).
(8) (a) R. H. Lane and L. E. Bennett, *J. Am. Chem. Soc.*, **92**, 1089 (1970); (b) C. J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973).
(9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N.Y., 1970, p 238.
(10) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).
(11) (a) R. J. Cozens, G. B. Deacon, P. W. Felder, K. S. Murray, and B. O. West, *Aust. J. Chem.*, **23**, 481 (1970); (b) Y. Yamano, I. Masuda, and K. Shinra, *J. Inorg. Nucl. Chem. Lett.*, 729 (1969); (c) M. Kubota and B. M. Loeffler, *Inorg. Chem.*, **11**, 469 (1972).
(12) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).
(13) However, the 1055-$\mathrm{cm^{-1}}$ absorption in III is more intense, relative to other features in the spectrum, than is the 1055-$\mathrm{cm^{-1}}$ band in I, suggestive of a sulfur–oxygen absorption in this region.
(14) An alkoxysulfenate-*S* structure, $\mathrm{Co{-}S(O)OCH_2{-}}$, expected to have absorptions similar to those of the sulfinate-*O*,[7,10] appears to be ruled out as well.
(15) The quantities in parentheses indicate the shift (ppm) upfield from internal $\mathrm{H_2O}$ and the relative area associated with the absorption, respectively. In general the areas observed support the assignments, although the values are somewhat arbitrary for multiplets which overlap to some extent.
(16) (a) S. Isied and H. Taube, *Inorg. Chem.*, **13**, 1545 (1974); (b) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *ibid.*, **12**, 2690 (1973); (c) P. H. Tewari, R. W. Gaver, H. K. Wilcox, and W. K. Wilmarth, *ibid.*, **6**, 611(1967); (d) H. Siebert and G. Wittke, *Z. Anorg. Allg. Chem.*, **399**, 43 (1973); (e) J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).
(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, New York, N.Y., 1969, pp 130–131.
(18) A similar difficulty arises in analysis of the more complex features in Id which may be the result of nonequivalence of the methylene protons.
(19) Base-promoted exchange of the methine proton occurs in the cobalt(III)–alaninato complex in which the amino and carboxylate groups are coordinated. (a) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5133 (1967); (b) D. H. Williams and D. H. Busch, *ibid.*, **87**, 4644 (1965).
(20) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).
(21) Shorter wavelength transitions are masked by charge-transfer bands at 371 nm in II and at 287 nm in III.
(22) W. E. Savige and J. A. MacLaren in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N.Y., 1966, p 379.
(23) Recently, alkyl sulfenates have been trapped by reaction with activated alkynes and alkenes: (a) E. Block and J. O'Connor, *J. Am. Chem. Soc.*, **96**, 3929 (1974); (b) J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem., Part C*, **8**, 205 (1973).
(24) (a) J. P. Barton, J. E. Packer, and R. J. Sims, *J. Chem. Soc., Perkin Trans. 2*, 1547 (1973); (b) J. P. Danehy, *Int. J. Sulfur Chem., Part C*, 6, 159 (1971).
(25) C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).

Contribution from the Research School of Chemistry,
The Australian National University, Canberra, A.C.T. 2600, Australia

Site of Deprotonation in the Base Hydrolysis of Chloropentaaminecobalt(III) Ions

D. A. BUCKINGHAM, P. J. CRESSWELL, and A. M. SARGESON*

Received September 4, 1974 AIC406275

Proton-exchange studies at the amine centers, base hydrolysis studies, and steric strain calculations on the two isomers of $\mathrm{[Co(tren)NH_3Cl]^{2+}}$ (tren = tris(2-aminoethyl)amine are reported. The results indicate that deprotonation at the N center trans to bound $\mathrm{Cl^-}$ leads to the most reactive intermediate for loss of $\mathrm{Cl^-}$ and the stereochemistry of the two reaction paths is discussed in relation to likely structures for the intermediates.

Introduction

Much evidence has now appeared to support a dissociative mechanism for hydrolysis of cobalt(III)–amine complexes in basic media.[1-7] The proposed mechanism, Figure 1, requires a preliminary deprotonation at a primary or secondary N center which is usually a preequilibrium but may be rate determining.[1,2,6] This is followed by dissociation of the leaving group X, usually rate determining, to give an intermediate of reduced coordination number.[4,7] The intermediate then rapidly captures nucleophiles in solution to give the products.[8] The evidence which supports the proposal involves studies of H exchange,[1,2] capture of the intermediate by competing species to give common products[4,6] and stereochemistry[7] independent of the leaving group and gross accelerations in rates when steric compression is introduced in the parent ions.[9] At least two points of uncertainty in the mechanistic proposals are the position of deprotonation in the parent ion which leads to hydrolysis[10-12] and the stereochemistry of the intermediate of reduced coordination number. The present work was designed to examine both these aspects.

It is conceivable that the two isomers[13] or $\mathrm{[Co(tren)NH_3Cl]^{2+}}$ depicted in Figure 2 could be revealing in the context of the deprotonation problem since there is no N proton trans to $\mathrm{Cl^-}$ in one instance, while there is in the other. Superficially the complexes appear to be electronically equivalent and strain free or at least equally strained and no undue influence should arise from these sources. It seemed therefore that an analysis of base hydrolysis and proton exchange rates along with some quantitation of the strain problem might allow an evaluation of which deprotonated reactant leads on to hydrolysis.

Experimental Section

Synthesis of $\mathrm{[Co(tren)NH_3Cl]Cl_2}$, Purple Isomer. tren·3HCl (25.6 g) and NaOH (12 g) were dissolved in water (200 ml) and $\mathrm{NaClO_4 \cdot H_2O}$ (50 g) was added after a clear solution had formed. $\mathrm{Co(ClO_4)_2 \cdot 6H_2O}$ (36.7 g) in water (100 ml) was added, followed immediately by $\mathrm{NaNO_2}$ (10 g) in water (100 ml). A brown solution containing some greenish precipitate was formed, but on vigorous passage of air for 45 min the precipitate dissolved and a crystalline, khaki-colored solid was deposited. This was washed on the filter with a little ice water and then with $\mathrm{CH_3OH}$ and $\mathrm{H_2O}$; yield 35 g (95%) presuming a constitution of $\mathrm{[Co_2(tren)(NO_2)_2O_2](ClO_4)_2}$.

Peroxo dimer (35 g) was added in portions to hot concentrated HCl (200 ml) and heating (steam bath) was continued for 10 min after the final addition. Ethanol (300 ml) was mixed into the deep blue solution and, on cooling, a nearly quantitative yield of flaky blue crystals was obtained (31 g).

$\mathrm{[Co(tren)Cl_2]Cl}$ (1.0 g) was suspended in a saturated solution of ammonia in methanol (50 ml) and warmed to 30–40° for 30 min, during which time the suspension changed from blue to pink. The mixture was cooled and anhydrous ether (100 ml) added. The solids

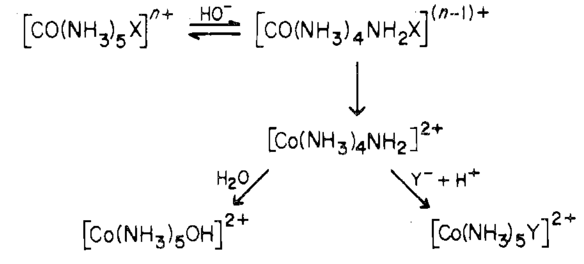

Figure 1. Base-catalyzed dissociative mechanism (SN1cB) for $[Co(NH_3)_5X]^{n+}$ ions.

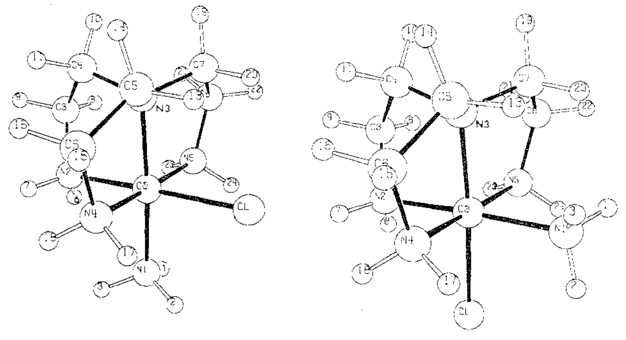

Figure 2. Minimum energy configurations of p- and t-[Co(tren)-NH_3)Cl]$^{2+}$ (left and right, respectively) derived from strain energy minimization calculations. The designations p and t refer to the position of the substituent trans to a primary or a tertiary N atom, respectively.

were collected and dissolved in water (90 ml). NaOH (10 ml, 1 *M*) was added and the solution stirred for 10 sec before acidifying with concentrated HCl. The resulting mixture was diluted with water, sorbed on an ion-exchange column (Dowex 50-WX2, 200–400 mesh, H^+ form, 5 × 10 cm), and washed with water. $[Co(tren)NH_3Cl]Cl_2$ was obtained by eluting the purple band with 1 *M* HCl and evaporating the solution to dryness (ϵ_{530} 136, ϵ_{363} 126 M^{-1} cm^{-1}). The complex was recrystallized from 1 *M* HCl by adding ethanol. Anal. Calcd for $[Co(C_6N_4H_{18})NH_3Cl]Cl_2 \cdot {}^1/_2H_2O$: C, 21.34; H, 6.58; N, 20.75. Found: C, 21.4; H, 6.7; N, 20.9.

Synthesis of $[Co(tren)NH_3Cl]Cl(ClO_4)$, Red Isomer. Freshly prepared $[Co_2(NH_3)_{10}O_2](NO_3)_4 \cdot 2H_2O$[14] (20 g) was added to a solution of tren (10 g) in water (150 ml) and a steam of air was bubbled through the mixture for 2 hr. Concentrated HCl (50 ml) was added; the mixture was heated to 80° on a steam bath and evaporated to low volume. The solution was cooled and sodium perchlorate added. The red crystals were collected and washed with ethanol (ϵ_{512} 94.3, ϵ_{367} 98.7 M^{-1} cm^{-1}). Anal. Calcd for [Co-$(C_6H_{18}N_4)(NH_3)Cl]Cl \cdot ClO_4$: C, 18.35; H, 5.40; N, 17.84. Found: C, 18.3; H, 5.4; N, 17.6.

PMR and Proton Exchange. The PMR spectra were obtained with a JEOL MH 100 spectrometer using solvents DMSO-d_6 and 0.1 *M* DCl. In the latter instance D_2SO_4 (98%) was used to move the HOD signal downfield and away from the N proton signals. Proton exchange for the purple isomer was followed at 25° using 0.1 *M* acetate and imidazole buffers. The faster exchange rate of the red isomer was measured by dissolving the complex (200 mg) in 0.1 *M* acetate buffer (5 ml) at 25°. Samples (0.5 ml) were withdrawn at intervals and quenched with D_2SO_4 (98%, 0.2 ml), and their PMR spectra were measured under identical conditions. The slower exchange rates for the red isomer in imidazole buffer were observed by scanning the spectrum at selected times.

Base hydrolysis was followed spectrophotometrically (Cary 16K) at 25 ± 0.05° in buffer solutions (0.1 *M* diethanolamine) for the red isomer and sodium hydroxide solutions for the purple isomer using stopped-flow techniques. The ionic strength was maintained at μ = 1.0 with $NaClO_4$ ([Co] ≈ 2 × 10^{-3} *M*).

The pH measurements were carried out using Radiometer equipment, pH meter TTT1C with scale expander type PHA630T, glass electrode type G202B and a saturated calomel electrode as reference. For the perchlorate buffers a special salt bridge (1.6 *M* NH_4NO_3, 0.2 *M* $NaNO_3$ (pH 7)) was used to calibrate the pH meter and measure the buffer solutions. The same equipment was used to determine the "pH" of the D_2O buffers and the empirical conversion[14] pD = "pH" + 0.4 was applied to evaluate [D^+].

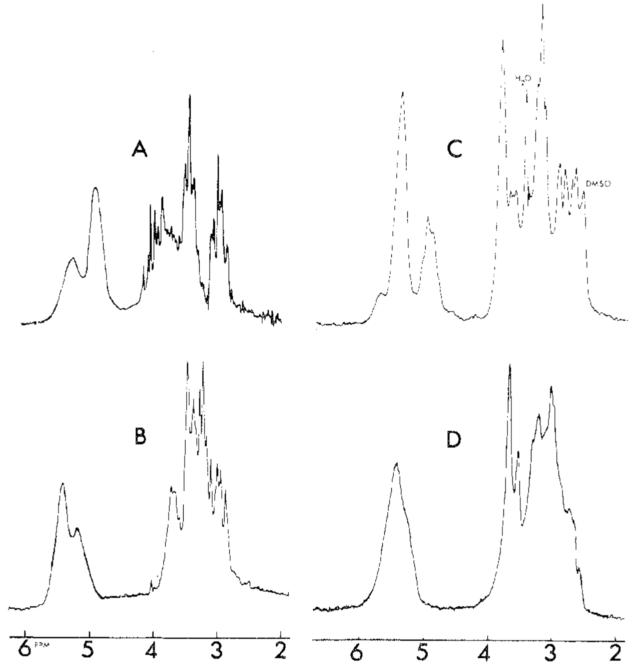

Figure 3. The 100-MHz PMR spectra of $[Co(tren)NH_3Cl]^{2+}$ ions: A and C, red isomer in 0.1 *M* DCl and DMSO-d_6, respectively; B and D, purple isomer in 0.1 *M* DCl and DMSO-d_6, respectively (chemical shifts (δ) in ppm relative to TMS).

Base Hydrolysis Product Analysis. Purple Isomer. [Co(tren)-$NH_3Cl]Cl_2$ (46.1 mg) was dissolved in 0.10 *M* NaOH solution (μ = 1.0, 10 ml) at 25°. After 10 min at 25 ± 0.1°, 5 ml of mixture was withdrawn ($t_{1/2}$ for base hydrolysis at this pH is 6 min), quenched with acetic acid, and diluted; the complexes were sorbed on a cation-exchange column (Bio-Rad Analytical Resin, Dowex 50-WX2, 200–400 mesh, 4 × 1 cm). The column was eluted with 1 *M* $NaCl_4$ (pH 4) to collect the unreacted chloro complex followed by 3 *M* HCl to collect the aqua complexes. The aqua complexes were rcanated to the corresponding chloro complexes by heating the 3 *M* HCl solution on a steam bath to dryness. The anated chloro complexes were dissolved in a little water and resorbed on a cation-exchange column (~15 × 1 cm) and eluted with 1 *M* $NaClO_4$ to separate the isomers. Product concentrations were determined spectrophotometrically. The remaining 5 ml of reaction mixture was quenched after 60 min and treated in a similar manner. This experiment was also conducted up to $150t_{1/2}$ without change in the products.

Red Isomer. Samples of $[Co(tren)NH_3Cl]Cl \cdot ClO_4$ (30.4 and 25.9 mg) dissolved in 10 ml of water at 25° were mixed rapidly with diethanolamine buffer at pH 10 (0.2 *M*, 25°, 10 ml) and quenched with acetic acid after 20 sec ($t_{1/2}$ for base hydrolysis at this pH) and 2 min, respectively. The product mixtures were then treated in the same manner as described for the purple isomer. Also the red isomer was hydrolyzed in 0.1 *M* NaOH (μ = 1.0 $NaClO_4$) for 15 hr without change in product ratio.

Stereochemistry of Anation. A sample of purple isomer (28.9 mg) was dissolved in dilute nitric acid (~0.1 *M*, 5 ml). Excess silver nitrate (0.1 g) was added and the mixture was kept at ~50° for 30 min. The mixture was cooled, concentrated HCl (2 ml) was added to precipitate the remaining silver, and the solution was filtered. The filtrate was heated to 100° for 10 min, cooled, and diluted with water; the anated complexes were sorbed onto an ion-exchange column (Dowex 50-WX2, 1 × 10 cm, Na^+ form. The column was eluted with 1 *M* $NaClO_4$ (pH ~4). A sample of the red isomer (46.0 mg) was treated in an identical manner.

Results

PMR and Proton Exchange. The 100-MHz PMR spectra of the two isomers in 0.1 *M* DCl and DMSO-d_6 are presented in Figure 3. In 0.1 *M* DCl both isomers show broad resonances due to the six NH_2 protons, partially resolved into peaks integrating for two and four protons. For the purple isomer these peaks are at δ 5.2 and 5.4 (ppm relative to TMS) and

Table I. Proton-Exchange Rates for $[Co(tren)NH_3Cl]^{2+}$ Isomers at 25°[a]

Purple Isomer: t-$[Co(tren)(NH_3)Cl]^{2+}$

pD^{15}	$10^4 k_{obsd}$, sec^{-1} (δ 5.4)	$10^{-5} k_{ex}$,[e] M^{-1} sec^{-1}	$10^4 k_{obsd}$, sec^{-1} (δ 5.2)	$10^{-5} k_{ex}$,[e] M^{-1} sec^{-1}	$10^4 k_{obsd}$, sec^{-1} (δ 5.2)	$10^{-5} k_{ex}$,[e] M^{-1} sec^{-1}
5.33[b]	4.6 (4)[f]	6.8	2.9 (2)	4.3	2.1 (3)	3.2
5.40[c]	4.0 (4)	5.0	[g]		2.6 (3)	3.3
5.67[b]	6.8 (4)	4.6	4.9 (2)	3.3	4.1 (3)	2.8
6.15[d]	32 (4)	7.2	21 (2)	4.6	18 (3)	4.1

Red Isomer: p-$[Co(tren)(NH_3)Cl]^{2+}$

pD^{15}	10^4 k_{obsd}, sec^{-1} (δ 5.2)	10^{-5} k_{ex},[e] M^{-1} sec^{-1}	10^4 k_{obsd}, sec^{-1} (δ 4.9)	10^{-7} k_{ex},[e] M^{-1} sec^{-1}	10^4 k_{obsd}, sec^{-1} (δ 3.7)	10^{-5} k_{ex},[e] M^{-1} sec^{-1}
3.71[b]			5.7 (2)	3.5		
4.32[b]			23 (2)	3.5		
4.68[b]			49 (2)	3.4		
6.15[d]	~6 (2)	~1			~6 (3)	~1

[a] $\mu \approx 1$ with complex; [Co] ≈ 0.2 M. [b] 0.1 M acetate buffer. [c] 0.05 M acetate buffer. [d] 0.1 M imidazole buffer. [e] Using $pK_{D_2O} = 14.50$ (25°, $\mu = 1$) obtained by extrapolation of data in ref 16 and 17, $k_{OD} = k_{obsd}/[OD^-]$. [f] The figure in parentheses gives the number of protons involved in the exchange. [g] Exchange obscured by HOD signal.

for the red isomer at δ 5.2 and 4.9. The NH_3 resonance for the purple isomer occurs at δ 3.7 partially resolved from the complex methylene resonances. In D_2O this signal vanished as NH_3 was deuterated. For the red isomer the NH_3 resonance lies in the region δ 3.7–3.8 but is obscured by fine structure due to the methylene protons. On addition of D_2SO_4 this resonance sharpened and shifted to δ 3.6. On deuteration the NH_3 region lost intensity but the overlying methylene signals remained.

The PMR spectrum of the purple isomer in DMSO-d_6 shows a single broad NH_2 resonance at δ 5.4 and a sharp NH_3 resonance at δ 3.7. For the red isomer there are two NH_2 resonances, δ 5.4 and 4.9, integrating for 4:2 protons. The sharp resonance at δ 3.83 is due to NH_3.

Proton exchange in the isomers was followed by collapse of the NH_2 and NH_3 signals in D_2O buffer solutions. Plots of log [(peak height)$_t$ − (peak height)$_\infty$] against time were linear over at least 2 half-lives. For the red isomer, the signal at δ 4.9 showed an initial rapid loss of two protons and a subsequent slower loss of the remaining two. The observed rate constants are given in Table I.

The results are consistent with the rate law

$$\frac{-\mathrm{d}[\mathrm{H\ complex}]}{\mathrm{d}t} = k_{ex}[\mathrm{OD}^-][\mathrm{H\ complex}]$$

for both isomers.

Base hydrolysis of the isomers in various buffers was consistent only with loss of Cl^-. Ion exchange of the quenched reaction mixtures and final products showed only unreacted chloro complexes (Figure 4) and aqua products. The spectral change is also consistent with this analysis and the rates were followed by the absorbance change. Plots of log $(A_t - A_\infty)$ against time were linear for at least 3 half-lives, and the reactions were followed for at least $10t_{1/2}$. The observed rate constants are given in Table II. There was no buffer dependence and the observed rate law for both isomers, over the conditions used, has the form

$$\frac{-\mathrm{d}[\mathrm{chloro\ complex}]}{\mathrm{d}t} = k_{OH}[\mathrm{chloro\ complex}][\mathrm{OH}^-]$$

Products of Base Hydrolysis. The products from base hydrolysis of each of the isomers were analyzed by separating the aqua complexes from any unreacted material, reanating them with chloride ion, and separating the resulting chloro complexes by ion-exchange chromatography. To prove that the anation reaction goes with retention of stereochemistry, a sample of each isomer was induced to aquate with Ag^+ ion. Induced reactions of this type occur with retention in pentaaminecobalt(III) systems.[7,10] The aqua species were reanated with chloride ion and ion-exchange chromatography showed only one product in each case, corresponding to the starting material. Analysis of the products from base hydrolysis of the purple isomer showed 15.3 ± 1.0% of aqua product with the same configuration as the purple isomer, with the remainder isomerized to the configuration of the red form. Hydrolysis of the red isomer gave only aqua product with the configuration of the red product (>98%). Reaction mixtures were analyzed after about 1 and 10 half-lives and after 15 hr (~$150t_{1/2}$) with no change in the result. Yang and Grieb[13] have suggested that the red isomer is unstable with respect to the purple form, but we have not observed isomerization in either direction.

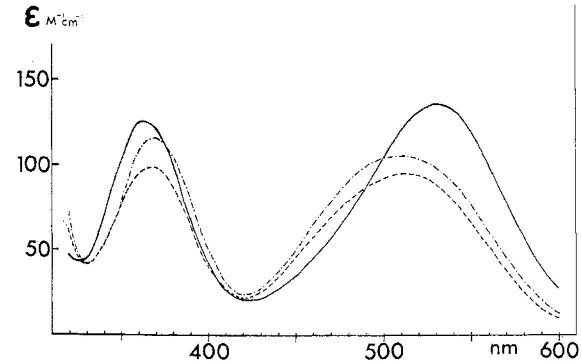

Figure 4. Visible absorption spectra (ε vs. λ) of purple (——) and red (- - - -) $[Co(tren)NH_3Cl]^{2+}$ and of red $[Co(tren)(NH_2CH_2CHO)Cl]^{2+}$ (- · · · -) in 1 M HCl.

Table II. Rate Constants for Base Hydrolysis of $[Co(tren)NH_3Cl]^{2+}$ Isomers at 25° and $\mu = 1.0$ ($NaClO_4$)

Purple Isomer:[a,e] t-$[Co(tren)(NH_3)Cl]^{2+}$

[NaOH], M	$10^4 k_{obsd}$, sec^{-1}	$10^2 k_{OH}$,[b] M^{-1} sec^{-1}
1.00	200	2.0
0.400	87	2.2
0.100	20	2.0
0.040	7.9	2.0

Red Isomer:[c,e] p-$[Co(tren)(NH_3)Cl]^{2+}$

pH	$10^3 k_{obsd}$, sec^{-1}	$10^{-2} k_{OH}$,[d] M^{-1} sec^{-1}
9.63	26.2	3.6
9.46	17.8	3.6
9.02	7.37	4.1
8.69	3.61	4.3
8.44	1.52	3.6

[a] Followed at 550 nm. [b] $k_{OH} = k_{obsd}/[OH^-]$. [c] Followed at 490 nm, in 0.1 M diethanolamine buffers. [d] Calculated using $pK_{H_wO} = 13.77$ (25°, $\mu = 1.0$) from ref 17. [e] [Complex] = 2 × 10^{-3} M.

Strain Energy Minimization. The two structures p- and t-$[Co(tren)NH_3Cl]^{2+}$ (Figure 2) have been studied by the strain energy minimization technique using the program MOL originated by Boyd[18] and subsequently developed by Snow,[19] Maxwell,[20,21] Dwyer,[22] and Gainsford.[23] The program uses a Newton–Raphson method to minimize total molecular strain energy, considered as the sum of terms due to bond length deformation, bond angle deformation, nonbonded interactions, and torsional interactions. Details of the energy functions and the force field used are given in Table III. Initial coordinates for the calculations were obtained by modification of structural

Table III. Force Field Potential Function Constants[a]

Nonbonded atoms	Nonbonded potential function constants[b] a_{ij}	b_{ij}	c_{ij}	Ref
H· · ·H	45.8	4.08	0.341	*g*
C· · ·H	218	4.20	0.84	*g*
N· · ·H	195	4.32	0.69	*h*
C· · ·C	1640	4.32	2.07	*g*
C· · ·N	1472	4.44	1.695	*h*
H· · ·Cl	234.7	3.85	1.84	*g*
C· · ·Cl	1597	3.96	4.528	*g*
N· · ·Cl	1479	4.06	3.708	*h, i*

$$U(r_{ij})_{NB} = a_{ij} \exp(-b_{ij}r_{ij}) - c_{ij}/r_{ij}^6$$

Bond angle type	Bond angle force constants, $k_{ijk}\theta^c$	θ^0_{ijk}, radians	Ref
H-C-H	0.52	1.911	*d*
H-N-H	0.53	1.911	*e*
N-C-H	0.65	1.911	
C-N-H	0.55	1.911	
C-C-H	0.65	1.911	*d*
C-C-N	1.00	1.911	
N-Co-N	0.68	1.571	*e*
N-Co-Cl	1.00	1.571	*e*
Co-N-H	0.20	1.911	*e*
Co-N-C	0.40	1.911	
C-N-C	1.0	1.911	

$$U(\theta_{ijk}) = {}^1\!/_2 k_{ijk}^{\theta}(\theta_{ijk} - \theta^0_{ijk})^2$$

Bond type	Bond length force constants,[c] $k_{ij}r$	r^0_{ij}, Å	Ref
N-H	5.6	1.03	*e*
C-H	5.0	1.09	*d*
C-C	5.0	1.50	*d*
C-N	6.0	1.49	
Co-N	1.75	1.925	*e*
Co-Cl	1.41	2.20	

$$U(r_{ij})_B = {}^1\!/_2 k_{ij}^{r}(r_{ij} - r^0_{ij})^2$$

Bond type	Torsional force constants,[f] $V_{ijkl}\phi$	Ref
C-C	0.0173	*j*
C-N	0.0107	*j*

$$U(\phi_{ijkl}) = {}^1\!/_2 V_{ijkl}^{\phi}(1 - \cos 3\phi_{ijkl})$$

$$U = \Sigma_{ij}U(r_{ij})_{NB} + \Sigma_{ijk}U(\theta_{ijk}) + \Sigma_{ijkl}U(\phi_{ijkl}) + \Sigma_{ij}U(r_{ij})_B$$

[a] Constants which are not referenced have been estimated and in some instances fitted to give best agreement with the structural data. [b] The units for parameters a_{ij}, b_{ij}, and c_{ij} respectively are 10^{-11} erg molecule^{-1}, Å^{-1}, and 10^{-11} erg Å^6 molecule^{-1}. [c] Force constants are given in 10^5 dyn cm^{-1}. [d] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963). [e] I. Nakagawa and T. Shimanouchi, *ibid.*, **22**, 759, 1707 (1966). [f] Force constants are given in 10^{-11} erg molecule^{-1}. [g] J. L. De Coen, A. M. Liquori, A. Damiani, and G. Elefante, *Nature (London)*, **216**, 910 (1967). [h] A. M. Liquori, A. Damiani, and G. Elefante, *J. Mol. Biol.*, **33** (1968). [i] From the geometric means of the parameters of the Cl-Cl (see footnote *g*) and N-N functions. [j] J. P. Lowe, *Prog. Phys. Org. Chem.*, **6**, 1 (1968).

Table IV. Calculated Atomic Coordinates (Å) for the $[Co(tren)(NH_3)Cl]^{2+}$ Ion

	t isomer			p isomer		
	x	*y*	*z*	*x*	*y*	*z*
Co	0.000	0.000	0.000	0.000	0.000	0.000
N(1)	0.027	−1.971	−0.005	1.945	0.000	0.000
N(2)	0.059	1.950	0.000	0.034	1.948	0.000
N(3)	−1.928	0.170	0.018	−1.933	0.123	−0.002
N(4)	−0.064	−0.075	−1.945	−0.054	−0.079	−1.948
N(5)	−0.068	−0.071	1.946	−0.102	−0.072	1.948
Cl	2.215	0.000	0.000	0.021	−2.235	0.010
C(3)	−1.203	2.449	0.619	−1.260	2.429	0.564
C(4)	−2.343	1.617	0.106	−2.367	1.567	0.026
C(5)	−2.403	−0.426	−1.274	−2.370	−0.534	−1.278
C(6)	−1.492	0.052	−2.379	−1.483	−0.044	−2.395
C(7)	−2.369	−0.610	1.219	−2.393	−0.618	1.218
C(8)	−1.493	−0.239	2.391	−1.531	−0.213	2.386
H(1)	−0.220	−2.376	0.907	2.304	0.156	0.952
H(2)	0.976	−2.297	−0.232	2.321	−0.891	−0.352
H(3)	−0.601	−2.378	−0.708	2.290	0.755	−0.609
H(6)	0.861	2.295	0.547	0.810	2.293	0.584
H(7)	0.137	2.323	−0.956	0.152	2.327	−0.950
H(8)	−1.146	2.405	1.705	−1.238	2.405	1.652
H(9)	−1.359	3.492	0.335	−1.427	3.464	0.257
H(10)	−3.197	1.732	0.776	−3.250	1.690	0.655
H(11)	−2.643	2.005	−0.868	−2.632	1.923	−0.969
H(13)	−2.406	−1.514	−1.236	−2.296	−1.619	−1.206
H(14)	−3.426	−0.105	−1.478	−3.410	−0.280	−1.492
H(15)	−1.660	−0.556	−3.270	−1.610	−0.692	−3.265
H(16)	−1.712	1.090	−2.631	−1.756	0.970	−2.689
H(17)	0.323	−0.967	−2.285	0.390	−0.947	−2.281
H(18)	0.495	0.684	−2.361	0.460	0.709	−2.365
H(19)	−3.411	−0.385	1.453	−3.438	−0.384	1.432
H(20)	−2.302	−1.681	1.034	−2.325	−1.696	1.072
H(21)	−1.862	0.677	2.853	−1.899	0.719	2.816
H(22)	−1.548	−1.032	3.140	−1.598	−0.981	3.159
H(23)	0.325	0.792	2.347	0.305	0.781	2.357
H(24)	0.504	−0.854	2.295	0.446	−0.874	2.294

Table V. Minimized Strain Energy Terms (kcal/mol) for the Two structures

Term	t structure	p structure	$U_t - U_p$
Bond deformation	0.91	0.79	0.12
Valence angle deformation	3.20	2.70	0.50
Nonbonded interaction	0.67	0.59	0.08
Torsional interaction	5.93	5.84	0.09
Total strain energy	10.71	9.93	0.78

coordinates for s-$[Co(trenen)N_3]^{2+}$.[21] The calculated structures of minimum energy are illustrated in Figure 2. Atomic coordinates are listed in Table IV. A comparison of the energy sums is given in Table V. An important point about the present calculations is that nonbonded interactions are summed over the entire molecule rather than over a limited range.[23] The inclusion of many small nonbonded terms, both attractive and repulsive, gives improved comparison of strain energies and lower absolute energies with little or no effect on the structural parameters.[23]

A comparison of the data for the two structures shows that the t isomer is ~0.8 kcal more strained than the p isomer and that the larger part (0.5 kcal) of this difference occurs in bond angle deformations. The energy difference cannot be ascribed to any particular interaction but appears to be spread evenly over the molecule. Also a strain energy difference of 0.8 kcal is too small to have any gross effect on the relative rate of reaction of the two isomers, especially when strain is expected to be relieved as the Co–Cl bond is stretched in the transition state.

Some comment is needed on the validity of the steric strain calculations. For numerous structures studied the calculations reproduce the geometry observed in the crystal.[19-23,24] In those instances where isomers have been equilibrated the calculations predict the correct stability relationship and the energy difference within ~1 kcal mol^{-1}. Over this tolerance therefore the calculations probably have significance in determining the strain contribution to $\Delta H°$. The calculations were performed on a Univac 1108 computer and the perspective drawings were prepared using the program ORTEP and a Calcomp plotter on line to a PDP-11.

Discussion

Structural Assignment. The p and t structures were assigned previously[13] to the "purpureo" and red isomers, respectively. The assignment was made on the basis of infrared spectra and a supposed splitting of the NH_3 proton resonance of the red

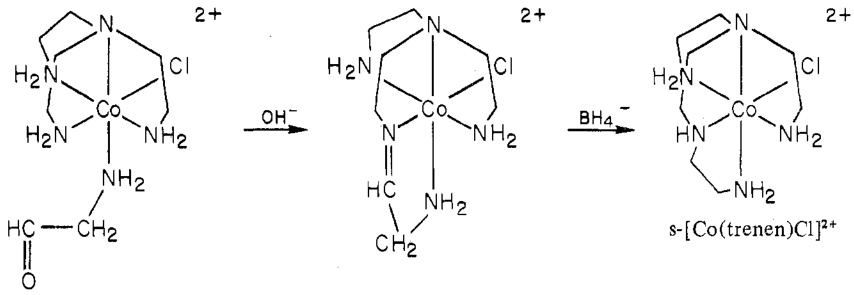

Figure 5. Intramolecular condensation of p-$[Co(tren)(NH_2CH_2CHO)Cl]^{2+}$.

isomer. This splitting was not observed in the present study. Moreover our data lead us to reverse the assignment.

For complexes of the cobalt(III)–chloropentaamine type amine protons trans to chloride exchange in D_2O much faster than those cis.[11] This rate enhancement factor is 60 for the $Co(NH_3)_3Cl^{2+}$ ion, 300 for *trans*-$[Co(en)_2NH_3Cl]^{2+}$, and about 10^5 for the $[Co(trenen)Cl]^{2+}$ ion (Figure 5) (trenen = 3-(2-aminoethyl)-1,8-diamino-3,6-diazaoctane). Considering the two $[Co(tren)NH_3Cl]^{2+}$ isomers we find that the red isomer exchanges two protons with a rate constant 3.2×10^7 M^{-1} sec^{-1} while the purple isomer shows exchanges at rates no faster than 7×10^5 M^{-1} sec^{-1}. In addition, there is a factor of ~ 100 between the fast exchange of the red isomer and any subsequent exchange. Moreover, all exchange rates for the purple isomer lie within a factor of 3 (($\sim$3–7) $\times 10^5$ M^{-1} sec^{-1}) and are about the same as the slow exchange rates for the red isomer. These results imply that the two rapidly exchanging protons of the red isomer are trans to Cl^- consistent with the red isomer having the p structure. In the purple t isomer all the amine protons are cis to Cl^-. The assignments give comparable exchange rates for all N protons cis to coordinated Cl^-.

Additional evidence for this assignment arises from the reactions of the $[Co(tren)(NH_2CH_2CHO)Cl]^{2+}$ ion.[25] The carbonyl function of coordinated aminoacetaldehyde undergoes a base-catalyzed intramolecular condensation with a primary amine center of the tren ligand. The process gives stereospecifically one isomer of the imine condensation product which can then be reduced to give the isomer s-$[Co(trenen)Cl]^{2+}$ (Figure 5) containing the saturated quinquedentate ligand 3-(2-aminoethyl)-1,8-diamino-3,6-diazaoctane. This isomer has been characterized previously[11,21] and has the structure shown in Figure 5. The product can only arise if the aminoacetaldehyde complex has the p configuration. The visible spectra of p-$[Co(tren)(NH_2CH_2CHO)Cl]^{2+}$ and p-$[Co(tren)NH_3Cl]^{2+}$ coincide closely and differ from that of t-$[Co(tren)NH_3Cl]^{2+}$.

Site of Deprotonation. The two isomers of $[Co(tren)NH_3Cl]^{2+}$ allow a test of the effect of the presence and absence of an exchangeable amine proton trans to the leaving group Cl^- on the rate of base hydrolysis of Cl^-. The ions are closely analogous; electronic differences are negligible compared with those in *cis*- and *trans*-$[Co(en)_2Cl_2]^+$ for example. The strain energy calculations indicate little difference in steric strain between the two isomers and we could expect therefore comparable reactivities from these sources for the deprotonated reactants. The difference in reactivity for the parent ions could come therefore from different concentrations of deprotonated reactants and from differences in the transition states for the reacting ions.

Previously it was shown that N protons trans to coordinated Cl^- deprotonate faster than those cis for comparable species. This might also be taken to indicate that those species are also more acidic than their cis counterparts. The proposal is supported by the collection of evidence for linear free energy relationships between proton exchange and equilibria especially for similar acids and we assume that holds here.[26] Neither isomer shows any general base dependence for proton exchange and this property is common for cobalt(III)–amine complexes. Estimates of the dissociation constants K_a for the N protons are in the vicinity 10^{-16}–10^{-17} for ions with 3+ charges.[27] We can expect therefore that for 2+ ions the values are even smaller and that the rate of reprotonation of the conjugate base by water is in the vincinity of diffusion control. We can also expect ideal behavior for the log k_{Hex}–ΔpK relationship between acid and base since the donor–acceptor groups form chemical H bonds and the electronic and spatial configurations of the acids and conjugate bases barely alter;[28] i.e., the system is in the state where Bronsted $\alpha = 0$ and $\beta = 1$. It follows that the species which exchanges its protons most rapidly, i.e., the most acidic isomer, p, could be more reactive that the t isomer which has no NH center trans to Cl^-. This is observed; in fact, p is $\sim 10^4$-fold more reactive than t. The proton exchange rates would presuppose a factor of 10^2 difference and the residue presumably should come from the reactivity difference between the two deprotonated reactants. The strain energy studies indicate that, if anything, isomer t should be a little more reactive than p. However a prospect exists that the five-coordinate intermediate arising from p is more readily generated than that from t and this thesis is examined in the next section.

In a previous publication[11] dealing with base hydrolysis of s-$[Co(trenen)Cl]^{2+}$ (Figure 5) it was argued that the NH trans to Cl^- was deprotonated to give the most reactive center. The argument arose from the fact that proton exchange at the site in question was $\sim 10^5$-fold faster than for NH sites cis to bound Cl^-. This required the cis-deprotonated species to be at least 10^6-fold more reactive than the trans-deprotonated ion if reaction was to occur through the cis-deprotonated form. It was felt at the time that this was an improbable difference in reactivity for cis- and trans-deprotonated species. The present study is also consistent with that opinion.

A consequence of such a conclusion is that in some circumstances there will be competing deprotonations at different sites and competing reactivities of deprotonated species for the same molecule. At the moment there appears to be no real evidence for this prospect probably because closely analogous complexes have been chosen for base hydrolysis studies where one site dominates the issue.

Nature of the Intermediate. Isomer p is nicely poised to generate the tripodal form of tren in the intermediate as shown in Figure 6. This seems a very reasonable prospect in view of the studies which show that ligands of this nature favor five-coordinate species of the trigonal-bipyramidal type.[29] Addition of a water molecule at any of the trigonal edges regenerates the same structure as the reactant which is consistent with the hydrolysis result. It is also unlikely that hydrolysis of the t isomer can produce a trigonal-bipyramidal intermediate without rearrangement of the ammonia ligand. The diaminoethane bridges of tren *cannot* be extended to span the 120° angle between equatorial sites of a trigonal bipyramid without extensive strain being generated in the chelate rings.

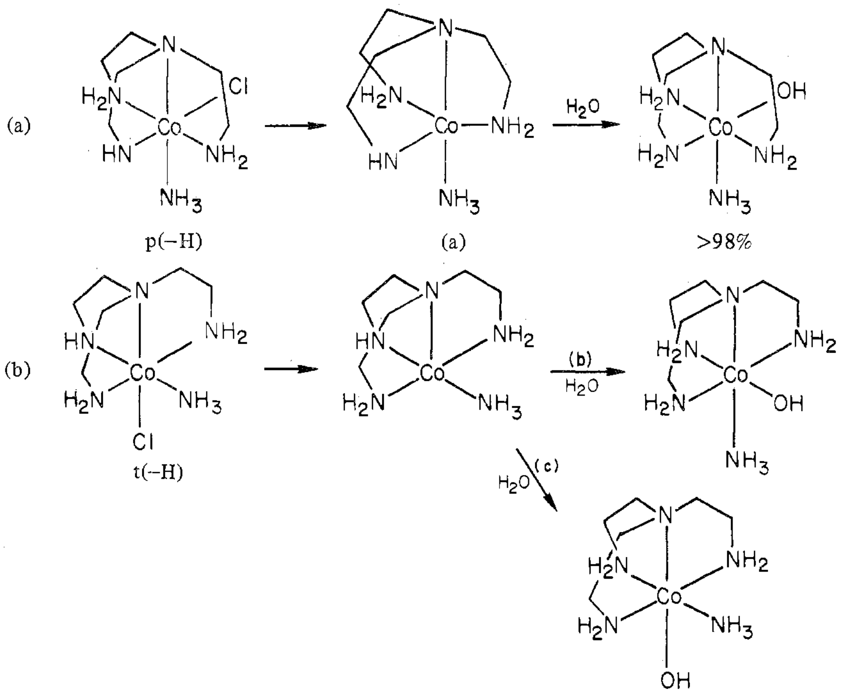

Figure 6. Likely intermediates in the base hydrolysis of (a) p-$[Co(tren)NH_3Cl]^{2+}$ and (b) t-$[Co(tren)NH_3Cl]^{2+}$ ions.

A square-pyramidal intermediate could be formed without rearrangement but it is clear that this is not sufficiently stable since it should lead to full retention of the t configuration which is not observed. Rather, there must be rearrangement of the NH_3 toward a p configuration. The observed product distribution, Figure 6, can then be explained in two ways: (a) by formation of an irregular intermediate which could give rise to a mixture of products or (b) by a kinetic effect in which the intermediate rearranges partly to the same regular intermediate seen for the p isomer. The observed product distribution (85% p and 15% t) presumably arises by entry of the nucleophile competitively at different sites (paths (b) and (c)) or in competition with the rearrangement process to the more regular trigonal-bipyramidal intermediate (paths (a) and (c)). Regardless of how the results are rationalized with respect to possible intermediates, two types at least appear to be required to explain the results for both isomers.

It was unfortunate that competition experiments in the presence of N_3^- which may have allowed the detection of the competitive rearrangement were inconclusive. The difference in the reactivities of the two azido isomers was such that under the conditions required to hydrolyze the slowest chloro isomer in the presence of N_3^- the azido product of the more labile isomer also partly hydrolyzed.

Acknowledgment. We wish to thank the Microanalytical Unit at The Australian National University for analyses.

Registry No. t-$[Co(tren)(NH_3)Cl]Cl_2$, 38161-93-2; p-$[Co(tren)(NH_3)Cl]Cl(ClO_4)$, 54713-96-1; p-$[Co(tren)(NH_2CH_2CHO)Cl]^{2+}$, 54713-97-2.

References and Notes

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N.Y., 1967.
(2) M. L. Tobe, *Acc. Chem. Res.*, **3**, 377 (1970).
(3) C. K. Poon, *Inorg. Chim. Acta, Rev.*, 123 (1970).
(4) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).
(5) F. Basolo, *Pure Appl. Chem.*, **17**, 37 (1968).
(6) A. M. Sargeson, *Pure Appl. Chem.*, **33**, 527 (1973).
(7) R. B. Jordan and A. M. Sargeson, *Inorg. Chem.*, **4**, 1849 (1965); D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).
(8) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).
(9) D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, **9**, 1790 (1970).
(10) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 5129 (1967); *Aust. J. Chem.*, **20**, 597 (1967).
(11) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).
(12) F. R. Nordmeyer, *Inorg. Chem.*, **8**, 2780 (1969).
(13) C. L. Yang and M. W. Grieb, *J. Chem. Soc., Chem. Commun.*, 656 (1972).
(14) M. Moni, J. A. Weil, and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).
(15) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).
(16) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).
(17) W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).
(18) R. H. Boyd, *J. Chem. Phys.*, **47**, 3736 (1967).
(19) M. R. Snow, *J. Am. Chem. Soc.*, **92**, 3610 (1970).
(20) D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Am. Chem. Soc.*, **92**, 3617 (1970).
(21) I. E. Maxwell, Ph.D. Thesis, The Australian National University, 1969.
(22) M. Dwyer, Ph.D. Thesis, The Australian National University (1971).
(23) D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dwyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson, and K. R. Turnbull, *J. Am. Chem. Soc.*, **96**, 1713 (1974).
(24) D. A. Buckingham and A. M. Sargeson, *Top. Stereochem.*, **6**, 219 (1971).
(25) J. MacB. Harrowfield, to be submitted for publication.
(26) R. P. Bell, "The Proton in Chemistry", Methuen, London, 1959, Chapter 10.
(27) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).
(28) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 825 (1967).
(29) M. Ciampolini, A. Cristini, A. Diaz, and G. Ponticelli, *Inorg. Chim. Acta*, **7**, 549 (1973), and references therein.