Configuration Effects on Electrode Processes: Optically Active Complexes of Quadridentate Schiff Bases. Part 1. Cobalt Complexes

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Diastereoisomeric cobalt chelate complexes of quadridentate Schiff bases derived from disubstituted ethylenediamines and salicylaldehyde show differences in the polarographic redox potentials and rates of electron transfer which are attributed to the different extent of tetrahedral distortion around the metal atom. In the oxygen adducts of the chelate complexes, inspection of the half-wave potentials corresponding to the reduction of co-ordinated oxygen shows that the ' activation ' of the molecular oxygen is also different in complexes with different conformations.

COBALT complexes having a quadridentate chelating system and delocalized electronic structure were proposed as models of vitamin B_{12} group coenzymes.[1-3] Several of these complexes are also suitable for the study of factors influencing the mechanism and reversibility of formation of adducts with molecular oxygen, and are thus models for biological oxygen carriers. Previous studies pointed out the electronic factors which influence the thermodynamic and kinetic aspects of reactivity at the axial positions relative to the macrocyclic ring; these sites are involved in the key steps of the action of coenzymes, as well as in molecular-oxygen transport.[4,5] On the other hand, existing theories of the control mechanism in enzymatic reactions emphasize the relevance of steric factors. As far as metalloenzymes are concerned, the entatic-state theory relates the biochemical behaviour to the special geometry of the reactive site in the co-ordination sphere of the metal.[6]

It is thus appropriate to extend the study of models by considering the steric effects on the mechanisms and rates of co-ordination reactions and of redox reactions. A suitable series of models is the Schiff-base chelates related to [*NN'*-ethylenebis(salicylideneiminato)]cobalt, [Co(salen)].[7] When the Schiff base is formed from salicylaldehyde and 2,3-disubstituted diamines, optically active, quadridentate, chelating agents are obtained.[8] The following cobalt chelate complexes [CoL] with optically active (±) and *meso* (*m*) conformations have been examined (Figure 1): [Co(salen)]; [Co{sal(±)pn}] [salpn = *NN'*-propane-1,2-diylbis(salicylideneiminato)]; [Co{sal(±)bn}], [Co{sal(*m*)bn}] [salbn = *NN'*-butane-2,3-diylbis(salicylideneiminato)]; [Co{sal(±)pen}] [salpen = *NN'*-1-phenylethylenebis(salicylideneiminato)]; [Co{sal(±)dpen}], [Co{sal(*m*)dpen}] [saldpen = *NN'*-1,2-diphenylethylenebis(salicylideneiminato)]; [Co{sal(±)chxn}], [Co{sal(*m*)chxn}] [salchxn = *NN'*-cyclohex-1,2-ylenebis(salicylideneiminato)]. *X*-Ray structure investigations have shown that the substituents of the diamine are pseudo-bis-axial [Figure 1(*a*)] in the optically active enantiomers of [Co{sal(±)bn}], pseudo-axial–pseudo-equatorial in [Co{sal(*m*)chxn}] [Figure 1(*c*)] and [Co{sal(*m*)bn}] [Figure 1(*b*)], and must be pseudo-bis-equatorial [Figure 1(*d*)] in [Co{sal(±)chxn}].[9-11] The present paper deals with the steric

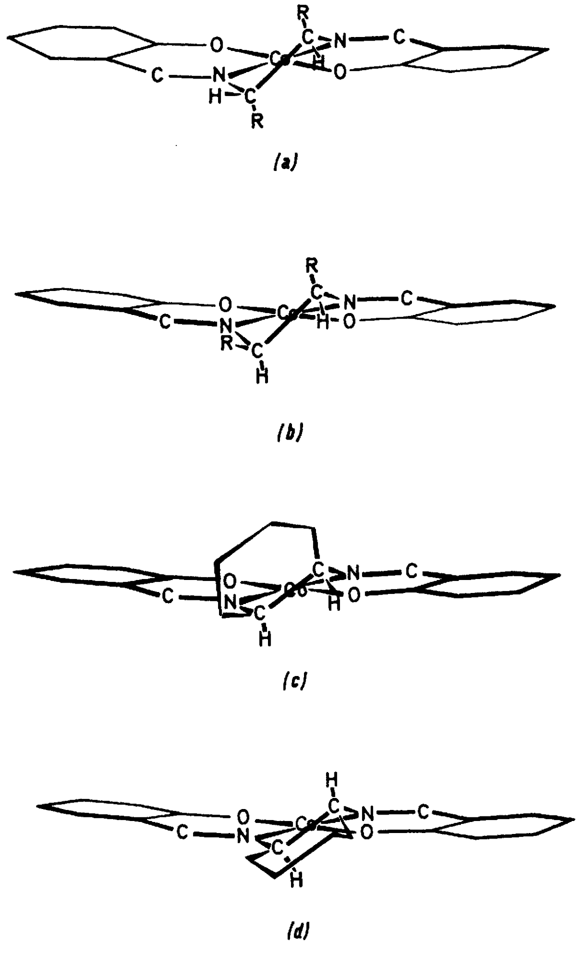

FIGURE 1 Side views of (*a*) [Co{sal(+)bn}], (*b*) [Co{sal(*m*)bn}], (*c*) [Co{sal(*m*)chxn}], and (*d*) [Co{sal(+)chxn}]

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effects on the electrochemical behaviour of the above chelate complexes and their oxygen adducts. Following previous studies on the effects of electronic structure on the redox properties of chelate complexes of general formula $[Co^{III}LL'_2]$,[12] the present work shows that the redox properties are also related to the steric structure, providing experimental data for the quantitative evaluation of steric influence on the heterogeneous electron-transfer process.

EXPERIMENTAL

Polarographic measurements were made on an AMEL model 448 polarograph with 448/YA and 448/XB attachments. The maximum sensitivity of the Leeds and Northrup recorder was 0.15 μA for full-scale deflection. The polarographic cell was a universal vessel,[13] connected to a commercial calomel electrode (s.c.e.) (Metrohm) as a reference electrode, in saturated aqueous NaCl solution. The connection was made with a salt bridge containing 0.1 mol dm^{-3} tetraethylammonium perchlorate in anhydrous pyridine. The auxiliary electrode was a platinum wire (10-cm length, 0.5-mm diameter) wound around the working electrode. The working electrode was a dropping mercury electrode with the following characteristics: when the height of the mercury level was 60 cm, the measured flow rate was 0.8 mg s^{-1} in anhydrous pyridine—0.1 mol dm^{-3} $[NEt_4][ClO_4]$ at a controlled drop time of 3 s (AMEL model 460 droptime control).

Cyclic-voltammetric measurements were carried out on PAR (Princetown Applied Research) model 170 equipment. Setting of the starting and reverse potentials was performed with ±1-mV accuracy. At sweep rates lower than 0.5 V s^{-1} the PAR recorder was used. For faster sweeps and measurements of electrode kinetics a Philips PM 3232 oscilloscope was used. Differences in the peak potentials were determined with ±2-mV accuracy. The oscilloscope was also used for testing full compensation of the resistance between the tip of the reference and working electrodes by means of positive feedback.[14] The cell, reference, and auxiliary electrodes were as in the polarographic measurements. As a working electrode for qualitative cyclic-voltammetric measurements, a Kemula's Metroohm electrode was used (hanging mercury-drop electrode). For quantitative measurements a small mercury-pool electrode (1-mm diameter) was obtained using a U glass capillary. The mercury pool was renewed before each run.

A working platinum electrode was prepared from a platinum wire (0.5-mm diameter). The electrode was cleaned by the Adams method [15] before each experiment.

Electrolyses were performed using an AMEL model 557/SU potentiostat with output voltage ±100 V, output current ±300 mA, and input impedance greater than 100 MΩ. The universal electrochemical vessel was again used. The reference electrode was the same as above. A mercury pool of *ca.* 4 cm^2 was used, as the working electrode, with magnetic stirring. The auxiliary electrode was a graphite electrode contained in a compartment separated from the cell by a sintered glass.

Chemicals.—An inert atmosphere was secured by use of extra-pure nitrogen which was further dried with K[OH] and saturated with the solvent before being passed through the electrochemical cell. The absence of dissolved oxygen in the solution was tested by exploiting the fast reactions of the examined complexes with trace amounts of oxygen. Pyridine (Carlo Erba, p.a.) was dried with K[OH] and distilled. Methanol (Carlo Erba, p.a.) was dried with Grignard reagents. The compound $[NEt_4][ClO_4]$ (Carlo Erba) was crystallized twice and dried *in vacuo* at 40 °C. Lithium perchlorate (Fluka A.G., anhydrous) was used without purification. Mercury was purified by conventional methods and distilled twice before use.

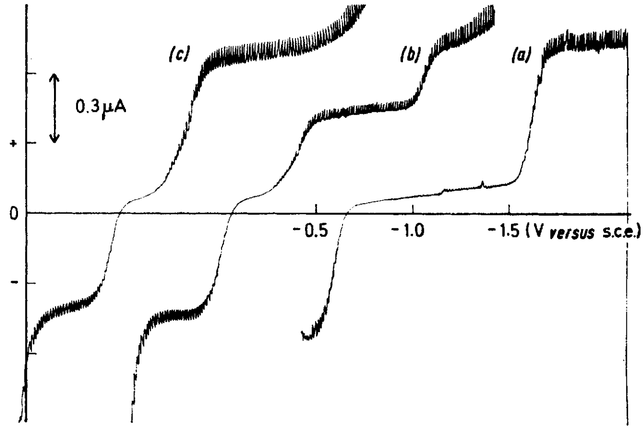

FIGURE 2 Polarographic patterns for: (*a*) [Co{sal(+)bn}] (1×10^{-3} mol dm^{-3}) in pyridine (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at 0 °C; (*b*) and (*c*) the same solution on increasing oxygenation by bubbling O_2

TABLE 1

Values of $E_{\frac{1}{2}}$ (in V) * in pyridine (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at 25 °C

	$Co^{II} \longrightarrow Co^{III}$		$Co^{II} \longrightarrow Co^{I}$	
Complex	±	*meso*	±	*meso*
[Co(salen)]	−0.540		−1.575	
[Co{sal(±)pn}]	−0.540		−1.600	
[Co{sal(±)pen}]	−0.525		−1.585	
[Co{sal(±)bn}]	−0.525		−1.580	
[Co{sal(*m*)bn}]		−0.460		−1.640
[Co{sal(±)dpen}]	−0.480		−1.495	
[Co{sal(*m*)dpen}]		−0.300		−1.530
[Co{sal(±)chxn}]	−0.545		−1.695	
[Co{sal(*m*)chxn}]		−0.425		−1.645

* *Versus* saturated aqueous calomel electrode; not corrected for NaCl liquid-junction potential. Average error ±0.002 V.

RESULTS

Polarography.—In pyridine solution all the chelate complexes showed the same polarographic pattern as previously found for [Co(salen)], with a first (anodic) and a second (cathodic) wave in the range −0.4 to −0.5 and −1.5 to −1.7 V *versus* the s.c.e. respectively [Table 1 and Figure 2(*a*)]. The diffusion character of both waves is demonstrated by the linear dependence of the limiting currents on the square root of the height of the mercury reservoir. The linear dependence of the diffusion current on the concentration of the depolarizer was ascertained at concentrations lower than 2×10^{-3} mol dm^{-3}. At higher

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concentrations or at low temperatures a maximum appeared in the anodic current. The ratio of the diffusion currents of both the first and second waves was unity within the limits of experimental error. The gradient of the plot of E against log $[i/(i_d - i)]$ for both the waves was between 59 and 65 mV^{-1} as expected for diffusion-controlled one-electron processes. The gradients for the first (anodic) wave had higher values in this range, suggesting that the corresponding electrode process is controlled simultaneously by the rates of diffusion and of electron transfer, and are on the borderline of quasi-reversible processes.

The cathodic wave, corresponding to the reduction of Co^{II} to Co^{I}, showed the characteristics of a reversible wave both in pyridine and in methanol. In methanol the half-wave potential of this wave for [Co(salen)] was displaced on addition of pyridine (py) and the gradient of the plot of $E_{\frac{1}{2}}$ against log [py] was 61 mV, showing that one molecule of pyridine is accepted into the inner co-ordination sphere of the Co^{II}. The chemical species in solution are thus [CoL(py)].

Coulometry and Controlled-potential Reduction.—Coulometric measurements confirm that both waves are due to one-electron process. Electrolysis at constant potential at a mercury-pool electrode showed that, by partial oxidation at a potential corresponding to the plateau of the anodic wave, the wave became anodic–cathodic, its total height and half-wave potential remaining constant. This suggests that the diffusion coefficients for the oxidized, D_o, and reduced species, D_r, of the first polarographic wave are very nearly the same. The diffusion currents of both waves obeyed the Ilkovic law with $D = (0.56 \pm 0.1) \times 10^{-5}$ $cm^2\ s^{-1}$ at 25 °C in pyridine (0.1 mol dm^{-3} $[NEt_4][ClO_4]$). There were no significant differences between the values of diffusion current for the diastereoisomers of each complex. Analogous behaviour was shown by the second, cathodic, wave of all the complexes $[Co^{II}L]$.

The polarographic pattern of a pyridine solution of [Co(salen)], oxidized at a constant potential corresponding to the plateau of the anodic diffusion current, was the same as that of a pyridine solution of an authentic sample of $[Co^{III}(salen)(py)_2]^+$. In each case the electrolysis at controlled potential could be reversed, yielding the starting polarographic pattern.

From the crude product containing the *meso* and ± enantiomers, two anodic waves were observed for [Co{sal(±,*m*)dpen}] at −0.300 and 0.480 V and from [Co{sal(±,*m*)chxn}] at −0.425 and −0.545 V. The ratios $i_1 : i_2 = 1 : 2$ for [Co{sal(±,*m*)dpen}] and for $[Co^{I}$\{sal(±,*m*)chxn\}] were obtained, the smaller wave being due to the *meso* form and the larger wave to the sum of the optically active enantiomers. Owing to a smaller difference in $E_{\frac{1}{2}}$ for the cathodic wave, the racemic mixture gave a single wave.

Cyclic Voltammetry.—The voltammetric pattern at either a platinum or mercury electrode was the same for all the complexes considered. The two sets of peaks corresponding to the first and to the second polarographic waves showed the same ratio of the cathodic and anodic peak currents, $i_p^c/i_p^a = 1$. However, at a platinum electrode the process corresponding to the first wave appeared to be complicated by absorption phenomena, and quantitative measurements were not possible.

For a low scan rate ($v = 0.01$ mV s^{-1}), the cathodic and anodic peak potentials, $E_p^{c,a}$, for each set at the mercury electrode are in agreement with the corresponding theoretical half-wave potentials. Under the same conditions, the peak current was linearly dependent on $v^{\frac{1}{2}}$. On increasing v the difference ΔE_p between the anodic and cathodic peak for each set increased and a plot of $i/v^{\frac{1}{2}}$ against $v^{\frac{1}{2}}$ was linear and of negative gradient. The heterogeneous electron-transfer rate constants k_s (Table 2) were evaluated by the Nicholson method [16] from $\Delta E_p^{a,c}$, assuming that $D_o \sim D_R = 0.5 \times 10^{-5}$ $cm^2\ s^{-1}$ and $\alpha = 0.5$ for all the complexes.

TABLE 2

Values of $10^2(k_s \pm 0.2)$ (in cm s^{-1}) [a] in pyridine (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at 25 °C

	$Co^{II} \longrightarrow Co^{III}$		$Co^{II} \longrightarrow Co^{I}$	
	±	*meso*	*b*	*c*
[Co(salen)]	4.6 [b]		4.5	3.6
[Co{sal(±)pn}]	2.8		2.5	6.2
[Co{sal(±)pen}]	2.8		2.5	6.2
[Co{sal(±)bn}]	1.7		2.3	6.1
[Co{sal(*m*)bn}]		1.5	5.7	6.4
[Co{sal(±)dpen}]	2.6		4.3	7.9
[Co{sal(*m*)dpen}]		0.8	6.1	5.2
[Co{sal(±)chxn}]	1.2		3.8	
[Co{sal(*m*)chxn}]		1.6	4.5	6.0

[a] Not corrected for the influence of the double layer. [b] Mercury electrode. [c] Platinum electrode.

Oxygen Adducts.—When oxygen was bubbled through pyridine solutions of the complexes, the limiting current of the first anodic wave decreased to one third of its value on increasing oxygenation, and the $E_{\frac{1}{2}}$ of this wave shifted toward more negative potentials by 20—50 mV. The current was diffusion controlled over the whole concentration range. A second, cathodic, wave developed at more negative potentials [Figure 2(*b*) and (*c*), Table 3] and the limiting current increased with increasing oxygenation of the solution until the ratio $Co : O_2 = 1 : 1$ was reached. This wave is attributed to electrochemical reduction of the oxygen adduct. Further oxygenation gave a third wave at −1.083 V *versus* the s.c.e. corresponding to the reduction of free-oxygen in the same solution. With the diphenylethylenediamine and cyclohexanediamine derivatives a catalytic increase of the second wave was observed. When the potential reached that of free-oxygen reduction, the current decreased again to the diffusion-limited value for the oxygen adduct.

TABLE 3

Values of half-wave potential $E_{\frac{1}{2}}$ [a] for the polarographic reduction of oxygen adducts

	$E_{\frac{1}{2}}$ in V for $[Co^{II}L(O_2)] \longrightarrow [Co^{II}L(O_2)]^-$		$10^3k_s \pm 0.1$ / cm^{-1}	α ±0.02
	±	*meso*		
$O_2 \longrightarrow [O_2]^-$	−1.083		>10 [b]	
[Co(salen)]	−0.873		2.11	0.68
[Co{sal(±)pn}]	−0.907		1.65	0.61
[Co{sal(−)pen}]	−0.878		*c*	
[Co{sal(+)bn}]	−0.964		2.11	0.71
[Co{sal(*m*)bn}]		−0.894	2.00	0.63
[Co{sal(−)dpen}]	−0.823		2.11	0.86
[Co{sal(*m*)dpen}]		−0.793	>10	
[Co{sal(−)chxn}]	−0.878		1.88	0.63
[Co{sal(*m*)chxn}]		−0.935	1.78	0.78

[a] Data in pyridine (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at 0 °C *versus* s.c.e.; not corrected for NaCl liquid junction potential. Average error ±0.002 V. [b] Reversible. [c] Catalytic.

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[16] R. S. Nicholson, *Analyt. Chem.*, 1965, **37**, 1351.

The cathodic wave due to the reduction of Co^{II} to Co^{I} in the starting complex decreased on increasing oxygenation, but the sum of the reduction currents of the adduct and of the free cobalt(II) complex was constant. On the other hand the character of this wave changed on increasing oxygenation from pure diffusion through semi-kinetic to pure kinetic control.

Oxygenation in excess of the stoicheiometric ratio of $Co : O_2 = 1 : 1$ gave a catalytic increase in the limiting current of the wave due to the Co^{II}–Co^{I} reduction. The oxygenation process could be reversed by bubbling inert gas and the starting polarogram was again obtained. In the presence of proton donors, irreversible oxidation took place yielding $[CoL(py)_2]^+$.

DISCUSSION

All the above results point to the conclusion that both the electrode processes of [CoL(py)] are one-electron transfers between the formal oxidation states Co^{II} and Co^{III} and Co^{II} and Co^{I} respectively. Breakdown of the chelate ring is not involved, and the only chemical changes which could influence the rate of the electron transfer take place at the axial positions and involve changes in co-ordination number, as is shown by the gradient of the plot of $E_{\frac{1}{2}}$ (for the first wave) against log [py] in methanol. The general formula of the depolarizer species is assumed to be [CoL(py)] as is actually found for [Co(salen)] and [Co(salbn)] crystallized from pyridine.[9-11] The following general mechanism for the electrode processes is thus proposed.

$$\begin{tikzcd}
 & {[CoL]} \arrow[d, shift left, "py"] & \\
{[CoL(py)]^+} \arrow[r, shift left] \arrow[d, shift left] & {[CoL(py)]} \arrow[l, shift left, "-e^-"'] \arrow[u, shift left] \arrow[r, shift left, "+e^-"] & {[CoL(py)]^-} \arrow[l, shift left] \\
{[CoL(py)_2]^+} \arrow[u, shift left, "py"] & &
\end{tikzcd}$$

Owing to the difference in $E_{\frac{1}{2}}$ values for the anodic wave, the diastereiosomers of the cyclohexane and diphenylethylene derivatives can be isolated from the mixture containing the ± and *meso* forms by controlled-potential oxidation of only one diastereoisomer of the mixture. The differently charged diastereoisomers could be separated from the electrolyzed mixture by electrophoresis. The separation process is being studied and compared with the classical methods.

For the oxygen adducts the above results are consistent with the assumption of mobile equilibrium (1) involving

$$[Co^{II}L] + O_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [Co^{II}L(O_2)] \qquad (1)$$

the equatorial ligand system. The behaviour of the anodic wave suggests that both the chelate complex and its oxygen adduct undergo oxidation, which is not influenced by the above equilibrium. The second cathodic wave is attributed to the reduction (2). The

$$[Co^{II}L(O_2)] + e^- \rightleftharpoons [Co^{II}L(O_2)]^- \qquad (2)$$

polarographic behaviour confirms the 1 : 1 stoicheiometry for the oxygen adducts. Equilibrium (1) is strongly displaced toward adduct formation and the changes in the character of the wave due to the Co^{II}–Co^{I} reduction confirm that k_b is relatively small.

Electronic and Steric Effects.—The inductive effects of the R_1 and R_2 substituents in the N-CHR_1-CHR_2-N ring is reflected by the shift in the $E_{\frac{1}{2}}$ values toward more negative potentials with increasing pK of the diamine from diphenylethylene to the butane-2,3-diamine (Table 1). This inductive effect appears to occur for both the oxidation and reduction waves.

While no difference was found, as expected, in electrochemical behaviour between the enantiomers, the differences in structure of the chelating agents of the diastereoisomers are reflected both in the half-wave potentials and in the kinetic parameters of the electrode processes for [CoL(py)] and their oxygen adducts.

The differences of $E_{\frac{1}{2}}$ values between diastereoisomers for the Co^{II}–Co^{III} process are in the range of 60—180 mV. The chelates in the *meso* form show a more positive $E_{\frac{1}{2}}$ than in the optically active form.

The same direction of shift was observed between the *meso* and ± forms of the dimethylethylene and cyclohexanediamine derivatives.

The differences of $E_{\frac{1}{2}}$ values between diastereoisomers are less pronounced for the Co^{II}–Co^{I} process, lying in the range 30—60 mV. In the cyclohexanediamine derivatives the chelate in the bis-equatorial conformation [± form, Figure 1(*d*)] shows more negative $E_{\frac{1}{2}}$ values than the diastereoisomer having axial–equatorial conformations [*meso* form, Figure 1(*c*)]. The contrary is true for the couples of diastereoisomers of the salbn and saldpen derivatives.

For the Co^{II}–Co^{I} process there is thus an inversion in the sign of the differences between the $E_{\frac{1}{2}}$ values of the *meso* and ± forms from salbn and saldpen to chxn diastereoisomeric couples. It is worth noting that the same inversion between the dimethyl- or diphenylethylene and the cyclohexane derivatives was also observed for the Cotton effect[11] of the same chelate complexes.

For the dimethyl- and diphenyl-ethylene compounds the influence of conformation is opposite in the Co^{II}–Co^{I} and in the Co^{II}–Co^{III} process shifting the oxidation process toward more negative values in the *meso* form for the latter process.

If the above shifts in the $E_{\frac{1}{2}}$ values between diastereoisomers for the Co^{II}–Co^{I} and Co^{II}–Co^{III} processes are due to conformational effects a distinction can be made from the electronic effects.

As $E_{\frac{1}{2}}$ values of sufficiently rapid electron-exchange processes reflect mainly the relative thermodynamic stability toward electrochemical oxidation or reduction, these results lead to the conclusion that in the dimethyl- and diphenyl-ethylene derivatives the stability of the formal oxidation state Co^{II} (relative to both the Co^{III} and Co^{I} states) is higher in the *meso* conformation than in the ± forms.

In fact, on increasing the donor power of a σ-bonded organic group in the axial position (Me, Et, *etc.*) both the Co^{II}–Co^{I} and Co^{III}–Co^{II} polarographic waves are shifted toward more negative potentials while in the present study, for the dimethyl- and diphenyl-ethylene derivatives, the shift is observed in the *opposite* direction.

Considering now the conformational effects which can be responsible for the *opposite* shift in the $E_{\frac{1}{2}}$ values from the *meso* to the ± forms for processes involving Co^{I} (reduction) and Co^{III} species (oxidation) of dimethyl and diphenyl derivatives, as compared with the *parallel* shift for the cyclohexyl derivatives, we should take into account the preferred co-ordination number.

In pyridine the Co^{III} species are likely to be six-co-ordinated with two pyridine molecules in the axial position to the metal atom, while in the Co^{I} species the interaction of the solvent molecules are at least very weak and they are essentially four-co-ordinate. The presence of the axial ligands in the Co^{III} species may cause the conformation of the optically active forms to change from the bis-axial to bis-equatorial. Different conformations are thus involved in the Co^{II}–Co^{III} and in the Co^{II}–Co^{I} process for the ± dimethyl- and diphenyl-ethylene derivatives, while this change is not possible for the cyclohexane derivatives.

We propose that the difference of $E_{\frac{1}{2}}$ between diastereoisomers is determined by the conformation which may be bis-axial or bis-equatorial (in the ± forms) with the exception of the cyclohexane derivative but only axial–equatorial in the *meso* form. The conformation influences the electronic structure through the distortion of the ligand field.

The difference in the k_s values for the diastereoisomers is also significant, at least in the case of the cyclohexane and diphenylethylene derivatives. For the process Co^{II}–Co^{III} the rate constant is smaller for *meso* than for ± diastereoisomers of the diphenylethylene derivatives but higher for the cyclohexane derivatives.

The $E_{\frac{1}{2}}$ values for process (2) lie in the range −0.793 to −0.935 V *versus* the s.c.e. and are also clearly influenced by the stereochemistry of the parent chelate. The process is assumed to involve mainly the co-ordinated oxygen, while the preceding anodic wave and the following cathodic wave are assigned as in the parent complexes to the processes Co^{II}–Co^{III} and Co^{II}–Co^{I} respectively, in view of the small shifts observed on oxygenation. A comparison of the $E_{\frac{1}{2}}$ values for process (2) and for $O_2 + e^- \longrightarrow [O_2]^-$ suggests that oxygen is activated by co-ordination. The $\Delta G^{\ddagger}$ of activation corresponds to a shift of *ca.* 120—180 mV toward less negative $E_{\frac{1}{2}}$ values. The differences between two diastereoisomers are of the order of 30—70 mV. The ± forms show more negative values, again with the exception of the cyclohexane derivatives. It follows that *meso* isomers, *i.e.* the pseudo-axial–equatorial conformation for the methyl- and phenyl-ethylene derivatives, and ± isomers, *i.e.* the pseudo-bis-equatorial conformation for the cyclohexane derivatives, are more effective in activation of the co-ordinated oxygen. This may be explained by the lower steric hindrance in the formation of the adduct and in the stronger interaction between the O_2 molecule and the chelate complex.

Chelate complexes of the type examined in the present paper appear to be suitable for model studies of the influence of steric factors on reaction rates and mechanisms relevant to coenzyme functions.

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