APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 5, 221–228 (1991)

Syntheses and electrochemical behaviour of novel dmit or dmio (dithiolato) cobalt(III) complexes with a η^5-cyclopentadienyl or η^5-pentamethylcyclopentadienyl ring

Hirobumi Ushijima, Susumu Sudoh, Masatsugu Kajitani, Kunio Shimizu,
Takeo Akiyama and Akira Sugimori*
Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho,
Chiyoda-ku, Tokyo 102, Japan

Four novel cobalt(III) complexes with a cyclopentadienyl or pentamethylcyclopentadienyl ring and dmit or dmio ligands were synthesized, and their electrochemical behaviour was investigated. All these complexes exhibited three one-electron transfer steps: one reduction and two oxidation steps. In addition, a novel organosulphur compound was afforded by electrochemical oxidation of dmit cobalt complex. Thus, these complexes may have considerable synthetic potential as precursors for electron reservoirs and organosulphur compounds.

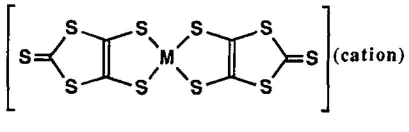
Keywords: dmit, dmio, metal complexes, cyclopentadienyl, cobalt(III) complex, cyclic voltammetry, controlled potential coulometry, electron reservoir, sulphur-rich organic electron donor

INTRODUCTION

Multinuclear organometallic complexes can exhibit mono- or multi-step electron transfer.[1] Mononuclear organometallic complexes with electron-rich or electron-poor ligands can be expected to exhibit electron transfer in a manner similar to multinuclear organometallic complexes. Recently, the conductive behavior of organometallic complexes with 1,2-dithiolato ligands has attracted interest.[2] The dmit (1,3-dithiole-2-thione-4,5-dithiolato) ligand is a class of 1,2-dithiolato ligand, the most attractive ligand in the field of conductive organometallic complexes.[3] Especially, Langmuir–Blodgett films of tridecylmethylammonium gold(dmit)$_2$ exhibit remarkable conductivities at room temperature.[4] By appropriate selection of the central metal and the counter-cation, dmit complexes which exhibit room-temperature conductivities and metallic behaviour have been prepared.[5]

The semiconductive, metallic and superconductive behaviour of symmetrical bis-dmit complexes (Scheme 1) has been of interest to many investigators, but mixed-ligand dmit complexes have been studied in only a few cases.[6–8] There is only one report concerning the synthesis of an organometallic complex with a cyclopentadienyl ring and dmit ligand.[8] The reported organometallic complex with a cyclopentadienyl ring and dmit ligand, [Ti(cp)$_2$(dmit)], was interesting from the viewpoint of its synthetic potential as a precursor for novel organosulphur compounds. The electrochemical behaviour of this organometallic complex with a cyclopentadienyl ring and dmit ligand has not been studied to date.

The present paper is an extension of our preliminary note[9] on the electrochemical behaviour of two novel (η^5-cyclopentadienyl)(dmit)cobalt(III) complexes (Scheme 2). The purpose of this study is to determine their synthetic potential as precursors for conductive organometallic complexes and for organosulphur electron donor compounds by investigating their electrochemical behaviour.



(cation)[M(dmit)$_2$]
(M = Ni, Pd, Pt, *etc.*)

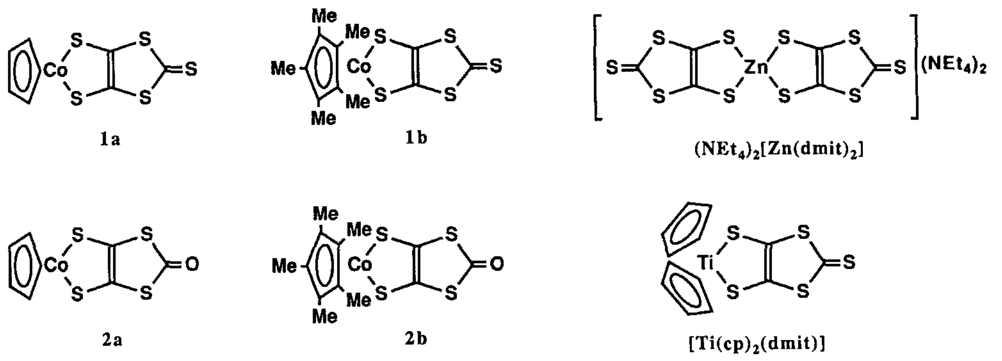
Scheme 1

---

* Author to whom correspondence should be addressed.

0268-2605/91/040221-08$05.00

Received 8 March 1991
Revised 25 April 1991



Scheme 2

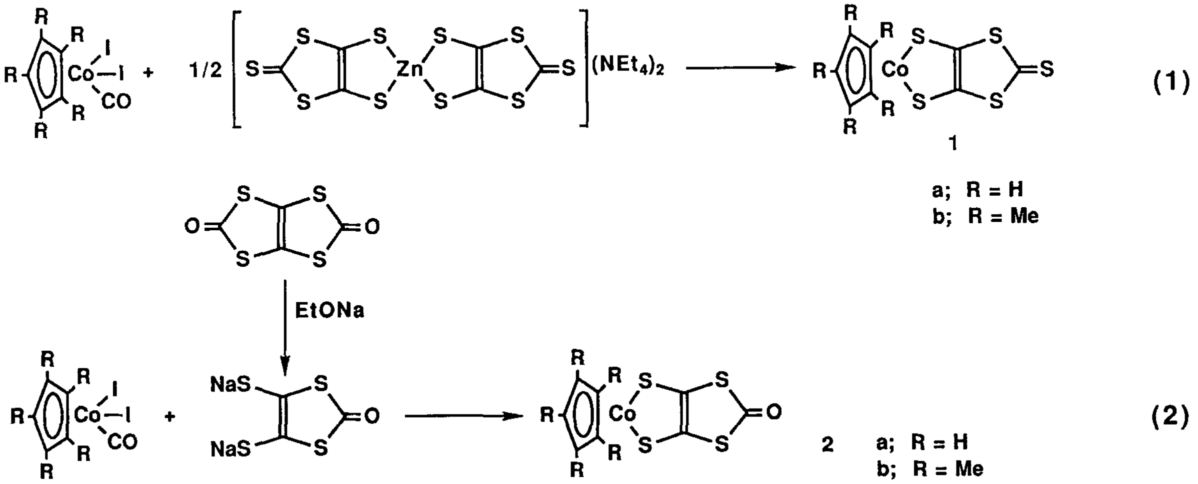
EXPERIMENTAL

Materials

The treatment of $[CoI_2(cp)(CO)]$ with $(NEt_4)_2[Zn(dmit)_2]$ in stirred methanol resulted in a colour change from red to green. After 1 h the resulting solution was passed through a silica gel chromatographic column to afford dark green crystals of [Co(cp)(dmit)] (**1a**) in 81 % yield [MS 70 eV), *m/z* (rel. intensity) 320 (M^+, 80.3), 168(100), 124(71.5); ^{1}H-NMR ($CDCl_3$) $\delta = 5.45$ (s, 5H, cp).[9] When $[CoI_2(cp^*)(CO)]$ (cp* = pentamethylcyclopentadienyl) is used instead of $[CoI_2(cp^*)(CO)]$ (cp* = pentamethylcyclopentadienyl) is used instead of $[CoI_2(cp)(CO)]$ in the treatment, [Co(cp*)(dmit)] (**1b**) was produced in 72% yield [MS (70 eV), *m/z* (rel. intensity) 390 (M^+, 100), 238(82.8), 133(58.0)).[9]

After the treatment of $[CoI_2(cp)(CO)]$ with 1,3,4,6-tetrathiapentalene-2,5-dione with sodium ethoxide in stirred ethanol, the resulting solution was passed through a silica gel chromatographic column to afford dark green crystals of [Co(cp)-(dmiol)] (**2a**). By using $[CoI_2(cp^*)(CO)]$ instead of $[CoI_2(cp)(CO)]$ in the above treatment, [Co(cp*)(dmiol)] (**2b**) was obtained (Scheme 3).

Tetraethylammonium perchlorate (TEAP) of special polarographic grade (Nakarai Chemicals Co. Ltd) was used as the supporting electrolyte. Silver perchlorate for the reference electrode was prepared by recrystallizing the guaranteed reagent grade salt (Aldrich Chemical Co. Inc.) from



Scheme 3 Preparations of dmit or dmio complexes.

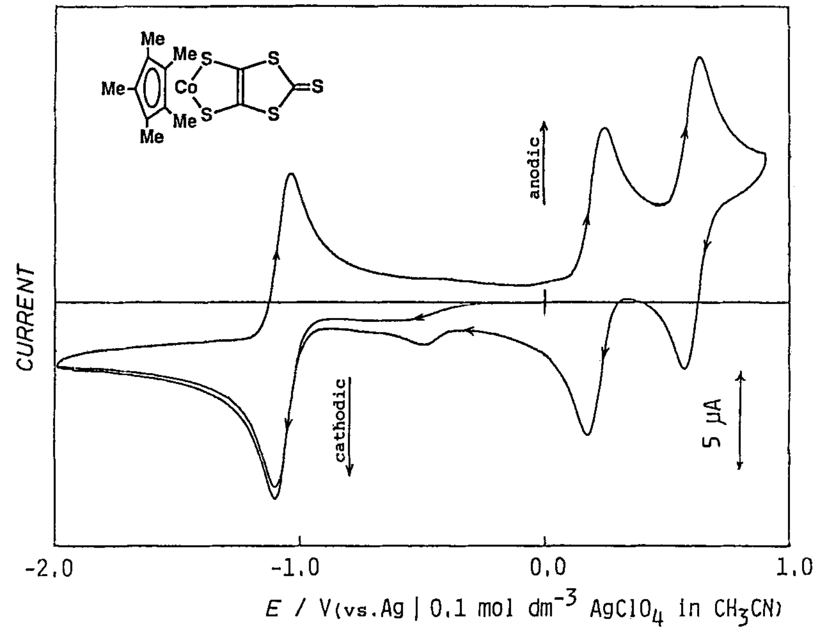


Figure 1 Cyclic voltammogram of **1b**; scan rate = 100 mV s^{-1}.

water and by vacuum-drying the crystals in the dark at room temperature for five days, then at 50 °C for two days. Acetonitrile was purified as described earlier.[14] Deuterochloroform (Aldrich Chemical Co. Inc.) was used as the solvent for NMR measurements. Other chemicals were of reagent grade.

Measurement

Normal pulse, hydrodynamic and cyclic voltammograms were recorded on a Huso polarograph Model 312 equipped with a Riken Denshi *X*–*Y* recorder Model F-42DG and a Huso potential scanning unit Model 321. When hydrodynamic

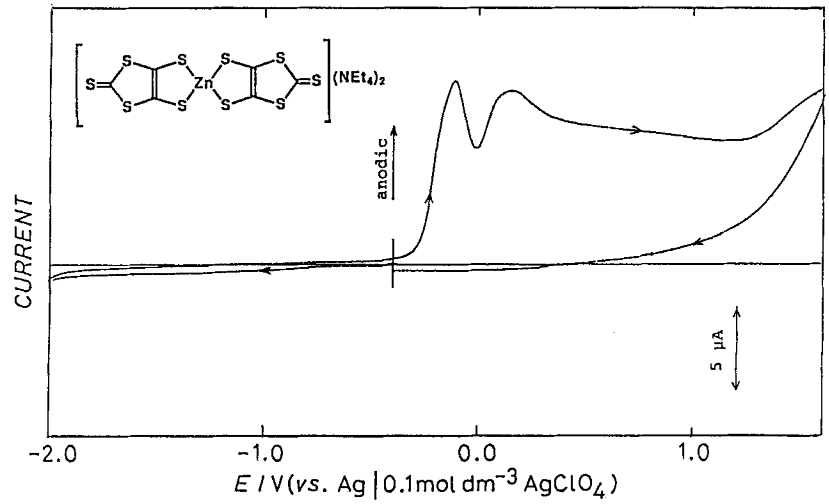


Figure 2 Cyclic voltammogram of $(NEt_4)_2[Zn(dmit)_2]$; scan rate = 100 mV s^{-1}.

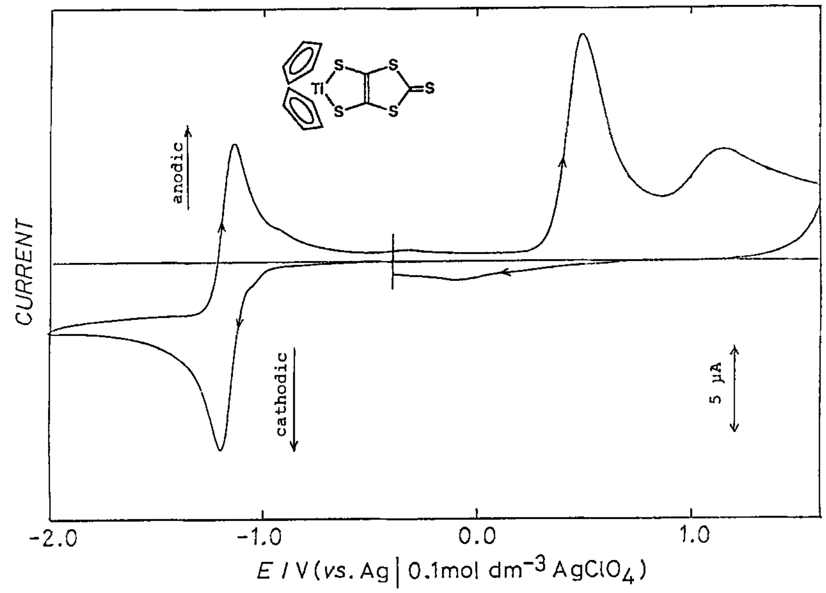


Figure 3 Cyclic voltammogram of [Ti(cp)$_2$(dmit)]; scan rate = 100 mV s^{-1}.

voltammetry was performed with a rotating platinum disc electrode, a Nikko Keisoku Motor Speed Controller SC-5 was used. All the electrochemical measurements were carried out in 0.1 mol dm^{-3} TEAP–acetonitrile solutions at 25 °C under an argon atmosphere. A platinum disc (2 mm diameter) embedded in poly(tetrafluoroethylene) was used as the stationary or rotating test electrode, and a spiral of platinum wire served as the auxiliary electrode. The reference electrode was a silver–silver ion electrode, Ag|0.1 mol dm^{-3} AgClO$_4$ in acetonitrile. All the potentials cited here are referred to this electrode. The reversible half-wave potential of the ferricinium–ferrocene couple in acetonitrile solution, $E^{r}_{1/2}(FcH^+/FcH)$, at 25 °C was 0.025 V against this reference electrode. Platinum gauze was used as the working electrode for controlled-potential coulometry.

The ^{1}H- and ^{13}C-NMR spectra at ambient temperature were obtained with a JEOL JNM GX-270. All the chemical shifts (δ) were referred to tetramethylsilane as the internal standard.

Mass spectra were obtained on a JEOL JMS-D300 (EI; 70 eV) spectrometer.

Table 1 Reversible half-wave potentials[a] of dmit and dmio complexes

Computer	Reduction	Oxidation 1st	Oxidation 2nd
1a	−0.794	0.388	0.680
1b	−1.076	0.211	0.605
2a	−0.863	0.427	0.694
2b	−1.153	0.285	0.630

[a] In *V* (vs Ag|0.1 mol dm^{-3} AGClO$_4$ in acetonitrile), reversible half-wave potentials determined by logarithmic plot analysis of the hydrodynamic voltammograms or normal pulse voltammograms.

RESULTS AND DISCUSSION

Voltammetry

Cyclic voltammetric studies confirmed that both **1** and **2** undergo a reversible reduction process and two reversible oxidation processes (a typical cyclic voltammogram is presented in Fig. 1). The dmit complexes with other metals such as (NEt$_4$)$_2$[Zn(dmit)$_2$] and [Ti(cp)$_2$(dmit)] showed complicated oxidation waves with subsequent chemical processes. The reduction of the titanium complex proceeded as a reversible one-electron process without any complication (Figs 2 and 3). In the case of (η^5-cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedithiolato)cobalt(III) complexes which have both a cyclopentadienyl ring and a 1,2-ethylenedithiolato ligand, one reversible reduction wave and one reversible or quasi-reversible oxidation wave were exhibited on the cyclic voltammograms. Although **1** and **2** are analogues of (η^5-cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedithiolato)cobalt(III) complexes, they have two reversible or two quasi-reversible oxidation processes.

The cyclic voltammogram of **1b** (Fig. 1) showed that the reduction step occurs in a reversible one-electron transfer process. Each anodic peak current of the first and second oxidation steps is equal to the cathodic peak current of the reduction step. Analyses of normal pulse and hydrodynamic voltammograms for **1b** reveal that the reduction is a Nernstian one-electron process with the limiting currents controlled by diffusion or convective diffusion, and that the first and second oxidation steps of **1b** are also Nernstian one-electron processes with the limiting current controlled by diffusion or convective diffusion, but they have some subsequent chemical reactions. The two-step oxidation processes and the following reactions are discussed later.

All reversible half-wave potentials of **1b** are more negative than those of **1a** (Table 1). These negative shifts of the half-wave potentials of **1b** can be explained by the fact that the electron-donating effect of the five methyl groups at the cyclopentadienyl (cp) ring is greater than that of hydrogen. The reported ESR data for the reduced form of the (η^5-cyclopentadienyl)(1,2-dicyano-1,2-ethylenedithiolato)cobalt(III) complex suggested that the reversible reduction of the (η^5-cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedithiolato)cobalt(III) complexes can be ascribed to the reduction of Co(III) to Co(II).[10-13] The difference in the reversible half-wave potentials of the reduction steps between **1a** (with cp) and **1b** (with cp*) (282 mV) is larger than those in the first and second oxidation steps (177 mV and 75 mV).

Similarly, in the case of the complexes with the dmio ligand, **2a** (with cp) and **2b** (with cp*), the difference in the half-wave potentials of the reduction step between **2a** and **2b** (290 mV) is larger than that in the first and the second oxidation steps (142 mV and 64 mV).

The effect of replacing cp by cp* on the half-wave potentials is greater in the reduction step than in the oxidation steps. This result is explained by hypothesizing that the reduction site is the central cobalt, while the oxidation sites are the dmit ligands. The dmit ligand is farther away from cp or cp* than the cental cobalt, and it is affected less by cp and cp*. A similar effect is observed for the complexes in which dmit ligand

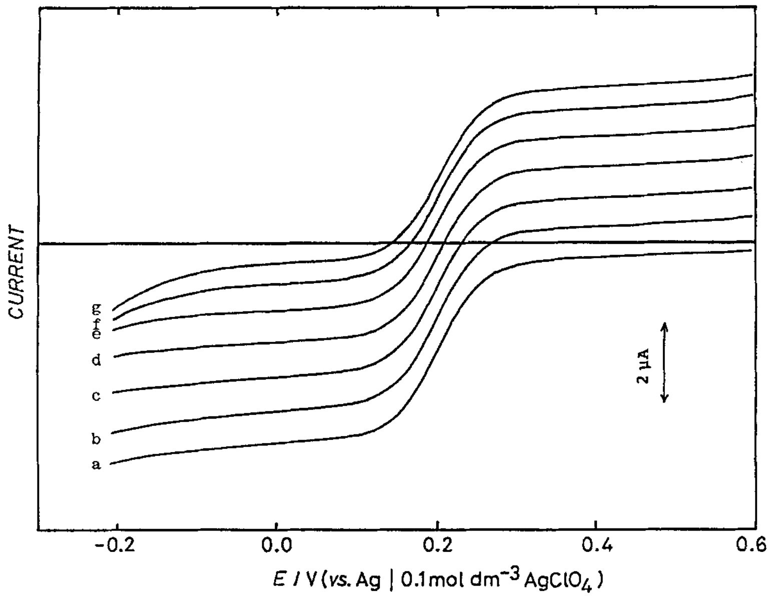


Figure 4 Change of hydrodynamic voltammograms for electrolytic reduction of **1a**; electrolytic potential = −1.0 V; quantity of electricity (C) = (a) 0.0, (b) 0.4, (c) 0.8, (d) 1.2, (e) 1.6, (f) 2.0, (g) 2.4.

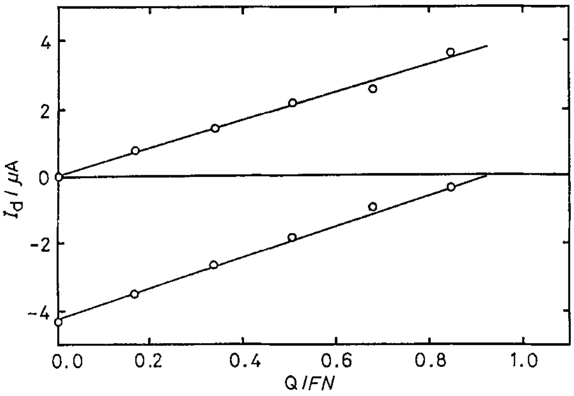


Figure 5 I_d vs Q plot for electrolytic reduction of **1a**.

is replaced by dmio ligand.

The two dmio complexes, **2**, in which the sulphur atom of the thioketone in the dmit ligand is replaced by oxygen, showed more positive half-wave potentials for the two oxidation steps than the corresponding dmit complexes. These positive shifts of their half-wave potentials for the oxidation steps are thought to be attributable to the fact that oxygen is more electronegative than sulphur. On the other hand, the half-wave potential of the reduction step was more negative than those of the corresponding dmit complexes. These results suggest that the electron-attracting inductive effect of the oxygen atom is transmitted directly to the dithiolato moiety of the dmio ligand, not to the cobalt atom. This observation is important for the analysis of the electronic and molecular structure, especially the coplanarity, of the dmit or dmio ligand.

Coulometry

A solution of **1a** was electrochemically reduced at −1.0 V with a platinum gauze electrode. During the electrolysis, hydrodynamic voltammograms with a rotating platinum disc electrode were recorded intermittently (Fig. 4). As the electrolytic reduction advanced, the limiting current of the cathodic current decreased and the anodic current increased linearly (Fig. 5). The oxidation limiting current for the reduced form, $[Co^{II}(cp)(dmit)]^-$, did not change with time when the electrolysis was suspended for about two hours. These facts confirm that the reduction process is a one-electron reduction to $[Co^{II}(cp)(dmit)]^-$ without any side reaction or consequent reactions. When **1a** was oxidized at the potential of the first oxidation step (0.55 V), the limiting currents of the hydrodynamic voltammograms plotted against the quantity of electricity gave curved lines as seen in Fig. 6 and Fig. 7. The increase in cathodic

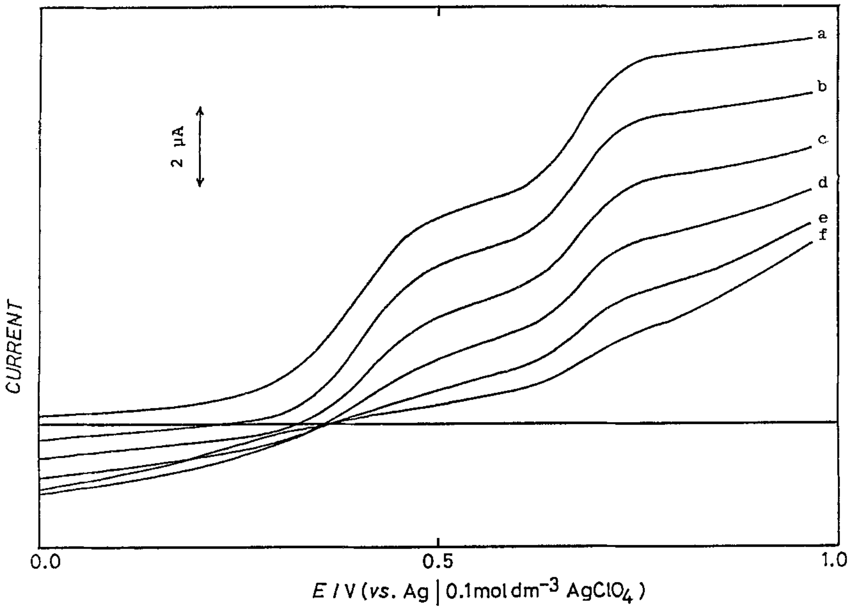


Figure 6 Change of hydrodynamic voltammograms for electrolytic oxidation of **1a**; electrolytic potential = 0.55 V; quantity of electricity (C) = (a) 0.0, (b) 0.5, (c) 1.0, (d) 1.5, (e) 2.0, (f) 2.4.

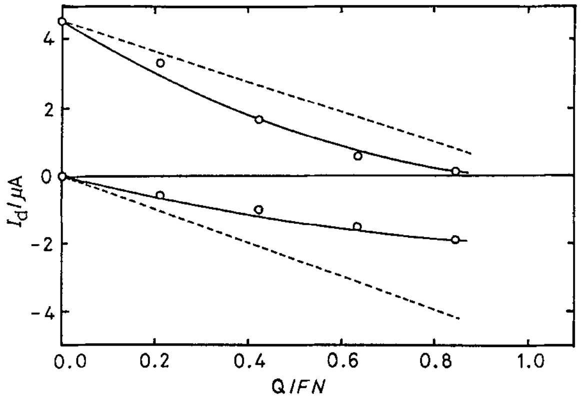


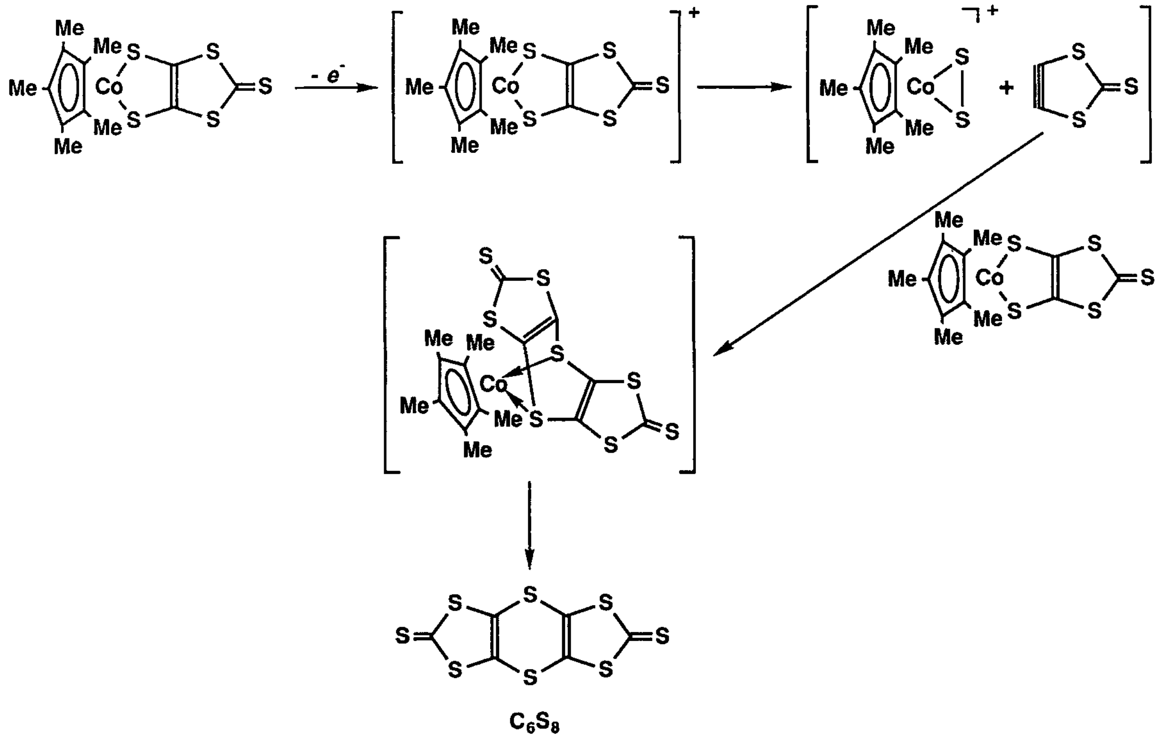
Figure 7 I_d vs Q plot for electrolytic oxidation of **1a** (dotted lines represent theoretical one-electron oxidation).

currents was smaller than the decrease in anodic currents. These facts indicate that the one-electron oxidation product, [Co(cp)(dmit)]$^+$, reacted with the original complex, [Co(cp)(dmit)], to afford the electro-inactive substance.

Controlled potential coulometry of **1b** revealed that the one-electron reduction product is less stable than that of **1a**. In contrast, the oxidation product of **1a** is less stable than that of **1b**. A yellow insoluble solid was deposited on the working electrode by electrolytic oxidation of **1b** at the first oxidation potential (0.4 V). High-resolution MS of the yellow solid showed a peak for the parent ion which was attributable to C_6S_8 (Found: m/z 327.7767; Calcd for C_6S_8: M, 327.7766). An EC mechanism is postulated for the electrolytic oxidation process in Scheme 4. The highly reactive intermediate, produced in the one-electron oxidation form, reacted with the original complex to afford the electro-inactive organosulphur compound. This result also supports the conclusion that the oxidation site of the first step is in the cobaltadithiolene ring, and the oxidation of the second step is in the 1,3-dithiole-2-thione ring.

CONCLUSION

Both dmit and dmio cobalt(III) complexes exhibited three one-electron transfer steps, in spite of the fact that the complexes have only one metal. These results suggest that these complexes



C_6S_8

Scheme 4 Proposed EC mechanism for electrolytic oxidation process of **1b**.

may be able to store and transfer electrons stoichiometrically or catalytically without decomposition. Thus, these complexes could be used as molecular electron reservoirs.

The organosulphur compound, produced by electrochemical oxidation of the dmit cobalt(III) complex might be a sulphur-rich organic electron donor, as is TTF or BEDT–TTF. (TTF, tetrathiafulvalene; BEDT-TTF, leis(ethylenedithio)tetrathiafulvalene.)

REFERENCES

1. Astruc, D, *Acc. Chem. Res.*, 1986, 19: 377
2. Ahmad, M M and Underhill, A E *J. Chem. Soc., Dalton Trans.*, 1982: 1065
3. Kobayashi, A, Kim, H, Sakaki, Y, Kato, R, Kobayashi, H, Moriyama, S, Nishino, Y, Kajita, K and Sakaki, Y *Chem. Lett.*, 1987: 1819
4. Nakamura, T, Kojima, K, Matsumoto, M, Tachibana, H, Tanaka, M, Manda, E and Kawabata, Y *Chem. Lett.*, 1989: 367
5. Hawkins, I and Underhill, A E *J. Chem. Soc., Chem. Commun.*, 1990: 1593
6. Vicente, R, Ribas, J, Solans, X, Font-Altaba, M, Mari, A, de Loth, P and Cassoux, P *Inorg. Chim. Acta*, 1987, 132: 229
7. Matsubayashi, G, Hirao, M and Tanaka, T *Inorg. Chim. Acta*, 1988, 144: 217
8. Yang, X, Rauchfuss, T B and Wilkson, S R *J. Am. Chem. Soc.*, 1989, 111: 3465
9. Ushijama, H, Sudoh, S, Kajitani, M, Shimizu, K, Akiyama, T and Sugimori, A, *Inorg. Chim. Acta.*, 1990, 175: 11
10. McCleverty, J A *Prog. Inorg. Chem.*, 1968, 10: 49
11. Dessy, R E, Stary, F E, King, R B and Waldrop, M *J. Am. Chem. Soc.*, 1966, 88: 471
12. Dessy, R E, King, R B and Waldrop, M *J. Am. Chem. Soc.*, 1966, 88: 5112
13. Kajitani, M, Akiyama, T, Sugimori, A, Hirakata, K, Hoshino, Y, Satsu, Y, Satô, G P, Shimizu, K, Kaise, M and Nishihara, C *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, 251: 421
14. Ushijima, H, Kajitani, M, Shimizu, K, Satô, G P, Akiyama, T and Sugimori, A *J. Electroanal. Chem. Interfacial Electrochem.*, 1991, 303: 199