Spin-canting in heavy atom heterocyclic radicals

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A pair of isostructural *bis*-selenathiazolyl and *bis*-diselenazolyl radical conductors display weak (spin-canted) ferromagnetism with T_c values of 18 K and 27 K respectively.

To date the development of molecular materials displaying both conductive and magnetic properties has focused on the use of charge transfer salts, that is, two component systems.[1] The incorporation of multifunctionality into single component systems is more of a challenge. Within this context the use of neutral radicals as the molecular building blocks is appealing, as the unpaired electrons hosted by the radicals can, in principle, serve as both spin and charge carriers. Recent research[2–4] on radical-based materials has, however, focused on the pursuit of systems displaying either magnetic activity or conductivity, but not both. In the separate arenas considerable progress has been made using heterocyclic thiazyl radicals,[2] as the lattice-wide networks of intermolecular S–S and S–N interactions found in their solid state structures provide direct or metal-mediated[5] pathways for magnetic exchange and/or charge transport. A number of thiazyl radicals exhibiting magnetic[6,7] or conductive[8] properties have been described.

We have reported the preparation and properties of the family of radicals (Chart 1) generated from the resonance stabilized *bis*-dithiazolyl **1** (R_1 = Me, R_2 = H) by replacement of sulfur by its heavier and more spatially extensive congener selenium,[9] and established that selenium incorporation affords a dramatic improvement in electronic bandwidth and hence conductivity. As a continuation of the exploration of structure–property relationships for radicals based on the frameworks **1–4** we have prepared the *bis*-selenathiazolyl **3** and the *bis*-diselenazolyl **4** (R_1 = Et, R_2 = H). These two selenium-based radicals are isostructural with each other and with the corresponding *bis*-dithiazolyl **1**. As seen earlier,[9,10] the presence of selenium has the desired effect of decreasing the activation energy for conduction. In addition, it provides a mechanism, *via* spin–orbit coupling, for the generation of a weak (canted) ferromagnetic state.

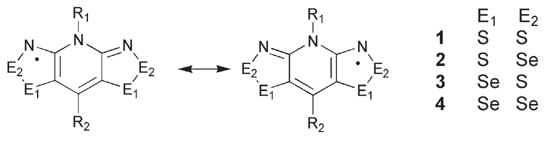
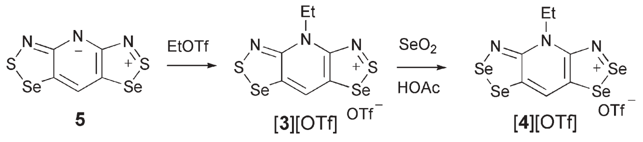


Chart 1



Scheme 1

The synthesis of **3** and **4** (Scheme 1) involves alkylation of previously prepared[9] zwitterion **5** with ethyl triflate in $C_2H_4Cl_2$, to afford deep red crystals (from MeCN) of the triflate salt [**3**][OTf]. Treatment of the latter with selenium dioxide in acetic acid at reflux for 90 min produces a dark green solution which, upon cooling, yields dark purple crystals of [**4**][OTf]. Black needles of the two radicals **3** and **4** can then be prepared by reduction of the triflate salts [**3**][OTf] and [**4**][OTf] with octamethylferrocene or *tetrakis*-dimethylaminoethylene.†

The crystal structures of **3** and **4** (R_1 = Et, R_2 = H) have been determined by single crystal X-ray diffraction,‡ which confirms that the two radicals, space group $P2_1/c$, are isostructural with each other and the corresponding all-sulfur radical **1**.[11] A drawing of the unit cell of **4** is shown in Fig. 1, and Table 1 provides the unit cell parameters of the three radicals and a summary of the pertinent intermolecular E–E′ (E = S, Se) contacts.

In contrast to **2** (R_1 = Et, R_2 = H), which associates in the solid state as laterally Se–Se σ-bonded dimers,[12] compounds **1**, **3** and **4** crystallize as discrete radicals packed into slipped π-stacks (along *x*) which are aligned into herringbone arrays (Fig. 2) running along the *y*-direction. Within these arrays there are close intercolumnar E–E′ (E = S, Se) contacts (d1–d3) that knit together adjacent π-stacks. There are also close interactions (d4, d5) that lace radicals together in the *z*-direction.

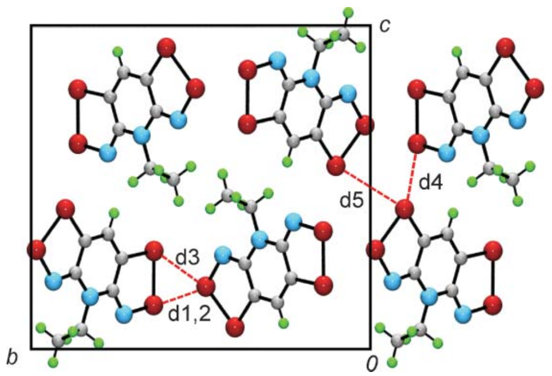


Fig. 1 Unit cell drawing of **4** (R_1 = Et, R_2 = H). Intermolecular contacts d1–d5 are defined in Table 1.

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Table 1 Crystal data,[a] intermolecular contacts, and physical properties

Radical	**1**[b]	**3**	**4**
a	4.9128(18)	4.9799(2)	4.9965(4)
b	14.764(5)	14.9351(7)	15.1932(11)
c	13.671(5)	13.8244(6)	13.8630(11)
β	98.129(6)	99.9350(10)	100.1480(10)
d1	3.353(1)	3.420(1)	3.409(1)
d2	3.593(1)	3.660(1)	3.640(1)
d3	3.623(1)	3.657(1)	3.528(1)
d4	3.563(1)	3.539(1)	3.466(1)
d5	3.654(1)	3.583(1)	3.663(1)
σ(295 K), S cm^{-1}	6×10^{-6}	7×10^{-6}	5×10^{-4}
E_{act}, eV	0.41	0.22	0.19
C, emu K mol^{-1}	0.343	0.330	0.334
θ, K	−4.5	6.3	−8.0
T_c, K	—	18	27
M_{rem}, Nβ	—	2.7×10^{-4}	2.6×10^{-4}
H_{cr}, Oe	—	130	390
ϕ, deg	—	0.024	0.024
g	2.0082	2.0188	2.0275

[a] Distances in Å and angles in degrees. [b] Data from reference 11.

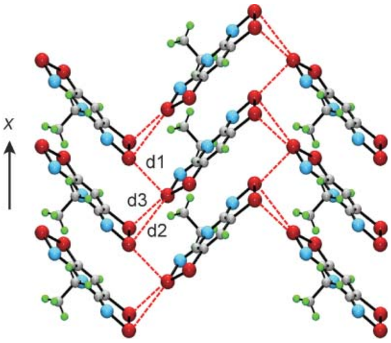

Fig. 2 Herringbone packing of slipped π-stacks of **4** (R_1 = Et, R_2 = H), showing close interstack Se–Se contacts d1-d3.

The results of four-probe, variable temperature conductivity measurements on **3** and **4** (R_1 = Et, R_2 = H) are illustrated in Fig. 3; derived parameters are summarized in Table 1. While the conductivity value σ(295 K) for **3** is comparable to that previously observed for **1**,[11] that of **4** is markedly higher. The conductivity is activated for all three compounds, indicative of a Mott insulating ground state. However, as in the corresponding series with R_1 = Me, R_2 = H, there is a significant decrease in the thermal activation energy (E_{act}) occasioned by the incorporation of selenium.

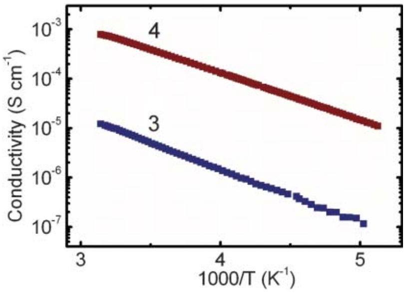

Fig. 3 Log plots of conductivity of **3** and **4** (R_1 = Et, R_2 = H) as a function of inverse temperature.

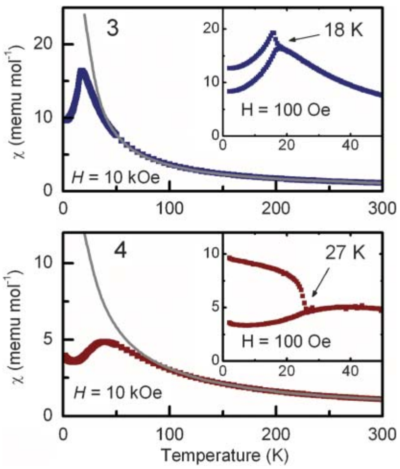

Fig. 4 ZFC-FC plots of χ *vs.* T for **3** and **4** (R_1 = Et, R_2 = H) at 10 kOe. Inserts show expansion of 0–50 K region at 100 Oe. Curie–Weiss fits to the high T data at 10 kOe are also shown.

We have examined the dependence of the magnetic susceptibility (χ) of **3** and **4** (R_1 = Et, R_2 = H) on temperature (T) and applied field (H). ZFC-FC plots of χ, measured at a relatively high field (H = 10 kOe) over the temperature range 2–300 K are essentially coincident (Fig. 4) for both compounds. At elevated temperatures ($T > 100$ K) the $\chi(T)$ dependence suggests essentially paramagnetic S = ½ behavior. Curie–Weiss fits to the data, corrected for diamagnetic contributions,[13] afford the C and θ values listed in Table 1. Below 100 K the susceptibility of the two compounds drops well below the Curie–Weiss fits, indicative of a phase transition to an antiferromagnetic state. Upon lowering the field to 1 kOe a discontinuity appears in the FC and ZFC plots of **3** and **4**, creating a point of divergence between the two curves which we interpret as heralding the onset of weak (spin-canted) ferromagnetism. The effect is amplified at H = 100 Oe, as shown in Fig. 4, which illustrates the well-defined blocking temperatures T_c of 18 K (**3**) and 27 K (**4**). In light of these results we re-examined the magnetic susceptibility of **1** (R_1 = Et, R_2 = H), which was previously measured at 5 kOe.[11] Although its ZFC-FC behavior at 100 Oe shows a slight inflexion in both curves below 10 K, there is no indication of bifurcation.

Further evidence of ferromagnetism in **3** and **4** is provided by measurements of the field-independent or spontaneous magnetization M_{sp} (Fig. 5). In both cases M_{sp} is strongly temperature dependent, decaying with increase in temperature and reaching a value of zero at T = 18 K and 27 K for **3** and **4** respectively, in

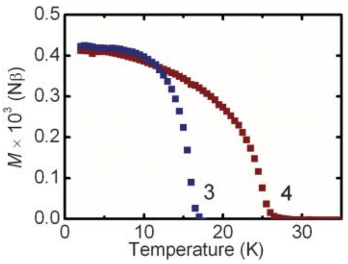

Fig. 5 Spontaneous magnetization of **3** and **4** (R_1 = Et, R_2 = H) as a function of temperature.

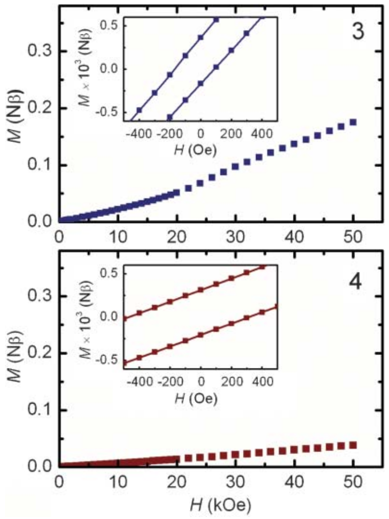

Fig. 6 Magnetization of **3** and **4** (R_1 = Et, R_2 = H) at 5 K as a function of field, with low field expansions of each, showing hysteresis.

accord with the blocking temperatures T_c noted in the ZFC-FC experiments. The values of M_{sp} extrapolated to $T = 0$ K are very much lower than that expected for a pure ferromagnet. Estimates of the canting angles ϕ, where $\phi = \sin^{-1}(M_{sp}/M_{sat})$, and M_{sat} is arbitrarily taken as the saturation value for a $S = ½$ ferromagnet, are provided in Table 1. Compound **1** shows no measurable spontaneous magnetization.

Magnetization measurements on **3** and **4** at $T = 5$ K as a function of field ($H = 0$ to 50 kOe) reveal a weak, nearly linear response; the shallower slope (dM/dH) observed for **4** indicates stronger antiferromagnetic exchange with increasing selenium content (Fig. 6). The slight break in the slope of the two M *vs.* H plots near $H = 20$ kOe may arise from a transition to a spin-flop state.[13] For both compounds the low-field $M(H)$ dependence is weakly hysteretic (Fig. 6). Remanent magnetizations M_{rem} and coercive fields H_{cr} are listed in Table 1.

While spontaneous magnetization arising from spin-canting has been observed before in thiazyl radicals,[6] the effect has been restricted to materials in which canting can be ascribed to an antisymmetric magnetic exchange arising from a polar space group. The centric space group $P2_1/c$ found for **3** and **4** militates against such an interpretation. The data are, however, consistent with the Dzyaloshinsky–Moriya mechanism,[13,14] within which the canting stems from spin–orbit effects, and a consequent departure of the g-value from the free-electron value (2.0023). Examples of materials displaying this effect are generally restricted to transition metal complexes.[15] In the all-sulfur radical **1** ($g = 2.0082$) the spin–orbit contribution is too small to produce an observable effect. However, the incorporation of selenium in **3** and **4**, and the concomitant increase in g-value (by EPR) to 2.0188 and 2.0275 respectively, affords sufficient magnetic anisotropy to allow spin-canting. Given their different g-values the similarity in the canting angles ϕ for **3** and **4** may seem surprising. However, the idea of an increase in ϕ between **3** and **4** assumes that the magnetic effect of selenium incorporation into the 1- and 2-positions of the heterocycles is the same. There is no reason that this should be so, and the structural data suggest that the close (and presumably magnetically important) interactions (d1–d5) are those involving the 1-positions. These are the positions occupied by selenium in **3**. The additional selenium atoms in **4** fill the 2-positions, and their effect on the canting angle may be small.

In summary, our results demonstrate that the isomorphous replacement of sulfur in thiazyl radicals by its heavier congener selenium increases intermolecular interactions, enhancing not only solid state charge transport but also magnetic properties. While the dominant low temperature exchange interaction in the present systems is antiferromagnetic, the spin–orbit contribution of selenium to the g-value allows for weak ferromagnetism arising from spin-canting. These conclusions augur well for the pursuit and development of magnetic, electronic and spintronic applications of these and other heavy atom heterocyclic radicals.

Notes and references

† Satisfactory chemical analyses were obtained for compounds **3**, **4**, [**3**][OTf] and [**4**][OTf] (R_1 = Et, R_2 = H).

‡ Crystal data at 295(2) K for **3** (R_1 = Et, R_2 = H): $C_7H_6N_3S_2Se_2$, M = 354.19, space group $P2_1/c$, a = 4.9799(2), b = 14.9351(7), c = 13.8244(6) Å, β = 99.9350(10)°, V = 1012.78(8) Å^3, Z = 4, D_{calcd} = 2.323 g cm^{-3}, μ = 7.673 mm^{-1}; 127 parameters were refined using 3107 unique reflections to give R = 0.0318 and R_w = 0.0903. Crystal data at 295(2) K for **4** (R_1 = Et, R_2 = H): $C_7H_6N_3Se_4$, M = 447.99, space group $P2_1/c$, a = 4.9965(4), b = 15.1932(11), c = 13.8630(11) Å, β = 100.1480(10)°, V = 1035.92(14) Å^3, Z = 4, D_{calcd} = 2.872 g cm^{-3}, μ = 14.126 mm^{-1}; 127 parameters were refined using 2116 unique reflections to give R = 0.0284 and R_w = 0.0710. CCDC 650268–650269. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708756j

1 E. J. Coronado and P. Day, *Chem. Rev.*, 2004, **104**, 5419.
2 J. M. Rawson, A. Alberola and A. Whalley, *J. Mater. Chem.*, 2006, **16**, 2560.
3 R. G. Hicks, *Org. Biomol. Chem.*, 2007, **5**, 1321.
4 F. Breher, *Coord. Chem. Rev.*, 2007, **251**, 1007.
5 K. E. Preuss, *Dalton Trans.*, 2007, 2357.
6 A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tanner, W. Clegg, M. R. Elsegood and F. Palacio, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2533; A. Alberola, R. J. Less, C. M. Pask, J. M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi, D. M. Murphy and R. D. Farley, *Angew. Chem., Int. Ed.*, 2003, **42**, 4782; W. Fujita and K. Awaga, *Chem. Phys. Lett.*, 2004, **388**, 186.
7 W. Fujita and K. Awaga, *Science*, 1999, **286**, 281; G. D. McManus, J. M. Rawson, N. Feeder, E. J. L. McInnes, J. J. Novoa, R. Burriel, F. Palacio and P. Oliete, *J. Mater. Chem.*, 2001, **11**, 1992; J. L. Brusso, O. P. Clements, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, *J. Am. Chem. Soc.*, 2004, **126**, 8256.
8 A. W. Cordes, R. C. Haddon and R. T. Oakley, *Adv. Mater.*, 1994, **6**, 798; A. A. Leitch, R. W. Reed, C. M. Robertson, J. F. Britten, X. Yu, R. A. Secco and R. T. Oakley, *J. Am. Chem. Soc.*, 2007, **129**, 7903.
9 J. L. Brusso, K. Cvrkalj, A. A. Leitch, R. T. Oakley, R. W. Reed and C. M. Robertson, *J. Am. Chem. Soc.*, 2006, **128**, 15080.
10 L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, R. T. Oakley, R. W. Reed, J. F. Richardson, R. A. Secco and X. Yu, *Chem. Commun.*, 2005, 5745.
11 L. Beer, J. F. Britten, J. L. Brusso, A. W. Cordes, R. C. Haddon, M. E. Itkis, D. S. MacGregor, R. T. Oakley, R. W. Reed and C. M. Robertson, *J. Am. Chem. Soc.*, 2003, **125**, 14394.
12 L. Beer, J. L. Brusso, R. C. Haddon, M. E. Itkis, A. A. Leitch, R. T. Oakley, R. W. Reed and J. F. Richardson, *Chem. Commun.*, 2005, 1543.
13 R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, 1986.
14 I. Dzyaloshinsky, *J. Phys. Solids*, 1958, **4**, 241; T. Moriya, *Phys. Rev.*, 1960, **120**, 91.
15 S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987; Y. Doi, T. Ishida and T. Nogami, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 2455; A. Rodríguez, R. Kivekäs and E. Colacio, *Chem. Commun.*, 2005, 5228.