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## Organic Selenium Compounds

### III. Dimethyl Selenoxide Complexes of Transition Elements

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Metal complexes of dimethyl sulfoxide (DMSO) have been studied extensively.<sup>1-7</sup> The present investigation was initiated to compare the tendency of dimethyl selenoxide (DMSeO) to form metal complexes to that of DMSO.

DMSeO complexes of iron, cobalt, nickel, copper, palladium, cadmium, and mercury could easily be prepared from the metal chlorides and dimethyl selenoxide. The complexes are soluble in water and insoluble in nonpolar solvents. In most cases the isolated complexes had a composition corresponding to the formula  $MCl_2 \cdot 2DMSeO$ , however, from  $FeCl_2$  and  $PdCl_2$  the  $FeCl_3$  and  $PdCl_4$  complexes were ob-

tained. The  $NiCl_2$  and  $NiBr_2$  complexes were only obtained with  $1\frac{1}{2}$  moles of DMSeO and the  $HgCl_2$  complex with 1 mole of DMSeO. The composition  $MCl_2 \cdot 2DMSeO$  would be in accord with the formation of tetrahedral (Cd, Co) or square-planar (Cu, Ni) complexes, but the structure may be more complicated (e.g. with  $MCl_4^{2-}$  ions), as is indicated by the composition of the nickel complexes.

In the DMSO complexes the S=O stretching frequency of the free ligand ( $1055\text{ cm}^{-1}$ ) in most cases decreases on coordination, indicating that the ligand is oxygen-bonded. However, in DMSO complexes of Pd,<sup>3</sup> Pt,<sup>3</sup> Th,<sup>6</sup> Zr,<sup>6</sup> and  $UO_2$ ,<sup>7</sup>  $\nu(S=O)$  increases and this has been explained by assuming that the ligand is sulfur-bonded in these cases. In dialkyl selenoxides the Se=O linkage has a more polar character than the S=O linkage in DMSO, and it therefore seems less probable that coordination should occur to selenium. Actually, it was found that the Se=O stretching frequency was lowered for all complexes studied here.

Paetzold and Vordank,<sup>8</sup> in a paper which appeared during the present investigation, have studied complexes of diphenyl selenoxide with some transition elements and similarly found a lowering of  $\nu(Se=O)$  for all the complexes studied (Pd or Pt complexes were, however, not prepared).

The infrared spectrum of DMSeO was determined in KBr, chloroform, acetonitrile, and dioxan (it was only slightly soluble in carbon tetrachloride or carbon disulfide). The absorption maxima due to  $CH_3$  stretching, deformation and rocking (in KBr:  $3010\text{ vw}$ ,  $2920\text{ vw}$ ,  $1425\text{ m}$ ,  $1275\text{ m}$ ,  $960\text{ m}$ ,  $906\text{ m}$ ) coincide essentially with the corresponding bands of DMSO in solution (the gas spectrum<sup>9</sup> is, of course, more fully resolved). The Se=O band appears as an extremely strong band at  $800\text{ cm}^{-1}$  in the solid spectra and at  $820\text{ cm}^{-1}$  in the solution spectra. In acetonitrile and dioxan, DMSeO also exhibits a strong band at  $760\text{ cm}^{-1}$ , which may be due to complex formation with the solvent. A weak band at  $585\text{ cm}^{-1}$  is assigned to antisymmetric C-Se stretching (corresponding to the C-S band of DMSO at  $690\text{ cm}^{-1}$ ). The symmetric stretch was not observed.

The infrared spectra of most of the DMSeO complexes in the NaCl region differ insignificantly from the spectrum of DMSeO, except for the Se=O stretching

Table 1. Complexes of dimethyl selenoxide (DMSeO).

| Composition                | Colour         | M.p., °C  |
|----------------------------|----------------|---|
| HgCl <sub>2</sub> ·1DMSeO  | colourless     | 128   |
| CdCl <sub>2</sub> ·2DMSeO  | colourless     | 158   |
| PdCl <sub>4</sub> ·2DMSeO  | orange-brown   | 110   |
| CuCl <sub>2</sub> ·2DMSeO  | yellow-green   | 150 (decomp.)   |
| NiCl <sub>2</sub> ·1½DMSeO | reddish yellow | turns red at 140<br>decomposes above 260                                    |
| NiBr <sub>2</sub> ·1½DMSeO | reddish yellow | ca. 260 (decomp.)   |
| CoCl <sub>2</sub> ·2DMSeO  | blue           | turns dark blue at 150 and then<br>decomposes (smell of Me <sub>2</sub> Se) |
| FeCl <sub>3</sub> ·2DMSeO  | light brown    | ca. 170 (decomp.)   |

band. The 800 cm<sup>-1</sup> band is shifted to lower frequencies in all cases and, except for the HgCl<sub>2</sub> complex, is doubled. A similar doubling has been found by Paetzold and Vordank<sup>8</sup> for the complexes of diphenyl selenoxide. It is more pronounced (separation 10–65 cm<sup>-1</sup>) in the spectra of the DMSeO complexes and so can hardly be due to a lattice effect but rather to a coupling of the Se=O vibrations through the metal atom. This would also explain why the mercury complex, which contains only one molecule of DMSeO, shows no doubling of this band.

The shift is exceptionally large in the spectrum of the palladium complex, which also differs from that of DMSeO by showing three weak bands (1210, 1250, 1290 cm<sup>-1</sup>) in place of the 1275 cm<sup>-1</sup> band. The platinum complex could not be obtained in a pure and crystalline state, but the spectrum of the amorphous reaction product is similar to that of the palladium complex and also shows a shift of the 800 cm<sup>-1</sup> band to lower frequencies (730 cm<sup>-1</sup>).

The 585 cm<sup>-1</sup> band of DMSeO is shifted very little in the spectra of the complexes, except in the spectrum of the Pd complex, where it is shifted to a higher frequency (610 cm<sup>-1</sup>). This would be in accord with the considerable weakening of the Se=O bond that is indicated by the exceptionally

large shift of the Se=O stretching band in this case.

The lowering of the frequency of the Se=O stretching band for all complexes investigated here indicates that coordination occurs through oxygen in all cases and that Pd especially is not bonded to selenium in the Pd complex.

In the spectra of the complexes (Table 2) there appears in most cases a medium to strong band in the 400–500 cm<sup>-1</sup> range. This may be due to metal-oxygen stretching as proposed for the corresponding band of DMSO complexes.<sup>10</sup> The infrared spectra of the Pd and Pt complexes of dimethyl selenide, [PdCl<sub>2</sub>(Me<sub>2</sub>Se)<sub>2</sub>] and [PtCl<sub>2</sub>(Me<sub>2</sub>Se)<sub>2</sub>], show no absorption between 900 and 400 cm<sup>-1</sup>, except an extremely weak band at 610 cm<sup>-1</sup>. Therefore, all other bands in this region of the DMSeO complexes must be due to the Se=O group.

The far infrared spectrum of DMSeO shows absorption bands at 382, 341, and 338 cm<sup>-1</sup>. They probably correspond to the bands at 382, 335, and 333 cm<sup>-1</sup> in the spectrum of DMSO,<sup>9</sup> and accordingly are due to C–Se–O deformation. Below 300 cm<sup>-1</sup>, DMSeO shows only a very diffuse series of weak bands. The spectra of the complexes below 400 cm<sup>-1</sup> increase in complexity and differ from complex to complex. The palladium, copper, and mercury complexes show several strong

Table 2. Principal infrared absorption bands of dimethyl selenoxide complexes.

| Compound                                  | $\nu(\text{Se}=\text{O})$ | $\nu(\text{C}-\text{Se})$ | $\nu(\text{O}-\text{M})$ | Far infrared bands   |
|---|---------------------------|---------------------------|--------------------------|--|
| DMS <sub>2</sub> SeO                      | 800vs                     | 585vw                     |                          | 392s, 341w, 328vw, (230-100)w, 72s   |
| HgCl <sub>2</sub> ·1DMS <sub>2</sub> SeO  | 770vs                     | 580vw                     |                          | 397vw, 387vw, 358vs, 348vs, 326vs, 278sh, 270s, 247w, 165m, 98s, br          |
| CdCl <sub>2</sub> ·2DMS <sub>2</sub> SeO  | 775vs<br>735vs            | 585w                      |                          |  |
| PdCl <sub>2</sub> ·2DMS <sub>2</sub> SeO  | 698vs<br>690vs            | 610w                      | 520w, br                 | 391w, 381vw, 337vs, 328vs, 321vs, 64s 258s, 200m, 170w, 150s, 124w, 80s, br, |
| CuCl <sub>2</sub> ·2DMS <sub>2</sub> SeO  | 760vs<br>720vs            | 595w<br>580w              | 515m<br>475m             | 394w, 318vs, 302vs, (260-180)vs, br 130s, br                                 |
| NiCl <sub>2</sub> ·1½DMS <sub>2</sub> SeO | 765s<br>700vs             | 590w                      | 403s                     | 397m, 376w, 350m, br, (270-230)s, br, 135m, br                               |
| CoCl <sub>2</sub> ·2DMS <sub>2</sub> SeO  | 760vs<br>705s             | 590w                      | 410s                     | 394s, 380m, 340m, (320-210)s, br, 148m, 124s                                 |
| FeCl <sub>3</sub> ·2DMS <sub>2</sub> SeO  | 760vs                     | 580w                      | 440s                     |  |

and rather sharp bands, some of which are undoubtedly due to metal-halogen stretching. The spectra of the cobalt and nickel chloride complexes are more similar to that of DMSeO, showing almost continuous absorption in the 200-300 cm<sup>-1</sup> region.

*Experimental.* Dimethyl selenoxide was prepared by oxidation of dimethyl selenide<sup>11</sup> with ozone.<sup>12</sup> The purity of the compound was checked by titrimetric analysis.<sup>12</sup> The complexes were prepared by adding saturated solutions of the metal halide hydrates in absolute ethanol to ethanolic dimethyl selenoxide. The complexes precipitated immediately and were isolated by centrifugation, washed with chloroform and dried over phosphorus(V) oxide *in vacuo*. For the preparation of the palladium complex, palladium(II) chloride (100 mg) was dissolved in hydrochloric acid (1 ml of water and 0.2 ml of conc. hydrochloric acid). To this solution a solution of DMSeO in ethanol was added dropwise, and after some time the precipitation started. The complex was washed with cold ethanol and recrystallized from chloroform. Analyses showed that the product was a Pd(VI) complex. (Found: Pd 21.00; Cl 28.37; DMSeO 52.34. Calc. Pd 21.36; Cl 28.47; DMSeO 50.18). Whether the oxidation was caused by oxygen of the air or by part of the DMSeO was

not ascertained. Oxidation also occurred when it was attempted to prepare a FeCl<sub>2</sub> complex.

With exception of the palladium compound the complexes could not be recrystallized without decomposition.

The complexes were analyzed by complexometric titration of the metal,<sup>14</sup> Volhard titration of the halide ion, and determination of dimethyl selenoxide by the method described by Ayrey *et al.*<sup>12</sup> In most cases the analyses corresponded well to a stoichiometric formula, but the nickel complexes were only obtained with approximately 1.5 DMSeO. Melting points and colours of the complexes have been listed in Table 1.

The infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer and far infrared spectra on a Fourier spectrophotometer FS 520.

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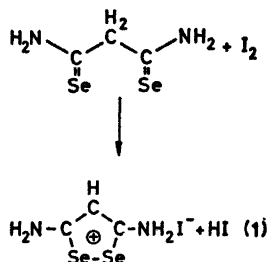
### V. Diselenolylium Salts

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By oxidation of dithiomalonamide, salts of the 3,5-diaminodithiolylium cation or 3,5-diaminodithiolylium ion\* have been obtained.<sup>1,2</sup> When diselenomalonamide be-

\* In the literature, the dithiolylium cation is often called the "dithiolium" ion. As was pointed out earlier,<sup>1</sup> this name is misleading because stoichiometrically the dithiolylium cation is a didehydrodithiolium ion. According to the IUPAC rules for organic chemical nomenclature,<sup>4</sup> cations formed by loss of an electron from an -yl radical may be denoted by the ending -ylium (this ending being considered as an entity and not to imply that the ion is formed by addition of a proton to the radical). Accordingly, the dithiolylium and diselenolylium cations may be called dithiolylium and diselenolylium ions.



came available in this laboratory,<sup>3</sup> we tried to prepare the corresponding 3,5-diselenolylium salts, but our first attempts, using hydrogen peroxide as oxidant, were unsuccessful.<sup>3</sup> However, when iron(III) chloride or iodine were used as oxidants, 3,5-diaminodiselenolylium chloride or iodide (1) were obtained without difficulty.

The properties of these diselenolylium salts are very similar to those of the corresponding dithiolylium salts and their infrared spectra are very similar. The infrared bands of the chloride (in KBr) were 3400m, 3250s, 3100s, 1630m, 1604s, 1510–1520vs, 1355m, 1272m, 1140w, br, 800m, 785w. As in the case of the dithiolylium salts the iodide showed a shift of some of the bands to lower frequencies (1610m, 1590s, 1330m), probably due to a lattice effect (for discussion of the infrared spectra, see the paper on the dithiolylium salts<sup>1</sup>).

*Experimental.* **3,5-Diaminodiselenolylium chloride.** Diselenomalonamide<sup>3</sup> (1.14 g; 5 mmol) was dissolved in ethanol by heating at 40°C. The solution was cooled and filtered from some selenium that had separated, and one equivalent of iron(III) chloride, dissolved in ethanol, was added with stirring. After  $\frac{1}{2}$  h, pentane was added, which induced the precipitation of a yellow crystalline solid. Yield 0.90 g (76%). It was recrystallized from aqueous methanol. On heating it decomposed above 200°C without melting. (Found: C 13.79; H 2.02; N 10.61. Calc. for C<sub>3</sub>H<sub>5</sub>Se<sub>2</sub>Cl: C 13.73; H 1.92; N 10.68).

**3,5-Diaminodiselenolylium iodide.** An ethanolic solution of diselenomalonamide (0.456 g) was oxidized with one equivalent of iodine (0.508 g) dissolved in ethanol. The solution was stirred for  $\frac{1}{2}$  h at room temperature and the resulting salt isolated as above. Yield 0.45 g (68%) of a yellow crystalline substance, which decomposed on heating above 200°C without melting. It was recryst-