Preparation and Solid State Characterization of 1,2,3,5-Diselenadiazolyl $[HCN_2Se_2]^{\cdot}$

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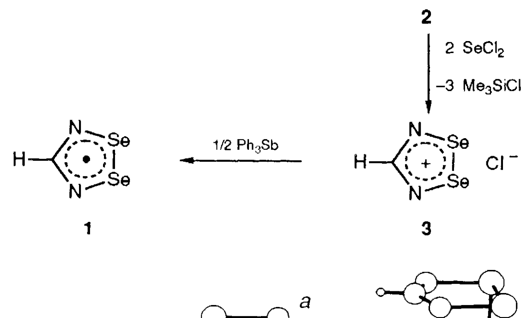
The reaction of *N,N,N'*-tris(trimethylsilyl)formamidine with $SeCl_2$ affords 1,2,3,5-diselenadiazolium chloride, which can be reduced with triphenylantimony to the corresponding diselenadiazolyl radical $[HCN_2Se_2]^{\cdot}$; the solid state structure and conductivity of the dimer $[HCN_2Se_2]_2$ are reported.

Interest in the design of molecular conductors based on neutral π-radicals has prompted the study of heterocyclic thiazyl and selenazyl radicals, in particular derivatives of 1,2,3,5-dithia- and diselena-diazolyl.[1] Several systems with different substituents in the 4-position have been characterized in the solid state.[2,3] Structure–conductivity correlations based on several selenium derivatives[4–6] indicate that the size of the 4-substituent plays an important role in determining the number and magnitude of close intermolecular interactions, and hence band dispersion.[7] In the belief that smaller organic substituents should lead to more densely-packed structures with narrower band gaps, we have prepared the prototypal diselenadiazolyl heterocycle **1**, in which the organic group has been removed entirely. The solid state characterization of the dimer is also described.



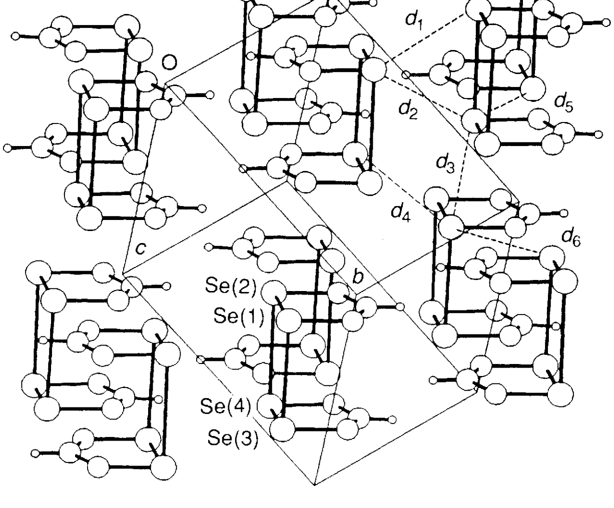


Fig. 1 General view of the crystal structure of $[HCN_2Se_2]_2$, showing head-over-tail stacking of dimers. Intradimer distances (Å) are Se(1)–Se(2) 2.329(4); Se(3)–Se(4) 2.322(4); Se(1)–Se(3) 3.215(3); Se(2)–Se(4), 3.345(3); interdimer contacts (Å) are d_1, Se(4)···Se(2′) 3.382(4); d_2, Se(4)···Se(4′), 3.376(5); d_3, Se(1)···Se(4′), 4.049(4); d_4, Se(1)···Se(1′), 3.445(5); d_5, Se(2)···Se(4′) 3.724(4); d_6, Se(1)···Se(3′), 3.774(5).

Our primary synthetic route to both 1,2,3,5-dithia- and diselena-diazolium cations has involved the condensation of persilylated amidines $RCN(SiMe_3)_2NSiMe_3$ with ECl_2 (E = S, Se). However, the method of preparation of the amidines, the addition of $LiN(SiMe)_2$ to a nitrile RCN,[8] appears to be limited to aryl nitriles. We have now discovered that the parent compound *N,N,N'*-tris(trimethylsilyl)formamidine **2** can be conveniently generated by the reaction of $LiN(SiMe_3)_2 \cdot Et_2O$ (54.1 g, 224 mmol) with 1,3,5-triazine (6.2 g, 76 mmol) in 200 ml toluene, followed by treatment of the intermediate lithiated amidine with Me_3SiCl (25.7 g, 237 mmol); **2** distils at 35 °C/10^{-2} Torr (1 Torr = 133.3 Pa; yield, 41.5 g, 66%); ^1H NMR, δ ($CDCl_3$) 7.96 (s, 1 H, HC), 0.16 (s, 27 H, Me_3Si). Addition of **2** (6.38 g, 24 mmol) to selenium dichloride (3.60 g, 24 mmol, prepared *in situ* from Se and $SeCl_4$) in acetonitrile (140 ml) affords the diselenadiazolium cation **3** (E = Se) as a reddish-brown powder in virtually quantitative yield. Reduction of this crude salt (1.27 g, 5.4 mmol) with triphenylantimony (0.96 g, 2.7 mmol) in acetonitrile (20 ml) yields 1,2,3,5-diselenadiazolyl **1**, which can be purified by sublimation at 50 °C/10^{-3} Torr as lustrous grey–black needles (0.56 g, 52%); decomp. > 100 °C; MS (70 eV) *m/z* 201 (M^+, 40%), 174 (Se_2N^+, 95%), 160 (Se_2^+, 100%), 107 ($HCNSe^+$, 8%), 94 (SeN^+, 20%), 80 (Se^+, 50%). The ESR signal (in CH_2Cl_2, 295K) of **1** consists of a featureless singlet, with $g = 2.041$.

The crystal structure of the dimer of **1** has been determined by X-ray diffraction.† The structure consists of antiparallel arrays of cofacial dimers $[HCN_2Se_2]_2$; Fig. 1 provides a general view of the structure, defines the interdimer contacts d_1–d_6, and illustrates the head-over-tail packing of dimers. All intramolecular bond lengths and angles are nominal, but the two interannular contacts Se(1)···Se(3) [3.215(3) Å] and Se(2)···Se(4) [3.345(3) Å] are notably different (*cf.* $[PhCN_2Se_2]_2$[3]). The interdimer Se···Se contacts d_5 and d_6 are well within the van der Waals separation,[9] and generate a strong network of lateral interactions. These lateral contacts help lace together interpenetrating spiral-like columns of dimers, one of which is shown in Fig. 2. Within these columns, which run parallel to *z*, there are many close Se···Se contacts. The interactions d_1, d_2 and d_4, which connect dimer units that approach one another in a side-slipped head-on manner, are all exceptionally short. The final contact d_3 runs almost parallel to *z* and connects (somewhat loosely) rings in a corner-to-corner fashion.

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† *Crystal data* for **1**: Se_2N_2CH, $M = 199.0$, triclinic, $P\bar{1}$, $a = 6.279(4)$, $b = 7.961(6)$, $c = 8.012(5)$ Å, $\alpha = 69.94(6)$, $\beta = 88.98(5)$, $\gamma = 84.03(6)°$, $V = 374.1(4)$ Å^3, $Z = 4$, $D_c = 3.53$ g cm^{-3}, $\mu = 19.4$ mm^{-1}. Data were collected with an Enraf-Nonius CAD-4 automated diffractometer, with graphite-monochromated Mo-Kα-radiation ($\lambda = 0.71073$ Å) using θ–2θ scans to a $2\theta_{max} = 50°$. The structure was solved by direct methods (SHELX) and refined by full-matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. 81 Parameters were refined using 700 unique observed reflections [$I > 2.5\,\sigma(I)$] to give $R = 0.048$ and $R_w = 0.050$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.

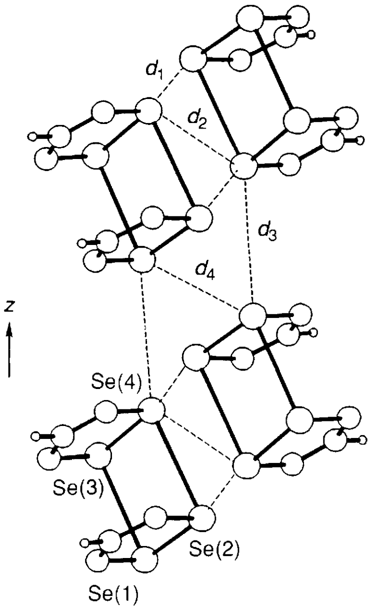

Fig. 2 Columns of dimers running parallel to z

In the solid state the dimer $[HCN_2Se_2]_2$ is diamagnetic, with a residual spin density, estimated by ESR, of 0.01%. The material exhibits a single crystal conductivity of 7×10^{-6} S cm^{-1}, a value which is at least three orders of magnitude higher than that seen in other monofunctional selenium-based radical dimers.[4] Collectively the interdimer Se···Se contacts, indicated above, generate a structure in which dispersion of the valence and conduction bands is more pronounced than in organo-substituted materials.

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