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The Crystal Structure of Selenium Diselenocyanate

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The crystal structure of selenium diselenocyanate has been determined by X-ray methods, from Patterson and Fourier projections along the *a*, *b* and *c* axes. The crystals are orthorhombic bipyramidal, with $a = 10.07$ Å, $b = 13.35$ Å, $c = 4.48$ Å. The space group is D_{2h}^{16}-*Pnma*, and there are four molecules per unit cell.

The molecule consists of an unbranched and non-planar $N{\equiv}C-Se-Se-Se-C{\equiv}N$ chain, with a Se—Se bond length of 2.33 ± 0.03 Å and a Se—Se—Se bond angle of 101 ± 2°. The following, less reliable values were found for dimensions involving carbon and nitrogen atoms: Se—C = 1.83 Å, C—N = 1.05 Å, ∠ Se—Se—C = 95°, ∠ Se—C—N = 164°, and the dihedral angle, SeSeSe/SeSeC = 94°. The middle selenium atom is located in a crystallographic mirror plane of symmetry, and the molecule thus occurs in a *cis* form in the crystals.

The sixth-group elements, sulphur and selenium, do both form many-membered chains and rings. Beside the S_8 rings of orthorhombic and monoclinic sulphur, and the very long chains of plastic and fibrous sulphur, there are polysulphides and polythionic compounds with six sulphur atoms or more in the molecule. Selenium occurs as Se_8 rings in the monoclinic forms, and as infinite spirals in the hexagonal state, and polyselenide anions up to and including hexaselenide appear to exist.

When, however, the selenium chains are terminated by other atoms, and thus are parts, only, of larger molecules, the chain-forming capacity of selenium becomes inferior to that of sulphur. The largest number of selenium atoms in the chains, in any such compound isolated hitherto, appears to be three. Even so, the representatives known are relatively few. The simplest, and one of the more stable, is selenium diselenocyanate [1-5], also called [3-5] cyanogen triselenide.

This compound, $Se(SeCN)_2$, was first prepared by Verneuil [1] in 1886, by treatment of potassium selenocyanate with oxidizing agents. The substance occurs, together with selenium dicyanide, as a rearrangement product of selenocyanogen [2], and the same products result from reactions of diselenium

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dibromide with silver cyanide [2] and of bromine with lead selenocyanate [3]. The molecular weight of selenium diselenocyanate in boiling benzene and chloroform corresponds to a single formula unit [4], and the electric moment, in benzene at 25° C, is 3.98 Debye units [5].

A preliminary note on the crystal structure of selenium diselenocyanate has been published [6]. Unit cell and space group data have earlier been reported for triselenium dibenzene- and di-*p*-toluenesulphinate [7], but no detailed structure determination is available for these nor for any other triselenium derivative.

CRYSTAL DATA

The compound was prepared from potassium selenocyanate and nitrogen dioxide as described by Muthmann and Schröder [4], and recrystallized from benzene. The substance consisted of orange-yellow prisms, which were elongated in the direction of the *c* axis. The faces $\{010\}$ were most prominently developed, with $\{110\}$ and $\{111\}$ also appearing. Recrystallization from chloroform gave thin plates, having a more yellow appearance but giving the same X-ray photographs as the crystals obtained from benzene.

The crystals are stable when kept in the dark, but decompose slowly, with liberation of selenium, when exposed to light or to X-rays. The slight deterioration did not, however, appear to influence the quality of the X-ray photographs.

Oscillation and Weissenberg photographs, using Cu$K\alpha$ radiation, $\lambda = 1.52_2$ Å, lead to the axial lengths: $a = 10.07 \pm 0.03$ Å, $b = 13.35 \pm 0.04$ Å, $c = 4.48 \pm 0.02$ Å. There are four molecules per unit cell; density, calc. 3.18, found 3.12 g/cm^3. On the basis of the systematic absences, $0kl$ when $k + l$ is odd, $hk0$ when h is odd, the centrosymmetric space group, D_{2h}^{16}-*Pnma*, was provisionally adopted, and this choise appears to be justified by the agreement ultimately obtained between observed and calculated structure factors. The space group implies that the selenium diselenocyanate molecule possesses either a mirror plane, or a centre, of symmetry.

Intensity measurements were made visually on zero layer Weissenberg photographs, using a double film technique. The crystals used for the *a*, *b* and *c* axis photographs had cross-sections of 0.05 × 0.06 mm, 0.08 × 0.09 mm, and 0.05 × 0.09 mm, respectively. 176 reflections out of a theoretically accessible 210 were measured in the principal zones, $0kl$, $h0l$, amd $hk0$. The intensities were corrected for the Lorentz and polarisation factors, but not for absorption. They were converted to relative structure factors, and later put to an approximately absolute scale by comparison with the calculated values.

The Patterson and Fourier summations were made with Beevers-Lipson strips, at intervals of 6° along the *a* and *b* axes and 12° (0.149 Å) along the *c* axis.

ANALYSIS OF THE STRUCTURE

The positions of the selenium atoms were determined from Patterson projections along the *a*, *b* and *c* axes, and the complete structure was subsequently worked out by means of Fourier projections along the same axes. The selenium

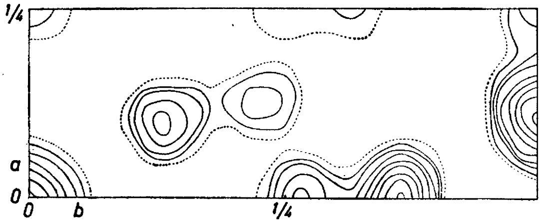


Fig. 1. Patterson projection along the c axis. Contours at arbitrary but equal intervals, except at the origin peak, where the intervals are three times as large.

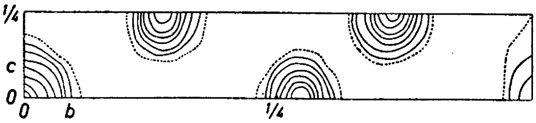


Fig. 2. Patterson projection along the a axis. Contours as in Fig. 1.

atoms, which account for 80 % of the electrons in the unit cell, were found to determine the signs of all observed structure factors in the three zones, except for a single one, 2,10,0.

The asymmetric parts of the Patterson projections are shown in Figs. 1 to 3. The number, heights and positions of vector peaks are in accordance with the requirements of the space group D_{2h}^{16}—*Pnma*, with one selenium atom situated in the mirror plane.

The following x and y coordinates were derived from the Patterson projection along the c axis: Se_1, $x = 0.536$, $y = 0.250$; Se_2, $x = 0.438$, $y = 0.116$. These values were used for the calculation of signs of the $hk0$ reflections for the first Fourier synthesis. The resulting map showed peaks corresponding to the carbon and nitrogen atoms, and the projection was refined by successive approximations in the usual way. The final electron density map, $\varrho(xy)$, is shown in Fig. 4.

The approximate z coordinates, 0.50 for Se_1 and 0.25 for Se_2, were derived from the Patterson projections along the a and b axes, and were employed, together with the x or y coordinates from $\varrho(xy)$, as a basis for the first Fourier projections along these axes. The refinement process, by Fourier methods as above, led to the electron density maps, $\varrho(yz)$ and $\varrho(xz)$, shown in Figs. 5 and 6.

Two sets of x, y and z coordinates were obtained from the three projections. The values finally adopted are listed in Table 1. The x and y coordinates are those derived from $\varrho(xy)$, since this projection is based on a larger number of

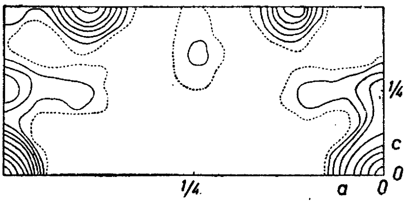


Fig. 3. Patterson projection along the b axis. Contours as in Figs. 1 and 2.

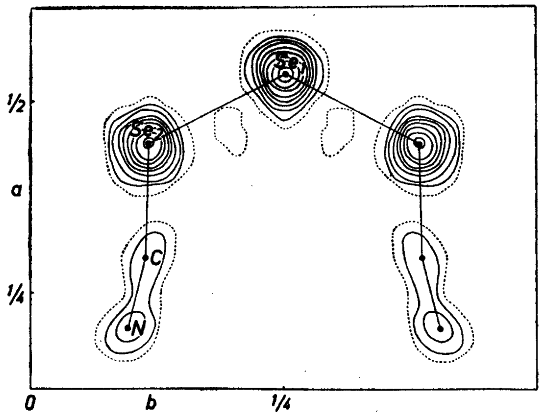


Fig. 4. Electron density projection of Se (SeCN)$_2$ along the c *axis,* ϱ(xy). *The area shown (from* x = $\frac{1}{8}$ *to* $\frac{5}{8}$*) is selected so as to cover one complete molecule. The 4-electron line is dashed. Contour intervals: 6 e.Å^{-2} for the selenium atoms and 2 e.Å^{-2} for the carbon and nitrogen atoms. In this and the two following figures, the positions corresponding to the final atomic coordinates are marked with dots, and lines are drawn to show the outline of a molecule.*

observed reflections (84) than the *a* axis (47) and *b* axis (45) projections. As for the *z* coordinates, overlapping occurs for Se$_1$ in $\varrho(xz)$ and for Se$_2$ in $\varrho(yz)$, but not *vice versa*. The carbon and nitrogen atoms are well resolved in $\varrho(xy)$ and $\varrho(xz)$ but not in $\varrho(yz)$, and the *z* coordinates chosen for these atoms are those derived from $\varrho(xz)$. Thus, all the coordinates of Table 1 have been determined from resolved peaks in electron density maps.

Table 1. Atomic coordinates, as fractions of corresponding cell edges. Origin at a centre of symmetry.

	x	*y*	*z*
Se$_1$	0.540	0.250	0.492
Se$_2$	0.442	0.115	0.249
C	0.295	0.112	0.488
N	0.203	0.095	0.586

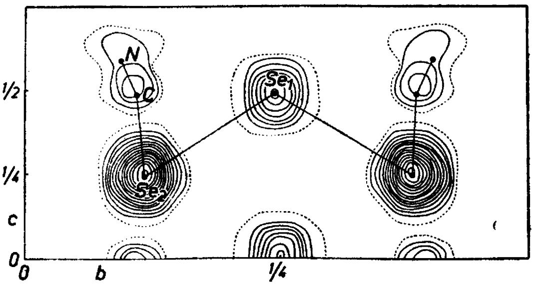
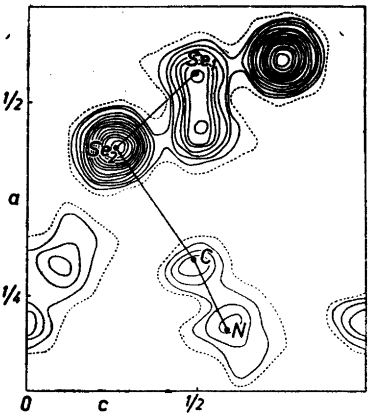


Fig. 5. Electron density projection of Se (SeCN)$_2$ along the a *axis,* ϱ(yz). *The Se$_2$ atoms are overlapped by other Se$_2$ atoms belonging to different molecules. The 6-electron line is dashed, and the contour intervals are 8 e.Å^{-2} for the selenium atoms and 2 e.Å^{-2} for the carbon and nitrogen atoms.*

Fig. 6. Electron density projection of Se $(SeCN)_2$ along the b *axis,* ϱ(xz). *As in Fig. 4, the drawing covers the* a *axis from $\frac{1}{8}$ to $\frac{5}{8}$. The two selenocyanate groups of a molecule overlap exactly because of the mirror plane normal to the projection axis, and Se_1 atoms, from different molecules, overlap partly across a centre of symmetry. The 8-electron line is dashed, and contour intervals are 8 e.Å^{-2} for the selenium atoms and 3 e.Å^{-2} for the carbon and nitrogen atoms.*



In Table 3, observed and calculated values of structure factors are compared for all *hk*0, 0*kl* and *h*0*l* reflections within the range of Cu*K*α radiation. The calculated values are based on the coordinates of Table 1, and the atomic scattering curves of the *International Tables*, with a temperature factor of $B = 3.0$ Å^2 for all three zones. The realiability factor, $R = \Sigma \,||F_{\text{obs}}| - |F_{\text{calc}}|| / \Sigma |F_{\text{obs}}|$, with non-observed reflections included in the difference only when $|F_{\text{calc}}|$ is greater than the lowest observable value of $|F_{\text{obs}}|$, is 0.15, 0.12 and 0.13, respectively, for the *hk*0, 0*kl* and *h*0*l* reflections.

THE SELENIUM DISELENOCYANATE MOLECULE

The analysis has shown that the molecule is built up of an unbranched and non-planar chain, with three divalent selenium atoms in the middle and the cyano groups at the ends. The dimensions, calculated on the basis of the

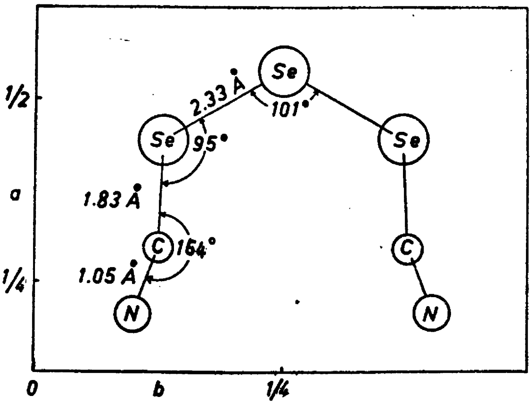


Fig. 7. The molecule as seen along the c *axis, showing bond distances and angles. The figure covers the same area as Fig. 4.*

coordinates of Table 1, are given in Table 2. The Se—Se bond length and Se—Se—Se bond angle are probably correct to within 0.03 Å and 2°. In view of the large contributions of the heavy selenium atoms to the observed X-ray intensities, but little reliance can be placed in the coordinates found for the carbon and nitrogen atoms. The coordinates may be in error by 0.1 Å or more, with corresponding errors in distances and angles involving these atoms. Due to the low and almost equal scattering power of the carbon and nitrogen atoms, the present analysis is incapable of deciding whether the structure of the selenocyanate groups is Se—C—N or Se—N—C. However, chemical evidence, and the close similarity with the thiocyanate group, leave little doubt that the former structure is the correct one.

Table 2. Bond lengths and bond angles.

Se—Se = 2.33 Å   ∠ Se—Se—Se = 101°
Se—C = 1.83   ∠ Se—Se—C = 95°
C—N = 1.05   ∠ Se—C—N = 164°

Shortest non-bonded distances within the molecule.

Se—Se = 3.60 Å   Se—C = 3.08 Å
C—C = 3.68   Se—N = 2.85

The length, 2.33 Å, found for the Se—Se bond, compares with the current value [8], 2.34 Å, for the Se—Se single bond distance. Recent determinations have given the values 2.34 ± 0.02 Å in α-monoclinic [9] and β-monoclinic [10] selenium, 2.29 ± 0.01 Å in diphenyl diselenide [11], and $2.33_5 \pm 0.032$ Å in perfluoromethyl diselenide [12]. In hexagonal selenium [8 p. 79] as well as in α- and β-monoclinic selenium [9,10] the Se—Se—Se bond angle is 105°, as compared with the present value of 101°. These are the only data available for the bond angle of divalent selenium when bonded to two other selenium atoms.

The selenium diselenocyanate molecule possesses a mirror plane of symmetry, which passes through the middle selenium atom. The cyano groups are rotated out of the plane of the selenium atoms, to the same side of the plane, and the molecule thus occurs in a *cis* form [13] in the crystals. The dihedral angle between the Se—Se—Se and Se—Se—C planes is 94°. It is interesting to note that the configuration of the triselenium group, including the directions of the bonds extending form the external selenium atoms, is the same as that of a triselenium group in the eight-membered rings of the element. In the crystals of triselenium di-*p*-toluenesulphinate[7, 13], a twofold axis of molecular symmetry is present, and the external valencies of the triselenium group are there extending to opposite sides of the plane of the selenium atoms.

This appears to be the first structure determination of a compound containing the selenocyanate group. The analogous thiocyanate group has always been found to be linear, except in the mercury tetrathiocyanate-copper diethylenediamine complex [14] where the weighted mean value, ∠ S—C—N = 163° 12′, was reported. The deviation from linearity in the present structure, ∠ Se—C—N = 164°, may, partly at least, be due to experimental errors. The bond lengths within the group, Se—C = 1.83 Å and C—N = 1.05 Å, are to be compared

Table 3. Observed and calculated values of structure factors for selenium diselenocyanate.

k	F_{obs}	F_{calc}
	*hk*0 zone	
	0*k*0	
2	58	−67
4	135	−156
6	161	−182
8	189	+194
10	46	+29
12	42	−17
14	100	−81
16	40	+38
	2*k*0	
0	163	+214
1	50	+45
2	93	−95
3	134	+202
4	9	−16
5	100	−108
6	95	−86
7	58	−54
8	126	+126
9	< 12	−1
10	23	−16
11	84	+83
12	< 13	−9
13	20	−16
14	57	−48
15	24	−25
16	40	+35
17	13	−16
	4*k*0	
0	98	+92
1	59	+46
2	49	−39
3	195	+216
4	24	+11
5	119	−110
6	62	−50
7	69	−59
8	53	+42
9	32	−31
10	13	−10
11	100	+93
12	21	+12
13	18	−19
14	27	−20
15	20	−15
16	11	+10
	6*k*0	
0	63	−67
1	< 12	−5
2	24	+12
3	139	+139
4	70	+65
5	102	−103
6	< 10	+15
7	31	−28
8	35	−38
9	34	−16
10	25	−23
11	76	+86
12	31	+24
13	24	−24
14	11	+15
15	9	−17
	8*k*0	
0	116	−123
1	39	−29
2	< 13	+4
3	58	+54
4	73	+70
5	45	−39
6	46	+49
7	20	+20
8	58	−68
9	32	−26
10	28	−26
11	30	+26
12	18	+19
13	12	−15
	10*k*0	
0	61	−66
1	38	−36
2	18	+23
3	< 13	−3
4	15	+15
5	12	−4
6	28	+29
7	30	+33
8	37	−47
9	20	−16
	12*k*0	
0	31	−42
1	25	−28
2	13	+15
3	16	−29
4	< 4	0
5	< 2	+12
6	16	+25
	0*kl* zone	
	0*k*0	
2	59	−67
4	138	−156
6	157	−182
8	183	+194
10	43	+29
12	29	−17
14	94	−81
16	40	+38
	0*k*1	
1	130	+147
3	131	+155
5	68	−77
7	123	−126
9	34	+32
11	93	+80
13	< 15	0
15	48	−47
17	8	−7
	0*k*2	
0	66	−55
2	105	−95
4	182	+193
6	35	−29
8	39	−30
10	91	−76
12	82	+75
14	< 12	+7
	0*k*3	
1	83	−75
3	108	−113
5	58	+49
7	84	+79
9	< 15	−3
11	62	−59
13	< 11	−3
15	16	+27
	0*k*4	
0	105	+118
2	36	−28
4	38	−37
6	56	−52
8	69	+77
10	< 12	+5
12	< 9	−12
14	27	−39

0k5

k	F_{obs}	F_{calc}
1	34	+ 38
3	33	+ 32
5	15	− 15
7	29	− 39

h0l zone

h00

h	F_{obs}	F_{calc}
2	151	+214
4	103	+ 92
6	66	− 67
8	125	−123
10	71	− 66
12	41	− 42

h01

h	F_{obs}	F_{calc}
1	101	+107
2	137	+152
3	85	+ 73
4	142	+149
5	44	+ 26
6	114	+107
7	< 16	− 9
8	21	+ 13
9	24	− 22
10	35	− 29
11	30	− 23
12	28	− 35

h02

h	F_{obs}	F_{calc}
0	59	− 55
1	27	− 23
2	70	− 73
3	< 14	+ 4
4	41	+ 29
5	< 16	− 8
6	80	+ 64
7	< 18	− 9
8	63	+ 49
9	< 18	+ 3
10	34	+ 32
11	< 14	− 2
12	8	− 10

h03

h	F_{obs}	F_{calc}
1	64	+ 61
2	72	− 68
3	32	+ 30
4	109	−114
5	35	+ 22
6	64	− 58
7	< 18	− 14
8	23	− 22
9	< 15	− 13
10	18	+ 19
11	9	− 15

h04

h	F_{obs}	F_{calc}
0	110	+118
1	< 18	− 6
2	89	+ 85
3	< 18	0
4	34	+ 26
5	< 18	− 4
6	28	− 29
7	< 15	− 6
8	37	− 50
9	< 11	− 1

h05

h	F_{obs}	F_{calc}
1	30	+ 22
2	27	+ 30
3	18	+ 8
4	32	+ 34
5	16	+ 14
6	18	+ 27

with the standard bond lengths [8], Se—C = 1.94 Å, Se=C = 1.74 Å, C=N = 1.27 Å, and C≡N = 1.15 Å. The rather large uncertainties in the carbon and nitrogen coordinates do hardly permit definite conclusions to be drawn concerning the multiplicity of the Se—C and C—N bonds.

The shortest intermolecular distances in the crystal are 3.04 Å and 3.24 Å and occur between selenium (Se_2) and nitrogen atoms. The figure, 3.04 Å, is rather low, considering the van der Waals radius of nitrogen [15], 1.4—1.5 Å, and of selenium [9,10], 1.75—1.80 Å. The closest approach between selenium atoms of different molecules is 3.98 Å.

The crystal structure of an isomorphous compound, *viz.*, selenium dithiocyanate, $Se(SCN)_2$, has been published recently [16]. The Se—S distance, 2.21 Å, corresponds to a single bond, as does the Se—Se distance in the present structure, and the selenium bond angle is the same, 101°. A van der Waals approach of 2.98 Å occurs between selenium and nitrogen atoms.

It appears possible that the relatively unstable crystals of sulphur dithiocyanate [17], $S(SCN)_2$, may be isomorphous with those of selenium dithiocyanate and diselenocyanate.

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