Electrochemical Studies of Perfluoroalkyl and Alkyl Derivatives of Cobalt(III) with Quadridentate Salicylaldimines at Mercury and Platinum Electrodes

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The electrochemical reduction at mercury and platinum electrodes of a series of perfluoroalkyl (R_F) and alkyl (R_H) cobalt(III) *NN'*-ethylenebis(salicylaldimines) [CoR(salen)] has been studied in tetrahydrofuran by several techniques. Each class of compound is reduced similarly, $[Co^{III}R(salen)] \xrightarrow{e^-} [Co^{II}R(salen)]^- \xrightarrow{e^-} [Co^{I}R(salen)]^{2-}$, with the $Co^{III}R_F$ complexes reducing most readily. Electron transfer and subsequent chemical reaction rates are different at the mercury and platinum electrodes implying that mercury-bridged intermediates may be formed at the mercury electrode. The $[CoR_F(salen)]^-$ species are more stable than the alkyl complexes but do decompose to [Co(salen)] and perfluorocarbanions. The $[CoR_H(salen)]^-$ anions rapidly yield $[Co(salen)]^-$ and the alkyl radical. Both complexes $[CoR(salen)]^{2-}$ decompose very rapidly to $[Co(salen)]^-$.

COSTA *et al.*[1,2] have examined the polarographic reduction of a variety of cobalt(III) organometallic compounds containing quadridentate ligands including the salicylaldimine anion derived from *NN'*-ethylenebis(salicylaldimine), *i.e.* $[Co^{III}R(salen)L]$ where $R = CH_3$ or C_2H_5 and L is water or dimethylformamide. They observed the reduction of [CoR(salen)] to be a reversible one-electron process but found that the cobalt(II) product was very unstable with respect to dissociation to $[Co^{I}(salen)]^-$ and alkyl radicals (R).

The analogous perfluoroalkyl cobalt(III) salicylaldimine complexes [3] have been reported to be more 'stable' to photochemical decomposition than their alkyl counterparts. They are also resistant to insertion of SO_2 into the Co–C bond [4] whereas the alkyl compounds readily form CoO_2SR species. Nor do the perfluoroalkyl groups undergo the ready redox exchange reactions between cobalt(III) and cobalt(II) centres found with alkyl cobalt compounds.[5]

The generally greater stability to reaction found for perfluoroalkyl transition-metal compounds compared to their alkyl derivatives [6] suggests that the products of the reduction of the perfluoroalkyl cobalt(III) salicylaldimine compounds may be considerably more stable than their alkyl counterparts. A polarographic and cyclic voltammetric study has therefore been made of the reductions of a series of perfluoroalkyl complexes $[CoR_F(salen)]$ where $R_F = CF_3$, C_2F_5, C_3F_7, or C_4F_9, together with a more detailed re-examination of the corresponding alkyl complexes in order to compare the electrochemical behaviour of the two classes of compound.

Tetrahydrofuran(thf) has been used as the solvent for the study since it has been widely used in synthetic procedures which involve the preparation of $[Co^{I}(chelate)]^-$ species by chemical reduction from $[Co^{II}(chelate)]$ which can then react with alkyl [7] or perfluoroalkyl [3] halides to yield organometallic cobalt(III) compounds. This solvent has not commonly been used for electrochemistry but is known to provide a large negative potential range.[8]

EXPERIMENTAL

Tetrahydrofuran was purified by successive treatment with potassium hydroxide, sodium, and lithium aluminium hydride. Samples were distilled from $Li[AlH_4]$ immediately before use. Tetra-n-butylammonium perchlorate (Eastman Kodak) was used as the supporting electrolyte without further purification since at the 0.1 mol dm^{-3} concentration used no reducible impurities could be detected in the accessible potential range.

Cobalt Compounds.—The alkyl compounds were prepared by the method of Schrauzer *et al.*[9] and recrystallized from methanol and water as the aqua-compounds $[CoR(salen)(OH_2)]$. The lability of the H_2O molecule makes it likely that the species in thf solution will be [CoR(salen)(thf)]. Perfluoroalkyl compounds were prepared by the reaction of perfluoroalkyl iodides R_FI with $[Co^{I}(salen)]^-$ prepared in turn by reduction of $[Co^{II}(salen)]$ with sodium amalgam.[3] They were also isolated as aqua-complexes.

The complex [Co(salen)] was prepared by reaction of $CoCl_2 \cdot 6H_2O$ with preformed ligand in methanol, 2 equivalents of sodium hydroxide in methanol being slowly added to the warmed mixture. All syntheses were carried out under an atmosphere of purified nitrogen.

Polarographic and cyclic voltammetric measurements were made on a PAR-170 electrochemical system using positive feedback IR compensation to allow for the high electrical resistivities of thf solutions. The working electrode was either dropping mercury or platinum wire (0.25 or 1 cm) with a 10-cm platinum wire coil as the auxiliary electrode.

The reference electrode was a $Ag-Ag^+$ couple prepared from a solution of silver pentafluoropropionate (0.01 mol dm^{-3}) in thf containing $[NBu^n_4][ClO_4]$ (0.1 mol dm^{-3}). This silver system was examined and found to be stable and reproducible giving a polarographic range of 0 to -3.7 V. Its potential with respect to the saturated calomel electrode (s.c.e.) was measured as $+0.618$ V. All results have been given with respect to the s.c.e.

Direct-current (d.c.) polarograms were obtained using an undamped recorder and maximum current readings were measured. Unless otherwise stated a mercury-column height of 60 cm was used with a capillary having the characteristics $m = 0.545$ mg s^{-1}, $t = 2.00$ s (controlled drop time), and $m^{2/3} t^{1/6} = 0.749$.

Cyclic voltammograms were measured using either a platinum wire or individual mercury drops from a dropping mercury electrode. It was found to be impossible to use a conventional hanging mercury-drop electrode since surface-tension effects in thf caused the drop to fall from the capillary after several seconds. In addition, even before the drop fell, the electrolyte solution was able to ' creep ' up the inner walls of the capillary causing the mercury thread to part, thus breaking electrical contact.

The technique eventually used of making measurements on single mercury drops had the disadvantage that it involved an expanding surface area but by recording curves at fast scan rates on a storage oscilloscope this effect was minimized. At a potential scan rate of 10 V s^{-1} over a 1 V range the surface area of a mercury drop from a capillary of the characteristics given above was calculated to change by 6% for a complete scan commencing 2 s after a previous drop had fallen. However, for cyclic voltammetry the mercury head was reduced to 40 cm and the change in drop area occurring between the cathodic and anodic peak current maxima and minima corresponding to E_p^c and E_p^a respectively was less than 2%. Since the drop surface areas however could not be known accurately under all conditions when using this method, individual current readings are not reported but only the quotients i_p^c/i_p^a at fast scan rates.

All electrochemical measurements were made at 25 °C in the dark because of the possible influence of light on the decomposition of the initial compounds or reduction products.

Constant-potential coulometry measurements were made in 0.4 mol dm^{-3} $[NBu^n_4][ClO_4]$-thf. The working electrode was a mercury pool with a diameter of 3.5 cm separated from the auxiliary electrode by two no. 5 sintered glass discs. A similar reference electrode to the above was used. Current was recorded with time at potentials 0.100 V more negative than $E_{\frac{1}{2}}^1$ for the perfluoroalkyl cobalt(III) complexes. The *i–t* curves were analysed in the usual way to determine *n*, the number of electrons involved in the charge transfer.

RESULTS

(*a*) *D.C. Polarography.*—(*i*) [Co(salen)]. The chemical reduction of this complex was first reported by Calderazzo and Floriani[10] who isolated and characterized the compounds Na[Co(salen)] and $Na_2[Co(salen)]$ after reduction of [Co(salen)] in thf with sodium. The polarographic reduction of the complex in thf proceeds in two stages. The first at $E_{\frac{1}{2}} = -1.200$ V is a monoelectronic process and is electrochemically reversible [equation (1)]. The second step at $E_{\frac{1}{2}} = -2.569$ V shows a larger limiting current per unit concentration (i_l/c) than would correspond to the passage of a single electron in the process (2). This phenomenon is also observed in the polarographic studies of the organometallic compounds which are discussed later. It is ascribed to a reaction (3) involving the supporting electrolyte cation.[11]

$$[\mathrm{Co(salen)}] \xrightleftharpoons{+e^-} [\mathrm{Co(salen)}]^- \qquad (1)$$

$$[\mathrm{Co(salen)}]^- \xrightleftharpoons{+e^-} [\mathrm{Co(salen)}]^{2-} \qquad (2)$$

$$[\mathrm{Co(salen)}]^{2-} + [\mathrm{NBu^n_4}]^+ \longrightarrow [\mathrm{CoBu^n(salen)}]^- + \mathrm{NBu^n_3} \qquad (3)$$

Costa *et al.*[12] have shown that $[Co(salen)]^-$ reacts with $[NR_4]^+$ species to yield [CoR(salen)] but the rate is sufficiently slow that no obvious contribution is observed on the electrochemical time scale during the reduction of [Co(salen)] to $[Co(salen)]^-$.

A similar reaction can be expected to occur with $[Co(salen)]^{2-}$ species but its enhanced nucleophilicity should lead to a faster reaction with $[NBu^n_4]^+$ being observed than with $[Co(salen)]^-$. The expected product $[CoBu^n(salen)]^-$ would be reduced at a less negative potential than $[Co(salen)]^-$ (see later) and hence at a potential of -2.57 V will in turn be immediately reduced thereby enhancing the current compared to a process derived solely from the second reduction step of [Co(salen)].

Oxidation of [Co(salen)] in thf was also observed ($E_{\frac{1}{2}} = +0.385$ V). This product is assumed to include two solvent molecules to provide a six-co-ordinate configuration [reaction (4)].

$$[\mathrm{Co(salen)}] \xrightleftharpoons[\mathrm{thf}]{-e^-} [\mathrm{Co(salen)(thf)_2}]^+ \qquad (4)$$

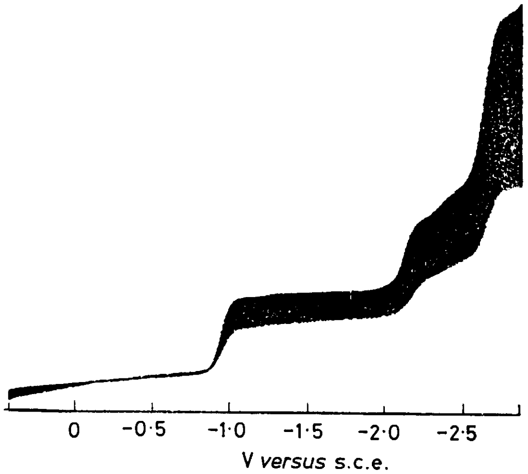


FIGURE 1 D.c. polarogram of 1 × 10^{-3} mol dm^{-3} $[Co(C_3F_7)(salen)]$ in thf (0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$). Drop time 0.5 s. Potential range +0.42 to −2.88 V *versus* s.c.e.

(*ii*) *Perfluoroalkyl and alkyl cobalt*(III) *salen compounds.* The perfluoroalkyl and alkyl complexes each show four polarographic reduction waves characterized by $E_{\frac{1}{2}}^1$, $E_{\frac{1}{2}}^2$, $E_{\frac{1}{2}}^3$, and $E_{\frac{1}{2}}^4$ (Figure 1). The previous studies of Costa *et al.*[1] on [CoMe(salen)(dmf)] detected four waves in dimethylformamide (dmf). The second and third were said to overlap and the fourth to be ill defined. For the ethyl complex[2] only two waves were reported.

In thf all four waves are resolved and complete assignments can be made for all except the third wave. The first reduction wave shows the characteristics of a diffusion-controlled process in the limiting-current region for each complex examined. Thus a linear dependence of limiting current i_l on the height of the mercury head $(h_{Hg})^{\frac{1}{2}}$ and i_l on concentration is observed. The wave slope (Table 1) is consistent with charge transfer being a reversible one-electron reduction process. The charge-transfer process can be assigned to reaction (5).

$$[\mathrm{CoR(salen)}] \xrightleftharpoons{+e^-} [\mathrm{CoR(salen)}]^- \qquad (5)$$

The perfluoroalkyl complexes are reduced at notably less negative potentials than the alkyl compound (Table 1).

TABLE 1

Electrochemical reduction of perfluoroalkyl and alkyl complexes of Co^{III}; [CoR(salen)] in tetrahydrofuran at 25 °C

R	Electron affinity of RH	$E_{\frac{1}{2}}^{1}$/V	i_l^1/c / mA mol^{-1}	Slope (mV)	$E_{\frac{1}{2}}^{2}$/V	i_l^2/c / mA mol^{-1}
CF_3	2.0	−0.989	1.42	−59	−2.04	1.1
C_2F_5	2.3	−0.977	1.53	−56	−2.05	1.1
C_3F_7	2.4	−0.930	1.43	−56	−2.06	1.2
C_4F_9		−0.908	1.45	−58	−2.06	*ca.* 1
CH_3	1.1	−1.563	1.44	−63	−2.20	0.6
C_2H_5	0.9	−1.703	1.47	−56	−2.16	0.4
C_3H_7	0.7	−1.697	1.43	−56	−2.2	*ca.* 0.4

$t_{Hg} = 2.00$ s. Slope = slope of plot of E against log $[i/(i_l - i)]$. $E_{\frac{1}{2}}^{3} \simeq -2.3$, $E_{\frac{1}{2}}^{4} = -2.57$ V.

This is in agreement with the relative pK_a values of the hydrocarbons, CF_3H (31) [13] and CH_4 ($\geqslant$40),[14] and the correlation detected by Costa *et al.*[2] that $E_{\frac{1}{2}}$ for reaction (5) becomes more negative as the acidity of RH decreases, *i.e.* as the donor power of the carbanion R^- increases.

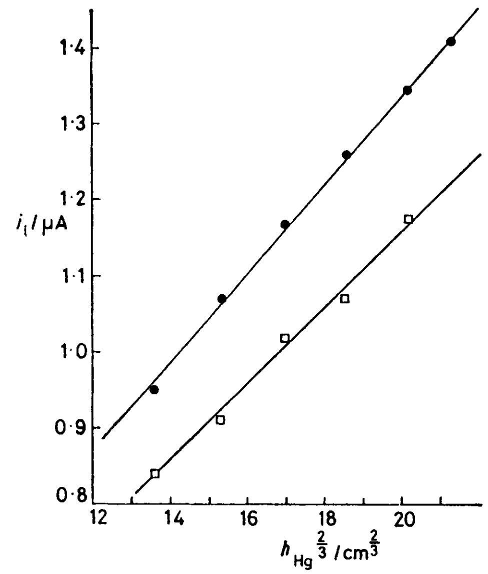


FIGURE 2 Plots of i_l against $h_{Hg}^{\frac{2}{3}}$ for the first ($E_{\frac{1}{2}}^{1}$, ●) and second reduction waves ($E_{\frac{1}{2}}^{2}$, □) of 1 × 10^{-3} mol dm^{-3} [Co(C_3F_7)(salen)] in thf (0.1 mol dm^{-3} [NBu^n_4][ClO_4]). Drop time 2.0 s

The second wave is smaller than the first for both the perfluoroalkyl and alkyl series, *i.e.* $(i_l^2/c) < (i_l^1/c)$, although the difference is smaller for the perfluoroalkyl than the alkyl series. The limiting current for the second reduction in the perfluoroalkyl series is partially kinetically controlled as shown by the variation of i_l with $h_{Hg}^{\frac{2}{3}}$ for the first two waves (Figure 2). The slope of the plot for the second wave is expected to be less than that for the first if the product of the first (which is the reagent for the second) is removed by reaction. A similar result is expected for the alkyl complexes; however, since i_l^2 is relatively small with respect to i_l^1 only small and imprecise changes of i_l^2 are observed with $h_{Hg}^{\frac{2}{3}}$.

These results indicate that a chemical reaction is reducing the concentration of $[CoR(salen)]^-$ formed in the first reduction step (5) before the second reduction can occur, for each class of complex. The second reduction process is considered to be (6).

$$[\mathrm{CoR(salen)}]^- \underset{}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{CoR(salen)}]^{2-} \longrightarrow \text{products} \quad (6)$$

The $E_{\frac{1}{2}}^{2}$ values are less separated for both perfluoroalkyl and alkyl species than for the first reduction stage and there is little variation with carbon chain length for either series. The values of i_l^2/c are much closer to those of i_l^1/c for the perfluoroalkyl than the alkyl series and this provides clear evidence for the greater ' stability ' of the perfluoroalkyl cobalt(II) species compared to the alkyl with respect to the decomposition reactions tending to break down these complexes.

A third reduction wave is observed in both perfluoroalkyl and alkyl series. It is smaller in height than the first and second waves, is poorly defined, and represents an irreversible process. It is not considered to relate to the process (7) since the evidence from cyclic voltammetry indicates a very low kinetic stability for the species $[CoR(salen)]^{2-}$. The potential at which such a process would be expected to occur is also likely to be much more negative. Presumably it results from one of the decomposition products of $[CoR(salen)]^{2-}$ and since this reduction is not observed at Pt it may be due to a mercury complex.

$$[\mathrm{CoR(salen)}]^{2-} \xrightarrow{+e^-} [\mathrm{CoR(salen)}]^{3-} \quad (7)$$

The fourth reduction process occurs with the same $E_{\frac{1}{2}}$ for all complexes examined ($E_{\frac{1}{2}}^{4} = -2.57$ V) and the value corresponds to the process (2). As in the same reduction

TABLE 2

Cyclic voltammetry (E in V, ΔE in mV) at mercury and platinum electrodes for [CoR(salen)] at a scan rate of 0.500 V s^{-1}

	Hg				Pt			
R	E_{p1}^{c}	E_{p1}^{a}	ΔE_{p1}	E_{p2}^{c} *	E_{p1}^{c}	E_{p1}^{a}	ΔE_{p1}	E_{p2}^{c} *
CF_3	−1.134	−1.064	70	−2.23	−1.177	−1.032	145	−2.25
C_2F_5	−1.027	−0.960	67	−2.23	−1.060	−0.914	146	−2.25
C_3F_7	−0.967	−0.907	60	−2.23	−1.057	−0.822	235	−2.30
C_4F_9	−0.957	−0.900	57	−2.28	−0.997	−0.850	147	−2.30
CH_3	−1.644			−2.3	−1.712			
C_2H_5	−1.778			−2.4	−1.805			
C_3H_7	−1.767			−2.5	−1.822			

* Cathodic peak for $[CoR(salen)]^- \longrightarrow [CoR(salen)]^{2-}$ is very small on Hg due to loss of the former by rapid chemical decomposition and is not observed as a distinctive peak on Pt. Anodic peak for the reverse (oxidation) process is not observed on either electrode even at very high scan rates.

TABLE 3

Cyclic voltammetry for [Co(CF$_3$)(salen)] on a 1-cm platinum wire

Scan rate (V s^{-1})	E_p^c/V	E_p^a/V	ΔE_p/mV	i_p^c/c (mA mol^{-1})	i_p^a/c (mA mol^{-1})	i_p^c/i_p^a
0.020	−1.135	−1.060	75	11.7	10.2	1.15
0.050	−1.133	−1.052	81	17.3	16.2	1.07
0.100	−1.140	−1.049	91	23.8	23.8	1.00
0.200	−1.146	−1.040	106	32.8	33.2	0.99
0.500	−1.177	−1.032	145	46.4	45.4	1.02

$\Delta E_p = E_p^c - E_p^a$; $i_p^a = i_p^a[\mathrm{CoR_F(salen)}]^- + i_p^a[\mathrm{Co(salen)}]^-$.

process observed for [Co(salen)], the current measured during this stage is greater than corresponds to a single electron process and this is ascribed to reaction with [NBu$^n_4$]$^+$ ions of the supporting electrolyte, as discussed previously.

(*b*) *Cyclic Voltammetry.*—A more detailed examination of the reduction stages of each class of compound has been carried out by cyclic voltammetry using platinum-wire and single mercury-drop working electrodes.

(*i*) *Platinum-wire electrode.* The first reduction stage (5) for alkyl cobalt(III) compounds appeared chemically irreversible at a platinum-wire electrode (Table 2). A definite anodic peak due to oxidation of [CoR$_H$(salen)]$^-$ was not observed at scan rates as high as 50 V s^{-1}. However, for each alkyl compound peaks could be observed for the reduction and oxidation of [Co(salen)]$^-$ [equation (8)] and

$$[\mathrm{Co(salen)}] \xleftarrow{-e^-} [\mathrm{Co(salen)}]^- \xrightarrow{+e^-} [\mathrm{Co(salen)}]^{2-} \quad (8)$$

oxidation of [Co(salen)]$^{2-}$ to [Co(salen)]$^-$. No evidence was found for the existence of [Co(salen)] on the first cathodic scan indicating that it was not produced by decomposition or reduction from a higher valent species.

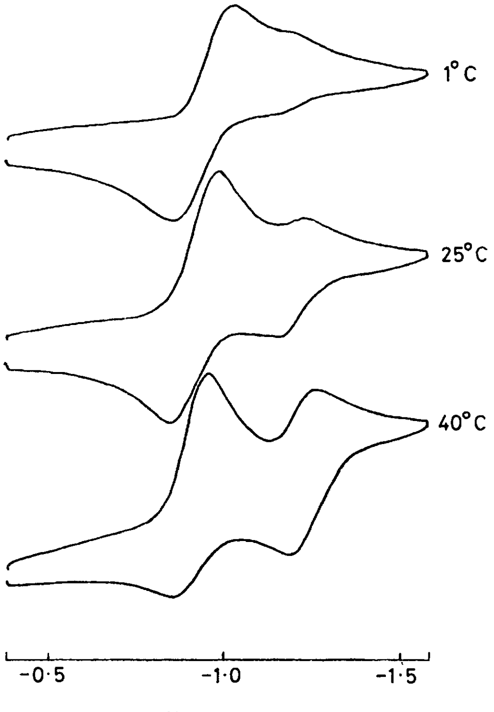


FIGURE 3 Effect of temperature on the rate of decomposition of [Co(C$_4$F$_9$)(salen)]$^-$. Cyclic voltammogram of 1 × 10^{-3} mol dm^{-3} [Co(C$_4$F$_9$)(salen)] in thf (0.1 mol dm^{-3} [NBu$^n_4$][ClO$_4$]) at a 1-cm platinum-wire electrode; scan rate 0.100 V s^{-1}, potential range −0.38 to −1.58 V *versus* s.c.e.

On Pt, no distinctive peak was observed for the reduction of [CoR$_H$(salen)]$^-$ to [CoR$_H$(salen)]$^{2-}$ which is consistent with the former being removed by a rapid chemical reaction.

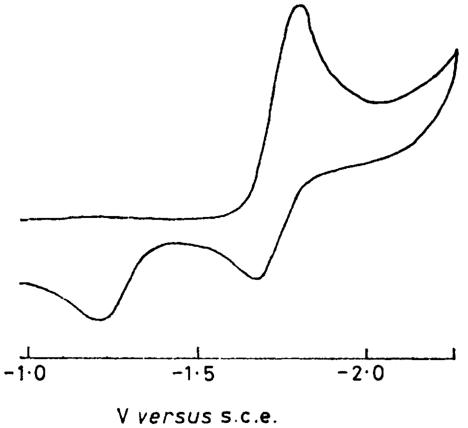


FIGURE 4 Cyclic voltammogram of 1 × 10^{-3} mol dm^{-3} [Co(C$_3$H$_7$)(salen)] in thf (0.1 mol dm^{-3} [NBu$^n_4$][ClO$_4$]). Hanging mercury-drop electrode, scan rate 10 V s^{-1}, potential range −0.92 to −2.28 V *versus* s.c.e.

The perfluoroalkyl complexes differed in two ways from the alkyl compounds. First the reduction step [CoR$_F$(salen)] $\overset{+e^-}{\rightleftharpoons}$ [CoR$_F$(salen)]$^-$ was quasi-reversible with E_p^c increasing, ΔE_p increasing, and i_p^c/i_p^a approaching 1.00 as the scan rate increased from 0.02 to 0.50 V s^{-1} (Table 3). Secondly, a peak was observed at these low scan rates for the reduction of [Co(salen)], so clearly a chemical step is associated with the charge transfer to produce this species. This complex can only have been formed by decomposition of the first reduction product [CoR$_F$(salen)]$^-$. The size of the peak for the reduction of [Co(salen)] decreases with increasing scan rate when compared to the peak for the reduction of the perfluoro-organometallic cobalt(III) complex. The extent of formation of [Co(salen)] increases with temperature (Figure 3) in agreement with an increase in the rate of decomposition.

The reduction step [CoR$_F$(salen)]$^-$ $\longrightarrow$ [CoR$_F$(salen)]$^{2-}$ was also observed at more negative potentials as an irreversible process at all scan rates.

(*ii*) *Mercury-drop electrode.* At slow scan rates the alkyl complexes showed apparently irreversible reduction behaviour as with a platinum electrode. However, as the scan rate increased above 5 V s^{-1} a well defined anodic peak was observed for the oxidation of [CoR$_H$(salen)]$^-$ when the switching potential was −2.3 V or less (Figure 4). The size of this oxidation peak, relative to the reduction, increased with scan rate while the current for the oxidation of [Co(salen)]$^-$ decreased. A comparison of relative stabilities to decomposition of the species [CoR$_H$(salen)]$^-$,

TABLE 4

Cyclic voltammetry for the first redox couple of $[Co(C_3F_7)(salen)]$ on a mercury-drop electrode

Scan rate ($V\ s^{-1}$)	E_p^c/V	E_p^a/V	ΔE_p [a]/mV	i_p^c/i_p^a [b]
0.5	-0.967	-0.907	60	<0.8
1.0	-0.972	-0.907	65	<0.8
2.0	-0.977	-0.907	70	<0.8
5.0	-0.982	-0.902	80	*ca.* 0.9
10.0	-0.962	-0.900	62	0.96
20.0	-0.967	-0.902	65	1.00
50.0	-0.967	-0.894	73	1.0

[a] At 2.0 and 5.0 $V\ s^{-1}$, ΔE_p was larger than expected for a reversible system. This is probably due to imperfect IR compensation since at higher scan rates $\Delta E_p \simeq 60$ mV again. [b] $i_p^c/i_p^a < 0.8$ at scan rates $<10\ V\ s^{-1}$ due to the expanding surface of the mercury drop.

$R = CH_3$, C_2H_5, or $n\text{-}C_3H_7$, was possible by measuring i_p^c/i_p^a for each complex at a scan rate of 10 $V\ s^{-1}$ over a 1 V range. The values were: CH_3, 1.7; C_2H_5, 2.8; $n\text{-}C_3H_7$, 2.5.

In contrast to reductions at a platinum electrode, at Hg the second reduction $[CoR_H(salen)]^- \longrightarrow [CoR_H(salen)]^{2-}$ is observed as a small peak. It appears to be completely irreversible with no peak for the oxidation of $[CoR_H(salen)]^{2-}$ being observed.

The third small reduction wave noticed in d.c. polarography of these complexes was not observed as a distinct peak using a mercury-drop electrode, but the process no doubt contributed to the rapidly rising baseline of the cyclic voltammogram immediately following the second reduction peak (Figure 5). The couple $[Co(salen)]^-$–$[Co(salen)]^{2-}$ was also observed as a reversible process and resulted in the appearance of the oxidation process $[Co(salen)]^- \longrightarrow [Co(salen)]$ in the anodic scan.

The first reduction process of $[CoR_F(salen)]$ was found to be electrochemically reversible at a mercury-drop electrode, at least up to scan rates of 20 $V\ s^{-1}$ using the criteria of Nicholson and Shain [15] (Table 4) and with the limitations of the use of a single growing mercury drop and the high resistance of the solutions.

A deviation from electrochemical reversibility in the results of Table 4 may be noted in that $E_p^c - E_{\frac{1}{2}} = ca.$ 40 mV rather than the expected 29 mV.[15] This is ascribed to the high resistance of the solution being used for measurements. When the supporting electrolyte concentration was increased to 0.3 mol dm^{-3}, to lower solution resistance, conditions for complete reversibility were found. Thus $E_{\frac{1}{2}}$ for the average current was -0.923 V, and at 10 $V\ s^{-1}$, $E_p^c = -0.952$, $E_p^a = -0.882$, $\Delta E_p = 60$ mV, $i_p^c/i_p^a = 1.00$, and $E_p^c = E_{\frac{1}{2}} - (0.029/n)$ when $n = 1$.

FIGURE 5 Cyclic voltammogram of 1×10^{-3} mol dm^{-3} $[Co(C_2F_5)(salen)]$ in thf (0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$). Hanging mercury-drop electrode, scan rate 10 $V\ s^{-1}$, potential range -0.58 to -2.98 V *versus* s.c.e.

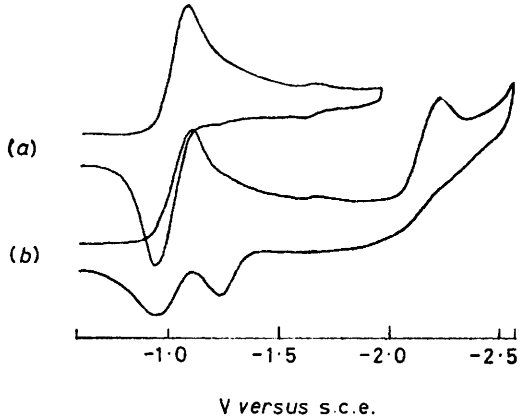


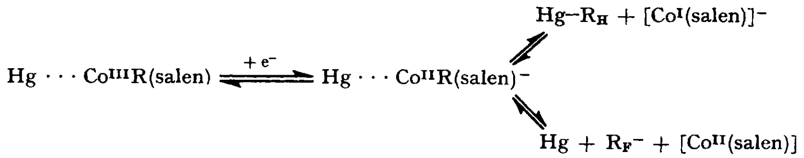
FIGURE 6 Cyclic voltammograms of 1×10^{-3} mol dm^{-3} $[Co(C_2F_5)(salen)]$ in thf (0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$). Hanging mercury-drop electrode, scan rate 10 $V\ s^{-1}$, potential ranges (*a*) -0.58 to -1.98, (*b*) -0.58 to -2.58 V *versus* s.c.e.

The second reduction step (6) appears to be chemically irreversible at all scan rates and at both mercury and platinum electrodes. However, on mercury the process does not shift markedly with large changes of applied scan rate. This may indicate that the electron-transfer process is actually reversible or quasi-reversible but that chemical decomposition of the product is extremely rapid. This rapid decomposition is demonstrated in Figure 6. At a scan rate of 10 $V\ s^{-1}$, curve (*a*) represents a cyclic voltammogram restricted essentially to the process $[CoR_F(salen)] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [CoR_F(salen)]^-$, but with a voltage sweep which would include the redox couple of $[Co(salen)]$. The reversibility of the process is demonstrated and no oxidation of $[Co(salen)]^-$ is observed. However, when the scan includes the reduction potential for the second step (*b*) a considerable amount of $[Co(salen)]^-$ is observed being oxidized on the anodic sweep.

It may be noted that, despite the absence of a clearly defined anodic peak for the oxidation of $[CoR(salen)]^{2-}$, there is nevertheless a definite anodic peak for the oxidation of $[CoR_F(salen)]^-$ although much reduced in height from the primary cathodic peak for $[CoR_F(salen)]$. It is believed that this is related to diffusion of $[CoR_F(salen)]$ into the volume next to the electrode during the time of the scanning process, thus allowing immediate reduction of the $[CoR_F(salen)]$ and subsequent oxidation of the product $[CoR_F(salen)]^-$.

The $[Co(salen)]^-$ must arise primarily by rapid decomposition of $[CoR_F(salen)]^{2-}$ giving $[Co(salen)]^-$ and presumably R_F^- carbanions. Furthermore the size of the oxidation peak for $[CoR_F(salen)]^-$ is somewhat smaller than expected, indicating that further chemical reactions may be occurring between the decomposition products and $[CoR_F(salen)]$ in the vicinity of the electrode.

In addition to the above, at slow scan rates ($\leqslant 0.5$ $V\ s^{-1}$), $[Co(salen)]$ is detected immediately following the reduction peak for $[CoR_F(salen)]$ as was observed in experiments with a platinum electrode. This compound must



Scheme 1

therefore arise by decomposition of $[CoR_F(salen)]^-$, a process that is not observed for the alkyl complexes.

The presence of [Co(salen)] as the source of the reduction peak following $[CoR_F(salen)]$ was confirmed by adding samples of the former to a solution of the organometallic cobalt(III) compound. An appropriate increase in the current flow was observed at the potential attributed to [Co(salen)] in the cathodic phase of the cyclic voltammogram without any evidence for broadening of the peak or appearance of a shoulder which might have indicated a separate complex of closely similar electrochemical behaviour being formed from $[CoR_F(salen)]$.

The faster electron-transfer rates and apparent stabilization of $[CoR_F(salen)]^-$ at mercury compared with platinum indicate the formation of a mercury-bridged intermediate and that electron transfer occurs *via* the bridge Hg · · · CoR(salen). That is, at mercury the electrode process may be best described as in Scheme 1 or similar reactions.

Further evidence for the formation of a mercury-bridged intermediate is provided by fast-scan cyclic voltammetry. Multiple scans of $[CoR_H(salen)]$ at 100 V s^{-1} give a result similar to that in Figure 4 with no significant reduction peak for [Co(salen)] on the second and subsequent cycles. It is known that alkyl radicals rapidly react with thf to give alkanes. It is also known that an alkyl radical can react with [Co(salen)] to form [CoR(salen)]. If a free radical were to result from decomposition of the first reduction product of the organometallic compound a reduction peak for [Co(salen)] would be expected. However, if the radical were stabilized by formation of a partial bond with mercury, the radical would be available to react with the [Co(salen)] and no reduction peak for this species would be expected.

(*c*) *Constant-potential Coulometry*.—Using this technique n was unambiguously shown to be one. When R was CF_3, C_2F_5, C_3F_7, and C_4F_9, n was measured as 0.97, 0.95, 0.95, and 0.96 respectively. Costa *et al.*[1,2] determined $n = 1$ for the methyl derivative. In the present work attempts to measure n for the other alkyl derivatives have proved unsuccessful. When the reduction potential was applied the current initially decayed but after some time became constant indicating that a cyclic process was occurring. The decomposition product of $[CoR_H(salen)]$ is $[Co(salen)]^-$ and this has been shown to react with $[NR_4]^+$ to produce [CoR(salen)] [12] which is immediately reduced. Attempts to measure n using other supporting electrolytes also proved unsuccessful. No supporting electrolyte, other than those containing tetra-alkylammonium salts, was found to be sufficiently soluble in thf and to give a low residual current at the negative potentials necessary.

DISCUSSION

There are three electrochemical processes that are observed in d.c. polarography for both the perfluoroalkyl and alkyl compounds and which have also been studied by cyclic voltammetry. In addition a fourth reduction is observed with a small current in the d.c. polarographic work but is not as clearly defined as a discrete cathodic peak in cyclic voltammetric studies and probably involves formation of a mercury compound. The products of reduction can undergo ready chemical decompositions. These reactions are shown in Scheme 2.

The first monoelectronic reduction process of organometallic Co^{III} to the organometallic Co^{II} is electrochemically reversible. The second monoelectronic reduction step for both types of complex is considered to involve reduction of organometallic Co^{II} to organometallic Co^I. The organometallic cobalt(II) species are however clearly unstable for both types of complex although the products of decomposition are different [equations (9) and (10)]. However, bridging at the

$$[CoR_F(salen)]^- \longrightarrow R_F^- + [Co(salen)] \qquad (9)$$

$$[CoR_H(salen)]^- \longrightarrow R_H\cdot + [Co(salen)]^- \qquad (10)$$

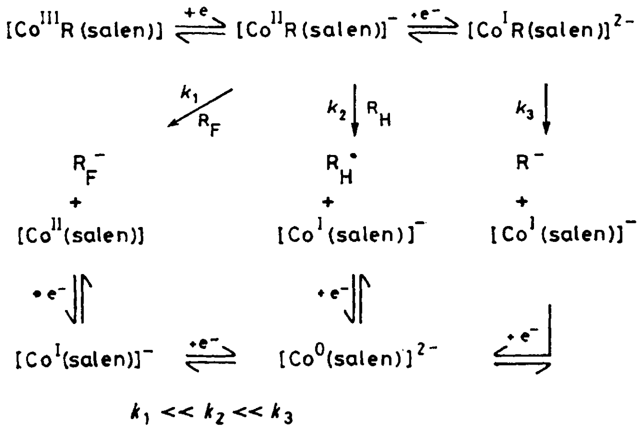
mercury electrode appears to stabilize $[CoR(salen)]^-$ somewhat so that intermediates of the kind [Hg · · · CoR(salen)] are probably formed during the electron transfer.

The further reduction product $[CoR(salen)]^{2-}$ must be considered as exceedingly unstable for both $R = R_F$ and R_H since no evidence for oxidation of such a species could be detected by cyclic voltammetry at very high scan rates. The process of decomposition in each system is thought to be (11). The final reduction step observed

$$[CoR(salen)]^{2-} \longrightarrow R^- + [Co(salen)]^- \qquad (11)$$

in d.c. polarography and cyclic voltammetry is unambiguously assignable to the reversible process (2).

The third wave observed in the d.c. polarographic measurement may relate to reduction of the subvalent organomercury compound (HgR) formed from reaction of the alkyl radical with mercury metal or from reaction



Scheme 2 The reduction and decomposition products of [CoR(salen)]

with the bridged mercury intermediate. Dessy *et al.*[16] have studied the reductions of a series of such species {derived from [HgR(X)]} and shown that the reduction (12) occurs at $E_{\frac{1}{2}} = -3.1$ and -3.2 V (*versus* Ag–Ag[ClO$_4$]) for the CH_3 and C_2H_5 derivatives respectively. The reduction potentials are precisely in the region observed for the third polarographic wave here. Furthermore, the wave reported by Dessy is electrochemically irreversible, again as is observed in this work.

$$HgR \xrightarrow{+e^-} R^- + Hg \qquad (12)$$

More recently Denisovich and Gubin [17] have studied similar HgR systems using different solvents, supporting electrolytes, and reference electrode. However, making allowances for these differences, similar irreversible reductions of HgR were obtained at very negative potentials.

A satisfactory explanation of the third wave for the perfluoroalkyl cobalt(III) complexes is not possible. First the R_F group is produced as a carbanion and as such is not as likely to react with mercury to form HgR_F. Secondly, if HgR_F were formed it would be expected to be reduced at less negative potentials and probably before the second reduction of the organometallic compound. Dessy *et al.*[16] give brief results for the reduction of $Hg(C_2F_5)$ which occurs at *ca.* -1.6 V *versus* Ag–Ag[ClO$_4$] in glyme.

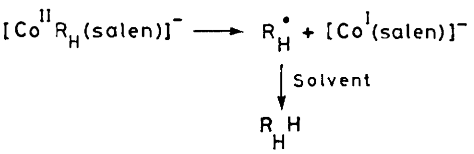
The final possible explanation for this wave would involve an exchange of the mercury-bridged intermediate with the supporting electrolyte to give HgBu.

It is noteworthy that for the alkyl series of compounds the trend in stability of the first reduced product follows the trend in $E_{\frac{1}{2}}^1$ regardless of the length of the carbon chain. The stabilities of the alkyls decreases in the order $CH_3 > C_3H_7 > C_2H_5$ following the trend in increasing reduction potential. The perfluoroalkyl cobalt(III) compounds show a steady decrease in $E_{\frac{1}{2}}^1$, $CF_3 > C_2F_5 > C_3F_7 > C_4F_9$, and this trend should be followed similarly for the stability of the perfluoroalkyl cobalt(III) anions, *i.e.* $CF_3 < C_2F_5 < C_3F_7 < C_4F_9$. However, the kinetic stabilities of these compounds is such that the order is difficult to distinguish, but they are much more stable than the analogous alkyls.

The correlation of pK_a of a protonated ligand group with $E_{\frac{1}{2}}$ is often observed in electrochemistry and appears to be followed here, although many workers have reported extremely variable values for the saturated hydrocarbons. Values of the pK_a of methane have been reported to vary from 40 to 58.[14] This variation is doubtless a function of the methods used for measurement and calculation. Nevertheless, it can be shown that as the pK_a of a protonated ligand increases the reduction potential becomes more negative. Thus the higher pK_a values of the hydrocarbons compared with the monohydrofluorocarbons is reflected in the $E_{\frac{1}{2}}^1$ values obtained. Furthermore the trend in $E_{\frac{1}{2}}^1$ observed for the perfluoroalkyl cobalt(III) complexes appears to follow that expected from the pK_a values determined by Andreades,[13] who found that as the length of the carbon chain increases the pK_a decreases as expected; CF_3H (31), $CF_3(CF_2)_5CF_2H$ (30).

The differences in electrochemical behaviour between the perfluoroalkyl and alkyl compounds relate to the electron affinity of the organo-group, and hence to the extent of electron distribution in the Co–C bond.[18] The reversible reduction [CoR(salen)] $\longrightarrow$ [CoR(salen)]$^-$ occurs at less cathodic potentials for the perfluoroalkyl than the alkyl compounds indicating that a suitable metal orbital is more readily available to receive the additional electron provided in the electrode process, for the perfluoroalkyl compounds. This would agree with a greater carbanion character for R_F groups and a smaller contribution of a metal *d* orbital in the Co–C bond. The superior electron-donating character of an alkyl compared to a perfluoroalkyl group would, on the other hand, favour considerably greater combination of metal *d* and ligand σ-type orbitals in bond formation.

The greater stability of the perfluoroalkyl cobalt(III) species to decomposition reflects the general observation that fluoroalkyl metal compounds are more resistant to decomposition than their alkyl analogues.[6] The reason for the enhanced kinetic and thermal stabilities of the perfluoroalkyl species may therefore relate more to the tendency to form carbanionic species which may stabilize a metal–carbon bond $\overset{\delta+}{M}-\overset{-\delta}{R_F}$ against dissociation. In contrast, a greater degree of electron sharing in a metal–alkyl bond may relate to the superior electron-donating character of alkyl groups. This bonding situation could more readily lead to transfer of an electron from a carbon orbital to the metal with formation of a reactive alkyl radical together with a 'stable' metal-containing species (Scheme 3).



SCHEME 3

Costa *et al.*[2] have shown that the aryl compound [CoPh(salen)]$^-$ also has a notably greater degree of kinetic stability than the methyl analogue and have indicated that solutions of the above anion may be prepared by exhaustive electrochemical reduction of the cobalt(III) complex. In such a case the stabilization of the cobalt(II) organometallic compound will be favoured by the ability of the aromatic ring to delocalize excess of electron density.

The stability of the metal–carbon bond is also influenced by the nature of the equatorial ligand.[2] The range of donor types incorporated in ligands of cobalt(III) organometallic compounds is still relatively limited. The compounds studied electrochemically include salicylaldimines and an oxime derivative,[1,2] methylcobinamide, methylcobalamin, and methyl(tetraphenylporphinato)-

cobalt(III).[19] Methyl(tetraphenylporphinato)cobaltate(II) is reported to be notably more stable than the analogous cobalamin derivatives and also [CoMe(salen)]$^-$. This suggests that delocalization of electron density by the porphine ring may again be contributing to the stability of the anionic species.

The perfluoroalkyl cobalt salen species appear to be more stable towards dissociation however than any of these compounds, indicating the dominating influence of the perfluoroalkyl group.

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