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Reactions of [CpCo(dmit)] (Cp = C_5H_5, dmit = C_3S_5) with Tetracyanoethylene Oxide (TCNEO): Synthesis of a New Complex Having a Novel Planar Ligand and Its Electrochemical Behavior

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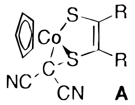
Summary: The title reaction resulted in desulfurization in the thiocarbonyl ligand to produce a new complex with a novel planar ligand, $[CpCoS_2C_2S_2C{=}C(CN)_2]$.

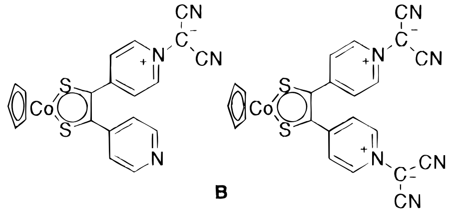
Recently, transition-metal dithiolene systems[1,2] have received much attention as precursors for low-dimensional molecular metals and superconductors.[3,4] Their electronic delocalization and intermolecular interactions are prerequisites for collective electronic properties such as conductivity[5] and ferromagnetism.[6] We have been interested in developing the synthesis of a novel ligand bearing a planar structure and in exploring the coordination of these ligands with the cyclopentadienylmetal group (CpM).[7,8]

We have already reported two types of reactions of cyclopentadienyl cobaltadithiolene complexes with tetracyanoethylene oxide (TCNEO);[9] one is the reaction of cobaltadithiolene complexes bearing phenyl or ester ligands, which result in the formation of Co−S dicyanomethylene-bridged complexes (**A**), and the other is the reaction where a cobaltadithiolene complex bearing 4-pyridyl ligands produces pyridinium dicyanomethylide complexes (**B**). Here we report a third type of reaction with TCNEO.



A

R = COOMe and Ph



B

A mixture of the dithiolene complex [CpCo(dmit)] (**1**; Cp = C_5H_5, dmit = C_3S_5)[10] and TCNEO (twice as much as **1**) was heated under reflux in THF.[11] The novel dicyanomethylene-substituted cobaltadithiolene complex [CpCo(dmiCN)] (**2**; dmiCN = 2-(dicyanomethylene)-4,5-disulfanyl-1,3-dithiole)[12] was obtained in 64% yield.

In this reaction some other products were expected, because TCNEO normally reacts with nucleophiles[13] or olefins.[14] However, only **2** was selectively obtained. The electron-poor carbon of TCNEO reacts with sulfur of the thiocarbonyl ligand.[15] The predicted mechanism of the reaction is shown in Scheme 1.

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(11) A solution of **1** (32 mg, 1×10^{-4} mol) and TCNEO (30 mg, 2×10^{-4} mol) in THF (30 mL) was refluxed for 3 h. After the solvent was removed under reduced pressure, the residue was chromatographed on silica gel (Wako-gel C300, eluent dichloromethane) and then the product was further submitted to HPLC (LC-08 produced by Japan Anal. Ind. Co. Ltd., column JAIGEL-H, eluent $CHCl_3$). The product **2** was obtained as a dark green crystalline solid in 64% yield (recovery of **1** 16%). Single crystals for the X-ray structural analysis were obtained from a dichloromethane−hexane mixture.

(12) $[CpCo\{S_2C_2S_2C{=}C(CN)_2]$ (**2**): ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 5.50 (s, 5H, C_5H_5); ^{13}C NMR (300 MHz, $CDCl_3$, TMS) δ 79.56 (C_5H_5), 112.80 (CN), 155.99; MS (EI^+, 70 eV) m/z (relative intensity) 352 (M^+, 100), 188 ($CpCoS_2^+$, 9.61), 168 ($CpCoSC^+$, 31.27), 124($CpCo^+$, 29.07); IR (KBr) 2207 (s) cm^{-1} (CN); UV−vis (CH_2Cl_2) λ_{max} (ϵ) 669 (11 782), 418 (9777), 392 (12 463), 288 nm (20 681).

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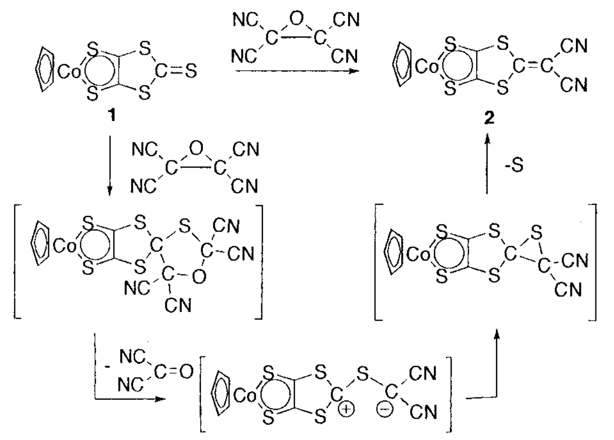
Scheme 1



The structure of [CpCo(dmiCN)] (**2**) was determined by single-crystal X-ray diffraction.[16] The ORTEP drawing of **2** is shown in Figure 1. The sulfur atom of the thiocarbonyl group is replaced by a dicyanomethylene group. The dmiCN ligand is almost coplanar (±0.0420 Å), and the cyclopentadienyl ring plane is nearly perpendicular to this ligand plane (the dihedral angle is 89.89°). The bond distances of the dithiolene ring and the molecular geometry are very close to those of the CpCo(dmit) complex[19] or those of $CpCo(S_2C_2R_2)$ (R = CN, COOMe, Ph) complexes.[20] A perspective drawing of the crystal packing is also given in Figure 1. The dmiCN ligand planes are parallel with each other. The crystal structure of complex **2** reveals a one-dimensional molecular interaction array. However, in complex **2**, the S(1)−S(4)′ distance (4.09 Å) is larger than that in [CpCo(dmit)] (3.608(3)−3.733(3) Å).

The redox behavior of [CpCo(dmiCN)] (**2**) has been examined by cyclic voltammetry (CV).[21] The CV result (Figure 2) shows a reversible reduction wave ($E_{1/2}$ = −0.90 V vs Fc^+/Fc), which can be attributed to the formation of a monoanion species. An oxidation wave appears at 0.57 V. Its rereduction wave was non-Nernstian-shaped; it was very similar to the oxidation couples of CpCo(dmit) and $Ni(dmit)_2$.[22] The rereduction wave is characteristic of a redissolution process. The monocation species afforded some insoluble product. This product, which had adsorbed on the electrode, redissolved when it was rereduced. It is assumed to be the dimer. We expect that the intermolecular interaction will appear due to oxidation. This electrochemical behavior is favorable for constructing noninteger-oxidation-state electrically conducting and superconducting molecular materials via electrocrystallization, the most general and widely used technique today.[23−25]

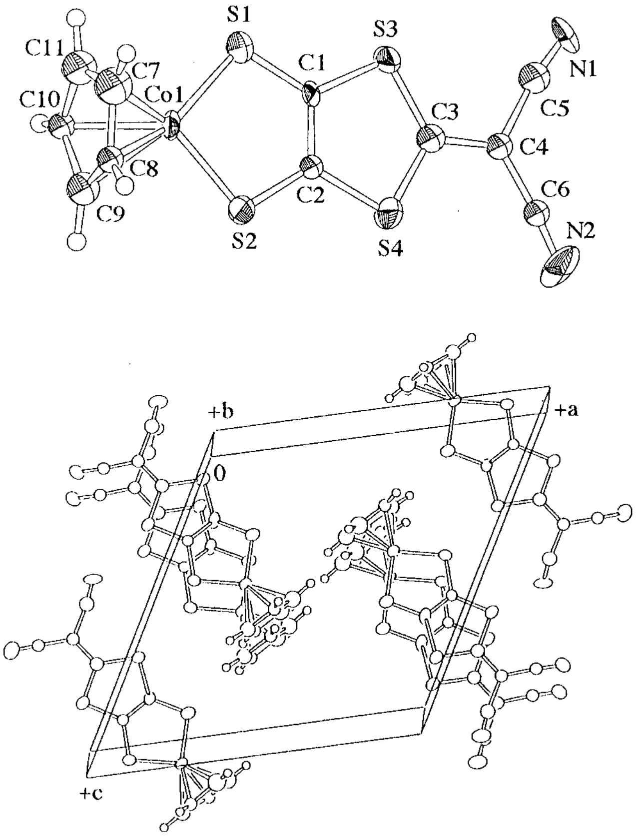


Figure 1. (Top) Molecular structure of **2**. Selected bond lengths (Å) and angles (deg) are as follows: Co−S(1), 2.125(7); Co−S(2), 2.115(7); S(1)−C(1), 1.68(2); S(2)−C(2), 1.70(2); C(1)−C(2), 1.39(3); C(1)−S(3), 1.77(2); C(2)−S(4), 1.76(2); S(3)−C(3), 1.71(2); S(4)−C(3), 1.71(2); C(3)−C(4), 1.41(3); S(1)−Co−S(2), 93.5(3)); Co−S(1)−C(1), 103.4(9); Co−S(2)−C(2), 102.8(8); S(1)−C(1)−C(2), 119(1); S(2)−C(2)−C(1), 120(1). (Bottom) View of the packing diagram with unit cell.

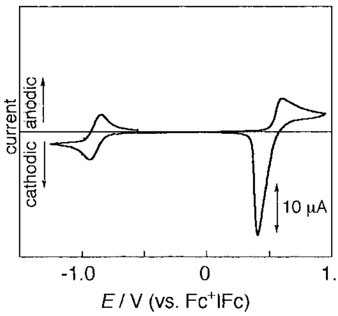


Figure 2. Cyclic voltammogram (v = 100 mV s^{-1}) of 1 mM complex **2** in CH_2Cl_2 containing 0.1 M TBAP.

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[16] All measurements were made on a Rigaku AFC5S diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Idealized positions were used for the teXsan crystallographic software package of Molecular Structure Corp.[18] Tables of atomic coordinates for non-hydrogen atoms, complete lists of bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters are available as Supporting Information.

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[21] The electrochemical measurements were undertaken in 0.1 M tetrabutylammonium perchlorate (TBAP)/CH_2Cl_2 at a Pt-disk working electrode using a Pt-wire counter electrode, with the reference electrode as Ag^+/Ag corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc^+/Fc) couple.

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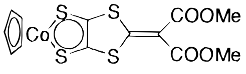
This reaction is also applicable to other complexes having a dmit ligand, such as $Cp_2Ti(dmit)$. The addition of TCNEO to a refluxing THF solution of $Cp_2Ti(dmit)$ afforded a novel Ti complex having a dmiCN ligand: $Cp_2Ti(dmiCN)$ (**3**).[26]

The analogous product $[CpCoS_2C_2S_2C{=}C(COOMe)_2]$ (**4**)[27] was obtained in the reaction with [CpCo(dmit)] (**1**) with dimethyl diazomalonate[28] (yield 49%). The CV result shows reversible redox waves at −1.01 and 0.41 V; here the redissolution process was not seen.

Although malononitrile is also known to be a precursor of dicyanomethylide,[29] this reaction did not occur with malononitrile in DMF solution. This reaction makes it possible to synthesize novel fully planar metal dithiolene complexes. They have a more elongated π system (CpCo(dmiCN); $\lambda_{max} = 669$ nm) than typical dithiolene complexes (e.g. $CpCo(S_2C_2(CN)_2$; $\lambda_{max} = 572$ nm).[20] Such complexes are expected to have interesting electronic properties and high functionality.



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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **2** (20 pages). Ordering information is given on any current masthead page.

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[26] $[Cp_2Ti(dmiCN)]$ (**3**): MS (EI^+, 70 eV) *m*/*z* (relative intensity) 406 (M^+, 43.72), 178 (Cp_2Ti^+, 100); ^1H NMR ($CDCl_3$) δ 6.24 (s, 10H, C_5H_5).

[27] $[CpCoS_2C_2S_2C{=}C(COOMe)_2]$ (**4**): MS (EI^+, 70 eV) *m*/*z* (relative intensity) 418 (M^+, 100), 387 ($M^+ -$ OMe, 20.76), 188 ($CpCoS_2^+$, 7.65), 168 ($CpCoSC^+$, 46.46), 124 ($CpCo^+$, 38.46); ^1H NMR ($CDCl_3$) δ 5.41 (s, 5H, C_5H_5), 3.83 (s, 6H, COOMe); ^{13}C NMR ($CDCl_3$) δ 78.88 (C_5H_5), 52.20 ($COOCH_3$), 126.05, 128.76 (dithiolene C═C), 161.86 ($COOCH_3$), 165.70 (C═C); UV−vis (CH_2Cl_2) λ_{max} (ϵ) 686 (14 103), 410 (9837), 384 (15 718), 289 nm (23 989).

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