Since the 10*Dq* values for all three metal systems are expected to be comparable (±20%), the only major differences between them appear to be their spin multiplicities and crystal field stabilization energies (CFSE). The CFSE of the octahedral complexes increase in the order high-spin iron(II) < cobalt(II) < nickel(II) < low-spin iron(II). Spin multiplicities increase in the reverse order. Thus, the satellite intensities are observed to follow the same order as the CFSE with high-spin iron(II) having the most intense satellite lines and low-spin iron(II) the least intense lines. The satellites in the cobalt(II) and nickel(II) spectra show a behavior consistent with a decomposition sensitivity analogous to that observed in the iron(II) systems, and these trends may provide a consistent qualitative explanation for the features of the 2p XPS spectra of all three sets of complexes. There is clearly reason to exercise considerable caution both in the assignment of satellites observed in the XPS of insulating solids and in the extension of theoretical models of satellite structure[14] until satisfactory experimental criteria for identifying decomposition can be established.

Acknowledgment. We wish to thank Dr. Morris L. Perlman for his valuable advice and comments. M.S.L. wishes to acknowledge Brookhaven National Laboratory and the City University of New York Faculty Research Award Program for their financial support. This research was carried out at Brookhaven National Laboratory under contract with the U.S. Energy Research and Development Administration and supported by its Division of Physical Research.

Registry No. Fe-I,, 55222-32-7; Fe-II, 55190-32-4; Fe-III, 55190-34-6; Fe-IV, 55190-36-8; Co-I, 63526-13-6; Co-II, 63449-04-7; Co-III, 63449-02-5; Co-IV, 63449-00-3; Ni-I, 56348-41-5; Ni-II, 56348-43-7; Ni-III, 56348-45-9; Ni-IV, 56348-47-1.

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Kinetics of the Formation and Bond Cleavage Reactions of an Alkyl-Bridged Dicobalt Organocobaloxime[1]

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Received April 26, 1977 AIC70293U

The reaction of the tributylphosphine–cobaloxime(I) complex with 1,4-dibromobutane forms, in succession, 4-bromobutylcobaloxime and a 1,4-butenyldicobaloxime, $BCo(dmgH)_2(CH_2)_4Co(dmgH)_2B$. The latter complex with $B = H_2O$ undergoes successive dealkylation reactions with Hg_{aq}^{2+}, forming first $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ and then $Hg(CH_2)_4Hg^{2+}$. The organocobaloximes also undergo protonation equilibria at oxime oxygen positions. Quantitative studies of the rates and equilibria of these reactions are reported, along with data for the comparison complex *n*-butylcobaloxime.

Introduction

Several examples are known of dimetallic complexes in which an alkyl (or aralkyl) bridges two cobalt chelates,[2] including $pyCo(dmgH)_2(CH_2)_nCo(dmgH)_2py$ (n = 2–5),[3] $pyCo(bae)(CH_2)_nCo(bae)py$ (n = 3, 4),[4] and $pyCo(dmgH)_2CH_2C_6H_4CH_2Co(dmgH)_2py$ (meta and para isomers).[5] Also, stable rhodium analogues, $BrRh(N_4chel)(CH_2)_nRh(N_4chel)Br$, are known,[6] and claims have been made for transient dichromium intermediates, $[(H_2O)_5Cr]_2(CHX)^{4+}$ (X = Cl,[7] Br[8]).

A key question for which the literature contains scant but discrepant data, for these difunctional compounds, is whether the two centers function independently. If they are indeed independent, one would expect the same chemistry at each site. One would also expect the chemical reactivity to be about the same at each center and comparable to monofunctional analogues, after making allowance for statistical factors. On the other hand the possibility of an interaction between the two centers cannot be excluded. In extreme instances this could result in new reactions such as alkyl coupling or cyclization or metallocycle formation, although it would perhaps more likely be manifest as altered reactivity and expressed in terms of neighboring group effects.

To explore these possibilities we first carried out work, which is the subject of the present paper, in which it seemed that such interaction might be relatively *unimportant*. The complex used in these studies is the well characterized,[3] bridged 1,4-butenyldicobaloxime $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2py$ (I). In this connection we have obtained data for three reactions which, at least for the monofunctional analogues, are relatively well characterized: (a) the nucleophilic displacement[9,10] of Br^- from alkyl bromide by $Co(dmgH)_2^-$ (eq 1), (b) the

$$RBr + Co(dmgH)_2^- \xrightarrow{k_{Co}} RCo(dmgH)_2 + Br^- \quad (1)$$

$$RCo(dmgH)_2(H_2O) + H^+ \overset{K_H}{\rightleftharpoons} RCo(dmgH)(dmgH_2)(H_2O)^+ \quad (2)$$

$$RCo(dmgH)_2(H_2O) + Hg^{2+} \xrightarrow{k_{Hg}} (H_2O)_2Co(dmgH)_2^+ + RHg^+ \quad (3)$$

protonation equilibrium[11-13] of coordinated dimethylglyoxime (eq 2), and (c) cleavage of the cobalt–carbon bond upon reaction with mercury(II)[11,12,14,15] (eq 3).

Experimental Section

Materials. Alkylcobaloximes were prepared according to the general method of Schrauzer,[16] that is, by reaction of the appropriate alkyl bromide with $Co^I(dmgH)_2^-$ prepared by borohydride reduction under an inert atmosphere in alkaline methanol. The compounds were isolated as their pyridine adducts. Purification was achieved by dual recrystallization: first by pouring a solution of the compound in the minimum quantity of glacial acetic acid into water containing several equivalents of pyridine; second by dissolving the crystals in a minimum volume of methylene chloride and reprecipitating by addition of two or more volumes of *n*-hexane. The filtered crystals were dried overnight under vacuum. The compounds $n\text{-}C_4H_9Co(dmgH)_2py$, $\omega\text{-}Br(CH_2)_4Co(dmgH)_2py$, and $pyCo(dmgH)_2(CH_2)_4Co(dmgH)_2py$ were prepared in this manner, the monobromo derivative by adding $(Co^I)^-$ slowly to a solution containing a large excess of 1,4-dibromobutane and the dicobaloxime by slowly adding a limited quantity of the halide to a stoichiometric excess of $(Co^I)^-$. Anal. Calcd for the *n*-butyl complex $CoC_{17}N_5O_4H_{28}$: C, 48.00; H, 6.64; N, 16.46; Co, 13.85. Found: C, 47.66; H, 6.65; N, 16.37; Co, 13.86. Calcd for the monobromo complex $CoC_{17}N_5O_4H_{27}Br$: C, 40.49; H, 5.40; N, 13.89; Co, 11.69; Br, 15.84. Found: C, 40.47; H, 5.51; N, 13.35; Co, 11.70; Br, 16.44. Calcd for the dicobaloxime $Co_2C_{30}N_{10}O_8H_{46}$: C, 45.46; H, 5.85; N, 17.67; Co, 14.87; Br, 0.0. Found: C, 45.07 ± 0.05; H, 5.72 ± 0.07; N, 17.96 ± 0.06; Co, 14.73 ± 0.12; Br, <0.1.

The data for reactions 2 and 3 were obtained in aqueous perchloric acid. The pyridinecobaloximes are instantaneously converted to the aquocobaloximes upon dissolution in dilute perchloric acid.

The sample of 1,4-dibromobutane was redistilled for use in kinetic runs, and other reagents were prepared as before.[14b] Solutions of the tributylphosphine adduct of $Co^I(dmgH)_2^-$ were generated as needed for kinetic studies by reduction of $Bu_3PCo(dmgH)_2Cl$ with excess borohydride in basic methanol as described by Schrauzer and Deutsch.[9]

Methods. Kinetic data for reaction 1 were obtained in the presence of a large excess of the alkyl halide by following the disappearance of the cobalt(I) complex spectrophotometrically at its 610-nm peak, $\epsilon \sim 1 \times 10^4$ M^{-1} cm^{-1}. These reactions were carried out at 25.0 °C in methanol containing traces of water, usually 1.5%.

The kinetic data for the dealkylation reactions (eq 3) of the organocobaloximes with mercury(II) were also followed spectrophotometrically, utilizing the absorption maximum of $RCo(dmgH)_2$ at 450 nm.[17] These reactions were studied at 24.8 °C in aqueous solution containing perchloric acid and/or lithium perchlorate to control $[H^+]$ and ionic strength.

Equilibrium constants for protonation equilibria (eq 2) were evaluated by two methods. The variation of the rate constant for the Hg^{2+} reactions with H^+ was used to determine these values as described previously.[11,14b] Also, the (small) changes in absorbance at λ 400–450 nm accompanying the protonation equilibrium[11] were used to evaluate the protonation constants.

The techniques used for obtaining and treating the pseudo-first-order kinetic data have been described previously.[11,14b] Some of the kinetic data for reaction with Hg^{2+} corresponds to a set of sequential pseudo-first-order reactions. The situation for the biphasic kinetics can be represented by the sequence shown in eq 4, where k_{obsd}^I and k_{obsd}^{II} are the respective pseudo-first-order rate constants.

$$A \xrightarrow{k_{obsd}^{I}} B \xrightarrow{k_{obsd}^{II}} C \tag{4}$$

In terms of absorbance values (D), the integrated rate expression for eq 4 is

$$D_t - D_\infty = C_1 \exp(-k_{obsd}^{I}t) + C_2 \exp(-k_{obsd}^{II}t) \tag{5}$$

For the case $k_{obsd}^I > k_{obsd}^{II}$, the constants are related to the initial concentration and molar absorptivity values (ϵ) by

$$C_1 = \frac{[A]_0\{k_{obsd}^{II}(\epsilon_A - \epsilon_C) - k_{obsd}^{I}(\epsilon_A - \epsilon_B)\}}{k_{obsd}^{II} - k_{obsd}^{I}} \tag{6}$$

$$C_2 = \frac{[A]_0 k_{obsd}^{I}(\epsilon_C - \epsilon_B)}{k_{obsd}^{II} - k_{obsd}^{I}} \tag{7}$$

The observed rate constants are functions of the concentrations of Hg^{2+} and H^+, constant in any run. The apparent molar absorptivities are also dependent on $[H^+]$ owing to the instantaneously established protonation equilibria of eq 2.

Table I. Data for a Typical Two-Stage Kinetic Experiment[a] on the Reaction of $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2(H_2O)$ with Hg^{2+}

t/s	$D_t - D_\infty$	Δ^b	t/s	$D_t - D_\infty$	Δ^b	t/s	$D_t - D_\infty$
0	0.734	0.219	180	0.457	0.061	540	0.235
20	0.690	0.190	200	0.437	0.052	640	0.202
40	0.653	0.167	220	0.418	0.044	760	0.166
60	0.615	0.143	240	0.402	0.039	820	0.152
80	0.584	0.126	260	0.386	0.034	940	0.130
100	0.552	0.107	280	0.370	0.028	1140	0.096
120	0.525	0.093	300	0.357	0.025	1360	0.070
140	0.500	0.080	380	0.308		1600	0.049
160	0.477	0.069	460	0.269		1900	0.030

[a] Conditions: 24.8 °C, 0.125 M H^+, 0.0613 M Hg^{2+}, 7.7 × 10^{-5} M $[(H_2O)Co(dmgH)_2]_2(CH_2)_4$, λ 450 nm, optical path 5 cm; ca. 20 s lag between time of mixing and tabulated zero time, [b] $\Delta = D_t - D_\infty - C_2 \exp(-k_{obsd}^{II}t)$; $C_2 = 0.515$.

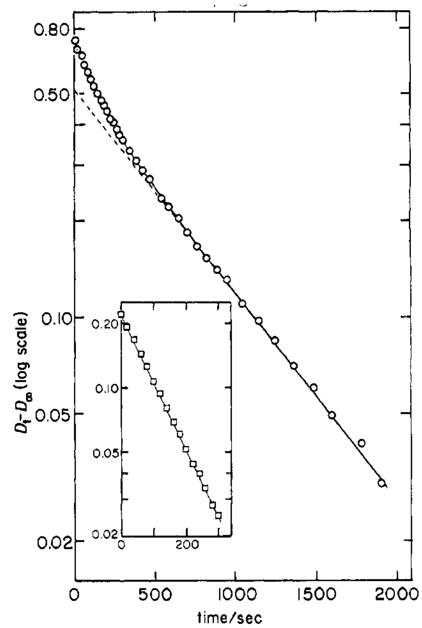

Figure 1. Plots for the two-stage kinetic data of Table I.

The biphasic kinetic data for reaction 3 were analyzed in terms of eq 5–7 by a plot of log $(D_t - D_\infty)$ vs. t. The second-stage rate constant, k_{obsd}^{II}, is given by the negative of the slope of the linear portion at long times. This straight line, extrapolated to zero time, is subtracted point-by-point from $D_t - D_\infty$; the logarithm of this difference, $D_t - D_\infty - C_2 \exp(-k_{obsd}^{II}t)$, is plotted against time giving as its slope the negative of the first-stage rate constant $-k_{obsd}^{I}$.

Data for a typical two-stage run are given in Table I, with the corresponding kinetic plots shown in Figure 1.

Results

Nucleophilic Reactions of $Bu_3PCo(dmgH)_2^-$. These reactions were studied under conditions quite similar to those used by Schrauzer and Deutsch,[9] utilizing a large excess of alkyl bromide. In view of this concentration excess, single-stage kinetics are closely adhered to, even by the potentially biphasic reaction of 1,4-dibromobutane.

The kinetic data, which are given in Table II, are consistent with the rate law

$$-d[Bu_3PCo(dmgH)_2^-]/dt = k_{Co}[Bu_3PCo(dmgH)_2^-][RBr] \tag{8}$$

Average values of k_{Co} at 25.0 °C in methanol with 1.5% H_2O and 0.05–0.18 M NaOH are the following: $n\text{-}C_4H_9Br$, 2.13 ± 0.03 M^{-1} s^{-1}; $Br(CH_2)_4Co(dmgH)_2py$, 2.04 ± 0.06 M^{-1} s^{-1}; $Br(CH_2)_4Br$, 9.51 ± 0.45 M^{-1} s^{-1}. For the latter, compare the published value,[9] 6.4 M^{-1} s^{-1} at ambient temperature; these results appear to be equivalent.

The reaction of 4-bromobutylcobaloxime with $Bu_3PCo(dmgH)_2^-$ was examined as a function of solvent composition, Scheme I

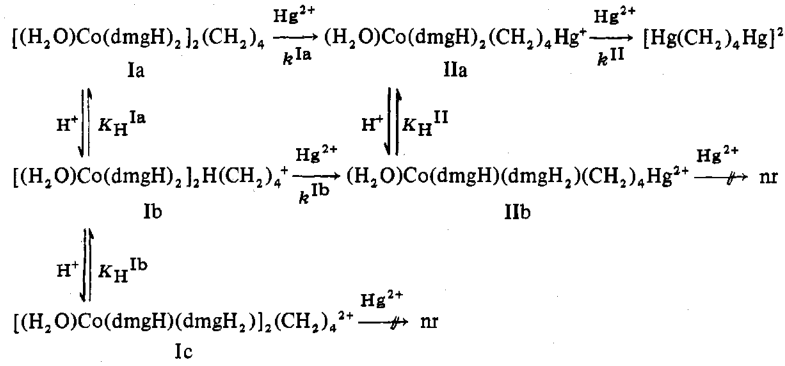

Table II. Kinetic Data for the Reaction of $Bu_3PCo(dmgH)_2^-$ with Alkyl Bromides[a]

RBr	10^3 × [RBr]/ M	C_{NaOH}/ M	k_{Br}/dm^3 mol^{-1} s^{-1}
n-C_4H_9Br	3.35	0.100	2.05
	3.35	0.183	2.12
	6.71	0.043	2.14, 2.20
	6.71	0.100	2.14
	6.71	0.183	2.13
$Br(CH_2)_4Co(dmgH)_2py$	0.81	0.100	2.06
	1.59	0.180	2.10
	1.63	0.100	2.04
	3.30	0.100	1.95
$Br(CH_2)_4Br$	1.53	0.090	8.95
	2.90	0.080	9.83
	2.90	0.190	10.4
	3.06	0.100	9.55
	3.06	0.183	9.83
	3.20	0.090	9.09
	5.66	0.100	8.94

[a] In CH_3OH (1.5% H_2O) at 25.0 °C; $[Bu_3PCo(dmgH)_2^-]_0 = 4.9 \times 10^{-5}$ M.

carrying data to much higher percent H_2O than the 2% level in methanol, which has been reported[9] to cause no change in rate compared to anhydrous methanol. Values of $k_{Co}/M^{-1}\ s^{-1}$ (H_2O/vol %) are 2.04 (1.5), 7.6 (4.6), 13.2 (8.2), and 20 (12.5).

Electrophilic Dealkylation and Protonation of Mononuclear Organocobaloximes. The reaction of n-butylcobaloxime in the presence of excess Hg^{2+} follows pseudo-first-order kinetics. The apparent second-order rate constant, $k_{obsd}/[Hg^{2+}]$, decreases with increasing $[H^+]$. The plot of $[Hg^{2+}]/k_{obsd}$ vs. $[H^+]$ is linear (Figure 2), consistent with the equation

$$-d \ln [n\text{-}C_4H_9Co(dmgH)_2H_2O]/dt = k[Hg^{2+}]/(1 + K_H[H^+]) \quad (9)$$

A least-squares fit gives the parameters $k = 0.095 \pm 0.005$ $M^{-1}\ s^{-1}$ and $K_H = 5.0 \pm 0.46\ M^{-1}$ from which are recalculated rate constants which differ from the experimental by an average of 3.0% and a maximum of 6.1%.

The reaction of Hg^{2+} with the butenyldicobaloxime occurs, as expected, in two stages. Using the procedure outlined in the Experimental Section (see Table I and Figure 1 also), the rate constants k_{obsd}^{I} and k_{obsd}^{II} were evaluated at different $[Hg^{2+}]$ and $[H^+]$. These data are summarized in Table III.

Consider first the values of k_{obsd}^{II}, which refers to the second-stage reaction of Hg^{2+} with the complex $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ (II). Using the symbolism in Scheme I, the rate expression, by analogy to eq 9, is given by eq 10.

$$-d \ln [II]/dt = k_{obsd}^{II} = k^{II}[Hg^{2+}]/(1 + K_H^{II}[H^+]) \quad (10)$$

A plot of $[Hg^{2+}]/k_{obsd}^{II}$ vs. $[H^+]$ is shown in Figure 2 and gives $k^{II} = 0.0336 \pm 0.0023\ M^{-1}\ s^{-1}$ and $K_H^{II} = 2.83 \pm 0.21\ M^{-1}$.

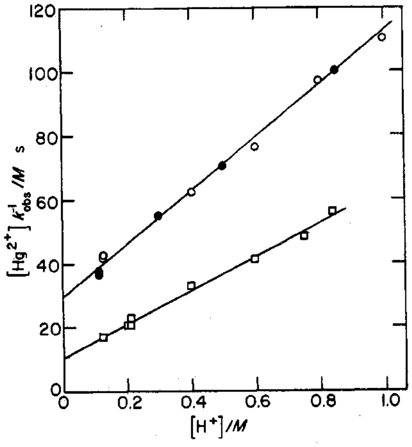

Figure 2. Linear variation of $[Hg^{2+}]/k_{obsd}$ with $[H^+]$ for the reaction of n-butylcobaloxime (□) and of the Co–Hg butenyl bridged complex II, the latter both from the second stage of reaction of I (○) and from the independently prepared and isolated sample of II (●).

Table III. Summary of Kinetic Data[a,b] for the Two-Stage Reaction of $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2(H_2O)$ with Hg^{2+}

$[H^+]$/M	$[Hg^{2+}]$/M	k_{obsd}^{I} × $[Hg^{2+}]^{-1}$/ $M^{-1}\ s^{-1}$	k_{obsd}^{II} × $[Hg^{2+}]^{-1}$/ $M^{-1}\ s^{-1}$	10^{-3} × ϵ_{II}/ $M^{-1}\ cm^{-1}$
0.125	0.0102	0.108	0.0219	1.49
0.125	0.0102	0.127	0.0272	1.26
0.125	0.0306	0.118	0.0236	1.50
0.125	0.0613	0.113	0.0238	1.27
0.125	0.0613	0.117	0.0238	1.29
0.402	0.0613	0.0625	0.0161	1.43
0.600	0.0613	0.0476	0.0131	1.52
0.800	0.0613	0.0392	0.0103	1.61
1.00	0.0102	0.0332	0.0091	1.41

[a] At 24.8 °C, $[[(H_2O)Co(dmgH)_2]_2(CH_2)_4]_0 = (4\text{–}9) \times 10^{-5}$ M, $\mu = 1.03$ M, in water. [b] In methanol–water, 22% CH_3OH by volume, at 0.125 M H^+, 24.8 °C, $\mu = 1.03$ M, $k_{obsd}^{I}/[Hg^{2+}] = 0.157 \pm 0.004\ M^{-1}\ s^{-1}$ and $k_{obsd}^{II}/[Hg^{2+}] = 0.032 \pm 0.001\ M^{-1}\ s^{-1}$.

In support of this interpretation, three further sets of experiments were done. First the complex $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ (II) was prepared and isolated by slow addition of Hg^{2+} to a well-stirred solution of the dicobaloxime and was precipitated with iodide. The complex could be redissolved in excess aqueous $AgClO_4$, and its subsequent reaction with Hg^{2+} was initiated by addition of $Hg(ClO_4)_2$. The latter reaction followed good pseudo-first-order kinetics, with rate constants in good agreement with k_{obsd}^{II} obtained from the biphasic kinetic treatment as illustrated in Figure 2.

The second verification for this part of the reaction scheme is based on a direct determination of K_H^{II}. Solutions of II were made up from the isolated iodide at various $[H^+]$, and the

Table IV. Summary of Statistically Corrected Rate and Equilibrium Constants

	Compd				
Parameter	n-C_4H_9X	$X(CH_2)_4X$	$(Co)(CH_2)_4Br$	$X(CH_2)_4Hg^+$	$X(CH_2)_4(Co)H^+$
k_{Co}/dm^3 mol^{-1} s^{-1} (X = Br)	2.13 ± 0.03	4.8 ± 0.2^a	2.04 ± 0.06		
k_{Hg}/dm^3 mol^{-1} s^{-1} (X = Co(dmgH)$_2$)	0.095 ± 0.005	0.103 ± 0.003^a		0.0336 ± 0.0023^c	0.064 ± 0.003^c
K_H/dm^3 mol^{-1} (X = Co(dmgH)$_2$)	5.0	5.0^a		2.8	3.0^b

[a] Statistically adjusted parameter, (experimental value)/2. [b] Statistically adjusted parameter, (experimental value) × 2. [c] At ionic strength 1.03 M.

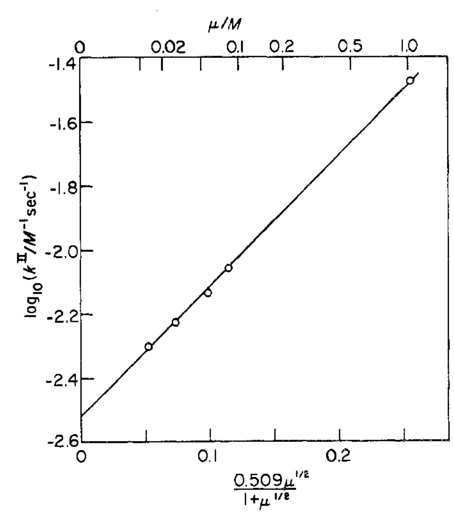

Figure 3. Ionic strength dependence of k^{II}.

absorbances measured at λ 400 or 450 nm, wavelengths at which the two forms, IIa and IIb, have slightly different molar absorptivities. The $[H^+]$ dependence of the absorption spectrum at a given $[Co]_T$ permits the evaluation of K_H^{II} as shown by eq 11

$$(D - D_0)/[H^+] = D_1K_H^{II} - DK_H^{II} \qquad (11)$$

in which D_0 represents the measured absorbance at $[H^+] \ll K_H^{II}$ (in practice, 0.010 M H^+) and D_1 represents that at $[H^+] \gg K_H^{II}$ (D_1 not measured but treated as a parameter). Values of K_H^{II} computed from the slopes in one determination at 400 nm and in three determinations at 450 nm are 3.2 ± 0.3, 3.9 ± 0.1, 4.0 ± 0.2, and 3.1 ± 0.2 M^{-1}. These values are in satisfactory agreement with that determined from the kinetic data, 2.8 ± 0.2. We regard the latter as likely to be more nearly correct.

A third set of experiments to verify the assignments made consists of a study of the effect of ionic strength variation upon k^{II}. These experiments utilized the independently prepared and isolated complex $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ and consisted of experiments having $[H^+] \ll K_H^{II}$, 0.0100 M H^+, to avoid corrections arising from the value of K_H^{II} and particularly its ionic strength dependence. Values of $10^3k^{II}/M^{-1}\ s^{-1}$ (24.8 °C) are 4.96, 5.94, 7.34, and 8.81 at μ/M = 0.0146, 0.0284, 0.0569, and 0.0855, respectively; in addition to these values there is the value 0.0336 $M^{-1}\ s^{-1}$ determined at μ = 1.03 M. Figure 3 shows a plot of log k^{II} vs. $0.509\mu^{1/2}/(1 + \mu^{1/2})$, which is linear with a slope of +4.06 and an extrapolated value of k^{II} (μ = 0) of $2.95 \times 10^{-3}\ M^{-1}\ s^{-1}$. In support of the assigned reaction step, this is consistent with the expected ionic strength dependence for the rate of reaction of dipositive Hg^{2+} with the unipositive $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ (theoretical slope, $2Z_AZ_B$ = +4.0).

Electrophilic Dealkylation and Protonation of the Binuclear Dicobaloxime. We return now to the first stage of reaction between the dicobalt complex and Hg^{2+}. Complexes Ia and Ib both contain an unprotonated alkylcobaloxime center, and hence will at least in principle react with Hg^{II}, whereas the fully protonated Ic will not.[11,12] Using the notation in Scheme I, the indicated kinetic scheme leads to the rate equation shown in eq 12. In view of the large number of parameters involved,

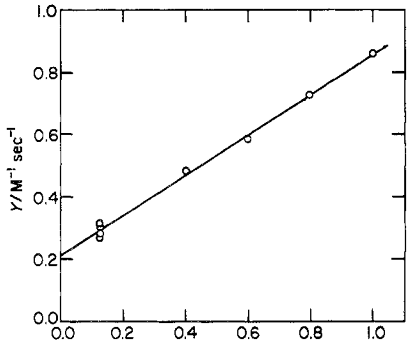

Figure 4. A plot of Y $(=k_{obsd}^{I}[Hg^{2+}]^{-1}(1 + K_H^{Ia}[H^+] + K_H^{Ia}K_H^{Ib}[H^+]^2))$ vs. $[H^+]$ in accord with eq 12.

$$\frac{-d\ln[I]}{dt} = k_{obsd}^{I} = \frac{(k^{Ia} + k^{Ib}K_H^{Ia}[H^+])[Hg^{2+}]}{1 + K_H^{Ia}[H^+] + K_H^{Ia}K_H^{Ib}[H^+]^2} \qquad (12)$$

the computation was based on values of protonation constants determined spectrophotometrically. The equation for the absorbance of the three-component protonation equilibrium by which species Ia, Ib, and Ic are related is given by eq 13.

$$\left(\frac{D - D_0}{D_1 - D}\right)\frac{1}{[H^+]} = K_H^{Ia} + K_H^{Ia}K_H^{Ib}\left(\frac{D_2 - D}{D_1 - D}\right)[H^+] \qquad (13)$$

The absorbances D_0, D_1, and D_2 represent respective values for the individual species Ia, Ib, and Ic, and D represents the measured absorbance[18] at a given $[H^+]$ (experimental range, 0.10–1.0 M). Values of D_0 and D_2 were determined directly, from measurements at 0.010 and 3.50 M H^+, respectively. Under the *assumption* that the half-protonated species Ib has an absorbance which is just the average of these two (i.e., $D_1 = {}^1/_2(D_0 + D_2)$), a plot of the data according to eq 13 is linear and gives the values K_H^{Ia} = 10.0 ± 1.0 M^{-1} and K_H^{Ib} = 1.48 ± 0.21 M^{-1}.

As suggested by a rearranged form of eq 12, a plot of $k_{obsd}^{I}(1 + K_H^{Ia}[H^+] + K_H^{Ia}K_H^{Ib}[H^+]^2)[Hg^{2+}]^{-1}$ vs. $[H^+]$ should be linear with intercept k^{Ia} and slope $k^{Ib}K_H^{Ia}$ (see Figure 4). The rate constants so obtained are k^{Ia} = 0.207 ± 0.007 $M^{-1}\ s^{-1}$ and k^{Ib} = 0.064 ± 0.003 $M^{-1}\ s^{-1}$.

Discussion

Previous work on monofunctional compounds has thoroughly delineated the nature of the nucleophilic displacement of halide by $Co(dmgH)_2^-$,[9,10] of the electrophilic dealkylation by Hg(II),[11,12,14,15] and of protonation of coordinated dimethylglyoxime.[11-13] The significance of the present work lies in the comparisons it provides of the possible change in chemistry or in the magnitudes of the parameters for difunctional compounds compared to their monofunctional analogues.

The data are summarized in Table IV and give rise to several interesting comparisons as follows. (1) Values of k_{Co}

for reaction 1 for the two monobromides $n\text{-}C_4H_9Br$ and $Co(dmgH)_2(CH_2)_4Br$ are virtually identical, 2.13 and 2.04 M^{-1} s^{-1}. The value of k_{Co} for the dibromide $Br(CH_2)_4Br$, after statistical correction, is more than twice this value, 4.8 M^{-1} s^{-1}. This appears to constitute a substantial neighboring group effect, although the discrepancy is hardly dramatic.

(2) Values of K_H for the *n*-alkylcobaloximes $RCo(dmgH)_2H_2O$ increase monotonically with the size of the alkyl: R = CH_3 (K_H = 3.5 M^{-1}),[11] C_2H_5 (4.2),[11] $n\text{-}C_3H_7$ (4.3),[11] and the present $n\text{-}C_4H_9$ (5.0). The changes although small are consistent with the expected inductive effect.

(3) Values of K_H for analogous complexes, once corrected for statistical effects,[19,20] are virtually identical. Thus the value of K_H^{Ia} (=10.0 M^{-1}) for protonation of $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2(H_2O)$ (Ia) becomes $K_H^{Ia}(\text{cor}) = 5.0\ M^{-1}$, a value identical with that of the neutral *n*-butylcobaloxime, and the value of K_H^{Ib} (=1.48 ± 0.21 M^{-1}) for protonation of the bridged dicobalt monocation $(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)(dmgH_2)(H_2O)^+$ (Ib) becomes $K_H^{Ib}(\text{cor}) = 3.0\ M^{-1}$, in good agreement with K_H^{II} (=2.8 ± 0.2 M^{-1}) for protonation of the monocationic Co–Hg bridged complex $(H_2O)Co(dmgH)_2(CH_2)_4Hg^+$ (Ic).

(4) Rate constants for dealkylation by Hg^{2+}, again corrected for statistical effects, afford interesting comparisons. The value of k^{Ia} (=0.207 ±0.007 M^{-1} s^{-1}) for the neutral dicobalt complex Ia becomes $k^{Ia}(\text{cor}) = 0.10\ M^{-1}\ s^{-1}$ which can be compared to the nearly identical value for *n*-butylcobaloxime, $k = 0.095 \pm 0.005\ M^{-1}\ s^{-1}$.

(5) A comparison can be made directly between the rate constants for reaction of Hg^{2+} with the two monocationic cobaloximes; the value for the half-protonated dicobaloxime is $k^{Ib} = 0.064 \pm 0.003\ M^{-1}\ s^{-1}$ and for the cobalt–mercury cation it is $k^{II} = 0.034 \pm 0.002\ M^{-1}\ s^{-1}$. Here the agreement is again not exact, although the discrepancy is small. Certainly no new or metal–metal interactive effects are suggested. This comparison, however, is the least satisfactory in any event, in that these cation–cation reactions are subject to significant salt effects.

(6) No valid comparison can be attempted between the reactions of Hg^{2+} with the unprotonated dicobaloxime ($k^{Ia}(\text{cor}) = 0.10\ M^{-1}\ s^{-1}$) and its half-protonated analogue ($k^{Ib} = 0.064\ M^{-1}\ s^{-1}$ at $\mu = 1.0$ M). Whereas the former value would be nearly independent of ionic strength, the latter should increase markedly with increasing ionic strength. The magnitude of the salt effect in k^{Ib} can be estimated from that determined experimentally for k^{II}. (The latter characterizes a similar reaction of the same charge-type ions, whose rate constant follows rather closely the extended Brönsted–Debye–Hückel relation). On this basis the estimate for k^{Ib} at $\mu = 0$ is ca. 0.006 M^{-1} s^{-1}. The (roughly μ independent) value of $k^{Ia}(\text{cor})$ exceeds this extrapolated value of k^{Ib} ($\mu = 0$) by over a factor of 16. A comparison of reactions of different charge types seems sufficiently questionable, however, that one could not confidently claim that one of these values is remarkable.

One comparison of reactivity that is particularly striking is afforded by the results of Collman and MacLaury[6] on the reaction of a neutral $Rh^I(N_4$ chelate) complex[21] with $Br(CH_2)_4Br$. The authors provide convincing evidence that their reactions occur by the same nucleophilic displacement mechanism found for $Co^I(dmgH)_2^-$. Yet they isolate only the 1,4-tetramethylenedirhodium product $BrRh(N_4chel)(CH_2)_4Rh(N_4chel)Br$, even at concentrations expected to favor the mononuclear product $BrRh(N_4chel)(CH_2)_4Br$. They thus infer that the second stage of reaction between the latter complex and $Rh^I(N_4chel)$ occurs very much faster than the first stage, which shows but a slight rate enhancement over the rate for *n*-bromobutane. This remarkable neighboring group effect is absent in the corresponding reactions of $Co^I(dmgH)_2^-$, although the cobalt and rhodium reactions and their mechanisms seem otherwise identical.

A final example from vitamin B_{12} chemistry is related to the present work. The product is less well characterized, and the rate effects only qualitatively noted, but Smith et al[22] examined the reaction of B_{12s} (=Co^I(corrin)) with $Br(CH_2)_4Br$. They easily isolated a material they suggested to be the bromide-free "tetramethylene dicobalamin", and only under forcing concentration conditions and even then in low yield was a sample of the 4-bromobutylcobalamin obtained. They attribute this unusual effect to a great but unexplained difference in reactivity toward the B_{12s} nucleophile. Thus these qualitative results in the cobalamin system resemble those for the $Rh(N_4chel)$ system far more than they do our findings for cobaloxime reactions.

Lack of an intramolecular dealkylation pathway for the cobalt–mercury complex II comes as no surprise; monoalkylmercury derivatives have been shown[11,12] to be quite unreactive with alkylcobaloximes, in contrast to their ready reaction with closely related but more reactive organochromium complexes.[23]

Registry No. I, 63848-49-7; Ia, 63848-48-6; Ib, 63902-71-6; IIa, 63915-10-6; $n\text{-}C_4H_9Co(dmgH)_2py$, 30974-87-9; $\omega\text{-}Br(CH_2)_4Co(dmgH)_2py$, 15228-02-1; $pyCo(dmgH)_2(CH_2)_4Co(dmgH)_2py$, 63902-70-5; $Bu_3PCo(dmgH)_2^-$, 63902-69-2; $n\text{-}C_4H_9Br$, 109-65-9; $n\text{-}C_4H_9Co(dmgH)_2H_2O$, 30974-86-8; $Br(CH_2)_4Br$, 110-52-1; Hg^{2+}, 14302-87-5.

References and Notes

(1) Work performed for U.S. Energy Research and Development Administration, Division of Physical Research, under Contract No. W-7405-eng-82.

(2) The chelates referred to are the following: $(dmgH)_2$, bis(dimethylglyoximato) or "cobaloxime"; bae, the dianion of bis(acetylacetone) ethylenediimine; dpnH, the monoanion of 3,3′-(trimethylenediimino)-bis(butan-2-one oximato).

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(17) In neutral methanol the various organocobalt complexes show the following peaks [λ, nm (ε, M^{-1} cm^{-1})]: $n\text{-}C_4H_9Co(dmgH)_2py$, 450 (1270), 330 (1740); $4\text{-}Br(CH_2)_4Co(dmgH)_2py$, 450 (1360), 325 (1850); $pyCo(dmgH)_2(CH_2)_4Co(dmgH)_2py$, 450 (2700), 340 (3500).

(18) Experimental absorbances (λ 405 nm, *b* = 2.00 cm on an arbitrary scale) for a series of solutions having identical cobalt concentrations, varying $[H^+]$, $\mu = 1.025$ M (with $LiClO_4$) at 23.5 ± 2 °C are the following: *D* = 0.300 ($[H^+]$ = 0.010 M), 0.420 (0.102), 0.443 (0.153), 0.463 (0.204), 0.500 (0.305), 0.531 (0.509), 0.560 (0.764), 0.594 (1.02), and 0.670 (3.50).

(19) These corrections are the same as those for the ionizations of a dicarboxylic acid and may be made based upon the respective number of sites available for protonation and deprotonation or more rigorously by the ratio of rotational symmetry numbers.[20]

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(21) The chelate structure[6] is quite similar to $(dmgH)_2$, although the chelate itself carries a charge 1− rather than 2−.

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