[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

The Crystal Structure of Selenium Dithiocyanate

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Selenium dithiocyanate, $Se(SCN)_2$, belongs to the orthorhombic system with a = 9.87 Å., b = 13.03 Å., c = 4.44 Å. and Z = 4. The space group is D_{2h}^{16}–Pnma and the molecules belong to point group Cs–m. The molecular parameters are Se–S = 2.21 Å., S–C = 1.69 Å., C–N = 1.13 Å., ∠S–Se–S = 101°, ∠Se–S–C = 104° and the dihedral angle between the S–Se–S and Se–S–C planes is 79°.

Ohlberg and van der Meulen[1] have recently described the preparation and some of the properties of selenium dithiocyanate. The two most probable configurations for this compound are $Se(SCN)_2$ and $Se(NCS)_2$. The present lack of information concerning the structure of the thiocyanate group provides additional incentive for determining the structures of this compound.

Experimental

Unit Cell and Space Group.—Crystals of $Se(SCN)_2$ were obtained from aqueous or dioxane–ether solutions as small prisms. Weissenberg photographs about the c (prism) axis showed that the compound is orthorhombic. Systematic absences observed on (hk0), (hk1) and (0kl) Weissenberg photographs indicate that the space group is either C_{2v}^{9}–Pn2a or D_{2h}^{16}–Pnma. That the latter is correct is evident from interpretation of Patterson projections.

The cell parameters were determined from indexed oscillation photographs. They are a = 9.87 Å., b = 13.03 Å. and c = 4.44 Å. The density calculated on the basis of four molecules per unit cell is 2.273 g./cc., which is in agreement with the density of 2.265 g./cc. determined by the flotation method.

Intensities.—The intensities of the (hk0) and (0kl) reflections obtainable with Cu Kα radiation were determined by visual comparison on triple Weissenberg photographs and converted to values of $|F|^2$ by division by the Lorentz and polarization factors. No corrections were made for absorption errors. However, very small crystals were used for the intensity measurements and we were able to obtain satisfactory agreement between observed and calculated data.

Structure Determination

The locations of the selenium and sulfur atoms were obtained from Patterson projections on (001) and (100). These projections were easily interpreted on the basis of four $Se(SCN)_2$ molecules, the Se atoms of which are in the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ of the space group D_{2h}^{16}–Pnma. The atomic coördinates[2] are 4 Se in 4(c): $x, \frac{1}{4}, z;\ \bar{x}, \frac{3}{4}, \bar{z};\ \frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z;\ \frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z;$ 8 S, C and N in 8(d) $x, y, z;\ \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z;\ \bar{x}, \frac{1}{2} + y, \bar{z};\ \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z;\ \bar{x}, \bar{y}, \bar{z};\ \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z;\ x, \frac{1}{2} - y, z;\ \frac{1}{2} + x, y, \frac{1}{2} - z.$

Parameters for Se and S obtained from the Patterson projections are given in Table I. Since the Se–S and Se–Se maxima on the Patterson projection on (100) were unresolved multiple peaks, the z coördinates were estimated from peak shapes and assignment of 2.21 Å. to the Se–S distance.[3]

Structure factors were calculated from the Se and S coördinates and the signs of these were used to calculate Fourier projections on (001) and (100). The C and N positions were not apparent from these

TABLE I

REFINEMENT OF PARAMETERS

Parameter	Patterson	First Fourier	Final
x_{Se}	−0.050	−0.045	−0.047
z_{Se}	.534	.513	.500
x_S	.059	.059	.058
y_S	.117	.119	.119
z_S	.281	.294	.285
x_C	.....	.196	.206
y_C	.....	.108	.111
z_C	.....	.522	.474
x_N	.....	.287	.305
y_N	.....	.100	.105
z_N	.....	.679	.600

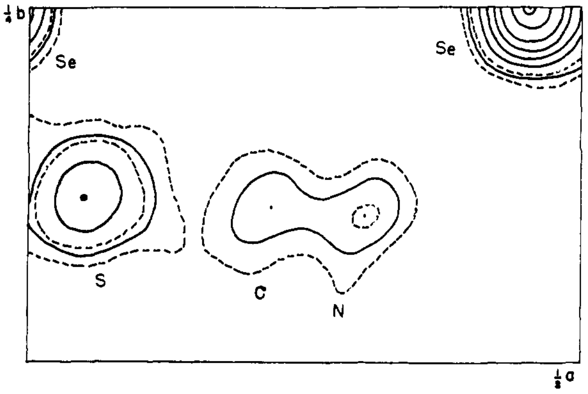

Fig. 1.—Fourier projection of $Se(SCN)_2$ on (001). Solid lines are at intervals of 4 electrons/Å.^{3}; dashed lines are at 3 and 5 electrons/Å.^{3}; dots are at positions corresponding to the final parameters.

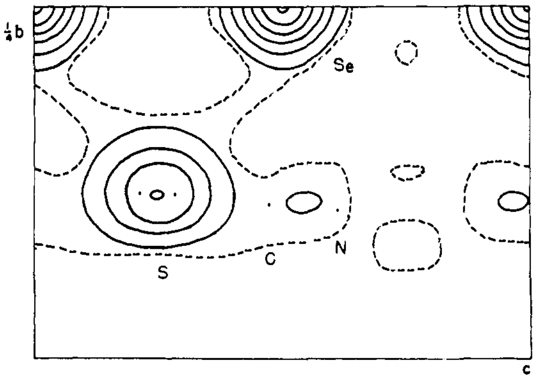

Fig. 2.—Fourier projection of $Se(SCN)_2$ on (100). Solid lines are at intervals of 4 electrons/Å.^{3}; the lowest solid line is at 8 electrons/Å.^{3}; the dashed line is at 6 electrons/Å.^{3}; dots are at positions corresponding to the final parameters.

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[1] S. M. Ohlberg and P. A. van der Meulen, THIS JOURNAL, **75**, 997 (1953).

[2] "International Tables for X-Ray Crystallography," Vol. I, the Kynoch Press, Birmingham, England, 1952, p. 151.

[3] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 164.

projections and projections were made using $F_{\text{obsd.}} - F_{\text{calcd.}}$ for the Fourier coefficients. Maxima corresponding to C and N appeared on these although the two atoms were unresolved in the (100) projection. The z parameters were calculated by making the assumption that C–N distance is 1.15 Å. The new parameters, which are given in Table I, were used to calculate structure factors, the signs of which were used to compute the final Fourier projections. These are shown in Figs. 1 and 2.

All of the atoms are clearly resolved on the (001) projection. On the (100) projection two sulfur atoms are unresolved. To obtain the final z parameters for sulfur the least squares[4] method was used. The observational equations were of the form

$$\sqrt{W_{hkl}}\ \ln |F_0|/|F_0| = \sqrt{W_{hkl}}\left\{-\Delta K - \Delta B(\sin\theta_{hkl}/\lambda)^2 + \Delta z_s(1/|F_c|)(\partial|F_c|/\partial z_s)\right\}$$

where e^K is the scale factor and $e^{-B(\sin\theta/\lambda)^2}$ is the temperature factor. The temperature factor was assumed to be isotropic since the resolved peaks are nearly isotropic in both projections and the temperature factors for the observed ($hk0$) and ($0kl$) reflections are nearly the same ($B = 3.82$ and 4.06, respectively). Solution of the normal equations gave $\Delta K = 0.0103$, $\Delta B = 0.27$ and $\Delta z_S = 0.0006$. The change in z_S is negligible; it amounts to only 0.0024 Å.

The C and N atoms are also unresolved in the (100) projection. To calculate final z parameters for C and N we assumed that the C–N maximum is at the center of the C–N bond and that the SCN group is linear. The latter assumption is consistent with the (001) projection. The final atomic coördinates are given in Table I and a drawing of the structure on Fig. 3.

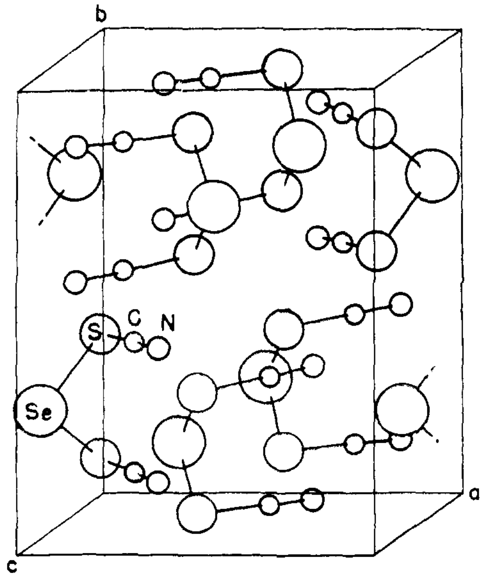

Fig. 3.—The crystal structure of Se(SCN)$_2$.

For the final structure, $R = \Sigma|F_{\text{obsd}} - F_{\text{calcd}}|/\Sigma|F_{\text{obsd}}| = 0.18$ for the ($hk0$) reflections and 0.12 for the ($0kl$) reflections. The observed and calculated structure factors are given in Table II.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

($hk0$) Reflections

hkl	$\|F_0\|$	F_c	hkl	$\|F_0\|$	F_c
200	117	111	860	51	66
400	72	56	10.6.0	<46	33
600	20	−33	12.6.0	<14	25
800	62	−75	270	21	19
10.0.0	29	−44	470	30	13
12.0.0	20	−22	670	38	30
210	20	−56	870	36	33
410	55	−53	10.7.0	<44	12
610	77	−64	080	117	125
810	58	−49	280	136	118
10.1.0	23	−17	480	46	53
12.1.0	16	−7	680	39	−42
020	81	−97	880	63	−79
220	198	−198	10.8.0	36	−44
420	66	−57	290	37	−25
620	<44	23	490	52	−52
820	36	43	690	44	−37
10.2.0	46	48	890	38	−26
12.2.0	16	−27	10.9.0	<34	−8
230	186	187	0.10.0	12	−13
430	236	260	2.10.0	78	−75
630	160	163	4.10.0	30	−16
830	86	58	6.10.0	35	7
10.3.0	30	0	8.10.0	<46	4
12.3.0	21	−31	10.10.0	<26	26
040	47	−39	2.11.0	23	74
240	120	118	4.11.0	94	58
440	33	22	6.11.0	78	76
640	37	15	8.11.0	33	25
840	<52	29	0.12.0	<28	4
10.4.0	<50	−28	2.12.0	37	22
12.4.0	<32	−8	4.12.0	<52	12
250	137	−149	6.12.0	<48	8
450	158	−181	8.12.0	<32	3
650	135	−135	2.13.0	<52	−24
850	60	−50	4.13.0	40	−36
10.5.0	<48	0	6.13.0	37	−41
12.5.0	<26	21	8.13.0	<18	−17
060	116	−121	0.14.0	40	−39
260	109	−107	2.14.0	39	−31
460	85	−57	4.14.0	<42	−18
660	28	16	6.14.0	<32	8
		($0kl$) Reflections			
020	95	−96	062	105	−105
040	49	−41	082	<52	36
060	114	−118	0.10.2	60	−63
080	111	120	0.12.2	61	64
0.10.0	19	−12	0.14.2	31	−22
0.12.0	19	1	0.16.2	24	8
0.14.0	35	−35	013	29	56
0.16.0	18	19	033	49	64
011	95	−103	053	41	−31
031	89	−90	073	47	−49
051	73	69	093	42	11
071	61	67	0.11.3	<48	25
091	40	−37	0.13.3	<38	−1
0.11.1	43	−42	004	51	45
0.13.1	<52	14	024	58	−56
0.15.1	<38	19	044	41	25
002	31	41	064	48	−47
022	161	−152	084	58	47
042	202	199			

[4] E. W. Hughes, THIS JOURNAL, **63**, 1737 (1941).

[5] P. Vaughan and J. Donohue, *Acta Cryst.*, **5**, 530 (1952).

Discussion

The dimensions of the $Se(SCN)_2$ molecule are Se–S = 2.21 Å., S–C = 1.69 Å., C–N = 1.13 Å., ∠S–Se–S = 101°, ∠Se–S–C = 104°, dihedral angle for S–Se–S–C = 79°. The sums of the covalent radii[3] are Se–S = 2.21 Å., S = 1.81 Å., S–C = 1.60 Å., C $\equiv$ N = 1.27 Å. and C $\equiv$ N = 1.15 Å. There is clearly no evidence for double-bond character in the Se–S bond. The S–C bond, however, is shorter than the normal single-bond distances found, for example, in dimethyl sulfide (1.82 Å.),[6] dimethyl sulfide (1.77 Å.)[7] and dimethyl trisulfide (1.78 Å.)[8] and corresponds to about 30% double-bond character. However, only small reliance can be placed on this result since the errors in the C coördinates could be as large as 0.15 Å. The C–N distance given above is certainly too small, although one expects this distance to be less than the value of 1.22 Å. found in HNCS.[9] The mean distances found in the compound $[Hg(SCN)_4][Cu(en)_2]$[10] are C–N = 1.34 Å. and S–C = 1.57 Å., which are in marked disagreement with our results. Since the SCN groups in the mercury compound appeared non-linear—a very unlikely result—we conclude that the interatomic distances are likely to be greatly in error.

The bond angles about Se and S are very close to those found in most sulfides, disulfides, trisulfides and comparable selenium compounds, although the S–S–S angle in 2,2′-diiododiethyl trisulfide[11] appears to have the abnormally large value of 113°. The dihedral angle between the S–Se–S and Se–S–C planes, 79°, seems small. Pauling[12] predicts that this type of angle should be 90° or larger in sulfur compounds and has used this concept to explain the stability of S_8. It is expected that selenium will show the same behavior, and Burbank[13] found the average dihedral angle in α-selenium to be 102°. On the other hand, Donohue[11] found the S–S–S–C dihedral angle in 2,2′-diiododiethyl trisulfide to be 82°, although he did not place much reliance in this result. We do not believe that the errors in this determination are sufficient to cause a deviation of 11° or more in this angle. It is easily shown that $\partial\varphi/\partial x'_C = -15$ deg./Å., $\partial\varphi/\partial y'_C = 21$ deg./A. and $\partial\varphi/\partial z'_C = 21$ deg./Å., where φ is the dihedral angle and x'_C, y'_C, and z'_C are the coördinates of carbon in Å. The corresponding derivatives for nitrogen are even smaller. Hence, changes in the coördinates of both C and N of the order of 0.4 Å. would be required to obtain a dihedral angle of 90°.

The packing of the molecules is such that the closest intermolecular distances are N · · · Se and N · · · S. The shortest of these are 3.03 Å., 3.32 Å., 3.58 Å. and 3.90 Å. for N · · · S, and 2.98 Å. and 3.58 Å. for N · · · Se.

(6) L. O. Brockway, THIS JOURNAL, **58**, 2036 (1936).

(7) D. P. Stevenson and J. Y. Beach, *ibid.*, **60**, 2872 (1938).

(8) J. Donohue and V. Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).

(9) C. I. Beard and B. P. Dailey, *ibid.*, **18**, 1437 (1950).

(10) H. Scouloudi, *Acta Cryst.*, **6**, 651 (1953).

(11) I. M. Dawson and J. M. Robertson, *J. Chem. Soc.*, 1256 (1948); J. Donohue, THIS JOURNAL, **71**, 2701 (1950).

(12) L. Pauling, *Proc. Nat. Acad. Sci.*, **35**, 495 (1949).

(13) R. D. Burbank, *Acta Cryst.*, **4**, 140 (1951).

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

Vapor Pressures of Inorganic Substances. XII. Zirconium Dioxide[1]

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The vapor pressure of ZrO_2 has been determined by the method of Knudsen, between 2014 and 2290°K. ZrO_2 vaporizes undissociated as $ZrO_2(g)$, the heat of vaporization being $\Delta H^\circ_{298} = 153.6 \pm 1$ kcal. The vapor pressure can be represented by the equation $\log p(\text{atm.}) = -(34{,}383/T) - 7.98 \times 10^{-4}T + 11.98$. The heat of dissociation of $ZrO_2(g)$ into gaseous atoms was found to be $D_0 = 365 \pm 5$ kcal.

Introduction

No experimental determination of the vapor pressure of zirconium dioxide is reported in the literature, and the question concerning which gaseous species are present when ZrO_2 vaporizes is still not settled.

The only available information on the vapor pressure of ZrO_2 is that of Searcy[2] who estimated a vapor pressure of 1.5×10^{-7} atm. at 2073°K. from measurements of Zintl, Morawietz and Gastinger.[3] Mott[4] reported the boiling point at 4570°K. Starodubtsev[5] observed ZrO_2^+ in a mass spectrograph, which indicates the existence of the gaseous ZrO_2 molecule.

In the present investigation, the Knudsen effusion method was used to determine the pressure over pure ZrO_2 and over a mixture of ZrO_2 and Zr.

Apparatus and Experimental Procedure

Two tantalum Knudsen cells were used, of dimensions 1 in. diameter and $^3/_4$ in. high, with an orifice diameter of $^1/_{16}$ in. The area of the orifice was corrected for thermal expansion by using the thermal expansion coefficient of tantalum determined previously in this Laboratory.[6] ZrO_2 was introduced into one of the cells, while a mixture of ZrO_2 and Zr was introduced into the other. Both cells were degassed for two hours at 2000° before the runs were made.

The samples were heated in our metal cell,[7] and the temperature was measured with a disappearing-filament optical pyrometer, calibrated against a standard tungsten-ribbon

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(1) This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) A. Searcy, University of California Radiation Laboratory, Report UCRL-1404 (1951).

(3) E. Zintl, M. Morawietz and E. Gastinger, *Z. anorg. Chem.*, **245**, 8 (1940).

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(6) J. W. Edwards, R. Speiser and H. L. Johnston, *J. Applied Phys.*, **22**, 424 (1951).

(7) J. W. Edwards, H. L. Johnston and P. E. Blackburn, THIS JOURNAL, **74**, 1539 (1952).