Organic Selenium Compounds

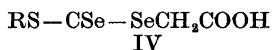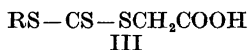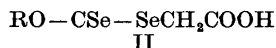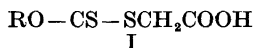## XIV.* Assignment of the C=Se Stretching Frequency of Dialkyl Diselenocarbonates and Diselenothiocarbonates

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Diselenocarbonates and diselenothiocarbonates of the types RO—CSe—SeCH$_2$CO$_2$H and RS—CSe—SeCH$_2$CO$_2$H exhibit a strong infrared band in the range 930—980 cm^{-1}. This band is missing in the infrared spectra of analogous dithiocarbonates and trithiocarbonates and is therefore ascribed to the C=Se stretching vibration.

Several [(alkoxythiocarbonyl)thio]acetic acids [1] (I) and [(alkoxyselenocarbonyl)seleno]acetic acids [2] (II) have been prepared in this laboratory. In this paper we report the preparation of corresponding {[(alkylthio)thiocarbonyl]thio}acetic acids (III) and {[(alkylthio)selenocarbonyl]seleno}acetic acids (IV).

$$RO-CS-SCH_2COOH \qquad\qquad RO-CSe-SeCH_2COOH$$
$$I \qquad\qquad\qquad\qquad\qquad II$$

$$RS-CS-SCH_2COOH \qquad\qquad RS-CSe-SeCH_2COOH$$
$$III \qquad\qquad\qquad\qquad\qquad IV$$

These compounds may also be considered as alkyl carboxymethyl esters of dithio-, trithio-, diseleno- and diselenothiocarbonic acids. One reason for studying these types of compound is that, since the carboxymethyl group is more reactive than the alkyl ester group, they give access to ester-amides and ester-hydrazides of thio- and selenocarbonic acids.[1,2] Another reason is that the carboxymethyl esters are crystalline solids which can be purified by recrystallization. This is of importance in the case of the selenium compounds because these are unstable and only available in small quantities. The compounds IV were obtained *via* the reaction of thiolates with carbon diselenide. Attempts to prepare the corresponding triselenocarbonates from selenolates and carbon diselenide were unsuccessful, only diselenides and bis(carboxy-

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methyl) triselenocarbonate being obtained. This result is in accordance with experiments by Henriksen,[3] which show that triselenocarbonates are very sensitive towards bases, including selenolate ions.

The infrared spectra of these compounds furnish additional evidence [4] for the location of the $C=S$ stretching band. The spectra of the corresponding compounds (I) and (II) or (III) and (IV) are very similar, except for differences in intensities, down to about 1100 cm⁻¹. Below this frequency all the compounds with a $C=S$ group (I and III) have a strong band near 1050 cm⁻¹ which is missing in the spectra of the compounds with a $C=Se$ group (II and IV). Instead these have a strong band near 950 cm⁻¹ which is missing in the spectra of the analogous $C=S$ compounds (Table 1). These facts can only be explained by assuming that the two bands are due to the $C=S$ and

Table 1. $C=S$, $C=Se$, and $C-SR$ stretching frequencies (in KBr; cm⁻¹) of dithio-, trithio-, diseleno-, and diselenothiocarbonates.

Compound	$\nu(C=S)$	$\nu(C-SR)$	Compound	$\nu(C=Se)$	$\nu(C-SR)$
$MeO-CS-SCH_2CO_2H$	1065vs		$MeO-CSe-SeCH_2CO_2H$	980s	
$MeS-CS-SCH_2CO_2H$	1058vs	815m			
$EtO-CS-SCH_2CO_2H$	1045vs		$EtO-CSe-SeCH_2CO_2H$	950}935}s	
$EtS-CS-SCH_2CO_2H$	1040s	825s	$EtS-CSe-SeCH_2CO_2H$	940s	775s
$Pr^nO-CS-SCH_2CO_2H$	1055vs		$Pr^nO-SCe-SeCH_2CO_2H$	960vs	
$Pr^nS-CS-SCH_2CO_2$	1060}1045}s	815m			
$Pr^iO-CS-SCH_2CO_2H$	1040vs		$Pr^iO-CSe-SeCH_2CO_2H$	930vs	
$Pr^iS-CS-SCH_2CO_2H$	1065}1042}vs	812s	$Pr^iS-CSe-SeCH_2CO_2H$	942vs	775s
$AllylS-CS-SCH_2CO_2H$	1062vs	807s			
$Bu^nO-CS-SCH_2CO_2H$	1060vs				
$Bu^nS-CS-SCH_2CO_2H$	1064}1047}s	812s			
$Bu^iO-CS-SCH_2CO_2H$	1060vs				
$Bu^iS-CS-SCH_2CO_2H$	1048vs	808s	$Bu^iS-CSe-SeCH_2CO_2H$	940vs	795s
$Bu^tS-CS-SCH_2CO_2H$	1062vs	800s			
$PhCH_2O-CS-SCH_2CO_2H$	1050vs				
$PhCH_2S-CS-SCH_2CO_2H$	1065vs	823m			
$S=C(SCH_2CO_2H)_2$	1050vs	870m	$Se=C(SeCH_2CO_2H)_2$	930s	
$S=C\binom{S}{S}$	1060vs	830s	$Se=C\binom{Se}{Se}$	870}880}s	
$EtO-CSSK$	1055vs		$EtO-CSeSeK$	940s	
$Ni(EtOCSS)_2$	1025vs		$Ni(EtOCSeSe)_2$	935vs	

$C=Se$ stretching vibration, respectively (at any rate as a major contribution). The frequencies of these bands are remarkably constant, in contrast to what has been found for the infrared spectra of dithiocarboxylates, $R-CSSR'$, and diselenocarboxylates, $R-CSeSeR'$.[5] In these cases the two bands are somewhat dependent upon the nature of R, which may be explained by a

coupling of the C = S or C = Se vibrations with vibrations of the alkyl or aryl groups. It seems reasonable that the influence of the R group should be negligible when it is not directly attached to the $-$ CSSR' or $-$ CSeSeR' group.

All the compounds with an RO group (I and II) have a very intense and generally broad band in the $1210-1250$ cm^{-1} range and a somewhat weaker band in the $1140-1190$ cm^{-1} range. These bands may be assigned to C $-$ O stretching vibrations of the R $-$ O group, as in the case of metal xanthates.[6-8] However, also the compounds with an RS group (III and IV) have rather intense bands around 1200 cm^{-1} and 1180 cm^{-1}. This indicates that these bands are, in part, caused by C $-$ O stretching vibrations of the carboxyl group, which are usually found near 1300 and 1200 cm^{-1} (cf. Ref. 9). In the spectra of type I compounds these vibrations apparently couple with the C $-$ O vibrations of the R $-$ O group resulting in a very strong and intense band near 1250 cm^{-1} with only a weak band, or a shoulder, at 1300 cm^{-1}. The spectra of the corresponding selenium compounds (II) and the RS compounds (III and IV) have instead two distinct bands at $1280-1300$ cm^{-1} and $1200-1250$ cm^{-1}. In addition they exhibit one or more bands of moderate intensity between 1100 and 1200 cm^{-1}.

The conclusion that the bands of compounds III and IV in the $1200-1300$ cm^{-1} region are caused by vibrations of the carboxyl group is corroborated by the observation that the bis(carboxymethyl) esters $S = C(SCH_2COOH)_2$ and $Se = C(SeCH_2COOH)_2$ similarly exhibit strong bands in this region (trithiocarbonate: 1208 cm^{-1}; triselenocarbonate: 1270 cm^{-1}) while dimethyl trithiocarbonate [10] and triselenocarbonate [3] do not have strong bands between 1200 cm^{-1} and 1300 cm^{-1}.

The assignment of two bands in the $1100-1300$ cm^{-1} to C $-$ O vibrations is also in accordance with the normal coordinate analysis of $(EtO-CSS)_2Ni$ by Agarwala et al.[11] However, these authors assume that there is a significant contribution from $\nu(C = S)$ to the 1115 cm^{-1} band of this nickel complex. This does not seem plausible because this band is only shifted to 1108 cm^{-1} in the spectrum of the corresponding selenium compound. Also, the spectra of the compounds of types I and III show very small differences in the $1000-1100$ cm^{-1} region.

The C = O stretching frequency is found at 1700 ± 10 cm^{-1} for all the compounds of types I $-$ IV.

The infrared spectra of alkali metal O-alkyl dithiocarbonates (xanthates) exhibit a strong infrared band near 1050 cm^{-1}. Although the two C $-$ S bonds of the $-$ CS$_2^-$ ion would be expected to be equivalent $-$ which is also evident from X-ray structure analyses [12-14] $-$ the anti-symmetric stretching vibration of the $-$ CS$_2^-$ ion apparently falls very close to the C = S stretching vibration. In the infrared spectrum of potassium O-ethyl diselenocarbonate, $C_2H_5O-CSe_2K$, the OC_2H_5 bands are found at almost the same wavenumber as in the spectrum of the corresponding sulfur compound, but instead of the 1055 cm^{-1} band there is a strong band at 940 cm^{-1} (Table 1). A similar difference between the sulfur and selenium compounds is found in the spectra of the chelate nickel complexes. This rules out the supposition, by Watt and McCormick,[7] that the strong band at 1042 cm^{-1} of nickel methylxanthate should be caused by a methyl rocking motion. In fact, their own experimental data

support the assignment of this band to a $C=S$ stretching mode because its wavenumber in transition metal complexes decreases in the order $Ni(II)>Pd(II)>Pt(II)$ and at the same time the wavenumber of the first $C-O$ band (near 1250 cm^{-1}) increases; also the second band has a much lower frequency (1115 cm^{-1}) than for xanthate esters (*ca.* 1180 cm^{-1}). This can be explained by assuming an increased contribution of the resonance structure $R\overset{+}{O}=CS\bar{S}$, which increases the donor ability of the sulfur atom.

All the RS compounds (III and IV) have a rather strong infrared band in the $795-825$ cm^{-1} range (Table 1). This is assigned to the $\nu(C-SR)$ vibration, which should appear with both increased wavenumber and intensity because of the contribution of the structure $\bar{S}-C=\overset{+}{S}R$. The $\nu(C-S)$ vibration of the $C-SCH_2CO_2H$ group cannot be ascertained, most compounds of the type $RO-CS-SCH_2CO_2H$ showing only weak bands in the $700-900$ cm^{-1} range. Possibly this vibration couples with the OH deformation vibration of the carboxyl group near 900 cm^{-1}. The same applies to the $C-Se$ vibration of the compounds of the type $RO-CSe-SeCH_2CO_2H$.

The symmetric stretching vibration of the $-CS_2^-$ and $-CSe_2^-$ groups cannot be identified; without doubt, coupling with other vibrations is extensive. Schmidt *et al.*[8] have assigned a band near 860 cm^{-1} in the spectra of xanthates of the type $Ph_3MSCSOEt$ ($M=Ge$, Sn, Pb) to $\nu(C-S)$, whereas Watts and McCormick[7] and Agarwala *et al.*[11] consider the 857 cm^{-1} band of $(EtO-CS_2)_2Ni$ to be due to $C-C$ stretching because it does not occur in the spectra of methyl-xanthates. We find that this band is shifted only to 825 cm^{-1} in the spectrum of $(EtO-CSe_2)_2Ni$, which indicates that contributions from $C-S$ or $C-Se$ vibrations, if any, can only be small. A more complete discussion of the spectra of diselenoxanthate complexes will be published in another paper.

EXPERIMENTAL

Microanalyses were carried out in the microanalysis department of this laboratory. Melting points were determined in capillary tubes and were not corrected. The IR spectra were, in most instances, recorded on a Perkin-Elmer model 21 double beam spectrophotometer. In addition, some of the spectra were recorded on a Perkin-Elmer model 337 Grating Infrared Spectrophotometer.

Method A. The compounds were prepared following the directions given by Holmberg[15] for {[(ethylthio)thiocabonyl]thio}acetic acid. However, this method failed in the case of benzyl and allyl derivatives.

Method B. A solution of freshly distilled mercaptoacetic acid (0.1 mol) in water (20 ml) was neutralized with potassium hydroxide (0.2 mol). Carbon disulfide (0.1 mol) was added dropwise to this solution, with stirring, over a period of 15 min. The solution was left at room temperature for 1 h, and benzyl or allyl bromide (0.1 mol) was added with stirring in one portion. The stirring was continued for a further 30 min, after which the solution was poured into excess of 1 N HCl cooled to 0°C. A semisolid product separated; it was isolated by decantation, and then dissolved in hot water. On cooling, crystals separated, which could be recrystallized from petroleum ether.

Method C. As method A, but the usual precautions in handling selenium compounds[2] were taken.

Method D. As method C, but the product separated as an oil. Purification was performed in the following way: The oil was dissolved in hexane and the solution filtered through a short column with Al_2O_3 (acid, activity grade 1) as column material. The column was subsequently washed with small portions of hexane containing 1 % of

Table 2. {[(Alkylthio)thiocarbonyl]thio}acetic acids, $RS-CS-SCH_2COOH$.

Method	R	Formula	Yield, %	M.p.,°C	Analyses (C, H, S)
A	Methyl [16]	$C_4H_6O_2S_3$	55[a]	73−74	Calc.: 26.38; 3.32 Found: 26.20; 3.36
A	Ethyl [15]	$C_5H_8O_2S_3$	60[b]	76−77	Calc.: 30.61; 4.08; 49.98 Found: 30.63; 4.12; 49.86
A	Propyl	$C_6H_{10}O_2S_3$	24[b]	38.5−39	Calc.: 34.30; 4.76; 45.70 Found: 34.22; 4.49; 45.60
A	Isopropyl	$C_6H_{10}O_2S_3$	43[b]	61−62	Found: 34.35; 4.59; 45.30
B	Allyl	$C_6H_8O_2S_3$	30[a]	64−65	Calc.: 34.62; 3.87 Found: 34.59; 3.91
A	Butyl	$C_7H_{12}O_2S_3$	45[b]	42−43	Calc.: 37.55; 5.36; 42.85 Found: 37.60; 5.65; 43.10
A	Isobutyl	$C_7H_{12}O_2S_3$	60[b]	81−82	Found: 37.40; 5.21; 42.84
A	*tert*-Butyl	$C_7H_{12}O_2S_3$	14[b]	78−79	Found: 37.85; 5.66; 42.93
B	Benzyl	$C_{10}H_{10}O_2S_3$	32[b]	104−105	Calc.: 46.53; 3.88; 37.21 Found: 46.20; 3.71; 37.31

Solvents used for recrystallization: [a] benzene-petroleum ether; [b] petroleum ether.

The directions given below refer to entry "Method", Table 2 and Table 3.

Table 3. {[(Alkylthio)selenocarbonyl]seleno}acetic acids, $RS-CSe-SeCH_2COOH$.

Method	R	Formula	Yield	M.p.,°C	Analyses (C, H)
C	Ethyl	$C_5H_8O_2SSe_2$	70[a]	61−62	Calc.: 20.69; 2.76 Found: 20.40; 2.95
D	Isopropyl	$C_6H_{10}O_2SSe_2$	3[b]	39−40	Calc.: 23.70; 3.29 Found: 23.83; 3.32
C	Isobutyl	$C_7H_{12}O_2SSe_2$	10[a]	59.5−60	Calc.: 26.42; 3.77 Found: 26.18; 3.99

Solvents used for recrystallization: [a] petroleum ether, [b] pentane, after chromatography (see text).

ethanol. Finally, the column was treated with hexane containing 1 % of formic acid to elute the carboxymethyl ester. After evaporation of the solvent the remaining crystals were recrystallized from pentane.

REFERENCES

1. Jensen, K. A., Anthoni, U. and Holm, A. *Acta Chem. Scand.* **23** (1969) 1916.
2. Jensen, K. A., Frederiksen, P. A. A. and Henriksen, L. *Acta Chem. Scand.* **24** (1970) 2061.
3. Henriksen, L. *Acta Chem. Scand. To be published.*
4. Jensen, K. A., Carlsen, J. B., Holm, A. and Nielsen, P. H. *Acta Chem. Scand.* **17** (1963) 550.
5. Jensen, K. A., Mygind, H. and Nielsen, P. H. *Acta Chem. Scand. To be published.*
6. Little, L. H., Poling, G. W. and Leja, J. *Can. J. Chem.* **39** (1961) 745.
7. Watt, G. W. and McCormick, B. J. *Spectrochim. Acta* **21** (1965) 753.

8. Schmidt, M., Schumann, H., Gliniecki, F. and Jaggard, J. F. *J. Organometal. Chem.* **17** (1969) 277.
9. Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, Methuen, London 1962.
10. Krebs, B. and Müller, A. *Z. anorg. allgem. Chem.* **348** (1966) 107.
11. Agarwala, U., Lakshmi, and Rao, P. B. *Inorg. Chim. Acta* **2** (1968) 337.
12. Shuzam, E. A. and Levine, V. M. *Kritallografiya* **5** (1960) 257.
13. Pignedoli, A. and Peyronel, G. *Gazz. Chim. Ital.* **92** (1962) 745.
14. Franzini, M. *Z. Krist.* **118** (1963) 393.
15. Holmberg, B. *J. prakt. Chem.* [2] **75** (1907) 169.
16. Sandström, J. *Acta Chem. Scand.* **17** (1963) 1380, p. 1389.