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Steric Acceleration in the Base Hydrolysis of Some Pentakis(alkylamine)cobalt(III) Complexes

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Base hydrolysis of a series of pentakisalkylamine complexes of the form CoA_5Cl^{2+} (A = CH_3NH_2, *n*-$C_3H_7NH_2$, *i*-$C_4H_9NH_2$) show a marked acceleration ($>10^6$) in rate relative to $Co(NH_3)_5Cl^{2+}$. The rate enhancement is attributed to steric compression in the deprotonated reactant which is relieved in the transition state. Evidence for the relative stabilization of the transition state and the deprotonated five-coordinate intermediate is given by an evaluation of nonbonded interactions and by competition studies using N_3^- and SCN^-. Smaller rate variations for aquation of Cl^- are also discussed.

Introduction

Although the concepts of the thermodynamic and kinetic effects of steric hindrance on rates of reaction have been successfully applied in organic chemistry,[1] there appear to be few well-documented cases extant in coordination chemistry.[2] If there are differences between the initial and transition states of a reaction in terms of nonbonding compressional energy and other effects are unimportant, kinetic steric effects will be observed.[1] If the compressional energy is greater in the transition state than in the initial state, *steric retardation* is observed; if steric strain is reduced in the transition state, *steric acceleration* is observed. Thus, in a series of analogous compounds where only steric crowding is important, marked retardation should be characteristic of a bond-making process, and marked acceleration, characteristic of a bond-breaking process.

In the last five years, much evidence has appeared which supports the proposal that the base hydrolysis of $Co(NH_3)_5X^{2+}$ ions (X = Cl, Br, I, NO_3) takes place by a dissociative mechanism (eq 1–3) which involves[3] an intermediate of reduced coordination number. The most recent experimental results which support this mechanism rely on (a) competition between isotopic H_2O (eq 3)[4] or different species in aqueous solution[5] for the postulated intermediate $Co(NH_3)_4NH_2^{2+}$, (b) the stereochemical course of the reaction,[6] and (c) deuterium-exchange studies on reactants and products of the base hydrolysis reaction.[7]

$$Co(NH_3)_5X^{2+} + OH^- \xrightleftharpoons{K_a/K_w} Co(NH_3)_4NH_2X^+ + H_2O \quad (1)$$

$$Co(NH_3)_4NH_2X^+ \xrightarrow{k_1} Co(NH_3)_4NH_2^{2+} + X^- \quad (2)$$

$$Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5OH^{2+} \quad (3)$$

$$Co(NH_3)_4NH_2^{2+} + Y^- + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5Y^{2+} + OH^- \quad (4)$$

Steric crowding in cobalt(III) complexes of this type should lead therefore to a marked acceleration in the rate of base hydrolysis by relief of steric strain as the reactant proceeds through the activated complex to the relatively stabilized five-coordinated deprotonated intermediate. Studies of the effect of nonbonded interactions on structure and equilibria in cobalt(III)–amine complexes have given an appreciation of the magnitude of the energies involved.[8] It was pertinent therefore to test the proposals above for a series of sterically hindered alkylamine complexes of the type $(RNH_2)_5CoCl^{2+}$ (R = CH_3 to *i*-C_4H_9).

For aquation of chloride ion from cobalt(III)–amine complexes in dilute acid, the mechanism is less well understood and effects arising from both bond making by water and bond breaking by Cl^- appear to be observed. This species of reactivity is also reviewed for these sterically hindered ions.

Experimental Section

$[Co(CH_3NH_2)_5Cl]Cl_2$ was prepared by the method of Mitzner, *et al.*[9] The perchlorate salt was prepared by treating the chloride with concentrated $HClO_4$ and cooling in ice. $[Co(n\text{-}C_3H_7NH_2)_5Cl]Cl_2$ and $[Co(i\text{-}C_4H_9NH_2)_5Cl]Cl_2$ were prepared by a modification of the above method. $[Co(C_5H_5N)_4Cl_2]Cl \cdot 6H_2O$[10] (4.0 g) was treated with alkylamine (10 ml). The mixture was cooled in ice for 5 min and evaporated under reduced pressure at ~25°. The purple residue was ground with 1 *M* HCl, filtered, and recrystallized from water by adding concentrated HCl. The method was unsuccessful with aniline, cyclohexylamine, and isopropylamine. A purple complex was isolated with benzylamine, but it was too insoluble in water (and unstable in organic solvents) for our purposes. *trans*-$[Co(CH_3NH_2)(NH_3)_4Cl]Cl_2$ was prepared by Dr. I. I. Creaser in a similar manner to the preparation of *trans*-$[Co(^{15}NH_3)(NH_3)_4Cl](ClO_4)_2$.[6]

Anal. Calcd for *trans*-$[Co(NH_3)_4(CH_3NH_2)Cl](ClO_4)_2$: C, 3.06; H, 4.36; N, 17.85. Found: C, 2.95; H, 4.30; N, 17.85. Calcd for $[Co(CH_3NH_2)_5Cl]Cl_2$: C, 18.73; H, 7.86; N, 21.85. Found: C, 18.82, 18.62; H, 7.99, 7.94; N, 21.37, 21.88. Calcd for $[Co(n\text{-}C_3H_7NH_2)_5Cl]Cl_2 \cdot HCl$: C, 36.23; H, 9.23; N, 14.08. Found: C, 36.06; H, 8.78; N, 13.65. Calcd for $[Co(i\text{-}C_4H_9NH_2)_5Cl]Cl_2 \cdot 0.5HCl$: C, 43.78; H, 10.20; N, 12.77. Found: C, 43.45; H, 10.03; N, 12.44.

Base Hydrolysis.—The complexes were dissolved in water or

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(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 400–418.

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 162, 387.

(3) See ref 2, p 183.

(4) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

(5) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88**, 5443 (1966).

(6) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **89**, 5129 (1967).

(7) C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).

(8) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970); D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *ibid.*, **92**, 3617 (1970), and references therein.

(9) R. Mitzner, P. Blankenburg, and W. Depkat, *Z. Chem.*, **9**, 68 (1969).

(10) P. Spacu, C. Gheorghiu, M. Brezeanu, and S. Popescu, *Rev. Chim.* (Bucharest), **3**, 127 (1958).

$NaClO_4$ solutions depending on the ionic strength requirements of the final solutions. The NaOH and 0.1 *M* tris(hydroxymethyl)aminomethane (Tris)–$HClO_4$ buffer solutions were prepared similarly. The reactant solutions were mixed rapidly at 25.0° in a stopped-flow reactor,[11] and the change in absorbance was followed using a Cary 14 recording spectrophotometer, in the region 270–290 nm.

Proton Exchange.—The exchange rate of H^+ for D^+ was followed at 34° using a Varian HR 100 nmr spectrometer. $[Co(CH_3NH_2)_5Cl](ClO_4)_2$ (0.050 g) was dissolved in NaOAc–DOAc buffer (0.1 *M*, 0.50 ml, pH 3.72).

Competition Experiment.—A solution (5×10^{-4} *M*) of $[Co(CH_3NH_2)_5Cl]Cl_2$ in water (pH 4-5) was mixed rapidly at 25.0° in the stopped-flow reactor with a 0.1 *M* Tris–$HClO_4$ buffer solution, containing NaN_3 (0.5 *M*) and $NaClO_4$ (0.5 *M*) (final pH 8.83). In another experiment a solution (5×10^{-4} *M*) of the complex was hydrolyzed at 25.0° for 6 half-lives in 0.1 *M* Tris–$HClO_4$ buffer (pH 8.70), 1 *M* in $NaClO_4$. This solution was then mixed rapidly with a 1 *M* NaN_3 solution in the stopped-flow reactor; changes in absorbance were followed at 325 nm. The same experiments were repeated (25–50 mg samples) and were allowed to stand (25°) for $6t_{1/2}$ for base hydrolysis. The products were sorbed on an ion-exchange resin (Dowex 50Wx2, 200–400 mesh) and eluted with acidified (HOAc) 1 *M* NH_4Cl. The aquo and azido samples were analyzed for [Co] on a Techtron AA4 atomic absorption spectrometer. Analogous experiments were carried out using fluoride, acetate, and thiocyanate.

Results

Hydrolysis Rates.—The rates of hydrolysis of the pentakisamine (A) complexes $A_5CoCl^{2+} + OH^- \rightarrow A_5CoOH^{2+} + Cl^-$ were measured under various conditions, and the rate constants and conditions are presented in Table I. Linear plots of log $(D_t - D_\infty)$ *vs.* time were obtained for at least 3 half-lives, and the second-order rate constants for base hydrolysis require a rate law of the form: $v_{\text{chloro}} = k_{\text{OH}}[A_5CoCl^{2+}][OH^-]$. It was necessary to correct the rates obtained for the chloropentakis(methylamine)cobalt(III) complex at pH 8.03 and 8.74 for a second, slower rate, which was observed as a linear increase in optical density (for a period of $\sim 10t_{1/2}$ for base hydrolysis) after the completion of the base hydrolysis reaction. This second rate appeared to be pH independent and was unimportant for the rate measurements made at pH >9; this complication is probably reflected in the slightly different derived rate constants at pH 8.03 and 8.74. It may correspond to loss of one of the amine groups; however, it was not investigated further.

TABLE I

RATE CONSTANTS[a] FOR BASE HYDROLYSIS OF CoA_5Cl^{2+} AT 25.0°

A	pH	10^2k_{obsd}, sec^{-1}	k_{OH}, M^{-1} sec^{-1}
NH_3	12–14		0.25[b]
cis-NH_3, *trans*-CH_3NH_2	14	6.4	0.64
CH_3NH_2	8.03	0.40	3,800
	8.74	1.9	3,400
	9.11	3.9	3,100
	10.18	47.5[c]	3,100[c]
	8.70	3.9[d]	7,700[d]
n-$C_3H_7NH_2$	7.49	0.35	11,000
i-$C_4H_9NH_2$	7.45	5.3[d]	150,000[d]

Rate Constants for Acid Hydrolysis of CoA_5Cl^{2+} at 25.0°

A	$10^6k_{H_2O}$, sec^{-1}	Conditions
NH_3	1.7[e]	0.1–0.2 *M* HNO_3
CH_3NH_2	37[f]	0.05–0.20 *M* HNO_3; 0.10–0.20 *M* $HClO_4$
i-$C_4H_9NH_2$	180[g]	0.05 *M* $HClO_4$

[a] $\mu = 1.0$; 0.1 *M* Tris–$HClO_4$ buffer. [b] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7**, 174 (1968). [c] Diethanolamine–$HClO_4$ buffer. [d] Measured in 0.1 *M* Tris–$HClO_4$; $\mu \approx 0.05$. [e] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937); **34**, 1088 (1938). [f] References 12 and 13. [g] This work.

One experiment to check the stoichiometry above was carried out. $[Co(CH_3NH_2)_5Cl]Cl_2$ (ϵ_{550} 60) was hydrolyzed at pH 8.74 for $6t_{1/2}$ at 25° and quenched with acid to pH 3. The molar absorptivity of the aquo complex obtained (ϵ_{510} 65) agreed with that generated by treating the chloro complex with Hg^{2+} (ϵ_{510} 66). It is apparent then that the complex hydrolyzes without interference from the second reaction. These results bear on a previous report[12] that the methylamine complex decomposes completely in neutral or basic solution. The apparent pH-independent path was not significant in the pH regions used for the measurement of base hydrolysis of the other pentakis-amine complexes. The principal result of the study (Table I) was an increase of $>10^5$ in the rate of base hydrolysis for substitution of NH_3 by the alkylamines.

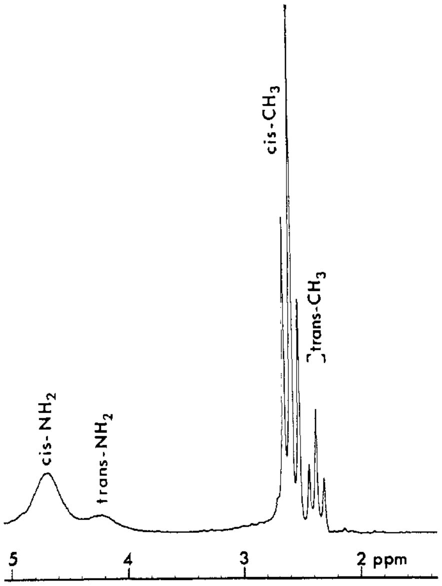

Figure 1.—The 100-MHz pmr spectrum of $Co(CH_3NH_2)_5Cl^{2+}$ (standard: external TMS, 0.4 *N* D_2SO_4, *J* = 6 Hz for both triplets).

In perchloric and nitric acid[12,13] the rates of acid hydrolysis for the complexes are first order with the rate law: $v_{\text{chloro}} = k_{H_2O}[A_5CoCl^{2+}]$. The rate constants are given in Table I, and compared with the results for base hydrolysis, the variation in rate constant is quite small (~100). The effects of variation of medium (HNO_3 or $HClO_4$) and complex concentration have been found to be insignificant for $Co(CH_3NH_2)_5Cl^{2+}$.[12,13]

Pmr and Proton Exchange—Figure 1 depicts the 100-MHz pmr spectrum of $[Co(CH_3NH_2)_5Cl](ClO_4)_2$.

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(11) Y. Inoue and D. D. Perrin, *J. Phys. Chem.*, **66**, 1689 (1962).

(12) S. C. Chan and K. Y. Hui, *Aust. J. Chem.*, **20**, 2529 (1967)

(13) M. Parris, *J. Chem. Soc. A*, 583 (1967).

Integration of the spectrum (10:12:3) supports the assignment. Similar spectra were obtained on a 60-MHz nmr instrument in 10 *M* H_2SO_4 and 0.1 *M* DCl, and while the resolution was less, the same general features were present. The result is not in agreement with that of Parris,[13] who observed a singlet resonance for the *trans* CH_3 in 0.1 *M* $HClO_4$ and concluded that rapid proton exchange occurred in acid solution. However, the present results (Table II) show that *trans*-proton exchange for D^+ occurred at a much slower rate than previously claimed.[13] Figure 2 shows the change in the *trans*-methyl resonance *vs.* time. The triplet slowly decays with concomitant formation of a doublet centered at the same frequency; this doublet collapses to give a sharp singlet as the final spectrum. The general features of the spectra indicate that these two processes occur at similar rates, and they are attributed to deuteration of the coordinated NH_2CH_3 to give $NHDCH_3$, and finally ND_2CH_3. The processes overlapped and were not separated, but after 814 sec the first reaction was essentially complete and a linear plot of log ((peak height)$_\infty$ − peak height) *vs.* time was obtained for $2t_{1/2}$. The plot was corrected for acid hydrolysis and gave a rate constant for H exchange in the *trans*-methylamine group of 1.5 × 10^{-4} sec^{-1}, pD 4.12, 34°. The rate constant for hydrolysis of Cl^- under these conditions was estimated from the change in peak heights at 2.14 ppm as 1.4 × 10^{-3} sec^{-1} which agrees with the previous value.[12]

Table II

Proton-Exchange Rates for CoA_5Cl^{2+}

A	Position exchanged	Ref	Temp, °C	10^4k_{obsd}, sec^{-1}	μ	k_{ex}, M^{-1} sec^{-1}
ND_3	*cis*	*a*	25		0.2	5×10^4
	trans	*a*	25		0.2	3×10^6
CH_3NH_2	*cis*	*b*	25	6.5	0.2	$3 \times 10^{5\,c}$
	trans	This work	34	1.5	0.8	$3 \times 10^{7\,c}$
			25		0.8	$1.4 \times 10^{7\,d}$

[a] I. I. Creaser, unpublished work. [b] Reference 13. [c] Estimated from first-order rate constants, pD measurements, and k_{D_2O}. Values of k_{D_2O} under various conditions were estimated from data of H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, **55**, 2194 (1933); W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936); V. K. La Mer and J. P. Chittum, *J. Amer. Chem. Soc.*, **58**, 1642 (1936); S. Korman and V. K. La Mer, *ibid.*, **58**, 1396 (1936); P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960). [d] Estimated using an activation energy of 28 kcal: *cf.* D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **89**, 3428 (1967).

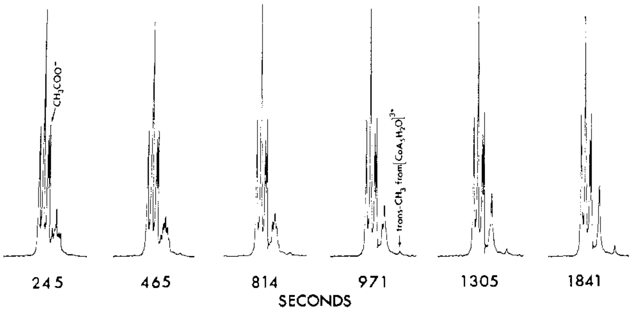

Figure 2.—Exchange of the *trans*-amine protons for deuterons in the $Co(CH_3NH_2)_5Cl^{2+}$ ion as followed by the change in the *trans*-methyl signal (pH 3.72, 34°).

Competition Studies.—Entry of N_3^- during base hydrolysis of $Co(CH_3NH_2)_5Cl^{2+}$ was monitored at 325 nm where azido product absorbs strongly (ϵ ~10^4). Linear plots of log ($D_t - D_\infty$) *vs.* time were obtained for at least 3 half-lives. The rate constant, 1.94 × 10^{-2} sec^{-1} (25°, μ = 1.0, 0.5 *M* NaN_3, 0.5 *M* $NaClO_4$, 0.1 *M* Tris buffer, pH 8.83), for entry of N_3^- agrees with that for hydrolysis of Cl^- under similar conditions, Table I. As mentioned previously, it was necessary to correct the data due to the presence of the second rate attributed to loss of amine. Azide entered only slowly after base hydrolysis at the same rate as that attributed to loss of amine (~2 × 10^{-4} sec^{-1}).

This experiment was repeated on a larger scale and the azido and aquo complexes were separated by ion-exchange chromatography. In 0.5 *M* N_3^- the azido: aquo ratio was 0.56, compared with 0.05 from the hydrolysis of $Co(NH_3)_5Cl^{2+}$ under similar conditions. This amount is corrected for azide which entered at the second rate mentioned above (0.26). The greater amount of azido complex formed here relative to the kinetic experiment was largely due to the time required to sorb the products on the ion-exchange column (~20 min).

The uncorrected thiocyanato:aquo ratio obtained from a similar competition experiment was 0.71, which is also much greater than that observed from the hydrolysis of $Co(NH_3)_5Cl^{2+}$ (0.03) under similar conditions. This ratio should also be corrected by about the same amount as for the azido complex.

Discussion

If the SN1CB mechanism obtains[3] in the form discussed in the Introduction, the derived rate law is

$$r_{\text{chloro}} = k_2\frac{K_a}{K_w}[A_5CoCl^{2+}][OH^-]$$

provided K_a/K_w is small (<10^{-2}). The mechanism requires H exchange at at least one N center to be faster than hydrolysis and loss of X^- to be assisted by the coordinated amide. In this process numerous factors can intervene to give variation in rate but in the closely analogous ions studied here these can be reduced to variations in the acidity of the protons of the coordinated amines (K_a), inductive effects of the alkyl substituents, the activity coefficients of the complex ions, and steric effects.

Both the ions $Co(NH_3)_5Cl^{2+}$ [14] and $Co(CH_3NH_2)_5Cl^{2+}$ obey the rate law and in the analogous complexes this property is assumed. For both ions proton exchange was much faster than loss of Cl^-.[15] Another property used to identify the mechanism was the competition characteristic[4] of the five-coordinate intermediate A_4NHRCo^{2+} for other species in solution. Both chloro complexes in the presence of N_3^- gave

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[14] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7**, 174 (1968).

[15] See ref 2, pp 183–185.

A_5CoOH^{2+} and $A_5CoN_3^{2+}$ ions at the same rate as the substrate hydrolyzed.[16] Similarly SCN^- competed effectively with water for the five-coordinate intermediate. These characteristics imply that the complexes hydrolyze by the SN1CB mechanism. It is pertinent now to analyze the factors which may account for the large variation in rate.

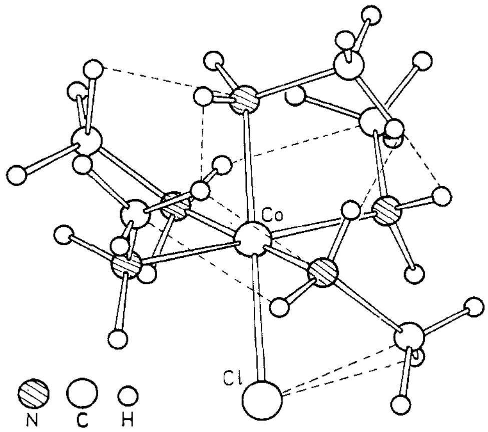

Figure 3.—A projected Dreiding model for $Co(CH_3NH_2)_5Cl^{2+}$ with minimized nonbonded interactions: ligand configurations eclipsed.

The measurement of K_a for the coordinated amines is precluded in water by the low dissociation constants ($pK_a > 14$). It was necessary, therefore, to use the rate of proton exchange (k_{ex}) of these centers as an approximate measure of relative acidity within and also between analogous ions. The assumption involved here is a direct proportionality between pK_a and log k_{ex}; these linear free energy relationships are common in many proton-transfer reactions.[17] In both $Co(NH_3)_5Cl^{2+}$ and $Co(CH_3NH_2)_5Cl^{2+}$ the *trans* protons exchanged ~50 times faster than the *cis* species (Table II), and this property was also assumed for the other alkylamine analogs. The results and LFER assumption imply that *trans*-NH_2R is ~50 times more acidic than the *cis*-NH_2R and we infer that the ion deprotonated *trans* is also the reactive species.[18] This is not required by the mechanism, however, and some of the stereochemical data can be rationalized more cogently by assuming that the reactive species is deprotonated *cis* to the leaving group in the pentamine system.[19] This question has yet to be fully resolved, but for the purposes of this paper it will be shown to be unimportant. The results in Table II for $Co(ND_3)_5Cl^{2+}$ and $Co(CH_3NH_2)_5Cl^{2+}$ imply that $K_a(cis)$ or $K_a(trans)$ do not differ by much more than a factor of 5. Therefore the difference between the base hydrolysis rate constants ($\sim 10^4$) for the two ions cannot be accounted for by differences between K_a either of *cis* or *trans* N protons. By analogy the same argument holds for the other pentakis-alkylamine complexes relative to $Co(NH_3)_5Cl^{2+}$.

The proton-exchange rates imply that coordinated methylamine is a stronger acid than ammonia although the inductive effects and relative pK_a's[20] would predict the reverse. The implication is therefore that the effect is small. It is also possible for the amine substituent to influence the release of Cl^- by donating negative charge to cobalt. The magnitude of this effect might be gauged from the relative rates of base hydrolysis of $Co(NH_3)_5Cl^{2+}$ and *trans*-$Co(CH_3NH_2)(NH_3)_4Cl^{2+}$ which should have similar proton acidities. The similar rate constants for base hydrolysis in both instances also imply the effect is small.

Finally for reactions under the same conditions the ratio of activity coefficients for the deprotonated reactant and activated complex

$$\frac{\gamma[CoA_4RNHCl^+]}{\gamma[CoA_4RNHCl^+]^{\ddagger}}$$

should be approximately constant for the series. The relative change in size of the ion in the two conditions will not be great and they both have the same charge. It appears therefore that this effect could not account for the rate differences observed.

The preliminary discussion implies that differences in proton acidity, activity coefficients, or inductive effects are not important in determining relative rates in the series of complexes. We assert therefore that the large rate enhancements are due to steric crowding in the ground states of the pentakis-alkylamine ions which is relieved in the transition state by substantially stretching the Co–Cl bond. Table I shows that the most striking increase (10^4) in the rate of base hydrolysis occurs between R = H and R = CH_3. Thereafter increasing alkyl substitution beyond the α-C atoms does not affect the rate greatly (20 times). An inspection of the nonbonding interactions in the alkylamine systems (Dreiding models) indicates that substitution at C atoms distant from the coordination site should not greatly increase the compressional effect. However, if substitution at the α-C atom is included, *e.g.*, isopropylamine, the nonbonded interactions become considerably magnified. Some support for this last effect might be inferred from our inability to prepare the pentakis-isopropylamine complex by the method which gave the other complexes and from the fact that monodentate secondary alkylamines in general have not been coordinated in octahedral cobalt(III)–pentamine complexes despite many attempts.

Evidence for steric effects in the ground state appears from other sources. The crystal structure analysis of $[Rh(NH_3)_5C_2H_5]Br_2$ shows that the *cis* N–Rh–C angle is distorted by over 10° from its expected value of 90°. It was suggested[21] that this occurs to equalize the nonbonded H···H contacts of methylene and

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[16] Present work and D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

[17] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 159.

[18] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **8**, 1595 (1969).

[19] F. Nordmeyer, *ibid.*, **8**, 2780 (1969).

[20] L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964.

[21] A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).

methyl with the *cis*-NH_3 groups. This example is comparable with the *trans*-$Co(NH_2CH_3)(NH_3)_4Cl^{2+}$ ion since $-CH_2CH_3$ and NH_2CH_3 are isoelectronic. A comparable distortion should be observed in the cobalt complex if the above explanation is correct, although the hydrolysis rate difference relative to $(NH_3)_5CoCl^{2+}$ would indicate that the energy arising from the distortion is small. However, for five such bulky groups the nonbonded interactions are more pronounced and an attempt has been made to show the severity of these interactions.

Two configurations of the $[Co(NH_2CH_3)_5Cl]^{2+}$ ion were considered. Figure 3 shows the structure obtained by minimizing nonbonded interactions for eclisped configurations of the ligands while Figure 4 shows the results of minimizing the interactions for a staggered ligand configuration. Dreiding models were constructed for Co–N distances of 2.0 Å and a Co–Cl distance of 2.2 Å and the distances between nonbonded atoms were used to calculate the energy terms from the conservative potential functions derived by Hill.[22] Representative interactions >0.7 kcal/mol are shown as dotted lines in the figures. No attempt was made to evaluate permutations of partially eclipsed and staggered ligand configurations or orientations, since this degree of sophistication was not warranted by the present analysis based solely on nonbonded interactions.

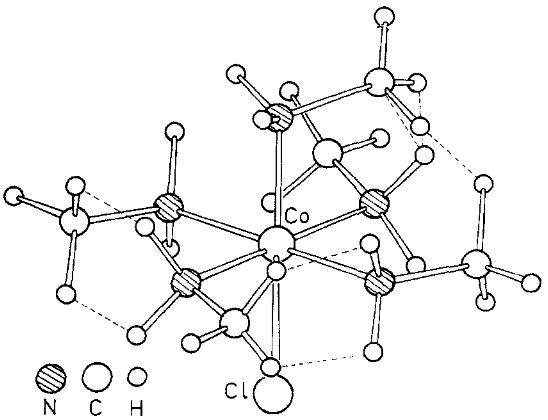

Figure 4.—A projected Dreiding model for $Co(CH_3NH_2)_5Cl^{2+}$ with minimized nonbonded interactions: ligand configurations staggered.

The calculations predict that the methylamine complex is 25–30 kcal/mol less stable than the corresponding ammonia complex in both configurations. However, it is clear from recent studies[8] that energies calculated in this manner may be reduced by 50–75% by angular deformations. Such distortions occur with relatively little expenditure of energy, in order to relieve severe nonbonded interactions. *Thus, while the depicted structures may not represent the true molecular structure, the significance of these calculations is that there must be large nonbonded interactions which lead to deformation and therefore reduced stability in the reactant ground state.* This situation will alter little for the deprotonated reactant where a proton is replaced by a lone pair of electrons.

A crystal structure analysis is planned for the pentakis-methylamine complex which should reveal the predicted substantial distortion. At that time a more elaborate calculation of the energy arising from the steric effects will be undertaken which will include not only the nonbonded terms but bond stretching, angle bending, and torsional terms.[8] It follows that if the transition state is stabilized relative to the ground state by relief of these steric interactions, the deprotonated five-coordinate intermediate, where Cl is lost, should be even more stabilized. It is likely then that reentry of coordinating species such as H_2O and anion in solution will be more hindered than for $Co(NH_3)_4NH_2^{2+}$ and that the lifetime of $Co(NH_2R)_4NHR^{2+}$ will be lengthened relatively. Under these circumstances the alkylamine intermediate should be more selective for the species in solution and will elect for the better competitor. Evidence for these characteristics might be inferred from the fact that N_3^- and NCS^- (0.5 *M*) capture $\sim ^1/_3$ of the alkylamine intermediate and $\sim ^1/_{20}$ of $Co(NH_3)_4NH_2^{2+}$ even though $[H_2O] \gg$ [competing anion]. Similar experiments with acetate and fluoride did not appear to give any competition products. However, the meaning of the latter experiments is obscured by unknown factors, *e.g.*, (a) the base hydrolysis rates of both species might be fast relative to the corresponding pentaammine complexes and (b) the entry of acetate could be sterically hindered to a substantial degree.

Acid Hydrolysis.—The relative order "bond breaking more important than bond making" appears to be characteristic of the aquation reactions of cobalt(III)–amine–halide complexes[23–28] in dilute acid, although there is some indirect evidence for some degree of bond making by the water molecule.[25,26,28] The results obtained for aquation of the present series of pentamine complexes, namely, an increase of 100 from R = H to R = *i*-C_4H_9, appear to agree with this analysis. The rate difference implies that bond breaking is less important here than for the SN1CB mechanism and could reflect the compromise between the need to release Cl^- to relieve steric strain and the difficulty of forming a seven-coordinate transition state.

For the analogous chromium(III) series[29] there is a (30 times) decrease in rate from R = H to R = CH_3 and then a gradual increase (10 times) with lengthening alkyl substituent. This could reflect again the balance between bond making by H_2O and breaking of the Cr–Cl bond except that here bond making is initially

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more important than for the cobalt series. Such a proposal would not be inconsistent with the expected abilities of low-spin d^6 and d^3 ions to form a bond with an incoming nucleophile. However, the rate differences for aquation are much smaller than for base hydrolysis and they could possibly arise from variations in other factors.

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The *trans–cis* Isomerization of Bis(malonato)diaquochromate(III)

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The rate of isomerization of *trans*-bis(malonato)diaquochromate(III) has been studied at 40, 50, 60, and 70° in aqueous solution at a constant ionic strength of 1.0 F ($NaClO_4$) and at pH 3. The rate law is $-d[trans\text{-}Cr(C_3H_2O_4)_2(OH_2)_2^-]/dt = k \cdot [trans\text{-}Cr(C_3H_2O_4)_2(OH_2)_2^-]$, where $k = 2.66 \times 10^{-5}$, 1.02×10^{-4}, 5.09×10^{-4}, and 1.95×10^{-3} sec^{-1} at 40, 50, 60, and 70°, respectively. The activation parameters for the isomerization are $\Delta H^* = 30.5 \pm 0.5$ kcal/mol and $\Delta S^* = 17.6 \pm 1.4$ cal/deg mol, where the associated uncertainties are standard deviations. The visible spectra of solutions of $Cr(C_3H_2O_4)_2(OH_2)_2^-$ at equilibrium with respect to the *trans–cis* isomerization were found to be identical within experimental error from 40 to 70° and to correspond to within 5% at 560 and 418 nm of that of a solution of pure *cis* isomer. This indicated that the *trans–cis* isomerization is greater than 95% complete in this temperature range.

Introduction

Few studies have been made of the isomerization reactions of chromate(III) complexes. The *trans–cis* isomerization of *trans*-bis(oxalato)diaquochromate(III) has been studied by several different groups.[1] Hamm and Perkins reported the preparation of the *cis* and *trans* isomers of potassium bis(malonato)diaquochromate(III) but did not study the kinetics of the isomerization reaction.[2] This paper reports the results of the investigation of the kinetics of the isomerization of *trans*-bis(malonato)diaquochromate(III) at pH 3. Comparisons with the bis(oxalato)diaquochromate(III) isomerization are made.

Experimental Section

Reagents.—All commercial chemicals were of reagent grade and were used without further purification, except as specified below. Hexaaquochromium(III) perchlorate was prepared by the procedure of Plane and Phipps.[3] The uv–visible spectrum of the product obtained compared favorably with that reported by Plane and Laswick.[4]

Potassium *trans*-bis(malonato)diaquochromate(III) was prepared in a manner similar to that described by Hamm and Perkins.[2] The product was recrystallized twice from water. *Anal.* Calcd for $K[Cr(C_3H_2O_4)_2(OH_2)_2] \cdot 3H_2O$: Cr, 13.49; C, 18.62; H, 2.59. Found: Cr, 13.2; C, 20.01; H, 2.97. The analysis for chromium, as chromate(VI), was performed spectrophotometrically. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.

The purity of the potassium *trans*-bis(malonato)diaquochromate(III) was established by using ion-exchange chromatography. The following procedure was used. A 25.0-ml solution containing 0.1444 g of the compound, which had isomerized at 25°, was run into a Dowex 50W-X8, 100–200 mesh, Na^+-form, cation-exchange column. The column was washed with 50 ml of water. A narrow purple band remained at the top of the column, indicating the presence of a positively charged chromium(III) species in the mixture. All of the effluent from the cation-exchange column was run into a Dowex 1-X8, 200–400 mesh, NO_3^--form, anion-exchange column. A purple band formed at the top of the column, and no chromium species remained in the effluent after passing through the column. Both columns were jacketed and cooled to 1° with circulating water. The cation-exchange column was eluted with 0.10 F sodium nitrate. The narrow band did not separate upon elution. This implied a 1+ species.[5] The effluent was analyzed for chromium as described above. This species, which probably was malonatotetraaquochromium(III), contained 2.03% of the recovered chromium. The anion-exchange column was eluted first with 0.10 F sodium nitrate. Two bands developed. One remained at the top of the column and the other was eluted. This behavior implied that the species which was removed was 1− charged and it was bis(malonato)diaquochromate(III).[5] By chromium analysis, this species was determined to be 93.7% of the recovered chromium. The second band was eluted with 1.0 F sodium nitrate, implying a 3− species which probably was tris(malonato)chromate(III).[5] This species was 4.24% of the total recovered chromium. Of the chromium taken 99.97% was recovered.

A sample of the *trans* isomer which had not isomerized was analyzed in the same manner. This analysis gave 1.56% 1+ species, 96.4% bis(malonato)diaquochromate(III), and 2.32% 3− species. Since this sample of potassium *trans*-bis(malonato)diaquochromate(III) had already been recrystallized twice

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(5) In this laboratory, under these same conditions, it has been found that 0.10 F sodium nitrate will elute *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ from anion-exchange resin or $Cr(C_2O_4)(OH_2)_4^+$ from cation-exchange resin and that 1.0 F sodium nitrate will elute $Cr(C_2O_4)_3^{3-}$.