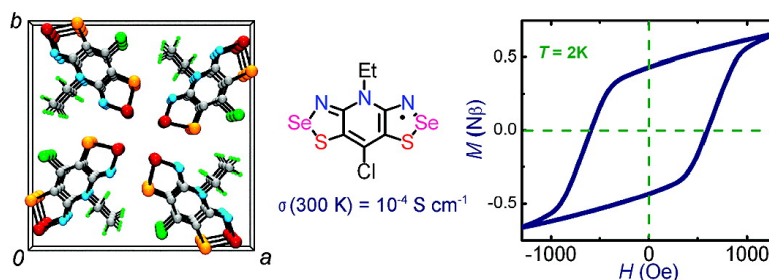Communication

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# Ferromagnetism in a Heavy Atom Heterocyclic Radical Conductor

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Molecular materials displaying both conductive and magnetic properties are typically based on the use of charge transfer salts.[1] Examples of single component molecular solids displaying multifunctional behavior are rare,[2] as the design of the necessary molecular building blocks is a challenging task. The basic electronic requirement for such molecules is the availability of at least one unpaired electron that can serve as both charge carrier and magnetic coupler. In principle, this condition is met by molecular radicals. A number of organic nitroxyls have been shown to order ferromagnetically, but their ordering temperatures (T_c) are less than 2 K.[3] Spin-canted antiferromagnetism (weak ferromagnetism) has been found for an oxoverdazyl at 5.4 K[4] and also in a heterocyclic dithiadiazolyl at 35.5 K.[5] In none of these systems, however, do the unpaired electrons serve as charge carriers, as the high molecular disproportionation energies lead to a large on-site Coulomb barrier (U) to charge migration.

Chart 1

	E_1	E_2
1	S	S
2	S	Se
3	Se	S
4	Se	Se
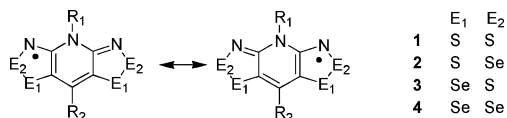
In order to lower the value of U and improve conductivity, we have explored the potential of resonance-stabilized bisdithiazolyl radicals **1** (Chart 1)[6] and their selenium-containing variants **2**, **3**, and **4**.[7] With careful choice of the R_1 and R_2 groups, these radicals crystallize in undimerized, slipped π-stack arrays. Intermolecular interactions along and between the π-stacks allow for the development of an energy band which, ideally, would be half-filled and thereby afford a metallic ground state. The bandwidth (W) of these materials is, however, insufficient to overcome U, and their conductivity remains activated, although the incorporation of the heavier heteroatom selenium has the desired effect of increasing intermolecular interactions and hence conductivity. The presence of selenium can also give rise to interesting magnetic effects. We have recently shown that **3** and **4** (with R_1 = Et, R_2 = H) behave as spin-canted antiferromagnets with T_c values of 17 and 28 K, respectively.[8] Here we report that the bisthiaselenazolyl **2** (R_1 = Et, R_2 = Cl) displays bulk ferromagnetism with a T_c of 12.3 K.

Black, air stable needles of radical **2** (R_1 = Et, R_2 = Cl) can be grown by reduction of salts of $[2]^+$ in acetonitrile solution with either octamethylferrocene or tetrakisdimethylaminoethylene. The crystal structure[9] belongs to the tetragonal space group $P\bar{4}2_1m$ (Figure 1) and is isomorphous with that of **1** (R_1 = Et, R_2 = Cl),

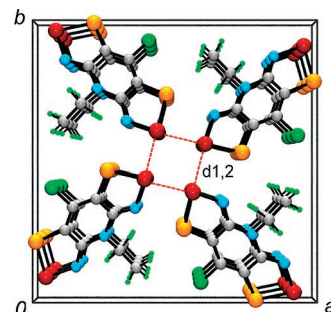[†] University of Waterloo.
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[#] McMaster University.
[§] Memorial University of Newfoundland.

Figure 1. Crystal structure of **2** (R_1 = Et, R_2 = Cl). Intermolecular Se−Se′ contacts (dashed lines) are d1 = 3.328(1) Å and d2 = 3.459(1) Å.

consisting of slipped π-stack arrays of radicals clustered about $\bar{4}$ centers and linked by weblike arrays of intermolecular Se−Se′ contacts (d1, d2). These interactions are well within the van der Waals separation for two selenium atoms and closer than the corresponding S−S′ contacts in **1** (R_1 = Et, R_2 = Cl).[6]

Variable temperature four-probe conductivity measurements on **1** and **2** (Figure 2) show that the conductivity (σ) is activated for both compounds, indicating that in neither case is the bandwidth W sufficient to overcome U and afford a metallic state. As observed elsewhere,[7] the replacement of sulfur in **1** by the more spatially extensive selenium in **2** nonetheless has the desired effect of increasing σ(300 K) from 3×10^{-6} to 1×10^{-4} S cm^{-1}. It also reduces the thermal activation energy E_{act} from 0.43 to 0.27 eV.
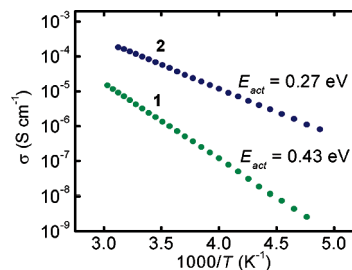

Figure 2. Electrical conductivity of **1** and **2** (R_1 = Et, R_2 = Cl) as a function of inverse temperature (data for **1** from ref 6).

Variable temperature magnetic susceptibility (χ) measurements have been performed on **1** and **2** (R_1 = Et, R_2 = Cl). Plots of the product χT (field cooled) as a function of temperature (T) at a magnetic field (H) of 100 Oe (Figure 3) confirm paramagnetic behavior for both compounds at ambient temperatures, with χT values at 300 K of 0.379 and 0.370 emu K mol^{-1} for **1** and **2**, respectively, that is, near that expected (0.375 emu K mol^{-1}) for an $S = 1/2$ system. Curie−Weiss fits to the data afford $C = 0.373$ emu K mol^{-1} and $\theta = 4$ K for **1** and $C = 0.349$ emu K mol^{-1} and
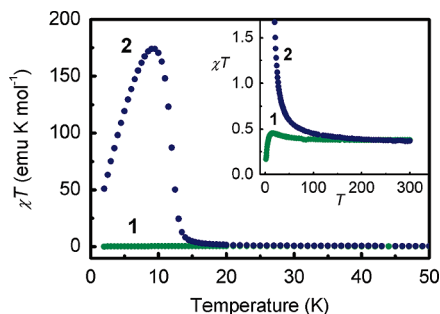
Figure 3. Plots of χT (field cooled) versus T for **1** and **2** ($R_1 = Et$, $R_2 = Cl$) at $H = 100$ Oe. Inset shows expansion of low χT region from 2 to 300 K.

$\theta = 19.3$ K for **2**. In accord with its positive (ferromagnetic) θ value, cooling **1** below 50 K leads to a slight increase in χT to 0.45 emu K mol^{-1}, followed by a decrease arising from weaker antiferromagnetic effects. The larger θ value of compound **2** leads to a more pronounced rise in the value of χT on cooling, starting near 100 K. A major surge in χT, suggestive of a transition to a ferromagnetically ordered state, then takes place just below 15 K, with χT reaching a maximum value $(\chi T)_{max} = 174$ emu K mol^{-1} at 9.0 K. The subsequent decrease in χT on further cooling can be ascribed to low-temperature magnetization saturation.

AC susceptibility measurements on **2** as a function of temperature, performed at frequencies of 1, 100, and 1000 Hz (Figure 4), provide further support for the presence of the ferromagnetic state and also allow an accurate assessment of the ordering temperature. Both the real, in-phase χ' and imaginary, out-of-phase χ'' components show well-defined maxima at $T_c = 12.3$ K. The invariance of T_c with cycling frequency confirms that the material is not a spin glass.
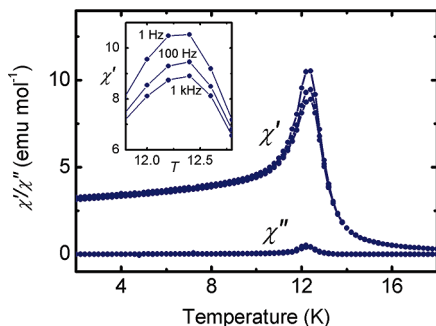

Figure 4. In-phase χ' and out-of-phase χ'' magnetic susceptibility of **2** ($R_1 = Et$, $R_2 = Cl$) as a function of temperature at 1, 100, and 1000 Hz. Inset shows expansion of χ' near T_c.

Magnetization (M) measurements on **2** show a rapid increase in M as a function of field (H), with M registering a value of 0.90 Nβ at $H = 5$ kOe (at 2 K). M continues to rise gradually thereafter, reaching 0.95 Nβ at $H = 55$ kOe. This behavior is consistent with a ferromagnetically ordered state composed of $S = 1/2$ radicals, for which the saturation magnetization would be 1 Nβ; the small discrepancy may reflect a slight spin-canting. The magnetization versus field dependence (Figure 5) shows strong hysteretic behavior. At 2 K, the remanent magnetization M_r is 0.43 Nβ and the coercive field H_c is 590 Oe. These values decrease to $M_r = 0.27$ Nβ and $H_c = 110$ Oe at 10 K.

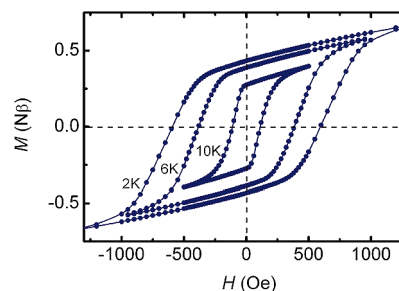**Figure 5.** Magnetization of **2** ($R_1 = Et$, $R_2 = Cl$) as a function of magnetic field at 2, 6, and 10 K.

In summary, the presence of the heavy heteroatom selenium in **2** affords a molecular, non-metal containing ferromagnet with one of the highest T_c values known[10] (the highest[10a] is in TDAE·C$_{60}$, $T_c = 16.1$ K). Perhaps more importantly, the material displays a coercive field H_c far larger than those found in conventional light atom molecular radical ferromagnets. The origin of the phenomenon is yet to be established, but the ratio $T_c/\theta = 0.64$ indicates some magnetic anisotropy,[11] a conclusion consistent with the tetragonal crystal system. The decrease in conductivity of **2** with temperature militates against measurements below T_c, but modification of the nature of the R_1/R_2 groups and/or the degree of selenium incorporation may increase both the ordering temperature and conductivity.

Supporting Information Available: Synthetic, magnetization, and crystallographic (CIF) data for **2** ($R_1 = Et$, $R_2 = Cl$). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **2** at 298(2) K: C$_7$H$_5$ClN$_3$S$_2$Se$_2$, $M = 388.63$, tetragonal, space group $P42_1m$, with $a = b = 16.0334(8)$, $c = 4.1090(4)$ Å, $V = 1056.30(13)$ Å^3, $Z = 4$, $D_{calcd} = 2.444$ g cm^{-3}, $\mu = 7.613$ mm^{-1}; 76 parameters were refined using 1150 unique reflections to give $R = 0.0447$ and $R_w = 0.1003$.
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