The Crystal and Molecular Structure of Selenium Bis(1-pyrrolidinecarbodiselenoate)

STEINAR ESPERÅS, STEINAR HUSEBYE and ÅGE ROLANDSEN

Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway

The structure of selenium bis(1-pyrrolidinecarbodiselenoate), $Se(C_4H_8NCSe_2)_2$, has been determined by three-dimensional X-ray crystallographic methods. The crystals are monoclinic with unit cell dimensions $a = 15.800(3)$ Å, $b = 6.590(1)$ Å, $c = 15.152(2)$ Å, $\beta = 100.42(2)°$ and $Z = 4$. The space group is $P2/c$. Reflection intensities were measured by means of a Siemens AED-1 diffractometer. The structure was solved by the symbolic addition procedure and refined by full-matrix least-squares methods to an R-value of 0.041. There are two types of crystallographically independent molecules in the unit cell, both being very similar to each other and both with the central selenium atom situated on a twofold rotation axis. The monomeric compounds can be regarded as four-coordinated trapezoid planar selenium(II) complexes with two bidentate diselenocarbamate ligands. Average bond lengths from the central selenium atoms to the ligand selenium atoms are 2.445(1) and 2.867(1) Å, respectively, for the short and long bonds which are *trans* to each other.

The average interbond angle in this system of two *trans* bonds, is 161.66(3)°.

In our studies of complexes of divalent selenium and tellurium with bidentate dithio-, thioseleno-, or diseleno ligands,[1–5] the central atom has always been found to be bonded to four ligand sulfur and/or selenium atoms in a trapezoid planar configuration. Two classes of such complexes have been found.[4] Class I consists of essentially monomeric molecules where the central selenium or tellurium atoms are coordinated to all four ligand donor atoms in the molecule with two relatively strong bonds and two relatively weak ones. Class II compounds are built up of essentially polymeric networks, where the central atom is strongly bonded to two ligand atoms in the parent molecule and weakly to two ligand atoms belonging to different neighbouring molecules. The only complex with a diseleno ligand whose structure has previously been solved in this laboratory, is selenium bis(diethyldiselenophosphinate),[1,6] which has a class II structure. With diselenocarbamate ligands, it was from analogy with tellurium and selenium dithiophosphinates and dithiocarbamates[1–4,7–9] thought more likely that both divalent selenium and tellurium would give class I complexes.

Diselenocarbamates have been prepared by several workers and metal complexes with such ligands have been prepared and characterized.[10–27] So far, only a few structures of such compounds seem to have been solved.[13,22,23,27]

EXPERIMENTAL

A sample of crystalline selenium(II) bis(1-pyrrolidinecarbodiselenoate), $Se(C_4H_8NCSe_2)_2$, was kindly supplied by Dr. L. Henriksen at the H. C. Ørsted Institute, University of Copenhagen, Denmark. The ligand itself was first made by Shankaranarayana.[19] Such diselenocarbamate ligands are easily oxidized to the corresponding diselenides which disproportionate into mono- and triselenides,[10–12] the latter may alternatively be termed selenium bis(diselenocarbamates).

For data recording, a Siemens off-line automatic AED-1 diffractometer was used. The diffractometer was operated as a three-circle instrument and $MoK\alpha$ radiation was used.

Intensity data were collected using a scintillation counter, the "five-value" measurement, and the $\theta - 2\theta$ scan technique.[28] Reflections out to $2\theta = 56°$ were scanned with scan speed 2.5° per min, but with automatic setting of greater speed for strong reflections. An automatic

Table 1. Atomic coordinates in fractions of cell edges. Standard deviations in parentheses.

	x	y	z
Molecule I			
Se1	$\frac{1}{2}$	0.4535(1)	$\frac{1}{4}$
Se2	0.41167(6)	0.6570(1)	0.09250(5)
Se3	0.44401(6)	0.1869(1)	0.14254(5)
C1	0.4011(5)	0.3881(9)	0.0559(5)
N1	0.3664(4)	0.3303(8)	−0.0233(4)
C2	0.3635(6)	0.1139(11)	−0.0544(5)
C3	0.3435(6)	0.1405(12)	−0.1581(5)
C4	0.2928(6)	0.3339(11)	−0.1773(5)
C5	0.3336(5)	0.4783(11)	−0.0975(5)
Molecule II			
Se4	0	0.6262(1)	$\frac{1}{4}$
Se5	0.08431(6)	0.4248(1)	0.40926(6)
Se6	0.05891(6)	0.8947(1)	0.35536(5)
C6	0.0979(5)	0.6935(9)	0.4420(4)
N2	0.1351(4)	0.7545(8)	0.5221(4)
C7	0.1445(5)	0.9743(11)	0.5473(5)
C8	0.1931(6)	0.9714(12)	0.6449(5)
C9	0.1720(7)	0.7661(12)	0.6822(5)
C10	0.1655(5)	0.6167(11)	0.5987(5)

attenuation filter insertion mechanism reduced counting losses, and the reflections were scanned between $\theta_1 = \theta - 0.41°$ and $\theta_2 = \theta + 0.41°$, where θ is the Bragg angle for the α_1 peak. Two reference reflections were meas-

ured twice at intervals of 50 reflections. Of the 3680 reflections measured, 2183 had intensities greater than twice the standard deviations, σ_C, based on counting statistics and were labelled as observed.[29] Unobserved reflections were given intensities equal to $2\sigma_C$.

The intensities were corrected for Lorentz and polarization effects and for absorption ($\mu = 126.5$ cm⁻¹).[30] The crystal used for data collection had the following dimensions measured as distances from a common origin to crystal faces: 100 and $\bar{1}00$; 0.043 mm, 010 and 0$\bar{1}$0; 0.089 mm, 011, 0$\bar{1}$1, 01$\bar{1}$ and 0$\bar{1}\bar{1}$, 0.097 mm.

Accurate cell dimensions were based on measurements of 20 high-order reflections and calculated using a least squares procedure. The crystals are monoclinic with $a = 15.800(3)$ Å, $b = 6.590(1)$ Å, $c = 15.152(2)$ Å, $\beta = 100.42(2)°$ and $Z = 4$. Based on systematic absences, the space group is either $P2/c$ or Pc. The calculated and observed (flotation) densities are 2.40 and 2.39 g/cm³, respectively.

STRUCTURE ANALYSIS

The structure factors were converted to normalized structure factors using a program written by Shiono.[31] The resulting E statistics clearly indicated that the space group was centric, *i.e.* $P2/c$. This was later confirmed by the successful structure refinement. Reflections with E values greater than 2.0 (196 of the reflections with $2\theta < 48°$), were used as input in program package MULTAN.[32,33] The correct

Table 2. Components of atomic vibration tensors, $U \times 10^4$, in Å² with standard deviations, referred to the crystallographic axes. The expression used is $\exp[-2\pi^2(h^2a^{-2}U_{11} + \cdots + 2hka^{-1}b^{-1}U_{12} + \cdots)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Se1	443(8)	315(6)	283(6)	0	0	53(5)
Se2	641(7)	276(5)	371(5)	8(4)	9(3)	4(5)
Se3	637(7)	278(4)	314(5)	−11(4)	21(3)	−34(4)
C1	388(51)	345(42)	360(44)	−25(33)	−11(30)	108(38)
N1	437(41)	411(38)	290(33)	−11(29)	−10(27)	−51(30)
C2	874(73)	368(47)	428(49)	−57(42)	−148(36)	76(48)
C3	931(79)	706(58)	328(45)	164(51)	−148(38)	−167(48)
C4	737(60)	563(50)	348(42)	99(47)	−34(38)	−22(41)
C5	763(69)	511(47)	325(45)	64(45)	124(35)	−75(43)
Se4	482(8)	320(6)	312(6)	0	0	49(6)
Se5	600(7)	292(5)	408(5)	23(3)	24(3)	26(5)
Se6	621(7)	301(4)	296(4)	43(4)	13(3)	−2(4)
C6	412(51)	395(44)	292(41)	20(34)	23(30)	16(38)
N2	472(43)	347(37)	416(40)	55(30)	35(28)	87(34)
C7	582(60)	461(49)	338(42)	−31(40)	−134(34)	−72(39)
C8	840(74)	620(55)	476(52)	16(50)	−21(40)	−101(48)
C9	1469(101)	513(53)	357(49)	−221(56)	31(37)	−47(56)
C10	561(59)	537(47)	351(45)	138(40)	137(36)	30(41)

Table 3. Bond lengths in Å with standard deviations in parentheses.

Molecule I		Molecule II	
Se1 − Se2	2.870(1)	Se4 − Se5	2.863(1)
Se1 − Se3	2.449(1)	Se4 − Se6	2.451(1)
Se2 − C1	1.856(6)	Se5 − C6	1.841(6)
Se3 − C1	1.902(6)	Se6 − C6	1.889(6)
C1 − N1	1.283(8)	C6 − N2	1.313(9)
N1 − C2	1.500(9)	N2 − C7	1.499(9)
C2 − C3	1.556(10)	C7 − C8	1.538(10)
C3 − C4	1.505(11)	C8 − C9	1.527(12)
C4 − C5	1.581(10)	C9 − C10	1.591(11)
C5 − N1	1.508(9)	C10 − N2	1.484(9)

Some intramolecular distances

Se3 − Se3′	3.413(1)	Se6 − Se6′	3.392(1)
Se3 − Se2	3.208(1)	Se5 − Se6	3.209(1)
Se2 − C5	3.148(7)	Se5 − C10	3.187(7)
Se3 − C2	3.062(7)	Se6 − C7	3.023(7)

structure emerged from the output, and was refined by a full matrix least squares program which minimizes the function $\sum w(|F_o| - K|F_c|)^2$, where $w = 1/\sigma_F$ and K is a scale factor. Unobserved reflections with $K|F_c|$ larger than the observable limit were included in the refinement with F_o put equal to the limit. There are two crystallographically independent half molecules in the asymmetric unit, the central selenium atoms of the molecules being located on the twofold axes $(0,y,\frac{1}{4})$ and $(\frac{1}{2},y,\frac{1}{4})$.

After introducing anisotropic temperature factors, the factor $R = \sum ||F_o| - |F_c||/\sum |F_o|$, converged to the value 0.041. The parameter shifts at this stage of refinement, were all less than 1/5 of the standard deviations. The hydrogen atom positions were not revealed in the final difference map which contained no spurious peaks.

The final observed and calculated structure factors may be obtained from the author S. H. upon request.

The scattering factors used were taken from the *International Tables for X-Ray Crystallography*,[34] those of selenium were corrected for anomalous dispersion using the $\Delta f'$ and $\Delta f''$ values calculated by Cromer.[35]

The final atomic coordinates are listed in Table 1 and components of atomic vibration tensors in Table 2. Interatomic distances and angles are listed in Tables 3 − 4. Some short intermolecular distances and least squares planes through the molecules are given in Tables 5 − 6.

RESULTS AND DISCUSSION

The two crystallographically independent molecules, with bond lengths and angles indicated, are shown in Fig. 1. There are hardly significant differences between corresponding bond lengths in the two molecules, but several differences in bond angles are significant. The ligands in molecules of type I and II (see Fig.

Table 4. Bond angles in degrees with standard deviations in parentheses.

Molecule I		Molecule II	
Se2 − Se1 − Se3′	161.95(3)	Se5 − Se4 − Se6′	161.37(3)
Se2 − Se1 − Se2′	124.28(3)	Se5 − Se4 − Se5′	124.76(3)
Se3 − Se1 − Se3′	88.34(3)	Se6 − Se4 − Se6′	87.58(3)
Se2 − Se1 − Se3	73.72(3)	Se5 − Se4 − Se6	73.84(3)
Se1 − Se2 − C1	78.8(2)	Se4 − Se5 − C6	78.2(2)
Se1 − Se3 − C1	90.0(2)	Se4 − Se6 − C6	89.1(2)
Se2 − C1 − Se3	117.3(3)	Se5 − C6 − Se6	118.7(3)
Se2 − C1 − N1	124.3(4)	Se5 − C6 − N2	123.7(4)
Se3 − C1 − N1	118.5(4)	Se6 − C6 − N2	117.6(4)
C1 − N1 − C2	124.0(5)	C6 − N2 − C7	122.6(5)
C1 − N1 − C5	122.4(5)	C6 − N2 − C10	124.3(5)
N1 − C2 − C3	101.5(5)	N2 − C7 − C8	104.0(5)
C2 − C3 − C4	107.1(6)	C7 − C8 − C9	105.2(6)
C3 − C4 − C5	103.5(6)	C8 − C9 − C10	103.9(6)
C4 − C5 − N1	102.6(5)	C9 − C10 − N2	102.0(5)
C5 − N1 − C2	113.2(5)	C7 − N2 − C10	112.9(5)

Table 5. Some short intermolecular distances in Å. Standard deviations in parentheses. The distances are calculated from atoms in the original molecules (extreme left) to atoms in molecules whose tranformations are given in the central column of the table.

Se1 − C5	$1-x, 1-y, -z$	3.83(1)
Se2 − Se3	$x, 1+y, z$	3.591(1)
Se2 − C2	$x, 1+y, z$	3.74(1)
Se6 − Se5	$x, 1+y, z$	3.594(1)
Se5 − C7	$x, -1+y, z$	3.66(1)
C3 − C8	$x, -1+y, -1+z$	3.64(1)
C4 − C9	$x, y, -1+z$	3.85(1)
C4 − C8	$x, -1+y, -1+z$	3.73(1)
C4 − C6	$x, 1-y, -\frac{1}{2}+z$	3.85(1)

1 and Table 6) are both planar within 0.05 Å, except for hydrogen and the two outer carbon atoms of the pyrrolidine rings. The central selenium atom is coordinated to all four ligand selenium atoms in the molecule, resulting in a trapezoid planar structure, quite similar to

Table 6. Least squares planes through the molecules.

Plane

1: Se1, Se2, Se3, Se2′, Se3′
2: Se1, Se2, Se3, C1, N1, C2, C5
3: Se4, Se5, Se6, Se5′, Se6′
4: Se4, Se5, Se6, C6, C7, C10, N2

Equation of planes based on coordinates of the monoclinic cell. Coordinates from Table 1 give distances of atoms from plane in Å.

Plane

1:   $14.648\ X + 8.086\ Z + 5.303 = 0$
2:   $15.052\ X + 0.362\ Y - 7.013\ Z + 5.833 = 0$
3:   $14.737\ X - 7.888\ Z - 1.972 = 0$
4:   $15.057\ X - 0.019\ Y - 7.073\ Z - 1.695 = 0$

Interplanar angle

Plane 1 − Plane 3: 0.88°
Atomic distances from planes in Å:
Plane 1. Se1: 0.0, Se2: −0.030, Se3: 0.043, Se2′: 0.030, Se3′: −0.043.
Plane 2. Se1: 0.104, Se2: −0.048, Se3: −0.082, C1: −0.047, N1: −0.035, C2: 0.061, C5: 0.046.
Plane 3. Se4: 0.0, Se5: −0.021, Se6: 0.032, Se5′: 0.021, Se6′: −0.032.
Plane 4. Se4: −0.085, Se5: 0.062, Se6: 0.051, C6: 0.029, N2: 0.022, C7: −0.019, C10: −0.060.
The ligand in molecule I is planar to within 0.042 Å, that in II is planar within 0.028 Å.

those found in divalent selenium and tellurium bis(dialkyldithiocarbamates).[1] Thus the selenium bis(1-pyrrolidinecarbodiselenoate) has a class I structure, and not a class II or class III (trichalcogenide) structure.[4] There is no short intermolecular contact from the central selenium atom in a molecule to ligand atoms in neighbour molecules. In this respect, selenium (bis(1-pyrrolidinecarbodiselenoate) is more like the dithiocarbamates of selenium than those of tellurium.[1] For comparison, the coordination around the central atom in the present investigation and in related compounds, is shown in Fig. 2.

In the SeSe$_4$ coordination groups, the stronger central atom to ligand bonds Se1 − Se3 and Se4 − Se6 are 2.449(1) and 2.451(1) Å, respectively. The weaker bonds, Se1 − Se2 and Se4 − Se5 which are *trans* to the strong ones, are 2.870(1) and 2.863(1) Å, respectively. The resulting three-center four-electron bonding systems, consisting of pairs of weak and strong Se − Se bonds *trans* to each other, have an average length of 5.32 Å. This closely corresponds to the length of the analogous three-center systems found in selenium dithiocarbamates, when the difference in covalent radius between sulfur and selenium, 0.13 Å, is taken into consideration.[1−3] It is also exactly equal to the average length of the almost linear three-center Se − Se − Se systems found in triselenocyanate and triselenourea ions.[36,37] The two different SeSe$_4$ groups are nearly planar (Table 6), the planes are nearly parallel with the molecular twofold axes and with each other. The SeSe$_4$ groups deviate less from square geometry than the SeS$_4$ and TeS$_4$ groups in the selenium- and tellurium bis(dialkyldithiocarbamates).[1−3,8,9] This is mainly due to sterical factors. When the sulfur atoms in a dithiocarbamate ligand are replaced by the larger selenium atoms, the ligand bite becomes larger, increasing from 2.94 to 3.20 Å. This results in an increase in the intraligand S − Se − S angle of about 3° when sulfur is replaced by selenium. The increased interligand Se3 − Se3′ and Se6 − Se6′ repulsions across the smaller of the two interligand angles are offset by the lengthening of the Se − Se bonds relative to a Se − S bond, so these angles remain close to 87°. As a result of these factors, the larger interligand Se − Se − Se angle have an average
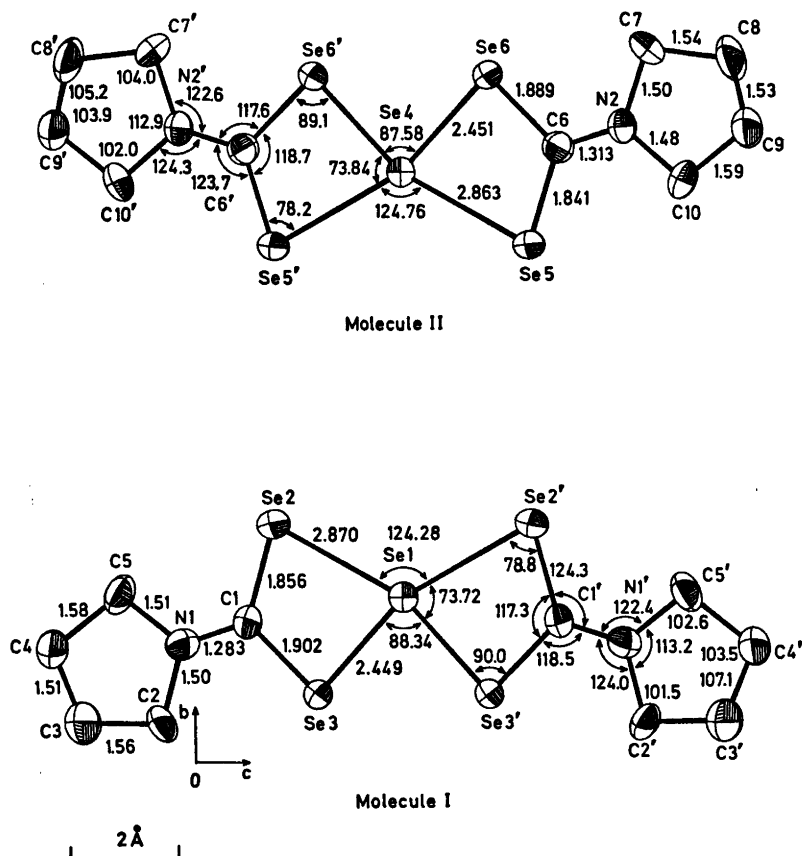
Molecule II

Molecule I

2 Å

Fig. 1. The two types of molecules in the unit cell as seen along *a*. Molecule II has been moved one unit cell length along *b*, to prevent overlap with molecule I. Primed letters denote atoms in one half of the molecules, related to those in the asymmetric unit by the twofold symmetry axes parallel with *b* through Se1 and Se4. Distances are in Å and angles in degrees.
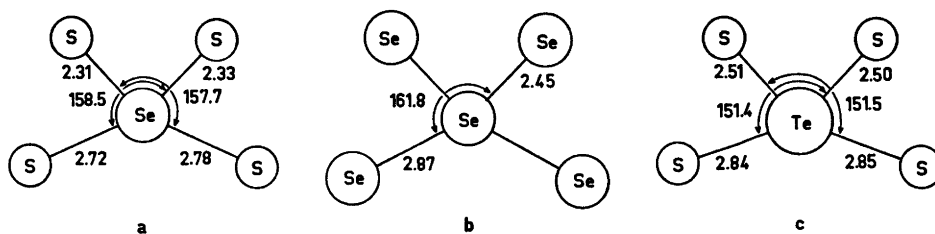

a   b   c

Fig. 2. The coordination around the central atoms in (a) selenium bis(diethyldithiocarbamate), (b) selenium bis(1-pyrrolidinecarbodiselenoate), and (c), tellurium di(methylxanthate). The bond lengths and angles in (b) are average values. All complexes are viewed along the normal to the least squares planes of the atoms shown. Bond lengths are in Å, angles in degrees.
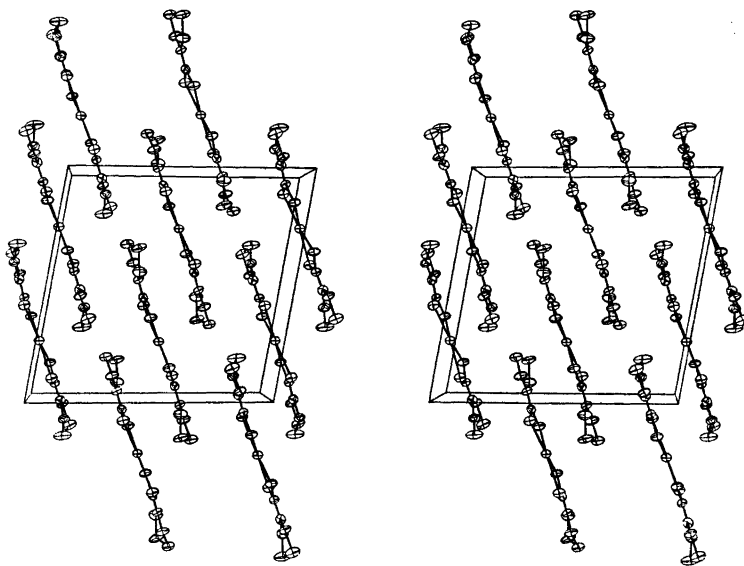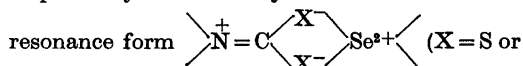
Fig. 3. The unit cell contents as seen along *b*. The *a* axis is horizontal, while *c* is represented by the nearly vertical edge (stereo drawing).

value of only 124.52(3)° in the present investigation. The corresponding angle is larger than 130° in the selenium dithiocarbamates,[2,3] and is found to have values up to 146° in analogous tellurium compounds.[1 5,8,9]

The asymmetry in the selenium-selenium bonds are reflected in the length of the selenium-carbon bonds. To a long selenium-selenium bond there corresponds a short selenium-carbon bond, and *vice versa*. For a short bond, the average length is 1.849(6) Å, for a long one, it is 1.896(6) Å. These values are not significantly different from those found in the diethyldiselenocarbamate of zink,[22] where there is asymmetry in the zink-selenium bonds, and they agree well with values found in other metal diselenocarbamates.[13,22,23 27] The bond lengths are intermediate between the values expected for carbon-selenium single (1.94 Å) and double (1.73 Å) bond lengths.

The average C⋯N bond length is found to be 1.30(1) Å in the present investigation. This corresponds to a π-bond order of 0.5 based on Paulings bond order/bond length relationship, with parameters used by Merlino.[38] The average π-bond orders for the short and long carbon-selenium bonds are 0.1 and 0.2. In the dithiocarbamates of divalent selenium and tellurium,

the average π-bond order for the C⋯N bond is close to 0.3, while the averages for the short and long C–S bonds are close to 0.5 and 0.1, respectively. This may indicate that the resonance form $\diagup\!\!\!\!\!\!\overset{+}{N}=C\diagdown^{X^-}_{X^-}\!\!\diagup Se^{2+}\!\!\diagdown$ (X = S or Se) contributes more to the structure in a selenium(II) bis(dialkyldiselenocarbamate) than in selenium(II) and tellurium(II) bis(dialkyldithiocarbamates). As in the dithiocarbamates,[1] there is uneven contribution from resonance forms of the types $\diagup\!\!\!\!\ddot{N}-C\diagdown^{X}_{X^-}\!\!\diagup Se^{2+}\!\!\diagdown$ and $\diagup\!\!\!\!\ddot{N}-C\diagdown^{X^-}_{X}\!\!Se^{2+}\!\diagup$.
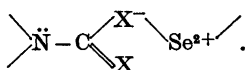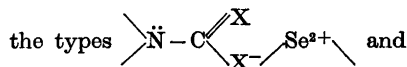
This increase in mesomeric shift of electron density from nitrogen to the ligand donor atoms may be part of the explanation why the structure found in the present investigation is that of a selenium(II) complex rather than that of a regular triselenide.

The angles on the CSe₂ carbon atoms and the nitrogen atoms correspond to sp^2 hybridization, in agreement with the suggested resonance forms. However, due to the strain in the pyrrolidine rings, the nitrogen ring angles are

small, only approximately 113°. The other ring angles and the bond lengths in the rings, have normal values.

In Fig. 3, the contents of a unit cell is shown as seen along the b axis. It can clearly be seen that the molecules are stacked nearly parallel to each other and that the molecular planes are nearly parallel with the b axis. The molecules are packed so that molecules of type I and II with a common z coordinate for their central selenium, are rotated about 180° relative to each other through a hypothetical axis lying along the length of each molecule. The central selenium atoms are not involved in any close contacts, but there are short intermolecular Se2···Se3 contacts between molecules of type I and Se5···Se6 contacts between molecules of type II. These contacts are 3.59 Å, which is considerably shorter than two times the van der Waals radius of selenium (4.00 Å). As a result, the molecules are connected into long chains parallel to the b axis by these weak Se···Se interactions. The intermolecular Se1−Se3···Se2 and Se4−Se5···Se6 angles are both close to 104°.

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