Inorganica Chimica Acta, 156 (1989) 125–137

Vitamin B_{12} and Coenzyme B_{12} Models. II.* An Electrochemical Investigation on Alkyl- and (Non-alkyl)cobalt(III) Complexes of 3,8-Dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione Dioxime by Cyclic Voltammetry and Polarography**

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(Received June 10, 1988)

Abstract

An electrochemical investigation has been carried out by polarography and cyclic voltammetry to evaluate the suitability of a new coenzyme B_{12} model built upon the quadridentate tetraza equatorial chelate, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [$(DOH)_2$bzo] as a non-biological mimic of coenzyme B_{12} and to establish a quantitative electrochemical comparison with the cobaloxime and Costa-type models. The (non-alkyl)cobalt(III) complexes of $(DOH)_2$bzo exhibit two polarographic reduction waves corresponding to the reductions, Co(III) → Co(II) and Co(II) → Co(I). The alkylcobalt(III) complexes exhibit adsorption/desorption phenomena, and the $E_{1/2}$ values have been obtained under conditions where the absorption/desorption processes and R–Co decomposition have been suppressed by the externally added base. The cyclic voltammograms of both alkyl and (non-alkyl)cobalt(III) complexes consist of two cathodic waves corresponding to the reductions, Co(III) → Co(II) and Co(II) → Co(I) and two anodic waves corresponding to the oxidations, Co(I) → Co(II) and Co(II) → Co(III). The ΔE_p is large for the Co(III)/Co(II) redox couple indicating irreversible electron transfer. For the Co(II)/Co(I) couple, ΔE_p is ~60 mV indicating reversible one electron transfer, but the i_{pc}/i_{pa} is ~0.5 indicating irreversibility. The irreversibility of the Co(III)/Co(II) and Co(II)/Co(I) redox couples can be attributed to the breaking of the Co–ligand bond in the axial sites during the reduction processes and the generation of the five-coordinate cobalt(II) complex, [RCo^{II}(DODOHbzo)] during the reduction of the organocobalt(III) complexes and the generation of the four-coordinate cobalt(I) complex, [Co^{I}(DODOHbzo)] during the reduction of the five-coordinate cobalt(II) complex are envisioned. The i_{pa}/i_{pc} ratio of 0.5 for the Co(II)/Co(I) redox couple indicates a 50% Co(I) yield probably due to the chemical reaction undergone by 50% of the electrogenerated Co(I). This suggests the involvement of a coupled chemical reaction such as an ECE mechanism. The near constancy of the E_{pc} values for the Co(II)/Co(I) couple of all the complexes indicates that both the axial ligands are lost during the electrolytic conversion of Co(II) to Co(I). The $E_{1/2}$ values for both redox couples are more negative for the alkyl complexes than that of the (non-alkyl) complexes indicating the high basicity of the coordinated alkyl groups. The externally added base has a pronounced effect of increasing the rate of electron transfer and suppressing the R–Co decomposition. The organocobalt(III) complexes undergo a quasireversible one electron oxidation without breaking either of the Co–ligand bonds in the axial sites. The $E_{1/2}$ value of the Co(IV)/Co(III) redox couple has a marked dependence on the nature of the organic ligand and is very sensitive even to the slight modifications of the Lewis base *trans* to the organic ligand. The results are discussed in the light of electrochemical studies of other models.

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*For Part I see ref. 1.

**The following abbreviations are used in this paper: $(DOH)_2$bzo = 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime; DODOHbzo = monoanion of 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime; DODOHpn = monoanion of 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime; C_2DODOHpn = monoanion of 2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diol; salen = *N,N'*-ethylenebis(salicylideneiminato) dianion; bae = *N,N'*-ethylenebis(acetylacetoneiminato) dianion; saloph = *N,N'*-*o*-phenylenebis(salicylideneiminato) dianion; TEAP = tetraethylammonium perchlorate; py = pyridine; Iz = imidazole; MeIz = 1-methylimidazole; 4-CH_3py = 4-methylpyridine (4-picoline); BIz = benzimidazole; Me_2BIz = 5,6-dimethylbenzimidazole; PPh_3 = triphenylphosphine; i-pr = isopropyl; $EtNH_2$ = ethylamine; Et_2NH = diethylamine; Et_3N = triethylamine; DMF = *N,N'*-dimethylformamide.

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A comparison of the electrochemical parameters, obtained under comparable conditions, of both alkyl- and (non-alkyl)cobalt(III) complexes of the present model with the corresponding literature values of cobaloxime and Costa-type models indicates that the present model is a closer electrochemical mimic of B_{12} than the cobaloxime and lies in between the Costa's modified derivative and the cobaloxime.

Introduction

Vitamin B_{12} coenzyme and methylcobalamin, the only known organocobalt compounds of nature, mediate the catalysis of a distinctive class of biologically important reactions together with an appropriate enzyme system [2]. Methylcobalamin is known to be operative in the catalysis of the methylation of homocysteine to methionine, the biosynthesis of methane and the reduction of carbon dioxide to acetic acid [3]. Vitamin B_{12} coenzyme, with an appropriate apoenzyme, mediates the catalysis of a diverse group of mutase or isomerase reactions [2]. The cobalt atom in vitamin B_{12} and its derivatives can exist in three main formal oxidation states, Co(III), Co(II) and Co(I), which display quite different chemical properties and hence oxidoreduction phenomena are very important in the chemistry of vitamin B_{12}.

Early electrochemical work employed mainly polarography as a technique to study the electrochemistry of vitamin B_{12} coenzyme and other alkylcobalamins [4], alkylcobinamides [4b, c] hydroxocobalamin [4b]. sulphitocobalamin [4c, d] and vitamin B_{12} [5]. Recently, cyclic voltammetry has been used to describe the electrochemical behaviour of B_{12} [6], B_{12a} [6b, c], B_{12r} [6a, 7], B_{12s} [6a] and methylcobalamin [6b, c]. Besides evaluating reversibility, these studies have provided characteristic potentials for the oxidoreduction of various B_{12} derivatives. The extensive work of Saveant and his co-workers [8] on the electrochemistry of vitamin B_{12} and its derivatives unravelled the complexities arising from the interplay between electron transfer and changes in axial ligation in the electrochemical reactions of B_{12} derivatives. Besides thermodynamic characterizations, the kinetics of the electrochemical reactions was investigated systematically with the aim of determining the reaction mechanisms and estimating the rate constants for the key steps.

The model studies, though primarily aimed at elucidating the mechanism of biological reactions mediated by coenzyme B_{12}, exceeded this objective and have become a general contribution to coordination chemistry [9]. It is well recognized that the credible cobaloxime and the Costa-type models have made rich contributions to the field of B_{12} chemistry and to inorganic chemistry in general [9, 10]. The still continuing task of model studies [1, 11] of myraid research interest has produced work remarkable for its elegance and perseverance. As models for coenzyme B_{12}, cobaloximes and the alkyl- and (non-alkyl)cobalt(III) complexes of Costa-type models have been subjected to extensive electrochemical studies [12]. The electrochemical oxidoreduction properties of these models have provided valuable kinetic information on redox coupled axial ligand

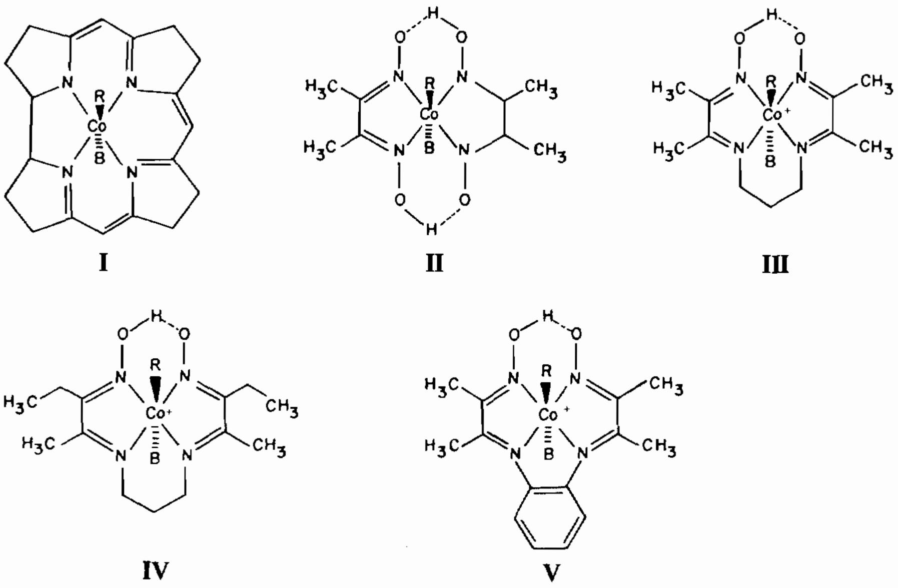

Fig. 1. I, Alkylcobalamin (only macrocyclic skeleton is shown); II, $[RCo(DH)_2B]$ (cobaloxime); III, $[RCo(DODOHpn)B]^+$ (Costa's model); IV, $[RCo(C_2DODOHpn)B]^+$ (Costa's modified model) and V, $[RCo(DODOHbzo)B]^+$.

changes and factors affecting the cleavage of the Co–C bond besides providing thermodynamic redox potentials important to mechanistic studies. It is worth mentioning that the electrochemical parameters reflect even small modifications on the electronic properties of the complexes brought by the axial and equatorial ligand changes.

We have recently reported a new conjugated quadridentate tetraaza ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime (**V**) [1], which forms stable organocobalt(III) complexes which serve as models of coenzyme B_{12}. This model differs from Costa's model (**III**) [13] and Costa's modified derivative (**IV**) [14] in that the conjugation extends over all donor atoms (Fig. 1). The present model has been designed with minimal alteration in structure from Costa's model so as to enable the study of the structure–reactivity correlation with minimal structural parameters as Murakami [15] has emphasized. The electrochemical investigation of Elliott *et al.* [12a] has established a quantitative comparison between the cobalamin chemistry and that of cobaloxime (**II**) and Costa's modified model. The conclusion is that the latter is a considerably closer electrochemical mimic of B_{12} than the more widely studied cobaloxime model. This, being an excellent electrochemical mimic of cobalamins, seems to promote better the types of reactions involved in B_{12}-dependent enzymic processes [2c, 16].

Cyclic voltammetry seems to be the most versatile tool for evaluating the redox chemistry of vitamin B_{12} and its model complexes because of its ability to reproduce the interconversion between the pertinent oxidation states of cobalt in these compounds. Therefore, a detailed electrochemical investigation has been undertaken to evaluate the suitability of this new model as a mimic of coenzyme B_{12} and to establish a quantitative electrochemical comparison with other well studied models. Since the biochemical reactivity of coenzyme B_{12} and methylcobalamin depend on the chemical reactivity of the axial coordination sites of cobalt, the probable coupling of the redox processes with the chemical reaction at the axial coordination sites of cobalt has also been explored with the present model complexes.

Experimental

Materials

Tetraethylammonium perchlorate (Fluka) recrystallized once from AR dry methanol and dried in vacuum was used as the supporting electrolyte. Ferrocene (crystalline, Sigma) was used as an internal standard in the cyclic voltammetric measurements. Dimethylformamide (E. Merck) was kept over potassium hydroxide pellets for 24 h, filtered and distilled over phosphorus pentoxide under reduced pressure and kept over 4 Å molecular sieves. Acetonitrile (extra pure, E. Merck) was dried over phosphorus pentoxide and distilled and dried over 4 Å molecular sieves. Pyridine (Sarabhai M. Chemicals) was refluxed over KOH pellets and distilled.

Synthesis of the Ligand and Complexes

The synthesis of the ligand and alkyl- and (nonalkyl)cobalt(III) complexes has been reported elsewhere [1]. The free ligand, 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,7-diene-2,9-dione dioxime [$(DOH)_2$-bzo] is neutral and coordinates with cobalt through its nitrogen donors in the equatorial position with the loss of one of the oxime protons with the concomitant formation of an intramolecular hydrogen bond. The dichloro and dibromo complexes have been synthesized by the direct reaction of the ligand with the respective cobalt(II) halide hexahydrate. Making use of the axial lability of the dibromo complex, [Co(DODOHbzo)Br_2], the (non-alkyl)-cobalt(III) complexes have been synthesized. Thus the azido complex, [N_3Co(DODOHbzo)Br]; the thiocyanato complex* [SCNCo(DODOHbzo)Br]; and, the cyano complex, [CNCo(DODOHbzo)Br]; the so-called cyanocobalamin models [CNCo(DODOHbzo)py]Br and [CNCo(DODOHbzo)Iz]Br; and the Lewis base complexes [pyCo(DODOHbzo)Br]-ClO_4 and [IzCo(DODOHbzo)Br]PF_6 were synthesized by replacing one of the axially bound bromide ions in [Co(DODOHbzo)Br_2].

The alkylcobalt(III) complexes, namely, [CH_3-Co(DODOHbzo)py]ClO_4, [CH_3Co(DODOHbzo)Iz]-ClO_4, [CH_3Co(DODOHbzo)PPh_3]ClO_4, [CH_3Co(DODOHbzo)Me_2BIz]ClO_4, [C_2H_5Co(DODOHbzo)py]-ClO_4, [C_2H_5Co(DODOHbzo)Iz]ClO_4, [i-prCo(DODOHbzo)py]ClO_4, [C_6H_{11}Co(DODOHbzo)py]ClO_4 and [$C_6H_5CH_2$Co(DODOHbzo)py]ClO_4 have been synthesized by the oxidative addition reaction of the *in situ* generated Co(I) nucleophile with the respective alkyl halide in an inert atmosphere. All these alkyl- and (non-alkyl)cobalt(III) complexes have been characterized by C, H, N and Co analysis, IR, UV–Vis, ^{1}H NMR spectroscopy, conductivity measurements and magnetic susceptibility [1]. The alkylcobalt(III) complexes exhibit a Co–C CT band in the region 21.5–23.8 kK [1].

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*The formation of the thiocyanato complex has been substantiated by IR and UV–Vis spectra. The IR spectrum of [SCN(DODOHbzo)Br] consists of a strong as well as sharp band at 2150 cm^{-1} assignable to ν(CN) of the coordinated SCN^-. The higher energy of this absorption is characteristic of S-bonded isomer since for the N-bonded isomer the same absorption occurs near and below 2050 cm^{-1} [17a]. The electronic absorption spectrum of this complex consists of an intense absorption band at 34.48 kK diagnostic of the Co^{III}–S bond and has been assigned to ligand to metal charge transfer (LTMCT) [17b–d].

Physical Measurements

Polarography

Polarograms were recorded using a Potentioscan Wenking POS 73 in conjunction with an Omniscribe recorder. A dropping mercury electrode (DME) with a mercury flow rate of 0.339 mg s^{-1} was used as the cathode and a pool of mercury as the anode. All measurements were referenced to the Ag/AgCl electrode. The polarograms of the alkyl derivatives were recorded in purified CH_3CN and that of the (non-alkyl) complexes in purified DMF containing 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. A salt bridge containing 0.1 M solution of TEAP in the respective solvent was employed between the reference electrode and the test solution. Each sample was deaerated by passing oxygen free dinitrogen saturated with the solvent vapour for 45 min. Baseline was recorded using a 0.1 M solution of TEAP in each solvent after deaeration and no polarographic wave was observed. Unless otherwise stated, all polarograms were recorded at a sweep rate of 4 mV s^{-1}.

Cyclic voltammetry

Cyclic voltammograms were recorded with a Princeton Applied Research (EG & G Instrument Co.) Model 170 Electrochemistry system using a PAR model 173 Potentiostat/Galvanostat in conjunction with a PAR model 175 universal programmer and a PAR model 900 2A X-Y recorder. A conventional two compartment glass cell was used with a standard three electrode configuration with a PAR glassy carbon (GC) disk working electrode, a platinum foil auxiliary electrode and a saturated calomel reference electrode. The auxiliary electrode was separated from the test solution (GC working electrode compartment) by a medium porosity glass frit. The cyclic voltammograms of the alkylcobalt(III) complexes were recorded in electrochemically pure CH_3CN dried over 4 Å molecular sieves and that of the (non-alkyl)cobalt(III) complexes in purified DMF dried over 4 Å molecular sieves using tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Every voltammetric measurement was carried out using $\sim 10^{-3}$ M solution of the complex containing 0.1 M TEAP. A salt bridge containing 0.1 M solution of TEAP in the respective solvent was employed between the reference electrode and the working compartment of the cell. Argon gas saturated with the solvent vapour was flushed through each sample solution for 1 h before voltammetry was performed and all measurements were carried out in an atmosphere of argon at 22 °C.

At the beginning of every set of experiments, the baseline was recorded for a 0.1 M solution of TEAP in each solvent. The absence of any extraneous wave ensured the electrochemical purity of the solvents and the supporting electrolyte. For every system, the voltammograms were recorded at the sweep rates of 20, 50, 100, 200 and 500 mV s^{-1}. Potentials were measured *versus* a saturated calomel reference electrode as well as with respect to the reference redox system, ferrocene/ferrocenium ion (Fc/Fc^+) in order to correct for differences in liquid junction potential between different solvents [18]. After recording the voltammograms of every system, a solution containing 0.1 M of the supporting electrolyte (TEAP) and 0.1 M of ferrocene in the respective solvent was added to the solution under study in the working electrode compartment of the cell. The solution was flushed with argon for 15 min to ensure complete expulsion of air and then the voltammograms were recorded *versus* the reference electrode. The potential data of each system, studied before and after the addition of ferrocene, agree within the experimental error of ±1 mV. The difference in potentials between the studied redox system and the reference redox system were then calculated. Peak potentials (E_p) were measured from cyclic voltammograms recorded at a scan rate of 50 mV s^{-1}. After every experiment, the surface of the GC disk electrode was activated by applying a sequence of extreme positive and negative potentials [19]. From the cyclic voltammograms electrochemical parameters such as the anodic peak potential (E_{pa}), the cathodic peak potential (E_{pc}), the anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic half-peak potential ($E_{p/2}$) and the half-wave potential ($E_{1/2}$) were computed.

The $E_{1/2}$ of the Fc/Fc^+ redox couple for our cell is +0.40 V (*versus* SCE) in CH_3CN, +0.49 V (*versus* SCE) in DMF, +0.45 V (*versus* SCE) in CH_3CN containing pyridine (10% *v*/*v*) and, +0.50 V (*versus* SCE) in DMF containing pyridine (10% *v*/*v*) at 22 °C.

Results and Discussion

Polarography of (Non-alkyl)cobalt(III) Complexes

The (non-alkyl)cobalt(III) complexes exhibit two well-defined reduction waves corresponding to Co(III) → Co(II) and Co(II) → Co(I) reductions. The half-wave potentials for both are presented in Table 1 along with the diffusion current constants, $i_{d/c}$. The first reduction takes place for all these complexes between −0.14 and −0.26 V, whereas the second reduction occurs in the range of −1.1 to −1.32 V except for $[Co\{(DO)_2bzoBF_2\}Br_2]$ for which the half-wave potential is −0.96 V. This low value may be due to the electron withdrawing nature of BF_2. In a study of copper complexes of cyclops* it has been observed by Addison

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*Cyclops is the BF_2 derivative of the Costa's model, $(DOH)_2pn$.

TABLE 1. Polarographic Half-wave Potentials[a] and Diffusion Current Constants for the Reduction of (Non-alkyl)cobalt(III) Complexes in CH_3CN Containing 0.1 M TEAP at 25 °C

	Concentration ($\times 10^{-3}$ M)	First reduction wave Co(III) → Co(II)		Second reduction wave Co(II) → Co(I)	
		$E_{1/2}$ (V)	i_d/c (log units)	$E_{1/2}$ (V)	i_d/c (log units)
$[Co(DODOHbzo)Br_2]$	3.84	−0.26	1.84	−1.1	1.84
$[Co\{(DO)_2bzoBF_2\}Br_2]$	0.92	−0.24	1.93	−0.96	1.93
$[pyCo(DODOHbzo)Br]PF_6$	1.17	−0.22	1.89	−1.02	1.74
$[IzCo(DODOHbzo)Br]BF_4$	1.04	−0.14	1.95	−1.32	2.08
$[SCNCo(DODOHbzo)Br]$	1.32	−0.13	1.52	−0.91	1.55
$[CH_3Co(DODOHbzo)py]ClO_4$	1.24	−0.78	1.5	−1.6[b]	1.55
$[C_2H_5Co(DODOHbzo)py]ClO_4$	1.72	−0.70	1.6	−1.48	1.57

[a] Potentials are reported in volts *vs.* Ag/AgCl. [b] The second reduction wave was well resolved in the presence of pyridine (10% *v*/*v*).

et al. [20] that Cu(cyclops) is reduced more readily than the hydrogen analogue, [Co(DODOHpn)] due to the greater electron withdrawing ability of BF_2^+ relative to H^+. Indirect evidence for the electron withdrawing nature of the BF_2 group comes from the slow rate of dealkylation of $[CH_3Co\{(DO)_2pnBF_2\}]^+$ by the Hg^{2+} electrophile [21]. The polarograms of $[Co(DODOHbzo)Br_2]$ and $[pyCo(DODOHbzo)Br]PF_6$ are given in Fig. 2a and b, respectively. The variation of i_d with concentration ($i_{d/c}$) is very nearly constant indicating that the waves were diffusion controlled. A comparison of the diffusion current constant confirms that a one electron transfer occurs for both reductions [12d].

The half-wave potential for the reduction of Co(III) to Co(II) depends on the field strength of the axial ligand*. Complexes with high field axial ligands are reduced at high negative potentials relative to those with low field ligands. That is in broad agreement with the general observation that as the electron donating power of the axial ligand increases, more electron density is transmitted to the metal ion thereby rendering the metal ion less susceptible for reduction. A similar variation of the polarographic $E_{1/2}$ values for the reduction of $[Co(III)LX_2]$ to $[Co(II)LX_2]$ ($L = Me_6$ [14] 4,11-dieneN_4) with the spectrally determined ligand field strength of X was observed by Rillema *et al.* [22] with a large potential variation of more than 1 V.

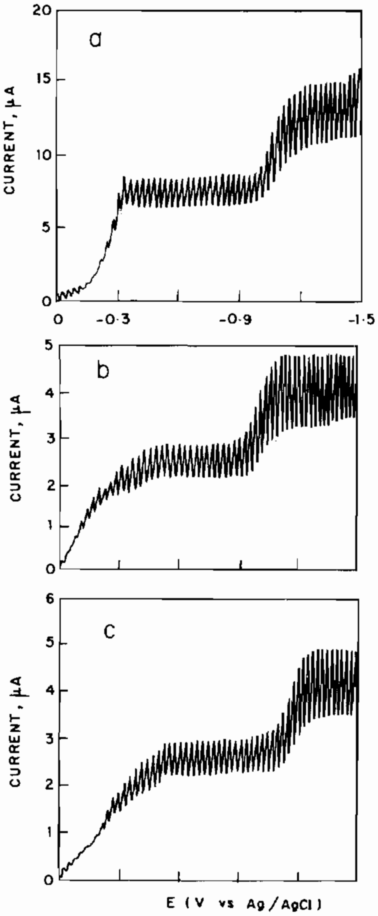

Fig. 2. Polarogram of (a) $[Co(DODOHbzo)Br_2]$ (3.845×10^{-3} M), (b) $[pyCo(DODOHbzo)Br]PF_6$ (1.166×10^{-3} M) and (c) $[4\text{-}CH_3pyCo(DODOHbzo)Br]ClO_4$ (1.245×10^{-3} M) in DMF containing 0.1 M TEAP at 25 °C. DME *vs.* Ag/AgCl. Sweep rate 4 mV s^{-1}.

Polarography of Alkylcobalt(III) Complexes

The polarograms of the alkylcobalt(III) complexes were complicated by adsorption/desorption processes. However, well defined polarograms could be obtained after the addition of pyridine (10% *v*/*v*). Both $[CH_3Co(DODOHbzo)py]ClO_4$ and $[C_2H_5Co(DODOHbzo)py]ClO_4$ exhibit two reduction

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*The field strength, Dq^z, of the axial ligands have been computed from the crystal field model of Wentworth and Piper since the (non-alkyl)cobalt(III) complexes exhibit D_{4h} microsymmetry as a result of tetragonal distortion from O_h symmetry. See ref. 1.

waves as do the (non-alkyl) complexes. The $E_{1/2}$ values for the reductions of these complexes are given in Table 1. From the $E_{1/2}$ values presented in Table 1 it is obvious that both Co(III) → Co(II) and Co(II) → Co(I) reductions take place at higher negative potentials for the alkyl complexes than for the (non-alkyl) complexes due to the higher electron donor ability of the alkyl groups. This observation is in conformity with the report of Hogenkamp and Holmes [23]. The reduction of $[CH_3Co(DODOHbzo)py]ClO_4$ occurs at a higher negative potential than $[C_2H_5Co(DODOHbzo)py]ClO_4$ indicating the higher electron donor ability of CH_3^- than $C_2H_5^-$. In the presence of added pyridine the reduction waves were well-resolved in both the ethyl and methyl complexes.

Cyclic Voltammetry

(Non-alkyl)cobalt(III) complexes

The cyclic voltammetric data for the reduction of $[Co(DODOHbzo)Br_2]$ are presented in Table 2 and the cyclic voltammogram in Fig. 3a. The various criteria [24], namely, ΔE_p, i_{pa}/i_{pc}, $i_{pc}/v^{1/2}$, and $E_{pc} - E_{p/2}$, employed to evaluate the electrochemical

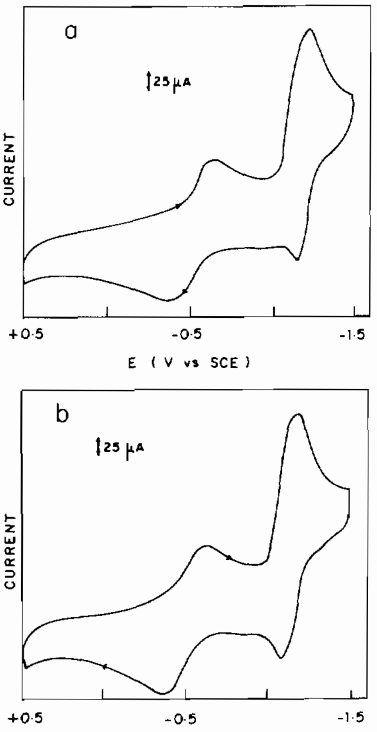

Fig. 3. Cyclic voltammogram of (a) $[Co(DODOHbzo)Br_2]$ (1.694×10^{-3} M) and (b) $[Co(DODOHbzo)Br_2]$ (1.694×10^{-3} M) (with pyridine 10% v/v) at glassy carbon electrode in DMF containing 0.1 M TEAP at 22 °C. Sweep rate 200 mV s^{-1}.

TABLE 2. Cyclic Voltammetric Data for the Reduction of $[Co(DODOHbzo)Br_2]$ at a Glassy Carbon Electrode in DMF Containing TEAP (~ 10^{-2} M) at 22 °C

Complex	Cobalt redox couple	Sweep rate, v (mV s^{-1})	E_{pc} (V, *vs.* SCE)	E_{pa} (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* Fc/Fc$^+$)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}	ΔE_p (mV, *vs.* SCE)	$i_{pc}/v^{1/2}$ (μAs$^{-1/2}$ mV$^{-1/2}$)	$E_{pc} - E_{p/2}$ (mV)
$[Co(DODOHbzo)Br_2]$ (1.69×10^{-3} M)	III/II	500	−0.65	−0.35	−0.450	−0.940	120	115	0.96	300	5.36	130
		200	−0.65	−0.37	−0.510	−1.000	77.5	75	0.97	280	5.48	130
		100	−0.63	−0.40	−0.515	−1.005	57.5	55	0.96	230	5.75	100
		50	−0.62	−0.43	−0.525	−1.015	45	44	0.98	190	6.36	110
		20	−0.61	−0.45	−0.530	−1.020	31	30	0.97	160	6.94	100
	II/I	500	−1.25	−1.13	−1.190	−1.680	300	145	0.48	120	13.41	130
		200	−1.23	−1.14	−1.185	−1.675	195	100	0.51	90	13.97	130
		100	−1.23	−1.15	−1.190	−1.680	130	65	0.50	80	13.00	120
		50	−1.22	−1.14	−1.180	−1.670	95	50	0.52	80	13.43	130
		20	−1.22	−1.15	−1.185	−1.675	60	30	0.50	70	13.42	130
$[Co(DODOHbzo)Br_2]$ + pyridine (10% v/v)	III/II	200	−0.63	−0.35	−0.490	−0.990	77.5	80	1.03	280	5.48	120
		20	−0.58	−0.39	−0.485	−0.985	29	30	1.03	190	6.49	110
	II/I	200	−1.19	−1.10	−1.145	−1.645	190	97	0.51	90	13.43	110
		20	−1.16	−1.10	−1.130	−1.630	60	30	0.50	60	13.42	110

reversibility of a redox couple are listed in the last four columns of Table 2.

It is seen in Table 2 that the ratio of the anodic peak current to the cathodic peak current is nearly unity indicative of the reversibility of the Co(III)/Co(II) couple. But the separation between the anodic and cathodic peak potentials ΔE_p is very high, indicative of electrochemical irreversibility. Though the anodic and cathodic peaks shift further apart with increasing scan rate characteristic of a quasireversible couple [19], the peaks are widely separated (160–300 mV) indicating that the electrochemical reduction of $[Co^{III}(DODOHbzo)Br_2]$ to the cobalt(II) form is irreversible. The observed irreversibility can be attributed to two reasons: (i) a slow rate of the Co(III)/Co(II) electrode reaction so that the initial cobalt(III) complex and the reduced Co(II) complex are not in equilibrium with each other at the electrode surface and (ii) the electrochemically generated Co(II) complex does not get recycled electrochemically to give back the original cobalt(III) complex. This indicates extensive bond breaking [19] during the course of the electrolytic reduction of $[Co(DODOHbzo)Br_2]$, probably one of the Co–Br bonds, to give a five-coordinate Co(II) complex, $[Co^{II}(DODOHbzo)Br]$ as shown in eqn. (1).

$$[Co^{III}(DODOHbzo)Br_2] + e^- \longrightarrow [Co^{II}(DODOHbzo)Br] + Br^- \qquad (1)$$

The near constancy of $i_{pa}/\nu^{1/2}$ indicates that the reduction of Co(III) → Co(II) is diffusion controlled at the glassy carbon electrode [25]. The (non-alkyl)-cobalt(III) complexes of $(C_2DODOHpn)$ also exhibit this behaviour as previously observed by Elliott *et al.* [12a]. Similarly, a slow rate of electron transfer for the Co(III)/Co(II) couple of aquacobalamin was observed by Lexa and Saveant, a behaviour which they ascribed to the increase in bond lengths accompanying reduction to Co(II) [8e].

The azido complex, $[N_3Co(DODOHbzo)Br]$ and the thiocyanato complex, [SCNCo(DODOHbzo)Br] exhibit the same cyclic voltammetric behaviour as does the dibromo complex. But, the latter undergoes reduction from Co(III) → Co(II) at a less negative potential (−0.47 V *versus* SCE) when compared to the dibromo complex (−0.525 V) and the complexes of pyridine (0.49 V) and imidazole (0.44 V) indicating that the Co–S bond renders cobalt more susceptible for reduction. This lends indirect evidence that sulphur is the donor atom in the complex, that is, that the thiocyanate linkage isomer is present. The cyclic voltammetric data for the reduction of the pseudohalogeno and the Lewis base complexes are given in Table 3. In the case of $[pyCo(DODOHbzo)Br]BF_4$ and $[IzCo(DODOHbzo)Br]PF_6$ the Co(III)/Co(II) reduction waves are poorly defined and the oxidation even more so.

In the case of the Co(II)/Co(I) redox couple the separation between the cathodic and anodic peak

TABLE 3. Cyclic Voltammetric Data for the Reduction of (Non-alkyl)cobalt(III) Complexes ($\sim 10^{-3}$ M) in DMF and Alkyl-cobalt(III) Complexes ($\sim 10^{-3}$ M) in CH_3CN Containing ~0.1 M TEAP at a Glassy Carbon Electrode at 22 °C

Complex	Cobalt redox couple	Sweep rate, ν (mV s^{-1})	E_{pc} (V, *vs.* SCE)	E_{pa} (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* Fc/Fc^+)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}	ΔE_p (mV, *vs.* SCE)
$[N_3Co(DODOHbzo)Br]$	III/II	50	−0.63	−0.35	−0.49	−0.98	33.0	32.0	0.97	280
	II/I	50	−1.19	−1.10	−1.14	−1.63	97.0	51.0	0.53	90
[SCNCo(DODOHbzo)Br]	III/II	50	−0.62	−0.32	−0.47	−0.95	12.0	13.0	1.08	300
	II/I	100	−1.18	−1.12	−1.15	−1.65	87.0	44.0	0.51	60
$[pyCo(DODOHbzo)Br]PF_6$[a]	III/II	50	−0.63	−0.33	−0.48	−0.97				300
	II/I	50	−1.18	−1.12	−1.15	−1.64				60
$[IzCo(DODOHbzo)Br]BF_4$[b]	III/II	50	−0.63	−0.34	−0.44	−0.93				290
	II/I	50	−1.18	−1.12	−1.15	−1.64				60
$[CH_3Co(DODOHbzo)py]ClO_4$[c]	III/II	100	−1.17	−1.08	−1.12	−1.52				90
	II/I	100	−1.65	−1.59	−1.62	−2.02				60
$[CH_3Co(DODOHbzo)py]ClO_4$ + py (10% *v/v*)	III/II	100	−1.15	−1.07	−1.11	−1.56	27.5	30.5	1.11	80
	II/I	100	−1.66	−1.60	−1.62	−2.07	162	80.0	0.49	60
$[C_2H_5Co(DODOHbzo)py]ClO_4$[d]	III/II	200	−1.46	−1.37	−1.41	−1.81	12.5	13.0	1.04	90
	II/I	200	−1.77							

[a] The anodic and cathodic waves are very broad. [b] For the Co(III)/Co(II) redox couple the waves are poorly defined and for the Co(II)/Co(I) couple i_{pc} is much higher than i_{pa} indicating the involvement of coupled chemical reaction. [c] The cathodic peak for the Co(III)/Co(II) couple and the anodic peak for the Co(II)/Co(I) couple are not well resolved. [d] Anodic peak corresponding to the oxidation of Co(I) to Co(II) is not observed.

potentials ranges from 70–90 mV at all sweep rates and the i_{pa}/i_{pc} ratio is less than unity indicating the electrochemical irreversibility of this couple. An interesting feature of the cyclic voltammetry of these complexes is the relative insensitivity of the Co(II)/Co(I) redox couple to the axial ligand. The near invariance of the position of the cathodic peak corresponding to the reduction of Co(II) to Co(I) is consistent with the weak axial interactions in these cobalt(II) complexes which are considered to be five coordinate as observed by Schneider *et al.* [26] and Endicott *et al.* [27]. The near invariance of the position of the anodic peak corresponding to the oxidation of Co(I) to Co(II) is attributed to the complete loss of the axial ligands during the generation of the Co(I) species as shown in eqn. (2).

$$[Co^{II}(DODOHbzo)Br] + e^- \longrightarrow [Co^{I}(DODOHbzo)] + Br^- \quad (2)$$

The same observation has been made by Swetik and Brown [28] in their cyclic voltammetric study of vitamin B_{12} derivatives. A weak axial interaction of the solvent (DMF) with a electrogenerated Co(I), as observed by Elliott *et al.* [12a] is not ruled out however.

In an attempt to get reversible electrochemical behaviour of $[Co^{III}(DODOHbzo)Br_2]$, the cyclic voltammogram was recorded in the presence of pyridine (10% *v*/*v*). In the presence of pyridine the reductions occur at less negative potentials indicating that pyridine renders cobalt more susceptible to reduction. Though the cathodic and anodic waves are now well resolved, irreversible behaviour is indicated for both redox couples as evidenced by the values of i_{pa}/i_{pc} and ΔE_p. ΔE_p is 60 mV for the Co(II)/Co(I) redox couple at the sweep rate of 20 mV s^{-1}, characteristic of a reversible one electron transfer [29], but i_{pa}/i_{pc} is 0.51 indicating irreversible Co(II)/Co(I) electrode reaction. The cyclic voltammogram of $[Co(DODOHbzo)Br_2]$ in DMF in the presence of pyridine is depicted in Fig. 3b and the data are presented in Table 2.

Alkylcobalt(III) complexes

The alkylcobalt(III) complexes undergo two sequential one electron reductions, Co(III) → Co(II) and Co(II) → Co(I) and two sequential one electron oxidations, Co(I) → Co(II) and Co(II) → Co(III). The anodic and cathodic waves were well defined for both redox couples in the case of $[CH_3Co(DODOHbzo)py]ClO_4$ whereas for other alkyl derivatives the waves were very poorly defined and are hidden in large background current. In the case of $[CH_3Co(DODOHbzo)py]ClO_4$, the Co(III)/Co(II) couple has a much slower rate of electron transfer (ΔE_p = 100 mV) than the Co(II)/Co(I) couple (ΔE_p = 60 mV). While the i_{pa}/i_{pc} is very nearly unity for the Co(III)/Co(II) redox couple, it is ~0.5 for the Co(II)/Co(I) couple. Thus both ΔE_p and i_{pa}/i_{pc} values indicate that both the Co(III) → Co(II) and Co(II) → Co(I) reductions are irreversible. This indicates bond breaking during the reduction processes. The cyclic voltammogram of $[CH_3Co^{III}(DODOHbzo)py]ClO_4$ is depicted in Fig. 4a and the data are presented in Table 3.

The $E_{1/2}$ values for both redox couples are more negative for the alkylcobalt(III) complexes than that of the dihalo, pseudohalogeno and Lewis base complexes. The same is true for the polarographic $E_{1/2}$ values also. The highly negative $E_{1/2}$ values indicate that the alkyl carbanions transmit more electron density to the cobalt ion thereby rendering it less susceptible for reduction. The higher negative $E_{1/2}$ potentials of the Co(II)/Co(I) redox couple of the alkylcobalt(III) complexes than that of the (non-alkyl) derivatives indicate that during the electrolytic reduction of $[RCo^{III}(DODOHbzo)py]ClO_4$ to the

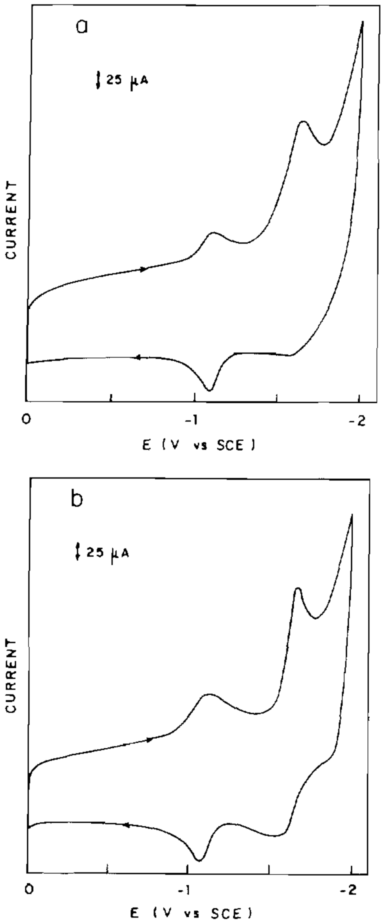

Fig. 4. Cyclic voltammogram of (a) $[CH_3Co(DODOHbzo)py]ClO_4$ (1.692×10^{-3} M) and (b) $[CH_3Co(DODOHbzo)py]ClO_4$ (with pyridine 10% *v*/*v*) at glassy carbon electrode in CH_3CN containing 0.1 M TEAP at 22 °C. Sweep rate 100 mV s^{-1}.

Co(II) form, the R–Co bond is not cleaved but the pyridine in the *trans* position is lost leading to the formation of the five-coordinate cobalt(II) complex, $[RCo^{II}(DODOHbzo)]$ as shown in eqn. (3).

$$[RCo^{III}(DODOHbzo)py]ClO_4 + e^- \longrightarrow [RCo^{II}(DODOHbzo)] + py \qquad (3)$$

The generation of this five-coordinate complex explains the electrochemical irreversibility of the Co(III)/Co(II) couple. The (non-alkyl) complexes also exhibit the same behaviour (*vide supra*). The anodic peak potential for the oxidation of Co(I) to Co(II) is very nearly the same for the alkyl complexes indicating complete loss of both the axial ligands during the generation of Co(I) and the formation of a four-coordinate Co(I) complex is envisioned as shown in eqn. (4). The formation of a

$$[RCo^{II}(DODOHbzo)] + e^- \longrightarrow [Co^{I}(DODOHbzo)] + R^- \qquad (4)$$

four-coordinate Co(I) complex was also observed by Saveant and his coworkers [8a, b] in their studies on vitamin B_{12} derivatives.

The value of i_{pa}/i_{pc} is very nearly 0.5 for the Co(II)/Co(I) redox couple indicating a 50% Co(I) yield. This indicates that nearly 50% of the electrogenerated Co(I) complex has undergone a chemical reaction. This illustrates the involvement of a coupled chemical reaction and it is almost surely a reversible *ECE mechanism*

$$E\ [RCo^{III}(DODOHbzo)py]^+ + e^- \rightleftharpoons [RCo^{II}(DODOHbzo)] + py \qquad (5)$$

$$C\ [RCo^{II}(DODOHbzo)] + [RCo^{III}(DODOHbzo)py]^+ \rightleftharpoons [R_2Co^{III}(DODOHbzo)] + [Co^{II}(DODOHbzo)]^+ \qquad (6)$$

$$E\ [Co^{II}(DODOHbzo)]^+ + e \rightleftharpoons [Co^{I}(DODOHbzo)] \qquad (7)$$

This ECE mechanism also predicts a 50% Co(I) yield (eqn. (8)).

$$2[RCo^{III}(DODOHbzo)py]^+ + 2e \longrightarrow [R_2Co^{III}(DODOHbzo)] + [Co^{I}(DODOHbzo)] \qquad (8)$$

To study the electrochemical properties under reversible conditions, the cyclic voltammogram of $[CH_3Co(DODOHbzo)py]ClO_4$ was recorded in the presence of pyridine (10% v/v). The cathodic wave corresponding to the reduction of Co(III) to Co(II) and the anodic wave corresponding to the oxidation of Co(I) to Co(II) which were poorly resolved in the absence of pyridine are now well defined, besides sharpening the cathodic wave for the reduction of Co(II) to Co(I) and the anodic wave for the oxidation of Co(II) to Co(III). This enabled the computation of all parameters. The cyclic voltammetric data for the reduction of $[CH_3Co^{III}(DODOHbzo)py]ClO_4$ in the presence of pyridine is presented in Table 3 and the cyclic voltammogram is depicted in Fig. 4b. The slow rate of electron transfer encountered for the reduction of the Co(III) to Co(II) ($\Delta E_p = 100$ mV) is made faster ($\Delta E_p = 80$ mV) by the externally added pyridine. The effect of added pyridine on sharpening the waves and increasing the rate of electron transfer clearly shows that the major role of pyridine is to inhibit the R–Co decomposition.

Oxidation of alkylcobalt(III) complexes

To study the oxidation of alkylcobalt(III) complexes, the cyclic voltammograms were recorded between the switching potentials 0 and +1.5 V in CH_3CN. Among the alkyl derivatives, $[CH_3Co(DODOHbzo)py]ClO_4$, $[C_2H_5Co(DODOHbzo)py]ClO_4$, and $[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$ exhibit well resolved anodic waves corresponding to the oxidation of $[RCo^{III}(DODOHbzo)py]ClO_4$ to $[RCo^{IV}(DODOHbzo)py]ClO_4$ and cathodic waves corresponding to the reduction of the Co(IV) complex to the initial $[RCo^{III}(DODOHbzo)py]ClO_4$. The cyclic voltammograms for the oxidation of $[CH_3Co(DODOHbzo)py]ClO_4$, $[C_2H_5Co(DODOHbzo)py]ClO_4$ and $[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$ are depicted in Fig. 5a, b and c, respectively, and the data are presented in Table 4. While both $[CH_3Co(DODOHbzo)py]ClO_4$ and $[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$ undergo oxidation to cobalt(IV) at

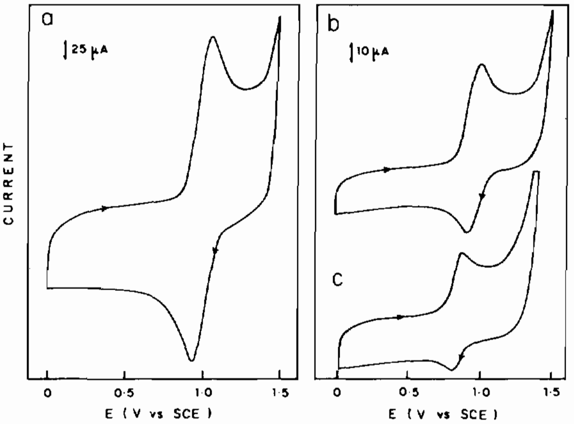

Fig. 5. Cyclic voltammogram for the oxidation of (a) $[CH_3Co(DODOHbzo)py]ClO_4$ (1.692×10^{-3} M), (b) $[C_2H_5Co(DODOHbzo)py]ClO_4$ (0.87×10^{-3} M) and (c) $[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$ at glassy carbon electrode in CH_3CN containing 0.1 M TEAP at 22 °C. Sweep rate 100 mV s^{-1}.

TABLE 4. Cyclic Voltammetric Data for the Oxidation of Alkylcobalt(III) Complexes (~ 10^{-3} M) at a Glassy Carbon Electrode in CH_3CN Containing ~0.1 M TEAP at 22 °C[a]

Complex	Sweep rate, ν (mV s^{-1})	E_{pc} (V, *vs.* SCE)	E_{pa} (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* Fc/Fc$^+$)	i_{pc} (μA)	i_{pa} (μA)	i_{pa}/i_{pc}	ΔE_p (mV)	$i_{pc}/\nu^{1/2}$ (μA$s^{-1/2}$ m$V^{-1/2}$)	$E_{pc} - E_{p/2}$ (mV)
$[CH_3Co(DODOHbzo)py]ClO_4$	200	0.90	0.80	0.85	0.45	112	125	1.11	100	7.92	70
$[C_2H_5Co(DODOHbzo)py]ClO_4$	200	0.82	0.73	0.77	0.37	97.5	117	1.20	90	6.90	60
	20	0.82	0.75	0.78	0.38	31.0	37	1.19	70	6.94	60
$[CH_3Co(DODOHbzo)Me_2BIz]ClO_4$	100	0.88	0.80	0.84	0.44	62.5	70	1.12	80	6.25	60
	20	0.87	0.80	0.83	0.43	29.0	23	1.21	70	6.48	60

[a] The cobalt redox couple is Co(IV)/Co(III).

0.8 V, $[C_2H_5Co(DODOHbzo)py]ClO_4$ undergoes oxidation at 0.73 V with subsequent reduction at 0.9, 0.88 and 0.82 V, respectively, at the scan rate of 100 mV s^{-1}. Though the ratio of i_{pa} to i_{pc} and ΔE_p are a little higher than that of a reversible one electron process, the increase in ΔE_p with increasing scan rate indicates that the electron transfer is quasi-reversible and consequently no bond breaking is presumed during the course of oxidation. This is further substantiated by the dependence of the Co(IV)/Co(III) $E_{1/2}$ values on the axial alkyl group. When pyridine is the *trans* axial base, the $E_{1/2}$ of the methyl complex is 0.5 mV as against 0.775 mV for the ethyl analogue. Such a wide variation in $E_{1/2}$ is indicative of the dependence of the oxidation/reduction processes on the alkyl group. This indicates that the Co–C bond is not cleaved during the electrolytic conversion of the original cobalt(III) complex to the cobalt(IV) complex as indicated in eqn. (9).

$$[RCo^{III}(DODOHbzo)L]^+ + e^- \rightleftharpoons [RCo^{IV}(DODOHbzo)L]^{2+} \quad (9)$$

Costa and his co-workers [30] and Benedetti *et al.* [31] in their studies on organocobalt(III) complexes of salen and bae also observed a reversible one electron redox process, $[RCo^{III}L]^+ \xrightleftharpoons{\pm e} [RCo^{IV}L]^+$ (L = salen or bae, R = $C_2H_5^-$ or $C_6H_5^-$), and the oxidation product was found to be stable. But in the case of $[CH_3Co\,salen]$ though one electron reversible oxidation was observed, the oxidized product was found to be unstable [32]. In the present study the oxidized products, $[RCo^{IV}(DODOHbzo)py]^{2+}$ was found to be stable as indicated by the i_{pa}/i_{pc} ratio. The other alkylcobalt(III) complexes of the equatorial chelates such as $(DH)_2$ [31, 33], salen [31, 32], saloph [31] and bae [31] also undergo oxidation to alkylcobalt(IV) complexes. When the pyridine of $[CH_3Co(DODOHbzo)py]ClO_4$ is replaced by 5,6-dimethylbenzimidazole, the $E_{1/2}$ is found to be 840 mV, very close to that of the former (850 mV). This indicates that though $E_{1/2}$ is very sensitive even to slight modification of the axial base, it has a marked dependence on the organic ligand. The constancy of the ratio of i_{pc} to the square root of sweep rate indicates that the oxidation–reduction is diffusion controlled at the electrode surface [25].

Electrochemical comparison of the (DODOHbzo) model with cobalamins and the cobaloxime and Costa's models

A comparison of the redox chemistry of alkylcobalamines and coenzyme B_{12} models should look at the properties of cobalt redox couples and draw conclusions regarding the positive attributes of the present model. Table 5 presents a comparison

TABLE 5. Cyclic Voltammetric Data for Cobalamin Derivatives and Coenzyme B_{12} Models

Compound	Cobalt redox couple	Solvent	Temperature (°C)	Scan rate (mV s^{-1})	$E_{1/2}$ (V, *vs.* SCE)	$E_{1/2}$ (V, *vs.* Fc/Fc^+)	ΔE_p (mV)	Reference
Aquacobalamin	III/II	H_2O	22	100	−0.042		450	8e
Methylcobalamin	III/II	DMF/propanol	−30	100	−1.6		100	8d
Diaquacobinamide	III/II	H_2O	22	200	+0.27		200	8e
Methyl(solvent)cobinamide	III/II	DMF/propanol	−20	100	−1.47		100	8d
Base-off-aquacob(II)alamin	II/I	H_2O	22	–	−0.74		59	8b
$[Co(C_2DODOHpn)I_2]$	III/II	CH_3CN	RT	200	−0.1		100	12a
	II/I			200	−0.71		63	12a
$[CH_3Co(C_2DODOHpn)OH_2]PF_6$	III/II	DMF/propanol	RT	200	-0.94^c		–	12a
$[CH_3Co(C_2DODOHpn)OH_2]PF_6$ *N*-methylimidazole, 10%	III/II	DMF/propanol	RT	200	−1.16		62	12a
$[CH_3Co(DH)_2OH_2]$	III/–	CH_3CN	−26	200	-2.2^c		–	12a
$[CH_3Co(DH)_2OH_2]^a$ +	II/–	CH_3CN	−26	200	-2.3^c		–	12a
N-methylimidazole, 10%					-2.5^c		–	12a
$[BzImCo(DH)_2Cl]^b$ +	III/II	CH_3CN	RT	200	−0.4		230	12a
excess *N*-methylimidazole	II/I				−1.12		80	12a
$[Co(DODOHbzo)Br_2]$	III/II	DMF	22	100	−0.515	−1.005	230	this work
	II/I				−1.19	−1.68	80	
$[Co(DODOHbzo)Br_2]$ +	III/II	DMF	22	20	−0.48	−0.98	190	this work
pyridine (10% *v*/*v*)	II/I				−1.13	−1.63	60	
$[CH_3Co(DODOHbzo)py]ClO_4$	III/II	CH_3CN	22	100	−1.12	−1.52	90	this work
	II/I				−1.62	−2.02	60	
$[CH_3Co(DODOHbzo)py]ClO_4$ +	III/II	CH_3CN	22	100	−1.11	−1.56	80	this work
pyridine (10% *v*/*v*)	II/I				−1.62	−2.07	60	

[a]Two waves were observed. [b]BzIm = 1,5,6-trimethylbenzimidazole. [c]E_p.

of the $E_{1/2}$ and ΔE_p values of cobalamin derivatives, cobaloximes and Costa's modified model with that of the present one. The solvent and temperature have a pronounced effect upon the rate of electron transfer and on the $E_{1/2}$ values. The Co(III)/Co(II) $E_{1/2}$ value of −1.6 V with methylcobalamin, −1.47 V with methyl(DMF)cobinamide, −1.10 V with $[CH_3Co(DODOHpn)N{-}MeIm]PF_6$* at 25 °C (−1.2 V at −21 °C) and −1.26 V with $[CH_3Co(C_2DODOHpn)solvent]PF_6$ (solvent = DMF or CH_3CN) at 25 °C (−1.3 V at −26 °C) are very closely reproduced by the DODOHbzo model, which exhibits a $E_{1/2}$ value of −1.1 V for $[CH_3Co(DODOHbzo)py]ClO_4$ under comparable conditions. On the other hand, the cobaloxime model undergoes reduction at too negative potentials. $[CH_3Co(DH)_2N{-}MeIm]$ exhibits a totally irreversible reduction wave at $E_{pc} = -2.5$ V in CH_3CN and $[CH_3Co(DH)_2(solvent)]$ (solvent = DMF or CH_3CN), at −2.2 V at −26 °C. In the presence of an externally added base, two waves were observed at $E_{pc} = -2.3$ and −2.5 V which are still highly negative. This is contrary to the behaviour of the $C_2DODOHpn$ and DODOHbzo models which undergo reduction at less negative potentials in the presence of the base. While $[CH_3Co(C_2DODOHpn){-}N{-}MeIm]PF_6$ and $[CH_3Co(C_2DODOHpn)(solvent)]PF_6$ are about −0.4 V easier to reduce on the average when compared to methylcobalamin and methyl(DMF)cobinamide, the DODOHbzo model is about −0.5 V easier to reduce. The cobaloximes, $[CH_3Co(DH)_2N{-}MeIm]$ and $[CH_3Co(DH)_2solvent]$, on the other hand, are about 0.7 V more difficult to reduce.

A comparison of the $E_{1/2}$ values of Co(II)/Co(I) redox couples of various models shows that the couple is relatively insensitive to the axial ligands and the solvents indicating that the axial ligands are lost during the electrolytic conversion of the initial Co(III) complex to the Co(I). Therefore it is concluded that the potential of the Co(II)/Co(I) couple measures only the electronic effects of the equatorial ligand [12f]. The same observation was made by Costa [34] that the polarographic $E_{1/2}$ values for the reduction of Co(II) → Co(I) are independent of the nature of the axial ligand and are influenced by the equatorial chelate to the same extent in both alkyl and (non-alkyl) complexes.

The complexes of other dibasic B_{12} model ligands such as salen, saloph and bae are even more difficult to reduce than the cobaloxime. However, the cobalt(III) complexes of the dibasic quadridentate equatorial chelate, tetraphenylporphyrin, studied by Lexa and Saveant [35] exhibit a RCo(III)/RCo(II) $E_{1/2}$ value of −1.3 V and the Co(II)/Co(I) $E_{1/2}$ value

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*N-MeIm = *N*-methylimidazole.

of -0.8 V which are very close to the Co(III)/Co(II) $E_{1/2}$ values of -1.47 V for methyl(solvent)cobinamide and the Co(II)/Co(I) $E_{1/2}$ value of -0.74 V for base off Co(II)cobalamin indicating the limitations of oxidation state formalism in deciding a suitable B_{12} model. The study of Murakami *et al.* [15b] on the cobalt complexes of 1,19-dimethyl-AD-didehydrocorrin (BDHC) and its tetrahydro analogue (TDHC) indicates that the former is a closer electrochemical mimic of vitamin B_{12}, the $E_{1/2}$ being 0.47 V for the Co(III)/Co(II) couple and -0.71 V for the Co(II)/Co(I) couple. Their study also indicates a wide variation in the Co(III)/Co(II) $E_{1/2}$ values on the formal charge of the equatorial ligand. The Co(III)/Co(II) $E_{1/2}$ values of the cobalt(III) complexes of a family of closely related quadridentate tetraaza equatorial macrocyclic ligands such as TDHC, aetioporphyrin and octaalkylcorrole, which carry 1−, 2− and 3− charges respectively, span over more than 1 V from +0.97 V for TDHC through +0.3 V for aetioporphyrin to -0.26 V for corrole.

Conclusions

To conclude, neither the cobaloxime model nor the Costa's modified derivative nor the present one exactly reproduces the electrochemistry of the cobalamin derivatives. The present model exhibits electron transfer for both redox couples faster than the cobaloxime and nearly as fast as Costa's modified derivative. The externally added base has a pronounced effect in increasing the rate of electron transfer by suppressing the Co–C bond cleavage. But in the cobaloxime, the electron transfer is slow even in the presence of the externally added base. Thus the present model is a closer electrochemical mimic of B_{12} than the cobaloxime and lies in between Costa's modified derivative and the cobaloxime. However, the Co(II)/Co(I) $E_{1/2}$ lies at too negative a potential when compared to that of the base off Co(II)cobalamins and Costa's modified derivative indicating the greater π-donating ability of the equatorial chelate of the present model which places excessive change density on the cobalt rendering its reduction to Co(I) difficult. This is one of the limitations of this model.

Acknowledgements

The funding of this research project by the Department of Science and Technology, Government of India, New Delhi is gratefully acknowledged.

We wish to thank Dr C. V. Suryanarayana, former Deputy Director and Dr K. I. Vasu, Director, Central Electrochemical Research Institute, Karaikudi-623 006, India, for granting permission to carry out the electrochemical investigations in CECRI. The valuable help rendered by the scientists of CECRI is acknowledged with gratitude.

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