LOCALIZATION OF THE C—Se VIBRATION IN THE INFRARED SPECTRA OF SELENOSEMICARBAZONES¹

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ABSTRACT

Few organic compounds of selenium are known and, consequently, very little published data are available concerning the various vibrations around the selenium atom. The present paper discusses the C—Se vibration in selenosemicarbazones by comparing their infrared spectra with those of corresponding Se-benzyl derivatives in which the C—Se group has been replaced by a C—Se—Bz. On this basis, it can be seen that a band at 800–780 cm⁻¹ in the spectra of selenosemicarbazones is absent in the spectra of the benzyl derivatives. This band is assigned to the C—Se vibration.

In recent years, a few organic compounds of selenium have been investigated with particular emphasis on the localization of the various infrared vibrations around the selenium atom, generally by comparison with infrared spectra of analogous sulfur compounds. For instance, a band at 942 cm⁻¹ was attributed to the CSe₂⁻ ion of diselenocarboxylates by comparison with the spectra of dithiocarboxylates which lacked that band (1). In metal complexes of iso- and seleno-cyanates, the C-Se stretching vibration was found to be in the regions 650 cm^{-1} for NCSe⁻, and 550 cm^{-1} for SeCN⁻ (2, 3). In selencesters of the type Ar—CSeOMe, the region 1.227 - 1.220 cm⁻¹ was suggested by Collard-Charon and Renson (4) for the C=Se by comparison with the spectra of the corresponding this and oxygen compounds, although these workers point out the great similarity between the spectra of sulfur and selenium compounds in this class as well as in all the other compounds of selenium and sulfur they have studied. Thus, in *n*-butyl-4-selenosemicarbazides a band at 1045 cm^{-1} was assigned to the C—Se vibration while in the corresponding this compound, a band at 1055 cm^{-1} was suggested for the C=S, and at 1070 cm^{-1} (C—Se) and 1075 cm^{-1} (C—S) in *n*-butyl-4-methyl-2-seleno- and thio-semicarbazides (5). By the same method of comparison, bands at 1.080 cm^{-1} and 1.082 cm^{-1} were assigned to the C—S and C—Se respectively in thio- and seleno-ureas, and at 1.115 cm^{-1} (C=S) and 1.110 cm^{-1} (C=Se) in substituted ureas (6).

In view of the results recently reported from this laboratory on the localization of the C=S in thiosemicarbazones (7), it seemed appropriate to extend this study to seleno-semicarbazones. Because of the great similarity between the spectra of thio and seleno compounds already mentioned and because this similarity was found to exist in the case of thio- and seleno-semicarbazones, it was felt that the method of comparison could lead to very misleading conclusions. Indeed, it was found by Jensen (8) that the spectra of thio- and seleno-amides, ureas, and semicarbazides were so much alike that it was impossible to discriminate between the various vibrations. Jensen even argues that all assignments of infrared bands to the C=S group of thioamides may have been erroneous since the same bands appear in spectra of selenoamides.

The present work describes a number of new selenosemicarbazones and their infrared spectra with particular emphasis on the C—Se vibration. Another purpose of this work

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GINGRAS ET AL.: LOCALIZATION OF THE C-Se VIBRATION

was to study the antifungal properties of selenosemicarbazones and their reaction with metals. Such studies were carried out earlier with thiosemicarbazones (7, 9, 10) and a relationship was found between antifungal activity and complex formation with copper.

The selenosemicarbazones investigated are listed in Table I, together with their melting points and analyses. The preparation of these compounds is complicated by the fact that the required starting material, selenosemicarbazide, is not readily available and cannot be obtained by the procedures used for the oxygen and sulfur analogs. Seleno-semicarbazide was obtained accidentally and in low yields during the isomerization of a selenocyanate in the presence of butyraldehyde (11, 12). The possible methods of pre-paration of selenosemicarbazones were reviewed by Mautner (13) and later by Renson *et al.* (11), who arrived at the conclusion that the best method was one involving an exchange of carbonyl radicals starting from acetone selenosemicarbazone which can be obtained in fair yields. This method was used in the present work.

TABLE	I	
Selenosemicarbazones: R—C H	≿=NNH H	-C—NH2 Se

No.	Carbonyl compounds	m.p. (°C)	Yield (%)	Formulae	Required (%)	Found (%)
1	n-Heptanal	70	75	C ₈ H ₁₇ N ₃ Se	C, 41.03 H, 7.26 N, 17.95	$ \begin{array}{r} 41.24 \\ 7.10 \\ 17.90 \end{array} $
2	n-Octanal	99	53	C ₉ H ₁₉ N ₃ Se	C, 43.55 H, 7.66 N, 16.94	$\begin{array}{r} 42.88 \\ 7.56 \\ 16.92 \end{array}$
3	<i>n</i> -Nonanal	77	46	$C_{10}H_{21}N_{3}Se$	C, 45.80 H, 8.02 N, 16.03	$46.26 \\ 7.97 \\ 16.18$
4	n-Decanal	103	71	C11H23N3Se	C, 47.83 H, 8.33 N, 15.22	$47.87 \\ 8.37 \\ 15.22$
5	<i>n</i> -Undecanal	80	60	$C_{12}H_{25}N_{3}Se$	C, 49.65 H, 8.62 N, 14.48	$\begin{array}{r} 49.43 \\ 8.25 \\ 14.38 \end{array}$
6	9-Undecenal	72	32	$C_{12}H_{23}N_{3}Se$	C, 50.00 H, 7.98 N, 14.58	$50.12 \\ 8.15 \\ 14.58$
7	<i>n</i> -Dodecanal	105	90	C ₁₃ H ₂₇ N ₃ Se	C, 51.31 H, 8.88 N, 13.82	$51.53 \\ 9.16 \\ 13.94$
8	Benzaldehyde	166*			·	

*Literature m.p. 167-168 (12, 17).

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Due to the greater mass of the selenium atom, the C=Se vibration is expected to occur at somewhat lower frequencies than the C=S. The latter does not give rise to as characteristic a band as the C=O group due to the complication of interaction, particularly in the case of thiosemicarbazones where the NH rocking vibrations can interfere; however, the C=S vibration was reviewed recently for several compounds by Colthup (14) and was found to be in the range $1 \ 200 - 1 \ 050 \ cm^{-1}$. Furthermore, in an earlier publication, we assigned a band at around $1 \ 100 \ cm^{-1}$ to this vibration in the case of thiosemicarbazones (7). The region between $1 \ 200 \ and \ 700 \ cm^{-1}$ is, therefore, the logical one for the C=Se vibration to occur, at least in the case of selenosemicarbazones. This is substantiated by the value obtained for $\nu_{C=Se}$ using Gordy's rule and the harmonic oscillator equation.²

The method used previously (7) for the localization of the C=S vibration by comparing spectra of thiosemicarbazones with those of their copper complexes could not be used with reliability in the present case because of the difficulty in obtaining the copper complexes in sufficient degree of purity. Selenosemicarbazone-copper complexes can be prepared by the method described in a previous publication (10) but purification of the complexes, except in a few cases, resulted in partial decomposition and formation of colloidal selenium. However, benzyl derivatives of selenosemicarbazones, in which the benzyl radical is bonded to the selenium atom, are conveniently prepared and were found suitable for infrared studies, since the required change from C=Se to C-Se-Bz takes place.

Benzyl derivatives were then prepared from the series of selenosemicarbazones listed in Table I, and the new compounds are shown in Table II. Bands between 1 200 and 700 cm^{-1} in the spectra of selenosemicarbazones and their corresponding benzyl derivatives are shown in Table III.

It can be seen from Table III that the bands appear with a striking regularity in the



No.	Carbonyl compounds	m.p. (°C)	Yield (%)	Formulae	Required (%)	Found (%)
1a	n-Heptanal	58	59	C15H23N3Se	C, 55.56 H, 7.10 N, 12.96	$55.61 \\ 6.88 \\ 12.99$
2a	<i>n</i> -Octanal	66	48	$C_{16}H_{25}N_{3}Se$	C, 56.80 H, 7.39 N, 12.43	$56.86 \\ 7.20 \\ 12.51$
3a	<i>n</i> -Nonanal	57	40	$C_{17}H_{27}N_{3}Se$	C, 57.95 H, 7.67 N, 11.93	$58.13 \\ 7.79 \\ 11.65$
4a	n-Decanal	68	30	C18H29N3Se	C, 59.02 H, 7.92 N, 11.48	$59.47 \\ 8.21 \\ 11.72$
5a	<i>n</i> -Undecanal	67	47	C ₁₉ H ₃₁ N ₃ Se	C, 60.00 H, 8.16 N, 11.05	$\begin{array}{r} 60.00\\ 8.25\\ 11.14\end{array}$
6a	9-Undecenal	53	40	C ₁₉ H ₂₉ N ₃ Se	C, 60.32 H, 7.67 N, 11.11	$59.80 \\ 7.89 \\ 11.07$
7a	<i>n</i> -Dodecanal	70	28	$C_{20}H_{33}N_{3}Se$	C, 60.91 H, 8.38 N, 10.66	${61.03 \atop 8.60 \atop 10.88}$
8a	Benzaldehyde	158	75	C ₁₅ H ₁₅ N ₃ Se	C, 56.96 H, 4.75 N, 13.29	$56.83 \\ 4.71 \\ 13.25$

²Professor R. A. Zingaro, Agricultural and Mechanical College of Texas, reviewed this paper, carried out the calculations, and suggested that they be included. Force constants are 2.7 and 5.9 \times 10⁵ dyn/cm for "isolated" pure C—Se bond and pure C—Se bond respectively. The corresponding values are $\nu_{C-Se} = 685$ cm⁻¹, $\nu_{C=Se} = 982$ cm⁻¹.

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GINGRAS ET AL.: LOCALIZATION OF THE C=Se VIBRATION

1653

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1	1 105m	1 030m		930m		800w	770m		
1a	1.125m	1 070w	975w	935w	870w	—	765s	725w	700s
2	1 110m	1 035w 1 045m	990w	935w	895w	780m	765w	725m	
2a	$1 \ 130 m$	1 070w 1 030w	980w	945w	865w		765s	725w	700s
3	1 110m	1 040m	990w	940w 925w	890w	800w	770m 750w	720m	
3a	$1\ 130 w$	1 070w 1 035w	980w	940w 915w	865w	_	765s	725w	700s
4	1 110m	1.040w	1 020w	925w	865w	780m	765m	725m	
4a	1.125m	1 070w 1 030w	1 005w 990w	965m 935m	825w		765s	725m	700s
5	1 110m	1 045m	1 015w	925m	850w	800w	775m	725m	
5a	1.125m	1 070w 1 030w	980w 965w	935w	865w	—	765s	725w	700s
6	1 110m	1.040 m	995w	920m	850w	790w	770m	725m	
6a	1 130m	1 070w 1 035w	1 000w 975w	945w 920w	865w	—	765s	725w	700s
7	1 105m	1 045w	980w	935w	865w	780m	765m	720m	
7a	1.125m	1 025w 1 070w 1 030w	970w	950w 950w 935w	865w	_	765m	725w	700s
$\frac{8}{8a}$	1 100m 1 140m	1 060m 1 075m	1 035w 1 035m	950m 950m	865w 865m	785m —	765m 765s		695s 695s

 TABLE 111

 Region 1 200 - 700 cm⁻¹ for seleno- and benzylseleno-semicarbazones

spectra of seleno- and benzylseleno-semicarbazones. For instance, a band at $1\,105$ – 1 110 cm⁻¹ in the spectra of the seleno compounds is shifted regularly by 15–20 cm⁻¹ in the benzyl derivatives while a band at 1030 - 1045 cm⁻¹ in the former is split into a doublet in the spectra of the latter. This regular pattern can be seen throughout the spectra. The spectra of selenosemicarbazones consistently show a group of two bands, of weak to medium intensity, at $800-780 \text{ cm}^{-1}$ and at $775-765 \text{ cm}^{-1}$, while the spectra of benzyl derivatives show only one band at 765 cm^{-1} . The band at $800-780 \text{ cm}^{-1}$ is therefore assigned to the C—Se vibration. It is realized that formation of benzyl derivatives not only replaces a C-Se by a C-Se-Bz, but also results in a change of configuration from =N-NH-C(Se)-NH₂ to =N-N=C(SeBz)-NH₂; hence, a loss of a hydrogen atom and replacement of a C-N bond by a C=N bond. The band at 800-780 cm⁻¹ (C—Se) in the spectra of selenoisemicarbazones is too low to have resulted from a C—N stretching vibration since this is usually found in the 1 400 cm⁻¹ region (15) or between 1 300 and 1 000 cm⁻¹ in amines (16). It could be argued that N—H rocking vibration can be found at such a low frequency but there remains in the molecules of benzylselenosemicarbazones free NH_2 groups, so that any N—H rocking should still be detected. The new C=N bond in benzylseleno compounds is likely responsible for an extra band at 1 650 cm⁻¹ in the spectra. The new band is at somewhat higher frequency than that normally associated with the aromatic ring. This was examined more closely by comparing the spectra of benzaldehyde selenosemicarbazone with its benzyl derivative. The former has a broad band at 1 600 cm⁻¹, probably due to overlapping of the C=N vibration of the benzilidene grouping with the double bond vibrations of the aromatic ring, while the benzyl derivative shows the same pattern at 1 600 cm⁻¹ but has an extra band at 1.650 cm^{-1} . This band is attributed to the C=N of the selenocarbohydrazide residue since it is probable that the vibrations associated with the benzyl radical will overlap with those of the benzene ring in the benzaldehyde portion of the

CANADIAN JOURNAL OF CHEMISTRY, VOL. 43, 1965

molecule. The strong absorption at 700 cm⁻¹ in the spectra of benzylselenosemicarbazones may be suggestive of a C—Se stretch but no definite assignment can be made since this band may be due to the aromatic ring. Thus, a similar band at 695 cm⁻¹ is present in both compounds 8 and 8*a* (Table III) which are aromatic, benzaldehyde seleno- and benzaldehyde benzylseleno-semicarbazone.

In the N—H stretching region, the spectra of selenosemicarbazones are identical with those of corresponding thiosemicarbazones reported earlier (10); they show three bands of medium intensity at 3 420, 3 280, and 3 180 cm⁻¹.

It should be mentioned that, although the preparation of selenosemicarbazone-copper complexes was not generally satisfactory, some were obtained in a fair degree of purity; e.g. dodecanal, *m*-nitrobenzaldehyde, and decanal selenosemicarbazone – copper (I). As with the thiosemicarbazone-copper complexes, the infrared spectra of the seleno-copper complexes are not well resolved but it is interesting to note that the band at 800–780 cm⁻¹ (C—Se) disappears while the one at 765 cm⁻¹ remains.

The biological properties of selenosemicarbazones will be reported elsewhere but it should be mentioned that the compounds were found to be generally more active than the corresponding thiosemicarbazones against the two organisms studied, *Chaetomium globosum* and *Aspergillus niger*. Furthermore, the activity of thiosemicarbazones was limited to the aliphatic ones, while a number of aromatic selenosemicarbazones (benzalde-hyde and *o*-hydroxy-, *o*-chloro-, and *p*-methoxy-benzaldehyde selenosemicarbazones) were found to be active at 10 p.p.m. against *C. globosum*.

Selenosemicarbazones

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EXPERIMENTAL

The method used was described by Huls and Renson (17). The new aliphatic compounds are listed in Table I.

Benzylselenosemicarbazones

An alcoholic solution of equivalent amounts of a selenosemicarbazone (from Table I) and sodium was refluxed for 5 min and allowed to cool. An excess (10%) of benzyl chloride was then added and the resulting solution was stirred for 1 h at room temperature, followed by a 5 min refluxing period. After cooling, the sodium chloride was separated out by filtration and the resulting solution was evaporated to a gum which was taken up in benzene-hexane (1:1), and passed through a column of silica gel. Benzene eluted a small amount of a by-product which was found to be benzyl diselenide (C₆H₆CH₂Se)₂; m.p. 89, lit. m.p. 92–93 °C (18).

Anal. Calcd. for C₁₄H₁₄Se₂: C, 49.41; H, 4.12. Found: C, 50.08; H, 4.94.

The infrared spectrum of this compound supports the diselenide structure instead of the benzyl selenol, since it shows no band in the region where the Se—H vibration is known to occur, at $2\,290 - 2\,295$ cm⁻¹ in phenyl selenol and $2\,300 - 2\,315$ cm⁻¹ for *n*-butyl selenol (6). Benzene-ether (1:1) eluted the required benzylselenosemicarbazones, listed in Table II.

Selenosemicarbazonato-Copper

Three 1:1 complexes were obtained in a sufficiently pure form for identification: decanal, dodecanal, and *m*-nitrobenzaldehyde selenosemicarbazone-copper (I). They were prepared by adding equimolar amounts of cupric chloride in ethyl alcohol to a warm solution of the selenosemicarbazone in the same solvent. The mixture turned brown and, after cooling, the precipitated complex was collected by filtration. The analyses are given for C, H, N only, since the presence of selenium interferes with the determination of copper.

Decanal selenosemicarbazonato-copper(I), m.p. 104 °C. Required for C₁₁H₂₂N₃SeCu: C, 38.98; H, 6.50; N, 12.40%. Found: C, 36.34; H, 5.82; N, 12.11%.

Dodecanal selenosemicarbazonato-copper(I), m.p. 155 °C. Required for C₁₃H₂₆N₃SeCu: C, 42.6; H, 7.1; N, 11.45%. Found: C, 42.86; H, 6.5; N, 11.4%.

m-Nitrobenzaldehyde selenosemicarbazonato-copper(I), m.p. 214 °C. Required for C₈H₇N₄O₂SeCu: C, 28.8; H, 2.1; N, 16.8%. Found: C, 29.2; H, 2.6; N, 17.0%.

Infrared Spectra

Infrared spectra were taken on a Perkin-Elmer, Model 21, Double-Beam spectrophotometer using KBr pellets.

1654

1655

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