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Electrode processes of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-substituted } 1,2\text{-ethylenedithiolato})\text{cobalt(III)}$ complexes in an ambient temperature molten salt

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Abstract

The electrochemistry of two derivatives of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-ethylenedithiolato})\text{cobalt(III)}$ complexes with substituents, cyano (CN) and 4-pyridyl (⁴Py) at the ethylenedithiolato moiety, was studied at a glassy carbon electrode in an ambient temperature ionic liquid composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride ($\text{AlCl}_3\text{-ImCl}$). The reduction of Co^{III} to Co^{II} in the two complexes was a diffusion-controlled reversible process in basic and neutral melts. The half-wave potentials for both complexes were slightly dependent on melt composition. Because the ethylenedithiolate ligands also participated in the electrode reaction, the CN-substituted complex showed an irreversible anodic peak, while the ⁴Py-substituted complex not only gave a quasi-reversible anodic peak but also displayed another irreversible cathodic peak at very negative potentials. The oxidation of the metalladithiolene ring is believed responsible for the anodic peaks of both complexes. The diffusion coefficients of the complexes in basic and neutral melts were estimated from the Cottrell equation. The Stokes radius estimated for the CN-substituted complex was 0.26 nm in the 0.8:1.0 melt and 0.29 nm in the 1.0:1.0 melt. The slightly larger radius in the 0.6:1.0 melt (0.38 nm) was interpreted in terms of the solvation of the complex in the more basic melt.

1. Introduction

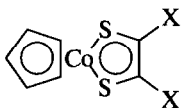
A considerable amount of research work has dealt with the chemistry and electrochemistry of various solutes in aluminum chloride–1-ethyl-3-methylimidazolium chloride ($\text{AlCl}_3\text{-ImCl}$) ambient temperature molten salt [1–3]. This solvent is characterized as acidic, basic, or neutral if the mole ratio of AlCl_3 to ImCl is greater than, less than or equal to unity. Our group has recently explored the electrochemistry of some complexes with unique structures, such as (tris-acetylacetonato)metal complexes [4] and 1,4-diferrocenyl-1,3-butadiyne [5]. Because of the Lewis acid-base character of the solvent, these solutes show electrochemical behavior quite different from that in acetonitrile solutions. As a continuation of this work, we report here on electrochemical studies of the derivatives of

$(\eta^5\text{-cyclopentadienyl})(1,2\text{-ethylenedithiolato})\text{cobalt(III)}$ complexes with substituents at the ethylenedithiolato moiety.

Our interest in studying these complexes stems from an expectation that we might observe interactions between the complexes and the Lewis acid, Al_2Cl_7^- , or base, Cl^- , moieties in the solvent. Both moieties can be present at high concentrations that depend on the relative mole ratio of AlCl_3 to ImCl . Interactions might also depend on the substituents on the dithiolene ring. Such interactions are of interest, and are important in understanding the use of these complexes as homogeneous catalysts [6]. It has also been noted that the ring is pseudo-aromatic, or the metal chalcogen bonds exhibit double-bond character, as demonstrated by various addition reactions at these bonds, such as the addition of an alkyne [7], quadricyclane [8], or alkyldiene [9]. The central metal atom is coordinatively unsaturated, and might be expected to accept an additional ligand or ligands in or from the solvent.

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An attractive feature of these complexes lies in their unique structure, as shown below, where X is a substituent,



Since the first report on a cyclopentadienyl complex $[\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CF}_3)_2)]$, the electronic structure of the metalladichalcogenolene has been controversial [10]. The actual structure can best be visualized as a resonance hybrid of two extreme olefinic and dithioketonic forms of the structure given above. The “metalladichalcogenolene ring”, which involves one metal cation, two ligating chalcogen atoms, and a carbon-carbon bond, is responsible for the interesting physicochemical properties and reactivity of the chelates. The central Co atom has an unoccupied d orbital which makes these complexes function as catalysts [6,7]. They also exhibit interesting chemical [8] and electrochemical properties [11–13]. The effects of the substituents and chalcogen atoms have been examined for a number of this class of compounds in acetonitrile by electrochemical techniques and NMR spectroscopy [11].

In the present paper, two typical complexes of this class, (η^5 -cyclopentadienyl)(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III) and (η^5 -cyclopentadienyl)(1,2-di(4-pyridyl)-1,2-ethylenedithiolato)cobalt(III) were selected to study the electrochemical aspects of these compounds in the ambient temperature molten salt. We focus our attention on voltammetric examinations in the melts, and compare the electrochemical responses of these two complexes to those in acetonitrile solutions.

2. Experimental details

2.1. Materials

(η^5 -Cyclopentadienyl)(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III) ($\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$) was prepared by the method given in Ref. 14. (η^5 -Cyclopentadienyl)(1,2-di(4-pyridyl)-1,2-ethylenedithiolato)cobalt(III) ($\text{Co}(\text{cp})(\text{S}_2^4\text{C}_2\text{Py}_2)$) was synthesized according to the procedure described in Ref. 15. The complexes were identified on the basis of IR, NMR (^1H and ^{13}C), and mass spectra.

The synthesis and purification of AlCl_3 and ImCl were performed as previously described [16,17]. Four melts with composition 0.6:1.0, 0.8:1.0, nominally 1.0:1.0 (slightly basic in fact), and 1.5:1.0 were employed. $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ readily dissolved in basic and neutral melts to give a violet solution that was stable for months; $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ displayed a dark-orange color when dissolved in basic and neutral melts.

Both complexes produced unidentified species in the 1.5:1.0 acidic melt, and showed null waves on voltammograms. Hence, the cyclic voltammetric characterization for both complexes as a function of melt composition was restricted to basic and neutral melts.

2.2. Measurements

Cyclic voltammetry (CV) was performed using a PARC Model 273 potentiostat. A Houston Ommigraph Model 2000 x - y recorder was employed for recording cyclic voltammograms. Normal pulse (NP) voltammetry was carried out using a PARC Model 273 potentiostat with a computer-controlled system as describe previously [18].

The electrochemical cell was assembled by fitting a glass bottle, having a volume of about 25 cm^3 , with a Teflon cap which served to introduce the three-electrode system. The working electrode was a glassy carbon disk (Bioanalytical System) with an area of 0.071 cm^2 . A Pt flag was used as a counter electrode. Aluminum wire immersed in a 1.5:1.0 AlCl_3 - ImCl melt was employed as a reference electrode. All potential values reported are referred to this reference electrode.

Electrochemical measurements were carried out in a Vacuum Atmospheres Co. dry box under a purified nitrogen atmosphere. Oxygen and water levels were maintained below 2 ppm, as tested by a bulb with its tungsten filament exposed to the dry box atmosphere. All experiments were performed at a temperature of ca. 30°C , controlled with a Selectrol Thermo Electric temperature controller in an aluminum heating block which contained the cell.

3. Results and discussion

3.1. Cyclic voltammetric results

Figure 1 shows the cyclic voltammetric response of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ in a 0.8:1.0 melt at various scan rates. The redox couple at E_{pa1} , -0.11 V , E_{pc1} , -0.17 V , results from the Co^{III} - Co^{II} couple in the complex. The separation of the cathodic and anodic peaks was 60 mV with no pronounced change with scan rate from 50 mV s^{-1} to 500 mV s^{-1} . The 1:1 relationship of the cathodic to anodic peak current was obtained and the peak current was proportional to the square root of the scan rate. Thus, the reduction process of Co^{III} to Co^{II} is Nernstian. The apparent formal potential, ($E^{0'} = (E_{\text{pa1}} + E_{\text{pc1}})/2$), shifted about 10 mV from the most basic to the neutral melts. $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ also shows an irreversible anodic peak at a potential of 0.75 – 0.80 V . The peak potential shifted slightly positive with increasing scan rate and melt acidity. The small, and ill-defined, cathodic peaks at more negative

potential may involve some adsorption processes or other complexities, and were not examined further. Unlike the complex with CN as the substituent, $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ with a weaker electrophilic substituent, 4-pyridyl, gave voltammetric responses in a 0.8:1.0 melt as shown in Fig. 2(A). Peak potentials of -0.30 V, cathodic, and -0.24 V, anodic, for the $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ couple were found, resulting in an apparent formal potential of -0.27 V and a peak potential difference of 60 mV. A shift of *ca.* 20 mV of $E^{0'}$ in the positive direction was observed in going from the 0.6:1.0 melt to the 1.0:1.0 melt. As expected, the $E^{0'}$ value is more negative than that of the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2\text{(CN)}_2)$ complex. The redox peak potentials and peak currents for $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ shown in Fig. 2(A) have the same characteristics as those in Fig. 1 for the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2\text{(CN)}_2)$ complex, indicating that the reduction of Co^{III} to Co^{II} in the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ complex is also a diffusion-controlled Nernstian electrode process. However, the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ complex exhibits a quasi-reversible oxidation peak at more positive potentials. The estimated apparent formal potential has a value of 0.68 V, based on $E_{\text{pa}2} = 0.74$ V and $E_{\text{pc}2} = 0.62$ V at a scan rate of 50 mV s^{-1} . The reversibility for the oxidation of these two complexes in these melts is opposite to that in acetonitrile, as observed by Ushi-

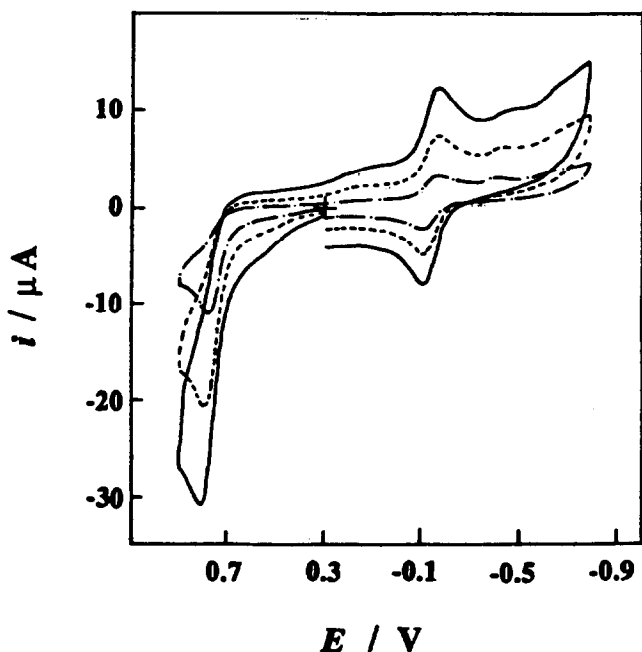


Fig. 1. Cyclic voltammometric responses of $3.08 \text{ mmol dm}^{-3}$ $\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$ in a 0.8:1.0 melt. Scan rate (mV s^{-1}): (dash-dotted) 50, (dashed) 200, (solid) 500.

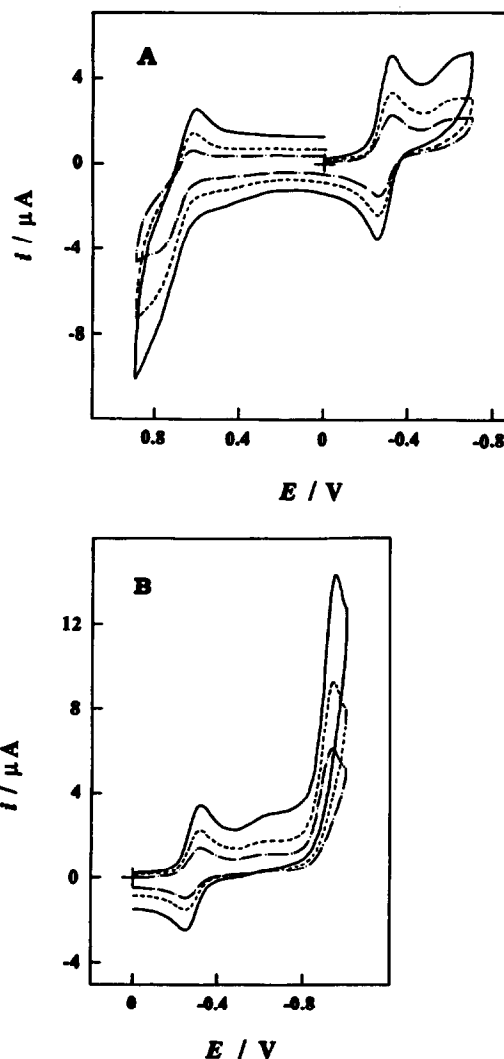


Fig. 2. Cyclic voltammometric responses of $1.80 \text{ mmol dm}^{-3}$ $\text{Co}(\text{cp})(\text{S}_2^4\text{C}_2\text{Py}_2)$ in a 0.8:1.0 melt. (A) Potential range 0.9– -0.7 V; (B) potential range 0.0– -1.0 V. Scan rate: (mV s^{-1}): (dash-dotted) 50, (dashed) 100, (solid) 200.

jima *et al.* [11], where the oxidation peak of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ showed quasi-reversible features, while that for $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ gave an irreversible oxidation peak. Comparison of the potential values of the two complexes in these melts and in acetonitrile solutions is shown in Table 1. The absolute values of the potentials shown between the melts and acetonitrile differ because of the use of different reference electrodes in the two solvents and the differences in the solvents themselves. It is thus the difference in the formal potentials between the two solvents that is of interest here. The difference of the formal potential values between the two complexes in the melts is smaller (0.15–0.16 V) than that in acetonitrile (0.44 V). These phenomena will be discussed later. In addition,

TABLE 1. Comparison of half-wave potentials for $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ and $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ complexes in melt and acetonitrile system ^a

System	$E_{1/2}^r(\text{CN})/\text{V}$	$E_{1/2}^r(\text{Py})/\text{V}$	$E_{1/2}^{\text{ox}}(\text{CN})/\text{V}$	$E_{1/2}^{\text{ox}}(\text{Py})/\text{V}$
0.6:1.0 melt ^b	-0.13	-0.29	ir ^d	0.67
0.8:1.0 melt	-0.13	-0.28	ir	0.68
1.0:1.0 melt	-0.12	-0.27	ir	^e
acetonitrile ^c	-0.59	-1.03	0.73	ir

^a $E_{1/2}^r(\text{CN})$ and $E_{1/2}^r(\text{Py})$ are reduction half-wave potentials for $\text{Co}^{\text{III}}-\text{Co}^{\text{II}}$; $E_{1/2}^{\text{ox}}(\text{CN})$ and $E_{1/2}^{\text{ox}}(\text{Py})$ is the oxidation half-wave potentials for the ligand. ^b Potentials in melts are measured against Al in a 1.5:1.0 melt at 30°C. Glassy carbon disk working electrode. ^c Potentials are referred to $\text{Ag}/0.1 \text{ mol dm}^{-3} \text{ AgCl}$ in acetonitrile at 25°C. Pt disk working electrode. ^d Irreversible. ^e Ill-defined wave.

a surprisingly large reduction peak occurred at about -0.93 V, which is shown in Fig. 2(B). This wave was not examined further.

3.2. Normal pulse voltammetric responses

More detailed electrochemical characterization for both complexes was performed using normal pulse voltammetry. Figure 3 shows NP voltammograms for the reduction of Co^{III} to Co^{II} in the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ complex obtained in a 0.8:1 melt at pulse widths of 20, 40, 60, 100 and 200 ms. Those voltammograms were fitted to a theoretical model for a simple reversible one-electron transfer reduction using the cool algorithm [19]. Plots of the limiting current i_l vs. $t_p^{-1/2}$ for NP voltammograms obtained in the 0.6:1.0, 0.8:1.0 and 1.0:1.0 melt all show good linear behavior and pass close to the origin, as displayed in Fig. 4.

Similar experiments were performed for $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ in the 0.6:1.0, 0.8:1.0, and 1.0:1.0 melt. Figure 5 shows typical NP voltammograms for $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ in a 0.8:1 melt that were fitted to a re-

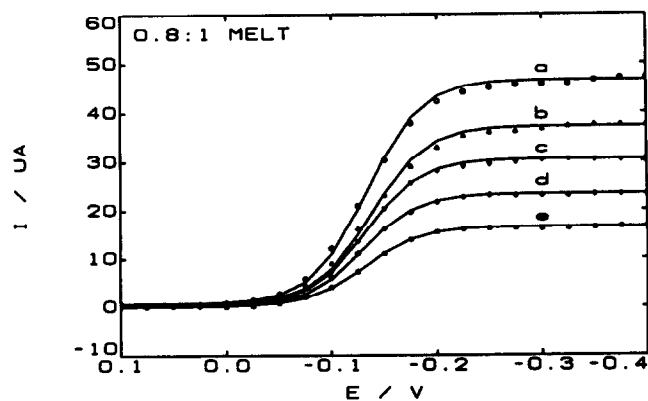


Fig. 3. Normal pulse voltammograms for the reduction of Co^{III} in $\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$ complex. t_p (ms): (a) 20; (b) 40; (c) 60; (d) 100; (e) 200. Curve fitted to cool algorithm is shown by solid lines. Other conditions are as in Fig. 1.

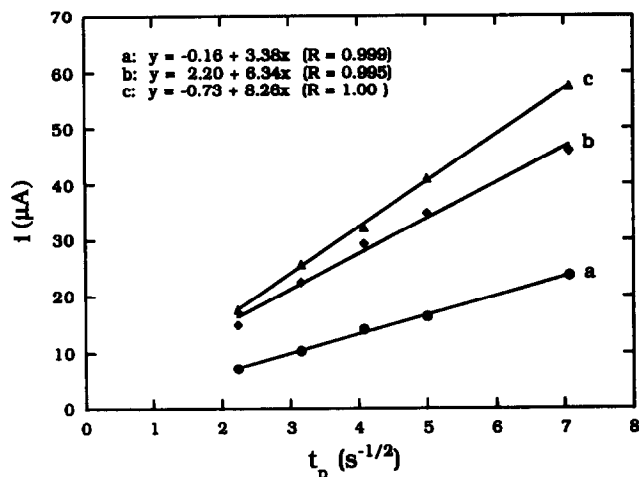


Fig. 4. Plots of the limiting current of NP voltammograms vs. $t_p^{-1/2}$ for the reduction of $3.08 \text{ mmol dm}^{-3} \text{ Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$ complex. Melt composition: (a) 0.6:1.0, (71.55 cP); (b) 0.8:1.0, (29.15 cP); (c) 1.0:1.0 (15.14 cP).

versible one electron reduction model as in Fig. 3. Similarly, the plot of i_l vs. $t_p^{-1/2}$ is linear. Thus, we conclude that the reduction of the Co^{III} to Co^{II} is a diffusion-controlled Nernstian process for both complexes. The diffusion coefficients (D) calculated from the slope of those lines, and other related parameters, such as the $\eta D/T$ product, the Stokes radii, estimated using the Stokes-Einstein equation and the viscosity of the melts [20] etc., are summarized in Table 2. It can be seen that the Stokes radius for the $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ complex is quite constant in the 0.8:1.0 and 1.0:1.0 melts, whereas, in the 0.6:1 melt, it shows a slightly larger value, which may be interpreted in terms of the solvated state of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ in the more basic melts. The larger Stokes radius of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ in basic melts is surprising. Two possible explanations are suggested.

The 1,2-ethylenedithiolatocobalt(III) complexes with a η^5 -cyclopentadienyl ligand have an unoccupied d orbital on the cobalt atom that can combine with a Lewis base to form adducts [21]. In our case, because of the strong electrophilic properties of both cyano and 4-pyridyl (the former is more electrophilic than the latter) substituents on the dithiolene ring, the central atom is expected to be positively charged. Thus, a strong Lewis base chloride in the melts, can more easily attack the vacant cobalt orbital. Formation of the bond between the cobalt and chloride would reduce the electrophilic character of both cyano and pyridyl groups on the central metal, and bring them closer together. Thus, the difference between the formal potentials would be reduced. This, however, does not explain the difference between the Stokes radii for the two complexes.

TABLE 2. Diffusion coefficients and Stokes radii of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ and $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ complexes in melts ^a

Melts	Method	C (mmol dm^{-3})	η (cP)	D ($10^{-7} \text{ cm}^2 \text{ s}^{-1}$)	$\eta D/T$ ($10^{-10} \text{ g cm s}^{-2} \text{ K}^{-1}$)	r (nm) ^b
0.6:1.0(CN)	NP	3.08	71.55	0.81	1.91	0.38
0.8:1.0(CN)	NP	3.08	29.15	2.86	2.76	0.26
0.8:1.0(CN)	RDE	3.00	29.15	3.00	2.89	0.25
1.0:1.0(CN)	NP	3.10	15.48	4.86	2.48	0.29
0.6:1.0(Py)	NP	1.77	71.55	0.23	0.54	1.34
0.8:1.0(Py)	NP	1.80	29.15	0.68	0.65	1.11

^a (CN) and (Py) are referred to $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ and $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ respectively. ^b Calculated from the Stokes-Einstein eqn. $r = kT/6\pi\eta D$, 30°C.

Another explanation seems more reasonable. Acetonitrile solutions of the complex with 4-pyridyl substituent are blue in color; however, in the basic and neutral melts the complex is a dark-orange color as mentioned above. The color change may be explained on the basis of an interaction between the nitrogen atom on the 4-pyridyl group and some species, presumably the Im^+ cation in the melts. Such an interaction would increase the electrophilic character of the 4-pyridyl group and change the color. In fact, the color of the complex with the 4-pyridyl group depends on the acidity of the solvent. For example, the complex is blue in neutral and basic aqueous solution but reddish orange in strongly acidic solutions. Essentially, the complex is acting as an indicator.

The latter interactions also offers a reasonable explanation for the large difference of the Stokes radii between the complexes with and without the 4-pyridyl group. The Stokes radii of the complexes with cyano or 4-pyridyl groups in 0.1 mol dm^{-3} TEAP-acetonitrile solution are 0.344 nm and 0.570 nm respectively, as obtained by hydrodynamic voltammetry using a rotating platinum disk electrode at 25°C; the difference of

the Stokes radii between the complexes with CN and ⁴Py substituents in acetonitrile solution is smaller than that in the melts. The fairly large radius for the 4-pyridyl complex measured in the melt may thus reflect the movement of the complex with solvation by the melt cation.

NP voltammetry for the large anodic peak of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ complex was performed in the 0.6:1.0, 0.8:1.0 and 1.0:1.0 melt. Figure 6 shows typical NP voltammograms obtained in a 0.8:1 melt, a plot of limiting current *vs.* $t_p^{-1/2}$ was linear throughout the basic to neutral melts, though resulting in an intercept on the y-axis, as shown in Fig. 7. NP voltammograms were fitted to a two-electron transfer oxidation for a quasi-reversible process using the COOL algorithm [19]. The apparent electrode-reaction rate constants, estimated by curve fitting of NP voltammograms (at $t_p = 40$ ms) with the COOL algorithm, are $2.8 \times 10^{-4} \text{ cm s}^{-1}$ (0.6:1.0 melt), $4.8 \times 10^{-4} \text{ cm s}^{-1}$ (0.8:1.0 melt) and $1.1 \times 10^{-3} \text{ cm s}^{-1}$ (1.0:1.0 melt), respectively. The rate constants decrease with increasing melt viscosity, which has been noted by others [22,23], and we have observed the same phenomenon in two other systems in these melts [24,25]. The anodic wave may result from the

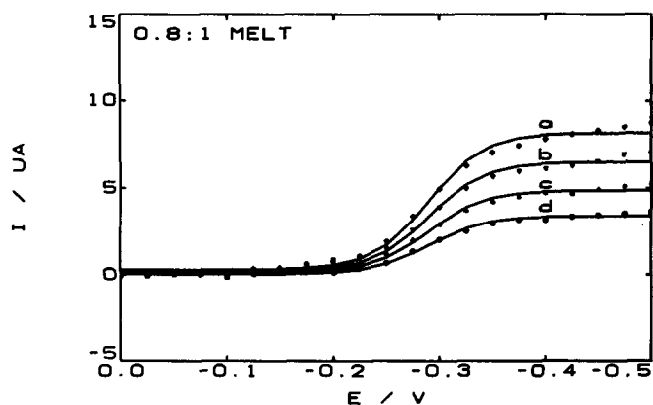


Fig. 5. Normal pulse voltammograms for the reduction of Co^{III} in $\text{Co}(\text{cp})(\text{S}_2^4\text{C}_2\text{Py}_2)$ complex in a 0.8:1.0 melt. t_p (ms): (a) 40; (b) 60; (c) 100; (d) 200. Concentration of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$: $1.80 \text{ mmol dm}^{-3}$.

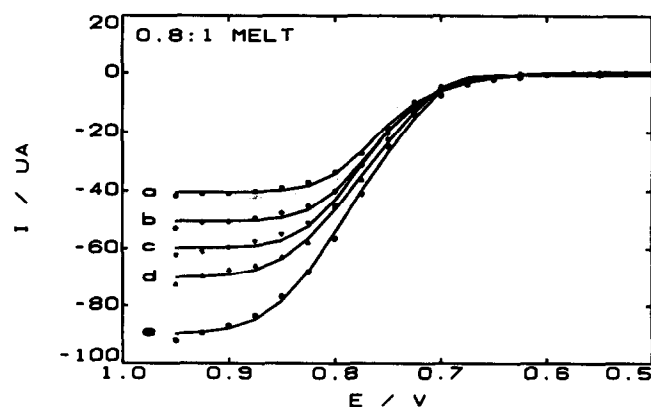


Fig. 6. Normal pulse voltammograms for the oxidation of the $\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$ complex. t_p (ms): (a) 200; (b) 100; (c) 60; (d) 40; (e) 20. Melt composition 0.8:1.0, Concentration: $3.08 \text{ mmol dm}^{-3}$.

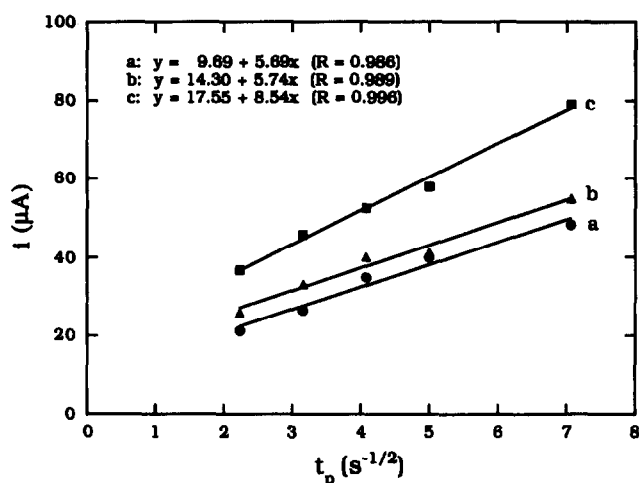


Fig. 7. Plots of the oxidation limiting current of NP voltammograms of $\text{Co}(\text{cp})(\text{S}_2\text{C}_2(\text{CN})_2)$ complex. Melt composition: (a) 0.6:1.0; (b) 0.8:1.0; (c) 1.0:1.0. Concentration of solute: 3.08 (in 0.6:1.0 and 0.8:1.0 melt), 3.10 (in 1.0:1.0 melt) mmol dm^{-3} .

oxidation of the metalladithiolene moiety in the complexes. In acetonitrile solutions, Kajitani and coworkers [11,12] reported that $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$ showed a reversible one-electron oxidation process that was assumed to result from the oxidation of the metalladithiolene moiety, and the oxidation of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ showed very complicated voltammograms consisting of several overlapping irreversible oxidation steps. In addition, the $\text{Ni}(\text{Ph}_2\text{C}_2\text{S}_2)_2$ complex also gave a quasi-reversible one-electron oxidation wave in dichloromethane solution [26]. Further, the electron density on the cyclopentadienyl ring should be low because of the electron-withdrawing effect of the substituents on the dithiolene ring. Another possibility is that it is the cyclopentadienyl ring that is oxidized. This possibility is based on our previous work in the melt, where the large oxidation peak after the oxidation of ferrocene to ferrocenium cation was considered to be a four-electron transfer oxidation for two cyclopentadienyl rings [27].

NP voltammograms for the oxidation of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$ were not analyzed owing to the poorly defined waves. Similar to the case of $\text{Co}(\text{cp})(\text{C}_2\text{S}_2(\text{CN})_2)$, the oxidation peak in Fig. 2 is assumed to correspond to the oxidation of the metalladithiolene ring in $\text{Co}(\text{cp})(\text{C}_2\text{S}_2^4\text{Py}_2)$. The fairly large reduction peak at the more negative potential might be attributable to the reduction of metalladithiolene moiety. This suggestion is based on the work conducted by Boyd *et al.* [26] who studied the ligand reduction in $\text{Ni}(\text{Ph}_2\text{C}_2\text{S}_2)_2$ complexes. It should be pointed out that in our case the fairly large reduction peak current compared to that of $\text{Co}^{\text{III}}\text{-Co}^{\text{II}}$ may involve multi-

electron transfer processes or other complicated kinetics, leading to the decomposition of the complex.

4. Conclusions

Both $(\eta^5\text{-cyclopentadienyl})(1,2\text{-dicyano-1,2-ethylenedithiolato})\text{cobalt(III)}$ and $(\eta^5\text{-cyclopentadienyl})(1,2\text{-di(4-pyridyl)-1,2-ethylenedithiolato})\text{cobalt(III)}$ complexes are stable in the neutral and basic melts, but unstable in the acidic melt. The reduction half-wave potentials of Co^{III} in both complexes shift from -0.13 V to -0.12 V, and -0.29 V to -0.27 V, from the 0.6:1.0 to 1.0:1.0 melt for the CN- and 4-pyridyl-substituted complexes respectively. The anodic process may result from the oxidation of the metalladithiolene moiety, whereas the pronounced larger reduction peak for 4-pyridyl-substituted complex may involve multi-electron transfer processes in the metalladithiolene ring, leading to the decomposition of the complex.

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