

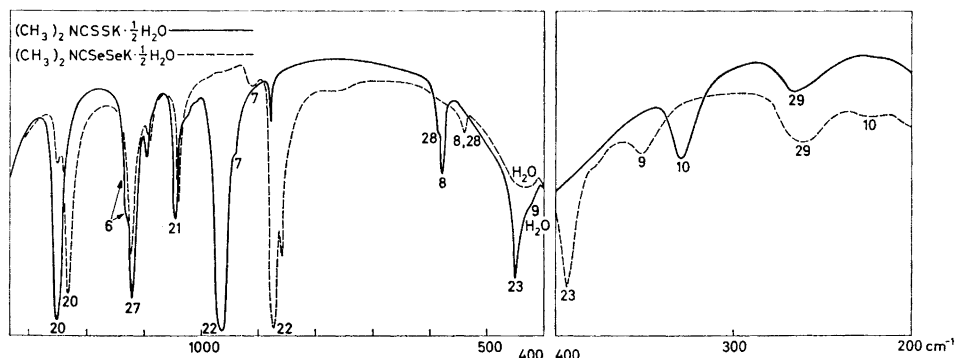
## Tentative Assignment of Fundamental Vibrations of Thio- and Selenocarboxylates III. The Dimethyl-diselenocarbamate Ion and the Concept of Selenation

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The vibrational spectra of potassium and lead(II) dimethyl-diselenocarbamate are reported. The fundamentals are assigned on the basis of (1) comparison with the spectra of the deuterated species, and (2) a normal coordinate analysis of the dimethyldiselenocarbamate ion with a 24-parameter generalized valence force field, mainly transferred from that previously derived for the dimethyldithiocarbamate ion.

For the purpose of analyzing the infrared spectrum attributed to the dimethyldiselenocarbamate (DDSC) ion,  $(\text{CH}_3)_2\text{NCSeSe}^-$ , the ion can conveniently be considered to be derived from the analogous dimethyldithio-



*Fig. 1.* The infrared spectra of potassium dimethyldithiocarbamate and its selenium analogue in the range 200–1333 cm<sup>-1</sup>. The numbering refers to the assigned fundamentals, discussed in the text.

Table 1. Observed infrared spectra of  $(\text{CH}_3)_2\text{NCSeSeK} \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $(\text{CD}_3)_2\text{NCSeSeK} \cdot \frac{1}{2}\text{H}_2\text{O}$  in KBr (400–4000  $\text{cm}^{-1}$ ) and polyethylene (40–400  $\text{cm}^{-1}$ ), and Raman spectra in 1 N aqueous NaOH solutions ( $\text{cm}^{-1}$ ). Observed infrared spectra of  $[(\text{CH}_3)_2\text{NCSeSe}]_2\text{Pb}$  and  $[(\text{CD}_3)_2\text{NCSeSe}]_2\text{Pb}$  in KBr (400–4000  $\text{cm}^{-1}$ ) and polyethylene (40–400  $\text{cm}^{-1}$ ).

$(\text{CH}_3)_2\text{NCSeSeK} \cdot \frac{1}{2}\text{H}_2\text{O}$		$[(\text{CH}_3)_2\text{NCSeSe}]_2\text{Pb}$		$(\text{CD}_3)_2\text{NCSeSeK} \cdot \frac{1}{2}\text{H}_2\text{O}$		$[(\text{CD}_3)_2\text{NCSeSe}]_2\text{Pb}$		Assignment <sup>b</sup>
Infrared <sup>a</sup>	Raman <sup>c</sup>	Infrared <sup>a</sup>	Raman <sup>c</sup>	Infrared <sup>a</sup>	Raman <sup>c</sup>	Infrared <sup>a</sup>	Raman <sup>c</sup>	
3004w		2992vw		2247w		2163m <sup>c</sup>		$\nu_{16}(\text{B}_1), \nu_{28}(\text{B}_2)$
2990w		2955vwsh <sup>c</sup>		2174vw <sup>c</sup>		2210m		$\nu_1(\text{A}_1)$
2954m <sup>c</sup>		2945vwsh		2223m	2225m,P	2123m		
2918m	2944s,P	2913m		2128w	2140m,P	2094m		
				2059m <sup>c</sup>	2107w,P	2057m <sup>c</sup>		$\nu_{17}(\text{B}_1)$
1601m	2868w,P	2835w		2059m <sup>c</sup>	2076w,P	2057m <sup>c</sup>		$\nu_2(\text{A}_1)$
				1601m				$\text{H}_2\text{O}$
1492s	1507m,P			1454vw				$\nu_3(\text{A}_1)$
1455vw <sup>c</sup> , 1444vw <sup>c</sup>	1450m,(DP?)	1508vs		1064w <sup>c</sup>		1056m <sup>c</sup>		$\nu_{18}(\text{B}_1)$
1455vw <sup>c</sup> , 1444vw <sup>c</sup>	1450m,(DP?)			1064w <sup>c</sup>		1056m <sup>c</sup>		$\nu_{20}(\text{B}_2)$
1434m		1437w		1050w		1040msh		$\nu_4(\text{A}_1)$
1425wsh				1413vs	1431s,P	1442vs		
1395m	1401wsh(?)	1396m		1038m <sup>c</sup>		1040msh <sup>c</sup>		$\nu_{19}(\text{B}_1)$
1359s	1382vs,P	1379s		1108m	1110m,P	1100s		$\nu_5(\text{A}_1)$

Table 1. Continued.

1252w		1240w,sh	1212s	1201s	$\nu_{20}(B_1)$ $\nu_7(A_1) + \nu_{23}(B_1)$ $\nu_6(A_1)$ $\nu_{27}(B_2)$ $\nu_{21}(B_1)$ $\nu_7(A_1)$ $\nu_{23}(B_1)$ $\nu_{28}(B_2)$ $\nu_9(A_1)$ $H_2O$ $\nu_{23}(B_1)$ $\nu_9(A_1)$ $\nu_{29}(B_2)$ $\nu_{10}(A_1)$ lattice modes
1232s		1227s	1128w 1038m <sup>c</sup> 945m	1040msh <sup>c</sup> 954s	
1130msh	1136m,(P?)	1137s <sup>c</sup> 1137s <sup>c</sup>			
1122s			956m,DP		
1091w		1040m			
1039m		898w	774m,(P?)	815m	
914w		871s	888m,DP	768w	
872vs, 860m	872s,DP,864s,DP	856wsh		867s	
846msh		511w		802msh	
536w	519s,P		451s,P	502w	
430m,br				449w	
391m		390m			
351m,br	355vs,P	349m	326vs,P	355m	
261m,br		263m		321m	
224w,br		213m		238m	
200w,br				214m	
127s,br		125m			
104s		103s		124m	
91s				101s	

<sup>a</sup> Abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, and sh = shoulder. The polarisation of a Raman line is indicated by P, depolarisation by DP.

<sup>b</sup> The numbering of the fundamentals refers to the undeuterated compound.

<sup>c</sup> Multiply assigned bands.

No.	(CH <sub>3</sub> ) <sub>2</sub> NCS <sub>2</sub> Se <sup>-</sup>					(CD <sub>3</sub> ) <sub>2</sub> NCS <sub>2</sub> Se <sup>-</sup>				
	ν <sup>calc</sup> <sup>a</sup>			Description <sup>b</sup>	ν <sup>obs</sup> IR/Raman	ν <sup>calc</sup> <sup>a</sup>			ν <sup>obs</sup> IR/Raman	Description <sup>b</sup>
	A	B	C			A	B	C		
A <sub>1</sub> ν <sub>1</sub>	2965	2964	2964	2918/2944	ν <sub>as</sub> CH(100)	2224	2221	2221	2223/2225	ν <sub>as</sub> CD(100)
ν <sub>2</sub>	2884	2884	2884	—/2868	ν <sub>s</sub> CH(100)	2081	2081	2081	2059/2076	ν <sub>s</sub> CD(100)
ν <sub>3</sub>	1473	1481	1481	1492/1507	δ <sub>as</sub> CH <sub>3</sub> (47-48), νCN(22-23), νCN(19-20), ν <sub>s</sub> CNC(9)	1054	1051	1051	1064/—	δ <sub>as</sub> CD <sub>3</sub> (95)
ν <sub>4</sub>	1427	1433	1434	1434/—	δ <sub>as</sub> CH <sub>3</sub> (42-43), νCN(26), ν <sub>s</sub> CNC(16)	1398	1423	1425	1413/1431	νCN(53), ν <sub>s</sub> CNC(21)
ν <sub>5</sub>	1380	1383	1384	1359/1382	δ <sub>s</sub> CH <sub>3</sub> (93-95)	1104	1116	1118	1108/1110	δ <sub>s</sub> CD <sub>3</sub> (52-53), ν <sub>s</sub> CNC(24)
ν <sub>6</sub>	1087	1109	1113	1130/1136	νCN(22-23), ν <sub>s</sub> CSeSe(16)	982	986	989	1038/—	δ <sub>s</sub> CD <sub>3</sub> (33-34), νCN(25), ν <sub>s</sub> CSeSe(15-16)
ν <sub>7</sub>	931	936	937	914/—	ν <sub>s</sub> CNC(53-58), νCH <sub>3</sub> (29-33)	766	766	766	772/774	νCN(57), ν <sub>s</sub> CNC(33)
ν <sub>8</sub>	546	525	526	—/519	δCNC(44), ν <sub>s</sub> CNC(28), ν <sub>s</sub> CSeSe(17), νCN(10)	477	469	470	—/451	δCNC(28), ν <sub>s</sub> CSeSe(24), ν <sub>s</sub> CNC(28), νCN(15)
ν <sub>9</sub>	341	342	342	351/355	ν <sub>s</sub> CSeSe(45), δCNC(40)	318	315	315	324/326	δCNC(48-49), ν <sub>s</sub> CSeSe(42)
ν <sub>10</sub>	220	221	226	224/—	δCSeSe(87)	215	215	220	224/—	δCSeSe(79)
B <sub>1</sub> ν <sub>16</sub>	2961	2962	2961	2954/—	ν <sub>as</sub> CH(100)	2213	2214	2213	2174/—	ν <sub>as</sub> CD(100)
ν <sub>17</sub>	2882	2882	2882	—/—	ν <sub>s</sub> CH(100)	2075	2074	2074	2059/—	ν <sub>s</sub> CD(100)
ν <sub>18</sub>	1461	1461	1461	1455/1450	ν <sub>as</sub> CH <sub>3</sub> (89)	1068	1052	1052	1064/—	δ <sub>as</sub> CD <sub>3</sub> (54), δ <sub>s</sub> CD <sub>3</sub> (30)
ν <sub>19</sub>	1385	1387	1387	1395/1401	δ <sub>as</sub> CH <sub>3</sub> (93-94)	1046	1042	1042	1038/—	δ <sub>s</sub> CD <sub>3</sub> (61), δ <sub>as</sub> CD <sub>3</sub> (28)
ν <sub>20</sub>	1247	1236	1238	1232/—	νCN(23-31), ν <sub>as</sub> CNC(20-21), νCN(14-17), νCSeSe(10-16), ν <sub>as</sub> CSeSe(8-9)	1230	1221	1228	1212/—	νCN(33-44), νCSeSe(17-24), ν <sub>as</sub> CNC(18-20), ν <sub>as</sub> CSeSe(13-15)
ν <sub>21</sub>	1040	1020	1031	1039/—	νCH <sub>3</sub> (63-65), ν <sub>as</sub> CSeSe(14)	792	783	784	806/—	νCN(72-73), ν <sub>as</sub> CNC(25)
ν <sub>22</sub>	957	888	890	872/872	ν <sub>as</sub> CNC(75-78), ν <sub>as</sub> CSeSe(19-22)	942	882	888	882/888	ν <sub>as</sub> CNC(39-42), ν <sub>as</sub> CSeSe(34-40)
ν <sub>23</sub>	405	396	385	391/—	νCN(46-48), ν <sub>as</sub> CSeSe(47-48)	368	361	352	356/—	ν <sub>as</sub> CSeSe(50-51), νCN(49-50)
ν <sub>24</sub>	137	137	151	—/—	νCSeSe(67-77), νCN(15-23)	127	128	141	—/—	νCSeSe(66-76), νCN(17-26)
B <sub>2</sub> ν <sub>25</sub>	2960	2960	2960	2954/—	νCH(100)	2209	2209	2209	2174/—	νCD(100)
ν <sub>26</sub>	1464	1464	1464	1455/1450	δCH <sub>3</sub> (87)	1049	1049	1049	1050/—	δCD <sub>3</sub> (90)
ν <sub>27</sub>	1120	1120	1120	1122/—	νCH <sub>3</sub> (85)	896	897	897	945/956	νCD <sub>3</sub> (83)
ν <sub>28</sub>	547	534	534	536/—	ωCSeSe(83)	541	527	527	529/—	ωCSeSe(86)
ν <sub>29</sub>	255	262	262	261/—	ωCNC(87)	230	237	237	238/—	ωCNC(89)
ν <sub>30</sub>	123	124	124	—/—	τCH <sub>3</sub> (80)	88	88	88	—/—	τCD <sub>3</sub> (83)

<sup>a</sup> Calculation A made, using the force field for the dimethylthiocarbamate ion.<sup>3</sup> Calculations B and C made with force fields (Table 3), modified with special reference to obtaining agreement with the frequencies observed for dimethylselenocarbamate.

<sup>b</sup> Abbreviations: ν = stretching, δ = deformation, ω = rocking, τ = torsion, and, as subscripts, s = symmetric, as = antisymmetric. The rounded percentage potential energy distribution values are shown in parentheses; small values have been neglected. For vibrations belonging to species A<sub>1</sub> and B<sub>1</sub>, intervals are given for the potential energy distributions, corresponding to the differences between the two calculations B and C. In cases where several vibrations contribute significantly, the most important ones are printed in italics.

carbamate (DDTC) ion,  $(\text{CH}_3)_2\text{NCSS}^-$ , by what may be called "selenation", *i.e.* the replacement of sulfur with selenium. The infrared spectra of the potassium salts of the ions in the range  $200-1333\text{ cm}^{-1}$  are shown in Fig. 1. By consideration of the superimposed spectra, it is seen that the infrared absorption bands can be divided roughly into two groups: (1) those hardly influenced by selenation (*e.g.* the bands numbered 20, 27, and 21), and (2) those displaced towards lower frequencies on selenation (*e.g.* the bands numbered 22, 23, and 10). A similar trend was observed when the infrared spectra of thioamides were compared with those of selenoamides<sup>1</sup> as well as in many other cases (see refs. in part I of this series<sup>2</sup>). It therefore seems a reasonable conclusion<sup>1</sup> that selenation allows an empirically useful classification of the infrared bands of sulfur compounds, containing the NCS grouping.

However, the question remains how this classification should be explained in terms of the changes in geometry, mass, and force field, induced in the molecule by selenation. For example, we should like answers to such questions as: Is the shift of the strong band at  $965\text{ cm}^{-1}$  in DDTC to  $872\text{ cm}^{-1}$  in DDSC due to a change in bond lengths, interbond angles, and the greater mass of selenium compared with sulfur, or to changes in the force constants in the ion? Such problems are discussed in the present paper by comparing the results of a vibrational analysis of the DDTC ion<sup>3</sup> with those reported below for the DDSC ion.

The experimental results (Table 1) comprise the infrared and Raman spectra of potassium DDSC and the infrared spectrum of lead(II) DDSC. The spectra of the perdeuterated compounds have also been recorded to provide a more reliable basis for the normal coordinate analysis. The differences in the spectra of the potassium and lead compounds should probably be explained in the same way as for the DDTC salts.<sup>3</sup> The spectra of potassium DDSC have been assumed to represent the free DDSC ion and have been used in the normal coordinate analysis.

#### NORMAL COORDINATE ANALYSIS

The symmetry, number, and type of fundamentals, internal coordinates, and symmetry coordinates for DDSC have been assumed to be identical with those previously employed for DDTC.<sup>3</sup> The geometry has also been transferred unchanged, except that the distance  $\text{C}-\text{Se}=1.91\text{ \AA}$  was used for DDSC. This is the mean value of the two  $\text{C}-\text{Se}$  distances found for the Ni(II) complex of diethyldiselenocarbamate.<sup>4</sup>

The force field was derived in the following way (*cf.* Table 2). First, a calculation (A) was made, using the force field previously reported for DDTC.<sup>3</sup> The calculated frequencies were then compared to the experimental values and a preliminary assignment made. Next, the Jacobian matrix elements, relating changes in frequency to changes in force constants, were calculated for the relevant force constants of the force field. From these it was deduced that agreement between the experimental and the calculated frequencies for DDSC could be obtained in several equally satisfactory ways. Actual calculations showed that the satisfactory force fields ranged between two extremes. The

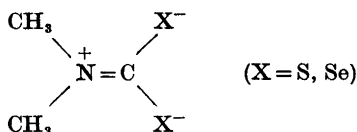
Table 3. Final valence force constants for dimethyldiselenocarbamate, which are not identical with those reported for dimethyldithiocarbamate.<sup>3</sup>

Force constant <sup>a</sup>	Dimethyldithio- carbamate	Dimethyldiselenocarbamate	
	Calc. A	Calc. B	Calc. C
$K_R$	4.80	5.35	
$K_P$	4.67	4.45	
$F_P$	0.83	1.05	
$K_D$	3.95	3.92	
$F_D$	0.95	1.57	
$H_{\omega_1}$	0.57	0.538	
$H_{\omega_2}$	0.167	0.18	
$H_\gamma$	1.40	1.60	1.40
$H_{\gamma'}$	1.40	0.90	1.00
$H_\delta$	0.80	0.80	1.10

<sup>a</sup> In units of mdyn/Å (stretch constants) and mdyn Å/(rad)<sup>2</sup> (bending constants).

final force fields of these two extremes are given in Table 3, and the calculated frequencies have been listed in Table 2 under the headings Calc. B and C.

It is interesting that the changes in force field from DDTC to DDSC (Table 3) are consistent with those expected from simple chemical arguments. For example, it is expected that selenation of DDTC will be followed by increased importance of the resonance structure



which means that the force constant for stretching of the central CN bond,  $K_R$ , should increase from DDTC to DDSC. In support of this argument, both calculations B and C show that the value  $K_R = 4.80$  in DDTC<sup>3</sup> should be increased to  $K_R = 5.35$  in DDSC.

The increased positive charge of the nitrogen atom in DDSC relative to DDTC is also expected to increase the polarity of the  $\text{CH}_3\text{-N}$  bond, *i.e.* decrease the corresponding stretching force constant,  $K_P$ . This is supported by the calculations, indicating that  $K_P$  should be decreased from 4.67 in DDTC to 4.45 in DDSC. In addition, several changes were necessary in the force field used for the NCSS/NCSeSe part of the molecule, but since the absolute values undoubtedly depend to a high degree on the assumption that the interbond angles are identical in DDTC and DDSC, we prefer not to comment on the remaining part of Table 3.

## DISCUSSION

We are now in a position to give a quantitative account of the changes observed in the infrared spectrum of DDTC on selenation. The experimental spectra are given in Fig. 1 in the range 200–1333  $\text{cm}^{-1}$ ; the region 1333–4000  $\text{cm}^{-1}$  has been omitted, because only insignificant changes are observed here. The calculated values for the frequencies and potential energy distributions can be found in Table 2 and in the previously reported analogous table for DDTC.<sup>3</sup>

Let us first consider the infrared region 1000–4000  $\text{cm}^{-1}$ . A total of 15 fundamentals in DDTC and DDSC have been assigned to bands in this region, characterized with a few exceptions by being found at almost identical positions in the two compounds. The explanation for this result is, according to the potential energy distribution of the contributing symmetry coordinates, that most of these bands are due to internal vibrations of the methyl groups, *i.e.* stretching, deformation, and rocking modes. The fundamentals  $\nu_3$ ,  $\nu_4$ , and  $\nu_6$  of species  $A_1$  have in some cases important contributions from the skeletal stretching motions (either a single symmetry coordinate or an out-of-phase combination), but these do not change from DDTC to DDSC to such a degree that the band positions differ much. The strongly mixed skeletal vibration  $\nu_{20}$  of species  $B_1$  exhibits a shift of 25  $\text{cm}^{-1}$  towards lower frequencies on selenation, partly because the force constant for the asymmetric CNC stretching motion has been lowered, partly owing to a slight change in composition. It seems justified in an empirical context to describe this strong characteristic band in both DDTC and DDSC, as  $\nu_{\text{as}}\text{CNC}$  coupled to  $\rho\text{CNC}$ ; *i.e.* when the  $\text{CH}_3\text{-N}$  distance changes, the angles  $\text{CH}_3\text{-N-CX}_2$  are also altered. More explicitly, this band can be characterized as an out-of-phase combination of  $\nu_{\text{as}}\text{CNC}$  and  $\nu_{\text{as}}\text{CXX}$ , strongly coupled to skeletal rocking motions.

The infrared region 600–1000  $\text{cm}^{-1}$  is dominated by the strong broad fundamental  $\nu_{22}(B_1)$ . This band is strongly influenced by selenation, and has accordingly generally been assumed to originate in asymmetric CSS/CSeSe stretching (see refs. in part I of this series<sup>2</sup>). Our results show that the band is insensitive to deuteration both in DDTC and DDSC, and the calculations confirm the reasonable conclusion that this band is due to skeletal vibrations. However, calculations on both DDTC and DDSC also agree, in showing that the band is due to an in-phase combination of  $\nu_{\text{as}}\text{CNC}$  and  $\nu_{\text{as}}\text{CXX}$  ( $X = \text{S, Se}$ ) in varying proportions. In contrast to the out-of-phase combination (in  $\nu_{20}$ ) this vibration is not coupled to the skeletal rocking modes. The shift of  $\nu_{22}$  on selenation of DDTC is mainly due to lowered force constants for asymmetric CNC stretching and asymmetric CXX stretching. The change in geometry and mass of the CXX grouping following selenation has only a small influence on the position of  $\nu_{22}$ .

In the range 500–600  $\text{cm}^{-1}$ , the fundamentals  $\nu_8(A_1)$  and  $\nu_{28}(B_2)$  occur, both showing a shift of *ca.* 50  $\text{cm}^{-1}$  towards lower frequencies on selenation. Based on the L-matrix, the former band can be described as  $\delta\text{CNC}$  coupled to an in-phase combination of  $\nu_s\text{CNC}$ ,  $\nu_s\text{CXX}$ , and  $\nu\text{CN}$ . The coupling of  $\delta\text{CNC}$  to  $\nu_s\text{CNC}$  represents an interaction similar to that discussed above

for  $\nu_{20}$ . A descriptive term for this motion would be a "skeletal breathing vibration" coupled to CNC deformation; from this description, the band is expected to be weak in the infrared and strong in the Raman spectrum, as is also found. The calculations indicate that approximately one half of the frequency shift of  $\nu_8$  on selenation is due to the changes in mass and geometry of the molecule; the other half of the shift is the result of the changes in force constants. The fundamental  $\nu_{28}$  is approximately described as the CXX wagging motion. In this case, most of the shift on selenation is due to the greater mass of the selenium atom, compared to sulfur and to the increased C-X distance in DDSC; the force constant is almost unchanged.

In the range 200–500  $\text{cm}^{-1}$ , four fundamentals have been identified. One of these,  $\nu_{29}$  ( $B_2$ ), is almost unaffected by selenation, but is displaced by *ca.* 20  $\text{cm}^{-1}$  on deuteration. This fundamental is identified as the wagging motion of the dimethylamino group, and the shift on deuteration primarily reflects the greater mass of the  $\text{CD}_3$  groups. It is noteworthy that the force constant for the CXX wagging motion is approximately three times as big as the force constant of the CNC wagging motion. A reasonable explanation would be that the difference originates in the  $\pi$ -electron density in the CXX part of the molecule.

The three remaining bands shift towards lower frequencies on selenation,  $\nu_{23}$  ( $B_1$ ) by *ca.* 50  $\text{cm}^{-1}$ ,  $\nu_9$  ( $A_1$ ) and  $\nu_{10}$  ( $A_1$ ) by *ca.* 100  $\text{cm}^{-1}$ . The first two of these bands can be described as  $\nu_{23}$  CXX coupled to  $\rho$ CNC, and  $\nu_9$  CXX coupled to  $\delta$ CNC, respectively. This description is valid also for the deuterated ions. A trait common to both skeletal vibrations is that stretching of the CX bonds is followed by a bending motion of the methyl group relative to the central CN bond (*i.e.* a change in the  $\text{CH}_3\text{-N-CX}$  angle). The calculations show that the shifts of the fundamentals  $\nu_{23}$  and  $\nu_9$  on selenation originate in the increased mass of selenium and the greater C-Se distance, not in changes in the force field. The same applies to the remaining fundamental  $\nu_{10}$ , which can to a reasonable approximation be described as the symmetrical deformation motion of the CXX group.

To summarize, the usefulness of the selenation method rests on a good separation between the skeletal vibrations and the internal vibrations of the methyl groups. In so far as this condition is fulfilled, selenation and isotopic substitution can both be of value to the spectroscopist.

## EXPERIMENTAL

The experimental details of obtaining the spectra and performing the normal coordinate analyses were described in part I of this series.<sup>2</sup>

*Dimethylammonium dimethyldiselenocarbamate.* At 0°C, 10 N aqueous sodium hydroxide (2 ml) was added to a suspension of dimethylammonium chloride ( $2 \times 10^{-2}$  mol) in ether (100 ml). The reaction mixture was shaken and then dried over potassium hydroxide pellets. To the filtered and stirred ethereal solution of dimethylamine, cooled in an ice-salt bath, a solution of carbon diselenide ( $10^{-2}$  mol) in dry ether (25 ml) was added dropwise over a period of 20 min. The reaction was performed under nitrogen. The precipitated yellow salt was filtered off, washed with pentane, and dried *in vacuo*. Yield 90%. The product was purified by dissolution in the minimum amount of absolute ethanol, followed by precipitation with ten times the volume of pentane.



*Potassium dimethyldiselenocarbamate hemihydrate.* Dimethylammonium dimethyldiselenocarbamate ( $1.5 \times 10^{-3}$  mol) was dissolved in the minimum amount of absolute ethanol and added to a solution of potassium hydroxide ( $1.5 \times 10^{-3}$  mol) in absolute ethanol (2 ml). Nitrogen was passed through the reaction mixture at room temperature for approximately 4 h, to remove dimethylamine. The volume of the solution was adjusted to 5–6 ml, if necessary by adding oxygen-free ethanol. Pentane (50–90 ml) was added, and small amounts of impurities removed from the clear solution by filtration. More pentane was added, until the solution became turbid. After standing for a few minutes, the mixture was stirred gently, and light yellow crystals of potassium dimethyldiselenocarbamate precipitated. The addition of pentane and stirring were repeated, until no more salt separated. The compound was isolated by decantation and dried *in vacuo*. Yield 40 %. (Found: C 13.93; H 2.68; N 5.20. Calc. for  $C_3H_6KNSe_2 \cdot \frac{1}{2}H_2O$ : C 13.74; H 2.69; N 5.34.)

*Lead(II) dimethyldiselenocarbamate.* On mixing the calculated amounts of aqueous solutions of lead(II) acetate and dimethylammonium dimethyldiselenocarbamate, yellow lead(II) dimethyldiselenocarbamate precipitated in excellent yield. (Found: C 11.31; H 1.82; N 4.42. Calc. for  $C_6H_{12}N_2PbSe_4$ : C 11.34; H 1.91; N 4.41.)

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