The Electrochemical Reduction Mechanism of [*N,N'*-1,2-Phenylenebis(salicylideneiminato)]cobalt(II)

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The electrochemical reduction mechanism of [CoL] [L = *N,N'*-1,2-phenylenebis(salicylideneiminate)] has been investigated in dimethylformamide by means of cyclic voltammetry and controlled-potential electrolysis. The cobalt(II) complex shows three successive one-electron reduction processes. The first electron uptake is metal-centred yielding $[Co^IL]^-$, whereas the second and third electron transfers are both ligand based, corresponding to the reduction of one imine double bond. This leads to the formation of a new cobalt complex $[Co^I(HL^-)]^{2-}$ which has the Co^{II}–Co^I redox couple located at a potential *ca.* 600 mV negative of the potential of the same redox couple of the original [CoL] complex. Decay reactions of some reduction intermediates have been kinetically characterised and the corresponding rate constants have been determined.

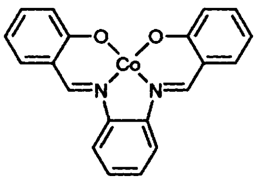
Chelate complexes of cobalt with quadridentate Schiff bases derived from salicylaldehyde have attracted considerable interest due to their ability to form stable organometallic derivatives[1] and to bind reversibly molecular oxygen[2] and CO_2.[3] Electrocatalytic reduction of CO_2 to CO by cobalt Schiff-base complexes such as [CoL][4] [L = salphen = *N,N'*-1,2-phenylenebis(salicylideneiminate)] and [Co(salen)][5] [salen = *N,N'*-1,2-ethylenebis(salicylideneiminate)] has also been reported recently.

The electrochemistry of cobalt(II) Schiff-base complexes has been extensively studied.[6] It has been shown that Co^{II} undergoes two one-electron, reversible charge transfers corresponding to the reduction and oxidation to Co^I and Co^{III}, respectively. The redox potentials of the Co^{III}–Co^{II} and Co^{II}–Co^I couples have been shown to be markedly affected by the nature of the solvent and background electrolyte and by the structure of the chelating ligand and of the complex as a whole.[6c–f] Even though cobalt Schiff-base complexes exhibit a rich redox chemistry, most of the electrochemical investigations carried out on these complexes were restricted to the three easily accessible oxidation states of cobalt, Co^{III}, Co^{II} and Co^I. Reduction processes beyond the Co^I stage have been reported for various complexes,[6c] but mechanistic interpretations were never attempted. This paper describes the electrochemical reduction mechanism of [CoL], containing a Schiff base ligand with a highly conjugated structure.

Experimental

Dimethylformamide (dmf) (C. Erba, RPE) was vacuum-distilled and stored in a dark bottle under a nitrogen atmosphere. For measurements under very anhydrous conditions, the solvent was repeatedly percolated, before use, through a column of neutral alumina (Merck, activity grade I), previously activated by heating at 360 °C for 12 h. Tetrabutylammonium perchlorate was prepared by neutralisation of the corresponding hydroxide with perchloric acid, recrystallised from ethanol–water and dried at 60 °C under vacuum. Anhydrous lithium perchlorate (Janssen) was further dried in a vacuum oven at 100 °C. The complex [Co(salophen)] was synthesized according to a published procedure.[2a]

Electrochemical measurements were performed with an EG&G-PAR apparatus formed by a 173 potentiostat and a 179 Digital Coulometer, and equipped with a programmable function generator Amel model 568 and a 2090 Nicolet digital oscilloscope. Cyclic voltammetric studies were carried out using a mercury sphere as working electrode and a platinum wire as auxiliary electrode. The reference electrode was Ag–AgI in dimethylformamide (dmf) containing $[NBu^n_4]I$ (0.1 mol dm^{-3}) whose potential was always measured *vs.* an aqueous saturated calomel electrode (SCE) to which all potentials are referred. Controlled-potential bulk electrolysis experiments were carried out in a two-compartment cell using a mercury-pool as the working electrode. All experiments were performed at 25 °C.



[CoL]

Results and Discussion

Fig. 1 illustrates the voltammetric behaviour of $[Co^{II}L]$ in dmf containing 0.1 mol dm^{-3} $[NBu^n_4]ClO_4$ as background electrolyte. On the negative-going scan, three well defined reduction peaks A, C and E are formed whereas, on the reverse sweep, up to four oxidation peaks B, D, F and H can be observed [Fig. 1(*a*)].

The anodic response is strongly dependent on the potential of scan reversal. If the negative-going scan is limited to the second reduction peak C, only two reversible peak couples A/B and C/D are observed [Fig. 1(*b*)]. Analyses of the voltammetric data, showing an anodic to cathodic peak separation, $E_{pa} - E_{pc}$, of *ca.* 60 mV, unit ratio of anodic to cathodic peak currents (i_{pa}/i_{pc}) and constancy of peak current function $i_{pc}/v^{\frac{1}{2}}$, indicate that both reduction processes correspond to reversible one-electron transfers. The standard potentials of the two processes determined as $(E_{pc} + E_{pa})/2$ are -1.12 and -1.93 V, respectively. The third cathodic process, E, with $E_p = -2.57$ V at a sweep rate $v = 0.1$ V s^{-1}, is chemically irreversible, no

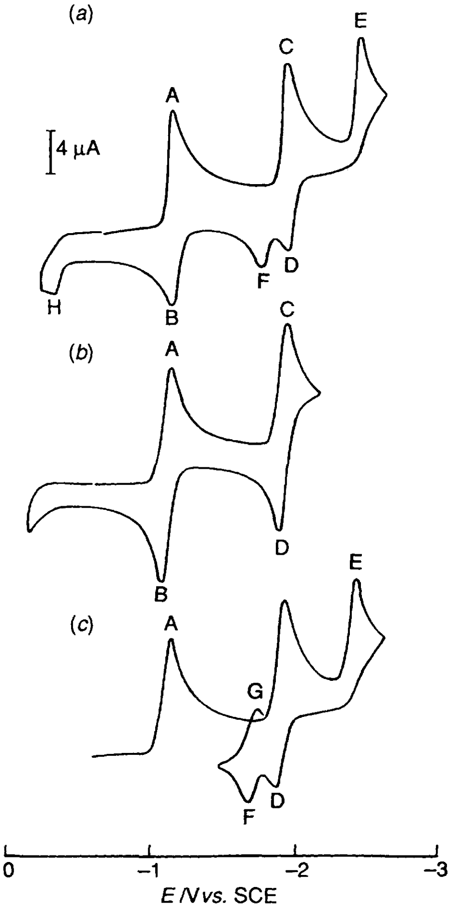


Fig. 1 Cyclic voltammograms of $[Co^{II}L]$ (1.70 mmol dm^{-3}) in dmf–$[NBu^n_4]ClO_4$ (0.1 mol dm^{-3}); $v = 0.1$ V s^{-1}

anodic partner being observed at scan rates as high as 500 V s^{-1}. The peak potential $E_p(E)$ shifts cathodically on increasing the scan rate with a variation of *ca.* 30 mV for each ten-fold increase in v and the peak width at half peak, $E_p - E_{p/2}$, is *ca.* 60 mV, whereas the peak current $i_p(E)$ is approximately equal to that of the first reversible one-electron peak A. These findings reveal the underlying process to be a reversible one-electron transfer followed by a fast first-order chemical reaction.[7]

Extending the potential scan in the negative direction to include the third reduction process, E, causes significant changes on the anodic response. Two new oxidation peaks (F and H) appear while the anodic peaks D and B decrease considerably. The anodic peak F is associated with a cathodic partner G, which can be observed, even at very low v values, if the positive-going potential scan is reversed back in the negative direction at −1.5 V [Fig. 1(*c*)]. The peak separation, ΔE_p, for this newly formed peak couple F/G is 60 mV, characteristic of a reversible one-electron transfer, with $E^\circ = -1.70$ V. The anodic peak H is totally irreversible at all sweep rates in the range 0.05–500 V s^{-1}.

This voltammetric pattern shows that the electrochemical reduction mechanism of $[Co^{II}L]$ is quite complex. The first cathodic process can unambiguously be assigned to the reduction of Co^{II} to Co^{I}, as previous electrochemical[6c,f] and ESR[8] studies have clearly shown [equation (1)]. The assignment of the remaining reduction processes is less straightforward.

$$[Co^{II}L] + e^- \rightleftharpoons [Co^{I}L]^- \quad \text{peaks A/B} \qquad (1)$$

West and co-workers[8] have previously described the electrochemical reduction mechanism of $[Co^{II}L]$ in tetrahydrofuran. They observed a voltammetric pattern which appears to be substantially coincident with that we have found in dmf, except for minor peak potential shifts. According to these authors, the second cathodic process of $[Co^{II}L]$ corresponds to the reduction of Co^{I} to Co^{0} which then reacts slowly with the tetrabutylammonium background cation, to give an organometallic derivative [equations (2) and (3)]. The peak couple F/G has been attributed to the Co^{III}–Co^{II} redox couple of the newly formed organometallic complex [equation (4)].

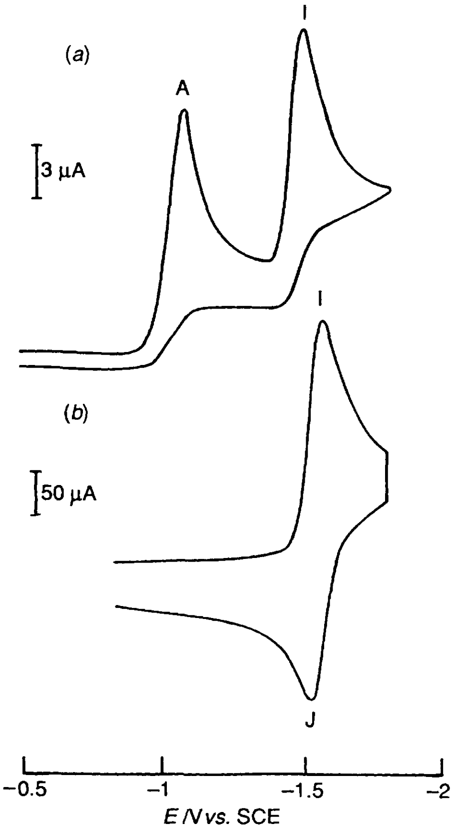


Fig. 2 Cyclic voltammograms of $[Co^{II}L]$ (2.10 mmol dm^{-3}) in dmf–$[NBu^n_4]ClO_4$ (0.1 mol dm^{-3}) in the presence of Bu^nI (2.30 mmol dm^{-3}): (*a*) before electrolysis, $v = 0.2$ V s^{-1} and (*b*) after exhaustive electrolysis at −1.25 V, $v = 100$ V s^{-1}

$$[Co^{I}L]^- + e^- \rightleftharpoons [Co^{0}L]^{2-} \qquad (2)$$

$$[Co^{0}L]^{2-} + [NBu^n_4]^+ \longrightarrow [Bu^n\text{–}Co^{II}L]^- + NBu^n_3 \qquad (3)$$

$$[Bu^n\text{–}Co^{II}L]^- - e^- \rightleftharpoons [Bu^n\text{–}Co^{III}L] \qquad (4)$$

In order to verify this, we compared the voltammetric pattern of the complex $[Co^{II}L]$ with that of the supposed organometallic intermediate $[Bu^n\text{–}Co^{II}L]$. This latter was prepared electrochemically, making use of the well known reactivity of cobalt(I) square-planar complexes towards alkyl halides,[9,10] according to equation (5). This is a fast reaction, even on the time-scale of high sweep rate voltammetry, as indicated by the disappearance of the anodic peak B, corresponding to the oxidation of $[Co^{I}L]^-$, by addition of Bu^nI to a dmf solution of $[Co^{II}L]$. At the same time a new cathodic peak I is formed at a potential *ca.* 400 mV more negative than that of peak A [see Fig. 2(*a*)]. In the presence of excess of Bu^nI, sufficient for reaction (5) to occur under pseudo-first-order conditions, the potential of peak A is shifted by *ca.* 30 mV in the cathodic direction and *ca.* 30 mV in the anodic direction, for a ten-fold increase of the

$$[Co^{I}L]^- + Bu^nI \xrightarrow{k_s} [Bu^n\text{–}Co^{III}L] + I^- \qquad (5)$$

Table 1 Kinetic data for the formation of [Bu^n–Co^{III}L] by reaction of electrogenerated [Co^{I}L]$^-$ with Bu^{n}I in dmf–[NBu^n$_4$]ClO$_4$ (0.1 mol dm^{-3})

[Bu^{n}I]^a/ mmol dm^{-3}	$10^{-3}k_5'^b$/s^{-1}	$10^{-5}k_5$/ dm^3 mol^{-1} s^{-1}
5.54	2.04	3.68
9.93	3.36	3.38
20.90	7.33	3.51

[a] Concentration of [Co^{II}L] = 0.33 mmol dm^{-3}. [b] Average of the values determined at various sweep rates, in the range 0.1–10 V s^{-1}, for each [Bu^{n}I].

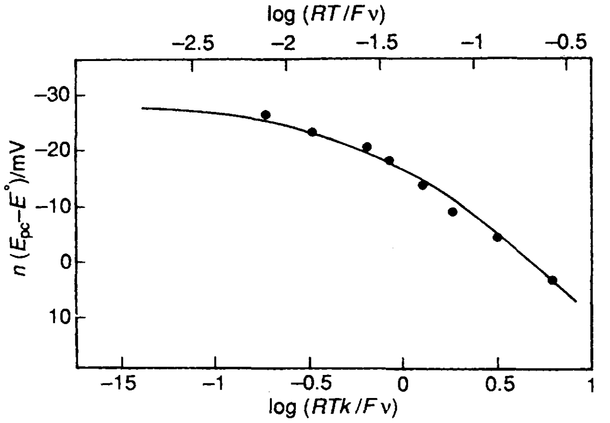


Fig. 3 Variation of $E_{pc} - E^0$ as a function of log (RTk/Fv). Solid line: theoretical curve; (●) experimental values measured for [Bu–Co^{III}L] (1.26 mmol dm^{-3}) in dmf–[NBu^n$_4$]ClO$_4$ (0.1 mol dm^{-3})

sweep rate and of the Bu^{n}I concentration, respectively. This behaviour, featuring pure kinetic conditions,[7,11] allows the rate constant of reaction (5) to be calculated from relationship (6)

$$\ln k_5' = 1.56 + \frac{2nF}{RT}(E_p - E^0) + \ln (nFv/RT) \quad (6)$$

where $k_5' = k_5[\text{Bu}^n\text{I}]$, E^0 is the standard potential of the A/B peak couple and $n = 1$ for the case under discussion. The pseudo-first-order rate constant k_5' was calculated at different concentrations of Bu^{n}I and at several sweep rates for each [Bu^{n}I]. The data reported in Table 1 provide for k_5 an average value of (3.5 ± 0.1) × 10^5 dm^3 mol^{-1} s^{-1}.

By controlled-potential bulk electrolysis at −1.25 V of [Co^{II}L] in the presence of Bu^{n}I, peak A diminishes and eventually disappears after passage of *ca.* 1 F (96 485C) per mole of [Co^{II}L], which is quantitatively transformed into the organometallic compound [Bu^n–Co^{III}L], reducible at peak I. This latter process is irreversible at scan rates up to 5 V s^{-1}, but, increasing v, its anodic partner J appears and increases in height [see Fig. 2(*b*)]. The standard potential determined as (E_{pc} + E_{pa})/2 for the peak couple I/J is −1.51 V. The peak I potential is practically independent of the organometallic compound concentration, but varies with the sweep rate as shown in Fig. 3, together with the theoretical curve showing the variation of $E_{pc} - E^0$ as a function of log (RTk/Fv), calculated for a fast one-electron transfer coupled with a first-order follow-up reaction.[11] The underlying process can be outlined[10] by the mechanistic pathway given in equations (6), (7) and (7′).

$$[\text{Bu}^n\text{–Co}^{III}\text{L}] + e^- \rightleftharpoons [\text{Bu}^n\text{–Co}^{II}\text{L}]^- \quad (6)$$

$$[\text{Bu}^n\text{–Co}^{II}\text{L}]^- \xrightarrow{k_7} [\text{Co}^I\text{L}]^- + \text{Bu}^{n\bullet} \quad (7)$$

$$[\text{Bu}^n\text{–Co}^{II}\text{L}]^- \xrightarrow{k_7'} [\text{Co}^{II}\text{L}] + \text{Bu}^{n-} \quad (7')$$

Whether the carbon–cobalt bond cleavage in the organometallic cobalt(II) complex follows path (7) or (7′) depends on the nature of the organic moiety bound to the metal centre.[10] In the present case the characteristics of peak I indicate an homolytic rather than an heterolytic bond cleavage. In fact the current function $i_{pc}/cv^{\frac{1}{2}}$ undergoes a small, theoretically predicted, decrease of *ca.* 10% in passing from irreversibility to full reversibility for peak *I*, indicating that the number of electrons exchanged is same at all sweep rates. This behaviour is in agreement with path (7) since neither the [Co^{I}L]$^-$ complex nor *n*-butyl radical[12] is reducible at the formation potential. Should the heterolytic bond cleavage path (7′) prevail over the homolytic one, the peak current function would be expected to decrease from a two-electron level at low sweep rates, owing to the contribution of [Co^{II}L], reducible at the potential of peak I, to a one-electron level at high sweep rates when the effect of reaction (7′) becomes negligible. The rate constant of the homolytic cleavage reaction k_7 was calculated by fitting the experimental values of $E_{pc} - E^0$ with the theoretical curve as shown in Fig. 3. The best fit gave a value of 24 s^{-1} for k_7.

The value of the standard potential of the peak couple I/J (E^0 = −1.51 V), which is 190 mV more positive than that of the F/G peak couple ($E°$ = −1.70), and the different degree of reversibility of the two processes cast doubt on the attribution of peak couple F/G to the redox reactions of the organometallic compound supposed to be formed according to reactions (2) and (3). A more convincing evidence that this is not the case, at least with dmf as a solvent, is provided by some experiments carried out using LiClO$_4$ as background electrolyte. Under such conditions, only the first two reduction processes, which appear to be uncomplicated one-electron transfers, can be observed prior to the Li$^+$ discharge [Fig. 4(*a*)]. The standard potentials of these two processes, $E°$ = −0.97 and −1.78 V, are shifted 150 mV towards more anodic potentials compared to their values in dmf–[NBu^n$_4$]ClO$_4$ (0.1 mol dm^{-3}). This suggests the existence of a strong interaction between electrogenerated anions, such as [Co^{I}L]$^-$, and counter cations. Cobalt(I) Schiff-base complexes were in fact reported to interact strongly with alkali-metal cations,[6a] forming contact ion pairs with association constants of the order of 10^4 dm^3 mol^{-1} for the case of Li$^+$, or even bimetallic complexes.[13]

Controlled-potential bulk electrolysis of [Co^{II}L] in dmf–LiClO$_4$ performed at −1.10 V led to the generation of a green solution of Co^I with the consumption of *ca.* 1 electron per molecule of complex. When the electrolysis was continued at the potential of the second cathodic peak, −1.90 V, two more electrons per molecule of complex were consumed.* Cyclic voltammograms recorded after electrolysis at −1.90 V are shown in Fig. 5. On an initially positive-going potential cycle only the peak couple F/G can be observed, provided the switching potential is lower than −0.4 V [Fig. 5(*a*)]. When the potential cycle goes up to 0.0 V, a well formed oxidation process at a potential corresponding to that of peak H can be observed [Fig. 5(*b*)]. If, after having scanned through the anodic peak H, the potential is swept backward in the negative direction and then again in the positive one, the resulting cyclic voltammogram shows all the voltammetric features of the original complex [CoL] [Fig. 5(*b*)]. In fact, bulk reoxidation at 0.0 V of a solution previously reduced at −1.90 V regenerated quantitatively the original [CoL] complex.

The above results show clearly that tetrabutylammonium cations do not play any significant role in the formation of the peak couple F/G, which is observable also in the presence of LiClO$_4$ as background electrolyte. However, the question

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* When the solvent was not carefully dried, charge consumption was higher than 2 e$^-$ per molecule of complex and H$_2$ could be detected among the electrolytic products. Reduced cobalt complexes such as [Co^{I}L]$^-$ possibly react slowly with water or other acidic impurities present in the medium, leading to a catalytic evolution of H$_2$.[4b,14]

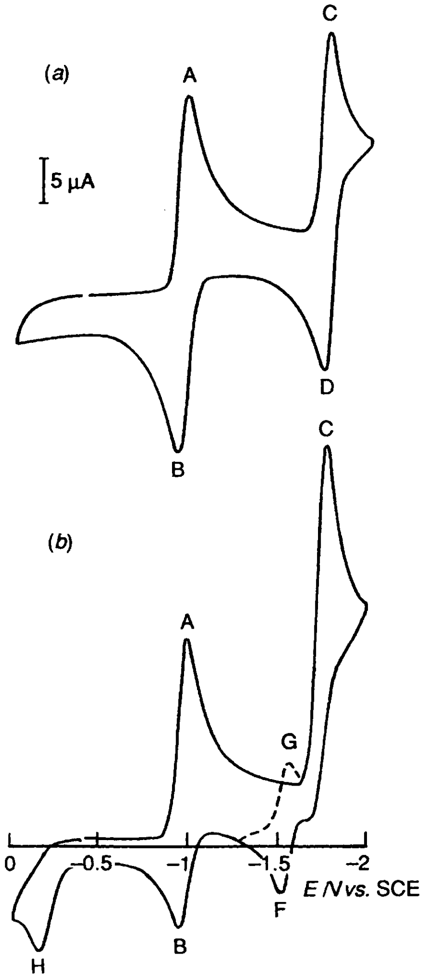


Fig. 4 Cyclic voltammograms of [Co^{II}L] (1.98 mmol dm^{-3}) in dmf–LiClO$_4$ (0.1 mol dm^{-3}) recorded (*a*) in absence and (*b*) in the presence of phenol (1.98 mmol dm^{-3}); (– – –) potential scan swept back in the cathodic direction at −1.30 V, v = 0.5 V s^{-1}

remains still open as to the nature of the species responsible for this peak couple as well as for the peaks C, D, E and H.

Further insight into the reduction mechanism of the complex is gained by the effect of proton donors. Addition of an equimolecular amount of phenol to a solution of [Co^{II}L] in dmf–[NBu$^n_4$]ClO$_4$ (0.1 mol dm^{-3}) produces a considerable amount of changes to the voltammetric pattern of the complex as can be seen comparing Figs. 1 and 6. While the reduction of Co^{II} to Co^{I} remains substantially unaffected [see Fig. 6(*a*), dashed curve], both the second and third reduction processes are strongly modified. Peak C increases approximately two times in height, its anodic partner D and the third reduction peak E are strongly reduced, while the anodic peaks F and H are both enhanced [Fig. 6(*a*)]. It is noteworthy that, by addition of the proton donor, the anodic peaks F and H can be observed even if the negative-going scan is limited to the potential of the second reduction peak C, *i.e.*, involvement of the third reduction process is no longer necessary in order to produce the species responsible for such peaks [see Fig. 6(*b*)].

Similar effects are brought about on the voltammetric pattern of the complex in a dmf–LiClO$_4$ medium, by addition of phenol as shown in Fig. 4(*b*). The cathodic peak C approximately doubles in height and becomes irreversible, while the reversible peak couple F/G (E° = −1.55 V) and the irreversible peak H (E_p = −0.15 V at v = 0.2 V s^{-1}) are formed [Fig. 4(*b*)]. Results of controlled-potential bulk reduction at −1.80 V, carried out under these conditions, are qualitatively the same as those obtained in absence of phenol (see Fig. 5), except for a more pronounced catalytic evolution of H$_2$.

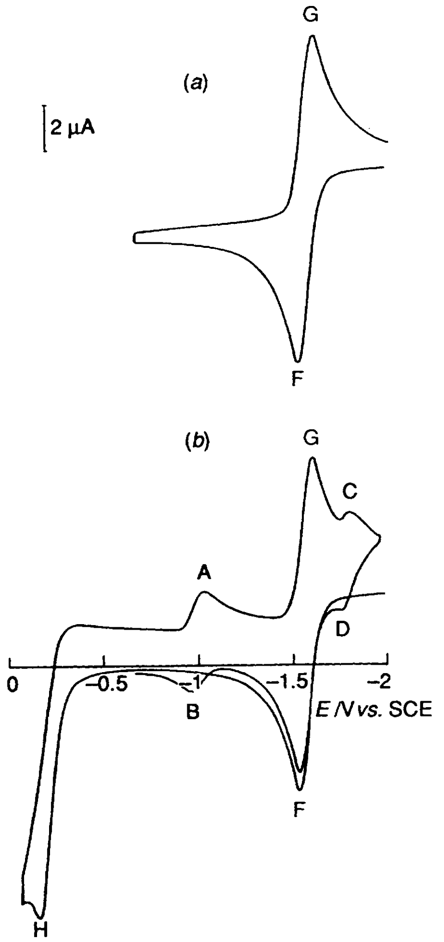


Fig. 5 Cyclic voltammograms of [Co^{II}L] (1.98 mmol dm^{-3}) in dmf–LiClO$_4$ (0.1 mol dm^{-3}) after electrolysis at −1.90 V. Potential scan reversal: (*a*) −0.65, (*b*) −0.06 V; v = 0.2 V s^{-1}

Variations of the second peak potential, E_p(C), were examined in dmf–[NBu$^n_4$]ClO$_4$ (0.1 mol dm^3) both as a function of v and phenol concentration, [PhOH]. Logarithmic analysis of E_p(C) as a function of v were performed at several concentrations of phenol, which was always in excess with respect to the complex. An average value of *ca.* −29 mV was obtained for the slope of $\partial E_p/\partial \log v$, whereas a value of 30 mV was found for the slope of $\partial E_p/\partial \log[\text{PhOH}]$. These results indicate[7,15] a pseudo-first-order reaction between the charge-transfer product formed at peak C and phenol.

Since the metal centre is not expected to be involved in a proton transfer reaction, the effect of proton donors on the voltammetric pattern of [Co^{II}L] suggests that reduction of the ligand rather than of the metal gives rise to peaks C and E. It is in fact well known that transition-metal complexes containing highly conjugated macrocyclic ligands may undergo, besides metal-centred, also ligand-centred reduction processes.[16] The electrochemical behaviour of Schiff bases has been widely studied.[17] The reduction of the imine function is characterised by two successive one-electron steps, in the potential range of the second and third cathodic peaks of [Co^{II}L] [equations (8) and (9)].

$$R^1CH{=}NR^2 + e^- \rightleftharpoons [R^1CH{=}NR^2]^{\cdot -} \qquad (8)$$

$$[R^1CH{=}NR^2]^{\cdot -} + e^- \rightleftharpoons R^1\overset{-}{C}H{-}\overset{-}{N}R^2 \qquad (9)$$

The second step is chemically irreversible because of the fast protonation of the dianion [equation (10)] where DH is any

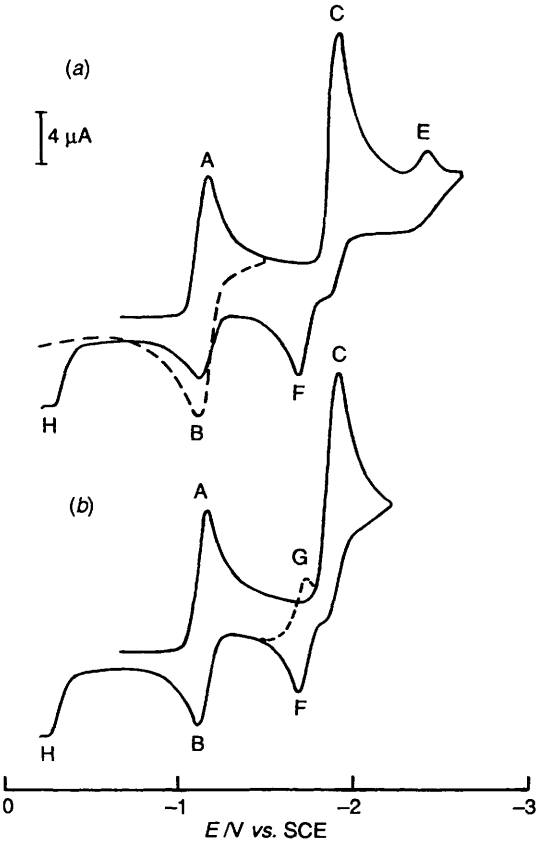


Fig. 6 Cyclic voltammograms of $[\mathrm{Co^{II}L}]$ (1.98 mmol $\mathrm{dm^{-3}}$) in dmf–$[\mathrm{NBu^n{}_4}]\mathrm{ClO_4}$ (0.1 mol $\mathrm{dm^{-3}}$) in the presence of phenol (2 mmol $\mathrm{dm^{-3}}$); potential scan reversal: (*a*) (——) −2.70, (– – –) −1.50 V; (*b*) (——) −2.30, (– – –) −1.45 V back in the cathodic direction; $v = 0.1\ \mathrm{V\,s^{-1}}$

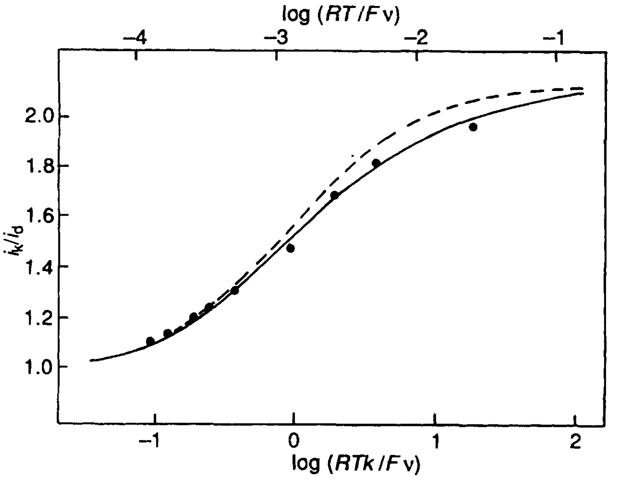


Fig. 7 Variation of peak current ratio i_k/i_d as a function of log (*RTk*/*Fv*) for $[\mathrm{Co^{II}L}]$ in the presence of phenol. (●) Experimental results. The solid and dashed line represent theoretical curves calculated for a disproportionation and an ECE process, respectively

$$\mathrm{R^1\bar{C}H{-}\bar{N}R^2} + \mathrm{DH} \longrightarrow \mathrm{R^1CH_2{-}\bar{N}R^2} + \mathrm{D^-} \quad (10)$$

proton donor present in solution. Oxidation of the resulting monoanion is often observed[18] at a potential more positive than the first reduction peak. When a strong proton donor is added to the medium also the less basic radical anion may undergo proton transfer yielding a neutral radical, reducible at the formation potential, whereby an overall two-electron reduction occurs directly at the first peak [equations (11) and (12)].

$$[\mathrm{R^1CH{=}NR^2}]^{\bullet-} + \mathrm{DH} \longrightarrow [\mathrm{R^1CH_2{-}NR^2}]^{\bullet} \quad (11)$$

$$[\mathrm{R^1CH_2{-}NR^2}]^{\bullet} + \mathrm{e^-} \longrightarrow \mathrm{R^1CH_2{-}\bar{N}R^2} \quad (12)$$

All the experimental results reported above and, in particular the characteristic effect of phenol on the voltammetric pattern, point to the reduction of a ligand imine function as responsible for the second and third cathodic peaks of $[\mathrm{Co^{II}L}]$. The reaction sequence underlying peaks C/D and E can thus be outlined by equations (13)–(15).

$$[\mathrm{Co^{I}L}]^- + \mathrm{e^-} \rightleftharpoons [\mathrm{Co^{I}(L^{\bullet-})}]^{2-} \quad \text{peaks C/D} \quad (13)$$

$$\left.\begin{aligned} &[\mathrm{Co^{I}(L^{\bullet-})}]^{2-} + \mathrm{e^-} \rightleftharpoons [\mathrm{Co^{I}(L^{2-})}]^{3-} && (14)\\ &[\mathrm{Co^{I}(L^{2-})}]^{3-} + \mathrm{DH} \longrightarrow [\mathrm{Co^{I}(HL^{-})}]^{2-} + \mathrm{D^-} && (15)\end{aligned}\right\}\ \text{peak E}$$

Electron transfer to the $[\mathrm{Co^{I}L}]^-$ complex stemming from reaction (1) leads to a cobalt(I)-stabilised ligand radical anion, rather than to a cobalt(0) complex. A further fast electron transfer to this radical anion occurs at peak E potentials, yielding a ligand-based, very basic dianion. The latter can be rapidly protonated by any proton donor DH present in the medium, such as residual water, acidic impurities or even the solvent and the background electrolyte, to give the new complex $[\mathrm{Co^{I}(HL^{-})}]^{2-}$.

The less basic ligand radical anion $[\mathrm{Co^{I}(L^{\bullet-})}]^{2-}$, although quite stable on the voltammetric time-scale, can undergo proton transfer from DH species on the longer time-scale of bulk electrolysis, when the latter is carried out at peak C potential. The resulting ligand based radical $[\mathrm{Co^{I}(HL^{\bullet})}]^-$ is assumed to be further reducible at the formation potential [equations (16), (17) and (17′)], so that bulk electrolysis at −1.90 V requires

$$[\mathrm{Co^{I}(L^{\bullet-})}]^{2-} + \mathrm{DH} \longrightarrow [\mathrm{Co^{I}(HL^{\bullet})}]^- + \mathrm{D^-} \quad (16)$$

$$[\mathrm{Co^{I}(HL^{\bullet})}]^- + \mathrm{e^-} \longrightarrow [\mathrm{Co^{I}(HL^{-})}]^{2-} \quad (17)$$

or

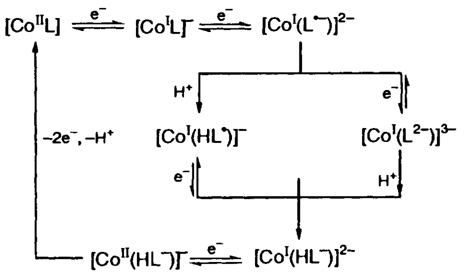
$$[\mathrm{Co^{I}(HL^{\bullet})}]^- + [\mathrm{Co^{I}(L^{\bullet-})}]^{2-} \rightleftharpoons [\mathrm{Co^{I}(HL^{-})}]^{2-} + [\mathrm{Co^{I}L}]^- \quad (17')$$

three electrons per molecule of $[\mathrm{Co^{II}L}]$.

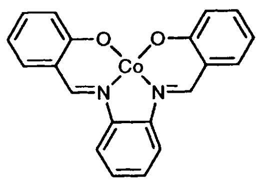
The same effect can be observed also on the voltammetric time-scale, provided that a stronger proton donor such as phenol is added to the medium [see Figs. 4(*b*) and 6], whereby the ligand radical anion complex $[\mathrm{Co^{I}(L^{\bullet-})}]^{2-}$ is rapidly protonated and further reduced to $[\mathrm{Co^{I}(HL^{-})}]^{2-}$, featuring an electrochemical–chemical–electrochemical (ECE) [equation (17)] or disproportionation [equation (17′)] mechanism.[15] This is in agreement with the doubling of peak C and decrease of peak E upon addition of phenol, since the two pathways leading to the new cobalt(I) complex [reactions (14), (15) or (16), (17), (17′)] are clearly alternative.

The rate constant of proton transfer from phenol to the anion radical, reaction (16), has been evaluated measuring the variation of the peak current i_k for peak C with sweep rate,[15] in the presence of a large excess of phenol. This was achieved by comparing the experimental data with the theoretical curves calculated from the above mechanisms.[7,15] The best fitting is obtained with the theoretical curve describing a disproportionation mechanism. This is shown in Fig. 7 where the ratio between the kinetic peak current i_k measured in the presence of phenol and the diffusion peak current i_d measured in the absence of it is plotted as a function of the kinetic parameter *RTk*/*Fv*. This fitting allows the pseudo-first-order protonation rate constant k_{11}' to be derived, from which the second-order rate constant $k_{11} = 8.8 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ has been calculated.

Whichever the pathway followed, the final reduction product of $[\mathrm{Co^{II}L}]$ is the species $[\mathrm{Co^{I}(HL^{-})}]^{2-}$. This is a square planar



Scheme 1



[Co(HL$^-$)]$^-$

cobalt(I) complex which is expected to undergo a reversible one-electron oxidation to the corresponding cobalt(II) partner [equation (18)].

$$[Co^{I}(HL^-)]^{2-} \rightleftharpoons [Co^{II}(HL^-)]^- + e^- \quad \text{peaks F/G} \quad (18)$$

The peak couple F/G can reasonably be assigned to this redox process. As to its standard potential one may question why two reversible one-electron transfer processes such as (1) and (18), both involving the redox couple Co^{II}–Co^{I} in complexes which differ in that one of the imine double bonds is reduced (see Scheme 1), are separated by *ca.* 600 mV. This might be partly attributed to the higher negative change of the redox partners of reaction (18), which entails a coulombic repulsion with the negatively charged electrode. It should be noted, however, that $E°$ of the Co^{II}–Co^{I} couple of cobalt Schiff-base complexes is very sensitive to the chemical structure of the equatorial ligand and in particular to its delocalisation ability. Progressive amounts of unsaturation in the cyclic ligand have been shown to cause an anodic shift of $E°$. Rohrbach *et al.*[6d] have reported a variation up to 490 mV for the standard potential of the reduction of Co^{II} to Co^{I} in a series of cobalt complexes with quadridentate ligands based on the Schiff bases salphen and salen. Greater variations of the redox potential have been observed by Busch and co-workers[6e] in electrochemical investigations carried out on cobalt complexes containing macrocyclic ligands based on 1,4,8,11-tetraazacyclotetradecane. These authors have shown that introduction of one isolated imine group caused an anodic shift of $E_{\frac{1}{2}}$ for the Co^{II}–Co^{I} couple of 155 mV whereas one α-diimine causes a shift of +860 mV. In view of these observations a considerable negative shift of $E°$ for the Co^{II}–Co^{I} couple of [CoL] is easily predictable upon destruction of the highly conjugated structure of the salphen ligand, as a consequence of the reduction of one imine double bond.

As to the irreversible anodic process occurring at peak H, whereby the original complex is quantitatively regenerated, it can reasonably be attributed to the oxidation of the anionic ligand of the $[Co^{II}(HL^-)]^-$ complex, according to the overall reaction (19).

$$[Co^{II}(HL^-)]^- - 2e^- \longrightarrow [Co^{II}L] + H^+ \quad (19)$$

The whole sequence of electron and proton transfer steps featuring the complex reduction pattern of $[Co^{II}L]$ are summarised in Scheme 1.

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