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Reactions of (n^5-Cyclopentadienyl)(1,5-cyclooctadiene)cobalt(I),
Diphenylacetylene, and a Mixture of S<sub>8</sub> and Se<sub>8</sub>.
Formation of (n^5-Cyclopentadienyl)(1,2-diphenyl-2-selenolato-
ethylenethiolato-S,Se)cobalt(III) Complex
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 $(\eta^5$ -Cyclopentadienyl)(1,2-diphenyl-2-selenolatoethylenethiolato-S,Se)cobalt(III) (1) is formed in the reaction of CpCo(1,5cyclooctadiene) (4), Ph-C=C-Ph (5), and a mixture of S₈ and Se₈, together with the dithiolato and diselenolato complexes. A possible mechanism for the formation of 1 is the attack of 5 to some S,Se-mixed clusters which are formed in the reaction of 4 with Se₈ and S₈.

The recent increase of interest in the physical and chemical properties of dithiolato- and diselenolato-metal complexes is notable.¹⁾ We have reported a convenient one-pot synthesis of (η^5 -cyclopentadienyl)(substituted ethylene-dithiolato or diselenolato)metal complexes.^{2,3)} We report here that the one-pot reaction of (η^5 -cyclopentadienyl)(1,5-cyclooctadiene)cobalt(I) (4), diphenylacetylene (5), and a mixture of elemental sulfur and selenium gives a new selenolatothiolato complex. We discuss the mechanism of the complex formation. Only three reports have appeared on the synthesis of S,Se-mixed complexes.⁴⁻⁶

A mixture of 4 (329 mg, 1.42 mmol), 5 (300 mg, 1.69 mmol), and an any molar mixture of S_8 and Se_8 was refluxed in xylene (25 cm³) for 24 h under an atmosphere of Ar. The selenolatothiolato complex 1 was obtained as a blue mixture with the corresponding dithiolato- and diselenolato-cobalt complexes (2 By means of silica gel chromatography [column, Wako gel C-300; and 3). developing solvent, $n-C_6H_{14}-CH_2Cl_2(1:1,v/v)$] and preparative HPLC which employed a column of GPC (developing solvent, CHCl₃), the separation of the selenolatothiolato 1 from the diselenolato complex 3 was unsuccessful. The formation of the S,Se-mixed complex 1, however, was confirmed by means of MS and 1 H and 13 C NMR spectroscopy. The mass spectra of the product mixture (Fig. 1) show the parent peaks of the S, Se-mixed complex: m/z (rel intensity) 416(4.5), 415(4.2), 414(19.2), 412(10.0), 411(3.5), and 410(3.3). The peaks due to the CpCoSSe were also observed at m/z = 238, 237, 236, 234, 233, and 232. The relative intensities of the peaks ascribable to the parent cation and CpCoSSe⁺

are consistent with the calculated ones on the basis of natural abundance of the isotopes. All the peaks due to the dithiolato (2) and diselenolato (3) complexes were also observed in the MS of the mixture.

In the ¹H NMR (JEOL FX-200, in CDCl₃) of the products, there exist three absorptions of the protons in the cyclopentadienyl rings at $\delta = 5.340$, 5.364, and 5.379. The authentic dithiolato (2) and diselenolato (3) complexes have the absorptions at $\delta = 5.340$ and 5.379, respectively. Thus, the absorption at $\delta =$ 5.349 can be assigned to the protons of the S,Se-mixed complex. ¹³C NMR spectra of the cyclopentadienyl rings of 2 and 3 appear at $\delta =$ 77.962 and 79.641, respectively. An absorption at $\delta =$ 78.789 which is situated at the middle of the corresponding absorptions of 2 and 3 can safely be ascribed to the cyclopentadienyl ring of 1.





Fig. 1. Mass spectra (EI, 70 eV) of mixture of 1, 2, and 3.

The yields of 1, 2, and 3, which are calculated from the ¹H NMR, are shown in Table 1 together with the correlation with the composition of sulfur and selenium in the starting mixtures.

Table 1. Yields of 1, 2, and 3 in reaction of 4, 5, and mixture of S_8 and Se_8 in various ratios Amount of 4, 1.42 mmol; Amount of 5, 1.69 mmol; Solvent, 25 cm³ of xylene; Reaction conditions, Reflux for 24 h.

Run	Molar ratio of S_8 and Se $_8$ to 4		Yiel	Yield of product ^a)		
			સ			
	s ₈	Se ₈	1	2~	3~	
1	2/8	2/8	18	45	0	
2	2/8	8/8	20	30	1	
3	1/8	1/8	17	16	1	
4	1/8	4/8	27	23	6	
5	1/20	4/20	21	9	6	
6	2/8	-	-	16	-	
7	-	2/8	-	-	20	

a) Yield = (Amount of product/Amount of 4 used) x 100.

The formation of the dithiolato complex 2 is always dominant over that of the diselenolato complex 3. However, the formation of the selenolatothiolato complex 1 is comparable to that of the dithiolato complex 2. When the molar ratio of sulfur/4 is less than 1, the formation of the S,Se- mixed complex is favored.

The exchange of S and Se in the metal complexes which occurs in the reaction of (n^5 -cyclopentadienyl)[1,2-(2-pyridyl)-1,2-ethylenediselenolato]cobalt(III) with $S_8^{(7)}$ does not occur in the reaction of 2 with Se₈ or in the reaction of 3 with S₈.

It was found that in the absence of diphenylacetylene, 4 reacts with the mixture of S₈ and Se₈ (molar ratio of S₈ and Se₈ to 4 are 1/20 and 1/5(=4/20), respectively) to give a dark brown solid which reacts further with 5 to afford a mixture of 1, 2, and 3. From the mass spectral analyses of the dark brown solid, it turns out that the solid consists of several S,Se-mixed clusters such as Cp₄Co₄SSe₃, Cp₄Co₄S₂Se₂, and Cp₄Co₄S₃Se (m/z(rel intensity) 768(1), 720(2), and 672(2)⁸).

The above results indicate that the S,Se-mixed complex is formed by the attack of diphenylacetylene to the S and Se in the S,Se-mixed clusters.

An intersting observation is that the reaction of 4, 5, and a mixture of sulfur and selenium gives the dithiolato complex in much higher yields than those of 4, 5, and sulfur. But the reason has not yet been clarified.

The pathways for the formation of 1, 2, and 3, from 4, 5, and a mixture of S₈ and Se₈ are illustrated in Scheme 1.

 $\begin{array}{c} \text{S}_8 \text{ and } \text{Se}_8\\ \text{CpCo(COD)} & \longrightarrow \text{Clusters such as } \text{Cp}_4\text{Co}_4\text{Sse}_3, \ \text{Cp}_4\text{Co}_4\text{S}_2\text{Se}_2, \ \text{Cp}_4\text{Co}_4\text{S}_3\text{Se} \text{ etc.} \end{array}$

An example of reaction of the cluster $Cp_4Co_4S_2Se_2$ with 5.



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- 8) Besides these S,Se-mixed clusters, of which the values of m/z were determined by using the isotopes of 32 S and 80 Se, the following typical peaks were observed at m/z(rel intensity) 624(1, Cp₄Co₄S₄⁺), 532(2, Cp₃Co₃Se₂⁺), 484(11, Cp₃Co₃SSe⁺), 436(23, Cp₃Co₃S₂⁺), 189(67, Cp₂Co⁺), 160(16,Se₂⁺), 124(10, CpCo⁺), 66(100, CpH⁺), 65(65, Cp⁺), and 64(12, S₂⁺).

A fraction most of which consists of $Cp_4Co_4S_2Se_2$ was separated by silica gel column chromatography method [column, Wako gel C-300; developing solvent, $CH_2Cl_2-Et_2O$ (3:1,v/v)] from the dark brown solid. The resulting cluster reacted with Ph-C=C-Ph in boiling xylene for 4 h to afford the S,Se-mixed complex 1, 2, and 3 in the ratio of 1:2:3=68:29:3.

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