Synthesis and X-Ray Crystal Structures of Dimorpholino-di-, -tri-, and -tetra-selane, and Dipiperidinotetraselane

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Summary The title compounds have been prepared by heating black selenium powder with the amine in the presence of red lead; their *X*-ray crystal structures have been determined.

Whereas di- and poly-sulphur diamides are well known,[1-5] the only example of a selenium analogue appears to be a brick-red solid of m.p. 90—95 °C described as being essentially dimorpholinotriselane.[6]

Levi[2] in 1931 prepared dipiperidino-tri- and -tetra-sulphane from sulphur and piperidine in benzene in the presence of an excess of PbO. The reaction was later used by others,[3,4] and HgO was also used instead of PbO as the sulphide acceptor.[3] The reaction has not, to our knowledge, been used in selenium chemistry. We found that selenium powder, when heated with piperidine or morpholine in the presence of PbO, reacts to give amides of divalent selenium. However, Pb_3O_4 was found to work markedly better than PbO. The yields varied with the brand of Pb_3O_4 used, probably depending on surface area and properties. Black selenium powder (Merck) (40 g), Pb_3O_4 (23—30 g), and piperidine or morpholine (50 ml) were heated with magnetic stirring close to the b.p. of the amine for 30—60 min. The mixture was filtered hot. In the case of the piperidine compound, the black residue was washed (× 2) with hot MeOH (50 ml), the combined washings and filtrate were kept overnight, and pure dipiperidinotetraselane crystallized; yield, 7—13 g. In the case of the morpholine compound hot cyclohexane (50 ml; ×2) was used instead of methanol, and the crude product was a green yellow mixture of dimorpholino-di-, tri-, and -tetra-selane.

The stabilities of the crystals in air increase with increasing selenium content. The crystals of dimorpholino- di- and -tri-selane used for *X*-ray analysis were coated with epoxy glue, whereas those of the tetraselane compounds were uncoated; in no case did the reference reflections show a decrease in intensity. Intensity data were collected on a Siemens diffractometer using Nb-filtered Mo-K_α radiation, and reflections with $I > 3\sigma(I)$ were used in the refinement.

Crystal data: $Se_4(NC_5H_{10})_2$: bipyramids, green-yellow to orange according to crystal size, m.p. 90—91 °C (decomp.); M = 484·1, tetragonal, space group $I4_1/a$ (No. 88), $a = b$ = 13·262(1), c = 17·713(4) Å, U = 3115·4 Å^3, Z = 8, D_c = 2·08 g cm^{-3}, μ = 101·1 cm^{-1}, 841 independent reflections within 2θ = 56°, refined to R = 0.036. The refinement began from the positional parameters of the corresponding atoms in dimorpholinotetraselane.

$Se_4(NC_4H_8O)_2$: bipyramids, colour as above, m.p. 123—124 °C (decomp.); M = 488·1, tetragonal, space group $I4_1/a$ (No. 88), $a = b$ = 13·074(1), c = 16·798(3) Å, U = 2871·3 Å^3, Z = 8, D_c = 2·26 g cm^{-3}, μ = 110·2 cm^{-1}, 803 independent reflections within 2θ = 56°. The structure was solved by Patterson and Fourier methods, and refined to R = 0·037. The crystals are isomorphous with those of dipiperidinotetraselane.

$Se_3(NC_4H_8O)_2$: rhombs or elongated plates, pale green, m.p. 104—105 °C (decomp.); M = 409·1, orthorhombic, space group *Pbcn* (No. 60), a = 5·445(1), b = 9·473(2), c = 25·408(2) Å, U = 1310·4 Å^3, Z = 4, D_c = 2·07 g cm^{-3}, μ = 90·4 cm^{-1}, 899 independent reflections within 2θ = 60°. The structure was solved by direct and Fourier methods, and refined to R = 0·035.

$Se_2(NC_4H_8O)_2$: prisms, colourless, larger crystals with a green tinge, m.p. 129—130 °C (decomp.); M = 330·1, monoclinic, space group $P2_1/c$ (No. 14), a = 8·871(1), b = 5·716(1), c = 23·820(3) Å, β = 98·59(1)°, U = 1194·3 Å^3, Z = 4, D_c = 1·84 g cm^{-3}, μ = 66·4 cm^{-1}, 2019 inde-

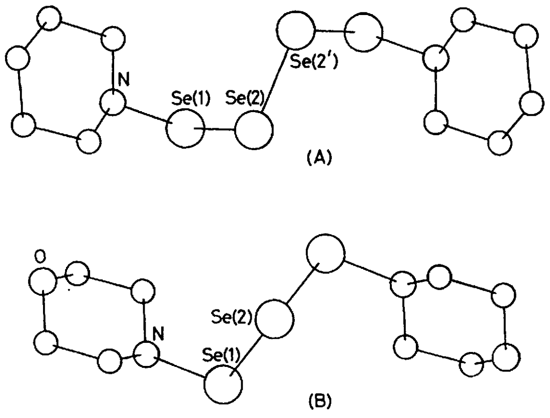

Figure. (A) Dipiperidinotetraselane and (B) dimorpholinotriselane as seen along the two-fold axes.

Table. Dimensions of the N–Se–Se–Se–Se–N, N–Se–Se–Se–N, and N–Se–Se–N chains

	Bond length[a]/Å			Bond angle/° at		Dihedral angle[a,b]/° at	
Compound	N–Se(1)	Se(1)–Se(2)	Se(2)–Se(2′)	Se(1)	Se(2)	Se(1)–Se(2)	Se(2)–Se(2′)
$Se_4(NC_5H_{10})_2$	1·832(6)	2·328(2)	2·346(2)	107·2(2)	104·1(1)	88·6	76·3
$Se_4(NC_4H_8O)_2$	1·836(6)	2·336(2)	2·356(2)	106·8(2)	102·1(1)	90·2	75·7
$Se_3(NC_4H_8O)_2$	1·841(5)	2·352(1)	—	105·2(2)	101·7(1)	97·1	—
$Se_2(NC_4H_8O)_2$	1·845(4)[c]	2·346(1)	—	109·0(1)	109·2(1)	94·6	—

[a] Se(2)–Se(2′) across molecular two-fold axis. [b] Zero for planar *cis*. [c] Se(2)–N = 1·851(4) Å.

pendent reflections within $2\theta = 56°$. The structure was solved by direct and Fourier methods, and refined to $R = 0{\cdot}035$.†

In the tetraselane compounds and in dimorpholinotriselane the molecules lie across crystallographic two-fold axes. The N–Se–Se–Se–Se–N and N–Se–Se–Se–N chains occur in the extended-helix rotational–isomeric forms (Figure), while the six-membered rings of the organic groups occur in the chair form, with N–Se equatorial. The Se–Se bond lengths along the tetraselenium chains (Table) alternate slightly but significantly. The average length of the nine Se–Se bonds in the four compounds, 2·342 Å, compares with the overall average of 2·335 Å in different forms of cyclo-octaselenium.[7] In dimorpholinotriselane, a close intermolecular contact, 3·404(2) Å, occurs between Se(1) atoms across the two-fold axis, in a direction which makes an angle of 152·4° with the Se(1)–N bond and an angle of 98·5° with the Se(1)–Se(2) bond.

The crystal structures of compounds containing chains of three selenium atoms have been reported earlier.[8] The present ones, as far as we are aware, are the first of compounds containing tetraselenium chains.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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