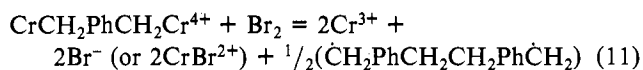react with aqueous bromine, iodine, and iodine monobromide in a reaction of straightforward stoichiometry and kinetics ($CrCH_2Ph^{2+}$ + X_2 → Cr^{3+} + $PhCH_2X$ + X^-), for which kinetic comparisons suggest an S_E2 mechanism, like that between organochromium cations and mercury(II) ion.[18] One might thus have expected that the dichromium complexes would also have reacted sequentially, as they appear to do[4] with mercury(II), first forming a monochromium cation and then the dibromide: $[CrCH_2PhCH_2Cr]^{4+}$ → $[CrCH_2PhCH_2Br]^{2+}$ → $BrCH_2PhCH_2Br$. The middle member has been made for the two complexes II and VII,[4] but from reaction of the appropriate dibromide with chromium(II) and not via bromine. It proves to be a stable species, however, typical of other monochromium cations. We did not perform kinetic determinations, but the reactions between the dichromium cations and aqueous bromine occur very rapidly, appearing complete upon mixing. This establishes that the mechanism is direct attack and not unimolecular homolysis. Two possible explanations come to mind. Reaction may occur by an oxidative pathway in which an organochromium complex capable of initiating polymerization is produced. Or a low concentration of atomic bromine may prove sufficient to function similarly. Further resolution does not appear possible at this point, although we note the recent report[35] of reductive

coupling induced by oxidation. Similar chemistry applied to the systems at hand would lead to a reaction, eq 11, which would result ultimately in polymer formation.

$$CrCH_2PhCH_2Cr^{4+} + Br_2 = 2Cr^{3+} +$$
$$2Br^- \text{ (or } 2CrBr^{2+}) + \frac{1}{2}(\dot{C}H_2PhCH_2CH_2Ph\dot{C}H_2) \quad (11)$$

Registry No. I, 71837-75-7; II, 71886-74-3; III, 71837-76-8; IV, 71837-77-9; V, 71837-78-0; VI, 71837-79-1; VII, 69493-83-0; *m*-$CrCH_2C_6H_4CH_2OH^{2+}$, 71886-75-4; *p*-$CrCH_2C_6H_4OH^{2+}$, 71837-80-4; *p*-$CrCH_2C_6H_4Ph^{2+}$, 71886-76-5; Cu(II), 15721-63-8; Co(III), 22541-63-5; Fe(III), 20074-52-6; α,α'-dibromo-*m*-xylene, 626-15-3; α,α'-dibromo-*p*-xylene, 623-24-5; 4,4'-bis(bromomethyl)-biphenyl, 20248-86-6; 4,4'-bis(bromomethyl)diphenylmethane, 16980-01-1; 4,4'-bis(bromomethyl)-1,2-diphenylethane, 6337-67-3; 4,4'-bis(bromomethyl)diphenyl ether, 4542-75-0; 2,4-bis(bromomethyl)toluene, 56752-76-2; *p*-phenylbenzyl bromide, 2567-29-5; *p*-(bromomethyl)benzyl alcohol, 71831-21-5; *p*-pyCo-(dmgH)$_2$CH$_2$C$_6$H$_4$CH$_2$OH, 71837-81-5; *p*-[pyCo(dmgH)$_2$CH$_2$]$_2$C$_6$H$_4$, 36425-45-3.

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Kinetics and Mechanism of Adduct Formation between Iron(III) and Bis(dimethylglyoximato)cobalt(III) Complexes

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Iron(III) ion undergoes a reversible association with methyl(aquo)cobaloxime and with diaquocobaloxime in which it replaces the hydrogen-bonded proton in one O–H···O group of the parent cobaloxime. Equilibrium constants for the reaction Fe^{3+} + $[XCo^{III}(dmgH)_2H_2O]^n$ = $[XCo(dmg_2HFe)H_2O]^{n+2}$ + H^+ were evaluated at 25 °C, the values for X = CH_3^- being 16.2 ± 0.5 (μ = 0.10 M) and 15.3 ± 0.8 (μ = 1.0 M) and for X = H_2O, 2.55 ± 0.055 (μ = 1.0 M). The rates of both reactions were determined at various concentrations of iron(III) and hydrogen ion, with results consistent with the equilibrium nature of the reactions. The rate laws and rate constants determined are consistent with the mechanism being a process of ligand substitution on iron(III) but are perhaps better explained by a mechanism common to every pathway in which the rate-limiting step is neutralization of the hydrogen-bonded proton of O–H···O by $(H_2O)_5FeOH^{2+}$ with concurrent incorporation of iron into the oxime bridging position.

Introduction

Some metal complexes with planar, tetradentate chelating ligands are able to form adducts with a second metal ion. Most such adducts reported are formed between the bis(salicylaldimine) complexes of divalent transition metals and a variety of metal ions.[2–6] Shifts in the ^1H NMR spectrum and changes in the visible spectrum which occur when various metal ions are added to the organometallic complex $CH_3Co(salen)H_2O$ (salen = N,N'-ethylenebis(salicylideniminato)) have been ascribed to similar adduct formations[7] whereby cobalt(III) and

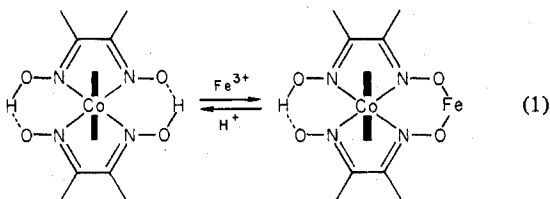the second metal ion are bridged by the two oxygen atoms of the macrocyclic salen ligand.

The possibility of bis(dimethylglyoximato)metal complexes forming similar Lewis acid–base adducts is less obvious owing to intramolecular hydrogen bonding in the pseudomacrocycle. However, replacement of hydrogen in such an O–H···O group takes place readily when $RCo(dmgH)_2B$ (R = alkyl group, B = H_2O or organic base such as pyridine or phosphine, and dmgH = the monoanion of dimethylglyoxime) reacts with boron trifluoride etherate forming $RCo(dmgBF_2)_2B$ containing two O–BF_2–O units.[8] Compounds such as $ClCo(dmgBF_2)_2PBu_3$[9] and $ClCo(dmg_2HBF_2)PBu_3$,[10] the latter

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having one O–H···O and one O–BF$_2$–O unit, have also been prepared and isolated. Similarly K$_3$[Co(dmg)$_3$], in which all three of the dmg^{2-} ligands are bound to cobalt(III) through nitrogen atoms, reacts with boron trifluoride[11] and with a variety of transition metal complexes[12] to form [Co(dmg)$_3$-(BF)$_2$]$^+$ and Co(dmg)$_3$(ML$_3$)$_2$]$^{n+}$, in which the arrays of oxygen atoms on opposite sides of Co(dmg)$_3$$^{3-}$ serve as a pair of tridentate ligands toward BF and ML$_3$ groups.
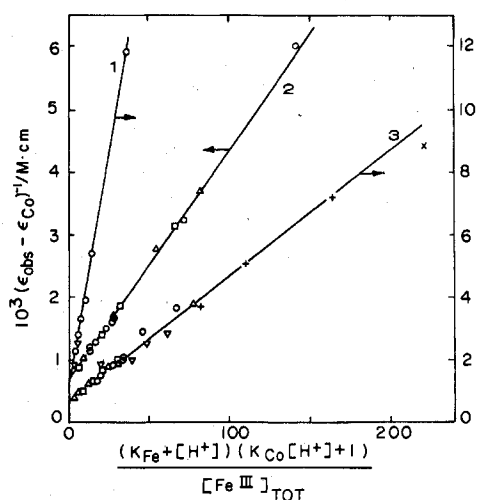
We have found that the hexaaquoiron(III) ion forms similar 1:1 complexes in aqueous solution with organometallic and inorganic bis(dimethylglyoximato)cobalt(III) complexes. A preliminary account of these findings has been published,[13] and we report here the complete results of a study of two such complexes. Equilibrium and kinetic data have been obtained for the two complexes CH$_3$Co(dmgH)$_2$H$_2$O and [(H$_2$O)$_2$Co-(dmgH)$_2$]$^+$, each of which reacts with iron(III) in aqueous solution to form a pseudomacrocycle (dmg$_2$HFe) in which one O–H···O group has been replaced by iron(III). The general reaction, charges omitted, is

$$
\text{(structure)} \quad \xrightarrow[\text{H}^+]{\text{Fe}^{3+}} \quad \text{(structure)} \quad (1)
$$

Experimental Section

Materials. Methyl(aquo)cobaloxime[14] was prepared by a published procedure.[15] The diaquo complex [(H$_2$O)$_2$Co(dmgH)$_2$](ClO$_4$) was prepared from [Cl$_2$Co(dmg$_2$H$_3$)][16] by stirring a suspension of the latter for several hours with an equivalent amount of silver perchlorate. After coagulation and filtration of silver chloride, the desired product was crystallized by addition of saturated, aqueous lithium perchlorate and prolonged cooling. The purity of both cobalt complexes was checked by UV–visible spectra and by cobalt analysis.[17] Methyl(aquo)cobaloxime has absorption maxima in 0.1 M perchloric acid at 440 nm (ϵ 1.4 × 10^3 M^{-1} cm^{-1}) and 385 (1.71 × 10^3). Anal. Calcd: Co, 18.3. Found: Co, 18.0 ± 0.2. The diaquo complex had λ_{max} 240 nm (ϵ 2.10 × 10^4 M^{-1} cm^{-1}); no maximum is seen in the visible spectrum, but the absorption rises sharply into the UV, with a point of inflection near 260 nm. Crystalline iron(III) perchlorate hydrate was prepared from the chloride;[18] some perchloric acid adheres to the crystals. Solutions of this salt were analyzed for iron and for perchloric acid by published methods.[18]

Equilibrium and Kinetic Data. Spectrophotometric measurements were made by using a Cary Model 14 recording spectrophotometer with a thermostated cell compartment. Most measurements were done at λ 525 nm where the cobaloxime reactants absorb weakly and the 1:1 adducts with iron(III) absorb strongly (ϵ ~>10^3 M^{-1} cm^{-1}). Temperature was controlled at 25.0 °C and ionic strength, using perchloric acid–lithium perchlorate, at 0.10 or 1.0 M as desired. Equilibrium constants were calculated from the equilibrated absorbance values with an iterative estimation of concentrations. Two types of kinetics experiments were done. In the first type, solutions of iron(III) and methyl(aquo)cobaloxime (or diaquocobaloxime) were mixed rapidly, and the absorbance increase at 525 nm accompanying formation of the adduct was recorded. In the second type of experiment, solution of the reactants equilibrated at a lower hydrogen ion concentration was diluted with a small volume of more concentrated acid. The dilution and increase in [H$^+$] caused a shift in the equilibrium position toward the left. The reaction was monitored by
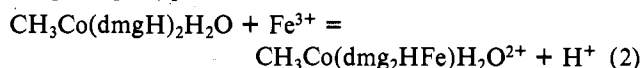

Figure 1. Evaluation of the equilibrium constants at 25.0 °C for reactions 2 and 6 according to a linearized form of eq 5. The lines shown are the least-squares fit to the nonlinear form of eq 5. Different [H$^+$] are shown as follows: 0.02 M H$^+$, △; 0.05, □; 0.10, ○; 0.20, ▽; 0.50, +; 0.90, ×. Line 1 refers to eq 6, and lines 2 and 3 to eq 2 at respective ionic strengths 0.10 and 1.0 M.

recording the absorbance decrease. The latter experiments were especially useful in deriving data at high [H$^+$] where direct mixing experiments are of marginal value since the adduct forms only to a slight extent.
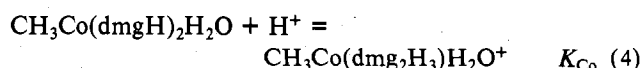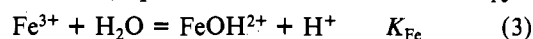
Concentration conditions were chosen such that the reaction approached equilibrium following pseudo-first-order kinetics. From the recording of absorbance, *D*, with time, plots of log [(*D*$_\infty$ – *D*$_t$)/(*D*$_\infty$ – *D*$_0$)] vs. time were constructed. These plots were linear and gave slopes from which were calculated values of k_{obsd}, a sum of apparent forward and reverse rate constants.

Results

Equilibrium. Addition of Fe^{3+} to a solution of CH$_3$Co-(dmgH)$_2$H$_2$O in dilute perchloric acid results in formation of a dark brown coloration and in intensification of the UV–visible spectrum. Conversely, acidification of the solution causes a reversible decoloration and a return at [H$^+$] > 1 M to the original spectrum of iron(III) ions and methyl(aquo)-cobaloxime. In terms of the predominant species in solution the principal equilibrium is

$$
\text{CH}_3\text{Co(dmgH)}_2\text{H}_2\text{O} + \text{Fe}^{3+} =
$$
$$
\text{CH}_3\text{Co(dmg}_2\text{HFe)H}_2\text{O}^{2+} + \text{H}^+ \quad (2)
$$

The form of this equilibrium reaction was confirmed, and its equilibrium constant at 25.0 °C evaluated, by spectrophotometric measurements over a range of concentrations of iron(III) ion, hydrogen ion, and methylcobaloxime. The quantitative treatment requires consideration of two additional equilibria which enter to minor but nonetheless appreciable extents; these are the acid ionization of the hydrated iron(III) ion, eq 3, and the protonation of the oxime oxygens of methyl(aquo)cobaloxime, eq 4. The former reaction[19] has K_{Fe} =

$$
\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+ \qquad K_{Fe} \quad (3)
$$

$$
\text{CH}_3\text{Co(dmgH)}_2\text{H}_2\text{O} + \text{H}^+ =
$$
$$
\text{CH}_3\text{Co(dmg}_2\text{H}_3)\text{H}_2\text{O}^+ \qquad K_{Co} \quad (4)
$$

2.9 × 10^{-3} M (μ = 0.10 M) and 1.65 × 10^{-3} M (μ = 1.0 M), and the latter[20,21] K_{Co} = 3.2 M^{-1} (μ = 1.0 M, assumed to be independent of ionic strength considering that ΔZ^2 = 0 for eq 4). The absorbance reading at equilibrium affords a value of ϵ_{obsd} (=D_{eq}/b[CH$_3$Co]$_{tot}$), and the molar absorptivity of the

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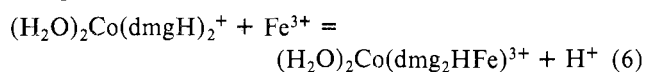(18) Carlyle, D. W.; Espenson, J. H. *Inorg. Chem.* **1967**, *6*, 1370.

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(20) Adin, A.; Espenson, J. H. *Chem. Commun.* **1971**, 653.
(21) Abley, P.; Dockel, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166.

parent cobaloxime, ϵ_{Co}, is known.[22] If $[Fe(III)]_f$ is used to represent $[Fe^{3+}] + [FeOH^{2+}]$, the equation relating these quantities is

$$\epsilon_{obsd} - \epsilon_{Co} = \frac{(\epsilon_1 - \epsilon_{Co})K[Fe(III)]_f}{P + K[Fe(III)]_f} \quad (5)$$

with P representing the known composite $(K_{Fe} + [H^+])(K_{Co}[H^+] + 1)$ and ϵ_1 the molar absorptivity of the adduct. Data can be fit graphically as $(\epsilon_{obsd} - \epsilon_{Co})^{-1}$ vs. $P/[Fe(III)]_f$ as shown in Figure 1 or by a nonlinear least-squares program directly to the form of eq 5. The latter method affords the values $K_2 = 16.2 \pm 0.5$ and $\epsilon_1 = (1.70 \pm 0.08) \times 10^3$ M^{-1} cm^{-1} at $\mu = 0.10$ M and $K_2 = 15.3 \pm 0.8$ and $\epsilon_1 = (1.67 \pm 0.12) \times 10^3$ M^{-1} cm^{-1} at $\mu = 1.00$ M. The lines drawn in Figure 1 correspond to these values. In this calculation it is necessary to estimate $[Fe(III)]_f$ using an approximate value of the equilibrium constant for the iron–cobalt complexation reaction; iron(III) was in considerable excess, however, and a single iteration provided convergence. The data that were obtained[23] gave an excellent fit, without any systematic deviations, to eq 5 over the range of concentrations $0.02 \le [H^+] \le 0.90$ M and $3 \times 10^{-4} \le [Fe(III)] \le 0.016$ M that no additional processes, such as complexation of a second iron(III), needed to be invoked under these conditions.
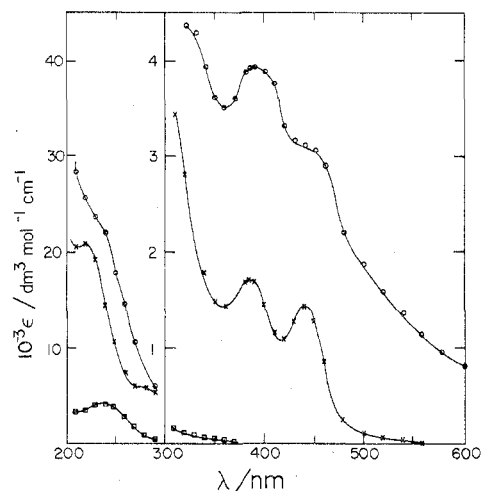
This interaction is not unique to the organometallic complex. The inorganic diaquocobalt(III) complex reacts similarly with iron(III) ion to produce a dark brown complex. This equilibrium is also reversed at high hydrogen ion concentration. The principal equilibrium is

$$(H_2O)_2Co(dmgH)_2^+ + Fe^{3+} =$$
$$(H_2O)_2Co(dmg_2HFe)^{3+} + H^+ \quad (6)$$

Similar equilibrium data[23] at 25.0 °C and 1.0 M ionic strength, covering 0.02–0.1 M H^+ and $(3.0–21) \times 10^{-3}$ M Fe(III), were evaluated according to eq 5 (now, however, with $K_{Co} = 0$). The graphical presentation is also shown in Figure 1 and a nonlinear least-squares fit gives the value $K_6 = 2.55 \pm 0.05$ with the molar absorptivity of the adduct at 525 nm found to be $(1.38 \pm 0.04) \times 10^3$ M^{-1} cm^{-1}.

With the equilibrium constants K_2 and K_6 known, the entire spectrum of each adduct can be calculated on the basis of the known molar absorptivities of the reactants. In both cases the adducts have spectra that are described most simply as intensified spectra of the parent cobaloxime itself. The spectrum of $CH_3Co(dmg_2HFe)H_2O^{2+}$, for example, shows λ_{max} 450 nm (sh, ϵ 3 × 10³) and 390 (ϵ 3.9 × 10³) which matches well the parent complex but with ϵ values over twice as great. The entire spectrum is shown in Figure 2.

Kinetics. The rate of approach to equilibrium in reaction 2 was evaluated under concentration conditions such that one product (H^+) and one reactant (usually Fe^{3+}, sometimes $CH_3Co(dmgH)_2H_2O$) were present at high and essentially constant concentration. In this case, the reaction should approach equilibrium following pseudo-first-order kinetics with contributions from forward and reverse reactions as expected for opposing first-order reactions. These determinations yielded values[23] of k_{obsd} as indicated in the Experimental Section. Studies were carried out at 25.0 °C and ionic strengths of 0.10 and 1.0 M. In the former case, concentrations were varied in the limit 0.02–0.10 M H^+ and $(1–10) \times 10^{-3}$ M Fe^{3+} and in the latter 0.02–0.90 M H^+ and $(1–16) \times 10^{-3}$ M Fe^{3+}.

(22) The value of ϵ_{Co} is assumed to be the same for both of the cobaloxime species in reaction 4. These species contribute so little to the absorbance at 525 nm, however, with $\epsilon_{Co} \approx 73$ M^{-1} cm^{-1}, that this assumption is not a serious limitation.

(23) The equilibrium and kinetic data are given in the supplementary material.

Figure 2. Measured absorption spectra for iron(III) (□) and $CH_3Co(dmgH)_2H_2O$ (×), and the calculated spectrum for the adduct $[CH_3Co(dmg_2HFe)H_2O]^{2+}$ based on the measured spectrum of a mixture and the determined value of the equilibrium constant as explained in the text.

At each $[H^+]$, k_{obsd} varies linearly with the concentration of the excess reactant, as in the expression

$$k_{obsd} = k_f'[Fe(III)] + k_r' \quad (7)$$

(For runs with the cobalt complex in large excess, its concentration is to be substituted for $[Fe(III)]$ in this expression.) The dependence of k_{obsd} upon $[H^+]$ is complex and will now be analyzed; the complexity arises from three effects of $[H^+]$: (1) its shift of the protonation equilibria of the reactants, eq 3 and 4; (2) its appearance in the equilibrium constant expression for the principal equilibrium under study, eq 2; (3) its authentic entry in the kinetic equations, the form and degree of which this analysis seeks to establish. The first of these factors is allowed for by expressing the forward rate as a function of the concentrations of individual species; for this purpose we chose $Fe(H_2O)_6^{3+}$ and $CH_3Co(dmgH)_2H_2O$, whose concentrations are related to the total concentration by the expressions

$$[Fe^{3+}] = [Fe(III)]_f[H^+]/(K_{Fe} + [H^+]) \quad (8)$$

$$[CH_3Co(dmgH)_2H_2O] = [Co]_T/(K_{Co}[H^+] + 1) \quad (9)$$

Since the equilibrium constant K_2 is known from direct determination, its value can best be incorporated into the calculation directly, rather than treating it as an additional variable in the kinetics analysis. That is, the condition accompanying eq 7 is

$$k_r' = k_f'[H^+]/K_2 \quad (10)$$

The incorporation of eq 8–10 into the kinetic analysis is most clearly seen if the results of this analysis are anticipated. The rate in each direction consists of two terms differing by one power of $[H^+]$. Expressed in terms of the species indicated, the rate can be written as

$$d[A]/dt = (k_{1f} + k_{2f}[H^+]^{-1})[Fe^{3+}] \times$$
$$[CH_3Co(dmgH)_2H_2O] - (k_{1r}[H^+] +$$
$$k_{2r})[CH_3Co(dmg_2HFe)H_2O^{2+}] \quad (11)$$

Incorporation of eq 8–10 gives the following expression for k_{obsd}:

$$k_{obsd} = \left\{ \frac{k_{1f}[H^+] + k_{2f}}{(K_{Fe} + [H^+])(K_{Co}[H^+] + 1)} \right\}[Fe(III)] + \frac{k_{1f}[H^+] + k_{2f}}{K_2} \quad (12)$$
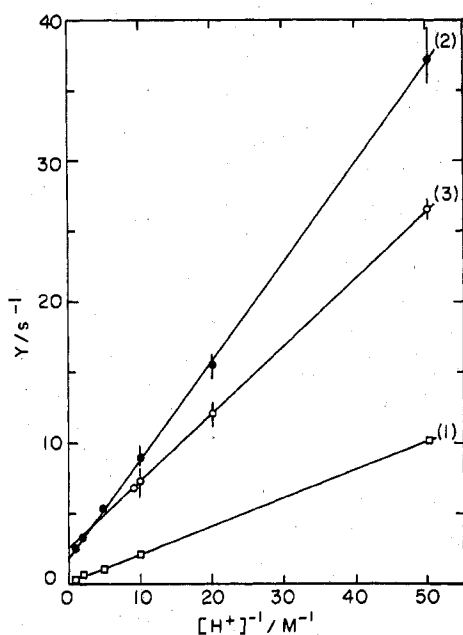
Figure 3. Treatment of the kinetic data at 25.0 °C for the reversible reactions of eq 2 and 6. The ordinate, Y, represents the left-hand side of eq 13, which is plotted against $[H^+]^{-1}$. The lines are numbered as in Figure 1.

If we symbolize the known composite $(K_{Fe} + [H^+])(K_{Co}[H^+] + 1)$ as P, eq 12 rearranges to

$$\frac{k_{obsd} P K_2}{[H^+]\{K_2[Fe(III)] + P\}} = k_{1f} + k_{2f}[H^+]^{-1} \qquad (13)$$

The left-hand side of this expression consists of known quantities;[23] a plot of this against $[H^+]^{-1}$ is linear at both ionic strengths as shown in Figure 3. The least-squares values are $k_{1f} = 2.37 \pm 0.17$ M^{-1} s^{-1} and $k_{2f} = 0.48 \pm 0.012$ s^{-1} ($\mu = 0.1$ M) and $k_{1f} = 1.80 \pm 0.04$ M^{-1} s^{-1} and $k_{2f} = 0.702 \pm 0.007$ s^{-1} ($\mu = 1.0$ M). Calculated values for the reverse reaction, based on the values of K_2 at each ionic strength, are $k_{1r} = 0.146 \pm 0.015$ M^{-1} s^{-1} and $k_{2r} = 0.030 \pm 0.002$ s^{-1} ($\mu = 0.10$ M) and $k_{1r} = 0.118 \pm 0.008$ M^{-1} s^{-1} and $k_{2r} = 0.046 \pm 0.003$ s^{-1} ($\mu = 1.0$ M). All values refer to 25.0 °C.

The diaquocobaloxime follows a similar kinetic pattern, but the reaction rate is dominated by the k_r' term of eq 7 since the equilibrium lies largely to the left of eq 6 except at high $[Fe^{3+}]$ and low $[H^+]$. Kinetic determinations covered these concentration ranges, 0.02–0.90 M H^+, (2.2–21.2) × 10^{-3} M Fe^{3+}, and (2–4) × 10^{-4} M $(H_2O)_2Co(dmgH)_2^+$, at ionic strength 1.0 M and 25.0 °C. Results were similar to those found for methylcobaloxime, except that the contribution of k_{1f}^{aq} (the rate constants are labeled as k^{aq} for the diaquo complex, for sake of clarity) proved to be negligible (0.01 $\pm$ 0.005 M^{-1} s^{-1}). The least-squares fit, now with $K_{Co} = 0$ for this complex, gave $k_{2f}^{aq} = 0.202 \pm 0.002$ s $^{-1}$. The calculated rate constant for the reverse reaction is $k_{2r}^{aq} = k_{2f}^{aq}/K_6 = 0.079 \pm 0.002$ s^{-1}.

An attempt was made to obtain a direct measure of the reverse rate of reaction 2, corresponding to decomposition of $[CH_3Co(dmg_2HFe)H_2O]^{2+}$. The plan was to add reagents known to react rapidly with free $CH_3Co(dmgH)_2H_2O$ and/or free Fe^{3+}, thereby pulling equilibrium 2 completely to the left. In one set of experiments, solutions of HF or $H_2C_2O_4$ were used to complex Fe^{3+} rapidly and thus remove it from the equilibrium. The reaction rates observed were, however, much higher than expected given the values of k_r' for eq 2 and were in addition a function of [HF] and $[H_2C_2O_4]$. These reagents thus react not only with Fe^{3+} but also directly with the adduct

$[CH_3Co(dmg_2HFe)H_2O]^{2+}$; consequently k_r' is not the rate-limiting step. In another set of experiments aqueous bromine was added to react rapidly with $CH_3Co(dmgH)_2H_2O$. The measured rate constant showed a dependence upon $[Br_2]$, again indicating a direct reaction of bromine and the adduct $[CH_3Co(dmg_2HFe)H_2O]^{2+}$. Similar runs were done with Hg^{2+}, and gave a pseudo-first-order reaction with $k_{obsd} = 0.083 \pm 0.003$ s^{-1} (20 runs), independent of $[Hg^{2+}]$ (0.02–0.11 M), $[H^+]$ (0.1–0.9 M), [Fe(III)] (0.5–5.0 mM), and $[CH_3Co(dmgH)_2H_2O]$ (0.1–1 mM). The value of k_{obsd} and its lack of variation with $[H^+]$ are not, however, characteristic of the values of k_r' for eq 2 (k_r' varies from 0.058 to 0.15 s^{-1} at 0.1–0.9 M H^+). Instead, the value 0.083 $\pm$ 0.003 s^{-1} corresponds quite well to that found for the reverse of reaction 6, decomposition of $[(H_2O)_2Co(dmg_2HFe)]^{3+}$, 0.079 $\pm$ 0.002 s^{-1}, independent of $[H^+]$. Thus these experiments did not succeed in their original purpose but did instead lead to the following conclusions: Hg^{2+} not only reacts rapidly to dealkylate $CH_3Co(dmgH)_2H_2O$ but also evidently dealkylates $[CH_3Co(dmg_2HFe)H_2O]^{2+}$ as well. The product of this reaction is then the adduct of iron(III) and the diaquo cobaloxime, but now present at a concentration exceeding its equilibrium value in eq 6. It is thus subject to reequilibrium by the reverse of this reaction, and under these concentration conditions equilibration in eq 6 is dominated nearly entirely by the contribution of the k_r' term to k_{obsd}.

Discussion

The Iron(III)–Cobaloxime Adduct. The principal equilibria of eq 2 and 6 are formulated as complexation of iron(III) at the oxime oxygen position. The evidence for coordination in this manner is in part negative; axial binding to give a structure such as $[L-Co-O(H)-Fe(aq)]$, leaving intact the $(dmgH)_2$ pseudomacrocycle, is not likely to occur with comparable formation constants for L = CH_3 ($K = 16$) and L = H_2O ($K = 2.6$), considering the very different acidity constants of the axial water molecules in the parent complexes.[24,25] That is to say, formation of $LCo(dmgH)_2OH^{n+}$, which has $pK_a \sim 12.7$ for L = CH_3 and ~ 4 for L = H_2O, reflects the strength with which the trans water molecule is coordinated in the parent complex. Clearly the methyl complex binds this water (and other bases) much less tightly than does the aquo complex, as reflected not only in these pK_a's but also in the kinetic trans effect[24,26,27] and chemical shifts[28] found for methylcobaloxime as well as the easy conversion of the related complexes $CH_3Co(salen)H_2O$ and $CH_3Co(bae)H_2O$ to stable, five-coordinate species by ready loss of axial water.[29] Displacement of the hydrogen bonded proton in the bridging O–H···O unit of $(dmgH)_2$ complexes by the Lewis acid BF_3 to form O–B-F_2–O was alluded to in the Introduction.

Still another argument that axial coordination of iron(III) is not the process under study is based on the kinetic results. The high rates of water exchange and of other substitution reactions[24,26,27] of methyl(aquo)cobaloxime would suggest that equilibrium would be established much more rapidly than found here, whereas the very low rate[30] of substitution of

(24) Crumbliss, A. L.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1970,** *92,* 2593.
(25) Ablov, A. V.; Bovykin, B. A.; Samus', N. M. *Russ. J. Inorg. Chem.* **1966,** *11,* 978.
(26) Brown, K. L.; Lyles, D.; Pencovici, M.; Kallen, R. G. *J. Am. Chem. Soc.* **1975,** *97,* 7338 and references therein.
(27) Tauzher, G.; Dreos, R.; Costa, G.; Green, M. *J. Chem. Soc., Chem. Commun.* **1972,** 413.
(28) Fox, J. P.; Banninger, R.; Proffitt, R. T.; Ingraham, L. L. *Inorg. Chem.* **1972,** *11,* 2379.
(29) (a) Costa, G.; Mestroni, G. *J. Organomet. Chem.* **1968,** *11,* 325. (b) Costa, G.; Mestroni, G.; Pellizer, G. *Ibid.* **1968,** *11,* 333. (c) Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Nucl. Chem. Lett.* **1972,** *8,* 477. (d) Brückner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1969,** *3,* 308.
(30) Samus', N. M.; Luk'yancts, T. S. *Russ. J. Inorg. Chem.* **1972,** *17,* 390.

$(H_2O)_2Co(dmgH)_2^+$ by pyridine suggests that axial substitution by iron(III) would occur more rapidly. Moreover these processes occur by dissociative mechanisms, and indeed the rate of the latter reaction is independent of the pyridine concentration. In contrast, the rates we have seen show an exact first-order dependence on each reactant over the entire range studied.

The spectral changes, too, are consistent with planar rather than axial coordination. The intensities of the visible absorption bands of methylcobaloximes are greatly increased in the iron(III) adduct, but the positions of the absorption maxima are not significantly altered (Figure 2). The UV maximum at 220 nm is shifted toward lower energy and appears as a shoulder at 240 nm. These are the effects to be expected for substitution at the oxime oxygens. Similar effects on the UV–visible spectra have also been observed[12] for the adducts formed upon chelation of transition metal complexes by the triangular array of oxygens in $Co(dmg)_3^{3-}$.

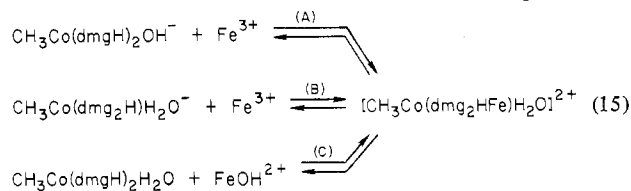The formation constant for reaction 2 can be reformulated as the substitution of hydroxoiron(III), as in eq 14. Such a

$$CH_3Co(dmgH)_2H_2O + HOFe(OH_2)_5^{2+} =$$
$$CH_3Co(dmg_2HFe)H_2O \quad (14)$$

formation constant would appear very high were it to be attributed to formation of the axial product $[CH_3Co(dmgH)_2OHFe(aq)]^{2+}$ rather than $[CH_3Co(dmg_2HFe)H_2O]^{2+}$, in that axial ligation of methyl(aquo)cobaloxime by such stronger bases as NH_3,[24] dimethoxyethylamine,[31] pyridine,[24,26] and 4-substituted pyridines[32] all replace water in $CH_3Co(dmgH)_2H_2O$ with formation constants $<10^4$ M^{-1}. Only cyanide ion[24] and thiolate ions,[33] very potent ligands for this soft acid center, have formation constants $>10^4$ M^{-1}.

The difference between the formation constants for the two reactions, $K_2 = 16$ vs. $K_6 = 2.5$, may well be ascribed to the 1+ charge on the diaquocobaloxime reactant of the latter equilibrium, an effect which should surely tend to reduce the binding constant for cationic groups such as the iron(III) ion. On the other hand, little success was realized in our attempts to confirm this by exploring adduct formation in a related complex containing the N_4-donor ligand dpnH⁻. (This ligand[34] is related to $(dmgH)_2$ in that one of the two O–H···O units has been replaced by $(CH_2)_3$.) The methyl complex is now a monocation, $[CH_3Co(dpnH)H_2O]^+$, and one might expect a reduced formation constant compared to the neutral methyl(aquo)cobaloxime. We found that, within experimental error, the spectrum remained unchanged upon addition of iron(III) perchlorate, even to the most favorable conditions studied, 0.025 M Fe^{3+} and 0.020 M H^+, and thus we set an upper limit, $K < 0.1$ M^{-1}.
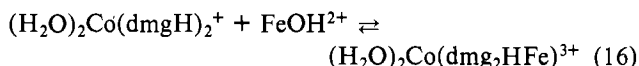
Kinetics. The rate law for adduct formation between iron(III) ion and methyl(aquo)cobaloxime, given by eq 11, indicates that the reaction proceeds by two parallel pathways. One pathway for formation and dissociation of $[CH_3Co(dmg_2HFe)H_2O]^{2+}$, and indeed the only pathway for $[(H_2O)_2Co(dmg_2HFe)]^{3+}$, corresponds to an activated complex with one proton less. The question here is a familiar one, and is the issue generally known as "proton ambiguity": For two reactants each containing acidic protons, which species comprise the kinetically active pair? In the case of methylcobaloxime we consider three different formulations, each consisting of the bimolecular reaction of one complex with an appropriately deprotonated form of the other, the latter present

at low concentration albeit highly reactive. The possibilities we consider, based on the structures of the complexes are

$$(15)$$

The acid ionization constants for each of the deprotonated precursors is known, at least roughly. The K_a for ionization of Fe^{3+} is 1.6×10^{-3} M; for axial water of methyl(aquo)cobaloxime[24] the K_a is ca. 3×10^{-13} M. Ionization of the hydrogen bonded proton of the O–H···O unit is estimated to have K_a ca. 10^{-12} M based on values[35] for a series of $XYCo^{III}(dmgH)_2$ complexes in which the range is 3×10^{-13} to 1.6×10^{-11} M and on $K_a = 2.5 \times 10^{-14}$ M for $CH_3Co(dmgH)_2py$.[32,36]

Using these estimates and the equation $k_{15} = k_{2f}/K_a$, we obtained the following values at 25 °C; $\mu = 1.0$ M: $k_{15A} = 2 \times 10^{12}$ M^{-1} s^{-1}, $k_{15B} = 7 \times 10^{13}$ M^{-1} s^{-1}, and $k_{15C} = 4.25 \times 10^2$ M^{-1} s^{-1}. The first two of these substantially exceed the diffusion-controlled limit and for this reason alone can be excluded from further consideration. We thus conclude that the reaction proceeds by the combination of the pair of reactants shown and ask whether k_{15C} is reasonable for a process which might be envisaged as consisting of substitution on iron(III). The value is 4.2×10^2 M^{-1} s^{-1}, compared to the range of values 3×10^3–4×10^4 M^{-1} s^{-1} generally accepted[36] for $(H_2O)_5FeOH^{2+}$. The value found does not preclude the mechanism of 15C; rather, it suggests that additional activation is necessary. Reaction of the O–H···O unit of $XYCo^{III}(dmgH)_2$ complexes with OH⁻ occurs abnormally slowly[35] ($k \sim 10^5$–10^6 M^{-1} s^{-1}), compared to the usual diffusion-controlled rate of neutralization by OH⁻ of proton donors which are not internally hydrogen bonded. This same factor may well be the source of the additional activation barrier of this reaction. Turning to the aquo complex, we must also consider the analogous rate constant for equilibrium 6, $k_{2f}^{aq} = 0.202$ s^{-1}. By analogy to the methylcobaloxime reaction, however, it seems reasonable to suggest that the mechanism for the aquo complex is the same as for the methyl, consisting of the reaction of $(H_2O)_5FeOH^{2+}$ as represented by the elementary reaction

$$(H_2O)_2Co(dmgH)_2^+ + FeOH^{2+} \rightleftharpoons$$
$$(H_2O)_2Co(dmg_2HFe)^{3+} \quad (16)$$

with $k_{16} = k_{2f}^{aq}/K_{Fe} = 1.2 \times 10^2$ M^{-1} s^{-1}. The similarity between this value and k_{15C} is additional evidence that the chemistry as well as the kinetic equations are the same. The value of k_{15C}/k_{16} is 3.5, the direction of which is consistent with the charge types involved, and the magnitude unimpressive, consistent with the activation barriers being (a) the S_N1CB process by which substitution on $FeOH^{2+}$ occurs and (b) the special nature of neutralization of the O–H···O function.

The parallel pathway, important for methylcobaloxime only, may possibly be viewed as substitution into the primary coordination sphere of $Fe(H_2O)_6^{3+}$. To do so would be consistent with the generally accepted patterns[37] of iron(III) substitution reactions, but before accepting this formulation, two aspects

(31) Brown, K. L.; Awtrey, A. W. *Inorg. Chem.* **1978**, *17*, 111.
(32) Brown, K. L.; Chernoff, D.; Keljo, D. J.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6697.
(33) Brown, K. L.; Kallen, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1894.
(34) The ligand dpnH⁻, sometimes referred to by others as (DO)(DOH)pn⁻, is 3,3'-(trimethylenediimino)bis(butan-2-one)oximato.
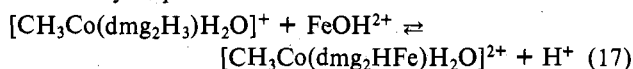
(35) Birk, J. P.; Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1968**, *90*, 6959.
(36) We choose to use the value based on the compound containing axial pyridine rather than water, so there is no doubt about which proton is undergoing ionization; we assume for purposes of this rough calculation that the value of K_a for ionization of an oxime hydrogen of $CH_3Co(dmgH)_2H_2O$ is the same.
(37) Wilkins, R. G. "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Allyn and Bacon: Boston, 1974; pp 69–71.

of reactivity must be considered: (1) the magnitude of k_{1f} and the substitution mechanism being considered and (2) the relative magnitude of the rate constants for the two complexes, i.e., $k_{1f}/k_{1f}{}^{aq}$. The first consideration leads to a comparison of the value $k_{1f} = 1.8$ M^{-1} s^{-1} to the range of values generally accepted[36] as representing ligand substitution of $Fe(H_2O)_6{}^{3+}$ by the acid-independent pathway, 3.4–800 M^{-1} s^{-1}. That this particular reaction is the slowest found is not surprising in view of the O–H···O barrier already discussed. On the other hand, the latter effect is of much less relative importance for $Fe(H_2O)_6{}^{3+}$ compared to $FeOH^{2+}$ perhaps because of the inherently lower rate of the former processes compared to which the O–H···O neutralization is, relatively speaking, of much less importance. The second point is clearly more difficult to account for by the iron(III) substitution mechanism, for if the analogous reaction pathway for the aquocobaloxime is to be interpreted as consisting of substitution on $Fe(H_2O)_6{}^{3+}$, then its rate constant, represented as $k_{1f}{}^{aq}$, at $<10^{-2}$ M^{-1} s^{-1} is some 10^2 or more smaller than expected, some 3.4–800 M^{-1} s^{-1}. The premises behind the expectation are open to question: Maybe $Fe(H_2O)_6{}^{3+}$ substitution reactions show a greater degree of ligand dependence than previously encountered, particularly in this case where the entering "ligand" is the cationic species $(H_2O)_2Co(dmgH)_2{}^+$. Since the standard ligands do not appear to react at rate constants which systematically vary with their ionic charge, however, we seek an alternative explanation.

One such alternative mechanism, suitable to account for all of the results we have obtained, is termed by us the *neutralization mechanism*. According to this, each pathway is the reaction of the hydrogen-bonded O–H···O proton with the base $FeOH^{2+}$. In the case of methylcobaloxime, its reaction is represented by two parallel pathways in which $FeOH^{2+}$ reacts with $CH_3Co(dmgH)_2OH_2$ and with $[CH_3Co(dmg_2H_3)H_2O]^+$. The former pathway has already been shown in reaction 15C, $k_{15C} = 4.2 \times 10^2$ M^{-1} s^{-1}, and the latter is represented by the elementary step

$$[CH_3Co(dmg_2H_3)H_2O]^+ + FeOH^{2+} \rightleftharpoons$$
$$[CH_3Co(dmg_2HFe)H_2O]^{2+} + H^+ \quad (17)$$

Substitution of the equilibrium constant expressions from eq 3 and 4 gives the following values: $k_{-17} = k_{1r} = 0.146$ M^{-1} s^{-1} and $k_{17} = k_{1f}/K_{Fe}K_{Co} = 3.4 \times 10^2$ M^{-1} s^{-1} (25 °C, $\mu = 1.0$ M).

Consider the consequences of the neutralization mechanism for the aquocobaloxime reaction. One would again expect two pathways, the first being that already given by reaction 16, having $k_{16} = 1.2 \times 10^2$ M^{-1} s^{-1} (25 °C, $\mu = 1.0$ M). It is evident, by comparing the values for the three rate constants computed for these reactions based on this assumed mechanism, that the values fall into a narrow range indeed,[38] 120–425

M^{-1} s^{-1}, consistent with (but hardly proof of) a mechanism such as that being considered where a single mode of activation is common to all. (A corollary of this is, of course, that the other ligands on cobalt are largely immaterial in setting the neutralization rate.) If this is accepted for the moment, then a very natural explanation arises for the absence of the second pathway for aquocobaloxime. The neutralization mechanism would consist of the step

$$[(H_2O)_2Co(dmg_2H_3)]^{2+} + FeOH^{2+} \rightleftharpoons$$
$$[(H_2O)_2Co(dmg_2HFe)]^{3+} + H^+ \quad (18)$$
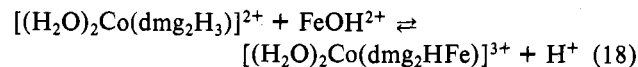
The very small (but unknown) protonation constant for this cobaloxime coupled with a value for k_{18} taken to lie within the same narrow range would result in an insignificantly small contribution from this pathway (for consistency, $K_{Co}{}^{aq}$ would need to be ≤ 0.02 M, certainly not unreasonable).

It should be noted that the steps referred to as "neutralization" of the group O–H···O in each of three cobaloxime substrates by the common base $FeOH^{2+}$ occurs much more slowly than does neutralization by OH^- (10^5–10^6 M^{-1} s^{-1}). This rate reduction by a factor of some 10^3–10^4 is also a reasonable one considering the base strengths of $FeOH^{2+}$ and OH^-. It must be recognized that each of the neutralization processes envisaged must also effect a substitution, since the oxime oxygens eventually penetrate into the inner coordination sphere of iron(III). It would be unreasonable to propose this as occurring in a fast step subsequent to neutralization, as this would require an impossibly high rate of substitution on iron(III) by the minute trace of $Co(dmg_2H)$ species. Instead, the neutralization mechanism would require, in an intramolecular fashion, loss of OH^- bound to iron(III) concurrent with its neutralization vacating one coordination position for concurrent or subsequent entry of the oxime oxygen.

The discussion given here has been as protracted as this that we might point out the complexity of the molecular changes involved and the care required in assigning the mechanism. The present situation, as is often the case when questions of protonation of such substrates are considered, is not easily resolved, although the best understanding is that a process other than substitution better accounts for the results obtained.

Registry No. $CH_3Co(dmg_2HFe(aq))H_2O^{2+}$, 71831-19-1; $(H_2O)_2Co(dmg_2HFe(aq))^{3+}$, 71831-20-4; $CH_3Co(dmgH)_2H_2O$, 25360-55-8; $(H_2O)_2Co(dmgH)_2{}^+$, 28124-53-0; $Fe(H_2O)_6{}^{3+}$, 15377-81-8.

Supplementary Material Available: Tables of data used for the evaluation of the equilibrium constants and of kinetic data giving the value of k_{obsd} in each experiment (8 pages). Ordering information is given on any current masthead page.

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(38) The neutralization mechanism would suggest, however, a statistical correction for the two complexes containing two such O–H···O groups but not for the third, having but one. The values to be compared are thus: $k_{15C}/2 = 2.1 \times 10^2$, $k_{16}/2 = 0.6 \times 10^2$, and $k_{17} = 3.4 \times 10^2$ M^{-1} s^{-1}.