

Refinements of the Crystal Structures of Selenium Dithiocyanate and Selenium Diselenocyanate

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The crystal structures of selenium dithiocyanate and selenium diselenocyanate have been refined by full-matrix least-squares procedures. The crystals of the dithiocyanate and the diselenocyanate are isomorphous, space group *Pnma* (No. 62) with four formula units per unit cell. The selenium dithiocyanate has the cell dimensions, $a=9.8899(15)$ Å, $b=13.0364(20)$ Å, $c=4.4231(10)$ Å. The cell dimensions of the selenium diselenocyanate are, $a=10.1397(10)$ Å, $b=13.4514(15)$ Å, $c=4.5139(7)$ Å.

The molecules possess mirror plane symmetry in the crystals, and thus occur in the *cis* form. The dimensions of the selenium dithiocyanate molecule are, $\text{Se}-\text{S}=2.2136(10)$ Å, $\text{S}-\text{C}=1.695(3)$ Å, $\text{C}-\text{N}=1.129(4)$ Å, $\angle \text{S}-\text{Se}-\text{S}=101.59(4)^\circ$, $\angle \text{Se}-\text{S}-\text{C}=99.12(11)^\circ$, $\angle \text{S}-\text{C}-\text{N}=178.2(3)^\circ$ and the dihedral angle, $\text{SSeS/SeSC}=94.8^\circ$. The selenium diselenocyanate has the dimensions, $\text{Se}-\text{Se}=2.3343(11)$ Å, $\text{Se}-\text{C}=1.852(7)$ Å, $\text{C}-\text{N}=1.131(9)$ Å, $\angle \text{Se}-\text{Se}-\text{Se}=102.97(6)^\circ$, $\angle \text{Se}-\text{Se}-\text{C}=97.1(2)^\circ$, $\angle \text{Se}-\text{C}-\text{N}=176.9(7)^\circ$ and the dihedral angle, $\text{SeSeSe/SeSeC}=93.2^\circ$.

The crystal structures of selenium dithiocyanate, I, and of selenium diselenocyanate, II, have been determined by Ohlberg and Vaughan¹ and by Aksnes and Foss,² respectively. The data from II have later been used by McDonald and Pettit³ in a full-matrix least-squares refinement.

The present refinements have been undertaken to get more accurate dimensions of the molecules and of the intermolecular contacts.

CRYSTAL DATA

Selenium dithiocyanate, I, was prepared according to Ohlberg and van der Meulen⁴ and selenium diselenocyanate, II, as described else-

where.⁵ The crystals of the two compounds are yellow-orange prisms elongated along the *c* axis. They are isomorphous, with space group *Pnma* (No. 62) and with four molecules in the unit cell. The unit cell dimensions of I are, $a=9.8899(15)$ Å, $b=13.0364(20)$ Å, $c=4.4231(10)$ Å, and of II, $a=10.1397(10)$ Å, $b=13.4514(15)$ Å, $c=4.5139(7)$ Å. The dimensions of the crystal used for data collections were about $0.13 \times 0.10 \times 0.20$ mm for I and $0.12 \times 0.07 \times 0.25$ mm for II. The crystals were protected against decomposition by coating them with epoxy glue.

Collection of X-ray data was done by means of a Siemens AED diffractometer, using Nb-filtered $\text{MoK}\alpha$ radiation, $\lambda(\alpha_1)=0.70926$ Å. The determination of cell parameters were done by the method of Maartmann-Moe,⁶ using 20 reflections with θ values between 21 and 26° for I and 19 reflections with θ values between 23 and 27° for II.

Intensity data were collected using a "five value" measuring procedure. The scale factors based on the net counts of three reference reflections, each measured two times at intervals of 50 reflections, varied within 5% for I and 3% for II. The lower limit for observed reflections was set equal to two times the standard deviation in net intensity. Of 869 reflections with $\theta < 30^\circ$, 623 were found to be stronger than the lower limit for I, and the numbers for II were 940 and 683. The remaining reflections were judged unobserved and set equal to the limit.

The intensities were corrected for absorption. The linear absorption coefficient, $\mu(\text{MoK}\alpha)$, is 76.3 cm^{-1} for I, and 191.5 cm^{-1} for II. The data of II were also corrected for extinction and the coefficient was found to be 3.7×10^{-3} . The data of I showed no sign of extinction.

With weighting scheme $w=1/\delta^2(F)$ and use of

Table 1. Positional and thermal parameters for the atoms in selenium dithiocyanate and selenium diselenocyanate. The temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{23}klb^*c^*)]$. The values of the thermal parameters are multiplied by 10^3 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Se(SCN)₂									
Se	0.54179(3)	0.25	0.50320(10)	30.3(2)	31.3(2)	37.6(2)	0	-1.5(2)	0
S	0.44287(7)	0.11843(5)	0.27702(17)	41.3(3)	36.5(3)	42.5(4)	-5.0(3)	4.8(4)	-7.9(4)
C	0.3026(2)	0.1093(2)	0.4956(7)	38.5(11)	30.0(12)	41.6(15)	-0.1(10)	-3.7(16)	2.6(17)
N	0.2079(2)	0.1014(2)	0.6360(6)	42.8(13)	44.8(13)	59.2(17)	-8.0(12)	5.0(13)	0.5(13)
Se(SeCN)₂									
Se ₁	0.53707(7)	0.25	0.4953(3)	28.2(4)	29.2(4)	35.7(5)	0	-3.2(5)	0
Se ₂	0.44230(6)	0.11422(5)	0.2536(2)	35.6(3)	32.1(3)	42.1(4)	-4.2(3)	4.3(3)	-5.5(4)
C	0.2920(5)	0.1056(4)	0.4852(17)	34(3)	26(3)	42(4)	-3(2)	-7(3)	0(4)
N	0.1974(5)	0.0985(5)	0.6159(15)	41(3)	43(3)	57(4)	-7(3)	5(3)	3(3)

Table 2. The environments of selenium and sulfur in selenium dithiocyanate and of selenium in selenium diselenocyanate. Distances and deviations from least squares planes (Å).

Atoms defining plane	Distance from central atom	Deviation from plane
Se(SCN)₂		
Se	0	-0.018
S	2.2136(10)	0.005
S ^I	2.2136(10)	0.005
N ^{II}	3.000(3)	0.003
N ^{III}	3.000(3)	0.003
Se(SeCN)₂		
Se ₁	0	-0.018
Se ₂	2.3343(11)	0.006
Se ₃	2.3343(11)	0.006
N ^{II}	3.142(6)	0.003
N ^{III}	3.142(6)	0.003
Se ₂	0	-0.166
Se ₁	2.3343(11)	0.172
C	1.852(7)	0.090
N ^{IV}	3.253(6)	-0.126
N ^V	3.085(6)	0.030

Superscript I denotes an atom at $(x, \frac{1}{2} - y, z)$, II at $(\frac{1}{2} + x, \frac{1}{2} - y, 1.5 - z)$, III at $(\frac{1}{2} + x, y, 1.5 - z)$, IV at $(\frac{1}{2} - x, \bar{y}, z - \frac{1}{2})$, and V at $(\frac{1}{2} + x, y, \frac{1}{2} - z)$.

full-matrix least-squares procedures, the structure of I was refined to an *R*-value of 0.028 and of II to 0.044. The value of $s F[\sum w_i(\Delta F_i)^2/(N - V)]^{1/2}$, where *N* is the number of reflections and *V* is the number of variables, is 1.43 for I and 2.36 for II. The three-dimensional Fourier difference map based on the final refinement showed no peak higher than 0.3 e Å⁻³ for I and 1.2 e Å⁻³ for II.

Calculations were made by the X-Ray System, Version of June 1972,⁷ with some adjustments made by K. Maartmann-Moe of this Institute.

The final atomic parameters are listed in Table 1. Lists of observed and calculated structure factors are available from the author on request.

RESULTS

The dimensions of the selenium dithiocyanate and selenium diselenocyanate molecules, based on the coordinates of Table 1, are given in Fig. 1. The packing of the molecules, and close intermolecular distances S...N and Se...N, are also shown in Fig. 1. The environments of the selenium and sulfur atoms and distances from least-squares planes are given in Table 2. The dihedral angles SSeS/SeSC in I and SeSeSe/SeSeC in II are 94.8 and 93.2°, respectively.

Since the middle atom in both I and II is situated in a mirror plane, the molecules have the *cis* form.

The Se-S bond length, 2.2136(10) Å in I and the Se-Se bond length 2.3343(11) Å in II are very near the values found in the previous determinations.¹⁻³

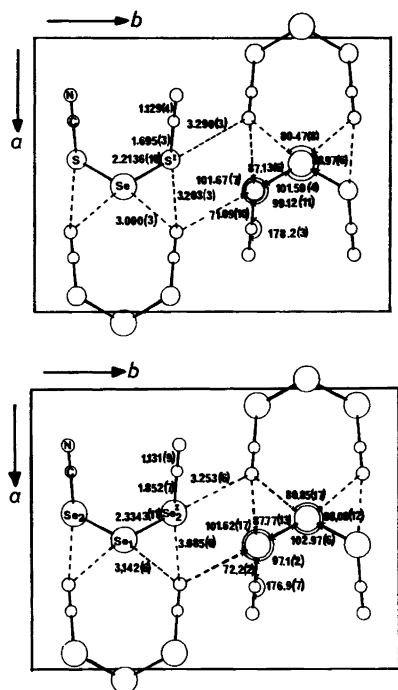


Fig. 1. Above, the crystal structure of Se(SeCN)₂ viewed along the *c*-axis, and below, the crystal structure of Se(SeCN)₂ viewed along the same axis.

As seen from Fig. 1 and Table 2, the environments of the selenium atoms in the two compounds indicate a tendency to square-planar coordination at these atoms, as has been pointed out by Foss.⁸ In the case of the sulfur compound, the S···N distances have previously¹ been found to be 3.03 and 3.32 Å, in the present refinement the values are 3.203(3) Å and 3.290(3) Å and the S···N contacts, if any, must be very weak.

The Se—Se bond length in crystal structures has been found to be 2.373(5) Å in trigonal selenium,⁹ 2.336(6) Å in α -monoclinic selenium,¹⁰ 2.334(5) Å in γ -monoclinic selenium,¹¹ 2.334(12) Å in bis(diethylthiophosphoryl) diselenide;¹² the dihedral angle, PSeSe/SeSeP, in the last one is 104.5°. In crystal structures of dimorpholino-di-, -tri-, and -tetra-selenane, and dipiperidinotetraselane¹³ the Se—Se bond lengths are from 2.328(2) to 2.356(2) Å. The dihedral angles at Se—Se are in the range 75.7 to 97.1°. From data listed by Aleby,¹⁴ the Se—Se bond lengths in five diselenides where selenium is bonded to carbon, are in the range 2.285(5) to

2.333(15) Å and the dihedral angles at Se—Se are in the range 56.0 to 89.5°.

In one case, α,α' -diselenobis[formamidinium] dichloride,¹⁵ the Se—Se bond length is 2.380(6) Å. This structure has a nearly linear Cl···Se—Se···Cl system with Se···Cl distances of 3.19 Å, and these contacts probably lengthen the Se—Se bond. This influence is still more evident in the isomorphous diiodide¹⁶ where the Se—Se bond length is 2.4037(10) Å and the Se···I distance is 3.4030(10) Å. The bonding system in these two diselenides can be looked upon as a linear four-centre six-electron system.

Two-sided linear approaches to Se—Se bonds are also found in the structures of the dimerized Se(SeCN)₃⁻ ion as it occurs in the potassium¹⁷ and rubidium¹⁸ salts. The ion can be looked upon as built up of two Se(SeCN)₂ molecules bridged together through the selenium atoms of two selenocyanate ions. In the Se(SeCN)₂ parts of the ion, the Se—Se bond lengths are in the range 2.391(2) to 2.419(2) Å and the angles Se—Se—Se are from 97.55(7) to 99.32(7)°. The Se···Se—Se···Se systems in these structures are asymmetrical with the shortest Se···Se distances in the range 3.089(2) to 3.331(2) Å and the long ones from 3.462(2) Å and upwards.

In the present structure of selenium diselenocyanate, the Se—Se bond has two-sided linear asymmetrical approaches by two nitrogen atoms, N···Se—Se···N. The Se···N distances are 3.142(6) and 3.253(6) Å. The approaches may lengthen the Se—Se bond a little. From what is said above a value of 2.32 Å should be reasonable for a normal Se—Se bond length when the dihedral angle at Se—Se is about 90°.

The Se—S bond length in three crystal structures of salts of the selenopentathionate ion^{19–21} is from 2.153(4) Å to 2.181(3) Å, with 2.178 Å as weighted mean value. The S—Se—S angle is from 103.1(1) to 104.9(2)°, the weighted mean value is 103.9°. The dihedral angle at Se—S is from 83.3 to 106.7°. In a mixed selenide-sulfide, the adduct of *o*-nitrobenzeneselenenyl thiocyanate with thiourea,²² the Se—S bond length is 2.189(3) Å and the dihedral angle CSeS/SeSC is 95.7°. The Se—S bond in this structure has a nearly linear O···Se—S approach which may lengthen the bond.

Approaches to Se—S bonds are also found in the structure of the dimerized KSe(SCN)₃·½H₂O.²³ This structure shows great resemblance to the structures of the corresponding selenocyanate com-

pounds. The dimerized $\text{Se}(\text{SCN})_3^-$ ion is built up of two $\text{Se}(\text{SCN})_2$ molecules bridged together through the sulfur atoms of two thiocyanate ions. The Se—S bond lengths in the $\text{Se}(\text{SCN})_2$ parts of the ion are from 2.252(2) to 2.318(3) Å and the two S—Se—S angles are 95.50(11) and 98.52(12)°. The Se···S distances in the nearly linear S···Se—S approaches are from 2.953(3) to 3.112(3) Å.

In the present structure of selenium dithiocyanate, a nearly linear N···Se—S system occurs with Se···N distance of 3.000(3) Å. According to the above, the N···Se contact must have a lengthening influence on the Se—S bond. A value near 2.18 Å as found in the structures of the selenopentathionates, will also from the present structure be reasonable for a normal Se—S bond when the dihedral angle is about 90°.

The dimensions of the thiocyanate and selenocyanate parts of the molecules are in the same range as previously found.^{15,16,21} In the structure of selenium diselenocyanate, the Se_2 atom has an approach by a nitrogen atom *trans* to the C— Se_2 bond. The Se_2 ···N distance is 3.085(6) Å. It is difficult, from the present data, to say whether the approach has any influence on the C— Se_2 bond length.

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