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# KINETICS AND MECHANISM OF BASE AQUATION OF CHLOROAMMINEBIS(DIMETHYLGLYOXIMATO)COBALT(III) AND CHLOROPYRIDINEBIS(DIMETHYLGLYOXIMATO)COBALT(III) *

W.K. WILMARTH, K.R. ASHLEY, J.C. HARMON, J. FREDERICKS and
A.L. CRUMBLISS **

*P.M. Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, NC and the Department of Chemistry, University of Southern California, Los Angeles, CA 90007 (U.S.A.)*

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CONTENTS

## A. INTRODUCTION

Cobalt(III) complexes containing coordinated amines have long been known to undergo aquation in basic medium at a significantly faster rate than in acidic solution. These systems have been reviewed extensively in the

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* Dedicated to the memory of Wayne Keith Wilmarth.

** Author to whom correspondence should be addressed: P.M. Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, NC 27706, U.S.A.

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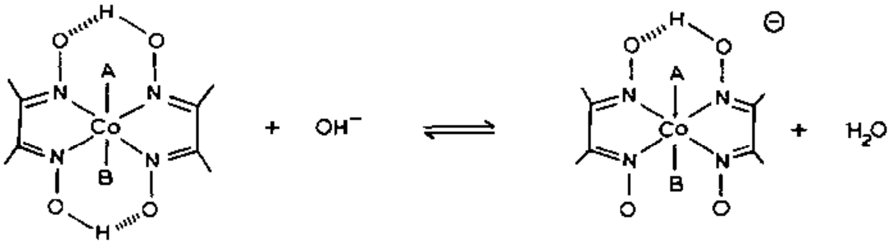
literature [1–6] and the currently accepted reaction path is the $S_N1$ CB mechanism. A key feature of this mechanism is initial deprotonation of an amine proton by $OH^-$ to produce a coordinated amido group, which then presumably accelerates the metal-leaving group bond dissociation to produce a reactive intermediate of reduced coordination number (D mechanism [1,7]). These reactions and mechanistic concepts have been expanded to include macrocyclic amine ligand complexes [8–10].

We report here on the kinetics and mechanism of base aquation for two dimethylglyoxime complexes of cobalt(III), $Co(dmgH)_2(Cl)(py)$ and $Co(dmgH)_2(Cl)(NH_3)$ *, as shown in reaction 1.

$$Co(dmgH)_2(Cl)(L) + \underset{L = NH_3, py}{OH^-} \rightarrow Co(dmgH)_2(OH)(L) + Cl^- \qquad (1)$$

Mechanistic interpretation of accelerated aquation rates in basic medium compared with acidic solution may be simplified for the cobaloximes (relative to the cobalt–amine systems) by the fact that the oxime proton is sufficiently acidic that it may be titrated to produce the conjugate base complex. (The existence of an amido intermediate complex in the cobalt–amine systems is normally inferred from kinetic data.) [11]



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The results of this study will enable us to comment on the relative reactivities of the neutral (**1**) and deprotonated (**2**) complexes, and the possible involvement of the tautomeric amido complex $Co(dmgH)_2(Cl)(NH_2)^-$ for the case where $L = NH_3$. The amido complex corresponds to a true $S_N1CB$ process and would test the applicability of the classical conjugate base mechanism [1] to base aquation of amine-cobaloximes.

Previous investigators have reported on the aquation of some acido- [9,12–15] and organo-cobaloximes, [16,17] and related organo-(DO)(DOH)pn cobalt(III) complexes ** [18] in basic medium. In general, an acceleration in

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* $dmgH_2$ represents dimethylglyoxime, $CH_3C(=NOH)C(=NOH)CH_3$, and $dmgH^-$ and $dmg^{2-}$ the corresponding mono- and di-anions. Cobalt complexes containing bis(dimethylglyoximato) ligands, $Co(dmgH)_2AB$, are referred to as cobaloximes.

** (DO)(DOH)pn = diacetylmonoximediacetylmonoximatopropane-1,3-diyldiimino; a tetradentate oxime-type ligand.

rate has been observed over that in acidic medium by a factor of ca. 3 to 100. However, this is not as dramatic an effect as that found for the cobalt(III) amine and cyclic amine systems [1,6,8,10]. Concurrent with and subsequent to the completion of our study two closely related studies have been published at different conditions and using alternative experimental techniques [14,15]. This report confirms the published results for Co(dmgH)$_2$(Cl)(py) [15] and extends these results over a wider [OH$^-$] range. For the case of Co(dmgH)$_2$(Cl)(NH$_3$) we report aquation kinetics at a significantly higher [OH$^-$] range where we observe second-order [OH$^-$]-dependent kinetics not observed in the previous study [14]. This necessitates a reinterpretation of the mechanism of base aquation and allows for a direct comparison of Co(dmgH)$_2$(Cl)(py) and Co(dmgH)$_2$(Cl)(NH$_3$) at identical reaction conditions.

## B. EXPERIMENTAL

### *(i) Reagents and solutions*

All commercial chemicals were of reagent grade and used without further purification. Stock solutions of $NaClO_4$ were prepared and analyzed as previously reported [19]. Standard solutions of $AgNO_3$ were prepared from weighed amounts of analytical grade $AgNO_3$ which had been dried at 120°C for 2 h. Sodium hydroxide solutions were prepared by diluting 50% analytical grade NaOH to the required volume. The solutions were standardized against $KHC_8H_4O_4$, using phenolphthalein as the indicator.

### *(ii) Preparation of complexes*

Bis(dimethylglyoximato)chloroamminecobalt(III) [20], bis(dimethylglyoximato)chloropyridinecobalt(III) [21] and bis(dimethylglyoximato)chloroaquocobalt(III) [22] were prepared according to published procedures. The possibility of ionic impurities was eliminated by passing aqueous solutions of the product through Dowex 50 WX8 (acid form) and Amberlite IRA-400 (basic form) or Dowex 1 × 8 ion-exchange columns. No colored material was eluted from either resin.

*Anal.* Calculated for Co(dmgH)$_2$(Cl)(NH$_3$)$\cdot$H$_2$O; C, 26.75; H, 5.29; N, 19.50; Cl, 9.87; Co, 16.22. Found: C, 26.75; H, 5.15; N, 19.55; Cl, 10.05; Co, 16.42. Calculated for Co(dmgH)$_2$(Cl)(py); C, 38.67; H, 4.75; N, 17.35; Cl, 8.78. Found: C, 38.55; H, 4.72; N, 17.15; Cl, 8.55. Calculated for Co(dmgH)$_2$(Cl)(OH$_2$) N, 16.35. Found: N, 16.35. The bis(dimethylglyoximato)aquopyridine ion was prepared in solution by the acid aquation of Co(dmgH)$_2$(Cl)(py).

### *(iii) Analyses*

Elemental analyses were made by Galbraith Laboratories, Inc., Tennessee and Elek Laboratories, Los Angeles, California. Nitrogen determinations for $Co(dmgH)_2(Cl)(py)$ and $Co(dmgH)_2(Cl)(OH_2)$ were made by the Kjeldahl method. Chloride determinations for these two complexes were made by potentiometric titrations, using $AgNO_3$ as the titrant. Complete aquation was ensured by dissolving the complex in 0.25M NaOH for 24 h prior to titration.

### *(iv) Apparatus*

Absorbancy measurements and UV–VIS spectra were obtained using Beckman DU, Cary 14 or Cary 15 spectrophotometers equipped with thermostatted cell compartments. Hydroxide ion concentrations were determined using a Beckman Research Model pH meter equipped with a Type E or Sargent S-30050-15A glass electrode. The reference electrode was filled with 4.0M NaCl, rather than the usual saturated KCl solution, to prevent clogging of the fritted electrode disk when measurements were made in solutions containing perchlorate ions. The pH values read from the pH meter under conditions of unit ionic strength ($NaClO_4$) were corrected to a formal concentration $p[OH^-]$ by the use of a calibration curve. The calibration curve was constructed in the following way. Solutions containing from 1.00 to $1.00 \times 10^{-4}$M NaOH were prepared at $I = 1.00$ ($NaClO_4$). The concentration $p[OH^-]$, calculated from the known amount of NaOH in the solutions, was plotted vs. the pH read directly from the pH meter. The calibration curve did not change during the duration of the experiments. Hydroxide ion concentrations given in this work are based on the use of this calibration. Potentiometric titrations were carried out using the same instrument equipped with a Ag/AgCl electrode and a calomel reference electrode which was isolated from the solution by a $NaNO_3$/Agar bridge.

### *(v) Neutralization quotient*

The acidity of a single bridge proton, as shown in eqn. 2, was measured spectrophotometrically for $Co(dmgH)_2(Cl)(L)$ ($L = NH_3$ and py). The measurements were made at 395 and 255 nm, respectively, for $L = NH_3$ and py. The solutions contained no buffer and were maintained at 25.0°C and $I = 1.00$ ($NaClO_4$). In the most basic solutions, $Cl^-$ aquation became significant so that it was necessary to use individual aliquots of the stock complex solution for each absorbance measurement at a particular $[OH^-]$ concentration and to extrapolate the measured absorbancy as a function of time to zero time. The p[$OH^-$] was determined from the calibration curve. The concentration of the complex in each solution was ca. $10^{-4}$ to $10^{-5}$M.

### *(vi) Kinetic measurements*

The rate of loss of chloride ion from Co(dmgH)$_2$(Cl)(py) and Co(dmgH)$_2$(Cl)(NH$_3$) was followed spectrophotometrically and titrametrically. The temperature was 25.0 ± 0.1°C and I = 1.00 (NaClO$_4$). The general titrametric procedure was as follows. A stock complex solution was mixed with a solution of known [$OH^-$] concentration and maintained at a constant temperature of 25 ± 0.1°C. At various time intervals, aliquots were withdrawn using a calibrated blowout pipette and quenched in cold dilute HClO$_4$ (pH 4). A drop of Tergitol NPX (Union Carbide Co.) was added to prevent coagulation of the AgCl and the quenched solutions titrated to an end-point potential with 0.0100M AgNO$_3$. Independent experiments indicate that additional $Cl^-$ release due to acid hydrolysis in the quenched solutions is not significant. The end-point potential was determined by titrating a standard NaCl solution with 0.0100M AgNO$_3$ under the same conditions as the kinetic experiments and was periodically rechecked throughout the course of this study. Pseudo-first-order rate constants at a given [$OH^-$] concentration (determined from the pH meter calibration curve described above) were taken as 2.303 times the slope of the linear plots of $\log(1 - V/V_\infty)$ vs. time, where $V$ represents the volume of AgNO$_3$ used to titrate the sample at time $t$, and $V_\infty$ is the total volume of AgNO$_3$ used to titrate the sample after 10 half-lives. Kinetic data for the aquation of Co(dmgH)$_2$(Cl)(py) above p[$OH^-$] 3 were obtained using 0.05M phosphate-buffered solutions.

The spectrophotometric rate determinations for the aquation of Co(dmgH)$_2$(Cl)(NH$_3$) were performed at 410 nm. The complex concentration was $1 \times 10^{-4}$M, below p[$OH^-$] 2.08. The p[OH] was determined by the amount of 1.00M NaOH added. The change in absorbance was ca. 1.0 when 2.00-cm path length cuvettes were used. Above p[$OH^-$] 2.08 the complex concentration was $6 \times 10^{-4}$M and 10.00-cm cuvettes were used. The change in absorbance varied from 0.65 at p[$OH^-$] 2.08 to 0.15 absorbancy units at p[$OH^-$] 2.67. These solutions were buffered with 0.100M sodium phosphate. The buffer solutions were prepared by dissolving 0.100 molecular weight of anhydrous Na$_3$PO$_4$ in ~ 100 ml of water in a 1 l volumetric flask. The desired amount of standardized HClO$_4$ and NaClO$_4$ solutions were added and the volume diluted to the mark. In order to calculate the ionic strength the concentration of $HPO_4^{2-}$ was assumed to be equal to the amount of HClO$_4$ added. The p[$OH^-$] was determined, after the complex was dissolved in the solution, by measuring the pH and using the calibration curves. The pseudo-first-order rate constants were taken as 2.303 times the slope of the linear $\log(A - A_\infty)$ vs. time plots, where $A$ is the absorbance at time $t$ and $A_\infty$ is the absorbance after 10 half-lives. The rate of aquation of $Co(dmgH)_2(Cl)(py)$ below p[$OH^-$] 1 was also determined spectrophotometrically at 250 nm. The complex concentration was ca. $10^{-6}$M and 1.0-cm cells were used. The p[$OH^-$] and the pseudo-first-order rate constants were determined as described above.

The rate of pyridine release from $Co(dmgH)_2(Cl)(py)$ at high [$OH^-$] concentrations was measured spectrophotometrically by an ether extraction method. Aliquots of the reaction mixture containing ca. $10^{-5}$M complex and $p[OH] \leq 2$ were pipetted into separate funnels containing $H_2O$-saturated ether. After the reaction time, $t$, was noted the flasks were shaken vigorously. The ether layer was then removed and the concentration of released pyridine determined spectrophotometrically at 256 nm. Pseudo-first-order rate constants were calculated as 2.303 times the slope of the linear plots of $\log(1 - A/A_\infty)$ vs. time, where $A$ is the pyridine absorbance at time $t$, and $A_\infty$ is the absorbance after 10 half-lives. A large uncertainty must be assigned to these results due to the experimental difficulties encountered in their determination. At high [$OH^-$] the release of pyridine is rapid and the time recorded for each measurement is uncertain as the reaction proceeds while shaking and separation of the ether layer occurs. The high vapor pressure of ether was an additional source of error. We estimate the uncertainty in our reported values for pyridine relase to be ~ 20%.

## C. RESULTS

### *(i) Neutralization quotient*

The general equation for the neutralization reaction depicted by reaction 2 is

$$K[OH^-] = \frac{[Co(dmgH)(dmg)(Cl)(L)^-]}{[Co(dmgH)_2(Cl)(L)]} \tag{3}$$

where $K$ is the neutralization quotient and the brackets denote molar concentrations. If we assume Beer's law and that the only absorbing species present are $Co(dmgH)_2(Cl)(L)$ and its conjugate base, Co(dmgH)-(dmg)(Cl)(L), then eqn. 4 is readily derived

$$\frac{A}{l\mathrm{Co_t}} = \frac{\varepsilon_A K[OH^-] + \varepsilon_{HA}}{1 + K[OH^-]} \tag{4}$$

where $A$ is the absorbance at a particular [$OH^-$] value, $l$ is the optical path length, $\mathrm{Co_t}$ is the total complex concentration, $\varepsilon_A$ is the molar absorptivity of Co(dmgH)(dmg)(Cl)(L), and $\varepsilon_{HA}$ is the molar absorptivity of Co-

(dmgH)$_2$(Cl)(L). Figure 1 is a plot of the experimental data for Co(dmgH)$_2$(Cl)(NH$_3$) and Co(dmgH)$_2$(Cl)(py) according to eqn. 4. The solid lines represent a non-linear least-squares analysis of these data.

In the non-linear least-squares analysis of the data for Co(dmgH)$_2$(Cl)(NH$_3$), $\varepsilon_{HA}$ was fixed at 378 M$^{-1}$ cm$^{-1}$, the independently determined value of $\varepsilon_{HA}$ at 395 nm, 25° and I = 1.00 (NaClO$_4$). The values of $\varepsilon_A$ and $K$ were allowed to vary. The data were weighted as $(Co_t\ 1/A)^2$. The calculated values for $\varepsilon_A$ at 395 nm and $K$ are 2.2 (0.1) × 10$^3$ M$^{-1}$ cm$^{-1}$ and 1.1 (0.1) × 10$^2$ M$^{-1}$, respectively. The reported value of $K_w$ in 1.00M NaClO$_4$ at 25° is 1.70 × 10$^{-14}$ [23]. Thus, the value of $K_a$, the acid dissociation

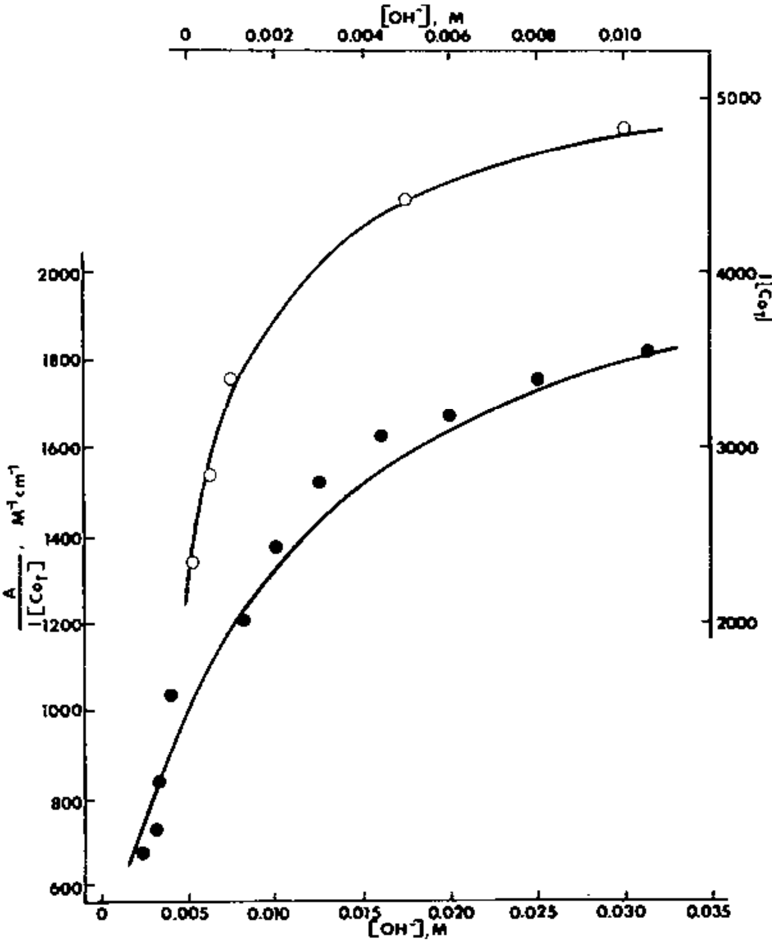

Fig. 1. Plot of eqn. 4 for Co(dmgH)$_2$(Cl)(NH$_3$) (●, left-hand ordinate) and Co(dmgH)$_2$(Cl)(py) (○, right-hand ordinate). Symbols represent actual data points; the solid line is a non-linear least-squares analysis of the experimental data according to eqn. 4.

constant, for $Co(dmgH)_2(Cl)(NH_3)$ is $1.64 \times 10^{-12}$ (p$K$a = 11.79) at 25° and I = 1.00 ($NaClO_4$). Similarly, the data for $Co(dmgH)_2(Cl)(py)$ were analyzed according to eqn. 4 by using the fixed value for $\varepsilon_{HA}$ of $2.35 \times 10^4$ $M^{-1}$ $cm^{-1}$ at 255 nm, 25°C and I = 1.00 ($NaClO_4$). The calculated values for $\varepsilon_A$ at 255 nm and $K$ are 5.3 (0.1) $\times 10^4$ $M^{-1}$ $cm^{-1}$ and 5.0 (0.7) $\times 10^2$, respectively. Consequently, the calculated value of the acid dissociation constant, $K_a$, for $Co(dmgH)_2(Cl)(py)$ is $8.4 \times 10^{-12}$ (p$K_a$ = 11.08) at 25°C and I = 1.00 ($NaClO_4$).

### *(ii) Stoichiometry*

The base aquation of $Co(dmgH)_2(Cl)(NH_3)$ produces one $Cl^-$ per molecule of complex. No $NH_3$ is released within 10 half-lives in 1.00M NaOH at 25°C, as determined by Nessler's technique [24]. The UV–VIS spectrum of the aquated product is the same as that of $Co(dmgH)_2(OH)(NH_3)$. The base aquation of $Co(dmgH)_2(Cl)(py)$ also produces one $Cl^-$ per molecule of complex and at higher p[$OH^-$] values the UV–VIS spectrum of the product is consistent with the formation of $Co(dmgH)_2(OH)(py)$. Thus the overall reaction studied kinetically is that shown in eqn. 1 for $Co(dmgH)_2(Cl)(NH_3)$ and $Co(dmgH)_2(Cl)(py)$.

TABLE 1

Aquation rate data for $Co(dmgH)_2(Cl)(py)$, $Co(dmgH)_2(OH_2)(py)^+$ and $Co(dmgH)_2$-$(Cl)(OH_2)$ [a]

| Complex | p[$OH^-$] | $k_{Cl}$ ($s^{-1}$) [b] | $k_{py}$ ($s^{-1}$) [c] |
|---|---|---|---|
| $Co(dmgH)_2(Cl)(py)$ | 0.3 | $2.5 \times 10^{-3}$ | $> 3.5 \times 10^{-4}$ |
| | 1.0 | $5.1 \times 10^{-4}$ | $3.5 \times 10^{-4}$ |
| | 2.0 | $1.2 \times 10^{-4}$ | $2.6 \times 10^{-5}$ |
| | 3.0 | $5.9 \times 10^{-5}$ | very slow |
| $Co(dmgH)_2(OH_2)(py)^+$ | 0.3 | | $2.7 \times 10^{-3}$ |
| | 1.0 | | $5.6 \times 10^{-4}$ |
| | 2.0 | | $9.1 \times 10^{-5}$ |
| | 3.0 | | $4.6 \times 10^{-5}$ |
| $Co(dmgH)_2(Cl)(OH_2)$ | 1.3 | $2.5 \times 10^{-2}$ | |
| | 2.0 | $4.4 \times 10^{-3}$ | |
| | 1.0 (pH) | $1.2 \times 10^{-4}$ | |
| | 1.0 (pH) | $1.0 \times 10^{-4}$ [d] | |

[a] Aqueous solution, I = 1.00 ($NaClO_4$) and 25°C. [b] Pseudo-first-order rate constant for $Cl^-$ release; reproducibility within 10%. [c] Pseudo-first-order rate constant for py release measured by ether extraction method for $Co(dmgH)_2(Cl)(py)$ and by spectrophotometrically monitoring the rate of $Co(dmgH)_2(OH_2)_2^+$ product formation in $Co(dmgH)_2(OH_2)(py)^+$. Reproducibility within 30% for ether extraction method. [d] A.V. Ablov and A.Y. Sychev, Russ. J. Inorg. Chem., 4 (1959) 1143; I = 0; T = 25°C.

For the aquation of Co(dmgH)$_2$(Cl)(py) a secondary reaction involving the release of py to yield the diaquo species as the product becomes significant at high alkalinity (p[OH$^-$] < 2). Table 1 is a compilation of rate constants for Cl$^-$ and py release from Co(dmgH)$_2$(Cl)(py), Co(dmgH)$_2$(OH)(py), and Co(dmgH)$_2$(Cl)(OH$_2$). These data were collected in order to determine in what order the release of Cl$^-$ and py occur in these strongly basic solutions.

If we consider the rate of py release from Co(dmgH)$_2$(Cl)(py), measured by the ether extraction method, we observe that at p[OH$^-$] $\geqslant$ 2 the rate of py release is slower than the rate of Cl$^-$ release (see Table 1), the rate of py release at p[OH$^-$] $\geqslant$ 3 being negligible. This is direct and conclusive evidence that at these conditions of alkalinity the release of Cl$^-$ occurs before any py release. However, at p[OH$^-$] 1 the rates are comparable and at p[OH$^-$] $\leqslant$ 1 we cannot make the comparison as the ether extraction technique is too slow to follow the rate of py release. At p[OH$^-$] 1 the rate of Cl$^-$ release from Co(dmgH)$_2$(Cl)(py) measured titrametrically is the same as the rate of Co(dmgH)$_2$(OH$_2$)$_2^+$ formation measured spectrophotometrically. This does not allow us to distinguish between initial Cl$^-$ or py release from Co(dmgH)$_2$(Cl)(py) at this p[OH$^-$] range.

If at p[OH$^-$] $\leqslant$ 1, Cl$^-$ is released before py from Co(dmgH)$_2$(Cl)(py), then the intermediate Co(dmgH)$_2$(py)(OH$_2$)$^+$ is formed which releases py to give Co(dmgH)$_2$(OH$_2$)$_2^+$. Given the above data that the rate of Cl$^-$ release and Co(dmgH)$_2$(OH$_2$)$_2^+$ formation from Co(dmgH)$_2$(Cl)(py) are comparable in the p[OH$^-$] region in question, then the rate of Co(dmgH)$_2$(OH$_2$)$_2^+$ formation from Co(dmgH)$_2$(py)(OH$_2$)$^+$ must be very much more rapid than its formation from Co(dmgH)$_2$(Cl)(py) (assuming Cl$^-$ is released from Co(dmgH)$_2$(Cl)(py) before py). The data shown in Table 1, however, for the rate of pyridine release from Co(dmgH)$_2$(py)(OH$_2$) is within the limits of error as being equal to the rate of Cl$^-$ release from Co(dmgH)$_2$(Cl)(py). We also see in Table 1 that the rate of Cl$^-$ release from Co(dmgH)$_2$(Cl)(OH$_2$) is indeed more rapid than the rate of Cl$^-$ release from Co(dmgH)$_2$(Cl)(py). When these data are considered in conjunction with the other data listed in Table 1 we must conclude that at p[OH$^-$] < 1 either py release from Co(dmgH)$_2$(Cl)(py) preceeds Cl$^-$ release, or both are released concurrently (within our limits of measurements). However, above this p[OH$^-$] range eqn. 1 clearly represents the stoichiometry of the Co(dmgH)$_2$(Cl)(py) aquation reaction for which kinetic data have been collected. This uncertainty at the extreme end of the p[OH$^-$] range studied does not seriously affect the interpretation of the kinetic data given below.

### *(iii) Kinetics*

The reaction of interest is depicted by eqn. 1. The kinetics of base aquation were investigated as a function of $[OH^-]$ at 25°C and $I = 1.00$ $(NaClO_4)$. Figure 2 is a plot of $pk_{obs}$ vs. $p[OH^-]$. The points represent experimentally obtained pseudo-first-order rate constants and the solid line represents a non-linear least-squares analysis of the data according to eqn. 5:

$$k_{obs} = \frac{A + B[OH^-] + C[OH^-]^2}{1 + D[OH^-]} \tag{5}$$

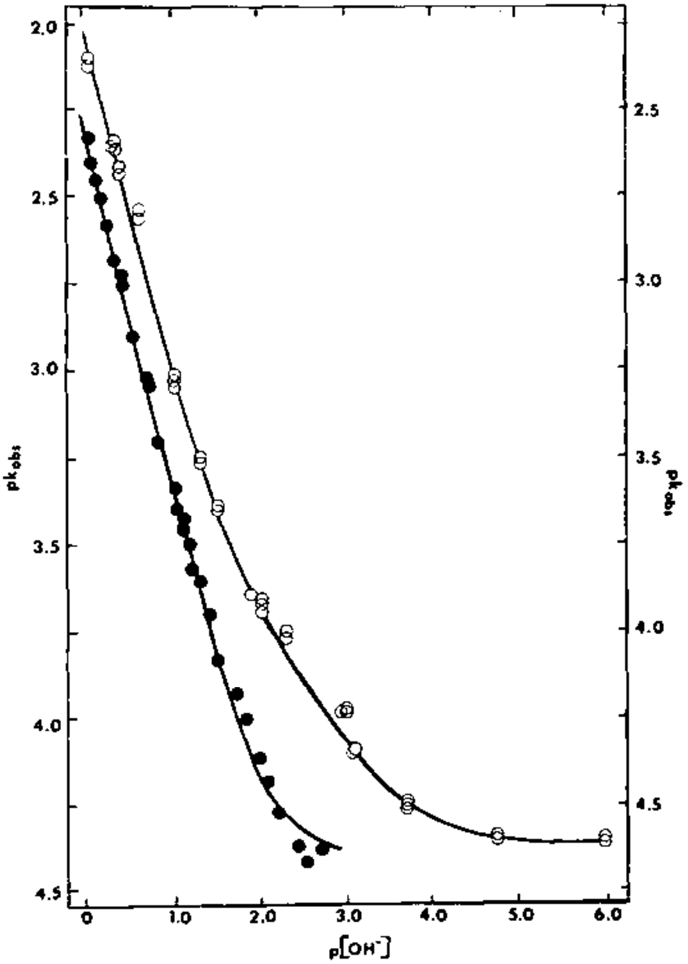

Fig. 2. $pk_{obs}$ as a function of $p[OH^-]$ for $Co(dmgH)_2(Cl)(NH_3)$ (●, left-hand ordinate) and $Co(dmgH)_2(Cl)(py)$ (○, right-hand ordinate). Symbols represent actual data points; solid line represents a non-linear least-squares analysis of the data according to eqn. 5.

TABLE 2

Kinetic parameters computed from a non-linear least-squares analysis of kinetic data using eqn. 5

| Parameter [a] | $Co(dmgH)_2(Cl)(NH_3)$ | $Co(dmgH)_2(Cl)(py)$ |
|---|---|---|
| A | $4.20 \times 10^{-5}$ [b] | $2.45\ (0.12) \times 10^{-5}$ |
| B | $5.52\ (0.80) \times 10^{-4}$ | $4.83 (0.24) \times 10^{-2}$ |
| C | $5.44\ (0.05) \times 10^{-1}$ | $2.28\ (0.07)$ |
| D | $1.05 \times 10^{2}$ [b] | $4.95 \times 10^{2}$ [c] |

[a] As defined in eqn. 5. [b] Parameter held fixed. When less than two of the four parameters were held constant for the $Co(dmgH)_2(Cl)(NH_3)$ aquation data convergence was not achieved. [c] Parameter held fixed at $4.95 \times 10^2$. When allowed to float, the calculated value is 6.52 $(1.91) \times 10^2$. See text.

Table 2 lists the values of the parameters resulting from the least-squares fit of eqn. 5 to the data for $Co(dmgH)_2(Cl)(py)$ and $Co(dmgH)_2(Cl)(NH_3)$.

## D. DISCUSSION

### *(i) Neutralization quotients*

The neutralization quotient reported here for $Co(dmgH)_2(Cl)(py)$ ($K = 5.0\ (0.7) \times 10^2\ M^{-1}$; I = 1.00 ($NaClO_4$); T = 25°C) is in reasonable agreement with that reported previously using kinetic ($K = 1.03\ (0.05) \times 10^3\ M^{-1}$) and spectrophotometric ($K = 1.55\ (0.01) \times 10^3\ M^{-1}$) techniques, given the differing experimental conditions (10 vol.% ethanol; I = 0.1 ($NaNO_3$); T = 30°C) [15]. Agreement between our neutralization quotient for $Co(dmgH)_2(Cl)(NH_3)$ ($K = 1.1\ (0.1) \times 10^2\ M^{-1}$; I = 1.00 ($NaClO_4$); T = 25°C) and that which may be calculated from kinetic data reported up to an $[OH^-]$ of 0.025M ($K = 1.9 \times 10^1\ M^{-1}$; I = 0.1; T = 25°C) [14] is not as good, probably because of the difficulty in extracting an accurate value of this parameter from kinetic data obtained over a limited $[OH^-]$ range.

Cobaloximes may act as acids in dissociating a proton bonded to an oxime oxygen atom. An acidic proton may also be lost from a coordinated water ligand in an aquocobaloxime. An examination of available data in the literature shows that for the aquocobaloximes the first acidic proton appears to come from the coordinated water:

$$Co(dmgH)_2(X)(OH_2)^n \rightarrow H^+ + Co(dmgH)_2(X)(OH)^{n-1} \qquad (6)$$

The $pK_a$ values for coordinated water in the cobaloximes depend on the *trans* ligand X and the charge $n$, but generally fall in the range from 5 to 7 [25–28]. When the aquo ligand is not present (or if initial loss of a proton from coordinated water has occurred) a proton is lost from the dimethylglyoximate ligand:

$$\mathrm{Co(dmgH)_2XY}^{n} \rightarrow \mathrm{H}^{+} + \mathrm{Co(dmgH)(dmg)XY}^{n-1} \qquad (7)$$

Again, the p$K_a$ value is dependent on the *trans* ligands X and Y and the charge $n$, but the normal range is 11–13, with the alkylcobaloximes extending this range to 14 [9,12,16,17].

The p$K_a$ values for $\mathrm{Co(dmgH)_2(Cl)(py)}$ (11.08) and $\mathrm{Co(dmgH)_2(Cl)(NH_3)}$ (11.79) reported here are similar, but differ in the direction expected as a result of the difference in donor ability between $NH_3$ and py, and difference in published p$K_a$ values for their corresponding aquo complexes [25,26]. It is clear from the p$K_a$ values that we are measuring the acidity of a dimethylglyoximate bridging proton, and not that of a coordinated water ligand resulting from aquation of the complex *. Furthermore, it is clear from the p$K_a$ value for $\mathrm{Co(dmgH)_2(Cl)(NH_3)}$ that we are not observing dissociation of an ammine proton, which would be expected to have a much higher p$K_a$ value.

### *(ii) Kinetics*

An examination of Fig. 2 indicates that the aquation of $\mathrm{Co(dmgH)_2(Cl)(NH_3)}$ could be described by assuming that the pseudo-first-order rate constant, $k_{\mathrm{obs}}$, can be represented by eqn. 8:

$$k_{\mathrm{obs}} = \mathrm{E} + \mathrm{F}[\mathrm{OH}^-] \qquad (8)$$

However, when one realizes that log $K$ for the neutralization of $\mathrm{Co(dmgH)_2(Cl)(NH_3)}$ is 2.02 (reaction 2), and that the protonated and deprotonated forms of the complex are in equilibrium over the p[$\mathrm{OH}^-$] range studied, the fit of the data to a simple expression such as eqn. 8 seems chemically unjustified. This consideration is equally valid for the aquation kinetics of $\mathrm{Co(dmgH)_2(Cl)(py)}$.

The concentrations of the protonated and deprotonated form of the complex are given by the following equations:

$$\mathrm{Co_T} = [\mathrm{Co(dmgH)_2(Cl)(L)}] + [\mathrm{Co(dmgH)(dmg)(Cl)(L)^-}] \qquad (9)$$

$$[\mathrm{Co(dmgH)_2(Cl)(L)}] = \frac{\mathrm{Co_T}}{1 + K[\mathrm{OH}^-]} \qquad (10)$$

$$[\mathrm{Co(dmgH)(dmg)(Cl)(L)^-}] = \frac{\mathrm{Co_T}K[\mathrm{OH}^-]}{1 + K[\mathrm{OH}^-]} \qquad (11)$$

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* The p$K_a$ for coordinated water in $\mathrm{Co(dmgH)_2(py)(OH_2)^+}$ (ref. 25) and $\mathrm{Co(dmgH)_2(NH_3)(OH_2)^+}$ (ref. 26) is 5.99 and 6.98, respectively.

If we now take eqns. 9–11 into account, eqn. 8 becomes

$$k_{obs} = \frac{G + HK[OH^-]}{1 + K[OH^-]} \tag{12}$$

where $K$ is the equilibrium quotient corresponding to the deprotonation reaction shown in eqn. 2. This expression is identical to that used by Birk and co-workers [12] to describe the kinetics of base aquation of $Co(dmgH)_2(NO_2)(Br)^-$, and that of Chan and Leung [14] to describe the kinetics of base aquation of $Co(dmgH)_2(Y)(NH_3)$ ($Y = Cl^-, Br^-$) at $[OH^-]$ up to 0.025M. Equation 12, however, does not adequately describe the kinetics of the base aquation of $Co(dmgH)_2(Cl)(NH_3)$ or $Co(dmgH)_2(Cl)(py)$ over the $p[OH^-]$ range described in this report. Equation 12 predicts a levelling off of the observed rate constant for base aquation in solutions of high alkalinity. As is evident from Fig. 2 the observed rate constant for aquation shows no sign of levelling off at low $p[OH^-]$ values. It should be noted that our kinetic results reported here ($k_{obs}$ values) are in good agreement with those previously reported [14] for $Co(dmgH)_2(Cl)(NH_3)$ in the region of overlapping $[OH^-]$, given the difference in conditions and experimental methods. Furthermore, although Chan and Leung [14] analyzed their results according to eqn. 12 they did not observe the expected plateau region and only observed slight curvature of the $k_{obs}$ vs. $[OH^-]$ plot at higher temperature (35°C).

The simplest expression describing the base aquation of both $Co(dmgH)_2(Cl)(py)$ and $Co(dmgH)_2(Cl)(NH_3)$ over the entire $p[OH^-]$ range studied is eqn. 5, described in the previous section. Therefore, any potential reaction schemes leading to the hydrolysis product must include paths which are zero, first, and second order in $[OH^-]$ dependence in order to be consistent with our analytical expression for $k_{obs}$. Also, eqns. 9–11 require that parameter D in eqn. 5 be represented by the equilibrium quotient, $K$. This requirement is met in the case of $Co(dmgH)_2(Cl)(py)$. When D is treated as a variable parameter the value calculated by a non-linear least-squares analysis of the kinetic data is $6.5\ (1.9) \times 10^2$, in reasonable agreement with the spectrophotometrically determined experimental value of $5.0\ (0.7) \times 10^2$ for $K$ (see Table 2).

A path zero order in $[OH^-]$ dependence represents the normal acid aquation of both complexes. The coefficient A in eqn. 5 may be interpreted as the aquation rate constant ($k_1$) for $Co(dmgH)_2(Cl)(py)$ ($k_1 = 2.5 \times 10^{-5}$ $s^{-1}$) and $Co(dmgH)_2(Cl)(NH_3)$ ($k_1 = 4.2 \times 10^{-5}\ s^{-1}$):

$$Co(dmgH)_2(Cl)(L) + H_2O \xrightarrow{k_1} Co(dmgH)_2(L)(OH_2)^+ + Cl^- \tag{13}$$

These results show that both complexes undergo acid aquation at about the same rate and are consistent with reported values of acid aquation rate constants for these and related cobaloximes [9,15,29]. Our observation of an acid aquation path for Co(dmgH)$_2$(Cl)(NH$_3$) is in contrast to the previous report of Chan and Leung [14].

The first order [OH$^-$] dependent term in eqn. 5 is consistent with, and fails to distinguish between, three alternative pathways. The first is a direct nucleophilic displacement of Cl$^-$ by OH$^-$:

$$\mathrm{Co(dmgH)_2(Cl)(NH_3) + OH^- \rightarrow Co(dmgH)_2(OH)(NH_3) + Cl^-} \qquad (14)$$

However, since we have established by spectrophotometric titration that Co(dmgH)$_2$(Cl)(L) (L = NH$_3$, py) undergoes deprotonation with OH$^-$, and in the absence of any definitive evidence for an associative mechanism in other cobalt(III) base aquation reactions, we do not propose reaction 14 as being the most probable explanation for the observed first-order [OH$^-$] dependence. A second, alternative path involving the hydrolysis of the conjugate base, Co(dmgH)(dmg)(Cl)(L)$^-$, appears to be a more reasonable explanation for the observed first-order [OH$^-$] dependence:

$$\mathrm{Co(dmgH)_2(Cl)(L) + OH^-} \overset{K}{\rightleftharpoons} \mathrm{Co(dmgH)(dmg)(Cl)(L)^- + H_2O} \qquad (15a)$$

$$\mathrm{Co(dmgH)(dmg)(Cl)(L)^- + H_2O} \xrightarrow{k_2} \mathrm{Co(dmgH)_2(OH)(L) + Cl^-} \qquad (15b)$$

If we assume that reaction 14 is not operating as a path parallel to 15a and 15b, then B in eqn. 5 can be expressed as the product $Kk_2$. Hence, calculated $k_2$ values for Co(dmgH)$_2$(Cl)(py) and Co(dmgH)$_2$(Cl)(NH$_3$) are $9.8 \times 10^{-5}$ s$^{-1}$ and $5.3 \times 10^{-6}$ s$^{-1}$, respectively. Reaction 15b could potentially be a two-step dissociative process involving an intermediate of reduced coordination number.

An additional possibility for the reacting species in the case of Co(dmgH)$_2$(Cl)(NH$_3$) is an ammido complex, Co(dmgH)$_2$(Cl)(NH$_2$)$^-$, which is a tautomer of the dimethylglyoxime ligand deprotonated complex, Co(dmgH)(dmg)(Cl)(NH$_3$)$^-$. The postulation of an ammido complex as the reactive species represents a classical S$_N$1CB mechanism. It is not possible to determine kinetically whether or not it is the Co(dmgH)(dmg)(Cl)(NH$_3$)$^-$ or Co(dmgH)$_2$(Cl)(NH$_2$)$^-$ complex which reacts via the $k_2$ path. However, since a corresponding tautomeric form is not available for Co(dmgH)$_2$ (Cl)(py), and since the $k_2$ path for this species is somewhat more efficient for aquation than it is for Co(dmgH)$_2$(Cl)(NH$_3$) (see above), we conclude that the S$_N$1CB mechanism (the existence of the ammido complex Co(dmgH)$_2$(Cl)(NH$_2$)$^-$ as a reactive species) is an unlikely possibility for Co(dmgH)$_2$(Cl)(NH$_3$). An S$_N$1CB mechanism involving an ammido intermediate is usually invoked to explain unusually high relative reactivity.

The form of eqn. 5 requires that we consider an additional path which exhibits second-order $[OH^-]$ dependence. These kinetics are consistent with a direct displacement of $Cl^-$ by $OH^-$ from the deprotonated form of the complex:

$$Co(dmgH)(dmg)(Cl)(L)^- + OH^- \xrightarrow{k_3} Co(dmgH)(dmg)(OH)(L)^- + Cl^- \quad (16)$$

In this case parameter C in eqn. 5 can be represented by the product $Kk_3$. The $k_3$ values computed in this way for $Co(dmgH)_2(Cl)(NH_3)$ and $Co(dmgH)_2(Cl)(py)$ are $5.2 \times 10^{-3}$ $M^{-1}$ $s^{-1}$ and $4.6 \times 10^{-3}$ $M^{-1}$ $s^{-1}$, respectively. Just as was indicated in our discussion of the $k_2$ path, the ammonia complex may react according to eqn. 16 via an ammido species, but the pyridine complex cannot. Since the calculated $k_3$ values are the same for both complexes there is no compelling argument to support the postulation of aquation via an ammido complex.

There is an additional reaction path which would result in second-order $[OH^-]$ dependence on the rate. It is possible that a second bridging proton may be lost from the dimethylglyoximato ligands to yield complexes with the structure $Co(dmg)_2(Cl)(L)^{2-}$. These species could then react in a rate-determing step zero order in $[OH^-]$ to give products:

$$Co(dmgH)_2(Cl)(L) + OH^- \overset{K}{\rightleftharpoons} Co(dmgH)(dmg)(Cl)(L)^- + H_2O \quad (15a)$$

$$Co(dmgH)(dmg)(Cl)(L)^- + OH \overset{K'}{\rightleftharpoons} Co(dmg)_2(Cl)(L)^{2-} + H_2O \quad (17)$$

$$Co(dmg)_2(Cl)(L)^{2-} + H_2O \xrightarrow{k_4} Co(dmgH)(dmg)(OH)(L)^- + Cl^- \quad (18)$$

However, if this doubly deprotonated species were formed, the pseudo-first-order rate constant, $k_{obs}$, would then be of the form:

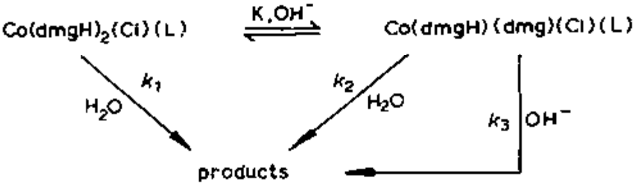
$$k_{obs} = \frac{A' + B'[OH^-] + C'[OH^-]^2}{1 + D'[OH^-] + E'[OH^-]^2} \quad (19)$$

Implicit in this equation is the expression for the concentration of $Co(dmg)_2(Cl)(L)^{2-}$:

$$\left[Co(dmg)_2(Cl)(L)^{2-}\right] = K'[Co(dmgH)(dmg)(Cl)(L)^-][OH^-] \quad (20)$$

where $K'$ is the neutralization quotient for the removal of the second dimethylglyoximato proton from the parent complex. Equation 19 gives a good theoretical fit to the available data for the hydrolysis of $Co(dmgH)_2$ $(Cl)(py)$ and $Co(dmgH)_2(Cl)(NH_3)$ over the $p[OH^-]$ range studied. This is not suprising since eqn. 19 has an additional parameter over eqn. 5. It is attractive to consider eqns. 17 and 18 as a possible reaction path, as it would not make a significant contribution to the production of aquated products until very low values of p[OH$^-$] were attained. The presence of a doubly deprotonated species could be the reason for py release from Co(dmgH)$_2$(Cl)(py) at very low p[OH$^-$]. However, there is no compelling reason to consider a doubly deprotonated form in the case of Co(dmgH)$_2$(Cl)(NH$_3$). Furthermore, we have no direct experimental evidence to verify the existence of the doubly deprotonated species Co(dmg)$_2$(Cl)(L)$^{2-}$. Judging from the experimentally determined values for the first deprotonation step ($K$), one would not anticipate the presence of a doubly deprotonated form to be kinetically detectable except at p[OH$^-$] values < 0. This is beyond the [OH$^-$] concentration range studied here, and studies in that region would be of questionable value due to changes in ionic strength necessary and the uncertain effects on the activities of the ions involved. Consequently, the less complex eqn. (5), which adequately describes the kinetics reported here, is used in the interpretation of our results.

Scheme 1 represents a summary of the three most probable reaction paths to products:



Scheme 1.

The corresponding microscopic rate constants are tabulated in Table 3. Scheme 1 represents an expansion of the previously reported mechanism for Co(dmgH)$_2$(Cl)(NH$_3$) [14] to include a zero- and second-order [OH$^-$]-dependent path ($k_1$ and $k_3$). The data reported here were collected over a much wider [OH$^-$] range and as such represent a more complete mechanistic picture. Moreover, the three parallel path mechanism for Co(dmgH)$_2$(Cl)(NH$_3$) is analogous to that observed for the similar complex, Co(dmgH)$_2$(Cl)(py). It is reasonable that similar reaction pathways be

TABLE 3

Summary of microscopic rate and equilibrium constants for Co(dmgH)$_2$(Cl)(L) (L = NH$_3$, py) aquation according to Scheme 1

| Constant | Co(dmgH)$_2$(Cl)(NH$_3$) | Co(dmgH)$_2$(Cl)(py) |
|---|---|---|
| $k_1$ | $4.2 \times 10^{-5}$ s$^{-1}$ | $2.5 \times 10^{-5}$ s$^{-1}$ |
| $k_2$ | $5.3 \times 10^{-6}$ s$^{-1}$ | $9.8 \times 10^{-5}$ s$^{-1}$ |
| $k_3$ | $5.2 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ | $4.6 \times 10^{-3}$ M$^{-1}$ s$^{-1}$ |
| $K$ | $1.1 \times 10^{2}$ M$^{-1}$ | $5.0 \times 10^{2}$ M$^{-1}$ |

available for these similar compounds. Our results for $Co(dmgH)_2(Cl)(py)$ confirm those of Vijayaraghavan and Santappa [15] in aqueous solution over a wider $[OH^-]$ range.

This study allows for a direct comparison of the relative influence of coordinated py and $NH_3$ in cobaloxime aquation reactions. A significant effect is seen only in the $k_2$ path, where the pyridine complex is 20 times more reactive than the ammine *. The reasons for this difference in reactivity are not clear, although a similar difference has been reported for the base aquation of $Co(en)_2(Cl)(NH_3)^{2+}$ and $Co(en)_2(Cl)(py)^{2+}$ [6,30,31]. The second-order base aquation rate constants for the ethylenediamine complexes represent the product of the equilibrium constant for deprotonation to form the conjugate base and the rate constant for the subsequent aquation step. Consequently, it is not possible to determine which of these processes is responsible for the increase in reactivity. Our results suggest that both processes may be a factor, since both $K$ and $k_2$ are larger for $Co(dmgH)_2(Cl)(py)$.

Aquation of the deprotonated form of $Co(dmgH)_2(Cl)(L)$ ($L = py, NH_3$) shows a slight decrease in reactivity over the neutral form when $L = NH_3$ ($k_2/k_1 \sim 0.1$) and a slight increase when $L = py$ ($k_2/k_1 \sim 4$). This is fairly consistent with other cobaloxime systems: e.g., $Co(dmgH)_2(NO_2)(Br)^-$ ($k_b/k_a = 30$ for $Br^-$ release [12]); and $Co(dmgH)_2(R)L$ ($k_b/k_a = 3$–$20$ for substituted pyridine or amine release with R = alkyl or substituted alkyl [16,17]). The relative reactivities for the two paths for the similar (DO)(DOH)pn ** chelate system is slightly higher; $Co[(DO)(DOH)pn](R)(NH_3)^+$, $k_b/k_a = 70$–$150$ for ammine release with R = alkyl or phenyl [18]. This behavior is in marked contrast to the cobalt(III) amine and cyclic amine systems where aquation of the deprotonated complex is several orders of magnitude more reactive. This serves to confirm further the unique labilizing influence when deprotonation occurs at a N atom bound to cobalt(III).

## REFERENCES

1 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions (2nd edn.). Wiley, New York, 1967, p. 177.

2 M.L. Tobe, Acc. Chem. Res., (1970) 377.

3 C.K. Poon, Inorg. Chim. Acta Rev., 4 (1970) 123.

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* This is in contrast to the case where the rate expression of Chan and Leung is used to calculate a value for $k_2$. (ref. 14) Note that in the region of $[OH^-]$ overlap, the $k_{obs}$ values reported here are in good agreement with those reported by these authors.

** (DO)(DOH)pn = diacetylmonoximediacetylmonoximatopropane-1,3-diyldiimino; a tetradentate oxime-type ligand.

4 A.M. Sargeson, Pure Appl. Chem., 33 (1973) 527.

5 R.G. Wilkins, The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes. Allyn and Bacon, Boston, 1974, p. 207.

6 D.A. House, Coord. Chem. Rev., 23 (1977) 223.

7 C.H. Langford and H.B. Gray, Ligand Substitution Processes. Benjamin, New York, 1965.

8 C.K. Poon, Coord. Chem. Rev., 10 (1973) 1.

9 A.V. Ablov and N.M. Samus, Coord. Chem. Rev., 17 (1975) 253.

10 J.F. Endicott and B. Durham, in G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds. Plenum Press, New York, 1979, p. 393.

11 The *trans* configuration shown in reaction 2 has been established for the cobaloximes. R.D. Gillard and G. Wilkinson, J. Chem. Soc., (1963) 6041.

12 J.P. Birk, P.B. Chock and J. Halpern, J. Am. Chem. Soc., 90 (1968) 6959.

13 J. Zsako, Z. Finta and C.S. Varhelyi, J. Inorg. Nucl. Chem., 34 (1972) 2887.

14 S.C. Chan and P.Y. Leung, Aust. J. Chem., 22 (1969) 2569.

15 V.R. Vijayaraghavan and M. Santappa, J. Inorg. Nucl. Chem., 36 (1974) 163.

16 K.L. Brown, D. Chernoff, D.J. Keljo and R.G. Kallen, J. Am. Chem. Soc., 94 (1972) 6697.

17 K.L. Brown, D. Lyles, M. Pencovici and R.G. Kallen, J. Am. Chem. Soc., 97 (1975) 7338.

18 G. Tauzher, R. Dreos, G. Costa and M. Green, Inorg. Chem., 19 (1980) 3790.

19 H.G. Tsiang and W.K. Wilmarth, Inorg. Chem., 7 (1968) 2535.

20 L.A. Tschugaeff, Ber., 39 (1906) 2692.

21 A.V. Ablov and M.P. Filippov, Russ. J. Inorg. Chem., 4 (1954) 1004.

22 A.V. Ablov, B.A. Bovykin and N.M. Samus, Dokl. Akad. Nauk., 16 (1965) 3635.

23 R. Nasanen and P. Meriloinene, Suom. Kemistil., B33 (1960) 149; Chem. Abstr., 55 (1961) 4130C.

24 A.I. Vogel, A Textbook of Quantitative Inorganic Analysis (3rd edn.). Wiley, New York, 1961, p. 783.

25 B.A. Bovykin and N.V. Ivanov, Russ. J. Inorg. Chem., 16 (1971) 370.

26 A.V. Ablov, B.A. Bovykin and N.M. Samus, Russ. J. Inorg. Chem., 11 (1966) 978.

27 B.A. Bovykin, Russ. J. Inorg. Chem., 17 (1972) 89.

28 D.M. Palade, T.N. Volokh, N.A. Breslavskaya and T.N. Golyshina, Russ. J. Inorg. Chem., 15 (1970) 1401.

29 N.M. Samus, A.V. Ablov and G.A. Konunova, Russ. J. Inorg. Chem., 18 (1973) 1409.

30 R.W. Hay and P.L. Cropp, J. Chem. Soc., A (1969) 42.

31 R.G. Pearson, R.E. Meeker and F. Basolo, J. Am. Chem. Soc., 78 (1956) 709; F. Basolo, J.G. Bergmann, R.E. Meeker and R.G. Pearson, Ibid 78 (1956) 2676.