Crystal and Molecular Structure of Bis(*NN*-diethyldiselenocarbamato)-selenium(II)

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Crystals of the title compound (II) are monoclinic, space group $P2_1/n$, with $a = 6.707(5)$, $b = 9.978(6)$, $c = 25.41(1)$ Å, $\beta = 90.75(5)°$. Except for the terminal methyl groups, the molecules are planar with non-crystallographic C_{2v} (*mm*) symmetry. There are two types of Se–Se bond of length 2.45 and 2.80 Å. The structure was solved by a combination of direct and heavy-atom methods from 1 890 photographic data. It was refined by least-squares techniques to *R* 0.08.

In an attempt to prepare bis(*NN*-diethylselenocarbamoyl)diselenide (I), an aqueous solution of sodium diethyldiselenocarbamate was allowed to react with atmospheric oxygen.[1] Two products were obtained by fractional crystallisation of the resulting orange solid from ethanol–chloroform: bis(*NN*-diethyldiselenocarbamato)selenium(II) (II), and bis(*NN*-diethylseleno-

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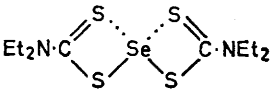
[1] P. Barnard and D. T. Woodbridge, *J. Chem. Soc.*, **1961**, **2922**.

carbamoyl)selenium(II) (III). The crystal structure of (II) is reported here.

$Et_2N{\cdot}C(Se){\cdot}Se{\cdot}Se{\cdot}C(Se){\cdot}NEt_2$ (I)

$Et_2N{\cdot}C(Se){\cdot}Se{\cdot}Se{\cdot}Se{\cdot}C(Se){\cdot}NEt_2$ (II)

$Et_2N{\cdot}C(Se){\cdot}Se{\cdot}C(Se){\cdot}NEt_2$ (III)



(IV)

EXPERIMENTAL

Crystal Data.—$C_{10}H_{20}N_2Se_5$, $M = 563$, orange monoclinic needles, $a = 6.707(5)$, $b = 9.978(6)$, $c = 25.41(1)$ Å, $\beta = 90.75(5)°$, $U = 1\,700$ Å^3, $D_m = 2.17$, $Z = 4$, $D_c = 2.20$ g cm^{-3}. Space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14). Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 144 cm^{-1}.

Structure Determination.—Data for layers 0—5*kl* were collected on multi-film packs, by the equi-inclination Weissenberg method. The crystal chosen was approximately cylindrical, elongated along [100] with a mean cross-sectional area of 0.06 mm². The intensities of 1 890 unique reflections were obtained by use of a Saab rotating-drum film scanner. No absorption corrections were applied.

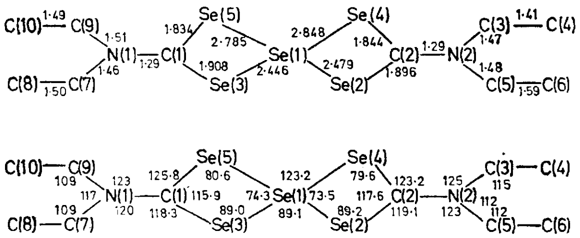


FIGURE 1

Fractional co-ordinates with standard deviations (× 10⁴) and thermal parameters (× 10³/Å²) for (II)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	1 984(3)	3 248(2)	8 842(1)	37	26	23	1	0	−5
Se(2)	−665(3)	1 872(2)	8 420(1)	27	27	43	3	4	−15
Se(3)	−568(3)	4 836(2)	9 124(1)	35	30	42	−2	2	−14
Se(4)	3 908(3)	967(2)	8 405(1)	30	41	39	6	−5	−11
Se(5)	4 049(4)	5 384(2)	9 298(1)	37	40	53	4	−16	−14
N(1)	997(30)	7 185(15)	9 536(7)	57	5	46	−1	0	−16
N(2)	797(24)	−336(15)	7 889(7)	29	20	14	12	−7	−8
C(1)	1 496(32)	6 016(21)	9 359(7)	45	29	13	2	−6	−18
C(2)	1 310(26)	646(18)	8 196(6)	4	24	18	8	3	7

	x	y	z	U		x	y	z	U
C(3)	2 174(40)	−1 352(26)	7 687(10)	48	C(7)	2 537(44)	8 189(31)	9 646(11)	59
C(4)	2 581(53)	−2 433(38)	8 032(14)	77	C(8)	3 234(68)	8 047(49)	10 208(18)	103
C(5)	−1 304(31)	−666(21)	7 756(8)	28	C(9)	−1 150(38)	7 600(26)	9 617(9)	46
C(6)	−2 037(44)	38(31)	7 225(12)	60	C(10)	−1 878(49)	8 316(34)	9 138(13)	69

The positions of the selenium atoms were found unambiguously by the MULTAN procedure,[2] and the remaining atoms were located by successive difference-Fourier syntheses. Refinement of interlayer scale factors and the positions and isotropic temperature factors of the selenium atoms led to R 0.13. No attempt was made to locate hydrogen atoms. For the final refinement cycles, all positional parameters, isotropic thermal parameters for the ethyl carbon atoms and anisotropic for all others, and a single scale factor were varied. Weights were of the form $W = X \,.\, Y$, where $X = \sin\theta/0.22$ for $\sin\theta < 0.22$ and 1.0 otherwise, and $Y = 150/|F_o|$ for $|F_o| > 150$ and 1.0 otherwise. The final R was 0.08.

Final atomic parameters are given in the Table, and intramolecular distances and angles in Figure 1. Among the atoms found, there are no intermolecular distances <3.6 Å. Structure factor tables are deposited as Supplementary Publication No. SUP 21657 (4 pp., 1 microfiche).[*] All standard crystallographic calculations were done by use of the '*X*-Ray '72' program system[3] at the Edinburgh Regional Computing Centre.

DISCUSSION

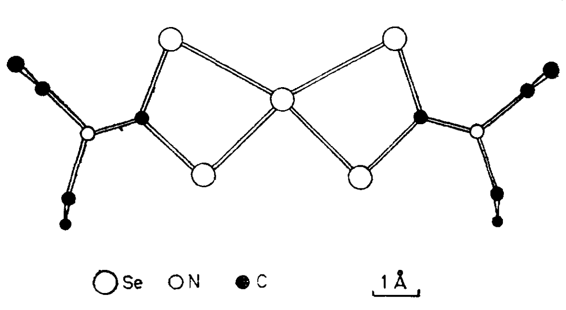


FIGURE 2 Projection of a molecule of (II) on its best plane

The projection of a molecule on its best plane is shown in Figure 2. Within experimental error, the molecules have C_s (*m*) symmetry; excluding terminal methyl groups, they are planar with C_{2v} symmetry, the maximum deviation from the plane being 0.4 Å [C(7)]. The corresponding bis(*NN*-diethyldithiocarbamato)-selenium(II) (IV) has been reported.[4] Its molecular structure is very similar: mean Se–S distances in (IV) are 2.32 and 2.76 Å, while in (II) the mean Se–Se distances are 2.46 and 2.82 Å. As would be expected,

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[*] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[2] P. Main, M. M. Woolfson, and G. Germain, 'MULTAN, a Computer Programme for the Automatic Solution of Crystal Structures,' University of York, 1971.

[3] '*X*-Ray' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of June 1972.

[4] S. Husebye and G. Helland-Madsen, *Acta Chem. Scand.*, 1970, **24**, 2273.

the difference between the two bonds in the $SeSe_4$ system is much less than that in the SeS_4 system. Similarly, the angles about the central atom are significantly nearer 90° in (II) than they are in (IV). The structures have very similar cell dimensions, but (IV) forms orthorhombic crystals, space group $P2_12_12_1$.[4] If the atom co-ordinates of (IV) are transformed to $1/4 + z, 3/4 - x, 1 - y$, the two molecules may virtually be superimposed, as may the two projections down the shortest axis of the entire structure. Clearly there is little difference in energy between the two packing arrangements, and this may explain the high thermal parameters for terminal groups, and the disorder found in (IV).[4]

Brøndmo *et al.*[5] distinguish three classes of structures for complexes of sulphur(II), selenium(II), and tellurium(II) with bidentate dithio- and related ligands. Classes (I) and (II) both have four-co-ordinate structures with two long and two short bonds, but in class (I) two bidentate ligands form a discrete complex molecule, while in class (II) the ligands are bridging and the 'intermolecular' bonds are particularly long. Both compounds (II) and (IV) are examples of class (I), while bis(diethyldiselenophosphinato)selenium(II) [6] is in class (II). In terms of their arguments, the diselenocarbamate ligand should thus have a greater donor capacity than the diselenophosphinate ligand. This distinction is well established for the sulphur analogues where, for example, the Ni–S bonds in bis(diethyldithiocarbamato)nickel(II) (2.202 Å) [7] are significantly shorter than those in bis(dimethyldithiophosphinato)nickel(II) (2.240 Å).[8]

We thank the S.R.C. for financial support (of C. L. J. and W. J. S.) and Professor E. A. V. Ebsworth and Dr. D. W. H. Rankin for encouragement and discussion.

[5/1757 *Received, 12th September*, 1975]

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[5] N. J. Brøndmo, S. Esperås, and S. Husebye, *Acta Chem. Scand.*, 1975, **A29**, 93.

[6] S. Husebye and G. Helland-Madsen, *Acta Chem. Scand.*, 1969, **23**, 1398.

[7] P. E. Jones, G. B. Ansell, and L. Katz, *Acta Cryst.*, 1969, **B25**, 1939.

[8] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 619.