Bis-1,2,3-thiaselenazolyl radicals and their σ-bonded dimers

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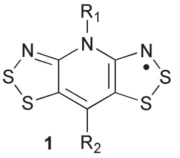
Resonance stabilized *bis*-1,2,3-thiaselenazolyl radicals associate in the solid state to afford Se–Se σ-bonded dimers.

The development of single component conductors based on neutral π-radicals[1] holds both appeal and challenge.[2] Most molecular radicals dimerize in the solid state, and even when association can be suppressed the resulting low bandwidth W, coupled with a high on-site Coulomb repulsion U, leads to a Mott insulating state. Improved conductivity requires radicals with larger W/U ratio and to this end we have pursued the resonance stabilized *bis*-1,2,3-dithiazolyl radicals **1**.[3]



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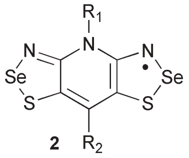

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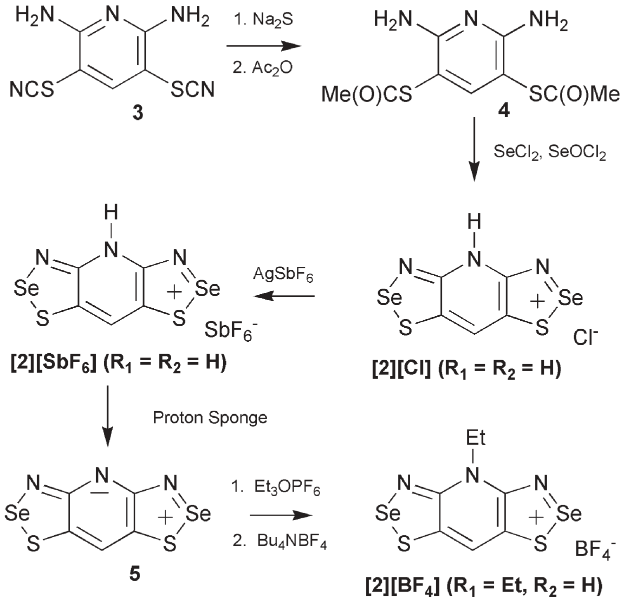
While computed gas phase disproportionation enthalpies ΔH_{disp} and solution cell potentials E_{cell} for these systems indicate a lower value of U, the bulk conductivity remains activated, with values of σ_{RT} near 10^{-5} S cm^{-1}, indicating that the electronic band width W is still insufficient to offset U.[3] In order to increase intermolecular interactions and hence conductivity we have sought to replace sulfur by its heavier congener selenium. Herein we report the preparation and solid state characterization of the selenium containing variant **2** (R_1 = Et, R_2 = H).

Simple 1,2,3-thiaselenazoles can be prepared by the condensation of aromatic *o*-aminothiols with $SeCl_4$,[4] but the reaction of 2,6-diaminopyridine-3,5-dithiol failed to afford the desired skeleton. However, use of the *bis*(thioacetate) **4**, prepared from the known *bis*(thiocyanate) **3**,[3a] was more successful (Scheme 1). Accordingly, addition of **4** to a solution of one eq. $SeOCl_2$ and one eq. $SeCl_2$ in MeCN in the presence of NEt_3 produced a black precipitate of [**2**][Cl] (R_1 = R_2 = H). Purification[3a] and metathesis of the latter with $AgSbF_6$ in MeCN generated a deep blue solution which, upon solvent removal, afforded golden crystals of [**2**][SbF_6] (R_1 = R_2 = H), the crystal structure of which (Fig. 1) consists of H-bonded cation/anion pairs with short intermolecular Se–N′ contacts.†

Deprotonation of [**2**][SbF_6] (R_1 = R_2 = H) with Proton Sponge in MeCN liberated the zwitterion **5** as an insoluble black solid which, upon alkylation with Et_3OPF_6 in the presence of Proton Sponge followed by anion metathesis afforded [**2**][BF_4] (R_1 = Et, R_2 = H) as deep red crystals (from MeCN). Cyclic voltammetry on MeCN solutions of the *N*-ethyl salt (Pt electrodes, *n*-Bu_4NPF_6 supporting electrolyte) revealed a reversible reduction wave ($\mathbf{2}^{+/0}$) with $E_{1/2}$ = −0.108 V *vs.* SCE.

Bulk reduction of [**2**][BF_4] (R_1 = Et, R_2 = H) was accomplished in high yield using octamethylferrocene (OMFc); bronze needles were grown by slow mixing of solutions of the salt and OMFc in MeCN.‡ Solutions of the radical in CH_2Cl_2 display an EPR signal (g = 2.0099) whose fine structure (Fig. 2) is consistent with equivalent spin density on the two terminal nitrogens (a_N = 0.30 mT), with additional smaller coupling to the unique CH



Scheme 1

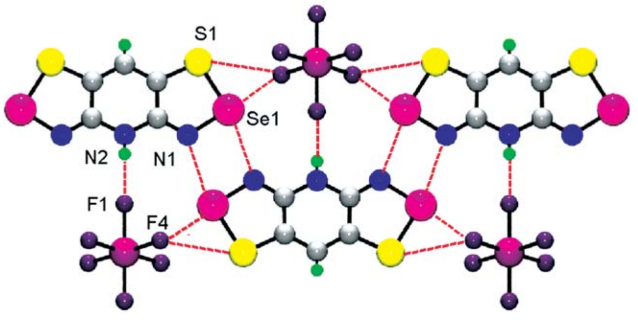


Fig. 1 Packing of [**2**][SbF_6] (R_1 = R_2 = H). Distances: S1–Se1, 2.205(2); N1–Se1, 1.793(4); NH–F, 2.977(7), N1–Se1′, 2.812(6) Å.

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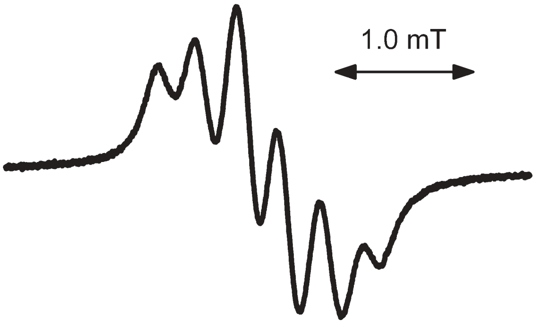


Fig. 2 EPR spectrum of **2** (R_1 =Et, R_2 = H) in CH_2Cl_2.

(a_H = 0.30 mT) and the pyridine nitrogen (a_N = 0.03 mT), as in **1** (R_1 = Et, R_2 = H).[3b]

The crystal structure of **2** (R_1 = Et, R_2 = H)† consists of pairs of highly distorted radicals linked across inversion centers to produce the approximately coplanar arrangement illustrated in Fig. 3. Within each radical the Se1–S1 bond is slightly shorter than in the cation (Fig. 1), but the Se2–S2 distance is severely elongated. At the same time the lateral intermolecular Se2–Se2′ contact is much less than the van der Waals separation,[5] indeed it approaches the value expected for a covalent bond. These features, taken with the mismatch in the C1–C5 and C4–C5 bonds, and in the C1–S1 and C4–S2 bonds, and the relative similarity of the N1–C2 and C3–N3 distances, militate in favor of a closed shell Se–Se σ-bonded framework with an exocyclic thione unit, *i.e.*, resonance structure [**2**]$_2$ (Scheme 2).

This unusual dimerization mode, particularly the otherwise exposed thione unit, is stabilized in the solid state by the head-to-tail intermolecular interactions S2–Se1′ and S2–S1′ (Fig. 4). The dimers are then aligned into approximately coplanar ribbons linked by Se1–N1′ contacts to produce slipped π-stacks in the *xy* plane. Alternate arrays of π-stacks along *z* are inclined in opposite senses so as to generate the cross-braced grid illustrated in Fig. 5.

A plot of the magnetic susceptibility χ of **2** (R_1 = Et, R_2 = H) as a function of temperature is shown in Fig. 6. The low value of χ at ambient temperatures may be interpreted in terms of the closed shell dimer formulation described above. The residual paramagnetism observed for **2** can be ascribed to defects in the lattice; the value of χT at 300 K suggests a defect concentration of about 5%. A Curie–Weiss fit to the data above 250 K provides values of $C = 0.033$ emu mol^{-1} K^{-1} and $\theta = -197$ K, *i.e.*, the defect spins are strongly antiferromagnetically coupled, presumably the result of pairwise interactions between unassociated radicals. While spin quenching in the solid state is the case for all known selenazyl radicals, dimerization has hitherto been of the cofacial π–π type.[6] The association of the π-radical **2** to afford a σ-bonded dimer [**2**]$_2$ is thus, to our knowledge, without precedent. B3LYP/6-31G** calculations on a model dimer ($R_1 = R_2$ = H) suggest a bond enthalpy of 18.9 kcal mol^{-1}. However, and inasmuch as the process requires a change of electronic configuration, there may be a substantial barrier to both association and dissociation.

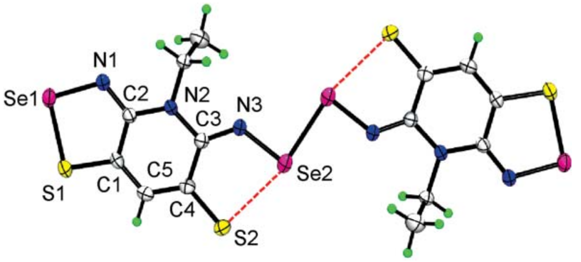
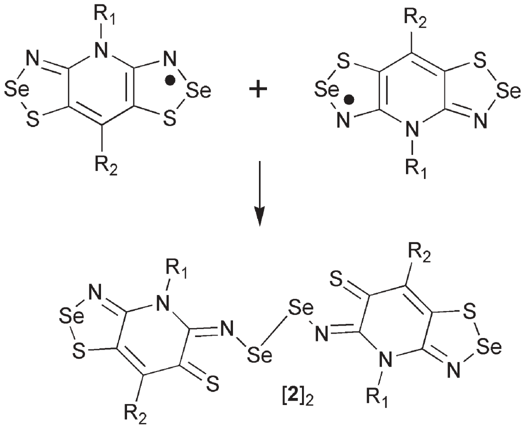


Fig. 3 ORTEP drawing of a dimer of **2** (R_1 = Et, R_2 = H). Distances: Se1–S1, 2.145(9); N1–Se1, 1.818(2); S2–Se2, 2.7847(9); Se2–Se2′, 2.4628(8); N3–Se2, 1.811(2); C1–C5, 1.359(4); C4–C5, 1.402(4); C1–S1, 1.719(3); C4–S2, 1.679(3); N1–C2, 1.303(4), C3–N3, 1.288(3) Å.



Scheme 2

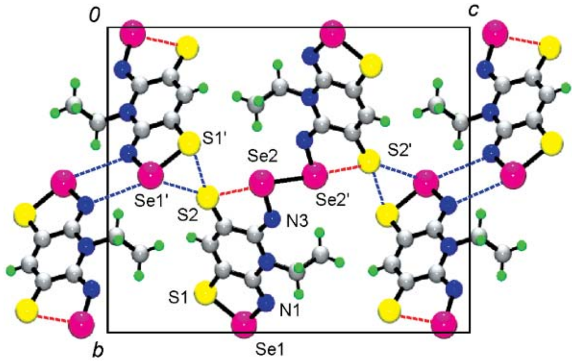


Fig. 4 Unit cell of **2** (R_1 = Et, R_2 = H). Intermolecular contacts S2–S1′, 3.245(1); S2–Se1′, 3.3348(9); Se1–N1′, 3.238(2) Å.

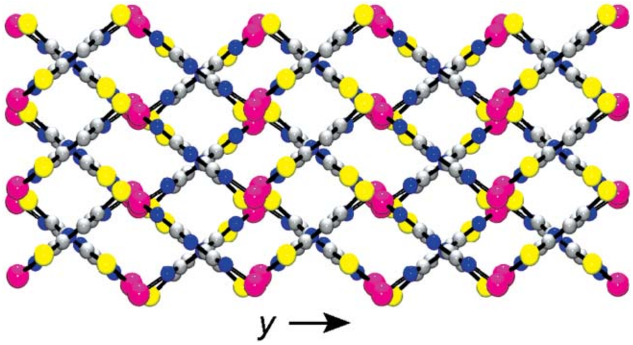


Fig. 5 Cross-braced π-stacking in **2** (R_1 = Et, R_2 = H); R-groups are omitted for clarity.

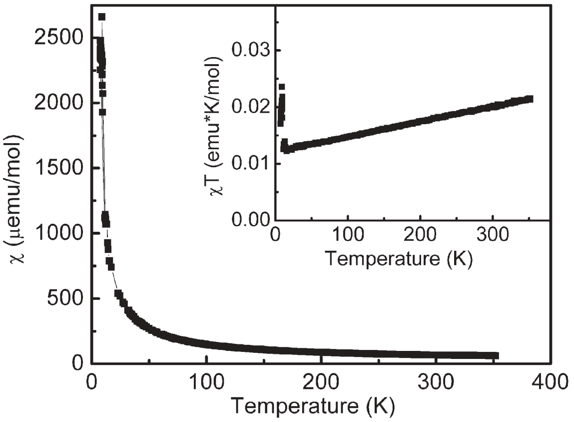


Fig. 6 Variable temperature magnetic susceptibility (χ) of **2** (R_1 = Et, R_2 = H). A plot of χT *vs.* T is inset.

Despite the fact that the bulk material is essentially diamagnetic, pressed pellet conductivity measurements on bulk **2** (R_1 = Et, R_2 = H) reveal a room temperature conductivity σ_{RT} of 10^{-6} S cm^{-1}. This relatively high value for a closed shell material can be attributed to the rich network of intermolecular interactions seen in the crystal structure, and the consequent development of wide valence and conduction bands so as to produce a small band gap semiconductor. This observation augurs well for the pursuit of these selenium containing heterocycles as building blocks for single component molecular conductors.

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Notes and references

† Crystal data at 295(2)K for [**2**][SbF_6] (R_1 = R_2 = H): $C_5H_2F_6N_3S_2SbSe_2$, *M* = 561.89, space group *Pnma*, *a* = 10.778(2), *b* = 14.142(3), *c* = 8.4526(2) Å, *V* = 1288.4(4) $Å^3$, *Z* = 4, D_{calcd} = 2.897 g cm^{-3}, μ = 8.175 mm^{-1}; 100 parameters were refined using 1666 unique reflections to give *R* = 0.0380 and R_w = 0.0729. Crystal data at 295(2)K for **2** (R_1 = Et, R_2 = H): C_7H_6 $N_3S_2Se_2$, *M* = 354.19, space group $P2_1/c$, *a* = 4.8546(8), *b* = 12.692(2), *c* = 16.472(3) Å, β = 97.624(3)°, *V* = 1005.9(3) $Å^3$, *Z* = 4, D_{calcd} = 2.339 g cm^{-3}, μ = 7.725 mm^{-1}; 128 parameters were refined using 2379 unique reflections to give *R* = 0.0280 and R_w = 0.0697. CCDC 254578 and 254579. See http://www.rsc.org/suppdata/cc/b4/b416352d/ for crystallographic data in .cif or other electronic format.

‡ Satisfactory chemical analyses were obtained for **2**, [**2**][BF_4] (R_1 = Et, R_2 = H) and **4**). The IUPAC name for **2** is 4-ethyl-4*H*-*bis*[1,2,3]thiaselenazolo[4,5-*b*:4′,5′-*e*]pyridin-2-yl.

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