Table I. Chromium(III) Physical and Spectroscopic Data

complex	% C[a]	% H	% X	% N	% Cr	color	ν(Cr–X), cm^{-1} [b]
$[NPr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$	45.3 (45.6)	7.9 (7.6)	24.3 (24.6)	2.2 (2.4)	...	purple	375 sh, 355 m, 330 s, 305 sh
$[NPr_4][Cr(o\text{-}C_6H_4(AsMe_2)_2)Cl_4]$	39.4 (39.6)	6.1 (6.6)	21.8 (21.3)	2.0 (2.1)	7.2 (7.8)	blue	358 sh, 333 m, 325 s, 312 sh
$[NPr_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$	58.5 (58.6)	6.1 (6.7)	17.0 (18.2)	1.9 (1.8)	5.9 (6.7)	purple	366 sh, 340 m, 315 sh, 300 s
$[NPr_4][Cr(Ph_2PCH{=}CHPPh_2)Cl_4]$	58.4 (58.7)	6.7 (6.4)	17.9 (18.3)	1.9 (1.8)	6.3 (6.7)	purple	340 s, 315 s
$[NPr_4][Cr(Ph_2AsCH{=}CHAsPh_2)Cl_4]$	52.2 (52.8)	5.4 (5.6)	16.2 (16.8)	1.7 (1.6)	6.0 (6.0)	purple	346 m, 335 s, 302 s
$[PPh_3CH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$	41.8 (41.5)	3.6 (3.8)	30.9 (31.7)	... ...	... ...	blue	312 m, 285 s, 258 s
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$	30.5 (30.7)	4.0 (4.1)	18.0 (18.1)	... ...	9.3 (8.8)	green	380 m, 333 sh, 321 s, 307 sh
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$	25.4 (25.0)	3.8 (3.3)	32.6 (33.3)	... ...	... ...	green	320, 285, 258 sh
$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]ClO_4$	30.3 (30.2)	4.3 (4.0)	...	...	...	bright green	380 m
$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Br_2]ClO_4$	27.2 (27.2)	3.6 (3.6)				bright green	320 m

[a] Found values are given, with calculated values in parentheses. [b] Nujol mulls. All complexes have magnetic moments close to μ_{eff} = 3.88 μ_B/Cr as expected for Cr(III).

identified (Table I). The characterization of these $[CrX_4(das)]^-$ complexes enabled us to definitely identify the structure present in $Cr(das)_{1.5}X_3$ (X = Cl, Br), by far-IR spectroscopy. (Attempts to grow crystals of $Cr(das)_{1.5}X_3$ for X-ray crystallographic examination were frustrated by the poor solubility, and only powders were produced from in situ syntheses.) The $[Cr(das)_2X_2]ClO_4$ were readily obtained by treatment of $Cr(das)_{1.5}X_3$ with $HClO_4$, and as can be seen from Table I, the bands in the IR spectrum of $Cr(das)_{1.5}Cl_3$ in the range 400–200 cm^{-1} are all accounted for by superimposition of the spectra of $[Cr(das)Cl_4]^-$ and $[Cr(das)_2Cl_2]^+$. Similar conclusions are drawn for $Cr(das)_{1.5}Br_3$, although here the overlapping of Cr–Br and ligand bands makes the spectral assignments more difficult. Thus the far-IR spectra demonstrate that the $Cr(das)_{1.5}X_3$ complexes are indeed [*trans*-$Cr(das)_2X_2]^+$ [*cis*-$Cr(das)X_4]^-$.

Experimental Section

All reactions were carried out under dry dinitrogen by using standard Schlenk tube and dry box techniques. $CrCl_3(THF)_3$ was prepared from anhydrous $CrCl_3$, zinc dust, and dry tetrahydrofuran,[6] and $CrBr_3(THF)_3$ analogously from anhydrous $CrBr_3$. Physical measurements were made as described previously.[7]

$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (X = Cl, Br). $CrX_3(THF)_3$ (1 mmol) was dissolved in dry dichloromethane (20 cm^3), the solution filtered, and *o*-phenylenebis(dimethylarsine) (0.57 g, 2 mmol) added. When the mixture was stirred at room temperature, green solids separated, which were filtered off, rinsed thoroughly with diethyl ether, and dried in vacuo; yield ca. 70%.

$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2X_2]ClO_4$. $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (1 mmol) was added to 40% aqueous perchloric acid and the mixture stirred for 4–5 h. The bright green solids were separated by filtration and washed with distilled water, until the washings were colorless. The solids were rinsed with diethyl ether and dried; yield ca. 65%.

$[N\text{-}n\text{-}Pr_4][Cr(L\text{-}L)Cl_4]$ (L–L = $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2AsCH{=}CHAsPh_2$). *n*-Pr_4NCl was dried by heating at 80–90 °C in vacuo for 2 days. The appropriate ligand (2 mmol), $CrCl_3(THF)_3$ (2 mmol), and *n*-Pr_4NCl (2 mmol) were dissolved in CH_2Cl_2 and the solutions combined and stirred for several hours. The solutions were filtered and concentrated in vacuo. The oils produced were stirred with petroleum ether until they were converted to fine powders, which were filtered off and dried in vacuo. $[N\text{-}n\text{-}Pr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$ was prepared similarly in acetone and $[Ph_3PCH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$ from the ligand, $CrBr_3(THF)_3$, and Ph_3PCH_2PhBr.

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Registry No. $[NPr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$, 82456-75-5; $[NPr_4][Cr(o\text{-}C_6H_4(AsMe_2)_2)Cl_4]$, 82456-77-7; $[NPr_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$, 82456-79-9; $[NPr_4][Cr(Ph_2PCH{=}CHPPh_2)Cl_4]$, 82469-03-2; $[NPr_4][Cr(Ph_2AsCH{=}CHAsPh_2)Cl_4]$, 82456-81-3; $[PPh_3CH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$, 82456-83-5; $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$, 82456-84-6; $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$, 82456-85-7; $[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]ClO_4$, 14127-30-1; $[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Br_2]ClO_4$, 60536-77-8; $CrCl_3(THF)_3$, 10170-68-0; $CrBr_3(THF)_3$, 82456-86-8.

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Electrochemical Oxidation and Reduction of Methylcobalamin and Coenzyme B_{12}

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Although the electrochemical reduction of alkylcobalamins has been reported, the number of electrons involved and the reaction products were in doubt.[1-3] The oxidation of these compounds has not previously been studied. We report here the spectroelectrochemical and product analysis of both the electrochemical oxidation and reduction of methylcobalamin and coenzyme B_{12}. The electrochemical reactions of the alkylcobalamins are completely different from those of vitamin B_{12}, cyano[Co(III)]cobalamin, and other cobalamins.[1,4,5]

Experimental Section

The cyclic voltammetric and coulometric studies of coenzyme B_{12} and methylcobalamin were carried out in 0.5 M Na_2SO_4. In both cases, Britton–Robinson buffer was used.

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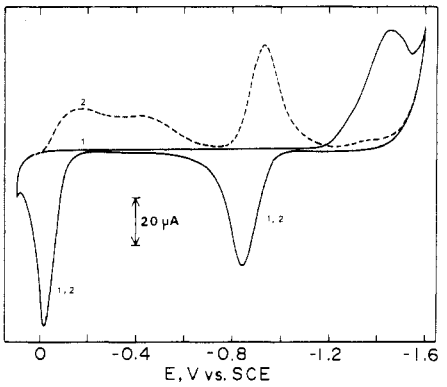

Figure 1. Cyclic voltammograms of methylcobalamin at pH 8.7. Details are discussed in the section on electrochemical reduction of methylcobalamin. Sweep rate was 2 mV s^{-1} at an Hg–Au minigrid.

The Britton–Robinson buffer, a combination of phosphate, borate, and acetate in equal measure, was found to exert a small but finite influence on the E peak values. The concentration of the buffer was, accordingly, kept constant between 24 and 27 mM in each ion: total acetate, borate, and phosphate. The pH was varied by adding concentrated KOH or NaOH to a stock solution before adding the buffer to the electrolyte solution.

The exhaustive reduction of methylcobalamin, to determine the products of the methyl group, was done in a solution of 0.5 M NaCl with 50 mM phosphate buffer at pH 7.4. The reduction was carried out under argon in a gastight cell in the dark for 30 min at −1.5 V vs. SCE. The products were transferred with a gastight syringe from the headspace to the mass spectrometer, a Kratos Model MS-80.

All chemicals employed were reagent grade, and solutions were deaerated with 99.99% water-pumped nitrogen or argon. All spectroelectrochemical, coulometric, and cyclic voltammetric measurements were carried out with the use of thin-layer cells as previously described.[4,6]

Results

Electrochemical Reduction of Methylcobalamin and Coenzyme B_{12}. A typical thin-layer cyclic voltammogram of methylcobalamin at an Hg–Au minigrid is shown in Figure 1. On the initial negative scan (solid line), there occurs a single irreversible reduction wave with a peak potential of −1.51 V vs. SCE at pH 7.3. The peak shifts to −1.45 V at pH 8.7. For reoxidation on the reverse scan, two anodic waves, at about −0.8 and 0.0 V, are observed. The subsequent negative scan, curve 2 of Figure 1 (broken line), shows two unresolved small cathodic waves between about −0.1 and −0.4 V. With decreasing pH, the −0.1-V peak increases in height while that of the −0.4-V peak decreases. A third cathodic wave is observed at about −0.9 V. No wave is seen in the −1.5-V range. The characteristics of all subsequent positive and negative scans remain the same.

After the first negative scan, the cyclic voltammograms at both pH values are identical with those found for aquocobalamin under identical conditions. [Co(II)]cobalamin (B_{12r}) and [Co(III)]cobalamin (B_{12a}) are formed sequentially during the positive scan. Spectroelectrochemical experiments further confirm that the product formed on reduction of methylcobalamin at −1.5 V is [Co(I)]cobalamin,[4,5] vitamin B_{12s} (see Figure 2A,B). Identical results were observed for coenzyme B_{12}. Thus, the cobalt–carbon bond is irreversibly broken during the reduction at −1.5 V.

GC–MS indicates that ethane is greater than 97% of the cleavage product of the reduction of methylcobalamin. Controlled-potential coulometry at −1.5 V using a thin-layer Hg–Au minigrid electrode cell[7,8] gave n values ranging from 0.94 to 1.07 in 20 separate determinations for both methylcobalamin and coenzyme B_{12}. This result is in contrast to the report of an n value of 2 for methylcobalamin in 0.1 M KCl solution at pH 7.0 in a paper of Swetik and Brown.[9] The production of [Co(I)]cobalamin and a radical species was also

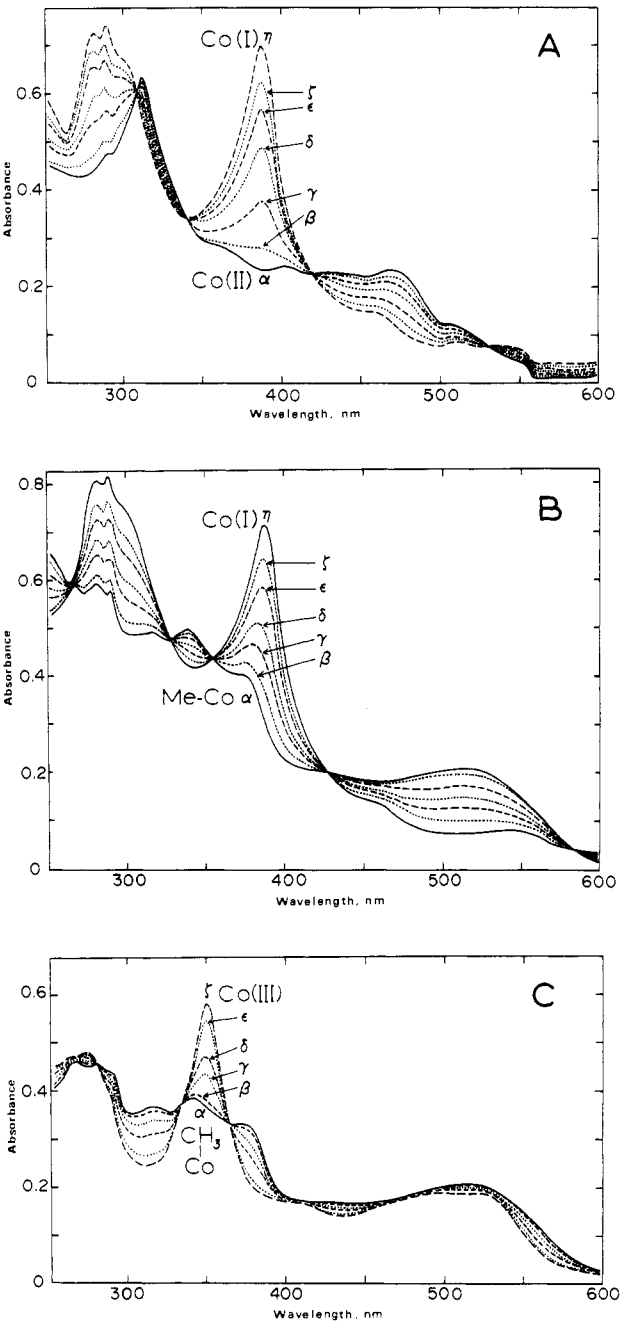

Figure 2. (A) Variation in the optical spectrum for the reduction of [Co(II)]cobalamin (B_{12r}) to [Co(I)]cobalamin (B_{12s}). The reduction was done in an Hg–Au minigrid thin-layer cell at pH 6.86 in 0.5 M Na_2SO_4 with 1 mM aquocobalamin. Equilibrium potentials, α to η: −0.770, −0.820, −0.860, −0.880, −0.900, −0.920, −1.000 V vs. SCE. (B) Optical spectral changes with time upon reduction of methylcobalamin to [Co(I)]cobalamin. Conditions are as in part A except the solution pH was 8.70 with 1 mM methylcobalamin. Time runs are from α to η. Compare with the α curve in part A to see lack of evidence for any intermediate Co(II) species. (C) Optical spectral changes with time for oxidation of methylcobalamin. Conditions were the same as in part B except the pH was 7.2. The final product is aquo[Co(III)]cobalamin, curve ζ at +0.800 mV vs. SCE.

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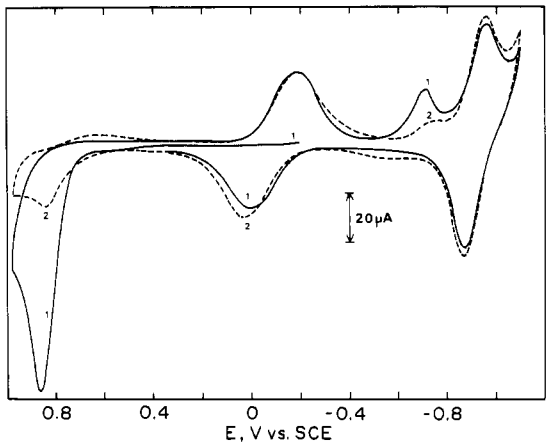

Figure 3. Cyclic voltammograms of methylcobalamin. Details are discussed in the section on electrochemical oxidation of methylcobalamin. The sweep rate was 2 mV s^{-1} at a gold minigrid, and the pH was 7.2.

observed upon reduction after a one-electron transfer produced by using γ-radiolysis methods.[10] Note that this scission must be classified as heterolytic.

Electrochemical Oxidation of Methylcobalamin. Figure 3 shows a typical thin-layer cyclic voltammogram for methylcobalamin at a gold minigrid electrode. A single irreversible wave is observed with a peak potential of +0.87 V vs. SCE on the initial positive scan. The subsequent negative scan and the second cycle (dashed line) exhibit peaks that are identical with those obtained for aquo[Co(III)]cobalamin (B_{12a}) under identical conditions. On the second cycle, the anodic peak at +0.87 V is much smaller, and on a third cycle (not shown), it cannot be observed.

Spectroelectrochemical experiments show that on oxidation of methylcobalamin at +0.80 V, B_{12a} is quantitatively produced (see labeled curve, Figure 2C). Methanol was identified by gas chromatography as the only other product. Thus, the cobalt–carbon bond is cleaved during the oxidation reaction. Controlled-potential coulometry at +0.8 V in an Au minigrid thin-layer cell gave an n value of 2.00 ± 0.07 for 10 determinations. It should be pointed out that neither B_{12a} nor vitamin B_{12}, cyano[Co(III)]cobalamin, show any oxidative wave before solvent breakdown in the pH range 1–11 at an Au minigrid electrode.

On the basis of these experimental results, the mechanisms for the redox reactions of the methylcobalamin and coenzyme B_{12} can be postulated. We find that the carbon–cobalt bonding and reactions can be explained with a simple two-level (σ, σ^*) molecular orbital model.[11] Oxidation at the electrode consists of a two-electron transfer out of the bonding orbital at about +0.9 V vs. SCE. The cobalt is formally Co(III). The methyl group leaves as its carbocation which, typically, will react with water as the nucleophile, producing methanol as the product.[12]

The mechanism of reduction is less obvious since only a one-electron reduction occurs. We postulate that the single electron does go into the σ^* orbital from the electrode. From electrochemical arguments at this large, negative potential, a two-electron transfer would be anticipated.[4,5] The second electron transfer is unobserved. This probably is due to the significant solvent reorganization required in analogy with the reduction of the methyl radical itself.[16] Thus, the one-electron product must be reacting relatively rapidly but away from the electrode interface to form [Co(I)]cobalamin and ethane. This formation of ethane parallels the results found when the methyl radical is formed from methylcobalamin by photolysis.[17] The reduction and concomitant heterolytic cleaving of the Co–C bond indicate that the cobalamin chelate is acting as a good leaving group. The mechanism can be explained[11,18] analogously to one-electron scission observed on reduction of alkyl halides and other organic species.[19]

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Registry No. Methylcobalamin, 13422-55-4; coenzyme B_{12}, 13870-90-1; aquo[Co(III)]cobalamin, 13422-52-1; [Co(I)]cobalamin, 18534-66-2; [Co(II)]cobalamin, 14463-33-3; Co, 7440-48-4.

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Neighboring Effects in the Ligand Field Photochemistry of the Pentacyano(ethylenediamine)ferrate(II) Complex

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The typical pattern observed[1,2] for the visible–near-UV photochemistry of substituted pentacyanoferrate(II) complexes, $Fe(CN)_5L^{3-}$, is the replacement of L by another ligand, as represented by reaction 1. The parallel photoreaction 2, leading to tetracyanoferrate species, has been reported to be minor or nonexistent at the irradiation wavelengths typically employed for the photolysis (e.g., 365 and 436 nm).

$$Fe(CN)_5L^{3-} + H_2O \xrightarrow{h\nu} Fe(CN)_5H_2O^{3-} + L \quad (1)$$

$$Fe(CN)_5L^{3-} + H_2O \xrightarrow{h\nu} Fe(CN)_4(H_2O)L^{2-} + CN^- \quad (2)$$

It has been suggested[3] that the photodissociation of a cyanide ligand would be less favored than for a neutral ligand, because of the charge separation involved in the process. Alternatively, the extent of labilization of the Fe–CN bond in the excited state would be insufficient to prevent the recombination of the quasi-dissociated species before the attack of the solvent molecules. With use of ethylenediamine as the

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