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Electrochemistry of cobalt mixed Schiff base/oxime chelates *,**

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Abstract

Diaquocobaloxime and three other chelating ligands obtained by substitution of the O · · · H · · · O bridge with $(CH_2)_3$ or BF_2 groups have been examined in order to compare the effects of changes in the in-plane ligand on the relative stability of different oxidation states of the cobalt atom and on the *cis*-effect of the equatorial structure with those observed in the corresponding organometallic derivatives.

The *cis*-effect of the in-plane ligand was evaluated from the electrochemistry of the Co^{III}/Co^{II} electron transfer which is dependent upon the Co–solvent bond strength changes in the axial positions. The axial interaction depends mainly on the nature of the axial ligand.

The introduction of either one $(CH_2)_3$ group or two BF_2 groups or both leads to a displacement of the stability range of the Co^{II} oxidation state towards more anodic redox potentials. The $(CH_2)_3$ group appears to be more effective both in the displacement of the redox potential and in the bathochromic shift of the visible band at 450–500 nm of the Co^{II} chelates.

Introduction

Chelates of the bis(dimethylglyoxime) pseudo-macrocyclic tetradentate ligand system have been used for a long time as models of metal porphyrins in prosthetic

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* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

** *Editor's note*. This paper was accepted in spite of its lack of organometallic content because it describes work, which forms part of a study or organometallic derivatives of the same chelating ligand as models of vitamin B_{12} coenzyme.

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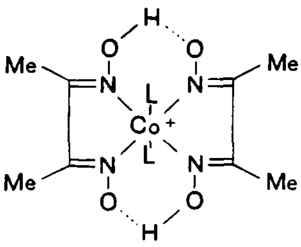
groups of important classes of proteins and enzymes [1]. Cobalt complexes with this ligand system were first proposed as models of cobalt corrinoids [2a–d,3]. We have suggested that some types of cobalt Schiff base chelates should provide models which more closely mimic the naturally occurring prosthetic group of Vit. B_{12} group coenzymes [4].

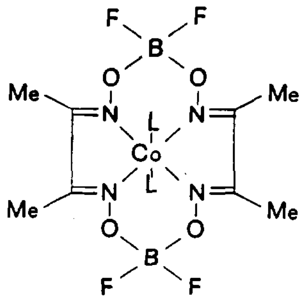
Investigations by our and other groups revealed that the cobalt-Schiff bases chelates and cobaloximes "bracket" many characteristic of cobalamins. From the cobalt complex of the bis(dimethylglyoximato) ligand **A**, which can be regarded as the parent compound, (diaquocobaloxime), other strictly related chelating ligands have been synthesized, and they have been suggested as further models of Vit. B_{12} group coenzymes.

The substitution of both the hydrogen atoms in the $O \cdots H \cdots O$ bridges of the bis(dimethylglyoxime)ligand $(DH)_2$ in the equatorial plane by the BF_2 group, leading to the ligand of the chelate **C** $[Co(DBF_2)_2L_2]$, was described previously by Schrauzer for the case of the bis(dimethylglyoxime)nickel complex [5]. A mixed Schiff base/oxime tetradentate ligand, obtained by substitution of one of the $O \cdots H \cdots O$ bridges by the $(CH_2)_3$ moiety to give the cobalt complex **B** $[Co(DO)(DOH)pn\text{-}L_2]^{2+}$, was described by one of us and Mestroni [4,6]. Finally, the substitution of the $O \cdots H \cdots O$ bridge by the BF_2 group in the latter to give the cobalt chelate **D** $[Co(DO)(DOBF_2)pnL_2]^+$ was described by Magnuson and Weber [7] and in a report from our laboratory [8].



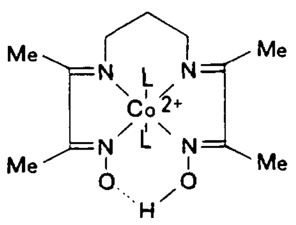
A

$[Co(DH)_2L_2]^+$



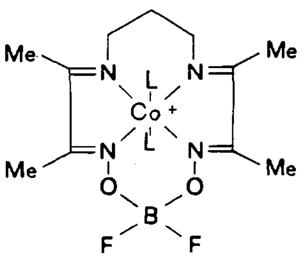
C

$[Co(DBF_2)_2L_2]$



B

$[Co(DO)(DOH)pnL_2]^{2+}$



D

$[Co(DO)(DOBF_2)pnL_2]^+$

The most relevant feature of the mixed Schiff base/oxime chelates is the monoanionic character of the macrocyclic equatorial ligands **C** and **D**. This feature represents a significant improvement in the resemblance to the corrin ring at least as far as the pseudosymmetry and charge of the chelating ring are concerned [6]. On the other hand the presence of the BF_2 group in the place of the $O\cdots H\cdots O$ bridge avoids the complications due to the reactivity of the hydrogen bond. Solubility in aqueous solutions is also an important property of the $[Co(DO)(DOH)pn(H_2O)_2]^{2+}$ and $[Co(DO)(DOBF_2)pn(H_2O)_2]^{+}$ chelates.

In recent times the choice of criteria for the evaluation of the appropriateness of Vit. B_{12} models has been a subject of discussion [9–12]. The more fundamental and ultimate objective of the present studies is the assessment of the factors influencing the physico-chemical behaviour of the models with reference to the naturally occurring system.

The mechanism of the biochemical reactions catalyzed by coenzymes of the Vit. B_{12} group, including homolytic cleavage of the Co–C bond, is probably related to the relative stability of the cobalt oxidation states [13]; the relevant thermodynamic and kinetic parameters can in principle be derived by determination of the standard potential and of the rate of the heterogeneous electron transfer (ET) or of the coupled chemical reaction. Moreover, changes in the oxidation state of the metal atom lead to reactive intermediates which have weaker and more readily cleaved bonds in the axial position. Information about these reactions relevant in the biochemical reactivity of the coenzyme can be also obtained by investigation of the chemical steps coupled with heterogeneous ET.

Polarographic redox potentials involving changes of the oxidation state of the central metal atom in the organometallic derivatives of the model series and of cobalamins related to the stability of the primary reduction product were first considered in our laboratory [14] and were further examined by Finke et al. [10]. The stability of five-coordinate species as models of possible intermediates in the coenzyme reaction mechanism was discussed by Marzilli et al. [15]. The influence of the equatorial ligand can be investigated by comparing closely related species bearing the same axial ligands and having the same mechanism for the reaction at the axial positions. The availability of the present series of chelates allows examination of the effects of controlled changes in the in-plane ligand arising from the changes of the equatorial pseudo macrocycle.

While the organometallic derivatives are the actual models for coenzyme B_{12}, the diaquo chelates can be regarded as the simplest representatives of the four series of complexes and most suitable for the study of the influence of the equatorial ligand with minimum interference from reactions in the axial positions.

On the other hand the "*cis*" effect of the equatorial ligand on coordination on axial positions can be most easily studied. The present paper is devoted to the assessment of the consequences of replacement of the $O\cdots H\cdots O$ bridge by the BF_2 and/or the $(CH_2)_3$ moiety in the macrocycle on (a) thermodynamic and kinetic aspects of ET; (b) UV-VIS spectra; and (c) the influence of the solvent on chemical steps coupled with the ET. The results are discussed in terms of the stability of the Co^{II} oxidation state and the reactivity at axial positions, and used in evaluation of the fitness of the present chelates as models of Vit. B_{12} group complexes.

Experimental

Materials

Caution: The perchlorates used in this paper must be handled with great care and in small quantities since they may explode violently when dry.

$[Co(DH)_2(H_2O)_2]^+$ (A). Co^{III} chelates of bis(dimethylglyoxime) of the type $X_2Co(D_2H_3)$ (where X is the anion of the reagent Co^{II} salt) are generally obtained in solution in the presence of molecular oxygen [16]. The corresponding Co^{III} diaquo complex $[Co(DH)_2(H_2O)_2] \cdot ClO_4$ was prepared as described by Bakac and Espenson [17] from $Cl_2Co(D_2H_3)$ by stirring a suspension of the latter for several hours with an equivalent amount of silver perchlorate; the product was precipitated by addition of concentrated sodium perchlorate solution and repeatedly washed with diethyl ether.

*$[Co(DO)(DOH)pn(H_2O)_2]^{2+}$ (**B**).* The $(Br_2Co(DO)(DOH)pn)$ chelate separates as a Co^{III} complex when dioxygen is bubbled through a solution containing $CoBr_2 \cdot 6H_2O$ and $(DOH)_2pn$ ligand [18]. The corresponding diaquo chelate perchlorate was obtained by treatment of a suspension of the dibromo complex in water with $AgNO_3$, followed by precipitation with concentrated perchloric acid from the filtered solution. The precipitate was repeatedly washed with diethyl ether [4].

The corresponding dianion $[Co(DO)(DOH)pn(DMF)_2]^{2+}$ was obtained in solution by performing the above reaction in anhydrous DMF, and was examined in this solution.

$[Co(DBF_2)_2(H_2O)_2]$ (C). This was prepared as described by Bakac and Espenson [19]. It is to be noted that the complex can be obtained stable only if the metal is in the Co^{II} oxidation state. Although not specified by Bakac and Espenson, the best results are obtained when the reaction with $(C_2H_5)_2O \cdot BF_3$ is performed at low temperature under nitrogen.

*$[Co(DO)(DOBF_2)pn(H_2O)_2]^+$ (**D**).* In contrast with $[Co(DO)(DOH)pn(H_2O)_2]^{2+}$, which was obtained as the Co^{III} chelate, $[Co(DO)(DOBF_2)pn(H_2O)_2]^+$ chelate is obtained as a Co^{II} complex.

The replacement of the $O \cdots H \cdots O$ bridge with the BF_2 group by treatment of $[Br_2Co(DO)(DOH)pn]$ with $(C_2H_5)_2O \cdot BF_3$ is very slow. Attempts to obtain the corresponding diaquo derivative by treatment with $AgNO_3$ were unsuccesful. Direct introduction of the BF_2 group into the $[Co(DO)(DOH)pn(H_2O)_2]^{2+}$ also failed.

The desired product was obtained by reduction of a suspension of the $[Br_2Co(DO)(DOH)pn]$ with slightly less than the stoichiometric amount of $NaBH_4$ at 0 °C under nitrogen. The reduced complex was then treated with $(C_2H_5)_2O \cdot BF_3$ in ether and precipitated with an excess of $NaClO_4$ [8].

Alternatively a solution of $[Co^{III}(DO)(DOH)pn(H_2O)_2]^{2+}$ is reduced with $NaBH_4$ and the resulting Co^{II} complex treated with $(C_2H_5)_2O \cdot BF_3$ and precipitated as above.

Solvents

Electrochemical experiments were carried out in dimethylformamide (DMF), acetontrile (AN), dimethylsulphoxide (DMSO) and CH_2Cl_2 (Carlo Erba) which had been dried and stored over molecular sieves. The supporting electrolyte was tetraethylammonium perchlorate (TEAP) or tetrabutylammonium perchlorate (TBAP), 0.1 mol dm^{-3}, which was recrystallized from water before use.

Apparatus

An Amel model 471 multipolarograph equipped with a model 460 stand was used for the voltammetric measurements at low scan rate.

Cyclic voltammetry (CV) was performed with an Amel model 551 potentiostat including positive feed-back compensation connected with an Amel model 568 function generator. A Nicolet 2090 IIIa digital oscilloscope was used as data buffer, from which data were transferred to an Amel model 863 X/Y recorder or by a IEEE 488 interface card to an Apple II computer for data handling.

All the measurements were performed in a three-electrode system: three different working electrodes were employed: (a) a Smoler's dropping mercury electrode (DME) with m 0.356 mg s^{-1} when $h = 55$ cm for polarography; (b) a Smoler's DME with m 0.07 mg s^{-1} and drop life > 50 s in solution for CV; (c) a Tacussel EDI rotating disk electrode (RDE) equipped with a Pt disk (radius 1 mm).

A NaCl saturated calomel electrode (SCE) was used as the reference electrode, and was separated from the cell by a salt bridge (Luggin's capillary) with the same solvent and supporting electrolyte. The counter electrode was a Pt wire. All measurements were performed with freshly prepared solutions deaerated with pure dry nitrogen.

Evaluation of reversible $E_{1/2}$

When the process was reversible, the value of $E_{1/2}$ was reproducible in the range ± 3 mV, whereas when it was quasi-reversible, the $E_{1/2}$ reversible was estimated by extrapolation of the straight line $\log[(i_l - i)/i]$ vs. E plot drawn for E values at the foot of the wave.

Evaluation of the ET rate constant

In view of the different orders of magnitudes of the ET rate constant for the processes Co^{III}/Co^{II} or Co^{II}/Co^{III} and Co^{II}/Co^{I}, two different techniques had to be used. For the former process we used the RDE system, following the procedure described previously [20]. For all the complexes examinated the voltammetric waves were recorded at a rotation speed of 60 to 2000 rpm and potential sweep rate of 2 mV s^{-1}. The $\log k_s$ values were reproducible within ± 0.1 units. For the reversible Co^{II}/Co^{I} process the CV technique at a DME was used, following the procedure described by Nicholson [21] in which the last portion of drop life is utilised, in order to minimize the effect of the increase of the electrode area.

The mean of the anodic and cathodic peak potentials measured by this technique was always in good agreement with the $E_{1/2}$ values of the corresponding reversible ET obtained by polarography.

Great care was taken to maintain the same cell geometry and to adjust the positive feed-back for all complexes under investigation. In this way the reproducibility of $\log k_s$ values was within ± 0.1 units.

Evaluation of reaction entropies

The $\Delta S = \Delta F(\Delta E/T)$ values were obtained for the reaction Co^{II}/Co^{I} on DME in DMF and TEAP from $E_{1/2}{}^{r}$ in a non-isothermal cell [22] using polarography or fundamental harmonic AC voltammetry. The temperature of the reference was maintained at 25.0 °C ± 0.1, while that of the cell was varied in the range -10.0 to 35.0 °C ± 0.1. The logarithmic analysis of the waves was always very close to the theoretical value for one electron reversible process at a given temperature.

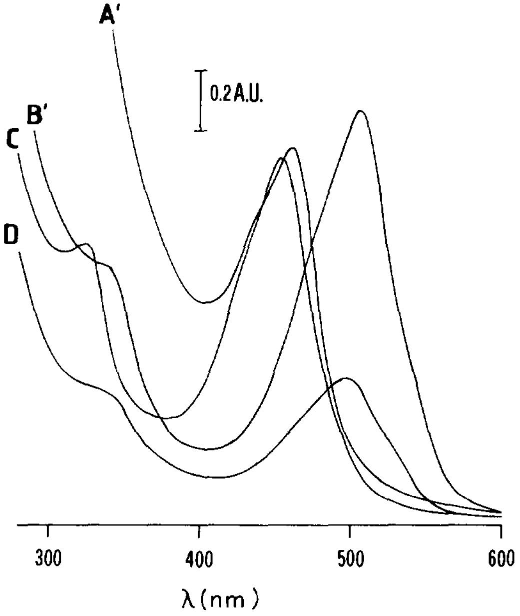


Fig. 1. Spectral data for the four chelates in water at 25° C under nitrogen: **A'** = $[Co^{II}(DH)_2(H_2O)_2]$; **B'** = $[Co^{II}(DO)(DOH)pn(H_2O)]^+$; **C** = $[Co^{II}(DBF_2)_2(H_2O)]$; **D** = $[Co^{II}(DO)(DOBF_2)pn(H_2O)]^+$.

Electronic spectra

Spectrophotometric measurements were performed on aqueous solutions under nitrogen at 25.0° C, with a double beam Perkin–Elmer Lambda 5 spectrophotometer.

Results

Electronic spectra

The observed absorptions of the Co^{II} chelates in water in the UV-VIS region are shown in Fig. 1; absorption maxima and extinction coefficients are listed in Table 1.

Each of the chelates **A** and **B** shows two well-defined bands, at 193 and 245 and at 193 and 216 nm, respectively. In these chelates, the substitution of one

Table 1

Electronic spectra

Complex	λ_{max}(nm) ($\epsilon \times 10^{-3}$)			
	λ_1	λ_2	λ_3	λ_4
$[Co^{III}(DH)_2(H_2O)_2]^+$	193 (15.0)	245 (13.6)	370 (sh)	
$[Co^{II}(DH)_2(H_2O)_2]$	216 (2.0)	246 (5.0)		462 (1.0)
$[Co^{III}(DO)(DOH)pn(H_2O)_2]^{2+}$	193 (22.0)	216 (24.0)	305 (4.0)	
$[Co^{II}(DO)(DOH)pn(H_2O)_2]^+$	217 (9.8)	242 (9.6)	336 (0.4)	507 (0.8)
$[Co^{II}(DBF_2)_2(H_2O)_2]$	198 (24.0)	257 (7.8)	330 (2.5)	454 (3.2)
$[Co^{II}(DO)(DOBF_2)pn(H_2O)_2]^+$	200 (16.0)	260 (sh)	340 (sh)	497 (1.4)

O · · · H · · · O bridge by the $(CH_2)_3$ moiety gives rise to an ipsochromic shift (29 nm) of the second, more intense, band. In the case of the boronic ester derivatives **C** and **D**, obtained by substitution of one (structures **B** to **D**) or two (structures **A** to **C**) of the O · · · H · · · O bridges by BF_2 groups, the strong bands at 245 and 216 nm are absent, and only an unshifted band at 200 or 198 nm, respectively, is still present in this region.

In order to compare the chelates in the same oxidation state of the central metal atom, the UV-VIS spectra of the solutions of chelates **A** and **B** reduced under nitrogen at controlled potential to the Co^{II} oxidation state (chelates **A′** and **B′**) were also obtained. The main spectrochemical characteristics of the Co^{II} species of the chelates **A′**, **B′**, **C** and **D** relative to the corresponding Co^{III} chelates, is the rather strong ($\log \epsilon \approx 3$) band at 462, 507, 454 or 497 nm, respectively.

Relative to that of the parent chelate **A′**, this band has undergone a bathochromic shift as a consequence of the presence of the $(CH_2)_3$ bridge (chelates **B′** and **D**) in place of one of the O · · · H · · · O bridges. A small ipsochromic shift is observed when one (chelate **D** relative to **B′**) or both of the O · · · H · · · O bridges (chelate **C** relative to **A′**) are substituted by BF_2 groups.

Since the absorption coefficients are between 10^3 and 10^4, all the bands in the above regions must be assigned to metal-to-ligand charge transfer.

Electrode processes

All the present diaquo derivatives undergo two heterogeneous redox processes, which were observed in DMF on DME and RDE (Table 2) as well as with CV experiments. DMSO was also used as solvent for voltammetry on RDE (Table 3).

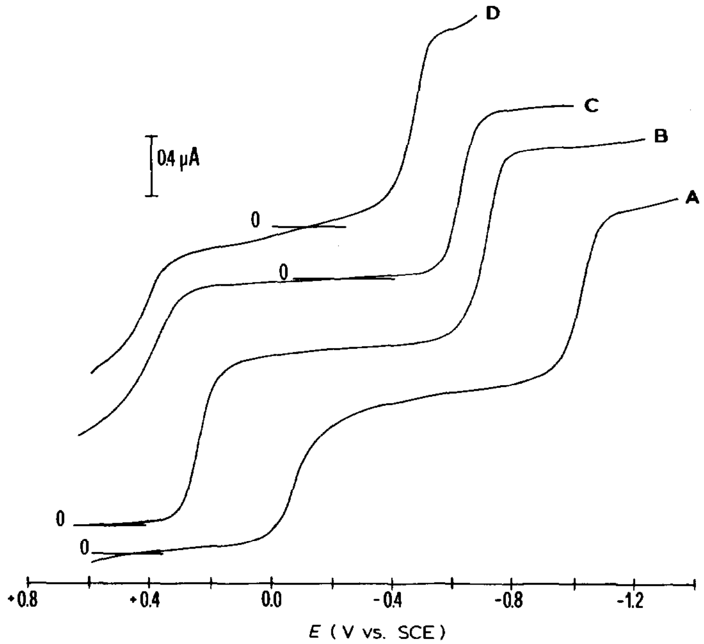


Fig. 2. RDE voltammograms on Pt disk at 60 rpm in DMF and TEAP 0.1 mol dm^{-3} at 0 °C for the four complexes: C 1.0×10^{-3} mol dm^{-3}.

Table 2

Electrochemical parameters in DMF and TEAP 0.1 mol dm^{-3} at 0 °C with RDE and DME

Complex	RDE (in DMF)				DME (in DMF)				
	$E_{1/2}^{r}(I)$ [a] (V vs. SCE)	$\log k_s$ [b]	$E_{1/2}^{r}(II)$ [a] (V vs. SCE)	Slope of log plot (mV)	$E_{1/2}^{r}(I)$ [a] (V vs. SCE)	I_d [c]	$E_{1/2}^{r}(II)$ [a] (V vs. SCE)	I_d [c]	$\log k_s$ [b]
$[Co^{III}(DH)_2(H_2O)_2]^+$	−0.081	−3.2	−1.061	56	−0.25	1.08	−1.04	1.16	−1.2
$[Co^{III}(DO)(DOH)pn(H_2O)_2]^{2+}$	+0.225	−2.8	−0.706	61	+0.18	0.89	−0.75	1.02	−1.0
$[Co^{II}(DBF_2)_2(H_2O)_2]$	+0.393	−3.2	−0.607	57			−0.57	0.80	−1.3
$[Co^{II}(DO)(DOBF_2)pn(H_2O)_2]^+$	+0.393	−2.6	−0.487	58			−0.48	0.93	−1.4

[a] Reproducibility ±0.003 V. [b] Reproducibility ±0.1. [c] $I_d = i/Cm^{2/3}t^{1/6}$.

The potential range on RDE was +0.40 to −0.10 V vs. SCE (range I) and −0.50 to −1.10 V vs. SCE (range II). The two redox processes are assigned to the redox couples Co^{III}/Co^{II} and Co^{II}/Co^{I}, respectively (Fig. 2). A third electrode process, which can be seen at more cathodic potentials, is not considered in the present work. In agreement with their chemistry (see preparative methods) the chelates **A** and **B** which are stable as Co^{III} complexes show cathodic waves in both the ranges I and II. With **C** and **D** chelates, which are stable in solution as Co^{II} complexes, the Co^{II} → Co^{I} ET is observed as a cathodic process in the range II, while the Co^{II} → Co^{III} couple is revealed by an anodic process in range I.

The ET in the potential range I. The appearance of both the anodic and cathodic peaks in CV experiments, with i_{pc}/i_{pa} very near to unity, suggests that the redox process is reversible in the chemical sense. In fact, controlled potential reduction (CPR) of chelates **A** and **B** at the potential of the first ET involves one electron per molecule yielding a stable Co^{II} species. The one electron character of the ET is confirmed by the value of the ratio $i_1/Cm^{2/3}t^{1/6}$, which is nearly the same for all the chelates examined (Table 2).

The main feature of the Co^{III} ↔ Co^{II} ET is its quasi-reversibility; the ET is not completely diffusion controlled in the time scale of the experimental technique used in the present study. Moreover, the extent of reversibility strongly depends on the nature of the solvent (see infra). The quasi-reversibility of the ET is quantitatively expressed by the separation of the potentials of the cathodic from that of the anodic peak $E_{pc} - E_{pa} = E$ in CV, which ranges from 140 to 280 mV (at a scan rate of 1 V s^{-1}) and by the slope of the log plot of the current $i/(i_1 - i)$ against the electrode potential E.

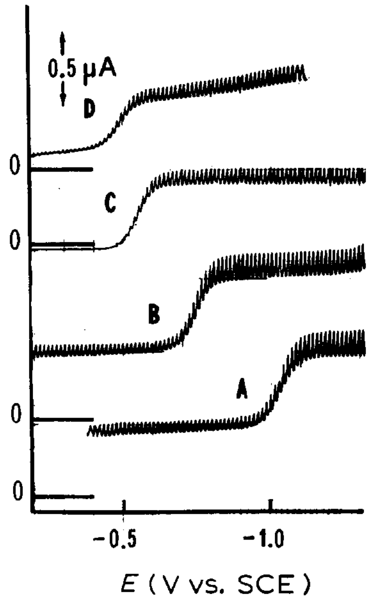


Fig. 3. Polarographic waves in DMF and TEAP 0.1 mol dm^{-3} at 0 °C for cathodic process Co^{II}/Co^{I} (range II) for the four complexes: C is about 1×10^{-3} mol dm^{-3} for all the compounds.

Table 3

Electrochemical parameters in different solvents (All measures were performed at 0 ° C except in DMSO (25 ° C). Supporting electrolyte was always TEAP 0.1 mol dm^{-3} except in CH_2Cl_2 where it was TBAP 0.1 mol dm^{-3} All $E_{1/2}$ refer to reversible ET and were measured with reference to ferrocene/ferricinium couple in the same solvent and supporting electrolyte)

Complex	DMF			DMSO				AN			CH_2Cl_2		
	$E_{1/2}$ (I) [a] (V)	$\log k_s$(I) [b]	$E_{1/2}$(II) [a] (V)	$E_{1/2}$(I) [a] (V)	Slope of log plot (mV)	$E_{1/2}$(II) [a] (V)	$E_{1/2}$(I) [a] (V)	$\log K_s$(I) [b]	$E_{1/2}$(II) [a] (V)	$E_{1/2}$(I) [a] (V)	$\log k_s$(I) [b]	$E_{1/2}$(II) [a] (V)
$[Co^{III}(DH)_2(H_2O)_2]^+$	−0.544	−3.2	−1.525	−0.442	57	−1.260						
$[Co^{III}(DO)(DOH)pn(H_2O)_2]^{2+}$	−0.239	−2.8	−1.170	−0.213	56	−0.919						
$[Co^{II}(DBF_2)_2(H_2O)_2]$	−0.071	−3.2	−1.071	−0.036	59	−0.808	0.153	−3.5	−0.919	0.209	−3.0	−0.940
$[Co^{II}(DO)(DOBF_2)pn(H_2O)_2]^+$	−0.071	−2.6	−0.951	−0.030	58	−0.779						

[a] Reproducibility ±0.006 V. [b] Reproducibility ±0.1.

The ET in the potential range II. This ET is very nearly reversible both in electrochemical and in the chemical sense, as shown by the slope of the log of $i/(i_d - i)$ vs. E, by the separation of the cathodic from the anodic peak potential, and by the ratio i_{pc}/i_{pa} in CV.

The trend of the $E_{1/2}$ values runs parallel to that of the first redox process. The ET in this range is also monoelectronic, as is shown by the I_d values as compared with those of the ET in the range I (Table 2) and by the log plot analysis. The trend is also the same in polarography in DMF (Fig. 3).

The effect of the solvent

The effect of the solvent was studied for the electrochemistry of $[Co(DBF_2)_2(H_2O)_2]$ in DMF, DMSO, AN and for CH_2Cl_2 with the RDE for both electrode processes. The assumption that the Co^{III} diaquo-derivatives in the solvent S are present as the di-solvato chelates $[Co(chel)S_2]^{n+}$ (where chel is one of the present chelating agents, and the solvent S is bonded to the axial positions, and $n = 1$ or 2 depending on the charge on the equatorial ligand) was checked by comparison of the polarograms of $[Co(DO)(DOH)pn(H_2O)_2]^{2+}$ and $[Co(DO)(DOH)pn(DMF)_2]^{2+}$ in DMF. No difference was found between the $E_{1/2}$ or k_s values in either range I or II.

The electrochemical behaviour of all chelates was also examined (Table 3) in DMF (Fig. 2) and in DMSO (Fig. 4): the RDE and CV patterns are qualitatively the same in all cases.

The only process which appears to be noticeably affected is the $Co^{III} \rightarrow Co^{II}$ or the $Co^{II} \rightarrow Co^{III}$ ET, which in DMSO are more reversible.

Relatively large shifts are observed for the $E_{1/2}$ values in the range, while the changes in the rate of the overall electrode process, as expressed by $\log k_s$, on going from DMF to AN to CH_2Cl_2 appear to be minor. In contrast to the results in other solvents, in DMSO all the chelates undergo a nearly reversible ET in both of the

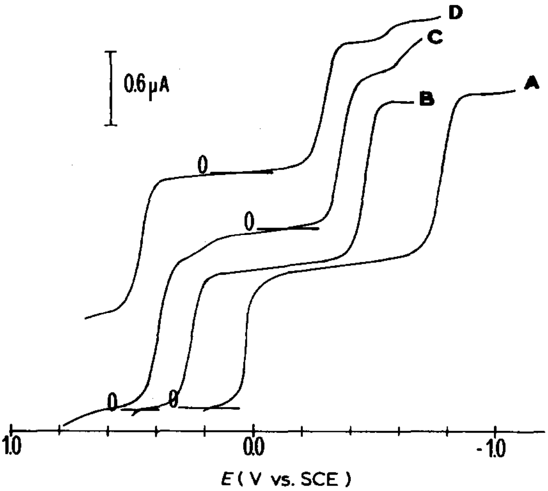


Fig. 4. RDE voltammograms on a Pt disk at 60 rpm in DMSO and TEAP 0.1 mol dm^{-3} at 25° C for the four complexes: C 1.0×10^{-3} mol dm^{-3}.

ranges I and II. The Co^{II}/Co^{I} ET at RDE is reversible in all solvents except CH_2Cl_2.

Discussion

The data for the polarographic behaviour of the non-organometallic derivatives of cobaloximes and of $[Co(DO)(DOH)pnL_2]^{2+}$ chelates [23], although sparse, indicated the existence of a correlation between the donor strength of the *axial ligand* and the shifts of the redox potentials of chelates containing a given equatorial ligand.

Thermodynamic and kinetic parameters for the ET in range I for the present chelates with a given in-plane ligand can be assumed to reflect the effect of changes in the axial bond on going from the Co^{III}, essentially d^6, chelates, bearing solvent molecules bonded in the axial positions, to the Co^{II} d^7 chelate, where the axial bonds are very weak.

Interaction of the solvent with Co^{III} chelates is revealed by the displacement of $E_{1/2}$ towards more cathodic values with increase in the donor power of the solvent molecules.

In fact the linear relationship

$$E_{1/2} = -0.014Ds + 0.3$$

(where Ds is the donor number [25]) holds for $[Co(DBF_2)_2L_2]$ when the solvent L = DMF, DMSO, or CH_2Cl_2 with deviations of less than 10 mV, whereas in AN the deviation is about 45 mV (Table 3). The displacement is about the same for all the four chelates examined, as indicated by the comparison of $E_{1/2}$ (I) DMF and DMSO.

If the kinetic behaviour is assumed to reflect mainly the activation energy related to the weakening of the Co–solvent interaction in the axial positions when Co^{III} chelates are reduced to the Co^{II} oxidation state (and vice versa), the k_s values do not suggest substantial differences between different solvents, except for DMSO, where, in striking contrast with the results in other solvents, the ET appears to be controlled only by diffusion.

The effect of changes in the *equatorial ligand* brought about by replacement of sections of the in-plane macrocycle can be best discussed on the basis of the reversible ET in the range II, where there is no complication from kinetic effects. The trend of the $E_{1/2}$ values is the same in RDE voltammetry and DME polarography, even though the differences in the $E_{1/2}$ obtained by the two techniques are slightly different.

The displacement towards more cathodic potentials observed resulting from replacement of one of the $O \cdots H \cdots O$ bridges in the chelate **A** by a $(CH_2)_3$ group, leading to the chelate **B**: $E_{1/2} = E_{1/2}(\mathbf{B}) - E_{1/2}(\mathbf{A}) = 355$ mV for RDE and 290 mV for DME, can be attributed to the reduction in electron delocalization. On the other hand the replacement of the $O \cdots H \cdots O$ bridge by the electron-withdrawing group BF_2 in the chelate **B**, already containing $(CH_2)_3$ group, leads to chelate **D** with $E_{1/2} = E_{1/2}(\mathbf{D}) - E_{1/2}(\mathbf{B}) = 219$ and 270 mV for RDE and DME, respectively.

Larger displacements are caused by replacement of both the $O \cdots H \cdots O$ bridges by the BF_2 group, i.e. on going from **A** to **C**: thus $E_{1/2} = E_{1/2}(\mathbf{C}) - E_{1/2}(\mathbf{A})$

= 454 and 470 mV in RDE and DME, respectively. Finally, the largest displacement is afforded by replacement of one O···H···O bridge by $(CH_2)_3$ and the other by BF_2: the values of $E_{1/2}$ are now 574 and 560 mV in RDE and DME, respectively.

It can be concluded that the introduction of the $(CH_2)_3$ aliphatic chain and/or the BF_2 group increases the electron affinity of the singly occupied MO of the Co^{II} chelates. The effect of the former is due to the decrease of the negative charge on the equatorial ligand, and is larger than that of the electron-withdrawing BF_2 group [26].

It is noteworthy that the same trend in $E_{1/2}$ values for the Co^{III}/Co^{II} couple caused by the same changes of the equatorial ligands was observed for the organometallic derivatives, for which the ET involves the reduction of the [RCo(chel)L] (where R is an organic group, (chel) is one of the present chelating ligands, and L a solvent molecule) to an unstable radical anion that undergoes Co–C bond cleavage [27].

Previous attempts to rationalize the effects of ligands on *redox potentials* together with these on the *electronic spectra* of the Co^{II} chelates were limited to changes of axial ligands in transition metal complexes of tetraaza-macrocycles [28], cobaloximes [29,30] and organocobaloximes [27,31]. A bathochromic shift was related to the increase in the donor and acceptor character of the axial ligand, but ligand field theory is apparently unable to explain the large shifts in the redox potentials of the metal ion caused by seemingly minor changes in the nature of the ligands [32,33].

Bathochromic shifts observed with organocobalt chelates of the present type (with the same axial ligand, a methyl or ethyl group) were attributed to an increase of the strength of the in-plane donation in the order: $(DPH)_2 < (DO)(DOH)pn < (DH)_2$, where $(DPH)_2$ is the dianion of the bis(diphenylglyoxime)ligand [30].

The almost linear correlation between the axial splitting parameters Dq^z and redox potentials $E_{1/2}$ for Co^{III}/Co^{II} ET in chelates of tetraaza-macrocycles [28] can be explained in terms of the interaction of the axial donor ligands which influence the same acceptor *d* orbital (mixed with in-plane ligand orbitals in a substantially unchanged equatorial electronic structure).

In the present complexes the changes in the electronic structure upon introduction of $(CH_2)_3$ and BF_2 strongly affect, the Co^{II}/Co^{I} redox potentials, but the shift in the values of λ_4 are much less consistent than those of the $E_{1/2}$ shift.

In the former case a substantial change of the electronic structure, and consequent decrease of charge donation from the in-plane ligand, can be assumed to result from the decrease of the charge of the equatorial anion ligand, and this could explain both the major anodic shift of the $E_{1/2}$ of about 300–350 mV and the bathochromic shift for λ_4 of about 45 nm on going from **B** to **A**.

In the latter case a large increase of the electron affinity of the acceptor *d* orbital is expected arise from the strongly electron withdrawing power of the BF_2 group. This could explain the strong anodic shift of about 450 mV on going from chelate **A** to **C** or of 250 mV on going from chelate **B** to **D**. In this case, however, the corresponding shift of λ_4 is ipsochromic and much less important (8 and 10 nm, respectively).

Thus, the shift in $E_{1/2}$ and λ_4 for the two oxime ligands and the two imine/oxime ligands resulting from the introduction of the BF_2 group is anodic and very slightly ipsochromic in both cases, while the shift due to the introduction of $(CH_2)_3$ group is anodic and bathochromic.

The anodic and bathochromic shifts observed on the introduction of the $(CH_2)_3$ group going from **A** to **B** and **C** to **D** can be explained in terms of a decrease in the charge on the equatorial ligand. This is also consistent with the correlation of the shift of λ_4 towards higher energies and of the cathodic shift of $E_{1/2}$ with the increase in the in-plane donation.

Entropy changes associated with Co^{II}/Co^{I} redox process appear to decrease significantly from 18 and 22 e.u. for **A** and **B** to 13 and 12 for **C** and **D** when the BF_2 group replaces the $O \cdots H \cdots O$ bridge in the equatorial ligand, and this may be attributed to the stiffening of the in-plane structure resulting from the presence of the more rigid $O{-}BF_2{-}O$ structure.

As far as the comparison with coenzyme B_{12} chemistry is concerned, we conclude that the replacement of the $O \cdots H \cdots O$ bridge by the BF_2 and/or the $(CH_2)_3$ group increases the stability of the Co^{II} oxidation state under ordinary ambient conditions.

The kinetics of Co^{III}/Co^{II} ET depends more on the nature of the axial than on that of the equatorial ligand, at least for ligands of the present series, confirming the observations arising from a study of organometallic derivatives of the present chelates [27], in which it was found that the mechanism of the Co–C bond cleavage is determined mainly by the nature of the organic group.

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