Effects of Cations on Electrode Processes of Cobalt–Schiff Base Complexes and Their Organometallic Derivatives

By **Edoardo Reisenhofer** * and **Giacomo Costa**, Istituto di Chimica, Università di Trieste, 34127 Trieste, Italy

In the dipolar aprotic solvent *NN*-dimethylformamide, the anionic species $[Co^{I}L]^-$ and $[Co^{II}L(R)]^-$, electrochemically generated from the corresponding cobalt(II) and cobalt(III) derivatives, interact strongly with counter cations forming contact ion pairs [L = *NN'*-*o*-phenylenebis(salicylideneiminato), *NN'*-ethylenebis(salicylideneiminato), *NN'*-ethylenebis(α,α'-dimethylsalicylideneiminato), and *NN'*-ethylenebis(acetylacetonediiminato)]. There is a linear relation between the reversible $E_{\frac{1}{2}}$(red) values and the ionic potential of the counter cations. Association constants for the complexes (ion pairs) thus formed have been evaluated by polarography. Destabilization effects of the counter cations on the cobalt–carbon bond in the organometallic derivatives have been detected by cyclic voltammetry.

COBALT chelate complexes with Schiff bases and their organometallic derivatives are suitable model compounds for the study of the chemistry of vitamin B_{12}. Relevant points under investigation are the factors influencing the mechanism and the rate of reactions leading to formation and cleavage of the cobalt–carbon bond. Both processes have been found to be related to the redox properties of the complexes in the different formal oxidation states of the cobalt atom.[1] In previous papers we have reported the polarographic behaviour of a series of the above complexes.[2] The electrode processes (1) and (2) are more relevant to the chemistry of the organometallic derivatives.*

$$[\mathrm{Co^{II}L}] \rightleftharpoons [\mathrm{Co^{I}L}]^- \qquad (1)$$

$$[\mathrm{Co^{III}L(R)}] \longleftarrow [\mathrm{Co^{II}L(R)}]^- \qquad (2)$$

In the present paper we attempt to establish to what extent the redox processes (1) and (2) are influenced by the nature of the counter cation M^{n+} of the supporting electrolyte, and to determine the stoicheiometry and the association constants of the complexes (ion pairs) formed from cobalt chelate anions and the counter cation. We also report on the influence of the counter cation on the stability of the cobalt–carbon bond in the organometallic derivatives. The detected destabilization effects are interesting in that the mechanism of formation and cleavage of the cobalt–carbon bond is important in understanding vitamin B_{12}-dependent enzymatic reactions.[3]

EXPERIMENTAL

All measurements were made in anhydrous *NN'*-dimethylformamide (dmf), at 0 °C and, for the organometallic derivatives, in the dark, because of their photolability. The ionic strength of the supporting electrolyte was 0.1 mol dm^{-3}.

Apparatus.—D.c. polarographic measurements were made with an operational amplifier-based three-electrode electronic Amel model 448 polarograph. A dropping mercury electrode was used as indicator; the drop time was controlled at 3.00 s. The potentials are referred to the standard calomel electrode (s.c.e.) which was separated by a fritted glass disc from a salt bridge containing the same solvent and supporting electrolyte as for the examined solution; the latter was also separated from the salt bridge by a fritted glass disc. Polarographic cells were of conventional types.

Materials.—The cobalt complexes were prepared following procedures reported previously.[4] *NN'*-Dimethylformamide was purified over magnesium sulphate and then distilled under reduced pressure before use. The anhydrous perchlorates used as supporting electrolytes were of analytical grade.

RESULTS

Reduction of Cobalt(II)*–Schiff Base Complexes in dmf: Influence of the Counter Cations of the Supporting Electrolyte*.—The polarographic behaviour of cobalt(II) chelates of the type [Co(salph)], [Co(salen)], [Co(dsalen)], and [Co(acen)] is well known;[2] in a dipolar aprotic solvent such as dmf they give a reversible one-electron reduction wave which is strongly influenced by the counter cation M^{n+} of the supporting electrolyte; on the other hand, the one-electron oxidation wave is not affected by the counter cations. The electrode processes are as in (3). The reversible half-wave potentials $E_{\frac{1}{2}}$(red) are shifted in a positive direction as the ionic potential of the counter cation increases (or the ionic radius decreases), implicating complex formation as in (4).

$$[\mathrm{Co^{III}L}]^+ \overset{E_{\frac{1}{2}}(\mathrm{ox})}{\rightleftharpoons} [\mathrm{Co^{II}L}] \overset{E_{\frac{1}{2}}(\mathrm{red})}{\rightleftharpoons} [\mathrm{Co^{I}L}]^- \qquad (3)$$

$$[\mathrm{Co^{II}L}] + e^- + M^{n+} \longrightarrow [\mathrm{Co^{I}L}]^- \cdots M^{n+} \qquad (4)$$

We investigated the polarographic reduction of $[\mathrm{Co^{II}L}]$ in dmf solutions with $[\mathrm{NBu_4}]^+$, $[\mathrm{NEt_4}]^+$, K^+, Na^+, Ba^{2+}, and Li^+ perchlorates as the supporting electrolytes; when $\mathrm{Mg[ClO_4]_2}$ is the supporting electrolyte, the irreversibility of the polarographic redox process $[\mathrm{Co^{II}L}] \rightleftharpoons [\mathrm{Co^{I}L}]^-$ precludes quantitative evaluation of the cation–anion interactions. The dependence of $E_{\frac{1}{2}}$(red) on the ionic potentials (evaluated from the effective ionic radii) of the counter cations is shown in Figure 1. The observed linearity of the plots suggests that the interaction between cation and anion is of the ' contact ion pair ' type, notwithstanding the solvation of the metal cation by dmf.[5]

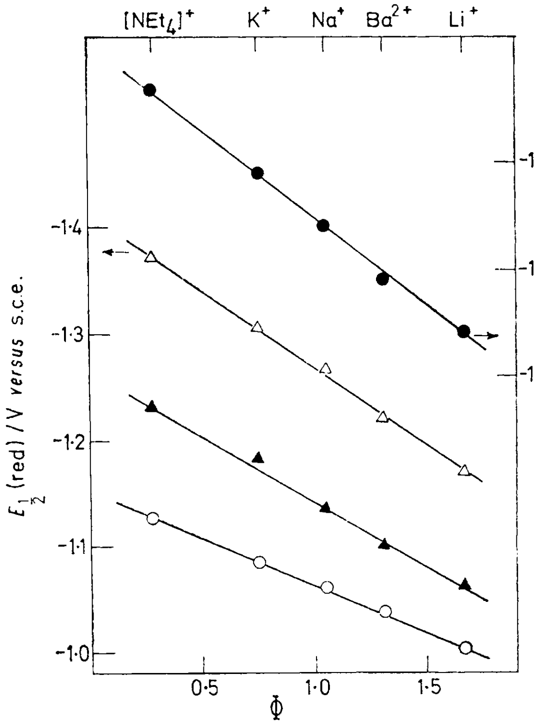

FIGURE 1 Variations in half-wave potentials for the processes $[\mathrm{Co^{II}L}] \rightleftharpoons [\mathrm{Co^{I}L}]^-$ with the ionic potential Φ of the cation of the supporting electrolyte in dmf. L = salph (○), salen (▲), dsalen (△), and acen (●)

According to the experimental data, we can assume that in solutions of tetra-alkylammonium salts the cobalt(I) anions

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* L is one of the following chelating ligands: *NN'*-*o*-phenylenebis(salicylideneiminato), salpn; *NN'*-ethylenebis(salicylideneiminato), salen; *NN'*-ethylenebis(α,α'-dimethylsalicylideneiminato), dsalen; and *NN'*-ethylene(acetylacetonedi-iminato), acen.

[1] H. A. O. Hill in ' Inorganic Biochemistry,' ed. G. L. Eichorn, Elsevier, 1973, vol. 2, p. 1067; J. M. Pratt, ' Inorganic Biochemistry of Vitamin B_{12},' Academic Press, New York, 1972.

[2] (*a*) G. Costa, G. Mestroni, A. Puxeddu, and E. Reisenhofer, *J. Chem. Soc.* (*A*), 1970, 2870; (*b*) G. Costa, A. Puxeddu, and E. Reisenhofer, *J.C.S. Dalton*, 1972, 1519; (*c*) G. Costa, A. Puxeddu, and E. Reisenhofer, *J.C.S. Dalton*, 1973, 2035.

[3] G. Costa, A. Puxeddu, and E. Reisenhofer, *Bioelectrochem. Bioenergetics*, 1974, **1**, 29.

[4] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefan, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41.

[5] M. K. Kalinowski, *Chem. Phys. Letters*, 1970, **7**, 55; 1971, **8**, 378.

are unaffected by the cation, whereas in solutions of smaller counter cations, such as lithium salts, the anions are associated as ion pairs. The reversible one-electron process $[\mathrm{Co^{II}L}] \rightleftharpoons [\mathrm{Co^{I}L}]^-$, *e.g.* in the presence of $\mathrm{Li^+}$, would involve ion-pair formation as in (5), the equilibrium constant

$$[\mathrm{Co^{I}L}]^- + p\mathrm{Li^+} \rightleftharpoons [\mathrm{Co^{I}L}]^- \cdots \mathrm{Li^+}_p \qquad (5)$$

being (6). From measurements of the positive shift of

$$K = \frac{[\mathrm{Co^{I}L^-} \cdots \mathrm{Li^+}_p]}{[\mathrm{Co^{I}L^-}][\mathrm{Li^+}]^p} \qquad (6)$$

$E_{\frac{1}{2}}$(red) at various concentrations of lithium perchlorate, keeping the ionic strength of the solution formally constant by addition of tetra-alkylammonium perchlorate (I 0.1 mol dm^{-3}), we evaluated the equilibrium constants and the stoicheiometry of complex formation for all the four cobalt chelates.

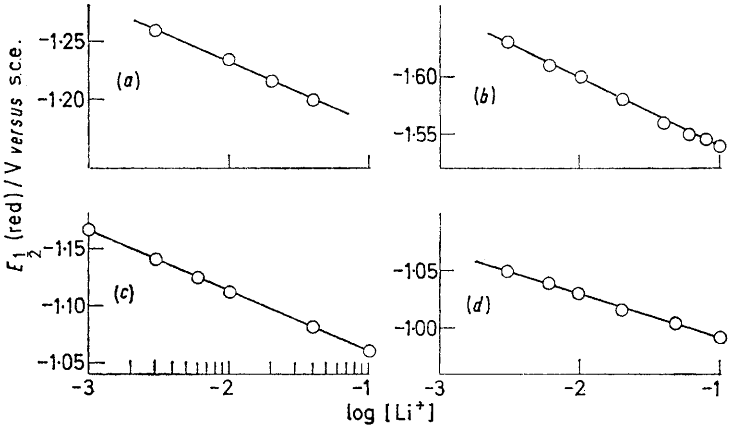

FIGURE 2 Variations in half-wave potentials for the processes $[\mathrm{Co^{II}L}] \rightleftharpoons [\mathrm{Co^{I}L}]^-$ with the concentration of the cation $\mathrm{Li^+}$ of the supporting electrolyte, at constant ionic strength (0.1 mol dm^{-3}) made up with $[\mathrm{NR_4}][\mathrm{ClO_4}]$. L = dsalen (*a*), acen (*b*), salen (*c*), and salpn (*d*)

According to the treatment of Peover and Davies,[6] when the shift of the half-wave potential depends on the concentration of the cation forming the ion pair, but not on that of the anion, relation (7) holds for a reversible one-electron

$$\Delta E_{\frac{1}{2}} = E_{\frac{1}{2}} - E_{\frac{1}{2}}^{0} = (RT/F)\ln K + p(RT/F)\ln[\mathrm{Li^+}] \qquad (7)$$

process, where $E_{\frac{1}{2}}$ represents the half-wave reduction potential of $[\mathrm{Co^{II}L}]$ in the presence of the counter cation, $E_{\frac{1}{2}}^{0}$ is the half-wave potential in the absence of ion association (*i.e.* in tetra-alkylammonium salt solutions, according to the above considerations), p is the number of cations involved in complex formation, and K is the complex-formation constant. In this relation, the association of the ions of the supporting electrolyte is neglected: this appears to be correct at ionic strengths not greater than 0.1 mol dm^{-3} (see refs. 6 and 7).

Plots of $E_{\frac{1}{2}}$(red) against log[Li$^+$] for the cobalt(II) chelate complexes are in Figure 2. From the derivative $\partial\Delta E_{\frac{1}{2}}/\partial\log[\mathrm{Li^+}]$, a 1 : 1 stoicheiometry for the ion pairs $[\mathrm{Co^{I}L}]^- \cdots \mathrm{Li^+}$ was established; moreover, applying equation (7), the association constants for the four complexes were evaluated (Table 1).

Reduction of Organometallic Cobalt(III)*–Schiff Base Complexes; Influence of the Supporting Electrolyte.*—The polarographic behaviour of the organometallic complexes $[\mathrm{Co^{III}L(R)}]$ shows similar features to the parent $[\mathrm{Co^{II}L}]$ complexes. The polarographically reversible processes (8)

$$[\mathrm{Co^{IV}L(R)}]^+ \xrightleftharpoons{E_{\frac{1}{2}}(\mathrm{ox})} [\mathrm{Co^{III}L(R)}] \xrightleftharpoons{E_{\frac{1}{2}}(\mathrm{red})} [\mathrm{Co^{II}L(R)}]^- \qquad (8)$$

were examined. Again $E_{\frac{1}{2}}$(red), but not $E_{\frac{1}{2}}$(ox), was influenced by the cations of the supporting electrolyte, though to a smaller extent. For instance, a plot of $E_{\frac{1}{2}}$(red) against ionic potential for $[\mathrm{Co^{III}Ph(salen)}]$ had a smaller gradient than that of $[\mathrm{Co^{II}(salen)}]$.* The shifts of $E_{\frac{1}{2}}$(red) at various concentrations of $\mathrm{Li[ClO_4]}$ for $[\mathrm{Co^{III}Ph(salen)}]$ are listed in Table 2.

From these data we infer a stoicheiometry of 2 : 1 for the complex formation between the anions $[\mathrm{Co^{II}L(R)}]^-$ and $\mathrm{Li^+}$. The association constants are considerably smaller than in the case of the $[\mathrm{Co^{II}L}]$ complexes: for [CoPh(salen)], using for $E_{\frac{1}{2}}^{0}$ the determined value of −1.425 V *versus* the s.c.e., we obtain a value of 2.41 for log K.

TABLE 1

Ion-pair formation constants

Complex	log K
$[\mathrm{Co^{I}(acen)}]^- \cdots \mathrm{Li^+}$	4.915
$[\mathrm{Co^{I}(dsalen)}]^- \cdots \mathrm{Li^+}$	4.918
$[\mathrm{Co^{I}(salen)}]^- \cdots \mathrm{Li^+}$	4.577
$[\mathrm{Co^{I}(salpn)}]^- \cdots \mathrm{Li^+}$	4.620

TABLE 2

Values of $E_{\frac{1}{2}}$(red) for $[\mathrm{Co^{III}Ph(salen)}]$ at various concentrations of lithium perchlorate; I = 0.1 mol dm^{-3} made up with $[\mathrm{NEt_4}][\mathrm{ClO_4}]$

$E_{\frac{1}{2}}$(red)/V *versus* s.c.e.	[Li$^+$]/mol dm^{-3}
−1.384	0.002
−1.373	0.004
−1.358	0.010
−1.349	0.020
−1.335	0.040
−1.320	0.100

Influence of the Counter Cation on the Rate of Cleavage of the Cobalt–Carbon Bond in $[\mathrm{Co^{II}L(R)}]^-$.—The stability of

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* See Figure 3, ref. 3.

[6] M. E. Peover and J. D. Davies, ' Polarography 1964,' vol. 2, MacMillan, London, 1966, p. 1003; *J. Electroanalyt. Chem.*, 1963, **6**, 46.

[7] J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, 1961, **57**, 1795

the reduced form $[Co^{II}L(R)]^-$ also appears to be affected by the counter cations of the supporting electrolyte. We have previously reported [8] that cyclic voltammetry of $[Co^{III}Ph(salen)]$ shows that the anodic peak due to reoxidation of $[Co^{II}Ph(salen)]^-$ can be seen several seconds after the reduction step, with an anodic–cathodic peak-current ratio of $I_{ap} : I_{cp} = 1 : 1$ when the experiment is carried out in the presence of $[NEt_4][ClO_4]$.

When the counter cations of the supporting electrolyte had ionic potentials higher than $[NEt_4]^+$, not only the reduction potentials but also the ratio $I_{ap} : I_{cp}$ was affected and distinctly decreased at low scan rates; the effect was most pronounced with Mg^{2+} which caused complete disappearance of the anodic peak of $[Co^{III}Ph(salen)]$ even at a scan rate as high as 40 V s^{-1}. This is attributed to the decomposition of the reduced species $[Co^{II}L(R)]^-$, which takes place through cleavage of the cobalt–carbon bond, as was previously shown for $[Co^{II}Me(salen)]^-$ in the presence of $[NEt_4]^+$ as counter cation.[8]

Influence of the Counter Cation on the Reaction Rate of $[Co^{I}L]^-$ *Complexes with Bromobenzene.*—Following the experimental procedure adopted in the studies of the reactivity of $[Co^{I}L]^-$ with organic halides, tetra-alkylammonium and trialkylsulphonium ions,[3] we found that the second-order rate constants for nucleophilic attack of $[Co^{I}(salen)]^-$ and $[Co^{I}(acen)]^-$ on bromobenzene in solutions of a very large counter cation such as $[NBu_4]^+$ are higher than the analogous constants obtained in solutions of a smaller counter cation, *e.g.* Li^+ (see Table 3). This means that the ion pair $[Co^{I}L^- \cdots Li^+]$ is less reactive towards nucleophilic attack than $[Co^{I}L]^-$ present in solutions of tetrabutylammonium counter cations.

TABLE 3

Second-order alkylation rate constants for $[Co^{I}L]^-$ electrochemically generated with PhBr in tetra-alkylammonium perchlorate and in lithium perchlorate media respectively

Complex	$10^3[PhBr]$/mol dm^{-3}	k'/s^{-1}	$10^{-3}\,k$/$dm^3\,mol^{-1}\,s^{-1}$
$[Co^{II}(acen)](0.3 \times 10^{-3}$	3.8	32.85	8.7
mol $dm^{-3})$	7.6	92.58	12.1
$[NBu_4ClO_4] = 0.1$ mol dm^{-3},	11.4	130.85	11.4
$\tau = 2.56 \times 10^{-3}$ s	15.2	146.87	9.7
$[Co^{II}(salen)](0.3 \times 10^{-3}$	38	0.260	6.85
mol $dm^{-3})$	76	0.384	5.05
$[NBu_4ClO_4] = 0.1$ mol dm^{-3},	114	0.562	4.93
$\tau = 0.126$ s	190	0.816	4.29
$[Co^{II}(acen)]$ *			84.5
$[LiClO_4] = 0.1$ mol dm^{-3}			
$[Co^{II}(salen)]$ *			(3.07×10^{-2})
$[LiClO_4] = 0.1$ mol dm^{-3}			

* Values from ref. 2*c*.

The dependence of the observed specific rates on the concentration of the lithium counter cation (at constant ionic strength, made up with $[NBu_4]^+$) was given by equation (9).

$$k_{obs.} = \frac{k_1 + k_2K[Li^+]}{1 + K[Li^+]} \qquad (9)$$

If the ion-pair formation equilibrium is attained rapidly compared to the subsequent nucleophilic attack, and the stoicheiometry is 1 : 1, k_1 and k_2 are the rate constants for the reaction in the presence of tetra-alkylammonium perchlorate and lithium perchlorate respectively, K is the association constant given in equation (6), and $[Li^+]$ is the concentration of the lithium counter cation. From equation (9) we can see that $k_{obs.} \cong k_2$, notwithstanding that values of k_1 are *ca.* 10^2 times higher than k_2, because of the high values of the association constants K (see Table 1).

DISCUSSION

The dependence of the shift of $E_{\frac{1}{2}}$(red), for both the $[Co^{II}L]$ and $[Co^{III}L(R)]$ complexes, on the reciprocal of the Pauling ionic radius of the cation of the supporting electrolyte shows that a mainly electrostatic interaction takes place between the reduced complex anions and the cations. The interaction is quantitated by the association constant calculated from $E_{\frac{1}{2}}$(red) according to Peover and Davies.[6] On the other hand, the influence of the size of the anion cannot be obtained from the formation constants of the different chelates in Table 1, suggesting that the interaction with the cation takes place on a negatively charged site which is little influenced by the delocalized electronic structure of the chelating macrocycle.*

It is reasonable to assume that the interaction involves the oxygen atoms of the chelating rings. The association product can be considered as a contact ion pair of a true complex in dmf. This is supported by recent ^1H n.m.r. and visible spectral investigations of $[CoMe(salen)]$ adducts with lanthanoids [10] and by the mechanism of transmethylation from $[CoMe(salen)]$ to Hg^{2+} which takes place through a detectable $[CoMe(salen)Hg]^{2+}$ intermediate.[11] Moreoever, the bonding of Na^+ to the oxygen atom of the chelating ring in $[Co(salen)]$ is indicated by the crystal structure.[12]

The results also yield some interesting though preliminary observations about the influence of the counter cation on the reactivity of the reduced species $[Co^{I}L]^-$ and $[Co^{II}L(R)]^-$. The effect of Li^+ as compared to $[NEt_4]^+$ on the rate of reaction with PhBr shows that the nucleophilicity of $[Co^{I}L]^-$ is decreased by the association with cations exhibiting high ionic potential. It is worth noting that both the ion pairs and the $[Co^{I}L]^-$ anions appear to react with PhBr, though with different rates. This is in agreement with the loss of negative charge from the axial position as a consequence of the interaction with Li^+. On the other hand, the decomposition of the reduced organometallic anion $[Co^{II}L(R)]^-$ involving rupture of the Co–C bond is easier in the presence of Li^+ or Mg^{2+}. In order to explain this effect further knowledge is required of the decomposition

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* As confirmation of this point, we reported that complex-formation effects were not detected in chelates of the type $Co^{II}N_4$, *e.g.* $[Co^{II}(amben)]$ where the oxygen atoms of salen are replaced by NH groups, which have more negative charge on the planar macrocyclic system, but are more delocalized than in $[Co^{II}(salen)]$.[9]

[8] G. Costa, A. Puxeddu, and E. Reisenhofer, *Experientia Suppl.*, 1971, **18**, 235.

[9] E. Reisenhofer, A. Puxeddu, G. Costa, and M. Green, VI Convegno Nazionale di Chimica Inorganica, Firenze, 24—29 September, 1973, A5.

[10] G. Tauszik, G. Pellizer, and G. Costa, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 717.

[11] G. Tauzher, R. Dreos, and G. Costa, *J. Organometallic Chem.*, 1974, **81**, 107.

[12] L. Randaccio, *Gazzetta*, 1974, **104**, 991.

mechanism, which is presently under investigation. The [Co^{II}L(R)Li] association product probably represents the intermediate in the decomposition reaction path. The relative position of the relevant carbon, cobalt, and lithium atoms should favour the transfer of the organic group from cobalt to lithium as the catalytic step of the cleavage reaction.

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