# Kinetics and Mechanism of the Oxidation of Ni$^{II}$cyclam by Aquocobalt(III) in Aqueous Perchloric Acid

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The facile oxidation of the Ni$^{II}$cyclam cation $[Ni^{II}L]^{2+}$ by cobalt(III) has been investigated kinetically in perchlorate media over the range $[H^+] = 0.4$–$1.50$ M at various temperatures (10.6–25.0 °C). The reaction stoichiometry indicates 1 mol of oxidant reacting/mol of Ni(II). The nickel(III) complex produced has been characterized with use of UV–vis and ESR techniques. Stopped-flow studies indicate the sole reaction pathway to be $[Ni^{II}L]^{2+} + CoOH^{2+} \xrightarrow{k_3} [Ni^{III}L]^{3+} + Co^{2+}(aq)$, with $k_3 = (4.7 \pm 0.1) \times 10^5$ M$^{-1}$ s$^{-1}$, $\Delta H^* = 6.5 \pm 0.9$ kcal mol$^{-1}$, and $\Delta S^* = -10 \pm 7$ cal deg$^{-1}$ mol$^{-1}$ (with $K_h = 2 \times 10^{-3}$ M for the hydrolysis constant of cobalt(III)). No rate effects are observed in the presence of sulfate although ESR data are consistent with formation of a nickel(III) sulfate complex. An outer-sphere electron-transfer process is proposed and comparisons are made with other reactions involving the hydroxocobalt(III) ion as oxidant.

Although complexes of nickel(II) with macrocylic ligands have been well established,[1,2] it is only recently that species involving other oxidation states have been characterized. Nickel(III) complexes with 14-membered tetraaza macrocycles have been prepared by electrochemical[3,4] means or by chemical oxidation[5,6] of the corresponding nickel(II) species. It is noteworthy that, whereas many of these species are stable in nonaqueous media, they exhibit ready reduction in basic solvents. An exception appears to be with deprotonated ligands which are stable[7] in aqueous solutions at pH ~9.

Studies on the formation and decay of short-lived nickel(III) complexes with nitrogen-donor ligands have been made with use of pulse radiolysis,[8–10] but in general the transient nature of these nickel(III) complexes has prevented study of the kinetics and mechanism of the oxidation of substrates by these species. The outer-sphere reactions of the relatively stable $[Ni(bpy)_3^{3+}]$ ion with Br$^-$ and H$_2$O$_2$ have been described.[11] Recently, we have been presented data on the formation and redox reactions of nickel(III) complexes with saturated macrocycles.[12] In the present study we describe the kinetics and propose a mechanism of formation of a nickel(III) macrocycle which shows considerable stability in acidic media. The facile oxidation of Ni$^{II}$cyclam (cyclam = 1,4,5,11-tetraazacyclotetradecane), (Ni$^{II}$L)$^{2+}$, by aquocobalt(III) ions is conveniently studied with use of stopped-flow techniques. In the course of completion of this work, a preliminary report appeared[3] in which the stable Ni(III)cyclam ion has been prepared by electrochemical oxidation at a platinum-screen working electrodes. Some of the present results are complementary to and agree with the data presented by Meyerstein. The study with cobalt(III) was undertaken since there is current interest in the rates and activation parameters for the various aquocobalt(III) species.[15]

## Experimental Section

[NiL(ClO$_4$)$_2$] (L = cyclam) was prepared from Ni(ClO$_4$)$_2$·6H$_2$O

**Table I.** ESR Parameters for Ni$^{III}$cyclam Complex Cations, $[NiLX_2]^{3+}$, in Frozen 1.0 M HClO$_4$ at $T = 77$ K

| X | $g_\parallel$ | $g_\perp$ | $\langle g \rangle^f$ |
|---|---|---|---|
| MeCN$^a$ | 2.0250 | 2.2148 | 2.1534 |
| OH$_2$$^b$ | 2.0332 | 2.2193 | 2.1590 |
| OH$_2$$^c$ | 2.0386 | 2.2138 | 2.1570 |
| OH$_2$$^d$ | 2.0240 | 2.210 | 2.1498 |
| H$_2$O/SO$_4$$^{2-}$ $^e$ | 2.026 | 2.232 | 2.163 |

$^a$ The solvent molecules are believed to be rapidly replaced on dissolution of a solid sample of [NiL(MeCN)$_2$](ClO$_4$) in acid media. $^b$ Electrolytic oxidation of Ni$^{II}$cyclam. $^c$ Reaction product of Co(III)(aq) with [Ni$^{II}$L]$^{2+}$. $^d$ Reaction of Co(III)(aq) with [Ni$^{II}$L]$^{2+}$ in the presence of 1.0 M Li$_2$SO$_4$ (pH 0). $^e$ Electrolytic oxidation of [Ni$^{II}$L]$^{2+}$ in 0.5 M Na$_2$SO$_4$[3] (pH 1.6). $^f \langle g \rangle = (g_\parallel^2/3 + 2g_\perp^2/3)^{1/2}$.

and cyclam (Strem Chemicals) and characterized by its UV–vis spectrum in methanol ($\epsilon_{max} = 67.5$ M$^{-1}$ cm$^{-1}$, $\lambda = 454$ nm). The nickel(III) complexes $[NiLX_2]^{n+}(ClO_4)_n$ (X = MeCN, NO$_3^-$, OH$_2$) were prepared by (i) electrolysis of [NiL(ClO$_4$)$_2$] in acetonitrile[4] or (ii) treatment of [NiL(ClO$_4$)$_2$] with concentrated HNO$_3$.[6] The [NiL'(ClO$_4$)$_2$] species (L' = Me$_6$[14]aneN$_4$) were prepared by literature methods.[16]

Solutions of aquocobalt(III) were prepared by electrolysis of Co$^{II}$ in perchloric acid (~4 M) under conditions of constant potential at 5 °C in the dark with a constant stream of O$_2$-free nitrogen passing through the solution. Stock solutions were analyzed spectrophotometrically for Co(III) ($\epsilon_{605} = 35.3$ M$^{-1}$ cm)[15] and by standard methods for [H$^+$] concentrations. Care was taken to ensure concentrations of $<5 \times 10^{-3}$ M in order to avoid any dimerization of the oxidant. Lithium perchlorate, prepared by neutralization of HClO$_4$ by Li$_2$CO$_3$ was recrystallized three times before use.

Kinetic runs were made with use of a stopped-flow apparatus described previously.[17] Thermostating was maintained to within ±0.05 °C. In general, runs were carried out in the presence of excess reductant especially at [H$^+$] < 0.5 M owing to the lower stability of the cobalt(III) species under these conditions. No effect of cobalt(II) was observed on the reaction rate. Pseudo-first-order kinetic plots were linear to at least 3 half-lives. Absorbance data were collected with use of a PCM-12 minicomputer, and rate constants were computed from ln (OD$_\infty$ – OD$_t$) vs. $t$ plots with use of a standard least-mean-squares program on an IBM 370 computer.

ESR spectra of magnetically dilute aqueous glasses containing the Ni(III) complexes ($<10^{-3}$ M) were measured at 77 K with use of a Varian E6S spectrometer. Magnetic field values are relative to DPPH as standard.

## Results

Reaction in solution of the nickel(II) complex with oxidant produced an immediate green coloration consistent with the formation of a nickel(III) ion. In solutions containing >1 M

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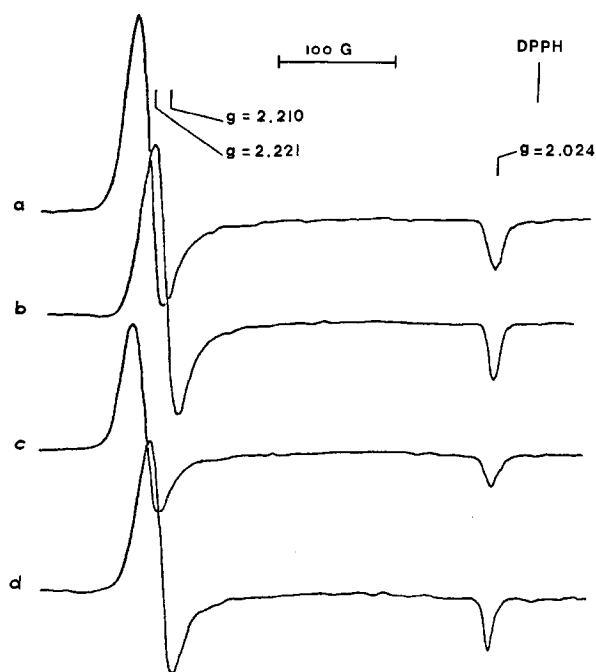
**Figure 1.** ESR spectra of various nickel(III) species: (a) product of reaction of $[Ni^{II}L]^{2+}$ with Co(III) ($HClO_4 = 1.0$ M), (b) same as part a with 1.0 M $Li_2SO_4$ present, (c) solution of $[Ni^{III}L]^{3+}$ in 1.0 M $HClO_4$, and (d) same as part c with 1.0 M $Li_2SO_4$ present.

$HClO_4$, and in the absence of light, the species were stable for >10 h. Confirmation of the oxidation of the metal center was given by comparison of the ESR spectra (77 K) of the frozen sample of reacted solution with both solid $[Ni^{III}cy$-$clam](ClO_4)_3$ prepared from acetonitrile and with a frozen aqueous acidic solution prepared from this salt (see Figure 1). The *g* values (Table I) are consistent with a tetragonally distorted low-spin nickel(III) complex with the unpaired electron located primarily in the $d_{z^2}$ orbital.[12]

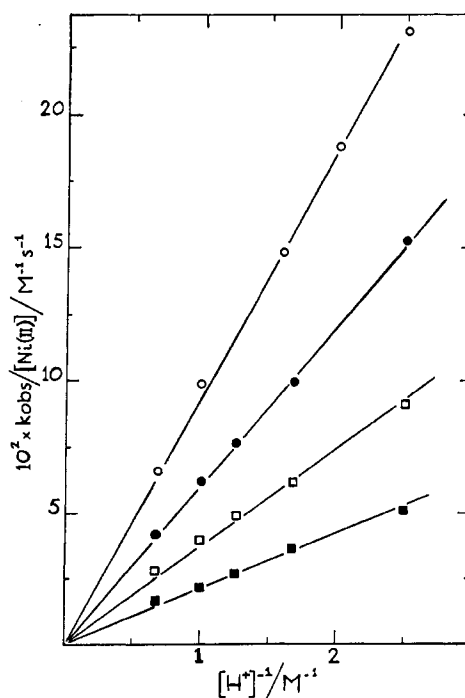The overall reaction (eq 1) was confirmed by spectropho-

$$Co(III)(aq) + [Ni^{II}L]^{2+} \rightarrow Co(II)(aq) + [Ni^{III}L]^{3+} \quad (1)$$
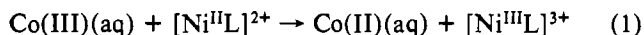
tometric titration, $1.1_0 \pm 0.05$ mol of Co(III) reacting/mol of reductant. After correction for absorbance of the reduced form of the oxidant, the spectrum of the resultant solution was identical ($\lambda_{max} = 308$ nm, $\epsilon = 11\,000 \pm 100$ $M^{-1}$ $cm^{-1}$) with that of a solution of Ni(cyclam)$^{3+}$(aq) prepared from dissolution of a solid sample. Even in the presence of a large excess of oxidant there is no evidence for oxidation of the ligand.

**Kinetic Studies**

The oxidation reaction was investigated over the range $\lambda$ = 360–390 nm at an ionic strength of 1.50 M ($HClO_4$/Li-$ClO_4$) over the range $T = 10.7$–25 °C. Rate data are presented in Table II. Experiments with both oxidant and reductant in excess confirmed a first-order dependence on both reagents. For hydrogen ion dependence studies, however, the nickel(II) concentration was maintained at 10–20-fold excess.

$Ni^{II}cyclam$ is known to be a square-planar ion in aqueous solution under the ionic strength conditions prevailing.[18] Also it has been shown recently[19] that, whereas in acidic media square planarity persists, a change in coordination to octahedral geometry is induced in basic conditions. We have attempted to measure the extent of any hydrolysis of axial water molecules (to produce $[NiL(OH)(OH_2)]^+$) by moni-

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**Figure 2.** Plots of $k_{obsd}/[Ni(II)]$ against $[H^+]^{-1}$ at various temperatures: ■, $T = 10.6$; □, $T = 16.0$; ●, $T = 21.0$; O, $T = 25.0$.

**Table II.** Rate Data and Thermodynamic Parameters for the Reaction of Co(III)(aq) with $Ni^{II}cyclam$

| First-Order Dependence on $[Co(III)]^a$ | | | | | | |
|---|---|---|---|---|---|---|
| $10^4[Co(III)]/M$ | 2.03 | 4.06 | 6.77 | 13.54 | 27.08 | |
| $k_{obsd}/s^{-1}$ | 0.13 | 0.25 | 0.43 | 0.85 | 1.74 | |
| $k_3K_h/s^{-1}$ | 987 | 933 | 969 | 945 | 966 | mean $959 \pm 17$ |

| First-Order Dependence on [Ni(II)] | | |
|---|---|---|
| $10^4[Ni(II)]/M$ | 6.367 | 4.80 |
| $k_{obsd}/s^{-1}$ | $1.43 \pm 0.03^{b,c}$ | $0.903^{b,d}$ |
| $k_3K_h/s^{-1}$ | 902 | 935 |

Dependence of Rate Constants on $[H^+]^e$

| $[Ni(II)] = 5.65 \times 10^{-4}$ M, $T = 10.6$ °C | | | | | |
|---|---|---|---|---|---|
| $[H^+]/M$ | 0.40 | 0.60 | 0.8 | 1.0 | 1.5 |
| $k_{obsd}/s^{-1}$ | 0.28 | 0.20 | 0.15 | 0.12 | 0.092 |

mean $k_3K_h/s^{-1} = 220 \pm 15$ $s^{-1}$

| $[Ni(II)] = 5.079 \times 10^{-4}$ M, $T = 16.7$ °C | | | | | |
|---|---|---|---|---|---|
| $[H^+]/M$ | 0.40 | 0.60 | 0.80 | 1.00 | 1.50 |
| $k_{obsd}/s^{-1}$ | $0.46 \pm$ | $0.313 \pm$ | $0.247 \pm$ | $0.200 \pm$ | $0.139 \pm$ |
| | 0.005 | 0.005 | 0.003 | 0.001 | 0.005 |

mean $k_3K_h = 385 \pm 17$ $s^{-1}$

| $[Ni(II)] = 5.08 \times 10^{-4}$ M, $T = 21.2$ °C | | | | | |
|---|---|---|---|---|---|
| $[H^+]/M$ | 0.4 | 0.60 | 0.80 | 1.00 | 1.50 |
| $k_{obsd}/s^{-1}$ | 0.77 | 0.50 | 0.38 | 0.31 | 0.21 |

mean $k_3K_h = 612 \pm 7$ $s^{-1}$

| $[Ni(II)] = 5.05 \times 10^{-4}$ M, $T = 25.0$ °C | | |
|---|---|---|
| $[H^+]/M$ | 0.628 | 1.00 | 1.50 |
| $k_{obsd}/s^{-1}$ | $0.75_1$ | $0.50_1$ | 0.335 |

mean $k_3K_h = 970 \pm 30$ $s^{-1}$

Composite Rate Constant Yields Parameters
$\Delta H^{\ddagger} = 16.5 \pm 0.9$ kcal mol$^{-1}$ (69.2 $\pm$ 3.6 kJ mol$^{-1}$)
$\Delta S^{\ddagger} = 12 \pm 7$ cal deg$^{-1}$ mol$^{-1}$ (49 $\pm$ 30 J K$^{-1}$ mol$^{-1}$)

$^a$ $T = 25.0$ °C, $[H^+] = I = 1.5$ M ($HClO_4$), $[Ni(II)] = 1.61 \times 10^{-5}$ M, $\lambda = 388$ nm. $^b$ $T = 25.0$ °C, $I = 1.5$ M ($LiClO_4/HClO_4$), $[Co(III)]_{aq} = (4.2$–$5.4) \times 10^{-5}$ M. $^c$ $[H^+] = 0.40$ M. $^d$ $[H^+] = 0.50$ M. $^e$ $I = 1.50$ M ($HClO_4/LiClO_4$), $[Co(III)] = (4.2$–$5.4) \times 10^{-5}$ M.

toring changes in the spectrum of $Ni^{II}cyclam$ in the regions 300–500 nm over the range $1.0 < pH < 12.2$. There is no

**Table III.** Effect of $SO_4^{2-}$ on Rate Constants at Various Hydrogen Ion Concentrations

$[H^+] = 0.40$ M, $[Co(III)] = 5.4 \times 10^{-5}$ M, $[Ni(II)] = 6.37 \times 10^{-4}$ M, $I = 1.50$ M $(LiClO_4/HClO_4)$

| $10^4[SO_4^{2-}]$/M | 0 | 1.16 | 2.31 | 5.78 | 11.6 | |
|---|---|---|---|---|---|---|
| $k_{obsd}/s^{-1}$ | 1.43 | 1.48 | 1.43 | 1.49 | 1.47 | mean 1.46 ± 0.02 |

$k_3K_h = 926 \pm 24$ s$^{-1}$

$[H^+] = 0.50$ M, $[Co(III)] = 4.2 \times 10^{-5}$ M, $[Ni(II)] = 4.80 \times 10^{-4}$ M, $I = 1.50$ M

| $10^4[SO_4^{2-}]$/M | 0 | 0.21 | 0.42 | 1.04 | 2.10 | |
|---|---|---|---|---|---|---|
| $k_{obsd}/s^{-1}$ | 0.90 | 0.89 ± 0.01 | 0.89 | 0.92 | 0.89 | mean 0.90 ± 0.01 |

$k_3K_h = 935 \pm 15$ s$^{-1}$

change observed within the range pH 6–10, and above pH ~10.5 a peak at 345 nm is observed with a corresponding decrease in the 450-nm absorbance. This could be due to axial ligand deprotonation but is more probably the result of a deprotonation of the N–H of the ligand. (For the free macrocycle tet a, the first p$K$ for the base is 10.5.)[20] There is therefore little evidence for any reaction of the type NiL(OH)$^+$ + Co$^{3+}$(aq), and we attribute the origin of the observed hydrogen ion dependence to the kinetically indistinguishable reaction of hydroxycobalt(III) from the hydrolysis of the aquocobalt(III) ion (see eq 2 and 3). The rate data may be

$$Co^{3+}(aq) \underset{K_h}{\rightleftharpoons} CoOH^{2+} + H^+ \qquad (2)$$

$$CoOH^{2+} + Ni^{II}L^{2+} \xrightarrow{k_3} Co(II) + Ni^{III}L^{3+} \qquad (3)$$
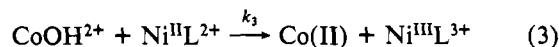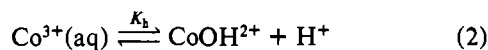
interpreted in terms of eq 3 where the rate law may be expressed in the form

$$d[Ni(III)]/dt = \frac{k_3K_h}{[H^+] + K_h}[Co(III)_{tot}][Ni^{II}L] \qquad (4)$$

Under the prevailing reaction conditions ($[H^+] = 0.4$–1.50 M), $[H^+] \gg K_h$ (see Table II) so that plots of the second-order rate constant $(k_{obsd}/[Ni(II)])$ against $[H^+]^{-1}$ are linear with slope $k_3K_h$ and zero intercept (Figure 2). From these data, thermodynamic parameters were derived for the composite constant $k_3K_h$ (Table II).

**Discussion**

The data are consistent with the formation of a nickel(III) cation, and as has been observed recently,[3,5] the stability of this oxidation state is enhanced if the nitrogen macrocycle is fully saturated. The oxidizing power of the product complex is also lowered when cyclam is the macrocyclic ligand involved as evidenced by our recent findings[12] that the interaction of this ion with Cl$^-$ or Br$^-$ leads to complex formation, with only I$^-$ of the halide ions being oxidized. Studies by Laurence[9] and Meyerstein[10] using the diene ring systems have confirmed that the redox potentials of these complexes are sufficient to oxidize all three halide ions.

Some insight into the reaction may be gained from the observation that in the case of the corresponding reaction with the tetra N-methylated Me$_6$[14]aneN$_4$ where there are no N–H protons, although an oxidation took place as evidenced by consumption of cobalt(III), no stable nickel(III) species was formed. In this case, a ligand oxidation may be involved. In a previous study[5] of the instability of the nickel(III) complexes at pH > 4, it was suggested that the mode of decomposition may be via a radical cation resulting from the base-catalyzed abstraction of a proton from the Ni(III)–N–H system leading to Ni(II)–N· (+BH$^+$). This finding has recently been challenged, however,[8,10] and it is considered that the first product of any redox decomposition is a nickel(III) complex of low symmetry. The nickel(II) radical has been found as an intermediate in the photochemical decay of [Ni$^{II}$(Me$_6$[14]aneN$_4$)].[21]

**Table IV.** Kinetic and Thermodynamic Data Involving Reactions of CoOH$^{2+}$(aq) in Perchloric Acid/Perchlorate Media ($T = 25$ °C, $I = 1.5$–3.0 M)

| reductant | $k_6K_h/s^{-1}$ | $\Delta H_m^{\ddagger a}/$ kcal mol$^{-1}$ | $\Delta S_m^{\ddagger a}/$cal deg$^{-1}$ mol$^{-1}$ | ref |
|---|---|---|---|---|
| NH$_3$OH$^+$ | 3.3 | 22.5 | 20 | b |
| NH$_3$NH$_2^+$ | 1.1 | 23.8 | 22 | b |
| H$_2$O$_2$ | 23 | 23.5 | 27 | c |
| HN$_3$ | 35 | 23.1 | 27 | d |
| H$_2$O$_x$ | 11 | 24.0 | 28 | e |
| Br$^-$ | 30 | 26.1 | 37 | c |
| HO$_x^-$ | 82 | 25.9 | 39 | e |
| SCN$^-$ | 80 | 25.6 | 37 | c |
| I$^-$ | 2860 | 21.5 | 30 | c |
| benzene-1,4-diol | 1280 | 18.6 | 17 | c |
| 2-methylbenzene-1,4-diol | 1120 | 19 | 19 | f |
| 2,3,5-trimethyl-benzene-1,4-diol | 2600 | 12 | −3 | g |
| ascorbic acid | 1480 | 12.1 | −2 | h |
| Ni$^{II}$cyclam | 935 | 16.5 | 12 | i |
| Fe$^{2+}$(aq) | 275 | 13.8 | 1.1 | j |
| Mn$^{2+}$(aq) | 46.5 | 12.3 | −7.7 | j |
| Co$^{2+}$(aq) | 1 | 21.8 | 16 | j |

$^a$ See Table III; data are uncorrected for enthalpy and entropy of dissociation ($K_h$). $^b$ Jijie, K.; Santappa, M. *Proc. Ind. Acad. Sci., Sect. A* **1969**, *69*, 117. $^c$ Davies, G.; Watkins, K. O. *J. Phys. Chem.* **1970**, *74*, 3388. $^d$ Thompson, R. C.; Sullivan, J. C. *Inorg. Chem.* **1970**, *9*, 1590. $^e$ Davies, G; Watkins, K. O. *Inorg. Chem.* **1970**, *9*, 2737. $^f$ Pelizzetti, E.; Mentasti, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2222. $^g$ Pelizzetti, E.; Mentasti, E.; Pramauro, E. *J. Chem. Soc., Dalton Trans.* **1976**, 23. $^h$ Reference 20. $^i$ Present work. $^j$ Reference 21.

It is of interest that the sole reacting ion is the hydroxo complex CoOH$^{2+}$. One possible mechanism for reaction is via a hydrogen atom abstraction. If such were the case a radical intermediate of the type described above would be formed with one of the N–H centers involved. We find no evidence in our kinetic traces for any transient absorbances in the region ($\lambda \approx 540$ nm) where such species absorb. We cannot, however, completely exclude this as a possibility since the intramolecular redox between the nickel(II) radical and a [Ni(III)–N$^-$] complex could be very fast. In any transfer involving a hydrogen atom, the cobalt species formed would be the reduced aquo ion.

We have also investigated the role of sulfate in these systems. A complex of moderate stability ($K \approx 10^3$ M) is known to be formed[3] between [Ni$^{III}$cyclam]$^{3+}$ and SO$_4^{2-}$. If this anion acted as an inner-sphere bridge between the two positive reacting centers, some acceleration of the rate might be expected. In Table III data are presented at two hydrogen ion concentrations where it is seen that even in 20-fold excess of SO$_4^{2-}$ no variation in rate is observed, the values again being consistent with CoOH$^{2+}$ reacting. Data for a variety of oxidation reactions of CoOH$^{2+}$ are listed in Table IV, where several reaction types have been identified. In systems where $k_3K_h$ < $10^2$ s$^{-1}$, a predominantly inner-sphere character has been proposed[15] whereas, for $k_3K_h$ > $10^3$ s$^{-1}$, the reactions are

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(21) Ferraudi, G. *Inorg. Chem.* **1979**, *18*, 3230.

considered outer sphere in nature. Davies[22] has analyzed the variations in rate constants for the latter reactions in terms of outer-sphere precursor formation and the attainment of a species in which the distribution of OH⁻ in the inner sphere of cobalt(III) is optimal for hydroxide-mediated electron transfer within the precursor complex. A specific interaction of this type is consistent with the present system.

The slower reaction ($k_3K_h$ = 935 s⁻¹) for the oxidation of Ni(cyclam) compared with other anionic or neutral substrates (e.g., I⁻, $k_3K_h$ = 2.9 × 10³ s⁻¹) may reflect either the higher redox potential of the Ni(II)L/Ni(III)L couple (0.95 V) or the fact that electrostatic repulsion terms will be greater in the case of cationic reductants. The former argument does not explain the relatively low reaction rates for the Co²⁺, Mn²⁺,

and Fe²⁺ reactions.[23] Differences in the rates will be however expected if a specifically oriented precursor is formed prior to the electron transfer. A series of preequilibria[22] describing such a process have been suggested as contributing to the compensating variation in $\Delta H^*$ and $\Delta S^*$ observed in these reactions. The fact that a metal complex ion is involved rather than the smaller aquo ions will have a bearing on these effects.

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# pH-Dependent Properties of a CoN₄(OH₂) Chromophore: A Spectroscopic Model of Cobalt Carbonic Anhydrase

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The complexes [Co(H₂O)L](ClO₄)₂ and [Co(N₃)L]ClO₄, where L stands for tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine, have been prepared and characterized. The aqua complex has been found to have two acidic groups in the pH range 5.5–9.5, which have been attributed to the bound water (p$K_a$ ≃ 9) and to the apical nitrogen (p$K_a$ ≃ 7.4). The behavior of this compound as well as of its azide derivative has been compared with that of cobalt(II)-substituted carbonic anhydrase; in particular, it is shown that the deprotonation of the coordinated water molecule can by itself cause a dramatic change in the electronic spectra of the cobalt(II) chromophore and a strong reduction of the anion affinity for the solvent coordination site, both puzzling properties of the above enzyme.

## Introduction

Carbonic anhydrase is a zinc(II) metalloenzyme with a water molecule in the metal coordination sphere, whose catalytic activity depends on an acid–base equilibrium with p$K_a$ of about 7.[2] The same equilibrium also controls the inhibiting ability of anions like NCO⁻, N₃⁻, halides, etc.[2] The identity of the acidic group involved is still controversial:[3] among various possibilities, the coordinated water molecule has been often regarded as a reasonable candidate.[4]

Cobalt(II) can be successfully substituted to the native metal ion yielding a still active enzyme with similar acid–base properties.[5] The electronic spectra of the latter derivative are strongly pH dependent;[2a] although they are probably sensitive to more than one acid–base equilibrium[6] (actually about four or five deprotonations take place in the enzyme in the pH range 5–9[2b]), the major variation can again be ascribed to a single acidic group with p$K_a$ of about 7. However, the observed spectral changes cannot be taken as diagnostic of ionization of the coordinated water molecule. Indeed, none of the few known cobalt(II) complexes with a single water molecule bound in water solution[7–11] are suitable to reproduce the spectral features and variations observed in the cobalt enzyme.

In order to investigate the acid–base properties of the coordinated water molecule, the influence of the water deprotonation on the electronic spectra, and the possibility of substitution of the H₂O or OH groups by other ligands, we have

prepared and characterized the complexes [Co(H₂O)L](ClO₄)₂ and [Co(N₃)L]ClO₄, where L is tris[(3,5-dimethyl-1-pyrazolyl)methyl]amine.
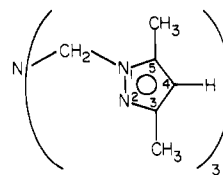


This ligand has been chosen for the following reasons: (i) pyrazolyl-containing ligands are known to stabilize low oxidation states[12] and therefore should protect cobalt(II) from

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