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Behavior Characteristic of (η^5-Cyclopentadienyl)(1,2-di-2-pyridyl-1,2-ethylenedithiolato)cobalt(III) and Its Diselenolato Analog. Elimination of 2S or 2Se and Exchange of S and Se

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(η^5-Cyclopentadienyl)(1,2-di-2-pyridyl-1,2-ethylendithiolato)cobalt(III) (**1**) and its selenium analog (**2**) show interesting reactivities at the S and Se moiety. A characteristic peak in MS of **1** and **2** measured using a direct inlet system under heating is found at m/z=304 assigned to ($(M-2S)^+$ or $(M-2Se)^+$). The reflux of **2** in toluene with S_8 causes the exchange of Se by S in the complex.

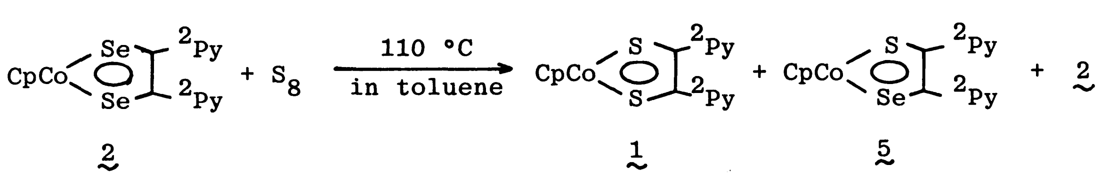
Increasing interest has been shown in several functions of dithiolato metal complexes: the catalytic activity for the synthesis of thiophene derivatives,[1,2] the stabilization of dyes against photo-decomposition, the quenching of singlet oxygen,[3] and electric conductivity.[4] Recently Hoffmann et al. analyzed the structural features and chemical and electrical properties of dithiolatometal complexes by the MO method.[5]

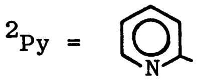
Owing to the development of a new and facile synthetic method for (η^5-cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) complexes in a one-pot reaction of $CpCo(CO)_2$ or CpCo(1,5-cyclooctadiene) with elemental sulfur and alkynes,[1] dithiolato and diselenolatometal complexes of this type with various substituents can be easily synthesized.[6]

We found that (η^5-cyclopentadienyl)(1,2-di-2-pyridyl-1,2-ethylenedithiolato)-cobalt(III)(**1**)[7] and its selenium analog, (η^5-cyclopentadienyl)(1,2-di-2-pyridyl-1,2-ethylenediselenolato)cobalt(III)(**2**),[8] show characteristic behavior which is not found in the aryl substituted complexes: 1) 2S or 2Se is eliminated and 2) the selenium atom(s) in **2** is replaced by sulfur atom(s) by refluxing **2** with S_8 in toluene.

A feature of dithiolato and diselenolatocobalt complexes with 2-pyridyl group as the substituent is the elimination of 2S or 2Se. When the mass spectra of **1** and **2** were measured using a direct sample inlet system at 220-350 °C (the conditions for the measurement are described in Ref. 9), a characteristic peak appeared at m/z = 304, which is assigned to $(M - 2S)^+$ and $(M - 2Se)^+$. $(M - 2S)^+$ and $(M - 2Se)^+$ should be formed by the fragmentation of $(\mathbf{1})^+$ or $(\mathbf{2})^+$ and/or the ionization of CpCo(di-(2-pyridyl)acetylene) species formed in the thermolysis of **1** and **2** in an ion source (in the probe for the direct inlet system) of a mass spectometer. In contrast, (η^5-cyclopentadienyl)(1,2-diphenyl-1,2-ethylenedithiolato)cobalt(III)(**3**) and its selenium analog (**4**) give strong mass-spectrometric peaks of [(M - diphenylacetylene)$^+$ = (CpCoS$_2$)$^+$ or (CpCoSe$_2$)$^+$] but give no peaks of (M-2S)$^+$ or (M-2Se)$^+$ under similar conditions. A differential thermal analysis of **1** shows the loss of weight at 305 °C. The weight loss of 15.7% suggests the elimination of 2S (theoretical weight loss, 17.4%). Similar results were not obtained for the unsubstituted dithiolato complex.

Another feature of the diselenolato complex with 2-pyridyl group is the facile exchange of Se by S. The reflux of **2** (0.026 mmol) with S$_8$ (0.095 mmol) in 3 cm^3 of toluene at 110 °C for 5 h under Ar gives a mixture of **1** , **2** , and (η^5-cyclopentadienyl)(1,2-di-2-pyridylethylene-1-selenolato-2-thiolato)cobalt(III) (**5**) in the mole ratio of 28:40:32.





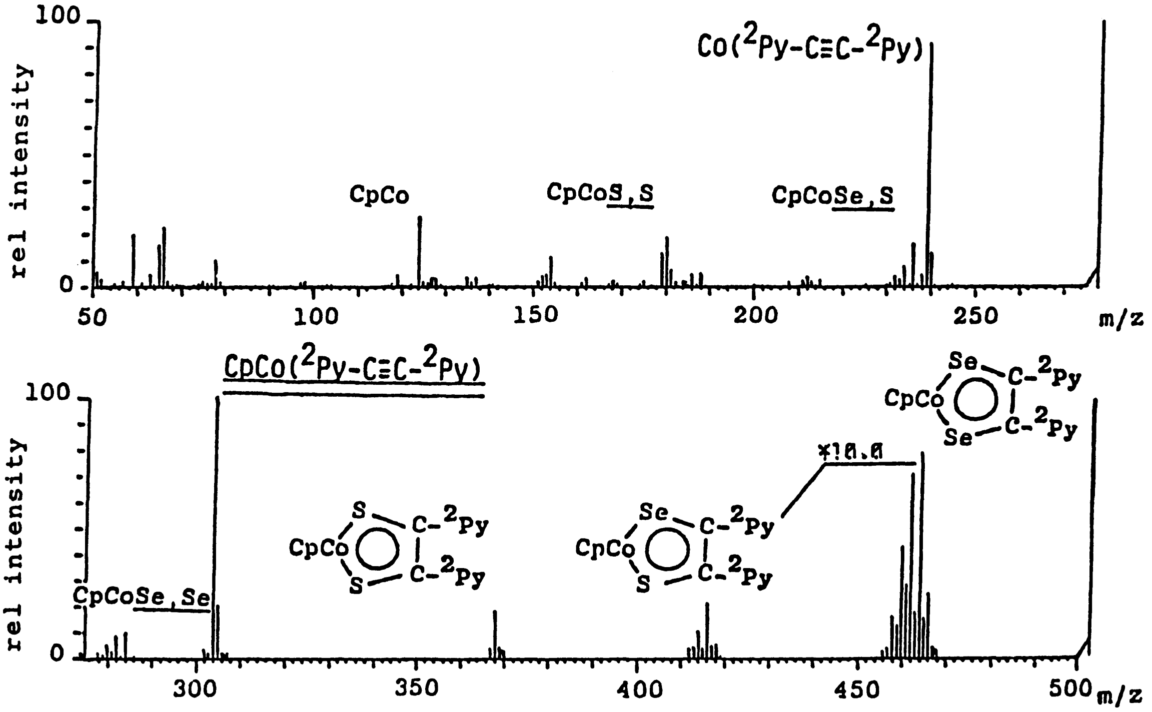


Fig. 1. Mass spectra (70 eV) of the reaction mixture from the reaction of **2** with S$_8$.

Complex **5** could not be isolated. It was identified by MS (Fig. 1) and ^1H NMR of the reaction mixture.

In MS the peaks at m/z (relative intensity) = 418 (5.1), 416 (21.4), 414 (10.9), 413 (4.6), and 412 (4.1) are ascribed to the parent peaks of **5**: Their relative intensities roughly agree with the calculated intensities on the basis of the isotope abundance of Se. The peaks for CpCoSSe were observed at m/z = 238, 236, 234, 233, and 232. These results indicate the formation of the complex **5**.

In ^1H NMR of the reaction mixture, three absorptions due to cyclopentadienyl group were observed at δ = 5.364, 5.396, and 5.416. The absorptions at δ = 5.364 and 5.416 agree with the absorptions of **2** and **1**, respectively. The absorption at δ=5.396 which is situated between the absorptions of diselenolato and dithiolato complexes can be assigned to the cyclopentadienyl group of the selenolatothiolato complex **5**. The composition of **1**, **2**, and **5** in the reaction mixture was determined by the relative intensities of the ^1H NMR absorptions.

The reaction with the use of excess S_8 (0.31 mmol for 0.032 mmol of **2**), at higher temperature (140 °C in xylene), and with longer reaction time (40 h) resulted in the complete exchange of Se in **2** by S. The corresponding exchange reaction of S by Se in the dithiolato complex (**1**) occurs but with much more difficulty. The reflux of **1** with Se_8 under similar conditions gives only trace amount of **2**. Such an exchange reaction does not occur in the complexes which lack the 2-pyridyl substituent.

Although the cause of the interesting behavior of the dithiolato and diselenolatocobalt(III) complexes with 2-pyridyl group is not yet clear, the donation of the lone pair electrons at the pyridine ring to the cobalt ion may cause the deformation of the dithiolato and diselenolato ring and the weakening of the metal-S (or Se) and C-S (or Se) bond. This would facilitate the elimination of 2S and 2Se and the exchange of S and Se.

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7) Complex **1** was synthesized in a one-pot reaction of CpCo(CO)$_2$ (1.29 mmol), S$_8$ (0.31 mmol), and di(2-pyridyl)acetylene (0.83 mmol) under the reflux in toluene (80 cm^3) for 24 h (yield, 36%): UV(CH$_3$OH) 293 (ε 60000) and 577 nm (ε 13860);IR(KBr disk) 3050, 1566, 1547, 1450, 1392, 1172, 1045, 992, 975, 820, 765, 732, 600, and 395 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 5.41 (s, Cp), 6.96, 7.15, 7.42, and 8.57; ^{13}C NMR (CDCl$_3$) δ= 80 (Cp ring), 121, 124, 136, 149, 159 (pyridine ring), and 168. Found: C, 54.64; H, 3.64; N, 7.16%. Calcd for C$_{17}$H$_{13}$CoN$_2$S$_2$: C, 55.43; H, 3.56; N, 7.61%.

8) Complex **2** was synthesized in a one-pot reaction of CpCo(CO)$_2$ (4.3 mmmol), Se$_8$ (1.20 mmol), and di(2-pyridyl)acetylene (2.3 mmol) under the reflux in xylene (20 cm^3) for 24 h (yield, 24%): UV(CH$_3$OH) 304, 590, and 802 nm; IR(KBr disk) 3060, 1715, 1572, 1532,1452, 1419, 1259, 812, 780, 748, and 605 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 5.36 (s, Cp), 6.86, 7.15, 7.30, and 8.58; ^{13}C NMR (CDCl$_3$) δ = 78 (Cp ring), 122, 123, 135, 145, 169 (pyridine ring) and 179. Found: C, 43.34; H, 2.87; N, 5.41%. Calcd for C$_{17}$H$_{13}$CoN$_2$Se$_2$: C, 44.12; H, 2.84; N, 6.06%.

9) Mass spectral measurements of the dithiolato and diselenolatocobalt complexes were done by introducing the solid samples directly into the ionization chamber of the mass spectrometer by using the direct inlet system and then heating the samples from room temperature to 350 °C.

MS of **1** (70 eV) at 280 °C: m/z (rel intensity) 370 ((M+2)$^+$; 11), 368 (M$^+$; 100), 304 ((M-2S)$^+$; 63), 239 ((Co(PyC≡CPy))$^+$; 60), 188 ((CpCoS$_2$)$^+$; 23), 180 ((PyC≡CPy)$^+$; 6), and 124 ((CpCo)$^+$; 3).

MS of **2** (70 eV) at 280 °C: m/z (rel intensity) 464 (M$^+$, calculated Se as ^{80}Se; 19), 304 ((M-2Se)$^+$; 100), 284 ((CpCoSe$_2$)$^+$; 22), 239 ((Co(PyC≡CPy))$^+$ 80), 180 ((PyC≡CPy)$^+$; 11), 124 ((CpCo)$^+$; 34), and 59 (Co$^+$; 19).

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