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Synthesis, Structure, and Dissociation Equilibrium of $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$, a Novel Metalladiselenolene Complex

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A (phenylenediselenolato)cobalt complex dimer, $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$ (**1**), was synthesized by a reaction of carbonyl(η^5-cyclopentadienyl)diiodocobalt(III) ($[Co(\eta^5\text{-}C_5H_5)I_2(CO)]$) with poly(*o*-diselenobenzene). The structure of **1**, determined by single-crystal X-ray crystallography, was found to be located in the space group $P2_1/c$ (No. 14), with $a = 9.3346(5)$ Å, $b = 11.6477(9)$ Å, $c = 10.2179(5)$ Å, $\beta = 111.491(1)°$, and $Z = 2$. Covalent Co–Se bonds bridge the metal centers. In solution, dimers and monomers coexist at equilibrium. The dissociation equilibrium constant of **1** in solution was evaluated by ^{1}H NMR spectra at several temperatures between 20 and 80 °C. Dissociation enthalpies/entropies were found to be 50/110, 60/120, and 88 kJ mol^{-1}/200 J K^{-1} mol^{-1} in dimethyl sulfoxide-d_6, benzene-d_6, and chloroform-d_1, respectively.

Introduction

Transition metal complexes involving a chalcogen atom such as sulfur or selenium are of importance as functional materials exhibiting peculiar electromagnetic properties[1] and an active site of a metal enzyme,[2] which participates in vital functions. A metalladichalcogenolene ring consisting of one transition metal atom, two coordinated chalcogen atoms, and two unsaturated carbon atoms is a very unique metal chelate ring.[3] By using one vacant d orbital of the metal atom, the ring constructs a conjugated system with 6 π-electrons,[3] exhibiting aromaticity and high thermal stability. Electron transfer can be made easily at the metal and chalcogen sites of the aromatic ring, leading to various reactivities.[4] Contrary to the vast chemistry of $[Co(\eta^5\text{-}C_5H_5)(S_2C_2R_2)]$-type cobaltadithiolene complexes,[3] cobaltadiselenolene has been studied little, if at all.[5] In this paper, we report the first synthesis of a representative cobaltaladiselenolene as a dimeric form, $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$ (**1**), and its crystallographic structure and dissociation reaction. The study of the dissociation equilibrium of **1** is interesting because at present no reports on such an equilibrium for metal−diselenolene complexes are available to our knowledge. The data presented here are fundamentally important to recognizing the difference between this compound and the corresponding cobaltadithiolene.[6,7]

Experimental Section

Materials. Poly(*o*-diselenobenzene)[8] and $[Co(\eta^5\text{-}C_5H_5)I_2(CO)]$[6] were prepared according to the literature. Sodium (Aldrich), 1,2-dibromobenzene (Tokyo Kasei), and other reagents and solvents (Kanto Chemicals) were purchased from commercial sources and used as received. Spectroscopic grade dimethyl sulfoxide (DMSO)

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Table 1. Experimental Data for the X-ray Diffraction Study of **1**

empirical formula	$C_{22}H_{18}Co_2Se_4$
fw	716.09
cryst dimens	0.10 × 0.10 × 0.10 mm
cryst system	monoclinic
lattice params	$a = 9.3346(5)$ Å $b = 11.6477(9)$ Å $c = 10.2179(5)$ Å $\beta = 111.491(1)°$ $V = 1033.72(10)$ Å^3
space group	$P2_1/c$ (No. 14)
Z value	2
μ(Mo Kα)	86.55 cm^{-1}
d(calcd)	2.300 g cm^{-3}
F_{000}	680.00
R1^a	0.026
wR2^b	0.072
GOF	0.81

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

(Kanto Chemicals) was used for UV−vis spectroscopy. The acetonitrile used for the electrochemical measurements was of HPLC grade (Kanto Chemicals).

Apparatus. UV−vis, IR, and ^1H NMR spectra were recorded with the Hewlett-Packard 8453 UV−vis spectrometer, Jasco FT/IR-620v spectrometer, and JEOL EX270 spectrometer, respectively.

Synthesis of $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$ (1). Under nitrogen, sodium borohydride (0.189 g, 5.00 mmol) was added in a small portion to a stirred, brown suspension of poly(*o*-diselenobenzene) (0.176 g, 0.752 mmol) in methanol (10 mL) at 0 °C and further stirred until it became a yellow homogeneous solution. To the solution was added $[Co(\eta^5\text{-}C_5H_5)I_2(CO)]$ (0.306 g, 0.754 mmol) in methanol (40 mL) at 0 °C. The temperature of the mixture was allowed to rise to room temperature over 20 h with stirring, resulting in the formation of a deep brown solid. Under nitrogen, the reaction mixture was filtered and the precipitate was dried under vacuum. The residue was eluted with chloroform and recrystallized from hexane to give dark purple, reflective crystals of **1** in a yield of 118 mg (0.329 mmol, 44%). Anal. Calcd for $C_{22}H_{18}Co_2Se_4$: C, 36.90; H, 2.53. Found: C, 36.92; H, 2.68. ^1H NMR (270 MHz, CD_2Cl_2, 20 °C): δ 4.42 (s, 10H, Cp), 6.78 (t, 2H, $J = 7.6$ Hz, Ph), 6.93 (t, 2H, $J = 7.0$ Hz, Ph), 7.18 (d, 2H, $J = 7.8$ Hz, Ph), 7.64 (d, 2H, $J = 8.4$ Hz, Ph). IR (KBr disk): ν_{C-H} (Cp) 3101 cm^{-1}, ν_{C-H} (Ph) 3047 cm^{-1}.

Crystal Structure Determination. Crystals of **1** were grown by vapor-diffusion evaporation of a hexane/chloroform solution (50/50 v/v). A dark purple crystal having approximate dimensions of 0.10 × 0.10 × 0.10 mm was mounted on a glass capillary. All measurements were made on a Rigaku Mercury diffractometer coupled with a CCD area detector with graphite-monochromated Mo Kα radiation (0.7107 Å). The structure was solved by direct methods and expanded using Fourier techniques. Hydrogen atoms were not included in the calculations. The final cycle of full-matrix least-squares refinement on F was based on 1805 observed reflections ($I > -10.00\sigma(I)$). All calculations were performed using the CrystalStructure crystallographic software package of the Rigaku Corp. and the Molecular Structure Corp. The crystallographic data are given in Table 1.

Results and Discussion

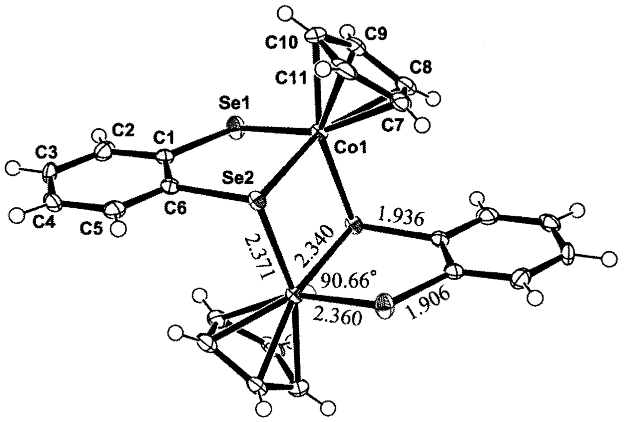

Figure 1. ORTEP drawing of **1** with 50% probability ellipsoids.

Table 2. Selected Bond Lengths and Bond Angles for **1** and Its Analogous Sulfur Complex[7]

	Se	S	Δ^a
	Bond Lengths (Å)		
E1−Co1	2.360 (1)	2.246 (1)	0.114
E2−Co1	2.340 (1)	2.230 (1)	0.110
E2−Co2	2.371 (0)	2.272 (1)	0.099
E1−C1	1.906 (5)	1.757 (4)	0.149
E2−C6	1.936 (5)	1.783 (3)	0.153
Cb ring ⟨av⟩	1.390	1.382	0.008
Cp ring ⟨av⟩	1.410	1.399	0.011
	Bond Angles (deg)		
E1−Co1−E2	90.66 (3)	89.73 (4)	0.93
Co1−E1−C1	102.1 (2)	103.0 (1)	−0.9
Co1−E2−C6	101.9 (1)	102.6 (1)	−0.7
E1−C1−C6	121.2 (4)	120.2 (3)	1.0
E2−C6−C1	120.2 (4)	119.7 (3)	0.5

[a] Δ is the difference of the values between $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$ and $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]_2$.[7]

Synthesis. The dianion $(Se_2C_6H_4)^{2-}$, which is a useful ligand for synthesizing (phenylenediselenolato)metal complexes, was prepared by reducing poly(*o*-diselenobenzene), which can be stored at room temperature for well over 1 year, by excess solid sodium borohydride in methanol. This anionic selenium ligand coordinates readily to the cobalt center of $[Co(\eta^5\text{-}C_5H_5)I_2(CO)]$ to give the product **1** with an elimination of iodine and carbon monoxide.

Crystallographic Structure. The molecular structure and labeling scheme for **1** are given in Figure 1. Covalent Co−Se bonds bridge the metal centers. The number of valence electron of cobalt atom in the dimer is 18, while that in the monomer is 16. Because two cobalt atoms in the dimer satisfy the 18-electron rule, the dimeric form is stabilized in the solid state where molecules are condensed and no other ligands (such as solvent molecules) are absent.

Table 1 summarizes the unit-cell parameters and details of data collection for the crystallographic studies of **1**. Selected bond lengths and angles from **1** are presented in comparison with those for $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]_2$[7] in Table 2. It should be noted that the structure of a crystalline monomeric form ($[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]$) determined by single X-ray crystallography has been also reported.[6] In our study, however, the monomeric complex $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]$ (**2**) has not been isolated owing to the high dissociation enthalpy and entropy (vide infra).

The difference in bond length of E−Co (E = Se or S) between $[Co(\eta^5\text{-}C_5H_5)(Se_2C_6H_4)]_2$ and $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]_2$[7]

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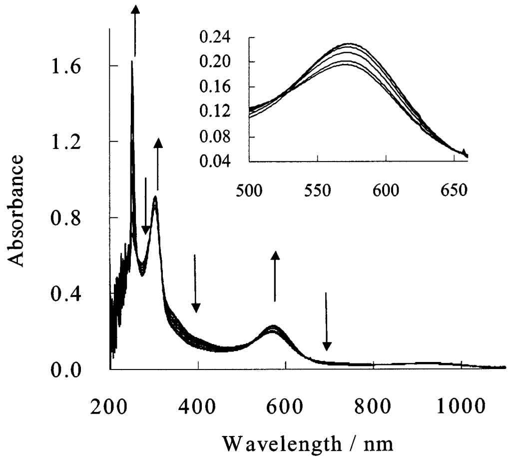
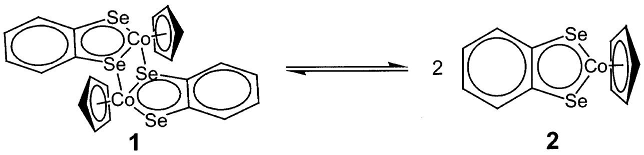


Figure 2. UV−vis spectral change of **1** in DMSO (4.72×10^{-4} M) with increasing temperature. Inset: Expanded view of the LMCT band of **1**, in DMSO.

is shorter than the difference between the covalent radius of Se and S, suggesting that the Se−Co bond is stronger than the S−Co bond. This occurrence might be explained that the 4p orbital of Se gives a much greater overlap with the cobalt 3d orbital than does the 3p orbital of S, with the Se−Co bond linking two monomer units being particularly strong. These results indicate that the thermodynamic stability of the dimeric form is greater than that reported for the compound's sulfur analogue.[7] The manner of dimerization has been also observed in other cobalt−dithiolene complexes,[9] in which the linkages between two monomer units are longer, and thus the thermodynamic stability of the dimeric form is weaker than that of **1**.

Dissociation Equilibrium in Solution. In solution, the dimer **1** and the monomer **2** coexist at equilibrium, while in the solid state **1** exists in its dimeric form. This is of interest in connection with the fact that $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]_2$ undergoes the single-crystal monomer/dimer transformation in the solid state.[7] Figure 2 shows UV−vis spectra of the product in dimethyl sulfoxide (DMSO) solution at several temperatures between 20 and 70 °C. Peaks that become more intense with increasing temperature are assigned to monomer absorbance, while those that are less intense are assigned to dimer absorbance.

The dissociation equilibrium of **1** in solution,



was studied by ^{1}H NMR spectra at several temperatures between 20 and 80 °C, as shown in Figure 3. The equilibrium constant, $K = [\mathbf{2}]^2/[\mathbf{1}]$, was determined by the monomer/dimer ratio, which was evaluated from integral values of two singlets of cyclopentadienyl protons in the dimer and the monomer.

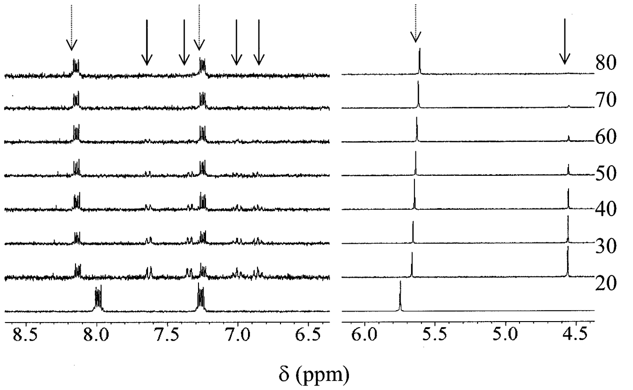


Figure 3. ^{1}H NMR spectral change of **1** (solid arrow) and **2** (dotted arrow) in DMSO-d_6 with increasing temperature, of which value in °C is given on the left side. A ^{1}H NMR spectrum of $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]$ in DMSO-d_6 solution is also shown at the bottom of the figure for comparison.

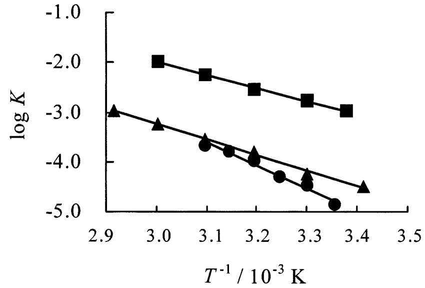


Figure 4. Van't Hoff plots of ln *K* vs 1/*T* for the equilibrium between **1** and **2** in dimethyl sulfoxide-d_6 (■), benzene-d_6 (▲), and chloroform-d_1 (●).

Dissociation enthalpies (ΔH) are evaluated from the slope of the Van't Hoff plots of ln *K* vs 1/*T* (Figure 4). The values of ΔH were obtained as 50, 60, and 88 kJ mol^{-1} in dimethyl sulfoxide-d_6, benzene-d_6, and chloroform-d_1, respectively. These values are larger than the of 18 kJ mol^{-1} in the case of the sulfur analogue.[7] This difference is consistent with the result of single-crystal X-ray crystallography: the Co−Se bond is stronger than the Co−S bond. The values obtained are not unusual considering the approximate value of 55 kJ mol^{-1} at the dissociation of $[Ni(SOCNR_2)_2]_2$,[10] which is an example of another metal complex dimer. Dissociation entropies were estimated at 110, 120, and 200 J K^{-1} mol^{-1} in dimethyl sulfoxide-d_6, benzene-d_6, and chloroform-d_1, respectively.

The values of ΔH and ΔS are dependent on the interaction between the monomeric form of **1** and the solvent. Because DMSO has the highest ability to donate an electron pair to a metal among the three solvents,[11] it can stabilize an electron-deficient monomer with 16 electrons. In contrast, chloroform, which is the least electron-donating solvent among the three, does not stabilize the monomeric form, leading to higher ΔH and ΔS values.

We have reported that metal−metal bonds with μ-S ligands can be formed by the reaction of $[Co(\eta^5\text{-}C_5H_5)(S_2C_6H_4)]$

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with metal carbonyl.[4] The stronger metal−selenium dimer linkage in **1** compared with the metal−sulfur analogue indicates a possibility of the formation of more stabilized metal−metal bonds with μ-Se ligands. Work along this line is in progress.

Conclusion

A (phenylenediselenolato)cobalt complex dimer, [Co(η^5-C_5H_5)($Se_2C_6H_4$)]$_2$, was synthesized, and its molecular structure was determined. The covalent Co−Se bonds bridging the metal centers are stronger than the Co−S bonds in the corresponding cobaltadithiolene compound. In solution, the dimer dissociates into the monomers to some extent, and the dissociation enthalpy and entropy determined by ^{1}H NMR spectra depend on the solvent.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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