# Organic Selenium Compounds

## VI. Diselenocarbamate Complexes of Transition Metals

K. A. JENSEN and V. KRISHNAN

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark*

Investigations of selenium-containing ligands are scarce. In connection with extensive studies of organic selenium compounds in this laboratory, their ability to form coordination compounds has also been investigated. Thus, metal compounds of selenoamides, selenosemicarbazides, alkoxyselenocarbonylhydrazines, diselenocarbamates, diselenocarbazates, and 1,1-diselenolates have been prepared. In this paper we describe some diethyldiselenocarbamates of transition metals.

Some years ago, Barnard and Woodbridge prepared the first dialkyldiselenocarbamates and also prepared some metal salts, *viz.* various zinc dialkyldiselenocarbamates and copper diethyldiselenocarbamate.[1] We have found it desirable to extend this material, especially with a view to investigating the spectra of transition metal complexes of diselenocarbamates. Various new dialkylselenocarbamates have been prepared in this laboratory,[2] but since their complex-forming properties seem to be very similar, we have concentrated on isolating complexes of diethyldiselenocarbamic acid (salts of this acid can be prepared more easily than those of the simpler dimethyldiselenocarbamic acid).

Sodium diethyldiselenocarbamate was prepared from diethylamine, carbon diselenide, and sodium hydroxide. On addition of an aqueous solution of the diselenocarbamate to solutions of transition metal salts, the corresponding diselenocarbamates usually precipitate in almost quantitative yields. The compounds are soluble in organic solvents. They were in most cases recrystallized from chloroform. They are somewhat darker coloured than the corresponding dithiocarbamates but otherwise resemble the dithiocarbamates very much, in appearance as well as in solubility and chemical properties. The new diselenocarbamate complexes * have been listed in Table 1. In addition, the copper(II) and zinc diselenocarbamates, already described by Barnard and Woodbridge,[1] were investigated. Further, it was found that the cobalt(II) and iron(II) diselenocarbamates (not isolated) easily absorbed nitrogen(II) oxide to form nitrosyl complexes similar to the known diethyldithiocarbamate compounds.

Like nickel(II) diethyldithiocarbamate,[3] the corresponding diselenocarbamate adds bromine to form a black compound, $Ni(Et_2NCSe_2)_2Br_2$, which contains formally quadrivalent nickel.

The electronic spectra of the diselenocarbamate complexes in chloroform solution show the expected red-shift of the *d-d* transition bands compared to those of dithiocarbamates, due to the lower optical electronegativity, $x_{opt}$, of the selenium ligand.[4]

The infrared spectra (KBr) of the nitrosyl compounds exhibit strong and sharp N—O stretching bands at 1623 $cm^{-1}$ (Co compound) and 1682 $cm^{-1}$ (Fe compound), practically at the same place as for the corresponding dithiocarbamates.[5]

The compound $Ni(Et_2NCSe_2)_2Br_2$ has an intense charge transfer band at 522 m$\mu$. This band is quite reproducible, but the ultraviolet bands show changes with time after addition of bromine to the chloroform solution of $Ni(Et_2NCSe_2)_2$ showing that the ligand undergoes some decomposition.

The electronic spectra of the diselenocarbamates do not change on addition of pyridine. For comparison, nickel *O*-ethyldiselenocarbonate ("diselenoxanthate") was prepared. The red solution of this compound instantly turns yellow on addition of pyridine, presumably because the low-spin square planar compound is transformed into a high-spin hexacoordinated compound, $NiL_2py_2$, as in the case of the corresponding xanthate.[6]

The spectra of the diselenocarbamate complexes will be discussed in more detail in a forthcoming paper.

*Experimental.* The diselenocarbamates were prepared from the metal chlorides and an aqueous solution of sodium diethyldiselenocarbamate. The latter was prepared in the following manner. A solution of diethylamine (1.46 g) in dry diethyl ether (10 ml) was added dropwise with frequent shaking to an ice-

* While this investigation was in progress, some of these compounds were also prepared by C. Furlani (private communication).

*Table 1.* Diethyldiselenocarbamates (L = $(C_2H_5)_2NCSe_2^-$).

| Formula | | Colour | M.p., °C | Analyses (C, H, N) | | | |
|---|---|---|---|---|---|---|---|
| TlL | ($C_5H_{10}NSe_2Tl$) | yellow | 134[a] | Found: | 13.45; | 2.37; | 3.18 |
| | | | | Calc.: | 13.47; | 2.24; | 3.13 |
| $NiL_2$ | ($C_{10}H_{20}N_2NiSe_4$) | dark red | 278[a] | Found: | 21.94; | 3.60; | 5.28 |
| | | | | Calc.: | 22.13; | 3.68; | 5.16 |
| $NiL_2Br_2$ | ($C_{10}H_{20}Br_2N_2NiSe_4$) | black | 154[b] | Found: | Br 22.6; | N 3.89 | |
| | | | | Calc.: | Br 22.7; | N 3.99 | |
| $PdL_2$ | ($C_{10}H_{20}N_2PdSe_4$) | red | 294[a] | Found: | 20.42; | 3.25; | 4.85 |
| | | | | Calc.: | 20.35; | 3.38; | 4.74 |
| $PtL_2$ | ($C_{10}H_{20}N_2PtSe_4$) | yellow | 303[a] | Found: | 17.62; | 3.01; | 3.97 |
| | | | | Calc.: | 17.68; | 2.94; | 4.12 |
| $CdL_2$ | ($C_{10}H_{20}CdN_2Se_4$) | yellow | 240[c] | Found: | 20.11; | 3.17; | 4.60 |
| | | | | Calc.: | 20.14; | 3.35; | 4.69 |
| $InL_3$ | ($C_{15}H_{30}InN_3Se_6$) | yellow | 280[d] | Found: | 21.35; | 3.63; | 5.16 |
| | | | | Calc.: | 21.41; | 3.57; | 4.99 |
| $TlL_3$ | ($C_{15}H_{30}N_3Se_6Tl$) | red | 210–215[a] | Found: | 19.38; | 3.17; | 4.53 |
| | | | | Calc.: | 19.36; | 3.22; | 4.51 |
| $CrL_3$ | ($C_{15}H_{30}CrN_3Se_6$) | violet | 283–285[a] | Found: | 20.07; | 3.26; | 4.24 |
| | | | | Calc.[e]: | 20.07; | 3.22; | 4.13 |
| $RhL_3$ | ($C_{15}H_{30}N_3RhSe_6$) | red | 301–302[a] | Found: | 21.87; | 3.51; | 5.12 |
| | | | | Calc.: | 21.73; | 3.62; | 5.06 |
| $CoL_2NO$ | ($C_{10}H_{20}CoN_3OSe_4$) | dark brown | *f* | Found: | 20.69; | 3.45; | 7.54 |
| | | | | Calc.: | 20.96; | 3.49; | 7.33 |
| $FeL_2NO$ | ($C_{10}H_{20}FeN_3OSe_4$) | dark brown | *g* | Found: | 20.16; | 3.45; | 7.54 |
| | | | | Calc.: | 21.08; | 3.51; | 7.37 |
| $Ni(EtOCSe_2)_2$ | ($C_6H_{10}O_2NiSe_4$) | black[h] | 180 (decomp.) | Found: | 14.73; | 2.02 | |
| | | | | Calc.: | 14.75; | 2.04 | |

[a] Recrystallized from chloroform.
[b] Precipitated from chloroform solution with petroleum ether.
[c] Recrystallized from benzene.
[d] Recrystallized from chloroform-acetone.
[e] For $C_{15}H_{30}CrN_3Se_6 \cdot 2CHCl_3$. The compound crystallized with two molecules of chloroform.
[f] Decomposes at 180°C on a Kofler hot plate.
[g] Decomposes at 230°C on a Kofler hot plate.
[h] Dark red in solution.

cooled solution of carbon diselenide (1.70 g) in ether (30 ml). A yellow precipitate began to separate during addition of the amine. As soon as the addition of the amine had been completed, the precipitate was collected on a glass filter and washed with ether. The precipitate was dissolved in 20 ml of 0.5 N NaOH to give a clear solution.

The chromium compound was prepared by refluxing an ethanolic solution of $CrCl_3 \cdot 6H_2O$ with the sodium diethyldiselenocarbamate solution for 12 h under nitrogen. The resulting greenish precipitate was filtered off and extracted with chloroform in a Soxhlet apparatus. On concentration of the solution, violet crystals separated. In other cases precipitation of the diselenocarbamates ensued on addition of the diselenocarbamate solution to solutions of the metal chlorides. Usually these were employed in aqueous solution, but thallium(III) chloride was dissolved in acetonitrile (1 g of $TlCl_3 \cdot 4H_2O$ in 30 ml of acetonitrile). In the case of the nickel compound, the precipitate was extracted immediately with chloroform, but in other cases the precipitate was filtered off, dried, and crystallized from chloroform.

The addition product of bis(*N*,*N'*-diethyldiselenocarbamato)-nickel(II) and bromine—presumably dibromobis(*N*,*N'*-diethyldiselenocarbamato)nickel(IV)—was prepared by addition of two equivalents of bromine to a solution of the diselenocarbamate in chloroform. On addition of petroleum ether and scratching of the sides of the flask, black crystals of the dibromo compound separated.

Bis(*N,N'*-diethyldiselenocarbamato)copper (II) and bis(*N,N'*-diethyldiselenocarbamato) zinc, reported by Barnard and Woodbridge,[1] were also prepared by the present method. The copper complex (black, m.p. 221°C) was recrystallized from chloroform and the zinc complex (yellow, m.p. 153–154°C) from benzene.

The yields of the complexes were almost quantitative. They were stored in a desiccator, over KOH and under nitrogen, in a cold room.

*Bis(O-ethyldiselenocarbonato)nickel(II).* Carbon diselenide (0.85 g) was added dropwise to a stirred and ice-cooled solution of potassium hydroxide (0.28 g) in ethanol, kept under nitrogen. This solution was added to a solution of $NiCl_2 \cdot 6H_2O$ (0.59 g) in water, with formation of a red precipitate. This was quickly extracted with chloroform, which on evaporation left black, glistening crystals of the complex.

*Bis(N,N'-diethyldiselenocarbamato)nitrosylcobalt(II).* Anhydrous cobalt(II) chloride (0.162 g) was dissolved in methanol, previously degassed with nitrogen, and the solution was saturated with nitrogen oxide. Sodium diethyldiselenocarbamate (0.66 g) dissolved in methanol was added to the $CoCl_2$ solution under nitrogen and nitrogen oxide was again passed through the solution. A brown precipitate resulted which was filtered off, washed with cold methanol under nitrogen and recrystallized from chloroform.

*Bis(N,N'-diethyldiselenocarbamato)nitrosyliron(II).* $FeCl_2 \cdot 4H_2O$ (0.245 g) was dissolved in degassed methanol, and diethyldiselenocarbamate (0.66 g) dissolved in methanol was added under nitrogen, with formation of a red precipitate. On saturation of the solution with nitrogen oxide, a brown precipitate separated. It was filtered off under nitrogen, washed with cold methanol, and crystallized from chloroform.

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# Mass Spectrometric and Gas Chromatographic Studies of *N*-Heptafluorobutyryl Derivatives of Peptide Methyl Esters

BENGT A. ANDERSSON

*Institute of Medical Biochemistry, University of Göteborg, Sweden*

The *N*-trifluoroacetyl (*N*-TFA) derivatives of peptide methyl esters have been found useful in the direct mass spectrometric sequence analysis of peptides.[1-3]

It has recently been found by Pollock [4] that the *N*-heptafluorobutyryl (*N*-HFB) derivatives of butyl esters of amino acids have significantly shorter gas chromatographic retention times than the corresponding *N*-TFA derivatives. It was therefore of interest to study the mass spectrometric behaviour of the *N*-HFB derivatives of peptide methyl esters. Two peptide methyl esters, DL-Ala-DL-Phe-OMe and Gly-Gly-Gly-OMe, were acylated using the TFA and HFB anhydrides.[5] The exchange of the trifluoroacetyl for the heptafluorobutyryl group reduced the gas chromatographic retention times on Carbowax 20M columns by approximately 50 %, and considerably lower temperatures were needed for the vapourization of the sample in the direct inlet system of the mass spectrometer. The mass spectra shown on Figs. 1 and 2 show the striking similarity in the fragmentation pattern between the TFA and HFB-derivatives, the only notable difference being that of 100 mass units in the *m/e* of ions containing the *N*-acyl group.

As peptide methyl esters *N*-acylated with long chain acyl groups give excellent mass spectra [6] the mass spectrometric behaviour of peptide esters with higher *N*-perfluoroacyl groups is being studied.