Electron transfer kinetics of cobaloxime complexes¹

Kefei Wang and R.B. Jordan

Abstract: The rates of oxidation of $Co^{II}(dmgBF_2)_2(OH_2)_2$ by $Co^{III}(NH_3)_5X^{2+}(X = Br^-, CI^-, and N_3^-)$ have been studied at 25°C in 0.10 M LiClO₄. The rate constants are 50 ± 9, 2.6 ± 0.2, and 5.9 ± 1.0 M⁻¹ s⁻¹ for X = Br^-, CI^-, and N_3^-, respectively, in 0.01 M acetate buffer at pH 4.7. The relative rates are consistent with the inner-sphere bridging mechanism established earlier by Adin and Espenson for the analogous reactions of $Co^{II}(dmgH)_2(OH_2)_2$. The rate constants with $Co^{II}(dmgBF_2)_2(OH_2)_2$ typically are ~10³ times smaller and this is attributed largely to the smaller driving force for the $Co^{II}(dmgBF_2)_2(OH_2)_2$ complex. The outersphere oxidations of cobalt(II) sepulchrate by $Co^{III}(dmgH)_2(OH_2)_2^+$ (pH 4.76–7.35, acetate, MES, and PIPES buffers) and $Co^{III}(dmgBF_2)_2(OH_2)_2^+$ (pH 3.3–7.42, chloroacetate, acetate, MES, and PIPES buffers) have been studied. The pH dependence gives the following rate constants (M⁻¹ s⁻¹) for the species indicated: (1.55 ± 0.09) × 10⁵ (Co^{III}(dmgBF_2)_2(OH_2)_2^+); (5.5 ± 0.3) × 10³ (Co^{III}(dmgH)_2(OH_2)_2^+); (3.1 ± 0.5) × 10² (Co^{III}(dmgH)_2(OH_2)(OH)); (2.5 ± 0.3) × 10² (Co^{III}(dmgBF_2)_2(OH_2)_2^+); (5.5 ± 0.3) × 10³ (Co^{III}(dmgBF_2)_2(OH_2)_2^+); (3.1 ± 0.5) × 10² (Co^{III}(dmgH)_2(OH_2)(OH)); (2.5 ± 0.3) × 10² (Co^{III}(dmgBF_2)_2(OH_2)_1) sepulchrate and the diaqua complexes, and the self-exchange rate for cobalt(II/III) sepulchrate, are used to estimate the self-exchange rate constants for the dioximate complexes. Comparisons to other reactions with cobalt sepulchrate indicates best estimates of the self-exchange rate constants are ~2.4 × 10⁻² M⁻¹ s⁻¹ for Co^{II/III}(dmgH)_2(OH_2)_2 and ~5.7 × 10⁻³ M⁻¹ s⁻¹ for Co^{II/III}(dmgBF_2)_2(OH_2)_2.

Key words: electron transfer, cobaloxime, inner sphere, outer sphere, self-exchange.

Résumé : Opérant à 25°C, en solutions à 0,10 M de LiClO₄, on a étudié les vitesses d'oxydation du Co^{II}(dmgBF₂)₂(OH₂)₂ par du Co^{III}(NH₃)₅X²⁺ (X = Br⁻, Cl⁻ et N₃⁻). Les constantes de vitesse sont de 50 ± 9, 2,6 ± 2 et 5,9 ± 1,0 respectivement pour X = Br⁻, Cl⁻ et N₃⁻ dans un tampon acétate à 0,01 M, à un pH de 4,7. Les constantes de vitesse sont en accord avec un mécanisme de formation de pont dans la couche interne démontrée antérieurement par Adin et Espenson pour les réactions analogues du Co^{II}(dmgH)₂(OH₂)₂. Les constantes de vitesse pour le Co^{II}(dmgBF₂)₂(OH₂)₂ sont en général 1000 moins rapides et on attribue ce résultat principalement à une force motrice plus faible pour le comlexe du Co^{II}(dmgBF₂)₂(OH₂)₂. On a aussi étudié es oxydations dans la couche externe du sépulcrate de cobalt(II) par le Co^{III}(dmgH)₂(OH₂)₂⁺ (pH de 4,76 à 7.35, tampons acétate, MES et PIPES) et par le Co^{III}(dmgBF₂)₂(OH₂)₂⁺ (pH de 3,3 à 7,42, tampons chloroacétate, acétate, MES et PIPES). Les relations avec le pH conduisent aux constantes de vitesse suivantes (M⁻¹ s⁻¹) pour les espèces indiquées : (1,55 ± 0,09) × 10⁵ (Co^{III}(dmgBF₂)₂(OH₂)₂⁺); (5,5 ± 0,3) × 10³ (Co^{III}(dmgH)₂(OH₂)₂⁺); (3,1 ± 0,5) × 10² (Co^{III}(dmgH)₂(OH₂)(OH)); (2,5 ± 0,3) × 10² (Co^{III}(dmgBF₂)₂(OH₂)(OH)). On a utilisé les potentiels connus de réduction du sépulcrate de cobalt(III) et des complexes diaqua ainsi que la vitesse d'autoéchange pour le sépulcrate de cobalt(II/III) pour évaluer les constantes de vitesse d'autoéchange sont d'autres réactions du sépulcrate de cobalt indiquent que les meilleures évaluations des constantes de vitesse d'autoéchange sont d'autres réactions du sépulcrate de cobalt indiquent que les meilleures forla⁻¹ s⁻¹ pour le Co^{II/III}(dmgH)₂(OH₂)₂ et d'environ 5,7 × 10⁻³ M⁻¹ s⁻¹ pour le Co^{II/III}(dmgBF₂)₂(OH₂)₂.

Mots clés : transfert d'électrons, cobaloxime, sphère interne, sphère externe, autoéchange.

[Traduit par la rédaction]

Introduction

The bis(dimethylglyoximato)cobalt(II) complexes $(Co^{ll}-(dmgH)_2)$ are models for the B_{12r} state of coenzyme B_{12} (1). They are mild reducing agents, and the electron transfer can be either by an inner-sphere or an outer-sphere mechanism,

Received November 16, 1995.

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- ¹ This paper is dedicated to Professor Henry Taube on the occasion of the celebration, at the University of Saskatchewan, of his many accomplishments.
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Scheme 1.

$(\mathrm{H}_{3}\mathrm{N})_{5}\mathrm{Co}^{\mathrm{III}}\mathrm{X} + (\mathrm{H}_{2}\mathrm{O})_{2}\mathrm{Co}^{\mathrm{II}}\mathrm{L}$	$\underbrace{fast}_{\text{fast}} (H_3N)_5 \text{Co}^{\text{III}} X - \text{Co}^{\text{II}} (OH_2)L + H_2O$
$(\mathrm{H_3N})_5\mathrm{Co}^{\mathrm{III}}\mathrm{-X-Co}^{\mathrm{II}}(\mathrm{OH_2})\mathrm{L}$	$\xrightarrow{k_{ct}} (H_3N)_5 Co^{II} - X - Co^{III} (OH_2)L$
(H ₃ N) ₅ Co ^{II} -X-Co ^{III} (OH ₂)L	fast Co ^{II} + 5NH ₃ + XCo ^{III} (OH ₂)L

depending on the nature of the oxidant. It has been shown (2) that the oxidation of $\text{Co}^{II}(\text{dmgH})_2(\text{OH}_2)_2$ by $\text{Co}^{III}(\text{NH}_3)_5 X^{2+}$ (X = halide and pseudohalide) proceeds by the classical X-bridged inner-sphere pathway (3) shown in Scheme 1 (L = (dmgH)₂, charges are omitted) by identifying the bridge-transferred product $\text{Co}^{III}(\text{dmgH})_2(X)(\text{OH}_2)$.

Part of the present study concerns the rates of oxidation of $Co^{II}(dmgBF_2)_2(OH_2)_2$ by $Co^{III}(NH_3)_5X^{2+}$ (X = Br⁻, Cl⁻, and N₃⁻). A comparison of these results with those of Adin and



Espenson (2) on $\text{Co}^{\text{II}}(\text{dmgH})_2(\text{OH}_2)_2$ provides some measure of the effect of the -BF₂ substituents on the inner-sphere reactivity of these systems.

Studies of the reduction of the cobalt(III) derivatives have yielded less definitive mechanistic results. Prince and Segal (4), Balasubramanian et al. (5), and Dayalan and Vijayaraghavan (6) have studied the reduction of various $Co^{III}(dmgH)_2(L)_2^+$ and $Co^{III}(dmgH)_2(X)(L)$ (X = halide or pseudohalide, L = amine or pyridine) complexes by aqueous V^{2+} , Fe²⁺, and Cr²⁺. These studies were done in acidic media (pH < 3), and the [H⁺] dependence of the reaction rate was used as an important criterion to assign the mechanism. The [H⁺] dependence is attributed to protonation equilibrium of the dmgH⁻ ligand, possibly as shown in eq. [1]. If eq. [1] is a rapidly maintained pre-equilibrium, then the apparent secondorder rate constant is given by eq. [2],

[2]
$$k_2 = \frac{k_0 K_a + k_H [H^+]}{K_a + [H^+]}$$

where $k_{\rm H}$ and k_0 are specific rate constants for reduction of the protonated (1) and unprotonated (2) complexes, respectively. In general, reductions by V²⁺ are either independent or first order in [H⁺] and may be controlled by substitution on V(OH₂)₆²⁺ in some cases. The reactions with Fe(OH₂)₆²⁺ show independent and inverse [H⁺] dependencies and the rate order is I⁻ > Br⁻ > Cl⁻ for the reduction of Co^{III}(dmgH)₂(py)(X) (6). This order is opposite to that for reduction of the Co^{III}(NH₃)₅X²⁺ complexes, and was suggested as evidence for bridging through the oximate rather than the halide ligand. The [H⁺]⁻¹ dependence of the Fe²⁺ reduction of Co^{III}(dmgH)₂(py)(X) (6) also was taken to support such an oximate ligand bridged pathway. The bridged intermediate may be pictured as in **3**, which has some precedent from the complexation of Co^{III}(dmgH)₂(OH₂)₂⁺ by aqueous iron(III) (7).



The most definitive criterion for establishing an innersphere mechanism is to identify the bridging ligand trans-

ferred product (3, 8). This is best done with Cr^{2+} as the reducing agent because the Cr^{III} product is substitution inert and can be separated and identified by standard methods. Unfortunately, only rather limited studies of this type have been done. Segal and Prince studied the $Cr^{2+} + Co^{III}(dmgH)_2(NH_3)_2^+$ reaction ($k_2 = 40 + 780 \times [H^+] M^{-1} s^{-1}$, 25°C) and initially reported no bridge-transferred product, but later (4*c*) separated, by ion-exchange chromatography, a fraction containing dmgH⁻ and Cr^{3+} . Balasubramanian and Vijayaraghavan (5*b*) did a product study for the Cr^{2+} reductions of $Co^{III}(dmgH)_2(N_3)(NH_3)$ and $Co^{III}(dmgH)_2(N_3)_2^-$ and reported the product ratios $Cr(dmgH)^+/CrN_3^{2+}$ of 2:1 and 1:2, respectively. These results indicate competitive bridging by the azide and oximate ligands, with the latter being more important for the neutral complex. However, it remains possible that the $Cr(dmgH)^+$ was produced by oxidation of a Cr^{2+} -dmgH complex during product analysis.

The main inconsistency between these studies is in the magnitude of K_a (eq. [1]). Prince and Segal (4) determined an approximate value of 0.25 M for Co^{III}(dmgH)₂(NH₃)₂⁺; Balasubramanian et al. (5) and Dayalan and Vijayaraghavan (6) find values of $(1-7) \times 10^{-3}$ M for various Co^{III}(dmgH)₂(X)(L) species. This difference might be ascribed to the charge on the complexes, but Adin and Espenson (9) had found earlier that $K_a \approx \text{ Å } 0.3$ M for various neutral alkyl species, Co^{III}(dmgH)₂(R)(OH₂).

There are no reports of definite outer-sphere reductions of the cobaloxime(III). However, outer-sphere reductions of structurally similar Co(III) tetraaza macrocyclic complexes have been studied extensively by Endicott and co-workers (10-14). In these complexes, the tetraaza ligands form a square-planar chelating ring binding to the Co cation, with the two axial positions of Co occupied by water ligands. The cross reactions between these $Co^{III}(N_4)(OH_2)_2^{3+}$ and $Co^{II}(N'_4)(OH_2)_2^{2+}$ (N₄ and N'₄ represent different tetraaza macrocyclic ligands) are supposed to be outer sphere, and the cross-reaction rates have been determined and used with Marcus theory to calculate the rates for the electron self-exchange. The self-exchange rates were discussed in terms of the Franck-Condon barrier, which is the inner-sphere reorganization energy resulting from the bond length changes accompanying the electron-transfer process. In addition to being structurally analogous to the tetraaza complexes, the cobalt(II)-dioximes are also low spin, and provide further examples to test the effect of this feature on Co(III)/Co(II) self-exchange rates. Most Co(III)/Co(II) exchanges involve high-spin cobalt(II) and there has been some disagreement (15-22) on the influence of the spin state change on the electron exchange rate.

The present study reports the first outer-sphere reduction of $\text{Co}^{\text{III}}(\text{dmgH})_2^+$ and $\text{Co}^{\text{III}}(\text{dmgBF}_2)_2^+$ by using the cobalt(II) sepulchrate ion (Co(sep)^{2+}) as the reducing agent. In Co(sep)^{2+} (4), the cobalt(II) ion is encapsulated within a macrocyclic ligand cage.



The cage ligand prevents substitution on the cobalt(II) ion, so that the electron-transfer from $Co(sep)^{2+}$ to the cobaloximes(III) must be via an outer-sphere mechanism. The observed reaction rates are used to estimate the cobaloxime(III)/(II) electron self-exchange rates by the Marcus cross relationship and the results are compared to those of various $Co(N_4)(OH_2)_2^{3+/2+}$ complexes.

Experimental section

Materials

Co(dmgBF₂)₂·2H₂O was prepared according to Bakac et al. (23) [Co^{III}(dmgH)₂(OH₂)₂]ClO₄ was prepared by the method of Ablov et al. (24–26) through a series of cobaloxime(III) intermediates as described below.

$[Co^{III}(dmgH_2)(dmgH)Cl_2]\cdot 2H_2O$, trans-

dichlorobis(dimethylglyoximato)cobalt(III) (ref. 24) A finely ground mixture of 2.38 g (0.01 mol) of CoCl₂·6H₂O (Fisher) and 2.32 g (0.01 mol) of dimethylglyoxime (dmgH₂, Fisher), was treated with \sim 15 mL of water and the slurry was stirred on a hot plate at 70-80°C for 15 min. The heating was turned off and 3-4 mL of H₂O₂ (30%, Fisher) were added slowly with stirring. The excess H_2O_2 was removed by boiling the solution for about 10 min, and \sim 30 mL of concentrated HCl (36%, BDH) was added to yield a dark-green precipitate. The mixture was cooled to room temperature, and then in an ice bath. The solid product was collected on a sintered glass filter and washed twice with dilute HCl (5% v/v), ethanol, and diethyl ether. Yield: 80%. The product was formulated as [Co^{III}(dmg₂H₃)Cl₂]·2H₂O according to the elemental analysis. Anal. calcd. for [Co(C₄H₆O₂N₂)₂H₃Cl₂]·2H₂O: C 24.2, H 4.78, N 14.1, Cl 17.9; found: C 24.4, H 4.88, N 13.9, Cl 18.2. The NMR spectrum of this complex in d_6 -DMSO shows methyl protons at 2.35 ppm and water as a broad peak at 7.5 ppm. The methyl proton resonance is shifted 0.44 ppm downfield from that in $dmgH_2$ (1.91 ppm). The shift upon coordination of dmgH⁻ to cobalt(III) is consistent with the reported value of ~ 0.4 ppm for other cobaloxime(III) complexes (27).

$[Co^{III}(dmgH)_2Cl(H_2O)]$, trans-chloroaquabis-(dimethylglyoximato)cobalt(III)

This product was prepared by aquation of [Colli-

 $(dm_2H_3)Cl_2]$ ·2H₂O (22). The dichloro salt (1.8 g) was covered with 6–8 mL of boiling water and the mixture was stirred for 20 min on a steam bath, and then cooled in ice. The greenish yellow solid obtained by filtration was washed twice with ice-cold water, ethanol, and diethyl ether. Yield: 75–85%.

[Co^{III}(dmgH)₂(OH)(OH₂)], trans-hydroxoaquabis-(dimethylglyoximato)cobalt(III) (ref. 23)

 $[Co^{III}(dmgH)_2Cl(OH_2)]$ (1.4 g) was covered with ~4 mL of a cold aqueous saturated Na₂CO₃ solution, and the mixture was stirred until the color changed from a yellowish green to gray-yellow. The precipitate was collected by filtration, washed twice with small amounts of cold water and cold ethanol, and finally with diethyl ether. Yield: 55%.

$[Co^{III}(dmgH)_2(OH_2)_2]ClO_4 \cdot H_2O$, trans-diaquo-

bis(dimethylglyoximato)cobalt(III) perchlorate (ref. 26) When 0.7 g of $[Co(dmgH)_2(OH)(OH_2)]$ was dissolved in 4 mL of 2 M HClO₄, a yellowish brown solid precipitated, and more was formed when a few drops of concentrated HClO₄ were added. The product was collected by filtration, and washed twice with small amounts of ice-cold water and methanol, and finally with diethyl ether. Yield: 35%. The product was formulated based on the elemental analysis. Anal. calcd. for [Co(C₄H₇O₂N₂)₂(OH₂)₂]ClO₄·H₂O: C 21.7, H 4.55, N 12.7; found: C 21.6, H 4.62, N 12.4. The NMR spectrum in d_{6} -DMSO shows the methyl protons at 2.54 ppm, and the water protons as a broad peak at 7.4 ppm. The electronic spectrum has a maximum at 240 nm with a molar absorptivity coefficient of 2.2×10^4 M⁻¹ cm⁻¹, consistent with the values of $2.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (240 nm) and $1.95 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (238 nm) reported by Heckman and Espenson (28) and Kita and Jordan (29), respectively. Reduction of this complex in aqueous solution with amalgamated zinc under an argon atmosphere produces a bright yellow solution of $Co^{II}(dmgH)_2(OH_2)_2$. This species has a distinctive absorption maximum at 462 nm, with a molar absorptivity coefficient of $3.42 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, in agreement with a reported value of $3.40 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (28). Solutions of Co^{III}(dmgBF₂)₂(OH₂)₂⁺ were prepared by election of M_{12}^{-1} were prepared by election of M_{12}^{-1} and M_{12}^{-1} and

trolysis of $Co^{II}(dmgBF_2)_2(OH_2)_2$ immediately before use. The electrolysis was done in an H-shaped electrolysis cell, with a sintered glass filter (10–20 μ m) separating the anode and cathode compartments. The cathode was Cu²⁺(aq)/Cu, and the anode was Pt in the Co^{ll}(dmgBF₂)₂ solution. LiClO₄ (Amend) was added as the supporting electrolyte at a concentration of 0.09 M in both compartments. To avoid diffusion of Cu²⁺ ion into the anode compartment, the small amount of $Cu(NO_3)_2$ solution was carefully placed with a dropper at the bottom of the cathode compartment, and only the anode tube was stirred during the electrolysis. The electrolysis was carried out at ~ 1 V and 0.4–0.6 mA for 0.5–1 h, during which time most of the yellow color of the Co^{II}(dmgBF₂)₂ solution faded. If acetate buffer was required for the kinetic studies, the buffer was added to the solution of Co^{II}(dmgBF₂)₂ at pH ~ 4.7. The pH was adjusted with NaOH to the desired values for kinetic studies after the electrolysis.

The two halopentaamminecobalt(III) complexes, $[(H_3N)_5-CoCl](ClO_4)_2$ (30) and $[(H_3N)_5CoBr](ClO_4)_2$ (30), and the azidopentaamminecobalt(III) complex $[(H_3N)_5CoN_3]Cl_2$ (31) were prepared according to the published methods. 1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]eicosanecobalt-(III) trichloride (cobalt(III) sepulchrate trichloride, or $Co(sep)Cl_3$) was obtained from Aldrich, and the solution of $Co(sep)^{2+}$ was prepared by reduction of the cobalt(III) sepulchrate solution over amalgamated zinc under argon.

Redistilled water was used in all preparations and kinetic studies. Other chemicals used in the preparations are of reagent or analytical grade. For buffer preparations, sodium acetate was from Fisher, chloroacetic acid from BDH, and MES hydrate and PIPES from Aldrich.

Kinetic measurements

All kinetic runs were carried out at $25 \pm 0.2^{\circ}$ C. The ionic strength was maintained at 0.100 M with LiClO₄, and the total buffer concentration is 0.01 M. Acetate buffer was used in the studies of Co^{II}(dmgBF₂)₂(OH₂)₂ with (H₃N)₅CoX²⁺, and the pH was kept at 4.72 ± 0.02 for all runs. Other buffers, MES, PIPES, and chloroacetic acid, were used in appropriate pH ranges in the studies of the cobaloxime(III)–Co(sep)²⁺ system. The pH of each solution was measured with a Corning 125 pH meter.

The absorbance decrease due to the oxidation of $Co^{II}(dmgBF_2)_2(OH_2)_2$ by $(H_3N)_5CoCl^{2+}$ and $(H_3N)_5CoN_3^{2+}$ was followed on a Hewlett Packard 8451 diode array spectrophotometer at 454 nm, with the oxidant in excess. A 5.0 cm cylindrical spectrophotometer cell was used, and the reactant solutions were degassed with argon before measurement. The absorbance-time data (80 points over 3–4 half-lives) were analyzed by least squares to obtain the first-order rate constants. The reported second-order rate constants are the average of three measurements at different $(H_3N)_5CoX^{2+}$ concentrations.

The reaction between $(H_3N)_5COBr^{2+}$ and $Co^{II}(dmgBF_2)_2^{-}$ $(OH_2)_2$ was observed on a stopped-flow spectrophotometer (Cantech Scientific Ltd) at 454 nm. The data (256 points/trace) were collected to an MS-DOS 486 computer and at least 150 points for each trace were analyzed by least squares to give the first-order rate constants. The reported rate constants are the averages of at least six runs at each of three oxidant concentrations.

The kinetics of reduction of $Co^{III}(dmgH)_2(OH_2)_2^+$ and $Co^{III}(dmgBF_2)_2(OH_2)_2^+$ by $Co(sep)^{2+}$ were followed by stopped-flow spectrophotometry at 460 nm and 452 nm, respectively, with the $Co(sep)^{2+}$ in excess. The kinetic measurements were performed under anaerobic conditions, since the $Co(sep)^{2+}$ can reduce O_2 in the acidic media to produce H_2O_2 , and $Co^{II}(dmgH)_2(OH_2)_2$ is extremely sensitive to O_2 and H_2O_2 . The $Co(sep)^{2+}$ solution was transferred to the stopped-flow storage syringe through a serum cap under argon and the cobaloxime(III) solution in the other syringe was capped with a serum cap and degassed with argon for at least 20 min. The reduction of $Co^{III}(dmgH)_2(OH_2)_2^+$ shows biphasic behavior due to the formation and then decomposition of $Co^{II}(dmgH)_2(OH_2)_2$. The absorbance–time profiles were fitted to a biphasic model to obtain the first-order rate constants for the reduction and decomposition.

Results and discussion

Oxidation of $Co^{II}(dmgBF_2)_2(OH_2)_2$ by $(H_3N)_5CoX^{2+}$ For each system, the rate was studied at three cobalt(III) com-

Table 1. Kinetic data for reactions between $(H_3N)_5Co^{III}X^{2+}$ and diaquacobaloximes(II).^{*a*}

	$k_2(M)$	$k_2(\mathbf{M}^{-1} \ \mathbf{s}^{-1})^b$		
X-	$(H_2O)_2Co^{II}(dmgH)_2^c$	$(H_2O)_2Co^{ll}(dmgBF_2)_2^{d}$		
Br	$(3.2 \pm 0.3) \times 10^5$	50 ± 9		
Cl	$(1.4 \pm 0.08) \times 10^4$	2.6 ± 0.2		
N ₃	$(6.4 \pm 0.3) \times 10^3$	5.9 ± 1.0		
NCS	$(1.4 \pm 0.08) \times 10^2$			
OH	$(7.7 \pm 1.5) \times 10^2$			
F	10.5 ± 0.9			

"At 25°C in acetate buffer (0.01 M) with $\mu = 0.10$ M by LiClO₄.

^bErrors quoted are one standard deviation.

"At 25°C in acetate buffer, from ref. 2.

 d pH = 4.74.

plex concentrations in at least 10-fold excess over the $Co^{II}(dmgBF_2)_2(OH_2)_2$ concentration in 0.01 M acetate buffer at pH 4.72. The observations indicate that the rate is first order in each reactant, and the second-order rate constants k_2 are collected in Table 1 along with the results reported by Adin and Espenson (2) on the oxidation of $Co^{II}(dmgH_2(OH_2)_2)$.

Adin and Espenson established a bridged inner-sphere mechanism for oxidation of $Co^{II}(dmgH)_2(OH_2)_2$ by $(NH_3)_5CoX^{2+}$ (Br⁻ > Cl⁻ \gg F⁻) by the identification of $Co^{III}(dmgH)_2(X)(OH_2)$ as the exclusive product. They interpreted the variation of k_2 with bridging ligands as the order of stability of the X-bridged precursor complexes following the analysis suggested by Haim (32). The order of k_2 values suggests soft-acid character for the Co^{II}(dmgH)_2(OH_2)_2 complex.

A common inner-sphere mechanism for the Co^{II}-(dmgBF₂)₂(OH₂)₂ and Co^{II}(dmgH)₂(OH₂)₂ reductants is consistent with the rate constant ratio $k_{2BT}/k_{2CI} \approx 20$ for both cobaloxime(II) complexes. For X = Cl⁻ and N₃⁻, the reactivity difference is smaller for both Co^{II}(dmgBF₂)₂(OH₂)₂ and Co^{II}(dmgH)₂(H₂O)₂, with k_{2CI}/k_{2N_3} ratio of ~0.4 in the former and ~2 for the latter. The different order may be due to some differences in affinity of Cl⁻ and N₃⁻ toward the two cobaloxime(II) complexes. For the outer-sphere reduction of (H₃N)₅CoX²⁺ by Ru(NH₃)₆²⁺ (33), the ratios k_{2BT}/k_{2CI} and k_{2CI}/k_{2N_3} of 6 and ~140, respectively, also indicate an innersphere mechanism of the cobalt(II) oximes.

The values of k_2 for Co^{II}(dmgBF₂)₂(OH₂)₂ oxidations are (1–6) × 10³ times smaller than those of the Co^{II}-(dmgH)₂(OH₂)₂ complex. Since the substitution lability for these two cobaloxime(II) complexes is not expected to differ substantially, based on our observed comparable solvent exchange rates for the two complexes (34), the large difference in the k_2 values indicate that the bridge-mediated electron-transfer process is rate controlling in the inner-sphere mechanism. The slower oxidation of Co^{II}(dmgBF₂)₂(OH₂)₂ may be due to its less favorable reduction potential of 0.65 V (NHE) compared to 0.36 V (NHE) for Co^{II}(dmgH)₂(OH₂)₂. If the Marcus theory (35) prediction of a square-root dependence of the rate on the equilibrium constant is also applicable to these inner-sphere electron transfers, then Co^{II}(dmgH)₂(OH₂)₂ is predicted to be ca. 2.8 × 10² more reactive. This factor would account in large part for the reactivity difference of the

Cobaloxime(III)	$k_{\rm a}$ or $k_{\rm b}$, ${\rm M}^{-1}~{\rm s}^{-1}$	pK _a	$E^{\circ} (\mathbf{V})^{b}$
$\begin{array}{c} (H_2O)_2Co(dmgBF_2)_2^+ \\ (H_2O)_2Co(dmgH)_2^+ \\ (HO)(H_2O)Co(dmgH)_2 \\ (HO)(H_2O)Co(dmgBF_2)_2 \end{array}$	$(1.55 \pm 0.09) \times 10^{5}$ $(5.53 \pm 0.33) \times 10^{3}$ $(3.11 \pm 0.45) \times 10^{2}$ $(2.46 \pm 0.30) \times 10^{2}$	4.40 ± 0.03 5.78 ± 0.07	0.36 0.65 0.17 0.38

Table 2. Kinetic results for reactions of cobaloxime(III) with Co(sep)^{2+, a}

^{*a*}At 25°C with $\mu = 0.10$ M. Errors quoted are one standard deviation.

^bEstimated as described in text vs. NHE by assuming a $pK_a' = 9$ for Co^{II}L(OH₂)₂

 $(L = (dmgH)_2 \text{ and } (dmgBF_2)_2).$

Fig. 1. pH dependence of the second-order rate constants for reduction of $Co^{III}(dmgH)_2$ by $Co(sep)^{2+}$ (25°C, $\mu = 0.10$ M, the calculated curve is generated by using parameters in Table 2).



Fig. 2. pH dependence of the second-order rate constants for reduction of $\text{Co}^{\text{III}}(\text{dmgBF}_{2})_2$ by $\text{Co}(\text{sep})^{2+}$ (25°C, $\mu = 0.10$ M, the calculated curve is generated by using parameters in Table 2).



cobaloximes, and the remaining factor of ~ 10 could be attributed to less favorable precursor complex formation with $Co^{II}(dmgBF_2)_2(OH_2)_2$.

Reduction of cobaloximes(III) by Co(sep)²⁺

The second-order rate constants for reduction of $Co^{III}(dmgH)_2(OH_2)_2^+$ and $Co^{III}(dmgBF_2)_2(OH_2)_2^+$ by co-

Scheme 2.

$$(H_{2}O)_{2}Co^{III}L^{+} \xleftarrow{k_{a}} (HO)(H_{2}O)Co^{III}L^{+} H^{+}$$

$$(H_{2}O)_{2}Co^{III}L^{+} Co(sep)^{2+} \xleftarrow{k_{a}} (H_{2}O)_{2}Co^{II}L^{+} Co(sep)^{3+}$$

$$(HO)(H_{2}O)Co^{III}L^{+} Co(sep)^{2+} \xleftarrow{k_{b}} (HO)(H_{2}O)Co^{II}L^{-} + Co(sep)^{3+}$$

$$L = (dmgH)_{2} \text{ or } (dmgBF_{2})_{2}$$

balt(II) sepulchrate decrease with the acidity, as shown in Figs. 1 and 2, respectively. This dependence suggests an equilibrium involving the dissociation of the proton from the axial coordinated water, as shown in Scheme 2, with the diaqua form more reactive than the hydroxoaqua form.

From Scheme 2, the observed second-order rate constant k_{obs} is given by eq. [3]:

[3]
$$k_{obs} = \frac{k_a[H^+] + k_b K_a}{K_a + [H^+]}$$

The values of pK_a , k_a , and k_b , obtained by least-squares analysis of the observed k_{obs} vs. [H⁺] data, are given in Table 2, and are used to obtain the calculated curves shown in Figs. 1 and 2.

The p K_a of 5.78 for Co(dmgH)₂(OH₂)₂⁺ is in reasonable agreement with the value of 5.14 ± 0.02 (at 25°C, in 0.1 M NaClO₄) obtained from potentiometric titration by Ablov et al. (36). For Co(dmgBF₂)₂(OH₂)₂⁺, the p K_a is lower by 1.4 units, as might be expected from the electron-withdrawing effect of the -BF₂ substituents in the modified macrocycle. In the pH ranges of our kinetic studies (4.8–7.4 for Co^{III}(dmgH)₂⁺ and 3.3–7.4 for Co^{III}(dmgBF₂)₂⁺), neither the ionization of the second proton (p K_{a2} = 8.38 ± 0.03 for Co^{III}(dmgH)₂(OH₂)₂⁺ (34)) nor the protonation of the dmgH ligand (eq. [1], p $K_a \sim 0.5$ (2) or ~2.5 (3, 4)) seems to have an influence on the k_{obs} measurement.

To analyse the reduction rate constants in terms of Marcus theory, one requires the reduction potentials of the reactants. These are known for $Co(sep)^{3+}$ and for the diaqua complexes, $Co(dmgH)_2(OH_2)_2^+$ and $Co(dmgBF_2)_2(OH_2)_2^+$, but not for the corresponding hydroxo complexes. The latter values have been estimated from the reaction cycle in Scheme 3.

From Scheme 3, the E_2^0 values are given by eq. [4]:

[4]
$$E_2^{0} = E_1^{0} - 0.059 (pK_a' - pK_a)$$

where the pK_a values are known from the kinetic results in

Wang and Jordan

Scheme 3.

$$(H_{2}O)_{2}Co^{III}L^{+} + e \xrightarrow{E_{1}^{0}} (H_{2}O)_{2}Co^{II}L$$

$$K_{a} \xrightarrow{H^{+}} H^{+} \xrightarrow{H^{2}O^{-9}} (HO)(H_{2}O)Co^{III}L^{-} + e \xrightarrow{E_{2}^{0} = ?} (HO)(H_{2}O)Co^{II}L^{-}$$

 $L = (dmgH)_2 \text{ or } (dmgBF_2)_2$

Table 2, but the pK_a' for diagua cobaloxime(II) complexes are unknown. A value of $pK_a' = 9$ has been assumed since this is typical for bivalent first-row transition metal ions (37). The E^0 values are given in Table 2.

The self-exchange rate constants for the cobaloxime(III)/ (II) couples have been estimated from the Marcus cross relationship (38), eq. [5],

[5]
$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12}$$

where k_{12} is the cross-reaction rate constant (= k_{obs}), k_{11} and k_{22} are the self-exchange rates for oxidant and reductant, and K_{12} is the equilibrium constant of the cross reaction. The f_{12} and work term corrections (W_{12} and w_{ii}) have been calculated from the following equations (39):

[6]
$$\ln f_{12} = \frac{\left[\ln K_{12} + (w_{12} - w_{21})/RT\right]^2}{4\ln(k_{11}k_{22}/Z^2) + (w_{11} + w_{22})/RT}$$

[7]
$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT]$$

[8]
$$w_{ij} = \frac{(4.225 \times 10^3) z_i z_j}{r(1 + 0.3285r \sqrt{\mu})}$$

where Z is the collision frequency, taken to be 1×10^{11}

Table 3. Summary of redox reactions of Co(sep)^{3+/2+} with various reactants with known self-exchange rates."

Reactant	<i>E</i> ⁰ , V (NHE)	$k_{11}, M^{-1} s^{-1}$		$k_{12}, M^{-1} s^{-1}$	
		obsd.	calcd.	obsd.	calcd.
$\overline{\operatorname{Co(en)}_{3}^{3+}}$	-0.18 ^b	$3.0 \times 10^{-5 c}$	2.3×10^{-5}	$5.0 \times 10^{-2 d}$	5.8×10^{-2}
$Co([9]aneN_3)_2^{2+}$	-0.41^{e}	$1.4 \times 10^{-1 f}$	5.2×10^{-1}	5.0 ^f	13
Co(sar) ²⁺	-0.43 ^b	2.1	0.13	20'	80
Co(dimsarH ₂) ⁵⁺	0.03^{b}	$2.4 \times 10^{-2 \ b}$	2.0×10^{-2}	$1.5 \times 10^{2 b}$	1.6×10^{2}
$Ru(NH_{3})_{6}^{3+}$	0.05^{g}	$6.7 \times 10^{3 h}$	0.39×10^{3}	$1.4 \times 10^{4 i}$	3.9×10^{4}
$Co(NH_3)_6^{3+}$	0.06 ⁱ	$4 \times 10^{-7 k}$	0.48×10^{-7}	0.15	0.44
$Co(terpy)_{2}^{3+}$	0.26 ^f	4.0×10^{2}	0.93×10^{2}	$1.5 \times 10^{5 f}$	3.1×10^{5}
$Co(bipy)_{3}^{3+}$	0.32‴	20'	4.8×10^{-2}	$1.0 \times 10^{4 n}$	20×10^{4}
Co(phen) ₃ ³⁺	0.38	6.7"	3.2×10^{-3}	$0.48 \times 10^{4 j}$	22×10^{4}
$Co([14]aneN_4)(OH_2)_2^{3+}$	0.42^{p}	$2.2 \times 10^{-4 p.q}$	0.5×10^{-4}	$1.6 \times 10^{3 j}$	3.4×10^{3}
$Co(Me_4[14])$ tetraene N_4 (OH ₂) ₂ ³⁺	0.56"	$14 \times 10^{-3 \ p,q}$	0.14×10^{-3}	$1.7 \times 10^{4 j}$	17×10^{4}
$Co(Me_{3}pyo[14]trieneN_{4})(OH_{2})_{2}^{3+}$	0.57 ^{<i>p</i>}	$2.5 \times 10^{-2 p.q}$	0.16×10^{-2}	$5.4 \times 10^{4 j}$	23×10^{4}
$Co(Me_{2}[14]-dieneN_{4}-13-one)(OH_{2})_{2}^{3+}$	0.60^{p}	$1.2 imes 10^{-3 \ p,q}$	0.15×10^{-3}	3.0×10^{4}	9.1×10^{4}
$Co(dmgH)_2(OH_2)_2^+$	0.36 ^r	$(2.4 \times 10^{-2})'$	2.4×10^{-3}	5.5×10^{3}	
$Co(dmgBF_2)_2(OH_2)_2^+$	0.65 ^s	$(5.7 \times 10^{-3})'$	5.7×10^{-4}	1.5×10^{5}	

^aAt 25°C and $\mu = 0.1$ M unless otherwise indicated. The self-exchange rates (k_{22}) for Co(sep)^{3+/2+} used are 3.5 and 5.1 M⁻¹ s⁻¹ at $\mu = 0.1$ and 0.2 M, respectively (ref. 43).

 ${}^{b}At \ \mu = 0.2 \ M \ (ref. 44).$

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'Adjusted to $\mu = 0.2$ using the μ dependence of Co(sep)^{3+/2+} and the value of 5 × 10⁻⁵ M⁻¹ s⁻¹ ($\mu = 0.5$) from ref. 45. ${}^{d}\mu = 0.2$, ref. 14. 'Reference 46. Reference 47. ⁸Reference 48 ^{*b*}Extrapolated with $\Delta H^* = 5$ kcal mol⁻¹ from measurements at 4°C (ref. 49). ⁱAdjusted to $\mu = 0.1$ as in footnote c from 3.5×10^4 ($\mu = 0.5$) (ref. 50). Reference 16. k Extrapolated using $\Delta S^{*} = -31$ kcal mol⁻¹ K⁻¹ (as for Co(en)₃^{3+/2+}) and ionic strength factor of 0.2 from 8 × 10⁻⁶ at 40°C in 2.5 M CF₃SO₃⁻ (ref. 51). 'Reference 52. "Reference 53. "At $\mu = 0.2$, from ref. 50. "Reference 54. "Reference 12. ^{*q*}Adjusted from $\mu = 1.0$ to $\mu = 0.2$ as in footnote *c*. 'Reference 28. 'Reference 22. 'Estimated as described in text.

Table 4. Summary of self-exchange rates (25°C) for low-spin Co(III)/(II) complexes.

Complex	$k_{11}, \mathbf{M}^{-1} \mathbf{s}^{-1}$	Δd , Å
$\frac{1}{\operatorname{Co}([9]\operatorname{aneS}_3)_2^{3+}}$	$9.5 \times 10^{4 a}$	0.07 ^b
Co(azacapten) ³⁺	$4.5 \times 10^{3 c}$	$0.06(N), 0.1(S)^{c}$
$Co(dmgH)_2(OH_2)_2^+$	$-2.4 \times 10^{-2} d$	$\sim 0.31(O)^{e}$
$Co(dmgBF_2)_2(OH_2)_2^+$	$\sim 5.7 \times 10^{-3} d$	$\sim 0.31(O)^{e}$
$Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$	$1.4 \times 10^{-2f} (5.0 \times 10^{-2})^{g}$	$0.38(O)^{e}$
$Co(Me_2[14]-dieneN_4-13-one)(OH_2)_2^{3+}$	$1.2 \times 10^{-3f} (4.4 \times 10^{-3})^{g}$	$0.43(O)^{e}$
$Co(Me_{6}[14]4, 11-dieneN_{4})(OH_{2})_{2}^{3+}$	$1.3 \times 10^{-5 f} (4.5 \times 10^{-5})^{g}$	0.57(O) ^e
$Co([14]aneN_4)(OH_2)_2^{3+}$	$8 \times 10^{-4 g}$	
$Co(Me_2pyo[14]trieneN_4)(OH_2)_2^{3+}$	$9.3 \times 10^{-2 g}$	

 $^{{}^{}a}\mu = 0.1$ (ref. 55).

^bReference 56.

Reference 57.

^dCalculated from the Marcus cross relationship as described in Table 3. These entries have a different charge type than the others and their relative values are somewhat influenced by the work term correction.

"Co-O bond length change, estimated as described in text.

Estimated at $\mu = 0.1$ as described in Table 3.

 ${}^{8}\mu = 1.0$ (ref. 12).

 $M^{-1} s^{-1}$, *r* is the sum of the radii of the reactants in Å, μ is the ionic strength, z_i is the charge on the ion, the numerical constants are for water at 25°C, and w_{ij} values are in cal mol⁻¹.

There has been a good deal of discussion (15-22) about the application of eq. [5] to cobalt(III)/(II) reactions because of the spin state changes involved and the possibility that the reactions are nonadiabatic. If the latter is the case, then a nonadiabatic factor κ of uncertain magnitude may be included on the right-hand side of eq. [5], and calculations of self-exchange rate constants become proportionately uncertain. Most recently, Shalders and Swaddle (22) have concluded that these reactions are essentially adiabatic.

For the specific case of reactions of $Co(sep)^{3+/2+}$, the justification and confidence in calculations based on eq. [5] can be tested by comparing observed and calculated values of k_{11} and k_{12} for systems in which these are known. Such results for 13 systems are summarized in Table 3, where the known k_{11} and k_{22} are used to give a calculated k_{12} , and k_{22} and k_{12} give a calculated k_{11} . For the vast majority of these systems, the observed and calculated values of k_{12} agree within a factor of \leq 10, although the calculated values are always larger. Since k_{11} depends on $(k_{12})^2$, the calculated k_{11} are ≤ 100 times smaller than the experimental values. The two exceptions are $Co(bipy)_3^{3+}$ and $Co(phen)_3^{3+}$ where the calculated k_{12} is 20 and 50 times, respectively, larger than the experimental value, and the calculated k_{11} are proportionately much smaller. These exceptions might be ascribed to conjugation in the ligand, making self-exchange more favorable than when a reaction partner has no such conjugation. However, this effect does not appear in the terpy system. It should be noted that the first eight cobalt complexes listed in Table 3 have cobalt(II) in the high-spin state, but cobalt(II) is low spin for the remaining entries. There does not appear to be any systematic difference between these two types of systems.

To estimate k_{11} for the cobalt-oxime complexes, one could simply use the k_{11} (calcd.) in Table 3. However, for the other systems, k_{11} (calcd.) is typically 5-10 times smaller than k_{11} (obsd.), so that one might expect as an upper limit for the oximes that the true k_{11} (obsd.) $\approx 10 \times k_{11}$ (calcd.) and this estimate has been entered in Table 3.

Endicott et al. (12) studied the variation of self-exchange rates with structure changes for a series of homologous *trans*- $Co(N_4)(OH_2)_2^{3+/2+}$ couples in which both Co(II) and Co(III) are low spin. The self-exchange rates were evaluated from the cross-reaction rates among these complexes. Structural studies have shown that the Co—N bond length changes very little between the Co(III) and Co(II) forms of these complexes, but the axial Co—OH₂ bond lengths are 0.38–0.57 Å longer for Co(II) because the unpaired electron occupies the antibonding d_{z^2} orbital. Endicott et al. attributed the variation of the self-exchange electron-transfer rates to the reorganization energies that result from changes in Co–OH₂ bond length Δd .

The cobaloxime systems are structurally similar to the $CoN_4(OH_2)_2$ complexes in that the equatorial Co—N bond lengths are 1.87–1.89 Å, and are very similar for the Co(III) and Co(II) forms (39). The lengthening of the axial Co—OH₂ bonds (Δd) for Co(II) compared to Co(III) is estimated as 0.31 Å for the (dmgH)₂ complex, from the Co—N(py) bond lengths in Co^{II}(dmgH)₂(py)₂ (40) and Co^{III}(dmgH)₂(py)₂⁺ (41). For the (dmgBF₂)₂ complex, Co(II)—OH₂ and Co(III)—OH₂ bond lengths can be estimated as 2.28 and 1.97 Å from the Co—O bond lengths in Co^{II}(dmgBF₂)₂(CH₃OH)₂ (23) and Co^{III}(dmgH)₂(X)(OH₂) (X = halide ions) (42). Therefore, Δd for both diaqua cobaloxime(II) complexes is estimated to be ~0.31 Å.

For these and other low-spin Co(II)/Co(III) systems, the self-exchange rates and structural change information are collected in Table 4. Our estimates for the cobaloxime complexes seem to conform reasonably with the suggestion of Endicott et al. (12) that larger structural change causes a smaller self-exchange rate constant for $CoN_4(OH_2)_2$ complexes. It is rather more surprising that the structurally quite different $Co([9]aneS_3)_2^{3+}$ and $Co(azacapten)^{3+}$ complexes also seem to follow this trend.

Acknowledgment

The authors thank the Natural Sciences and Engineering Research Council of Canada for financial support.

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