Hydrophobic Vitamin B_{12}. II. Coordination Geometry and Redox Behavior of Heptamethyl Cobyrinate in Nonaqueous Media†

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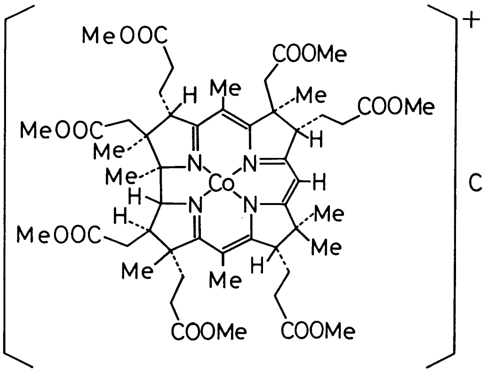
The nuclear cobalt(II) ion in heptamethyl cobyrinate iodide, Cob(II)ester·I, was found to assume a distorted square-planar geometry of $Co-N_4$ type with iodide as a counterion in a polar solvent (methanol) and a square-pyramidal one of $Co-N_4I$ type with the iodide ion coordinated at one of the axial positions in apolar solvents such as dichloromethane, benzene, and toluene. The redox chemistry of Cob(II)ester·I and heptamethyl cobyrinate perchlorate, $[Cob(II)ester]ClO_4$, was investigated in various organic solvents by means of cyclic voltammetry and controlled-potential electrolysis. The Co(II)/Co(I) and Co(III)/Co(II) redox potentials for $[Cob(II)ester]ClO_4$ exhibited cathodic shifts as either solvent basicity or polarity was raised, and were found to be in the anodic side relative to the corresponding potentials for Co^{II}(tpp) under identical conditions. The medium effect on the redox behavior of hydrophobic vitamin B_{12} was discussed in connection with the microenvironmental effect on vitamin B_{12} placed in the enzyme active sites.

We have been dealing with hydrophobic vitamin B_{12} derivatives in order to simulate various functions of vitamin B_{12} as exerted in the hydrophobic active sites of enzymes concerned. One of hydrophobic vitamin B_{12} derivatives involving a largely polarizable ion (iodide) shows different colors in solution as the solvent nature changes. Cob(II)ester·I has been prepared originally by Werthemann *et al.*,[1] and the X-ray diffraction analysis of its single crystal has shown that the complex is in a dimeric form which contains one bridging iodide per dimer complex and the second iodide ion is not coordinated.[2] However, any comprehensive structural clarification of the complex in solution has not been carried out yet. Thus, we studied firstly in this work the structures of Cob(II)ester·I in various organic solvents to clarify the origin of color change.

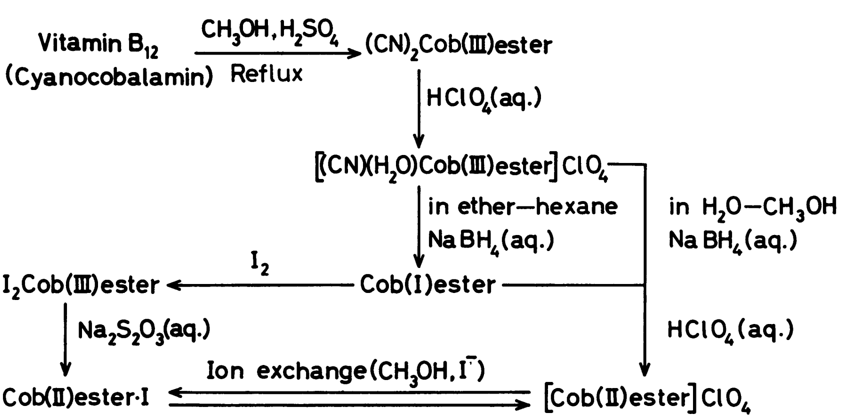
The redox behavior of vitamin B_{12} has recently been examined rather extensively,[3–9] and the studies on its catalytic reactions have been carried out by electrochemical means.[10–13] However, the redox chemistry of vitamin B_{12} in organic solvents has not been investigated because of its insolubility in most of such solvents. Thus, the redox behavior of hydrophobic vitamin B_{12} derivatives in various organic media was examined in this work by means of cyclic voltammetry in order to obtain useful information for the redox property of vitamin B_{12} under various microenvironmental conditions comparable to the enzyme active sites. In addition, the redox potentials of heptamethyl cobyrinate perchlorate, $[Cob(II)ester]ClO_4$, were compared with those of (5,10,15,20-tetraphenylporphinato)cobalt(II), Co^{II}(tpp), evaluated under identical conditions, so that the intrinsic ligand effect on the redox behavior of vitamin B_{12} is to be characterized.

Experimental

Materials. Cob(II)ester·I was prepared by the



$[Cob(II)ester]ClO_4$



Scheme 1.

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procedures outlined in Scheme 1 after the method of Werthemann *et al.*[1] [Cob(II)ester]ClO_4[14] and Co^{II}(tpp)[15] were synthesized according to the reported procedures. Tetrabutylammonium perchlorate (TBAP), tetrabutylammonium iodide (TBAI) of polarographic grade and ferrocene of guaranteed reagent grade were commercially obtained from Nakarai Chemicals. Organic solvents used for electrochemical measurements were purified and dried according to the standard procedures[16] and kept over 4-Å Molecular Sieves.

General Measurements. Electronic absorption spectra and diffuse reflectance spectra were recorded on a Hitachi 340 recording spectrophotometer. ESR spectra were obtained on a JEOL JES-ME 3 X-band spectrometer equipped with a 100-kHz field modulation unit; a standard MgO/Mn^{II} sample calibrated with a NMR magnetometer was employed for calibration of the magnetic field. Molecular weight measurements were carried out with a Hitachi Perkin-Elmer 115 vapor pressure osmometer by using benzene as a solvent.

Electrochemical Measurements. Cyclic voltammograms were obtained on a YANACO P-8 polarograph. An electrochemical cell similar to that reported in literature[17] was used and equipped with platinum wire of 0.5-mm diameter as working and auxiliary electrodes. A saturated calomel electrode (SCE) or an Ag/AgCl electrode was served as a reference which was separated from a bulk electrolyte solution by a salt bridge prepared with benzylidene-D-sorbitol[18] and a nonaqueous solution of TBAP (5.0×10^{-2} mol dm^{-3}). Nonaqueous solutions containing the cobalt complex (*ca.* 5×10^{-4} mol dm^{-3}) and TBAP (*ca.* 5×10^{-2} mol dm^{-3}) were deaerated prior to each measurement, and the inside of the cell was maintained under argon atmosphere throughout each measurement. All the measurements were carried out at 20 ± 2 °C. The scan rate was varied in a range from 10 through 200 mV s^{-1}. Half-wave potentials ($E_{1/2}$) and anodic and cathodic currents were evaluated according to the method described previously.[19]

Controlled-potential electrolysis was carried out in a three-electrode cell modified for electronic spectral measurements, as described previously.[19] An applied potential between the working and reference electrodes was maintained constant with a conventional potentiostat and monitored with a Takeda Riken TR-6656 digital multimeter.

Results and Discussion

Coordination Geometry of Cob(II)ester · I in Solution. Cob(II)ester · I shows two different kinds of electronic spectra in solution depending upon the nature of solvents (Figs. 1 and 2). The complex in methanol shows a spectral feature which is characteristic of the base-off vitamin B_{12r} in aqueous media and comparable to those of [Cob(II)ester]ClO_4 observed in methanol and dichloromethane. The diffuse reflectance spectrum of [Cob(II)ester]ClO_4 shown in Fig. 1 is apparently comparable to the spectrum of Cob(II)ester · I in methanol. Cob(II)ester · I has been known to be in a dimeric form with a single μ-iodo bridging between two cobalt atoms in the solid state as confirmed by the X-ray diffraction study.[2] The solution spectrum of Cob(II)ester · I in dichloromethane is apparently comparable to its diffuse reflectance spectrum as shown in Fig. 2. In order to identify the coordination geometry

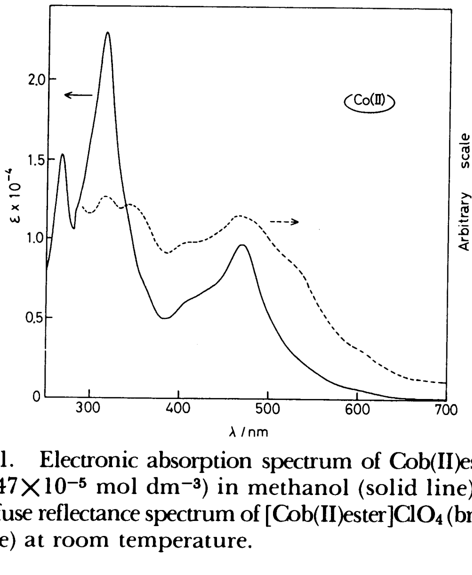

Fig. 1. Electronic absorption spectrum of Cob(II)ester · I (4.47×10^{-5} mol dm^{-3}) in methanol (solid line) and diffuse reflectance spectrum of [Cob(II)ester]ClO_4 (broken line) at room temperature.

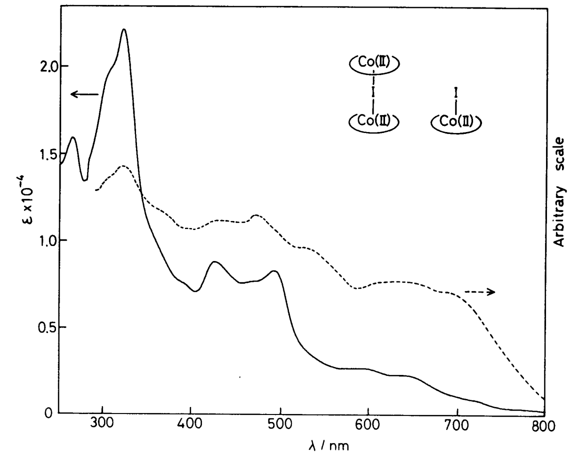

Fig. 2. Electronic absorption spectrum in dichloromethane (solid line; concentration of the complex, 4.90×10^{-5} mol dm^{-3}) and diffuse reflectance spectrum (broken line) of Cob(II)ester · I at room temperature.

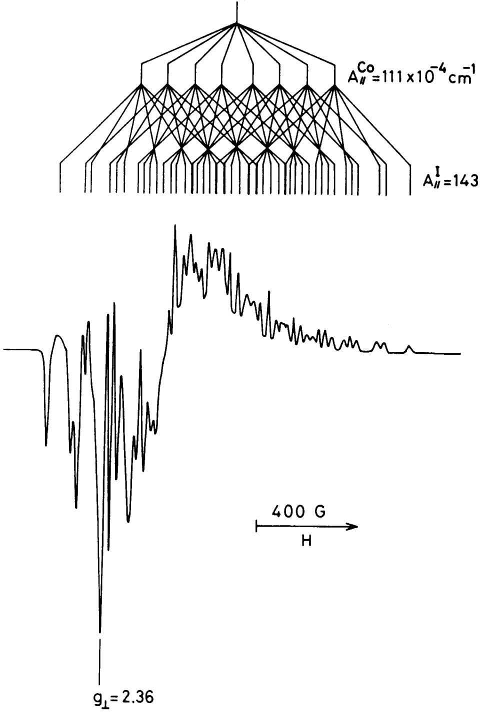

Fig. 3. ESR spectrum of Cob(II)ester · I (5.87×10^{-3} mol dm^{-3}) in toluene at 77 K.

of this complex in dichloromethane, another spectroscopic method was adopted in view of the advantageous property of Cob(II)ester · I in dichloromethane as being paramagnetic.

The ESR spectrum of Cob(II)ester · I in toluene at 77 K is shown in Fig. 3. Spin Hamiltonian parameters for the complex are as follows; $g_{\parallel}=2.00$, $g_{\perp}=2.36$, $A^{\mathrm{Co}}_{\parallel}=11.1\times10^{-3}\ \mathrm{cm}^{-1}$, and $A^{\mathrm{I}}_{\parallel}=14.3\times10^{-3}\ \mathrm{cm}^{-1}$. The superhyperfine structure observed in the $g_{\parallel}$ region is apparently due to the interaction between the iodine nucleus (I=5/2) and the cobalt nucleus (I=7/2). This indicates that one iodide ion is coordinated to the central cobalt at one of the axial positions of the latter. The spin Hamiltonian parameters thus evaluated are comparable to those for the same complex as measured by the Q-band ESR spectroscopy at 120 K in toluene; $g_{\parallel}=2.003$, $g_{\perp}=2.263$, $A^{\mathrm{Co}}_{\parallel}=11.2\times10^{-3}\ \mathrm{cm}^{-1}$, $A^{\mathrm{I}}_{\parallel}=14.0\times10^{-3}\ \mathrm{cm}^{-1}$, $A^{\mathrm{Co}}_{\perp}\approx0$, and $A^{\mathrm{I}}_{\perp}\approx0$.[20] An ESR signal due to forbidden transition, being characteristic of a dinuclear cobalt complex, was not observed for a wide scanning range of magnetic field. Consequently, the present complex is not associated with the interaction between cobalt–iodide–cobalt in dichloromethane. The ESR spectrum of Cob(II)ester · I measured in methanol at 77 K did not show such superhyperfine structure as caused by the interaction between the iodine and cobalt nuclei, but showed a spectral feature identical with that observed for [Cob(II)ester]ClO$_4$.[14] This again serves to confirm that the iodide ion is not coordinated to the cobalt atom at its axial position.

Cob(II)ester · I in methanol was readily converted into [Cob(II)ester]ClO$_4$ by ion-exchange chromatography on a column of Amberlite IRA-401. This result also indicates that the iodide ion is acting only as a counteranion in methanol.

The molecular weight of Cob(II)ester · I was determined in benzene by vapor pressure osmometry: 1120±70; calcd for Cob(II)ester · I as monomer, 1164. This result further serves to confirm that Cob(II)ester · I is not dimeric but monomeric in apolar solvents.

In summarizing the above results, the coordination geometry around the nuclear cobalt of Cob(II)ester · I is subjected to change by the nature of solvents employed. In polar solvents such as methanol, the complex assumes a distorted square-planar geometry around the cobalt atom and the anion of weak coordination ability, iodide, simply acts as a counterion species even though solvent molecules would possibly occupy the axial positions of cobalt. In apolar solvents such as dichloromethane, benzene, and toluene, however, the complex assumes a square-pyramidal geometry around the nuclear cobalt having coordination number 5, the iodide ion being coordinated to the cobalt atom at its axial position, and exists as a mononuclear species in solution. Such coordination structures are closely correlated with the redox behavior of the complex as described below.

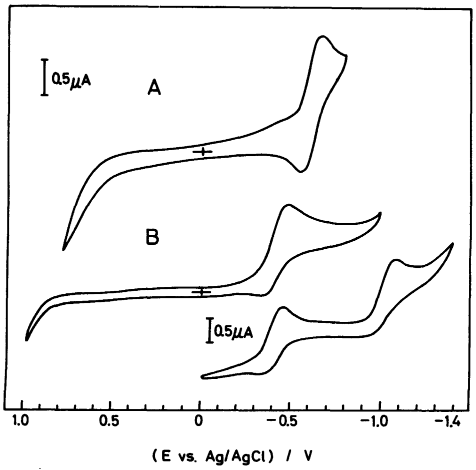

Fig. 4. Cyclic voltammograms of [Cob(II)ester]ClO$_4$ (5.0×10^{-4} mol dm^{-3}) containing 5.0×10^{-2} mol dm^{-3} TBAP in methanol (A) and dichloromethane (B) at 20±2 °C: scan rate, 100 mV s^{-1}.

Electrochemical Behavior of Cob(II)ester Species. Cyclic voltammograms of [Cob(II)ester]ClO$_4$ and Cob(II)ester · I in methanol and dichloromethane are shown in Figs. 4 and 5. The Co(II)/Co(I) redox couple for [Cob(II)ester]ClO$_4$ is observed at −0.61 V *vs.* Ag/AgCl (−0.65 V *vs.* SCE) in methanol and at −0.41 V *vs.* Ag/AgCl (−0.45 V *vs.* SCE) in dichloromethane. The redox reversibility observed with [Cob(II)ester]ClO$_4$ and

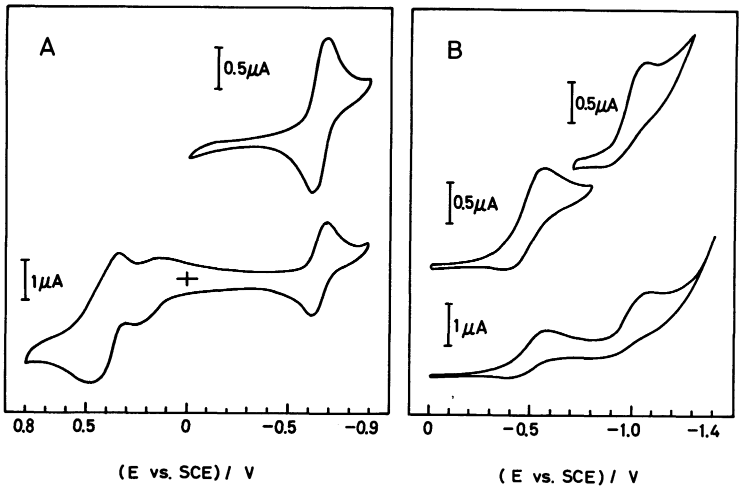

Fig. 5. Cyclic voltammograms of Cob(II)ester · I (7.0×10^{-4} mol dm^{-3}) containing 5.0×10^{-2} mol dm^{-3} TBAI in methanol (A) and dichloromethane (B) at 20±2 °C: scan rate, 100 mV s^{-1}.

Cob(II)ester·I in dichloromethane is less satisfactory as compared with that in methanol on the basis of relative potential peak intensities between the cathodic and anodic peaks; the redox process was irreversible in dichloromethane even at the scan rate as fast as 500 mV s^{-1} and the anodic peak disappeared at the slowest extreme. This is attributed to the fact that Cob(I)ester formed by electrochemical reduction undergoes reaction with dichloromethane to yield the corresponding alkylated complex [ClH_2C–Cob(III)ester] as confirmed independently by a preparative experiment. Scanning further to the cathodic side showed a one-electron reduction peak at −1.07 V *vs.* Ag/AgCl (−1.11 V *vs.* SCE). This reduction peak seems to be attributed to the alkyl complex derived from the reaction of Cob(I)ester with dichloromethane, ClH_2C–Cob(III)ester, in the light of the first reduction potential for [CH_3–Cob(III)ester]ClO_4 in dichloromethane (−1.23 V *vs.* SCE). The Co(III)/Co(II) redox peak was not observed under the above experimental conditions.

The cyclic voltammograms of Cob(II)ester·I in the presence of TBAI as a supporting electrolyte show redox peaks due to the iodide ion in the positive potential range (Fig. 5). The Co(II)/Co(I) redox peak for Cob(II)ester·I is observed at −0.65 V *vs.* SCE in methanol; comparable to that for [Cob(II)ester]ClO_4 in methanol. However, the same redox peak is observed at −0.52 V *vs.* SCE in dichloromethane; shifted by 70 mV to the cathodic side relative to the potential peak for [Cob(II)ester]ClO_4. Since the iodide ion acts as an axial ligand in dichloromethane, the reduction of Cob(II)ester·I requires greater cathodic potential relative to that of [Cob(II)ester]ClO_4. The Co(II)/Co(I) redox peak exhibits some anodic shift in dichloromethane relative to that in methanol even though the liquid junction potential difference between the two solvent systems is taken into consideration as described below. It is reasonable to expect that Cob(II)ester is more readily reduced in dichloromethane since this solvent is of noncoordinating nature and Cob(I)ester without charge on it is stabilized in highly apolar solvents.

Redox Potentials of [Cob(II)ester]ClO_4 in Various Solvents. The Co(II)/Co(I) and Co(III)/Co(II) redox potentials for [Cob(II)ester]ClO_4 in various organic solvents are summarized in Table 1. Cyclic voltammograms of the complex in dimethyl sulfoxide (DMSO) are shown in Fig. 6 as a typical example. The ratios between anodic and cathodic peak currents, i_{pa}/i_{pc}, were unity and independent of scan rate (from 10 to 200 mV s^{-1}) for the two redox couples in various organic solvents except dichloromethane. Plots of i_p ($=i_{pa}+i_{pc}$) *vs.* $v^{1/2}$(v for scan rate, mV s^{-1}) were linear, and potential separation between the anodic and cathodic peaks varied from 160 to 80 mV for the two redox couples, while $E_{1/2}$ values remained constant within an accuracy of ±3% regardless of scan rate variation. Thus, the present electrochemical redox reactions in various organic media except dichloromethane are consistent with reversible or quasi-reversible one-electron transfer processes.[21] In order to identify the complex species formed during each redox process, the controlled-potential electrolysis was performed at −1.20 and 0.80 V *vs.* SCE. The electrochemical reduction at −1.20 V *vs.* SCE was followed by electronic spectroscopy as shown in Fig. 7, where clear isosbestic points are observed at 308, 355, 417, and 547 nm. Since the developing absorption maximum at 394 nm during the reduction process is characteristic of Cob(I)ester, the redox potential at −0.64 V *vs.* SCE in DMSO is

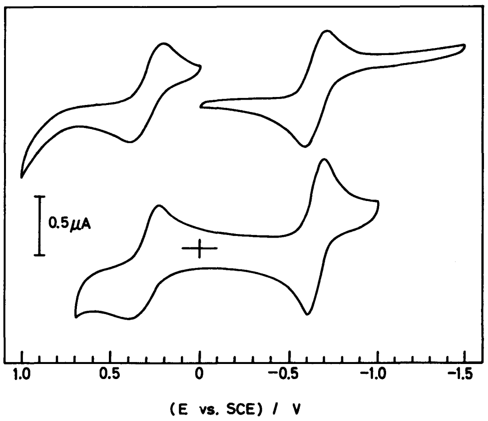

Fig. 6. Cyclic voltammograms of [Cob(II)ester]ClO_4 (5.2×10^{-4} mol dm^{-3}) in dimethyl sulfoxide containing 5.1×10^{-2} mol dm^{-3} TBAP at 20±2 °C: scan rate, 100 mV s^{-1}.

TABLE 1. REDOX POTENTIALS FOR Cob(II) ESTER AND Co^{II}(tpp) IN NONAQUEOUS MEDIA[a)]

Complex	Medium[b)]	Solvent parameters		*vs.* SCE/V		*vs.* (Fc^+/Fc)[c)]/V	
		DN	*Z*	Co(III)/Co(II)	Co(II)/Co(I)	Co(III)/Co(II)	Co(II)/Co(I)
[Cob(II)ester]ClO_4[d)]	CH_2Cl_2	0	64.2	—	−0.45	—	−1.00
	CH_3COCH_3	17.0	65.7	+0.77	−0.53	+0.30	−1.00
	DMF	26.6	68.5	*ca.* +0.40	−0.61	*ca.* −0.04	−1.05
	DMSO	29.8	71.1	+0.30	−0.64	−0.11	−1.05
	CH_3CN	14.1	71.3	*ca.* +0.45	−0.64	*ca.* +0.05	−1.04
	CH_3OH	19	83.6	—	−0.65	—	−1.05
Cob(II)ester·I[e)]	CH_2Cl_2	0	64.2	—	−0.52	—	−1.07
	CH_3OH	19	83.6	—	−0.65	—	−1.05
Co^{II}(tpp)[d)]	CH_2Cl_2	0	64.2	—	−0.88	—	−1.43
	DMF	26.6	68.5	+0.24	−0.83	−0.20	−1.27
	DMSO	29.8	71.1	+0.08	−0.87	−0.33	−1.28

a) Measured at 20±2 °C; scan rate, 100 mV s^{-1}. b) Abbreviations: DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide. c) Abbreviations: Fc, ferrocene; Fc^+, ferricinium ion. d) TBAP, 5×10^{-2} mol dm^{-3}. e) TBAI, 5×10^{-2} mol dm^{-3}.

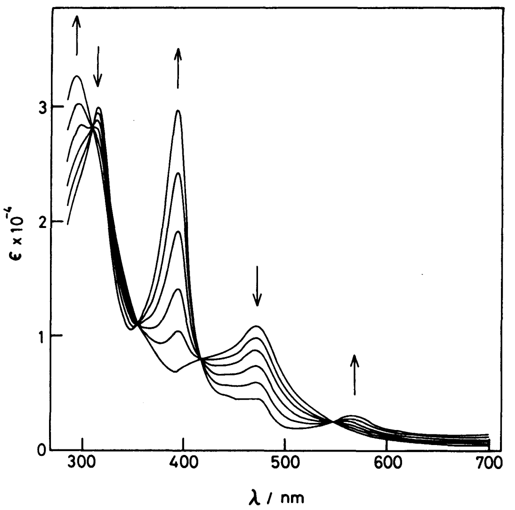

Fig. 7. Electrochemical reduction of [Cob(II)ester]ClO_4 (2.0×10^{-5} mol dm^{-3}) at −1.20 V *vs.* SCE in dimethyl sulfoxide containing 5.0×10^{-2} mol dm^{-3} TBAP at 20±2 °C: trends of spectral change with time are shown by arrows. About 80% of [Cob(II)ester]ClO_4 was reduced to Cob(I)ester after electrochemical reaction for 9 h.

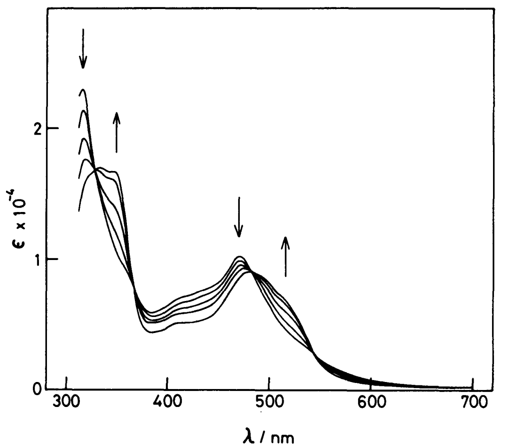

Fig. 8. Electrochemical oxidation of [Cob(II)ester]ClO_4 (2.0×10^{-5} mol dm^{-3}) at +0.80 V *vs.* SCE in dimethyl sulfoxide containing 5.0×10^{-2} mol dm^{-3} TBAP at 20±2 °C: trends of spectral change with time are shown by arrows. About 40% of [Cob(II)ester]$^+$ was oxidized to [Cob(III)ester]$^{2+}$ after electrochemical reaction for 3 h.

assigned to the Co(II)/Co(I) redox couple for the complex. Cob(I)ester thus produced was quantitatively reconverted into the original complex by oxidation at 0 V *vs.* SCE. The electronic spectral change during the electrochemical oxidation at 0.80 V *vs.* SCE in the same medium is shown in Fig. 8, and is accompanied with the increase in absorbance at 350, 490, and 520 nm. Since such absorption maxima are characteristic of Cob(III)ester, the redox potential at +0.30 V *vs.* SCE is assigned to the Co(III)/Co(II) redox couple.

Since the liquid junction potential is subjected to change by the nature of solvent system, the redox potentials observed in various solvents cannot be directly compared with each other among them. Though liquid junction potentials between electrolytic solutions in various solvents have been extensively investigated,[22] the most conventional and reliable means of eliminating the difference in liquid junction potential between various media is to adopt the observed redox potentials for the couple of ferrocene/ferricinium ion in various media as references. Because the true redox potential for the couple of ferrocene/ferricinium ion is considered to remain constant regardless of the nature of organic media,[23] the redox potentials corrected for the difference in liquid junction potential in the light of observed redox potentials for ferrocene/ferricinium ion are shown in Table 1. Gutmann investigated correlations between the half-wave potential of metal ion and the donor number of solvent (*DN*) for combination of various metal ions and solvents, and the half-wave potential for transition-metal ions was found to exhibit significant cathodic shift with the increase in solvent basicity (*DN*).[24] We claim here both polarity and basicity of solvents are primarily concerned with the redox potential after corrected for liquid junction potential. The solvent polarity is associated with the electrostatic stabilization of a metal complex; a polar solvent tends to favor the formation of a charged complex and such a solvent effect becomes more pronounced as the charge on a complex increases. On the other hand, the solvent basicity is concerned with the axial ligation behavior of solvent molecules; a sufficiently basic solvent tends to coordinate to the nuclear metal of a complex. Therefore, we discuss the Co(III)/Co(II) and Co(II)/Co(I) redox potentials for [Cob(II)ester]ClO_4 in correlation with both solvent polarity and basicity. Kosower's *Z*-value[25] and Gutmann's donor number (*DN*) are adopted here as polarity and basicity parameters, respectively. The correlations between the redox potential (Co(III)/Co(II) or Co(II)/Co(I)) and *DN* or *Z*-value are shown in Figs. 9 and 10. The Co(III)/Co(II) redox potential shows cathodic shift as the *DN* and *Z* parameters increase (Fig. 9); the higher the solvent basicity or polarity is, the more readily Cob(II)ester is oxidized. Such correlations are also observed for the Co(II)/Co(I) redox potential and level off beyond certain ranges of *DN* and *Z* parameters as shown in Fig. 10, but the extent of variation of the redox potential in various solvents is rather small as compared with that for the Co(III)/Co(II) couple. Since the overall charges on Cob(III)ester, Cob(II)ester, and Cob(I)ester are +2, +1, and 0, respectively, the tervalent cobalt complex is most stabilized in solvents of greater polarity. In addition, the tervalent cobalt in Cob(III)ester readily takes up the 5th and 6th ligand molecules at its axial sites while the univalent cobalt in Cob(I)ester has no tendency to interact with extra ligand molecules at its axial sites. Thus, the Co(III)/Co(II) redox potential is subjected to change by the variation of *DN* more effectively than the Co(II)/Co(I) couple. The correlations given in Figs. 9 and 10 apparently reflect such solvent effects. Similar solvent effects were observed on the Co(III)/Co(II) and Co(II)/Co(I) redox potentials for Co^{II}(tpp) (Table 1 and literature[26]). The Co(III)/Co(II) and Co(II)/Co(I) redox potentials for [Cob(II)ester]ClO_4 in various media appeared in the anodic side relative to the corresponding values for Co^{II}(tpp) as shown in Table 1. This must arise from the difference in ligand nature; the corrin and porphyrin

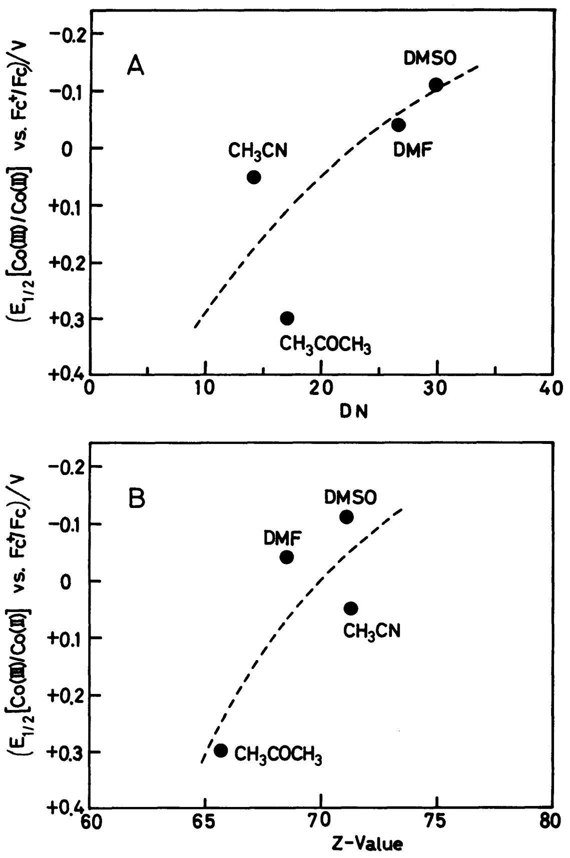

Fig. 9. Correlations of redox potential of [Cob(II)-ester]ClO$_4$ with solvent basicity and polarity: A, $E_{1/2}$[Co(III)/Co(II)] *vs.* *DN*; B, $E_{1/2}$[Co(III)/Co(II)] *vs.* *Z*-value.

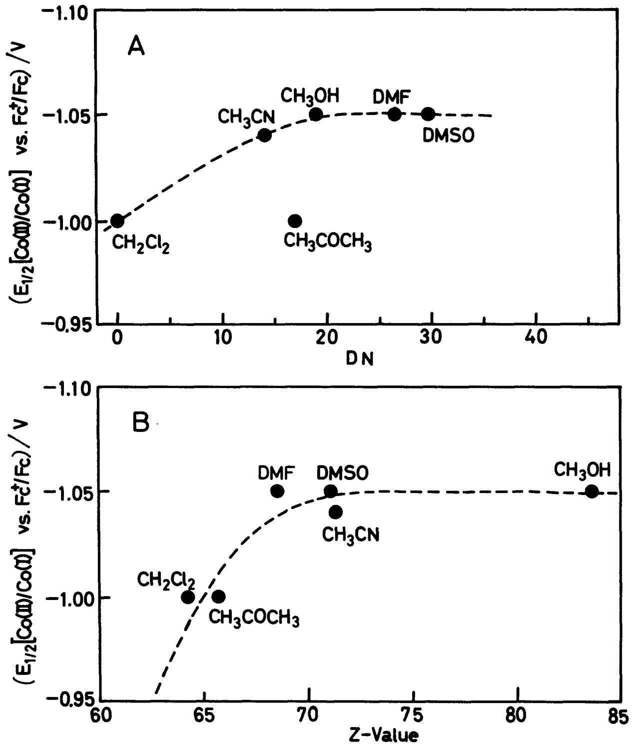

Fig. 10. Correlations of redox potential of [Cob(II)-ester]ClO$_4$ with solvent basicity and polarity: A, $E_{1/2}$[Co(II)/Co(I)] *vs.* *DN*; B, $E_{1/2}$[Co(II)/Co(I)] *vs.* *Z*-value.

ligands are mono- and dianionic, respectively, when coordinated to the cobalt ion. Thus, Co^{II}(tpp) is more readily oxidized and less readily reduced than Cob(II)ester. As reported in our previous paper,[14] the axial ligation behavior is subjected to change significantly by the nature of equatorial ligands, and the thermodynamic properties for the axial ligation of Cob(II)ester are much different from those observed for cobalt(II)-porphyrin. Such an equatorial ligand effect must be reflected on the redox behavior of cobalt.

The microenvironmental property effective on vitamin B$_{12}$ in enzyme systems is considered to vary rather extensively by the nature of apoenzymes concerned. In the light of the present results, the redox behavior of the nuclear cobalt of vitamin B$_{12}$ seems to be subjected to change from one enzyme to another depending upon the medium effects provided by the enzyme active sites. In particular, the Co(III)/Co(II) redox potential is sensitive to the nature of medium and the divalent cobalt state is more effectively stabilized in greater hydrophobic environments in the absence of coordinating ligands.

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