binuclear species, repulsion being least for the most highly solvated $(NH_3)_5$ species and greatest to the least solvated tetren analogue.

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Registry No. $Co(NH_3)_5SalH^{2+}$, 30931-74-9; *cis*-$Co(en)_2(NH_3)SalH^{2+}$, 59296-02-5; ($\alpha\beta S$)-Co(tetren)$SalH^{2+}$, 78715-92-1; Fe, 7439-89-6; $Fe(OH_2)_6^{3+}$, 15365-81-8; $Fe(OH_2)_5(OH)^{2+}$, 15696-19-2; H_2Sal, 69-72-7.

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Demethylation of Methylcobalamin by Tetrahaloaurates. Kinetics and Mechanism

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The stoichiometries and kinetics of reactions of methylcobalamin (CH_3-B_{12}) with AuX_4^- (X = Cl or Br) in acidic solution have been examined. Under anaerobic conditions, the reactions occur with a 2:1 stoichiometry (AuX_4^-:CH_3-B_{12}), producing aquocobalamin with an oxidized corrin ring, CH_3X, and metallic gold. The stoichiometry and reaction products are interpreted in terms of one-electron oxidative demethylation of CH_3-B_{12}. Kinetic data support a mechanism which involves an equilibrium prior to the electron transfer between CH_3-B_{12} and AuX_4^-. Effects of pH and ionic strength on the kinetics are also examined. The detailed mechanism for the Co–C bond cleavage is discussed.

Introduction

Oxidation–reduction reactions and their related cleavage of the cobalt–carbon bond are important in our understanding of the biological roles of methylcobalamin (CH_3-B_{12}).[1] They are also of considerable mechanistic interest.[2] Several modes of cleavage of the Co–C bond of CH_3-B_{12} induced by metal ions have been described in detail. These include electrophilic demethylation by Hg^{2+} [3] and $PdCl_4^{2-}$,[4], reductive demethylation by Cr^{2+} [5] and Sn(II),[6] and redox switch by $PtCl_6^{2-}$/$PtCl_4^{2-}$.[7]

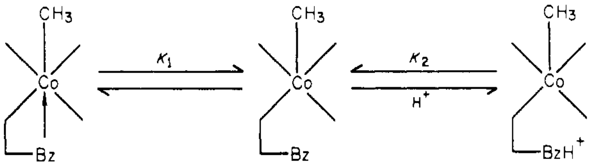
It has been briefly reported that CH_3-B_{12} can be demethylated by $AuCl_4^-$.[8] The mechanism for this reaction was suggested to be similar to that proposed for the methylation of platinum complexes by CH_3-B_{12}.[7] We undertook the study on the demethylation of CH_3-B_{12} by gold complexes to determine whether this mechanism occurs. In contrast to the previous report, our work provides results which support the single-electron oxidative demethylation of CH_3-B_{12} by gold complexes.

Experimental Section

Materials. Fine gold powder and $NaAuCl_4{\cdot}2H_2O$ were purchased from either Goldsmith or Ventron, Inc., and were used as received. $KAuBr_4{\cdot}2H_2O$ was synthesized by the method of Block.[9] AuX_2^- solutions were generated by reducing AuX_4^- with zinc amalgam in acidic solution under an atmosphere of argon. CH_3-B_{12} was synthesized by the method described by Dolphin[10] or purchased from Sigma, Inc. Cob(II)alamin (B_{12r}) solutions were generated by reducing aquocob(III)alamin (H_2O-B_{12}^+) with equimolar amounts of Eu^{2+} under argon. Concentrations of CH_3-B_{12}, H_2O-B_{12}^+, and B_{12r} in solution were determined from their published molar absorptivities.[11,12] All other chemicals were reagent grade and were used as received.

Stoichiometric Studies and Reaction Products. Consumption ratios for the reactions between CH_3-B_{12} and $AuCl_4^-$ or $AuBr_4^-$ were determined spectrophotometrically at 351 or 537 nm with a GCA/McPherson spectrophotometer in subdued light under an atmosphere of argon. B_{12} products were identified spectrophotometrically. Demethylation products under various conditions were identified with a Becker gas chromatograph Model 417 with a column (8 ft by 2 mm) of 5% FFAP on chromasorb W-AW-DMCS, 80–100 mesh at 45 °C, and with a Brüker 270 MHz proton NMR spectrometer.

Equilibrium Constant Measurements. The equilibrium constants for 5,6-dimethylbenzimidazole "base-on" and "base-off" conversion of CH_3-B_{12} (reaction 1) were estimated spectrophotometrically according to eq 2.[13] Measurements were made at 1.0 M ionic strength which was maintained with NaCl, NaBr, or $NaClO_4$ (23 °C).



(1)

$$\frac{A_{305nm}}{[CH_3\text{-}B_{12}]_T} = \frac{K_2\epsilon_{base\text{-}on} + K_1[H^+]\epsilon_{base\text{-}off}}{K_2 + K_1[H^+]} \qquad (2)$$

pK_2 can be considered as 4.7, which is the pK_a for free 5,6-dimethylbenzimidazole in aqueous solution.[14] According to eq 2, pK_1 in 1.0 M perchlorate, 1.0 M chloride, and 1.0 M bromide solutions were estimated to be 0.92, 1.7, and 2.1, respectively (at 23 °C).

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(13) Equation 2 was derived from equilibria presented in eq 1. The molar absorptivities at 305 nm for the base-on and base-off CH_3-B_{12} are given respectively by $\epsilon_{base\text{-}on} = 1.3 \times 10^4$ M^{-1} cm^{-1} and $\epsilon_{base\text{-}off} = 2.2 \times 10^4$ M^{-1} cm^{-1}. It is assumed that protonated base-off CH_3-B_{12} has the same molar absorptivity as unprotonated base-off CH_3-B_{12}.

(14) D. D. Perrin in "Dissociation Constants in Organic Bases in Aqueous Solution", International Union of Pure and Applied Chemistry (1972). The assumption that pK_2 is the same as that of free 5,6-dimethylbenzimidazole is justified on the basis that pK_a of 1-β-D-ribo-5,6-dimethylbenzimidazole has been estimated to be 4.68 (M. T. Davies, P. Mamalis, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol*, 3, 420 (1951)).

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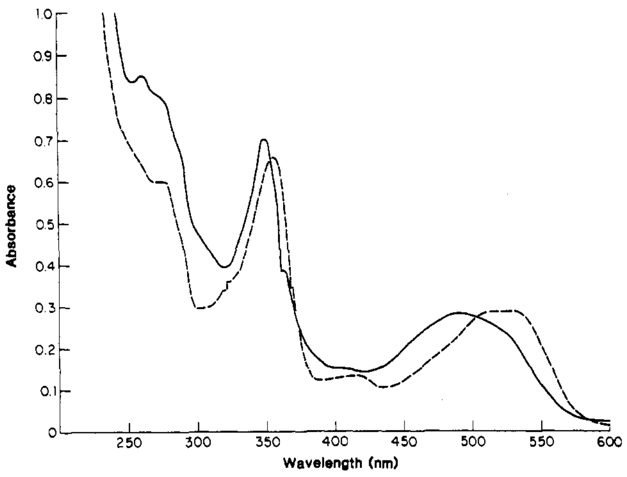

Figure 1. Absorption spectra of $H_2O\text{-}B_{12}^+$ (- - -) and the B_{12} product of the reaction between $CH_3\text{-}B_{12}$ and AuX_4^- under an atmosphere of argon (—). $[B_{12}] = 3.0 \times 10^{-5}$ M.

Kinetic Measurements. Reaction rates were estimated by absorbance increase at 537 or 351 nm (i.e., maxima of the α and γ bands of $H_2O\text{-}B_{12}^+$) with a GCA/McPherson spectrophotometer connected to a circulating thermostated cell. All reactions were performed at 23 ± 0.1 °C under a dim light. Ionic strength was maintained at 1.0 M with NaCl or NaBr throughout unless otherwise mentioned. pH values were controlled in the range 0.5–3 with HCl, HBr, or $HClO_4$. All reactions were initiated by injecting reagents with hypodermic syringes equipped with platinum needles.

Results

$NaAuCl_4$ is a yellow compound with an absorbance maximum at 315 nm ($\epsilon = 7.1 \times 10^3$ M^{-1} cm^{-1}). $KAuBr_4$ is a purple compound with an absorbance maximum at 380 nm ($\epsilon = 5.7 \times 10^3$ M^{-1} cm^{-1}). Both gold complexes are quite stable against hydrolysis in their corresponding hydrohalic acid solution ($[X^-] = 0.1$ M–1.0 M) in the pH range 0–3. However, dissolving large amounts of $KAuBr_4$ in Br^- solution results in the generation of Br_2. Therefore, relatively low concentrations of $AuBr_4^-$ were used throughout in this study. There is no spectral change for $AuCl_4^-$ or $AuBr_4^-$ upon mixing with equimolar amounts of Au(I) solutions, indicating that disporportionation reactions between Au(III) and Au(I) do not occur. This is consistent with the contention that Au^{II} species are extremely unstable. In the present time scale, $3Au^{I} \rightleftharpoons 2Au + Au^{III}$ is also unlikely to occur.

$CH_3\text{-}B_{12}$ (3.0×10^{-5} M) was quantitatively demethylated by $AuCl_4^-$ (1.0×10^{-4} M) at [HCl] = 0.28 M, $\mu = 1.0$ M (NaCl + HCl), 23 °C, under an atmosphere of air. The half-life of this reaction was estimated to be approximately 7 min. $H_2O\text{-}B_{12}^+$ was identified as the B_{12} product with isosbestic points at 493, 370, and 338 nm. Demethylation of $CH_3\text{-}B_{12}$ by twofold excess of $AuCl_4^-$ under an atmosphere of Ar also produced $H_2O\text{-}B_{12}^+$; however, the corrin ligand of $H_2O\text{-}B_{12}^+$ was modified during the course of reaction. Their absorption spectra are shown in Figure 1. A mixture of $CH_3\text{-}B_{12}$ (3.8×10^{-5} M) and $AuCl_4^-$ (1.4×10^{-4} M) at pH 3 did not show a spectrum indicative of base-off form of $CH_3\text{-}B_{12}$, indicating that $AuCl_4^-$ at this concentration does not coordinate to the 5,6-dimethylbenzimidazole portion of the B_{12} molecule.

When large amounts of $CH_3\text{-}B_{12}$ ($\geq 10^{-3}$ M) were mixed with a twofold excess of $AuCl_4^-$ under anaerobic conditions, a colloid of gold and $H_2O\text{-}B_{12}^+$ immediately formed. This indicates that $CH_3\text{-}B_{12}$ reduces $AuCl_4^-$ to metallic gold. However, because of the colloidal nature, it is difficult to obtain a quantitative analysis of the metallic gold produced. No reaction occurred upon mixing $H_2O\text{-}B_{12}^+$ with excessive amounts of $AuCl_4^-$ over a few hours. However, prolonged incubation of $H_2O\text{-}B_{12}^+$ (10^{-3} M) with $AuCl_4^-$ resulted in a slow precipitation of metallic gold under argon. B_{12r} was found to be quickly oxidized to $H_2O\text{-}B_{12}^+$ by $AuCl_4^-$ under an atmosphere of argon (23 °C). $AuCl_2^-$ does not react with $CH_3\text{-}B_{12}$ under strictly anaerobic conditions.

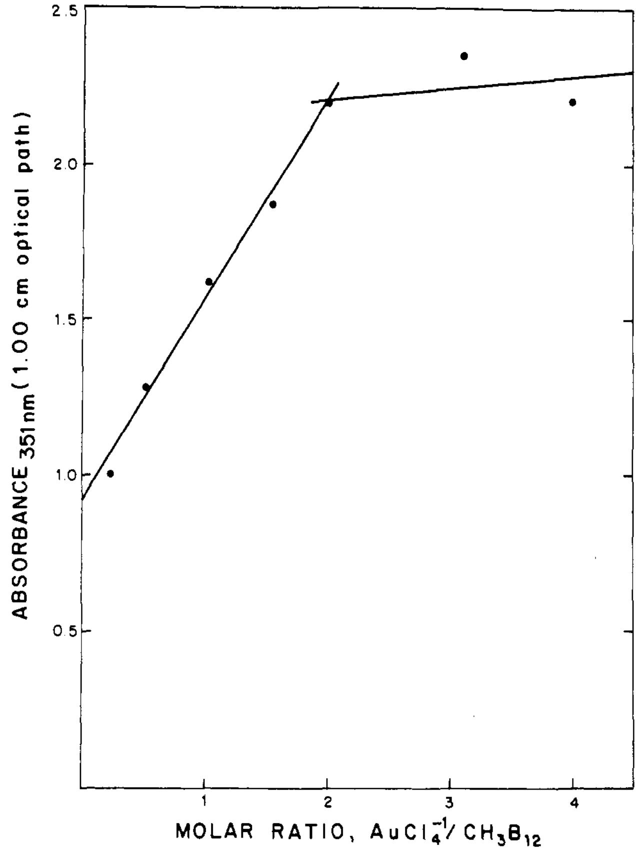

Figure 2. Spectrophotometric titration of 8.4×10^{-5} M $CH_3\text{-}B_{12}$ with various concentrations of $AuCl_4^-$ under anaerobic conditions at [HCl] = 0.28 M; $\mu = 1.0$ M (HCl + NaCl).

Stoichiometries and Reaction Products. Demethylation of $CH_3\text{-}B_{12}$ by $AuCl_4^-$ and $AuBr_4^-$ occurs according to eq 3 and 4.

$$CH_3\text{-}B_{12} + 2AuCl_4^- + H_2O \rightleftharpoons H_2O\text{-}B_{12}^+ + CH_3Cl + 2\text{“}Au^{II}\text{”} \quad (3)$$

$$CH_3\text{-}B_{12} + 2AuBr_4^- + H_2O \rightleftharpoons H_2O\text{-}B_{12}^+ + CH_3Br + 2\text{“}Au^{II}\text{”} \quad (4)$$

Au^{II} species are known to be extremely unstable, therefore, here “Au^{II}” represents a proposed intermediate gold product. To simplify these equations, we have omitted the halide ions. Plots of absorbance at 351 nm vs. the ratio of the added $AuCl_4^-$ and $CH_3\text{-}B_{12}$ under an atmosphere of argon are shown in Figure 2. A titration break is noted at a 2:1 ratio, which supports eq 3. This 2:1 stoichiometry is confirmed by calculation with the molar absorptivities of $CH_3\text{-}B_{12}$ and $H_2O\text{-}B_{12}^+$.[15] Similarly, the stoichiometry of $AuBr_4^-$:$CH_3\text{-}B_{12}$ was established to be 2:1 under an atmosphere of argon, in support of eq 4.

It should be stressed that exclusion of oxygen from the reacting solution is of crucial importance in these spectrophotometric titration experiments. When deficient amounts of AuX_4^- were mixed with a $CH_3\text{-}B_{12}$ solution under an atmosphere of air, the consumption ratio of AuX_4^-:$CH_3\text{-}B_{12}$ is

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(15) At 0.28 M H^+ and 1.0 M ionic strength (HCl + NaCl), molar absorptivities of $CH_3\text{-}B_{12}$ and $H_2O\text{-}B_{12}^+$ at 351 nm were determined to be 1.06×10^4 and 2.63×10^4 M^{-1} cm^{-1}, respectively. The absorbance of $AuCl_4^-$ at this wavelength can be neglected.

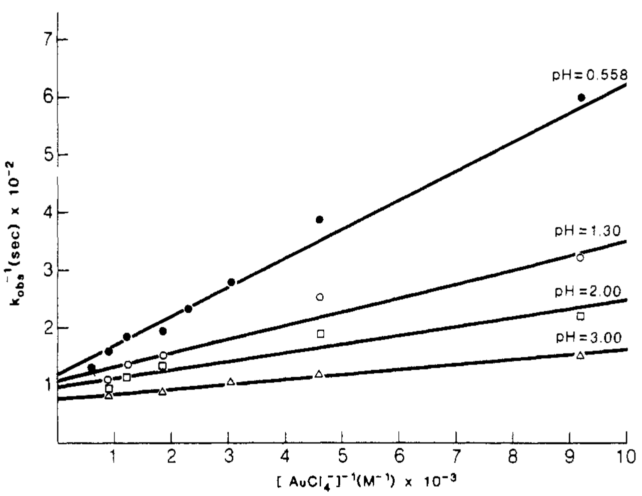

Figure 3. Kinetic measurements for the demethylation of CH_3-B_{12} by $AuCl_4^-$ as a function of $AuCl_4^-$ concentrations and pH values ($[CH_3\text{-}B_{12}]_{tot}$ = (1.5–3.0) × 10^{-5} M, μ = 1.0 M (HCl + NaCl), temperature = 23 °C). Average deviation from the linear least-squares calculation is ±7%.

found to be significantly less than 1. For example, adding 10^{-5} M $AuCl_4^-$ to a solution of threefold excess of CH_3-B_{12} under air would result in the conversion of more than 85% of CH_3-B_{12} to H_2O-B_{12}^+. This indicates that oxygen can oxidize the gold intermediate, e.g., Au^{II}, to regenerate AuX_4^- for further demethylation of CH_3-B_{12}.

CH_3Cl was identified as the demthylation product for the reaction between CH_3-B_{12} and $AuCl_4^-$, regardless the reaction was performed with $AuCl_4^-$ in excess over CH_3-B_{12} or vice versa. CH_3Cl was found to be the only demethylation product in the absence of Cl^- (e.g., in ClO_4^- solution). Similarly, CH_3Br was produced from the reaction between CH_3-B_{12} and $AuBr_4^-$ under all experimental conditions. Neither CH_3OH nor any other organic product has been detected in the present study. It should be noted that demethylation of CH_3-B_{12} by AuX_4^- is much faster than the hydrolysis of AuX_4^- in perchlorate solution in the pH range 0–3.

Kinetic Measurements. An excess of AuX_4^- over CH_3-B_{12} was used in all the rate measurements so that $[AuX_4^-]$ remained essentially constant. Under this condition, CH_3-B_{12} was quantitatively demethylated to H_2O-B_{12}^+ according to eq 5. No significant difference in rates was found whether the

$$d[H_2O\text{-}B_{12}^+]/dt = k_{obsd}[CH_3\text{-}B_{12}]_T \qquad (5)$$

reactions were performed aerobically or anaerobically. Plots of ln $(A_\infty - A_t)$ vs. time gave straight lines for more than 85% of reactions. Reproducibility was checked to be within 10%. Kinetic data for the demethylation of CH_3-B_{12} by AuX_4^- are found to obey rate law 6. Plots of k_{obsd}^{-1} vs. $[AuX_4^-]^{-1}$ for

$$k_{obsd} = \frac{kK[AuX_4^-]}{1 + K[AuX_4^-]} \qquad (6)$$

the reaction between CH_3-B_{12} and $AuCl_4^-$ are shown in Figure 3. Linear least-squares analysis of data listed in this figure provides values of k (reciprocal of intercept) and K (slope = $1/kK$). Their values are documented in Table I.

Addition of large amounts of $AuCl_2^-$ under anaerobic conditions does not affect the kinetic measurements for the reactions between CH_3-B_{12} and AuX_4^-. This is in contrast to the previous report by Agnes et al.[8] and clearly rules out the possibility of a redox switch mechanism. It should also be noted that in their study only equimolar amounts of $AuCl_4^-$ were used to demethylate CH_3-B_{12}. On the basis of our 2:1 stoichiometry for AuX_4^-:CH_3-B_{12}, apparently, their observation of an incomplete demethylation of CH_3-B_{12} is due to the deficiency of $AuCl_4^-$. Addition of stoichiometric amounts of cob(II)alamin (B_{12r}) does not have a significant effect on the rate measurements.[16] Rate measurements as a function of halide concentration at a constant pH and ionic strength (μ = 1.0 M, maintained with $NaClO_4$) indicate that halide ions (in a range 0.1–1.0 M) does not affect the rate-determining step (k). However, it does affect the equilibrium constant (K). Kinetic measurements are not affected by the nature of common cations in solution. For example, the same rates were obtained when LiCl or KCl were substituted for NaCl to control the ionic strength.

Discussion

The formation of colloidal gold from reactions of AuX_4^- with various reducing agents or biological compounds has been well documented.[17] For example, it was reported that $HAuCl_4$ can be reduced to metallic gold by hydroxyamine according to reaction 7.

$$HAuCl_4 + NH_2OH \rightarrow Au + 4HCl + NO \qquad (7)$$

It was further suggested that a hydrolysis of $AuCl_4^-$ is involved in this reduction.[18] Colloidal gold is formed upon treatment of AuX_4^- with CH_3-B_{12} ($[CH_3\text{-}B_{12}] > 10^{-3}$ M) under anaerobic conditions, indicating AuX_4^- is reduced to metallic gold during the course of reaction. It is of importance to note that, under present experimental conditions, hydrolysis of AuX_4^- prior to the interaction of CH_3-B_{12} with AuX_4^- is ruled out. The production of metallic gold and CH_3X, together with the 2:1 stoichiometry (AuX_4^-:CH_3-B_{12}), suggest that a mechanism involving direct electrophilic attack on the Co–C bond by AuX_4^- is unlikely to occur. This mechanism has been frequently suggested for the reactions between CH_3-B_{12} and electrophiles, e.g., Hg^{2+} [3] or $PdCl_4^{2-}$.[4] The direct electrophilic attack would produce H_2O-B_{12}^+ and $(CH_3)AuX_3^-$, followed by a reductive elimination of $(CH_3)AuX_3^-$ to give CH_3X and AuX_2^-. However, Au^{II} species are known to be extremely unstable, which clearly eliminates the disproportionation reaction between Au^{III} and Au^{I}. Also, disproportionation reaction of $3Au^{I} \rightleftharpoons 2Au^{0} + Au^{III}$ does not occur under the present conditions. Consequently, if electrophilic attack is operative in the demethylation of CH_3-B_{12} by AuX_4^-, one would expect a 1:1 stoichiometry to produce H_2O-B_{12}^+, CH_3X, and AuX_2^-, which is not the case. Therefore, in contrast to the substantial literature on methyl transfer from CH_3-B_{12} to metals, the plausible mechanism for the cleavage of Co–C bond by AuX_4^- appears to be a single-electron oxidative cleavage, as described in eq 8–10. "Au^{II}" produced in this reaction is

$$CH_3\text{-}B_{12} + AuX_4^- \overset{k_{et}}{\rightleftharpoons} CH_3\text{-}B_{12}^+ + \text{“}Au^{II}\text{”} \qquad (8)$$

$$CH_3\text{-}B_{12}^+ + AuX_4^- + H_2O \overset{\text{fast}}{\rightleftharpoons} H_2O\text{-}B_{12}^+ + \text{“}Au^{II}\text{”} + CH_3X \qquad (9)$$

$$2\text{“}Au^{II}\text{”} \xrightarrow[\text{corrin ring}]{\text{reduced by}} 2Au \qquad (10)$$

quickly reduced to metallic gold by corrin ring.[19] B_{12} product

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(16) The lack of significant kinetic effect upon addition of B_{12r} to the reaction solution eliminates the possibility of the mechanism proposed for the demethylation of CH_3-B_{12} by AuX_4^-, by Y.-T. Fanchiang, W. P. Ridley, and J. M. Wood, *ACS Symp. Ser.*, No. **82**, 54 (1978). Furthermore, we failed to repeat the experiment of acceleration of demethylation of CH_3-B_{12} by $AuCl_4^-$ due to the preincubation of Fe^{2+}.

(17) (a) J. Turkevich, P. C. Steveson, and J. Hiller, *Discuss. Faraday Soc.*, **11**, 55 (1951); (b) J. Turkevich, P. C. Steveson, and J. Hiller, *J. Phys. Chem.*, **57**, 670 (1953); (c) C. F. Shaw, III, M. P. Cancro, P. L. Witkiewica, and J. E. Eldridge, *Inorg. Chem.*, **19**, 3198 (1980).

(18) F. H. Fry, A. A. Hamilton, and J. Turkevich, *Inorg. Chem.*, **5**, 1943 (1966).

(19) Equation 10 (and also eq 18) suggests that the Au(II) species are reduced to Au(0) by the corrin ring with a net two-equivalent change. This reduction can proceed either by a two-electron transfer or by rapid successive one-electron transfer. A reviewer suggests that the successive one-electron transfer is more likely to occur.

Table I. Analysis of Kinetic Data for the Demethylation of CH_3-B_{12} by AuX_4^- (23 °C)

pH	10^3k, s^{-1}	$10^{-3}K$, M^{-1}
	$AuCl_4^-$	
0.558[a]	8.6	2.3
1.30[a]	9.3	4.4
2.00[a]	10.3	6.6
3.00[a]	13.0	9.2
1.00[b]	8.7	1.0
1.00[c]	10.0	0.75
1.00[d]	10.0	0.63
	$AuBr_4^-$	
1.00[e]	~4	~5
2.00[e]	4.5	5.1
3.00[e]	4.8	8.6

[a] μ = 1.0 M (HCl + NaCl). [b] μ = 0.10 M (HCl). [c] μ = 0.50 M (HCl + $NaClO_4$). [d] μ = 1.0 M (HCl + $NaClO_4$). [e] μ = 1.0 M (HBr + NaBr).

for the reaction between CH_3-B_{12} and AuX_4^- under anaerobic conditions shows a typical aquocob(III)alamin peak at ~350 nm. However, the entire absorption spectrum is significantly different from that of H_2O-B_{12}^+. It is known that changes in the side chains or even in the outer ring of carbon atoms of the corrin ligand have very little effect on the absorption spectra of B_{12} derivatives.[12] Therefore, the spectral change in Figure 1 suggests that the conjugated corrin ring is oxidized under anaerobic conditions, and eq 8–10 explain both the 2:1 stoichiometry and the production of metallic gold and CH_3X. It should be noted that if AuX_2^- is produced in significant amounts in this reaction (either by the disproportionation reaction of Au^{II} or by the direct electrophilic attack), then the stoichiometry of AuX_4^-:CH_3-B_{12} should be considerably less than 2. Therefore, the 2:1 stoichiometry can be considered as an indication that no significant amounts of AuX_2^- is produced during the demethylation of CH_3-B_{12}. When reactions were performed under air, the "Au^{II}" intermediate was quickly reoxidized by oxygen to regenerate AuX_4^- and produced unperturbed H_2O-B_{12}^+.

Oxidative cleavage of the Co–C bond of organocobaloximes has been well characterized by Halpern and co-workers.[20] One important feature of these studies is the relative stability of the organocobalt(IV) intermediates. Those intermediates are susceptable to nucleophilic attack to produce cob(II)aloximes with carbonium ion transfer to the attacking nucleophile. However, in some cases such as $[RCo^{IV}(acacen)L]^+$ or $[(CH_3)Co^{IV}(salen)L]^+$, the Co^{IV} carbon undergoes rapid homolytic cleavage leading to the production of R· and a Co(III) complex.[20f] This has been attributed to the high electron-donating ability of the chelating ligands and axial bases, as well as high ionization potential of the free radical R·. In light of these studies, it is apparent that the principal questions that should be addressed in studying the oxidative demethylation of CH_3-B_{12} are what is the electronic structure of the oxidized intermediate (e.g., R·–Co^{III}(corr), R–Co^{IV}(corr), or R–Co^{III}(corr·)?) and how does the Co–C bond of the intermediate cleave? While our present study does not allow an answer to the former question, it does provide some interesting information about the fate of the oxidized intermediate. If the Co–C bond of CH_3-B_{12}^+ cleaves heterolytically to transfer CH_3^+ to the nucleophile (e.g., H_2O or X^-) as in the case of organo(dimethyloximato)cobalt(IV) complexes, then one would expect CH_3OH as the demethylation product in the absence of X^-. Since we observed only CH_3X as the demethylation product, we suggest that CH_3-B_{12}^+ cleaves homolytically to release a CH_3· radical. This methyl radical then quickly extracts a halogen atom from a second molecule of AuX_4^- to produce CH_3X. This proposed mechanism is consistent with the contention that corrin ring is highly reduced. It is relevant to note that similar homolytic cleavage of the metal–carbon bond of oxidized organometals such as R_2Hg, R_4Pb, or R_4Sn has been well established by Kochi and co-workers.[21]

Kinetic data for the demethylation of CH_3-B_{12} by AuX_4^- obey the rate law expressed in eq 6, indicating that an equilibrium between CH_3-B_{12} and AuX_4^- is established prior to the demethylation of CH_3-B_{12}. An alternative explanation for the kinetic data is an "activation" of the corrinoid before the interaction with AuX_4^-. The latter explanation can be described in eq 11 and 12. Equations 11 and 12 would lead to

$$CH_3\text{-}B_{12} \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} CH_3\text{-}B_{12}^* \tag{11}$$

$$CH_3\text{-}B_{12}^* + AuX_4^- \xrightarrow{k_2'} \text{products} \tag{12}$$

rate law 13, which is kinetically indistinguishable from rate

$$\frac{d[H_2O\text{-}B_{12}^+]}{dt} = \frac{k_1'k_2'[AuX_4^-][CH_3\text{-}B_{12}]_T}{k_{-1}' + k_2'[AuX_4^-]} \tag{13}$$

law 6. However, nonenzymatic "activation" of the corrinoid is not known in cobalamin chemistry and seems unlikely to be operative in the interaction of CH_3-B_{12} and AuX_4^-. On the other hand, our recent work on the demethylation of CH_3-B_{12} by platinum complexes offers strong evidence for the complexation of corrinoid with Pt(II) complexes, e.g., $PtCl_4^{2-}$, $Pt(CN)_4^{2-}$,[22] andd $Pt(SCN)_4^{2-}$.[23] Furthermore, study of the demethylation of CH_3-B_{12} by tetracyanoethylene clearly shows a charge-transfer band in the visible region.[23] On this basis, the preequilibrium between CH_3-B_{12} and AuX_4^- is considered to be more likely the interpretation for the kinetic data shown in Figure 3. Table I shows that ionic strength has very little effect on the kinetics, which is consistent with the contention that CH_3-B_{12} is a neutral compound. It should also be noted that while there is a factor of 4 increase in the equilibrium constant from base-off CH_3-B_{12} to base-on form, there is virtually no difference in electron-transfer rates. The same phenomenon has been observed for the demethylation of CH_3-B_{12} by platinum complexes.[22] In view of these studies, it is reasonable to interpret the preequilibrium between CH_3-B_{12} and AuX_4^- in terms of d–π and d–π^* interactions. These interactions involve the d orbitals of AuX_4^- and π, π^* of the conjugated corrin ring.

In conclusion, the stoichiometries and kinetics suggest a single-electron-transfer mechanism for the demethylation of CH_3-B_{12} by AuX_4^-, as described in eq 14–18.

$$CH_3\text{-}B_{12} + AuX_4^- \overset{K}{\rightleftharpoons} CH_3\text{-}B_{12},AuX_4^- \tag{14}$$

$$CH_3\text{-}B_{12},AuX_4^- \xrightarrow{k_{et}} CH_3\text{-}B_{12}^+,Au^{II}X_4^{2-} \tag{15}$$

$$CH_3\text{-}B_{12}^+,Au^{II}X_4^{2-} + H_2O \xrightarrow{\text{fast}} H_2O\text{-}B_{12}^+ + \text{“}Au^{II}\text{”} + CH_3\cdot \tag{16}$$

$$CH_3\cdot + AuX_4^- \xrightarrow{\text{fast}} CH_3X + \text{“}Au^{II}\text{”} \tag{17}$$

$$2\text{“}Au^{II}\text{”} \xrightarrow{\text{corrinoid}} 2Au \tag{18}$$

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Registry No. CH_3–B_{12}, 13442-55-4; $AuCl_4^-$, 14337-12-3; $AuBr_4^-$, 14337-14-5; H_2O–B_{12}^+, 20623-12-5.

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Structure and Magnetism of Monomeric Chlorobis(*N*-(2-phenylethyl)salicylideniminato)iron(III), Fe(SANE)$_2$Cl

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Determination of the crystal structure of the monomeric form of the title complex has allowed the identification of structural distortions associated with pairwise molecular interactions in the previously reported "dimeric" form. In the "dimeric" species the coordination geometry of the iron ion is severely distorted from the distinctly trigonal-bipyramidal geometry observed in the monomer. Magnetic moment measurements for the monomer confirm that the temperature dependence of the magnetic moment of the dimer arises from interaction between the component molecules. The monomer, $FeC_{30}H_{28}N_2O_2Cl$, is monoclinic with space group *C*2/*c*, $Z = 4$, $a = 30.13$ (3) Å, $b = 8.689$ (6) Å, $c = 10.859$ (8) Å, and $\beta = 106.33$ (3)° at 293 K.

Introduction

In an examination of iron(III) Schiff base complexes, Bertrand, Breece, and Eller[1] discovered an unusual intermolecular interaction in the crystal structure of chlorobis(*N*-(2-phenylethyl)salicylideniminato)iron(III), Fe(SANE)$_2$Cl. In this material two molecules associate to form a "loose dimer", the components of which are related by a center of symmetry. The "dimers", however, differ from other species that contain four-membered Fe_2O_2 rings (for example, the dimeric form of Fe(salen)Cl[2]), in that the "intermolecular" Fe–O distance, 3.76 Å, is much longer than the corresponding "intramolecular" distance, 1.90 Å. Bertrand et al. suggest that the anomalous temperature dependence of the magnetic moment of this material could arise from a phase transition to a six-coordinate form at low temperature. Because of the similarity of the proposed transition to the structural transformation that often accompanies spin-state changes in ferric porphyrin complexes, several attempts were made in this laboratory to duplicate the reported synthesis of Fe(SANE)$_2$Cl. In all cases these efforts have resulted in the isolation of crystals with space group *C*2/*c* rather than $P2_1/c$ as reported by the previous authors. For the determination of the relationship between the two materials, the investigation reported herein was undertaken.

Experimental Section

Preparation of Fe(SANE)$_2$Cl. A solution of $FeCl_2{\cdot}4H_2O$ (0.695 g, 3.50 mmol) in 10 mL of methanol was added to *N*-(2-phenylethyl)salicylaldimine (1.70 g, 7.00 mm) in 10 mL of methanol. The mixture, exposed to the atmosphere, was stirred and then allowed to stand overnight. A small crop of red-black crystals formed. These were recrystallized from diethyl ether to produce crystals suitable for X-ray analysis.

Data Collection. Experimental parameters associated with the determination of the crystal structure are given in Table I.

Table I. Experimental Parameters

formula: $FeC_{30}H_{28}N_2O_2Cl$
color: red-black
habit: parallelepipeds
lattice parameters: $a = 30.13$ (3) Å, $b = 8.689$ (6) Å, $c = 10.659$ (8) Å, $\beta = 106.33$ (3)°
wavelength: Mo $K\overline{\alpha}$, 0.71969 Å
temp: 293 K
radiation: Zr-filtered Mo
space group: *C*2/*c*
cryst dimens: 0.30 × 0.30 × 0.35 mm
abs coeff: 4.62 cm^{-1}
abs cor: none
diffractometer: Picker FACS-1
diffraction geometry: $\theta/2\theta$
scan width: base width = 2.0°
scan rate: 2.0°/min
bkgd: 20 s each side
reflctns measd: $2\theta(\max) = 50°$; 2571 reflctns with h and $k \geqslant 0$
reflctns obsd ($I > 3\sigma$): 1147

Table II. Atomic Positions for the Monomeric Form of Fe(SANE)$_2$Cl

atom	*x*	*y*	*z*
Fe	0.5000	0.2303 (1)	0.2500
Cl(1)	0.5000	0.4899 (2)	0.2500
C(1)	0.5834 (2)	0.1426 (6)	0.4475 (5)
C(2)	0.6309 (2)	0.1097 (6)	0.4724 (6)
C(3)	0.6601 (2)	0.1249 (8)	0.5954 (7)
C(4)	0.6437 (2)	0.1720 (7)	0.6955 (6)
C(5)	0.5969 (2)	0.1981 (6)	0.6734 (5)
C(6)	0.5659 (2)	0.1853 (5)	0.5505 (5)
C(7)	0.5172 (2)	0.2046 (5)	0.5358 (5)
C(8)	0.4364 (2)	0.2209 (6)	0.4396 (5)
C(9)	0.4144 (2)	0.3764 (7)	0.3995 (5)
C(10)	0.3648 (2)	0.3826 (7)	0.4111 (6)
C(11)	0.3297 (3)	0.3028 (9)	0.3274 (6)
C(12)	0.2837 (3)	0.3095 (10)	0.3352 (8)
C(13)	0.2745 (3)	0.3968 (10)	0.4262 (10)
C(14)	0.3090 (4)	0.4719 (10)	0.5124 (9)
C(15)	0.3542 (2)	0.4640 (8)	0.5048 (7)
N(1)	0.4845 (1)	0.2137 (4)	0.4305 (4)
O(1)	0.5561 (1)	0.1286 (4)	0.3283 (3)

Magnetic Measurements. The magnetic moments of the monomer were determined at a magnetic field of 0.62 T with a Princeton Applied Research FM-1 vibrating-sample magnetometer. $HgCo(SCN)_4$ was used as a standard. Magnetic moments of 5.96 (3) μ_B at 298 K and 5.81 (3) μ_B at 80 K (corrected for diamagnetism[3]) were obtained.

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