Magnetic Ordering and Anisotropy in Heavy Atom Radicals

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ABSTRACT: Recent developments in stable radical chemistry have afforded "heavy atom" radicals, neutral open-shell (\(S = 1/2\)) molecular species containing heavy p-block elements (S, Se), which display solid-state magnetic properties once considered exclusive to conventional metal-based magnets. These highly spin-delocalized radicals do not associate in the solid state and yet display extensive networks of close intermolecular interactions. Spin density on the heavy atoms allows for increased isotropic and spin-orbit mediated anisotropy effects. Structural variations induced by chemical modification and physical pressure, coupled with ab-initio methods to estimate exchange energies, have facilitated the development of predictive structure/property relationships. These results, coupled with detailed theoretical analyses and magnetic resonance spectroscopic measurements, have provided insight into the magnetic structure of ferromagnetic and spin-canted antiferromagnetic ordered materials as well as an understanding of the importance of spin-orbit coupling contributions to magnetic hysteresis and anisotropy. Isotropic and anisotropic ferromagnetic exchange can also be enhanced indirectly by the incorporation of heavy atoms into nonspin-bearing sites, where they can contribute to multi-orbital spin-orbit coupling.

INTRODUCTION

Interest in magnetic materials, particularly those displaying magnetization associated with the ordering of unpaired electron spins, has a long history. In his 1928 treatise on the origins of ferromagnetism, Heisenberg considered the origins of bulk ferromagnetic (B-FM) order, in which spins on separate sites are aligned in parallel (Figure 1a), and concluded that the presence of atoms with principal quantum number (PQN) \(\geq 3\) was critical to achieve intersite magnetic exchange interactions sufficiently large to compete with thermal energies (\(>kT\)). Consistently, the design of ferromagnetic materials is, to this day, based largely on the use of d- and f-block elements and their compounds. In the light of Heisenberg's comments, reports in the early 1990s of B-FM order in crystals of the nitroxylic nitroxide \(^1\) and the bisnitroxyl \(^2\) (Chart 1), both neutral organic radicals with one unpaired electron (\(S = 1/2\)) per nitroxyl, were greeted with some surprise. Despite their low ordering (Curie) temperatures, \(T_C \approx 0.6\) K (1) and 1.48 K (2), these "light atom" (PQN = 2) radicals appeared to violate Heisenberg's axiom, prompting Peter Day to draw a parallel with the comment of Dr. Johnson on seeing a dog walk on its hind legs: the surprise is not that it is done well, but that it is done at all.\(^5\)

LIGHT VERSUS HEAVY ATOMS

In principle, the intrinsic limitations of light heteroatom radicals as magnetic materials can be overcome by the incorporation of heavy (PQN \(\geq 3\)) p-block elements (S, Se), which possess more spatially extensive valence orbitals capable of generating...
stronger magnetic exchange interactions. Enhanced magnetic anisotropy, with the potential for larger coercive fields, might also be expected as a result of spin–orbit coupling (SOC) occasioned by the presence of the heavier heteroatom. However, the introduction of heavy atoms in spin-bearing sites comes at a cost, as the tendency for the resulting radicals to associate into spin-quenched, diamagnetic ($S = 0$) dimers is increased. Consistently, early solid-state structural work on thiazyl radicals 3–7 revealed strongly associated dimers, with radical pairs often bound by multcenter or “pancake” π-bonds. Attempts to generate related phosphorus-centered radicals have met a similar fate, and for selenium-based analogues of thiazyls the dimer binding energies are larger. For some dithiazolyls 3 and 4, however, association in the solid state is sufficiently weak that heat- and light-induced magnostructural transitions between the dimer ($S = 0$) and a pair of radicals ($S = 1/2$) can be observed. Suppression of low-temperature dimerization in dithiazolyls 5 was eventually achieved by judicious choice of R-group, and was rewarded by the landmark discovery that the liberated spins can be magnetically active. The R = p-cyano-tetrafluorophenyl derivative enters a B-FM phase with $T_C = 1.3$ K, in the same range as that found for light atom radicals. In both cases, however, the resulting coercive field $H_C$ is very small. Bulk AFM (B-AFM) order, where the spins are in a perfectly parallel alignment (Figure 1c), has also been reported (with $T_N = 11$ K) in a 1,3,2-dithiazolyl derivative 3.

Figure 2. (a) Valence bond representation of a bisdithiazolyl 8, with four S/Se variations A–D. (b) Isotropic $\alpha_{fi}$ and $g$ values for $R_1/R_2 = Et/Cl$ and (c) Kohn–Sham SOMO for a model 8A ($R_1/R_2 = H$) are also shown.

The drive to produce heavy atom radicals in which dimerization is suppressed more by electronic rather than steric factors, thus facilitating more three-dimensional (3D) electronic and magnetic networks, led to the design of resonance stabilized bisdithiazolyl 8 (Figure 2). In these systems, spin density is equally partitioned between two 1,2,3-dithiazole rings on either side of an N-alkylated pyridine bridge. Synthetic strategies for site-specific incorporation of selenium were also developed, thereby allowing the generation of families of iso-electronic radicals 8A–D and affording an ideal opportunity for the systematic study of magnetic and charge transport properties as a function of S/Se content. Given the nodal properties of the $a_2$ symmetry SOMO of 8, neither the beltline $R_1/R_2$ ligands nor the S/Se content have much effect on the molecular spin distribution, as witnessed by the invariance to ligand exchange of the EPR hyperfine coupling constant $\alpha_{fi}$ to the “wing” nitrogens. However, the growth in the isotropic $g$-value with increasing Se content indicates an enhancement of SOC, which sets the scale of magnetic anisotropy in the solid state. While the beltline $R_1/R_2$ ligands have little effect on molecular properties, their influence on crystal packing, and hence on solid-state electronic and magnetic structure, is profound. In most cases, the combination of steric protection offered by the substituents, coupled with increased spin delocalization, is sufficient to offset solid-state dimerization, even for Se-based radicals. Thus, in contrast to simple dithiazolyls 5 and their Se analogues, where pancake dimerization predominates, the crystal structures of 8A–D almost always consist of slipped π-stacks of radicals packed into herringbone arrays (Figure 3). The structural diversity provided by different $R_1/R_2$ combinations, coupled with the fine-tuning of exchange interactions afforded by modification of S/Se content, has given rise to a wide range of magnetic phases, including B-FMs, SC-AFMs, metamagnets, and spin ladders.

### MAGNEOSTRUCTURAL MAPPING

The packing patterns of radicals 8A–D may be characterized by (i) the crystallographic space group and (ii) the specific direction and magnitude of relative slippage of adjacent radicals within the π-stacks. In order to quantify the latter parameters, it is convenient to define π-stack slippage (in Å) in terms of the local translation coordinates $x$ and $y$, which describe the relative position of radicals when viewed perpendicular to their molecular planes, as shown in Figure 4. Thus, in a perfectly superimposed π-stack, where the radicals are eclipsed, the slippage coordinates would be $[x, y] = [0.0, 0.0]$. However, as noted above, steric repulsion between $R_1/R_2$ groups enforces finite slippage, the extent and direction of which varies with specific $R_1/R_2$ combination. Of particular interest are those radical families, defined by space group and slippage, where magnetic order is indicated by the appearance of a net moment, suggesting a B-FM or SC-AFM state. Representative members 8D of two such families are shown in Figure 4. In the first, where $R_1/R_2 = Et/Cl$ (space group $P4_2/m$), slippage occurs exclusively in the $y$ direction, with $[x, y] = [0.0, 2.15]$. This tetragonal phase, found also for $R_1 = Et, R_2 = F, Br, I, Me$, hosts radicals displaying both B-FM and SC-AFM order. For the second family, shown in Figure 4b, where $R_1/R_2 = Et/H$ (space group $P2_1/c$), SC-AFM order is common, and slippage along the $x$ direction dominates, with $[x, y] = [3.3, 0.80]$. In each of the families of radicals 8A–D, the specific pattern of order, when it is observed, is determined by the sign and magnitude of the intermolecular magnetic interactions which,
In the absence of spin–orbit effects (to be discussed later), may be in described in terms of the Heisenberg Hamiltonian shown in eq (1).

\[ \mathcal{H} = -2J_{ij} S_i \cdot S_j \]  

(1)

In this expression \( J_{ij} > 0 \) corresponds to a preference for FM alignment of spins on adjacent radical sites \( i, j \), and \( J_{ij} < 0 \) denotes an AFM preference. From a theoretical perspective such interactions have been discussed in a variety of ways.\(^26, 27\)

Here we use the two-site Hubbard model (Figure 3c)\(^28\) including electron exchange between neighboring SOMOs, which affords the following expression for the value of \( J_{ij} \):\(^29\)

\[ 2J_{ij} = 2J_{ij}^{FM} + 2J_{ij}^{AFM} = 2K_{ij}^{(0)} - 4(\epsilon_{ij}^{(0)})^2 / U \]  

(2)

Of the various terms in eq (2), \( U \) is the onsite Coulomb potential, \( \epsilon_{ij}^{(0)} \) the intermolecular hopping integral, better known to chemists as a resonance integral, and \( K_{ij}^{(0)} \) the electron exchange integral (Figure 3c). For the latter two terms the superscripted "00" indicates that the interaction is between neighboring SOMOs; the influence of other orbitals will be in discussed in later sections. In most cases the magnitude of \( J_{ij} \) is set by the AFM (–ve) virtual hopping term \(-4(\epsilon_{ij}^{(0)})^2 / U \). However, with the inclusion of intersite electron exchange, which is generally small\(^30\) but always +ve, the balance may be shifted in favor of a net FM interaction. The challenge is to design materials in which this condition prevails.

As a result of the strongly antibonding (nodal) nature of the SOMO (Figures 2 and 3), orbital overlap and hence \( \epsilon_{ij}^{(0)} \) and \( J_{ij} \) are sensitive to solid-state packing, particularly the alignment (slippage) of neighboring radicals within the same \( \pi \)-stack. Moreover, for such neighbors, the sign of the associated intrastack exchange interaction \( J_{ij} \) is of critical importance for the emergence of B-FM and SC-AFM states. This is so because, for simple one- or two-sublattice ordered magnetic structures, symmetry restrictions require that a net magnetization may only appear when all crystallographic translation and inversion symmetries are maintained by the magnetic state. For this reason, B-FM and SC-AFM states in 8A–D require spins within the same \( \pi \)-stack, which are related by translation, to be ferromagnetically aligned. Thus, \( J_{ij} \) must be +ve, or sufficiently small that interstack interactions dominate the magnetic order. Quantitative estimation of this parameter may be achieved using density functional theory (DFT) broken symmetry (BS) methods.\(^31\) Results of this approach are illustrated in Figure 5, which shows the variations in calculated \( J_{ij} \) for sterically unhindered model radicals 8D \((R_1/R_2 = H)\), as a function of translation along \( x \) and \( y \) (computed at the (U)B3LYP/6-31G(d,p) level).\(^21\) The resulting two-dimensional (2D) energy surface shows regions of both FM (green) and AFM (blue) exchange, which may be related qualitatively to the expected pairwise overlap integral and hence \( \epsilon_{ij}^{(0)} \). All four radicals 8A–D produce qualitatively similar profiles, although the magnitude of \( J_{ij} \) (be it +ve or –ve) is enhanced with increasing selenium content.

Close inspection of Figure 5 allows the prediction of plate slippage regions conducive to either FM or AFM interactions along the \( \pi \)-stacks. For example, the deep AFM hole around \([x, y] = [0, 0]\) corresponds to the sterically unfavorable “pancake” overlap region, which would lead to formation of a diamagnetic \((S = 0)\) dimer, if found in nature. More subtle is the AFM well near \([1.5, 2.0]\), which may be loosely associated with strong Se1–Se2 intrastack overlap between adjacent radicals. Experimentally, radicals falling into this regime, such as 8B, D \((R_1/R_2 = Me/Cl, space group P2_1/n)\), with \([x, y] = [1.60, 1.54]\) and \([1.49, 1.64]\), respectively, indeed display strong AFM coupling along the \( \pi \)-stacks.\(^21\) Consistently, these radicals do not show the onset of a canted moment down to \( T = 2 \text{ K} \), which would be symmetry forbidden. The two remaining models shown in Figure 5c,d correspond to slippage coordinates where FM exchange dominates within the \( \pi \)-stacks. The first, close to the (green) FM ridge that meets the \([0, 0]\) plane near \( y \sim 1.8\), corresponds to the tetragonal \( P4_2_1/m \) family illustrated in Figure 4a. The second, found near the point of maximum slippage along \( x \) (with \( y \) near 0), is shown in Figure 4b. In both cases, the occurrence of a positive \( J_{ij} \) required for B-FM and SC-AFM order, respectively, can be understood in terms of the classical orthogonal overlap condition\(^32\) of neighboring SOMOs along the \( \pi \)-stacks, that is, where \( \epsilon_{ij}^{(0)} \) and hence \( J_{ij}^{FM} \sim 0 \).

Provided ferromagnetic \( \pi \)-stack interactions, whether a material orders as a B-FM or SC-AFM is determined by the details of magnetic coupling between stacks, which may be remarkably sensitive to S/Se replacement. This observation is apparent in the magnetic properties of the four isostructural radicals 8A–D.
The role of interstack interactions in determining the pattern of magnetic order is also apparent in 8D ($R_1/R_2 = Et/H$). Experimentally, this radical orders as a SC-AFM with $T_N = 28$ K; its isostuctural analogue 8C ($R_1/R_2 = Et/H$) behaves similarly, with $T_N = 18$ K. The former displays a weakly AFM Weiss constant ($\Theta = -8$ K), while the latter shows a net FM response at high temperatures, with $\Theta = +6$ K. In these materials, symmetry restrictions related to the crystallographic inversion center allow for unambiguous determination of the magnetic structure (Figure 7), which implies FM intrastack and AFM interstack interactions, as in the tetragonal materials. In this case, however, symmetry does not restrict the orientation of the observed canted moment, due to the low symmetry of the monoclinic space group.

- **CHEMICAL AND PHYSICAL PRESSURE**

The observation of ordering, be it B-FM or SC-AFM, hinges on the existence of a net ferromagnetic response along the $\pi$-stacks. For the tetragonal $P4_2/m$ family of 8, the DFT-BS structure map shown in Figure 5 suggests that intrastack exchange coupling $J_\pi$ should be extremely sensitive to variations in slippage along the $y$ direction (for $x = 0$). The orthogonal overlap condition where $J_\pi$ is ferromagnetic spans a very narrow range, essentially where the FM “ridge” abuts the $x = 0$ “wall”. Experimental support for this conclusion comes from the examination of the magnetic properties of a series of radicals of type 8B, all belonging to the $P4_2/m$ space group. While the changes in $R_1/R_2$ are not sufficient to alter the space group, they are enough to induce subtle changes in slippage coordinates. The variations of these are illustrated in Figure 8, along with an assessment of the magnetic consequences, that is, the resulting change in $J_\pi$. While there is not an exact correspondence between the calculated and observed geometry expected for a FM response, one may conclude that slippage along $y$ beyond that found for (i)–(iii) ($R_1 = Et; R_2 = Cl, Br, Me$) should eventually lead to AFM ($-ve$ $J_\pi$) values and loss of order in B-FM or SC-AFM order. Consistently, the more highly slipped (iv), (v) ($R_1 = CF_3CH_2; Pr; R_2 = Cl$) show no evidence for either order down to 2 K.

![Figure 6](image_url) (a) Unit cell of 8D ($R_1/R_2 = Et/Cl$), space group $P4_2/m$, showing mirror planes and $2_1$ axes. (b) Definition and (c) signs of interstack exchange interactions $J_1$ and $J_2$ in 8A–D about the 4 points.

![Figure 7](image_url) (a) Unit cell of 8D ($R_1/R_2 = Et/H$), space group $P2_1/c$, and (b) magnetic cell structure with associated symmetry operations (inversion centers and $2_1$ axes). The two magnetic sublattices are distinguished by blue and green shading.

![Figure 8](image_url) DFT-BS calculated $J_\pi$ energy surface for 8B ($R_1/R_2 = H$) as a function of $\pi$-stack slippage along the $y$ direction, with observed $y$ values of real systems. Radicals (i)–(iii) order as B-FMs, while (iv) and (v) do not order.

Exploration of the effect of changes in the ligands $R_1/R_2$ on the structure and magnetic response of a particular structure type represents an example of the use of “chemical pressure” to generate a magnetostructural response. An alternative approach, which allows for greater structural control, and hence more detailed insight, is to employ physical pressure. By way of example we summarize in Figure 9 the results of high pressure (HP) crystallographic and magnetic measurements on 8D ($R_1/R_2 = Et/Cl$). As expected, the application of pressure leads to the compression of the unit cell dimensions (Figure 9a), particularly the $c$-axis, which translates into a reduction of both the interlayer separation ($\delta$, Figure 8) and the slippage of the $\pi$-stacks along the $y$ direction. DFT-BS calculations of $J_\pi$ as a function of pressure, using geometries obtained from the HP crystallographic data (Figure 9b), reveal a trend anticipated in Figure 9, that is, an initial increase in $J_\pi$ as the FM “ridge” (where SOMO–SOMO overlap and $\delta^2$ is $\sim 0$) is traversed, followed by a rapid decrease as overlap and, hence, AFM interactions increase. The computational results provide a satisfying match with the pressure-induced variation in $T_C$ (Figure 9b), that is, an initial rise to near 22 K at about 1 GPa, followed by a rapid decline, and probable loss of order. While the maxima in the $J_\pi$ and $T_C$ plots as a function of pressure do not coincide, the qualitative correspondence between the two profiles is appealing. These results highlight the fact that subtle increase or decrease in the degree of $\pi$-stack slippage, through chemical or physical pressure, respectively, can profoundly affect magnetic ordering.

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HYSTERESIS AND ANISOTROPY

In previous sections, the enhancement of isotropic exchange interactions of resonance stabilized radicals \(8A - D\) served as a major motivation for pursuing the incorporation of selenium; it is the primary manifestation of the heavy atom effect. We now turn to the role selenium plays in mediating anisotropic exchange, as manifest in increased magnetic hysteresis and related phenomena. In contrast to \(S > 1/2\) metal-based systems, where single-ion anisotropy may arise from local crystal field effects, Kramers’ theorem forbids zero field magnetic anisotropy for isolated \(S = 1/2\) radicals. In the solid state, coercivity and spin canting must therefore arise, in radicals, from interactions between spins, either through long-range dipolar effects, or anisotropic SOC corrections to the magnetic exchange. The former interaction depends on crystal morphology and microstructure and as such is largely independent of Se-incorporation. In contrast, the latter SOC effects may be enhanced directly by introduction of heavy elements into the molecular framework. In this regard, it is not surprising that early organic ferromagnets including nitroxylics, thiazyls, and doped fullerenes displayed small coercive fields (\(H_c < 10\) Oe). In these light atom materials, spin–orbit effects are relatively weak. By contrast, the first reported heavy atom (Se-based) organic ferromagnets \(8B,D\) \((R_1/R_2 = Et/Cl)\) displayed significant hysteresis (Figure 10), with coercive fields (at \(2K\)) of \(250\) and \(1370\) Oe, respectively, indicating significant anisotropy.

This magnetic anisotropy has been probed in both \(8B,D\) \((R_1/R_2 = Et/Cl)\) through single crystal ferromagnetic resonance (FMR) measurements. In FMR, the resonance conditions are sensitive only to the anisotropic component of the magnetic interactions, making the technique uniquely suited for studying such effects. For tetragonal crystals, such as \(8B,D\) \((R_1/R_2 = Et/Cl)\), the lowest order anisotropic contribution to the magnetic free energy is uniaxial and is characterized by an anisotropy field \(H_A\) with an anisotropy energy \(E_{\text{aniso}} = -1/2H_A M \cos^2 \theta\). Here, \(\theta\) is the polar angle measured with respect to the crystallographic \(c\)-axis, and \(M\) is the magnetization. By convention, for \(H_A > 0\), magnetization is preferred along the \(c\)-axis (easy axis), while \(H_A < 0\) refers to easy \(ab\)-plane anisotropy. At high frequencies, the FMR resonant field of both radicals (Figure 11a) was found to vary in accord with the response predicted for easy \(c\)-axis anisotropy. As shown in Figure 11b, the magnitude of \(H_A\) was found to saturate, with decreasing temperature, toward values of 3.1 kOe for \(8B\) (at 4 K) and 8.8 kOe for \(8D\) (at 2 K), which may be compared with measured values for light atom ferromagnets, that is, 120 Oe for \(\beta\)-p-NPNN (at 0.4 K) and 58 Oe for TDAE-C\(_{60}\) (at 5 K). While dipolar interactions provide an adequate explanation of the anisotropy in light-atom radicals, the observed \(H_A\) (and \(H_c\)) is too large in \(8B,D\) \((R_1/R_2 = Et/Cl)\) to originate from dipolar interactions. Dipolar interactions also fail to explain the scaling of \(H_A\) with Se content, suggesting \(H_A\) arises primarily from spin–orbit anisotropic exchange interactions, as described in the following section.

SPIN–ORBIT COUPLING

Coupling of spin \(S\) and orbital \(L\) momenta may be expressed, for isolated atomic ions, via the Hamiltonian \(H_{SO} = \lambda L \cdot S\), with a magnitude set by the empirical constant \(\lambda\), which grows sharply with increasing atomic number (roughly as \(Z^4\)). In molecular systems, however, the presence of multiatom and multielectron SOC contributions implies that \(H_{SO}\) cannot be expressed in terms of a single atomic parameter \(\lambda\) or operator \(L\). Instead, one may introduce an effective one-electron molecular operator \(\mathcal{L}\), such that \(H_{SO} = \mathcal{L} \cdot S\), which may be computed in the spin–orbit mean field (SOMF) approximation. At first order, the effect of this interaction in orbitally nondegenerate radicals is to mix filled and virtual orbitals to induce nonzero orbital angular momentum at the expense of the spin moment. The physical consequence of this mixing is that the spin/orbital composition of the observable magnetic moment becomes orientation dependent, which results in increased anisotropy in the \(g\)-tensors of isolated \(S\)- and Se-based radicals. In the solid state, the interactions between composite spin–orbital moments are also rendered anisotropic and may be generally described by the Hamiltonian:

\[
\mathcal{H} = -2J_y S_y S_y + D_y S_y \times S_y + S_y G_y S_y
\]
The first term in eq (3) represents the isotropic Heisenberg exchange interaction $J_{ij}$ defined in eq (1) and described in terms of its ferromagnetic ($2K_{ij}$) and antiferromagnetic ($-4(\Delta_{ij}^\mu)^2/U$) components in eq (2). The second and third terms in eq (3) assess anisotropic exchange. Of these, the vector $D_{ij}$ is the celebrated antisymmetric Dzyaloshinskii–Moriya (DM) interaction, while the symmetric tensor $\Gamma_{ij}$ represents the pseudo-dipolar (PD) interaction. Both DM and PD effects may contribute to $H_{\text{ex}}$. The DM term prefers $S_i$ and $S_j$ to be canted with respect to one another, and lie in the plane normal to the $D_{ij}$ vector, with $H_{\text{ex}} \sim |D_{ij}|/|J_{ij}|$. The PD term prefers $S_i$ and $S_j$ to be parallel (perpendicular) to the largest positive principal axes of the $\Gamma_{ij}$ tensor for AFM (FM) aligned spins. The standard microscopic description of such terms is due to Moriya, who considered isolated $S = 1/2$ atomic centers and computed SOC corrections to the AFM exchange by means of eqs (4) and (5):

$$D_{ij}^{\text{AFM}} = \frac{4i}{U} \left( \Delta_{ij}^0 C_{ij}^{000} - C_{ij}^{00}\Delta_{ij}^0 \right) \tag{4}$$

$$\Gamma_{ij}^{\text{AFM}} = \frac{4}{U} \left( C_{ij}^{000} \otimes C_{\mu}^{00} + C_{\mu}^{00} \otimes C_{ij}^{000} \right) \tag{5}$$

where the SOMO–SOMO spin–orbit hopping term $C_{ij}^{00}$ is a (pseudo) vector, with Cartesian components given in eq (6):

$$C_{ij}^{00} = \frac{1}{2} \sum_a \left\{ \langle \phi_a \| L_a^\mu \phi_{ij}^0 \rangle \left( \varepsilon_a - \varepsilon_j \right) - \langle \phi_j \| L_a^\mu \phi_{ij}^0 \rangle \left( \varepsilon_a - \varepsilon_i \right) \right\} \tag{6}$$

In the above $\mu \in \{x, y, z\}$, $\phi_{ij}^0$ is the hopping integral between orbital $\phi_i^0$ at radical site $i$ and orbital $\phi_j^0$ at site $j$, the index $a$ runs over all orbitals, and $a = 0$ refers to the SOMO. The orientation and magnitude of $\Delta_{ij}^0$ completely determines the character of the magnetic anisotropy. While Moriya’s approach is equally valid for organic radicals, a conceptual disadvantage of writing $C_{ij}^{00}$ in terms of the molecular operator $L$ is that the energy scale for the interaction is no longer set by a single $\lambda$, complicating comparison of different molecular materials. Moreover, SOC may have varied effects on different orbitals, as discussed below. In order to address this complication, we introduce the orbital-dependent weighting functions shown in eqs (7) and (8), in which $\varepsilon_i - \varepsilon_j \leq \varepsilon_E$.

$$P_{\mu}(a, \varepsilon_E) = \sum_{b \neq a} \left| \frac{\langle \phi_b^0 \| L_a^\mu \phi_{ij}^0 \rangle}{\varepsilon_b - \varepsilon_a} \right| \frac{\langle \phi_a \| L_a^\mu \phi_{ij}^0 \rangle}{\varepsilon_a - \varepsilon_j} \tag{7}$$

$$P_{\text{tot}}(a, \varepsilon_E) = \sum_{b \neq a} \left( \sum_{\mu} \left| \frac{\langle \phi_b^0 \| L_a^\mu \phi_{ij}^0 \rangle}{\varepsilon_b - \varepsilon_a} \right|^2 \right) \tag{8}$$

Both functions quantify the degree of first-order spin–orbit mixing of orbital $\phi_i^0$ with all other orbitals lying within an energy window $\varepsilon_E$. The former function $P_{\mu}$ for $\mu \in \{x, y, z\}$ describes the relative weight of SOC induced by the different Cartesian components of $L$, which, for $a = 0$, is closely related to the orientation of $C_{ij}^{00}$ and therefore the character of the anisotropic exchange. The latter function $P_{\text{tot}}$ quantifies the total weight of mixing and is related to the overall scale of SOC, analogous to $\lambda$. Thus, for anisotropic exchange, $H_{\text{ex}} \propto C_{ij}^{00}$ and should therefore scale roughly as $(P_{\text{tot}}(0, \varepsilon_E))^2$ in the limit of large $\varepsilon_E$. Values of $P_{\text{tot}}(0, \varepsilon_E)$ and $P_{\mu}(0, \varepsilon_E)$, computed at the B3LYP/def2-SV(P) level using ORCA’s SOC module, are plotted in Figure 12 for $8A$–$D$ ($R_1/R_2 = \text{Et}/\text{Cl}$). The limiting values of $P_{\mu}(0, \varepsilon_E)$ appear in the same ratio as the average SOC constant for heavy ($S$, $Se$) atoms in the molecule. (b) Breakdown of Cartesian weights $P_{\mu}(0, \varepsilon_E)$ for $8D$ showing a negligible component perpendicular to the molecular plane ($\varepsilon_z$, direction).
monitor the resulting changes in $H_A$. Over the pressure range 0–2.2 GPa, $H_A$ was found to increase monotonically, more than doubling to a value of 18.2 kOe at 2.2 GPa. This pressure dependence is in marked contrast with the corresponding trend in $T_J$, which first rises and then begins to fall at pressures above 1 GPa, confirming that the isotropic and anisotropic interactions may scale differently with pressure. Ab-initio calculations correctly reproduced the pressure dependence of $H_A$ and revealed that the enhancement is largely due to the increasing magnitude of interstack hopping integrals upon compression of the crystal.

## MULTIPLE ORBITALS

While isotropic and anisotropic exchange interactions in radicals 8A–D have been well described in terms of a one-orbital Hubbard model, which includes only the SOMO explicitly, the importance of effects associated with other energetically nearby orbitals has recently been realized. These multi-orbital effects are relatively rare in radical-based magnetic materials, but study of their propensity to generate ferromagnetic exchange by virtual hopping between the SOMO and empty orbitals has a long history, going back to work by Anderson and Goodenough on inorganic oxides. The ideas have since been applied to the design of ferromagnetic radical ion salts and doped fullerenes.

In the context of bisdithiazolyl radicals, multi-orbital effects can be introduced by replacing the NR$_1$ unit of 8 with a carbonyl (CO) moiety, to afford the oxobenzene-bridged framework 9 shown in Figure 13.

![Figure 13](image)

(a) VB bond representation of an oxobenzene-bridged bisdithiazolyl radical 9. (b) Kohn–Sham $a_1$ SOMO and $b_1$ LUMO of 9 (R = H). (c) Four-orbital two-site orbital interaction diagram for two radicals 9 with a small SOMO–LUMO gap $\Delta c$. The SOMO–SOMO ($\epsilon_{ij}^{\text{01}}$) and SOMO–LUMO ($\epsilon_{ij}^{\text{10}}$) hopping integrals and the SOMO–LUMO electron exchange integral $K_{ij}^{\text{01}}$ are indicated.

While incorporation of the carbonyl group does not perturb the SOMO, mixing of the CO $\pi^*$-orbital results in a low-lying empty $\pi$-LUMO. The combination of a small HOMO–LUMO gap $\Delta c \sim 0.2–0.4$ eV with a large on-site SOMO–LUMO Hund’s rule coupling $K_{ii}^{\text{01}}$ requires modification of the FM exchange term in eq (2) to produce that shown in eq (9), in which the onsite Coulomb repulsion term $V (\ll U)$ refers to two electrons in different orbitals.

$$2J_{ij}^{\text{FM}} = 2K_{ij}^{\text{01}} + 2 - (t_{ij}^{\text{10}})^2 - (t_{ij}^{\text{01}})^2 + (V + \Delta c)^2 - (K_{ij}^{\text{01}})^2.$$

Structural studies on a range of oxobenzene-bridged radicals 9 (R = H, Me, Ph, F, Cl, Br, I) reveal no evidence for herringbone style $\pi$-stacking, as observed for 8. Instead, crystal packing is dominated by strong intermolecular S···O’ and S···N’ interactions which link adjacent radicals into coplanar ribbon-like arrays (Figure 14a). These “zig-zag” ribbons may then overlay to form slipped $\pi$-stacks, alternating ABABAB $\pi$-stacks and even brick-wall architectures (Figure 14b–d).

Magnetic studies on these materials have revealed several examples that display strong FM interactions along the $\pi$-stacks, with a pronounced tendency for SC-AFM order. When R = H, Ph, the radicals both order with $T_N \sim 4$ K and display strong ferromagnetic Weiss constants $\Theta = 16$ and 33 K, respectively. Consistent with the high $\Theta$ values, both materials undergo field-induced AFM alignment under relatively small applied field. For the SC-AFMs with R = F, I (the latter as its EtCN solvate), the ordering temperatures are significantly higher ($T_N = 13$ and 35 K respectively), and these values, combined with the high symmetry and simplicity of the crystal structures, have allowed a detailed analysis of their magnetic structures.

![Figure 14.](image)

The crystal structures of radical 9 (R = F), space group Cmce$_2$, and 9-EtCN (R = I), space group Pnma, are illustrated in Figure 15. Both consist of crystallographically coplanar arrays of radicals falling on a mirror plane. The canted moment is restricted to lie in the mirror plane (eq 9a) extend in both the $b$ and $c$ directions, to form 2D sheets at $x = 0, 0.5$ linked by a series of close, lateral S···O’ and S···N’ contacts. Neighboring radicals are related by C-centering or translation along $b$. In 9-EtCN (R = I), each radical lies on a mirror plane normal to $b$ at $y = 0.25$, 0.75 and is linked into ribbon-like arrays along the $a$-glide. The EtCN solvent molecules serve as buffers between adjacent radicals and inhibit magnetic interactions between them. Due to the high symmetry of the Cmce$_2$ and Pnma space groups and the fact that radicals fall on a special position, the magnetic structure of each of these materials can be uniquely specified. For R = F, canting requires that all spins within the $ab$ planes, which are related by translation (C-centering), belong to the same sublattice, that is, to be FM-aligned. Therefore, the only structure consistent with canting has ordering vector $0, 0, 2\pi$, with adjacent $ab$ plane layers AFM-coupled, as shown in Figure 15. The canted moment is restricted to lie in the $bc$ plane. This structure requires strong ferromagnetic $\pi$-stack interactions within the brick walls, which ab-initio calculations confirm arise from multi-orbital exchange.

In the case of the centric structure 9-EtCN (R = I), canting is possible only if sites related by either translation or inversion belong to the same magnetic sublattice. This condition is satisfied only for FM alignment of inversion-related spins on adjacent radicals in the same $\pi$-stack. Radicals related by the $a$-glide, coupled via lateral magnetic interactions, must be AFM-aligned, as shown in Figure 14, with individual moments lying in the $ac$ plane. Numerical estimates of pairwise isotropic exchange energies are consistent with this pattern of magnetic order.
In addition to promoting strong isotropic exchange interactions, multi-orbital effects also play an important role in determining the magnitude of the anisotropic exchange terms that influence spin canting and hysteresis. For the fluoro- and iodo-derivatives 9 (R = F, I) magnetic hysteresis measurements (Figure 16) reveal coercive fields \( H_c = 290 \) and 1060 Oe at \( T = 2 \) K, respectively, values comparable to those found in the Se-based ferromagnets 8B,D (R\(_1\)/R\(_2\) = Et/Cl). The anisotropy fields are, however, somewhat smaller. In the case of 9 (R = F) analysis of the powder antiferromagnetic resonance suggested easy plane anisotropy with \( H_A \sim -200 \text{ Oe} \) while estimation of \( H_A \) from the spin-flop field \( H_f \) in 9-ECN (R = I) indicated a value of \( H_A \sim +630 \text{ Oe} \).

In 9 (R = F), where the R-group is a light atom, the relative role of dipolar interactions and SOC remains to be investigated, but in the latter case, SOC effects play a prominent role which may be ascribed the heavy iodine substituent. The observed magnetic anisotropy can only be understood by modification of Moriya’s standard description to include spin-orbit corrections to the multi-orbital FM exchange. Accordingly, and in order to describe multi-orbital anisotropic exchange, arising from SOC corrections to the second terms in eq (9), the following expressions, eqs (10) and (11), apply:

\[
\mathbf{D}^{\text{FM}}_{ij} = -2\left\{ \mathbf{C}^{01}_{ij} \otimes \mathbf{C}^{10}_{ij} - t^{10}_{ij} \mathbf{C}^{10}_{ij} \right\} K^{01}_{ij} \tag{10}
\]

\[
\Gamma_{ij}^{\text{FM}} = -2\left\{ \mathbf{C}^{01}_{ij} \otimes \mathbf{C}^{10}_{ij} + \mathbf{C}^{10}_{ij} \otimes \mathbf{C}^{01}_{ij} \right\} K^{01}_{ij} \tag{11}
\]

These are distinguished from Moriya’s conventional anisotropic exchange by the superscript “FM”. The interorbital spin–orbit-mediated hopping \( C^{01}_{ij} \) is then given by eq 12:

\[
\mathbf{C}^{01}_{ij} = \frac{1}{2} \sum_x \left\{ \phi_x^0 \mathbf{L}_x^{\text{SOMO}} \phi_x^0 \right\} \left\{ \phi_x^1 \mathbf{L}_x^{\text{LUMO}} \phi_x^1 \right\} + \frac{1}{2} \sum_x \left\{ \phi_x^1 \mathbf{L}_x^{\text{SOMO}} \phi_x^1 \right\} \left\{ \phi_x^0 \mathbf{L}_x^{\text{LUMO}} \phi_x^0 \right\}
\]

It is important to note from eq (12) that, in contrast to \( C^{00}_{ij} \) defined in eq (6), the value of \( C^{01}_{ij} \) depends on SOC effects in both the SOMO and the LUMO, through the first and second terms, respectively. As a result, while the magnitude of \( C^{01}_{ij} \) is related only to \( \mathcal{P}_{\text{tot}}(0, E) \), the interorbital spin–orbit terms \( C^{10}_{ij} \) scale with both \( \mathcal{P}_{\text{tot}}(0, E) \) and \( \mathcal{P}_{\text{tot}}(1, E) \). To illustrate this point we show in Figure 17 the values of these two terms for 9 (R = F, Cl, Br, I), computed at the B3LYP/def2-SV(P) level, which reveal an important distinction between the behavior of the SOMO and LUMO. The \( a_9 \) SOMO contains a vertical nodal plane at the R-position (Figure 13), and consistently the SOC corrections are independent of both the R-group and the C=O moiety. For large \( E_n \), \( \mathcal{P}_{\text{tot}}(0, E) \) converges to the same value in 9 and 8A. By contrast, the \( b_1 \) LUMO, which possesses nonzero density at the R-position, shows spin–orbit effects that scale roughly with the spin–orbit constant \( \lambda_{b_1} \) as quantified by \( \mathcal{P}_{\text{tot}}(1, E) \).

![Figure 16. Magnetic hysteresis for (a) 9 (R = F) and (b) 9-ECN (R = I) at \( T = 2 \) K, where \( H_c = 290 \) and 1060 Oe, respectively. Adapted with permission from refs 55d and 56. Copyright 2012 and 2015 American Chemical Society.](https://example.com/fig16)

![Figure 17. Calculated weighting functions \( \mathcal{P}_{\text{tot}}(0, E) \) and \( \mathcal{P}_{\text{tot}}(1, E) \) for the (a) LUMO and (b) SOMO of 9 (R = F, Cl, Br, I), as a function of the width of the energy window \( E \).](https://example.com/fig17)

We conclude that in oxobenzene-bridged radicals 9, multi-orbital anisotropic exchange may be selectively tuned by substitution at the R-position. This point is particularly well illustrated in 9-ECN (R = I), where both \( \mathbf{D}^{\text{FM}}_{ij} \) and \( \Gamma_{ij}^{\text{FM}} \) are significantly enhanced by the heavy iodine substituent. By contrast, the symmetry of the SOMO and crystal conspires to restrict all conventional \( \mathbf{D}^{\text{FM}}_{ij} \) and \( \Gamma_{ij}^{\text{FM}} \) interactions essentially to vanish. In this way, 9-ECN (R = I) represents not only a definitive example of multi-orbital anisotropic exchange but also demonstrates that the observation of magnetic anisotropy in highly symmetric crystal structures may be explained in terms of departures from Moriya’s conventional theory.

**FUTURE PROSPECTS**

In 2007, Stephen Blundell remarked, regarding radical-based magnets, that “few (radicals) are stable enough to be assembled..."
into crystalline structures and, even when that is possible, aligning these spins ferromagnetically is usually impossible.\(^5^9\) The results summarized in this Perspective, which covers developments reported largely since that time, provide a more encouraging view of the opportunities available for such materials. It has been shown that significant improvement in the low ordering temperatures and small coercive fields which characterized early light atom (PQN \(< 3\)) radical magnets can be achieved by the incorporation of heavy heteroatoms. In materials such as \(8\)A−D, spin-pairing dimerization can be prevented by a combination of steric and electronic factors. These heavy atom (Se-based) organic magnets not only show strong isotropic exchange interactions but also display the effects (coercivity and spin-canting) of strong magnetic anisotropy arising from SOC. The recently introduced multi-orbital radical approach provides an alternative and potentially far-reaching means to enhance magnetic anisotropy, by incorporating heavy atoms into non-spin-bearing sites of a radical in which low-lying virtual orbitals are present. These virtual, heavy-atom-based orbitals can mix with the SOMO of a radical, thereby providing a means for the heavy atom to exert a spin−orbit effect while avoiding spin-pairing problems associated with the presence of spin density on a heavy atom.

Overall, the magnetic properties of the heavy atom radicals summarized here suggest a satisfying uniformity in the behavior of magnetic materials based on \(p\), \(d\), and \(f\)-electrons. Heisenberg was right, to generate strong exchange interactions all you need is \(PQN \geq 3\). Continued research into the magnetic properties of heavy \(p\)-block radicals may well provide a rich source of new spin−orbit related physics. For example, the possibility of realizing topologically nontrivial electronic or magnetic phases in organics and organometallics remains essentially unexplored.\(^6^0\) Likewise the impact of SOC effects on spintronic devices based on organic semiconductors deserves further study. In these materials, anisotropic terms must be suppressed for long-lived spin coherence, while enhanced SOC is of importance for applications involving spin-transport, spin-charge conversion (the spin Hall effect), and other spin-dependent processes.\(^6^1\) Engineering and tuning such properties in real systems requires a deep understanding of the relationship between spin−orbit parameters, molecular structure, and crystal architecture. As shown here, experimental and ab-initio probes of these relationships have already provided much insight.

From a practical perspective, the greatest challenges for the future, but also the greatest opportunities, lie in chemical synthesis, the demanding task of designing, building, and then crystalizing stable, main group heavy atom radicals in which dimerization is suppressed, and yet strong 3D magnetic exchange networks are preserved. While the neutral \(S−N\) and \(Se−N\) heterocycles described here have provided a rich array of magnetically active materials, exploration of \(\pi\)-delocalized inorganic ring systems based on other heavy \(p\)-block elements may eventually prove equally rewarding.\(^6^2\) In this regard, understanding of the structural properties of \(Te−N\) heterocycles is steadily emerging\(^6^3\) and may yield breakthroughs. The pursuit of ferromagnetically coupled \(S−N\) (and \(Se−N\)) heterocyclic radical ion salts where multi-orbital effects apply also holds great potential.\(^5^2,^6^4\) Likewise recent reports of \(\pi\)-delocalized radical cations of phosphorus-based heterocycles\(^6^5\) provide encouragement for the pursuit of heavy group 15 neutral radicals. An alternative application of radicals, not developed in this Perspective, is as mediators of magnetic exchange between coordinated metallic spin centers.\(^6^6\) The use of heavy atom radicals in this role, as a means of enhancing magnetic anisotropy, has yet to be fully explored.

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**Notes**

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