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# Methyl Transfer from *trans*-Dimethylcobalt(III) Complexes to Metal Ion Electrophiles. 1. Reactions of Zinc(II) and Cadmium(II) Ions

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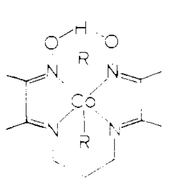
The *trans*-dimethylcobalt(III) complexes $(CH_3)_2Co((1-)N_4)$ and $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ rapidly transfer methyl groups to $Zn^{2+}$ and $Cd^{2+}$ ($M^{2+}$) in acetonitrile. (The ligands $(1-)N_4$ and $N_4$, which will be collectively designated as chel, are planar, quadridentate, macrocyclic ligands.) $^1H$ NMR studies demonstrate the presence of organozinc or organocadmium intermediates in acetonitrile. The organozinc and organocadmium intermediates vary with the $M^{2+}$:$(CH_3)_2Co(chel)$ reaction stoichiometry, but stable $CH_3Co(chel)$ is always a product. The $CH_3Zn^+$ or $CH_3Cd^+$ product in the 1:1 reaction slowly evolves methane, but only $CH_3Zn^+$ does so by pseudo-first-order kinetics. Reactions of excess $(CH_3)_2Co(chel)$ with $Zn^{2+}$ or $Cd^{2+}$ form the transient intermediates $(CH_3)_2Zn$ or $(CH_3)_2Cd$, which rapidly evolve methane via solvolysis reactions.

## Introduction

Trans-diorganic cobalt(III) complexes of macrocyclic ligands commonly act as carbanion donors toward electrophilic reagents such as $H_3O^+$,[1] $Hg^{2+}$,[1,2] $C_6H_5Hg^+$,[1,2] and $Ag^+$.[3] This research group[4-6] described previously the reactions of $(CH_3)_2Co((1-)N_4)$ (I, R = $CH_3$)[7] with $Zn^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ in 2-propanol. In the presence of excess $Zn^{2+}$ or $Cd^{2+}$,[4] $CH_3Zn^+$ or $CH_3Cd^+$ rapidly formed and slowly evolved $CH_4$ (eq 1). The half-lives for $CH_4$ evolution are 1.5 h for $CH_3Zn^+$ and 53 h for $CH_3Cd^+$. Analogous reactions[5] in the presence of excess $(CH_3)_2Co((1-)N_4)$ form transient $(CH_3)_2M$ species in biphasic reactions (eq 2). $(CH_3)_2Cd$ reacts with 2-propanol to form $CH_4$ and $^1/_4[CH_3Cd(i\text{-}C_3H_7O)]_4$, which solvolyzes to form $CH_4$ over several days. $(CH_3)_2Zn$ evolves 2 mol of $CH_4$ much more rapidly.



I

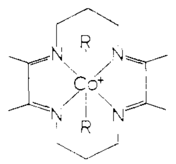
$$(CH_3)_2Co((1-)N_4) + \text{excess } M^{2+} \xrightarrow[\text{fast}]{\text{2-propanol}} CH_3Co((1-)N_4)^+ + CH_3M^+ \quad (1a)$$

$$CH_3M^+ \xrightarrow[\text{slow}]{\text{2-propanol}} CH_4 \quad (1b)$$

$$(CH_3)_2Co((1-)N_4) + M^{2+} \xrightarrow[\text{fast}]{\text{2-propanol}} CH_3Co((1-)N_4)^+ + CH_3M^+ \quad (2a)$$

$$(CH_3)_2Co((1-)N_4) + CH_3M^+ \xrightarrow{\text{2-propanol}} CH_3Co((1-)N_4)^+ + (CH_3)_2M \quad (2b)$$

The above papers left several unanswered questions. The organozinc and organocadmium intermediates were not directly identified. The presence of protic 2-propanol had a strong effect on reactions such as the formation of $[CH_3Cd(i\text{-}C_3H_7O)]_4$ from $(CH_3)_2Cd$. The results in this paper extend our past research in several ways including the first reactions of $[(CH_3)_2Co(N_4)]^+$ (II, R = $CH_3$)[7] with $Zn^{2+}$ and $Cd^{2+}$. The major themes are methyl transfer in $CH_3CN$ from neutral $(CH_3)_2Co((1-)N_4)$ and cationic $[(CH_3)_2Co(N_4)]^+$ to $Zn^{2+}$ and $Cd^{2+}$ during reactions of different stoichiometries and direct identification of alkylzinc and alkylcadmium intermediates by $^1H$ NMR. As discussed below, the reactions in $CH_3CN$ are quite different from those in 2-propanol. $(CH_3)_2Co(chel)$ is used in the following discussion to represent similar properties of $[(CH_3)_2Co(N_4)]^+$ and $(CH_3)_2Co((1-)N_4)$.



II

## Results and Discussion

**Spectrophotometric Titrations of $(CH_3)_2Co(chel)$ with $Zn^{2+}$ and $Cd^{2+}$.** Spectral titrations of both $(CH_3)_2Co(chel)$ with $Zn^{2+}$ or $Cd^{2+}$ gave similar results. All titrations confirmed the presence of the 1:1 and 1:2 $M^{2+}$:$(CH_3)_2Co(chel)$ reactions. Attempts to isolate the fast 1:1 reaction (eq 3a) by titrations yielded end point values between 1.0 and 0.5, which reflect the partial reaction of $CH_3M^+$ formed in eq 3a with a second mole of the dimethyl complex (eq 3b). Slow spectral titrations confirmed the overall 1:2 stoichiometry of the reaction. Plots of absorbance vs. mole ratio ($M^{2+}$:$(CH_3)_2Co(chel)$) (Figure 1, chel is $N_4$) yielded 0.5 mol ratio end points. The 0.5 value is indicative of the 1:2 reaction, in which 1 mol of $Cd^{2+}$ or $Zn^{2+}$ reacts with 2 mol of the dimethyl complex (eq 3). Two important points of the above results are that $CH_3M^+$ reacts quite rapidly with $(CH_3)_2Co(chel)$ to form $(CH_3)_2M$ (see below) and that during the time of the titrations organozinc or organocadmium compounds did not revert to $M^{2+}$ due to hydrolysis. If $M^{2+}$ had been formed in the latter process, the reaction would be catalytic in metal ion and metal ion: organocobalt ratios far less than 0.5 would occur.

$$(CH_3)_2Co(chel) + M^{2+} \xrightarrow{CH_3CN} CH_3Co(chel)(CH_3CN)^+ + CH_3M^+ \quad (3a)$$

$$(CH_3)_2Co(chel) + CH_3M^+ \xrightarrow{CH_3CN} CH_3Co(chel)(CH_3CN)^+ + (CH_3)_2M \quad (3b)$$

**NMR and $CH_4$ Evolution Studies of Reactions of $(CH_3)_2Co(chel)$ with $Zn^{2+}$.** $^1H$ NMR titrations in $CH_3CN\text{-}d_3$ and gas-liquid chromatographic (GLC) experiments provide evidence for the proposed organozinc intermediates. Addition

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[7] Ligand abbreviations: $(1-)N_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olato; $N_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

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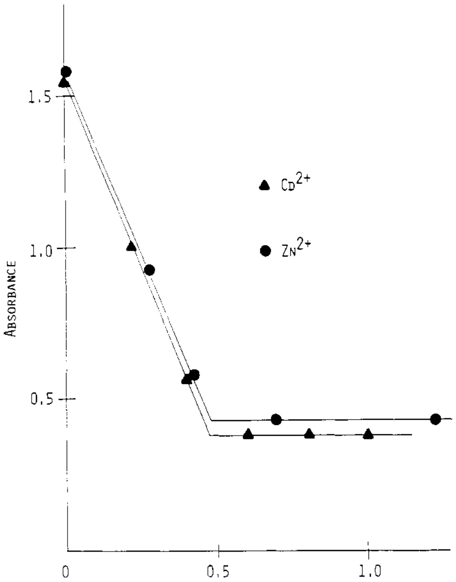

**Figure 1.** Representative slow spectral titrations of $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ with $Zn^{2+}$ (●) and $Cd^{2+}$ (▲).

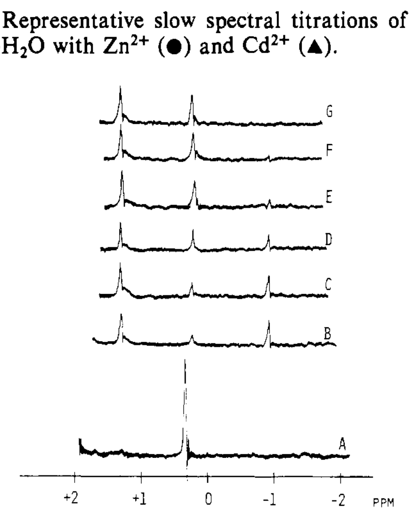

**Figure 2.** $^1H$ NMR spectra between +2.0 and −2.0 ppm: (A) $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$; (B) immediately after addition of excess $Zn^{2+}$; (C) after 6 min; (D) after 10 min; (E) after 18 min; (F) after 25 min; (G) after 35 min.

of an equimolar or excess quantity of $Zn^{2+}$ to an anaerobic solution of $(CH_3)_2Co(chel)$ (Figure 2, chel is $N_4$) in an NMR tube resulted in the instantaneous disappearance of the resonance due to $[(CH_3)_2Co(N_4)]^+$ (+0.35 ppm) and the appearance of two new resonances in addition to one at 1.30 ppm due to the monomethylcobalt complex. The −0.85-ppm resonance decreasing with time is the result of an organozinc species and the +0.2-ppm $CH_4$ resonance increasing with time is probably due to hydrolysis of an organozinc species.

Methane evolution studies from solutions of $Zn^{2+}$ and $(CH_3)_2Co(chel)$ (mol ratio ≥1.0) by GLC show linear plots of ln $(C_\infty - C)$ vs. time (Figure 3) and indicate that $CH_4$ is the product of a pseudo-first-order process. The half-life for $CH_3Zn^+$ decomposition in $CH_3CN$ depends on chel. It is 43 min ($k_{obsd} = 1.6 \times 10^{-2}$ min$^{-1}$) in the presence of $[CH_3Co((1-)N_4)(CH_3CN)]^+$ and 28 min ($k_{obsd} = 2.5 \times 10^{-2}$ min$^{-1}$) in the presence of $[CH_3Co(N_4)(CH_3CN)]^{2+}$. The greater stability of $CH_3Zn^+$ in the presence of $[CH_3Co((1-)N_4)(CH_3CN)]^+$ might be due to association of organozinc species with the oxime oxygens of the ligand, which renders it less susceptible to hydrolysis. Our previous work with the $(1-)N_4$ ligand[4] showed that $CH_3Zn^+$ has a longer half-life in 2-propanol (90 min) than in $CH_3CN$ (43 min) and is presumably stabilized by oxygen donors.

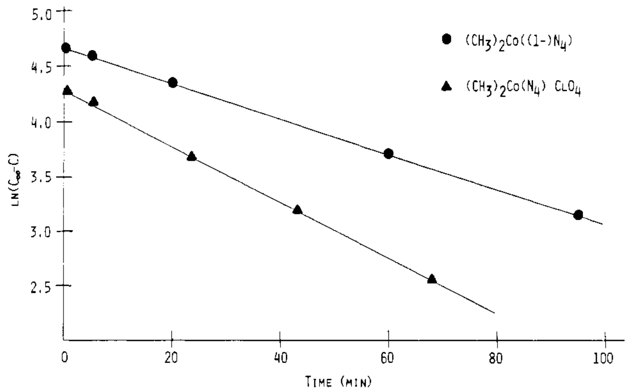

**Figure 3.** Rate of methane evolution for reactions of $(CH_3)_2Co((1-)N_4)$ (●) and $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ (▲) with a 4-fold $Zn^{2+}$ molar excess.

Spectral titrations, $CH_4$ evolution studies by GLC, and NMR results suggest that the resonance at −0.85 ppm (Figure 2) is due to $CH_3CN$-solvated $CH_3Zn^+$. Reviews[8,9] and papers[10,11] emphasize the complexity of solution organozinc chemistry. $(CH_3)_2Zn$ and polymeric $[CH_3Zn(OCH_3)]_n$ have $^1H$ NMR $CH_3Zn$ resonances at −0.67 and −0.40 ppm, respectively, in $C_6H_6$ at 40 °C.[10] Exchange between $(CH_3)_2Zn$ and $[CH_3Zn(OCH_3)]_n$ is slow on the NMR time scale at 0 °C in toluene and −5 °C in pyridine.[10] In similar studies,[11] exchange reactions (eq 4) in THF are slow on the NMR time

$$(CH_3)_2Zn + ZnI_2 \rightleftharpoons 2CH_3ZnI \qquad K \geq 500 \qquad (4)$$

scale only at −70 °C. Thus, our tentative assignment of the −0.85-ppm $^1H$ NMR resonance to solvated $CH_3Zn^+$ must be considered in terms of the possible disproportionation (eq 5).

$$2CH_3Zn^+ \rightleftharpoons (CH_3)_2Zn + Zn^{2+} \qquad (5)$$

Equilibrium 5 suggests, however, that $Zn^{2+}$ should catalytically decompose $(CH_3)_2Co(chel)$ because $Zn^{2+}$ is regenerated. Spectral titrations show that this does not occur. Instead, the broadness of the −0.85-ppm resonance in Figure 2 could be due to $CH_3Zn^+$ methyl self-exchange, which would be likely in a ligating solvent such as $CH_3CN$.

$^1H$ NMR spectra of solutions made from $Zn^{2+}$ and excess $(CH_3)_2Co(chel)$ showed no resonance attributable to $(CH_3)_2Zn$. A resonance at −0.85 ppm observed immediately after the addition of $Zn^{2+}$ disappeared within 2 min as the $CH_4$ peak (0.20 ppm) appeared. The rapid appearance of $CH_4$ is confirmed by GLC experiments, because 50% of the theoretical $CH_4$ appears in about 2 min and 100% within 20 min. In contrast to the 1:1 reaction $CH_3Zn^+$ is not a stable intermediate in the reactions containing excess $(CH_3)_2Co(chel)$. We postulate that $(CH_3)_2Zn$ formed (eq 3b) is instantaneously decomposed by $H_2O$ releasing 50% of the $CH_4$ and forming $CH_3Zn(OH)$ (eq 6), which rapidly releases the remaining 50%

$$(CH_3)_2Zn + H_2O \rightarrow CH_3Zn(OH) + CH_4 \qquad (6)$$

of the $CH_4$ by a second reaction with $H_2O$. This explanation is reasonable because reactions of dialkylzinc complexes with alcohols and $H_2O$ are well-known. For example $(C_2H_5)_2Zn$ reacts with $H_2O$ in diethyl ether at 0 °C in a 1:1 stoichiometry, and the presumed $(C_2H_5)Zn(OH)$ has a 6-min half-life at 30 °C.[12] The same paper describes the reactions of alcohols with $(C_2H_5)_2Zn$ to form $(C_2H_5)Zn(i\text{-}C_3H_7O)$ in hexane and Zn-

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$(OR)_2$ (R = primary, secondary, or tertiary alkyl) in ether. Thus, the literature agrees with our postulate of the unstable $CH_3Zn(OH)$ intermediate, but we cannot rule out the decomposition of $CH_3Zn^+$ via a reaction with a species such as $CH_3Zn(OH)$.

**NMR and $CH_4$ Evolution Studies of Reactions of $(CH_3)_2Co(chel)$ with $Cd^{2+}$.** Addition of equimolar or excess $Cd^{2+}$ to an anaerobic solution of $(CH_3)_2Co(chel)$ in an NMR tube resulted in the instantaneous disappearance of the $^1H$ NMR $CH_3Co$ signal due to $(CH_3)_2Co(chel)$ and appearance of the monomethylcobalt complex signal and a broad signal without satellites (see below) at −0.50 ppm. Attempts to obtain the half-life of $CH_4$ evolution as for $(CH_3)Zn^+$ (Figure 3) failed because $\ln (C_\infty - C)$ vs. time plots were not linear.

Reviews[8,9] and papers[10,13-15] emphasize exchange reactions of organocadmium species. Such exchange reactions are easy to detect because $^1H$ satellites due to $^{111}Cd$ and $^{113}Cd$ splittings are broadened and finally merged with the major band of Cd isotopes with spin = 0. Thus, the absence of satellites near the −0.50-ppm resonance demonstrates the presence of exchange reactions. The exchange could be either self-exchange or a Schlenk-type equilibrium (eq 7). Organocadmium exchange reactions can be very fast.

$$(CH_3)_2Cd^{2+} + Cd^{2+} \rightleftharpoons 2CH_3Cd^+ \qquad (7)$$

$(CH_3)_2Cd$ in THF lacks satellites even at −10 °C; added $CH_3Cd(OCH_3)$ or $CdI_2$ catalyzes the exchange, and $(CH_3)_2Cd$–$CdBr_2$ mixtures show broadened satellites at −110 °C.[13] Generally, polar solvents decrease the energy of activation of $(CH_3)_2Cd$ exchange reactions.[14] The absence of satellites of our −0.50-ppm resonance and the literature cited above strongly suggest that the $CH_3Cd^+$ species is in equilibrium with at least one other organocadmium species. It is not surprising that we cannot describe $CH_4$ evolution with the simple rate law described above for $Zn^{2+}$ reactions or our previous $Cd^{2+}$ reactions in 2-propanol.[4]

$^1H$ NMR spectra of solutions prepared from $Cd^{2+}$ and at least a 2-fold molar excess of $(CH_3)_2Co(chel)$ showed the usual rapid disappearance of the $(CH_3)_2Co$ resonance, the formation of the monomethyl analogue, and an organocadmium band at −0.06 ppm. The absence of $CH_4$ after 2 min in contrast to the analogous $Zn^{2+}$ reaction is explained by the rates of $CH_4$ evolution in $M^{2+}$–$(CH_3)_2Co((1-)N_4)$ reactions of 1:2 stoichiometry. The time for 50% of theoretical $CH_4$ evolution is about 50 min for $Cd^{2+}$ compared to about 2 min for $Zn^{2+}$.

The absence of satellites in this solution of 1:2 $Cd^{2+}$:$(CH_3)_2Co(chel)$ stoichiometry demonstrates the rapid exchange reactions expected for $(CH_3)_2Cd$ in polar solvents[13,14] or $(CH_3)_2Cd$ exchange catalyzed by $CdBr_2$, $CdI_2$, or $[(CH_3)Cd(OCH_3)]_4$.[13] These results agree with the observation that rates of exchange reactions are controlled by bridge formation.[9] Our experiments contain no alkoxide ion or coordinating anion, but $CH_3Cd(OH)$ formed via eq 6 could catalyze the exchange reaction. The chemical shift is more negative when the $Cd^{2+}$:$(CH_3)_2Co(chel)$ ratio is smaller because the equilibrium of eq 7 contains a higher fraction of $(CH_3)_2Cd$. It is generally known that proton resonances of $(CH_3)_2M$ (M = Cd, Zn) species are 0.2–0.5 ppm further upfield[8,10,15] than those of $CH_3MX$ (X = halide, alkoxide). To our knowledge species such as solvated $CH_3Zn^+$ or $CH_3Cd^+$ have not been subjected to NMR studies, but in $CD_3OD$, $CH_3Hg^+$[16] at +1.0 ppm is far downfield of $(CH_3)_2Hg$[8] at +0.2 ppm. Thus, increased $(CH_3)_2Cd$ in a $(CH_3)_2Cd$–$CH_3Cd^+$ mixture will result in the observed higher field proton resonance at lower $Cd^{2+}$:$(CH_3)_2Co(chel)$.

## Experimental Section

**General Information.** Reactions between the dimethyl complexes and $Zn^{2+}$ and $Cd^{2+}$ were performed in the dark under an atmosphere of purified nitrogen. Acetonitrile was purified by the method of Coetzee.[17] All other solvents were purified by standard methods.[18] $Zn(ClO_4)_2 \cdot 6H_2O$ and $Cd(ClO_4)_2 \cdot 6H_2O$ were obtained from G. F. Smith and were recrystallized from deionized water. The use of hydrated salts means that the solutions contain low water concentrations. The $Zn^{2+}$ and $Cd^{2+}$ solutions were standardized by the method of Flaschka.[19]

**Physical Measurements.** Elemental analyses (C, H, N) were performed on a Perkin-Elmer Model 240B elemental analyzer or an F and M Model 185 CHN analyzer. $^1H$ NMR spectra were recorded on a Varian EM360 NMR spectrometer. Electronic spectra in the 200–700-nm range were recorded on either a Cary Model 14 or 219 recording spectrophotometer. A Varian Aerograph series 1860-1 chromatograph equipped with a flame ionization detector and a 6 ft × $^1/_8$ in. OV-17 (3% on Chromsorb-W, 80–100 mesh) column maintained at 60 °C or a 6 ft × $^1/_8$ Porapak-Q (80–100 mesh) column maintained at 115 °C was used to determine volatile reaction products. With a 25 mL/min flow rate the following retention times were observed: $CH_4$, 66 s (OV-17), 30 s (Porapak-Q); $C_2H_6$, 54 s (Porapak-Q); $CH_3CN$, 90 s (OV-17), 21.5 min (Porapak-Q).

**Synthesis of Dimethyl Complexes.** $(CH_3)_2Co((1-)N_4)$ was prepared from $[Co((1-)N_4)(H_2O)_2](NO_3)_2$ by the method of Witman and Weber.[6] Anal. Calcd for $C_{12}H_{25}N_4O_2Co$: C, 47.57; H, 7.62; N, 17.07. Found: C, 47.53; H, 7.79; N, 17.16. UV–vis spectrum ($CH_3CN$): 236 nm ($\epsilon$ 19 600), 276 (13 000), 405 (7220). $^1H$ NMR spectrum ($CH_3CN$-$d_3$): $\delta$ 0.07 (s), 2.35 (s), 2.36 (s), 2.4–2.1 (m).

Initial attempts to prepare the intermediate complexes $[Co(N_4)X_2]^+$ (X = $Cl^-$, $Br^-$) by literature procedures[20] resulted in either very small yields (about 1–2%) or no product at all. A newer method[21] led to $[Co(N_4)Br_2]Br$ in 22% yield. Conversion to the $ClO_4^-$ salt[20] by removal of $Br^-$[6] resulted in $[Co(N_4)(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ in high yield. $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ was prepared from $[Co(N_4)(H_2O)_2](ClO_4)_3 \cdot 2H_2O$ by the procedure of Witman and Weber[6] for the preparation of $(CH_3)_2Co((1-)N_4)$. Anal. Calcd for $C_{16}H_{32}N_4O_5ClCo$: C, 42.26; H, 7.04; N, 12.33. Found: C, 42.50; H, 6.97; N, 12.50. UV–vis spectrum ($CH_3CN$): 252 nm ($\epsilon$ 19 400), 290 (sh), 442 (8630). $^1H$ NMR spectrum ($CH_3CN$-$d_3$): $\delta$ 0.35 (s), 2.40 (s), 2.1–2.4 (m).

*Caution!* Perchlorate complexes are potentially explosive and must be handled cautiously.

**Spectrophotometric Titrations.** Titrations were performed anaerobically in 1-cm quartz cells. Typically, $10^{-4}$ M solutions of $(CH_3)_2Co(chel)$ were titrated with standard solutions (0.2 M) of $Zn^{2+}$ or $Cd^{2+}$ by following the absorbance decrease due to the loss of $[(CH_3)_2Co(N_4)]ClO_4 \cdot H_2O$ at 442 nm or $(CH_3)_2Co((1-)N_4)$ at 405 nm. The overall biphasic reactions were titrated by injecting small volumes of the $M^{2+}$ titrant from a 1-$\mu$L syringe directly into a cuvette that contained a known amount of the $(CH_3)_2Co(chel)$. Attempts to titrate the fast first reaction of the overall biphasic reaction were done by using the same titration procedure just described except that the $M^{2+}$ titrant additions were made as rapidly as possible (10 s apart).

**$^1H$ NMR Titrations.** The titrations were performed in anaerobic 5-mm NMR tubes. Typically, a 0.50-mL aliquot of a 0.030 M solution of $(CH_3)_2Co(chel)$ in $CH_3CN$-$d_3$ was titrated with a standard $CH_3CN$-$d_3$ solution of $Zn^{2+}$ or $Cd^{2+}$. The titration progress was monitored by observing $^1H$ NMR spectral changes.

**Methane Evolution.** Anaerobic solutions of $(CH_3)_2Co(chel)$ ($4 \times 10^{-3}$ M) were made up in 50-mL hypo vials that were sealed with serum caps. The reactions were initiated by the addition of the appropriate volume of a standardized $Zn^{2+}$ or $Cd^{2+}$ solution from a

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syringe. The liberated $CH_4$ was sampled with a gastight syringe and detected by GLC. Infinity values were determined after acid hydrolysis of the reaction mixture.

**Acknowledgment.** We thank the National Science Foundation for partial funding for the Cary 219 spectrophotometer through Grant CHE 79-08399.

**Registry No.** $(CH_3)_2Co((1-)N_4)$, 33569-60-7; $[(CH_3)_2Co(N_4)]ClO_4$, 77310-45-3; Cd, 7440-43-9; Zn, 7440-66-6.

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# Kinetics and Mechanism of the Reduction of Hexacyanoferrate(III) by (Ethylenediaminetetraacetato)hydroxocobaltate(II)

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*Received May 14, 1981*

The formation and disappearance of the binuclear cyanide-bridged complex between $Fe(CN)_6^{3-}$ and $CoEDTA^{2-}$ were investigated between pH 6.0 and 13.44. No change in the rate is observed until pH ~12, after which a drastic rise in the observed first-order rate constant is seen with increasing pH. Concurrently, the intensity of the deep purple binuclear complex decreases. These observations are attributed to the formation of the hydroxo complex $CoEDTA(OH)^{3-}$, which reduces $Fe(CN)_6^{3-}$ via an outer-sphere reaction without first reacting to form a binuclear ($Fe^{II}$–CN–$Co^{III}$) species. The failure of this species to form is taken as strong evidence of the outer-sphere mechanism in these reactions.

## Introduction

The reduction of hexacyanoferrate(III) and substituted pentacyanoiron(III) complexes by (ethylenediaminetetraacetato)cobaltate(II) and related cobalt(II) chelates has been studied between pH 5 and 10 by several workers.[2-10] In each case the same pattern emerges: a rapid formation of a cyano-bridged binuclear complex followed by a slower formation of the final products, the mononuclear species $Fe^{II}(CN)_5X^{n-}$ and $Co^{III}$(chelate). The mechanism initially proposed[2,4,5,7] for these reactions involved the formation and subsequent dissociation of the cyano-bridged $Fe^{II}$–CN–$Co^{III}$ entity as represented by reactions 1 and 2, with use of $Fe(CN)_6^{3-}$ and $CoEDTA^{2-}$ as examples.

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \overset{K_1}{\rightleftharpoons} (EDTA)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5^{5-} \quad (1)$$

$$(EDTA)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5^{5-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoEDTA^{-} + Fe(CN)_6^{4-} \quad (2)$$

An alternate mechanism, initially proposed by Haim and co-workers[6] and later substantiated by this research group,[8,9] attributes the slow formation of mononuclear products to an outer-sphere process. In this mechanism the binuclear complex is a "dead end" to product formation. Instead, reaction 3 is proposed to account for the product formation.

$$CoEDTA^{2-} + Fe(CN)_6^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CoEDTA^{-} + Fe(CN)_6^{4-} \quad (3)$$

Recently,[10] evidence has been sought for the formation of a binuclear complex utilizing another bridging ligand, 4,4′-bipyridine. It was hoped that this species, which has served as an effective bridging ligand in earlier systems,[11,12] would act as a viable alternate to cyanide bridging, but this was not the case. In an effort to find such systems, we have continued our investigations using pentadentate cobalt(II) chelate complexes. Early work with (*N*-benzylethylenediaminetriacetato)cobaltate(II) and the parent iron complex $Fe(CN)_6^{3-}$ (performed as a model for cyanide-bridge formation) showed some interesting behavior above pH 10. The rate of production of products increased with pH, yet the apparent degree of formation of the binuclear complex decreased in this pH range. Similar results were obtained with (*N*-(hydroxyethyl)ethylenediaminetriacetato)cobaltate(II). To understand this effect more fully, the parent cobalt(II) complex, $CoEDTA^{2-}$, was investigated above pH 10. The results of this investigation are reported here.

## Experimental Section

**Materials.** $Na_3Fe(CN)_6$ was purchased from Pfaltz & Bauer. Hydrated reagent $NaClO_4$ was purchased from G. F. Smith, and the disodium salt of ethylenediaminetetraacetic acid was purchased from Matheson Coleman and Bell. Cobalt(II) nitrate and a 50% standard NaOH solution were Fisher reagent-grade chemicals. Steam-distilled water was passed through a Barnstead Ultrapure mixed-bed ion exchanger and filtered before use.

**Solution Preparation.** Stock solutions of all chemicals were prepared by weight except for the $Co(NO_3)_2$ solutions, which were standardized by titration with standard EDTA and xylenol orange indicator.[13] $Co^{II}$EDTA solutions were prepared just prior to each run by using 10% excess $Na_2H_2EDTA$. Hexacyanoferrate(III) solutions were analyzed spectrophotometrically by using a molar absorptivity of 1023 $M^{-1}\ cm^{-1}$ at 420 nm. Sample solutions were prepared so that kinetic runs were made at ionic strength 0.26 M and 25 °C. All pH adjustments were made with use of solutions prepared from carbonate-free standard 50% NaOH. No buffer was added. All pH measurements were made with a Fisher Accumet Model 520 pH meter equipped with a glass microprobe electrode. The electrode was placed in solutions for 30 s prior to measurement. Subsequent cleanings and standardization against pH 10 buffers were conducted between measurements.

**Spectrophotometric and Kinetic Measurements.** Kinetic measurements were obtained with a Cary 15 spectrometer equipped with a water-jacketed cell holder. Constant temperature in the cell compartment was maintained at 25 ± 0.01 °C by using a Lo-temptrol precision thermostatic bath. All solutions and the 2-cm absorbance cell were equilibrated to 25 °C before measurements were made. The

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