

## Organic Selenium Compounds

## IX. Infrared Spectra of Diselenocarbamate Complexes

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The infrared spectra of all the diethyl-diselenocarbamate complexes described in our earlier publication<sup>1</sup> exhibit (in addition to the C—H stretching bands and the CH<sub>2</sub> and CH<sub>3</sub> deformation bands in the 1300–1500 cm<sup>-1</sup> region) the following absorption maxima (in KBr; cm<sup>-1</sup>): 1395–1525 (vs), 1265–1275 (vs), 1190–1200 (s), 1140–1150 (s), 1090–1095 (w-m), 1070–1078 (s), 1060 (m or sh), 990–995 (w), 945–950 (w), 850–860 (w-m), 820–830 (w-m), 790 (vw or sh), 770–775 (w), 510 (vw), 445–460 (w-vw).<sup>\*</sup> The nitrosyl complexes [Fe(NO)(Et<sub>2</sub>NCSe<sub>2</sub>)<sub>2</sub>] and [Co(NO)(Et<sub>2</sub>NCSe<sub>2</sub>)<sub>2</sub>] in addition exhibit a strong NO stretching band<sup>1</sup> and a very weak band at 575 cm<sup>-1</sup>. None of the other spectra exhibits a band near 570 cm<sup>-1</sup>.

The only infrared band which exhibits a more pronounced variation in wavenumber is the band near 1500 cm<sup>-1</sup>. Like the corresponding band of dithiocarbamates,<sup>3</sup> this band is assigned to the R<sub>2</sub>N—CSe<sub>2</sub> bond, which has acquired some double-bond character because of the mesomeric electron releasing effect of the R<sub>2</sub>N group and the ability of S atoms to accept electrons. It is analogous to the B-band of thioamides and selenoamides.<sup>4</sup> As pointed out by Chatt *et al.*,<sup>5</sup> the frequency of this band decreases in dithiocarbamate complexes in the order planar > tetrahedral > octahedral. The same trend was found in the case of diethyldiselenocarbamate complexes:

planar (Ni, Cu, Pd, Pt):	1510–1525 cm <sup>-1</sup>
tetrahedral (Zn, Cd):	1502–1506 cm <sup>-1</sup>
octahedral (Cr, Co, Rh, In, Tl):	1495–1500 cm <sup>-1</sup>

These values are practically identical with those found for the diethyldithiocarbamate complexes.<sup>3</sup> Because a methyl group exerts a stronger inductive effect than an ethyl group, dimethyldithiocarbamate complexes exhibit this band at increased frequencies; it is found near 1550 cm<sup>-1</sup> in the spectra of both the planar complexes and the nitrosyl complexes.<sup>3,5</sup> This was also found to be the case with dimethyldiselenocarbamate complexes (see below).

As suggested by Cotton and McCleverty,<sup>5</sup> the increased frequency of the R<sub>2</sub>N—CSe<sub>2</sub> bond in planar complexes may be rationalized in terms of a donation of electrons from the dithiocarbamate group into a non-bonding orbital of the metal atom. The fact that the diselenocarbamate complexes exhibit an almost identical variation in frequency, again indicates that sulfur and selenium do not differ essentially in electronegativity (*cf.* the preceding paper).<sup>6</sup>

No significant differences have been found in the wavenumbers of the other bands of the various metal complexes. Further, their intensities are essentially independent of the metal atom, with one marked exception, however: In the planar complexes the 830 cm<sup>-1</sup> band is stronger than the 850 cm<sup>-1</sup> band while the opposite applies to tetrahedral complexes. The octahedral complexes exhibit these two bands with about equal strength. This indicates that these two bands should be correlated with the coordinated CSe<sub>2</sub> group.

This conclusion is corroborated by a comparison of the infrared spectra of diethyldithiocarbamate and diethyldiselenocarbamate complexes. Although most of the infrared bands of the two types of complexes are found at approximately the same wavenumbers (within a few cm<sup>-1</sup>) and with only slight differences in intensity, there are, however, two major exceptions: Firstly, the diethylthiocarbamate complexes exhibit a band near 910 cm<sup>-1</sup> which is not found in the spectra of the diselenocarbamate complexes and, conversely, these latter complexes exhibit two bands, at 950 cm<sup>-1</sup> and 820–830 cm<sup>-1</sup>, which are not found in the spectra of the diethylthiocarbamate complexes. Second-

<sup>\*</sup> The spectra were recorded on a Perkin Elmer Model 337 grating spectrophotometer. The customary abbreviations have been used to indicate intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

ly, the diethyldithiocarbamate complexes have two weak bands at  $575\text{ cm}^{-1}$  and  $490\text{ cm}^{-1}$  which are shifted to  $510\text{ cm}^{-1}$  and  $450\text{ cm}^{-1}$  in the spectra of diethyldiselenocarbamate complexes. It seems plausible that these bands should be correlated with the  $\text{CS}_2$  and  $\text{CSe}_2$  groups, respectively.

The assignment of the bands in the  $800\text{--}1000\text{ cm}^{-1}$  region is less unambiguous because there are other vibrations in this region with which  $\text{CS}_2$  and  $\text{CSe}_2$  vibrations could be coupled. However, since the  $830\text{ cm}^{-1}$  band is only observed in the spectra of the diethyldiselenocarbamates and is susceptible to changes of the stereochemistry of the complex, it seems plausible that this band should be assigned to the  $-\text{CSe}_2$  group. The  $850\text{--}860\text{ cm}^{-1}$  band is also present in the spectra of the diethyldithiocarbamates, but not in those of the dimethyldithiocarbamates; it is therefore assigned to C—C stretching vibration. Because it is located so near the  $830\text{ cm}^{-1}$  band of the diethyldiselenocarbamates, coupling with the latter vibration may occur. This may be the explanation of the fact that the intensity of this band is also dependent on the complexing metal. The  $950\text{ cm}^{-1}$  band, on the other hand, is not considered to be caused by the  $-\text{CSe}_2$  group for the following reasons: This band is only weak or very weak, whereas the  $-\text{CSe}_2$  band of the diselenocarbonates is a rather strong band.<sup>7</sup> Further the  $-\text{CSe}_2$  frequency of the diselenocarbamates should be lower than that of the diselenocarbonates, and for the latter the  $-\text{CSe}_2$  band is near  $935\text{ cm}^{-1}$ . Finally, the stretching frequency of the  $-\text{CS}_2$  group should undoubtedly be higher than that of the  $-\text{CSe}_2$  group, so the  $950\text{ cm}^{-1}$  band cannot be due to the  $-\text{CSe}_2$  group if the  $910\text{ cm}^{-1}$  band is due to the  $\text{CS}_2$  group.

An absorption band near  $990\text{ cm}^{-1}$  is common for the diethyldithiocarbamates and diethyldiselenocarbamates, but it is more intense for the dithiocarbamates and therefore probably has some contribution from the C=S stretching vibration.

Because of the ambiguities caused by the presence of the ethyl groups, we have prepared dimethyldiselenocarbamates of nickel and cobalt and compared their infrared spectra with those of the corresponding dimethyldithiocarbamates. In this case an unambiguous assignment of  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C}=\text{Se})$  is possible. The only major difference between the *N,N*-

dimethyldithio- and -diselenocarbamates is that a strong band at  $975\text{ cm}^{-1}$  in the spectra of the thio compounds is replaced by a medium strong band at  $890\text{--}900\text{ cm}^{-1}$  in the spectra of the seleno compounds.

Below  $500\text{ cm}^{-1}$  there are some differences between the corresponding sulfur and selenium compounds\* and also between analogous nickel and cobalt compounds, which indicates that some of the bands in this region are due either to ligand-metal vibrations or to deformation vibrations of the  $\text{CS}_2$  or  $\text{CSe}_2$  group which are influenced by the coordinated metal. Otherwise the spectra of the *N,N*-dimethyldithio- and -diselenocarbamates are very similar, except that, as in the case of the diethyl derivatives, the C=N frequency is lower for the cobalt compound.

When the methyl and ethyl compounds are compared the main differences are that the infrared bands of the methyl compounds at  $1550\text{ cm}^{-1}$ ,  $975\text{ cm}^{-1}$  (S-compound), and  $890\text{ cm}^{-1}$  (Se-compound) are shifted to lower wavenumbers, and those at  $1245\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  are shifted to higher wavenumbers, when  $\text{CH}_3$  is substituted by  $\text{C}_2\text{H}_5$ .

Among the additional bands which appear only in the spectra of the ethyl derivatives, the  $860\text{ cm}^{-1}$  band should probably be assigned to C—C stretch, as discussed above.

Accordingly, we come to the conclusion that the following infrared bands of metal dithiocarbamates and diselenocarbamates are essentially due to C=S and C=Se stretching vibrations:

	<i>N,N</i> -Dimethyl	<i>N,N</i> -Diethyl
$\nu(\text{C}=\text{S})$	$972\text{--}975\text{ cm}^{-1}$	$910\text{--}915\text{ cm}^{-1}$
$\nu(\text{C}=\text{Se})$	$890\text{--}900\text{ cm}^{-1}$	$820\text{--}830\text{ cm}^{-1}$

This result is, in the main, in accordance with the results of Pilipenko and Mel'nikova.<sup>8</sup> Durgaprasad *et al.*,<sup>2</sup> who have carried out a normal coordinate analysis of nickel dimethyldithiocarbamate, have come to other results.

The spectrum reported by Durgaprasad *et al.* for nickel *N,N*-dimethyldithiocarbamate is essentially in agreement with ours, except that their weak bands at

\* The spectra below  $500\text{ cm}^{-1}$  were recorded on a Perkin Elmer 225 infrared spectrophotometer. We thank Dr. F. A. Andersen for making these spectra available to us.

676, 650, 600, 590, 355, 341, 327, and 315  $\text{cm}^{-1}$  are absent from our spectra.

However, the Indian authors have also carried out a normal coordinate analysis of nickel *N,N*-dimethyldiselenocarbamate, but here the model used has been unsatisfactory. In fact, the spectrum of this compound (which was not available to the authors) shows none of the calculated frequencies, except the band near 1550  $\text{cm}^{-1}$ . Especially, there is no absorption between 1040 and 900  $\text{cm}^{-1}$  so the calculated frequency for  $\nu(\text{C}=\text{Se})$  as 946  $\text{cm}^{-1}$  cannot be correct.

Our empirical assignments have been corroborated by a normal coordinate analysis,<sup>9</sup> carried out in this laboratory, of nickel dimethyldithiocarbamate.

**Experimental.** The dimethyldithiocarbamates were prepared by known methods;<sup>10</sup> the nickel complex was recrystallized from dimethylformamide and the cobalt complex from chloroform-ethanol.

The dimethyldiselenocarbamates were prepared in a similar manner as the diethyldiselenocarbamates.<sup>1</sup> The nickel complex (yellow) could be recrystallized from dimethylformamide but was much less soluble than the corresponding dithiocarbamate. (Found: C 14.72; H 2.47; N 5.78. Calc. for  $\text{C}_6\text{H}_{12}\text{N}_2\text{NiSe}_2$ : C 14.81; H 2.49; N 5.76). The cobalt complex (brown) was recrystallized from chloroform-ethanol. (Found: C 15.40; H 2.53; N 5.64. Calc. for  $\text{C}_9\text{H}_{18}\text{CoN}_3\text{Se}_2$ : C 15.42; H 2.59; N 6.00).

**Infrared spectra.**  $\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Ni}\}$ : 1550vs, 1445m, 1379vs, 1232m, 1142vs, 1050m, 890m, 870vw, 375w, 325m.  $\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Co}\}$ : 1528vs, 1448m, 1390vs, 1235m, 1138vs, 1048m, 900m, 875w, 754w, 746w, 375w, 330w.

$\{[(\text{CH}_3)_2\text{NCS}_2]_2\text{Ni}\}$ : 1550vs, 1445m, 1400vs, 1245s, 1150vs, 1052m, 1015w, 975s, 894vw, 572vw, 550vw, 442m, 414m, 387s, 375s, 300m.  $\{[(\text{CH}_3)_2\text{CS}_2]_2\text{Co}\}$ : 1528vs, 1450m, 1390vs, 1255s, 1145vs, 1050w, 1025vw, 975s, 895vw, 580w, 442m, 360s, 324w.

- Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **21** (1967) 2904.
- Durgaprasad, G., Sathyanarayana, D. N. and Patel, C. C. *Can. J. Chem.* **47** (1969) 631.
- Chatt, J., Duncanson, L. A. and Venanzi L. M. *Suomen Kemistilehti B* **29** (1956) 75.
- Jensen, K. A. and Nielsen, P. H. *Acta Chem. Scand.* **20** (1966) 597.
- Cotton, F. A. and McCleverty, J. A. *Inorg. Chem.* **3** (1964) 1398.
- Jensen, K. A. and Krishnan, V. *Acta Chem. Scand.* **24** (1970) 743.<sup>1</sup>
- Jensen, K. A. and Anthoni, U. *Acta Chem. Scand.* *In press.*
- Pilipenko, A. T. and Mel'nikova, N. V. *Russian J. Inorg. Chem.* **14** (1969) 236.
- Jensen, K. A., Dahl, B. M., Nielsen, P. H. and Nielsen, O. Faurskov *Acta Chem. Scand.* *In press.*
- Delépine, M. *Bull. Soc. Chim. France* [4] **3** (1908) 643, p. 651.

Received March 12, 1970.

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### X. Coordination Compounds of 1,1-Diselenolates

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Lately much interest has centered around coordination compounds of 1,1-dithiols and 1,2-dithiols (*cf.* the reviews by Gray<sup>1</sup> and Jørgensen<sup>2</sup>) but, so far, the only selenium analogue investigated has been 1,2-bis(trifluoromethyl)-1,2-diselenol, of which some metal compounds have recently been described.<sup>3</sup> In connection with investigations, in this laboratory, of the reactions of carbon diselenide with active methylene compounds, alkali metal salts of 2,2-dicyanoethylene-1,1-diselenol,  $(\text{NC})_2\text{C}=\text{C}(\text{SeH})_2$ , and cyanimidodiselenocarbonic acid,  $\text{NC}-\text{N}=\text{C}(\text{SeH})_2$ , have been prepared,<sup>4</sup> from which some transition metal complexes have been obtained.

When a heavy metal salt is added to an aqueous solution of a 1,1-diselenolate an intensely coloured, brown or red-brown, solution is obtained, containing the anions I or II. The corresponding alkali metal salts are very soluble but, as in the case of the corresponding dithiolates, certain onium salts are only slightly soluble. Usually the anions I and II were isolated as tetraphenylphosphonium salts. When strong acid is added to solutions of the