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LETTER

Syntheses and electrochemical behaviour of novel (η-cyclopentadienyl)(dmit)cobalt complexes

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

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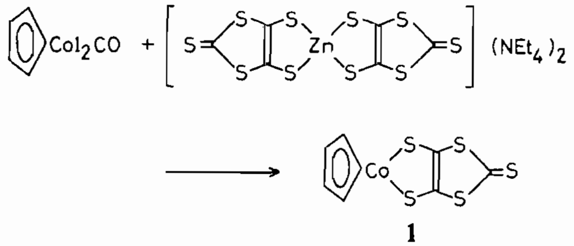
Multi-nuclear organometallic complexes can exhibit multi or multi-step electron transfer [1]. Mononuclear organometallic complexes with electron rich ligands can be expected to exhibit electron transfer in a manner similar to the multi-nuclear organometallic complexes. Recently, the superconductive behaviour of organometallic complexes with the ligand dmit (1,3-dithiole-2-thione-4,5-dithiolato) has attracted interest [2]. But there is only one report about the synthesis of an organometallic complex with a cyclopentadienyl ring and the dmit ligand [3]. In this report we describe the syntheses of two novel types of dithiolato cobalt complexes with the dmit ligand and their unique electrochemical behaviour.

Experimental

Treatment of [Co(cp)I_2CO] (cp = cyclopentadienyl) or [Co(cp*)I_2CO] (cp* = pentamethylcyclopentadienyl) with [Zn(dmit)$_2$](NEt$_4$)$_2$ 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 black–green crystals of [Co(cp)(dmit)] (**1**) in 81% yield and [Co(cp*)(dmit)] (**2**) in 72% yield. These complexes were characterized by MS spectra. [Co(cp)(dmit)] (**1**) MS (70 eV), *m/z* (rel. intensity) 320 (M^+, 80.3), 168(100), 124(71.5); ^{1}H NMR (CDCl$_3$) δ = 5.45 (s, 5H, cp). [Co(cp*)(dmit)] (**2**) MS (70 eV), *m/z* (rel. intensity) 390 (M^+, 100), 238(82.8), 133(58.0).



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All the electrochemical measurements were carried out in acetonitrile solutions containing 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ at 25 °C under an argon atmosphere by a three electrode system consisting of a test electrode (stationary or rotating platinum disk, 2 mm in diameter), a coiled platinum wire counter electrode, and Ag/0.1 mol dm^{-3} AgClO$_4$ in acetonitrile as a reference electrode. Platinum gauze was used as the working electrode for controlled potential coulometry.

Results and discussion

Cyclic voltammetric studies confirmed that both **1** and **2** underwent a reversible reduction process and two reversible oxidation processes (a typical cyclic voltammogram is presented in Fig. 1). In the case of the cobalt complexes with a cyclopentadienyl ring and the 1,2-ethylenedithiolato ligand, one reversible reduction wave and one reversible or one quasi-reversible oxidation wave were exhibited on the cyclic voltammograms. Although **1** and **2** are analogues of the cobalt complexes with a cyclopentadienyl ring and dithiolato ligand, these complexes have two reversible oxidation processes. Normal pulse voltammetry and hydrodynamic voltammetry with a

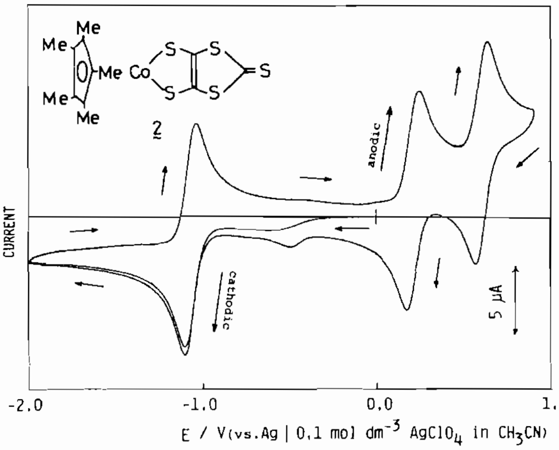

Fig. 1. Cyclic voltammogram of [Co(cp*)(dmit)] (**2**) in acetonitrile solution containing 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ at 25 °C. Reference electrode, Ag/0.1 mol dm^{-3} AgClO$_4$ in acetonitrile; test electrode, stationary platinum disc, 2 mm diameter; scan rate, 100 mV s^{-1}.

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*Author to whom correspondence should be addressed.

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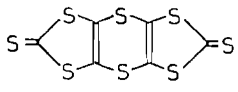
TABLE 1. Reduction and oxidation half-wave potentials of **1** and **2**[a]

Complexes	Reduction $E_{1/2}$ (V)	Oxidation (1st) $E_{1/2}$ (V)	Oxidation (2nd) $E_{1/2}$ (V)
[Co(cp)(dmit)] (**1**)	−0.794	0.388	0.688
[Co(cp*)(dmit)] (**2**)	−1.076	0.211	0.605

[a] E (V) (vs. Ag/0.1 mol dm^{-3} AgClO$_4$ in CH$_3$CN); $E_{1/2}$ as reversible half-wave potentials.

rotating disc electrode for **1** and **2** revealed that the reduction, the first and the second oxidation are nernstian one-electron processes with the limiting currents controlled by diffusion or convective diffusion. The reversible half-wave potentials for both reduction and oxidation processes determined by logarithmic plot analysis of the normal pulse voltammograms or the hydrodynamic voltammograms, are listed in Table 1. All reversible half-wave potentials of **2** are more negative than those of **1**. These negative shifts of half-wave potentials of **2** can be explained by the fact that the electron donating effect of the five methyl groups on the cp ring is greater than that of hydrogen. The reported ESR data for the reduced form of the (η-cyclopentadienyl)(1,2-dicyano-1,2-ethylene-dithiolato)-cobalt(III) complex suggested that the reversible reduction of the (η-cyclopentadienyl)(1,2-disubstituted 1,2-ethylenedithiolato)cobalt(III) complexes can be ascribed to the reduction of Co(III) to Co(II) [4]. The difference between the half-wave potentials of **1** and **2** in the reduction process (282 mV) is larger than those in the first and second oxidation processes (177 and 83 mV). The effect of replacing cp by cp* on the half-wave potentials was greater in the reduction process than in the oxidation processes. The reduction site is the central cobalt, while the oxidation sites are the dmit ligands, because the dmit ligand is farther from cp or cp* than the central cobalt.

Controlled potential coulometry revealed that the one-electron reduction product of **1** is more stable than that of **2**. In contrast with the above result, the oxidation product of **1** is less stable than that of **2**. A yellow insoluble solid was obtained on the working electrode by electrolytic oxidation of **2** at the potential given by the first oxidation wave (0.4 V versus Ag/0.1 mol dm^{-3} AgClO$_4$ in CH$_3$CN). HRMS of the yellow solid showed a peak for the parent ion which was attributable to C_6S_8. Found: m/z 327.7767. Calc. for C_6S_8: M, 327.7766.



C_6S_8

This result also supported the conclusion that the oxidation site of the first step is in ring A (cobaltadithiolene ring) and the oxidation site of the second step is in ring B (1,3-dithiole-2-thione ring).

In summary, we have succeeded in synthesizing two novel types of dithiolato cobalt complexes containing the dmit ligand and a substituted cyclopentadienyl ring. The new complexes showed three one-electron transfer steps, one reduction step and two oxidation steps, in spite of the fact that the complexes have only one metal. These new complexes have considerable synthetic potential as precursors for electron reservoirs and as new organosulfur compounds.

References

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