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Recent developments in the coordination chemistry of stable free radicals*

Martin T. Lemaire[‡]

Department of Chemistry, Memorial University of Newfoundland, St. John's, NL
A1B 3X7, Canada

Abstract: Several advances in the coordination chemistry of stable free-radical species over the past six years are documented in this review article. Specifically, a number of recent reports focused on the coordination chemistry of chelating nitroxide ligands are highlighted, with an emphasis on enhanced magnetic or optical properties in these complexes. Furthermore, very intriguing recent magnetic and optical studies with one-dimensional nitroxide chain complexes (new "Glauber" chains and chiral magnets) are also discussed. The *verdazyls* are another family of stable radicals whose coordination chemistry was literally unexplored prior to 1997. A summary of recent reports discussing metal-verdazyl coordination complexes is also presented, followed by an eye to the future of stable radical design and the coordination chemistry of these interesting molecules.

INTRODUCTION

The "metal-radical approach" toward magnetic materials was first expounded in an often-cited account by Dante Gatteschi that appeared in 1989 [1]. The strategy is simple: Strong *direct* metal-ligand magnetic exchange interactions are achieved from the coordination of stable free radicals to paramagnetic transition-metal ions, and if these interactions are extended in one, two, or three spatial directions, cooperative magnetic behavior is obtainable in these *molecule-based* systems. Since (and prior to) 1989, literally hundreds of metal-radical complexes have been reported, including a number of magnetically ordered materials [2a–o]. A wealth of knowledge about the structure and magnetic properties of coordination complexes containing stable radical ligands has been unearthed, and as a result, the metal-radical approach is recognized as one of the more fruitful efforts toward molecular magnetic materials [3a,b].

The purpose of this brief review is to summarize some of the major advances in stable radical coordination chemistry that have occurred between 1997 to the present. The families of radicals to be discussed are limited to stable, isolable free-radical species—i.e., radicals that can be prepared and stored under ambient conditions. The coordination chemistry of other very interesting radical anion molecules, such as the cyanocarbon family of acceptor ligands, including TNCE and TCNQ, as well as a variety of semiquinone radical anions and carbenes will not be discussed here [4a–j]. A topical overview of coordination complexes containing a variety of stable nitroxide and verdazyl radicals over the past six years will be given, along with a summary of future prospects, with particularly, the design of new stable radical ligands in mind.

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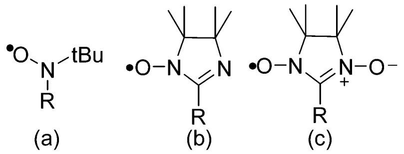
[‡] E-mail: mlemaire@mun.ca

ADVANCES IN THE COORDINATION CHEMISTRY OF NITROXIDE RADICALS: CHELATING RADICALS, OPTICAL STUDIES, AND REVISITING 1D CHAIN COMPLEXES

A variety of substituted nitroxide free radicals (Scheme 1) have been the focus of an enormous number of coordination chemistry studies over the past 30 years, or so (for examples, see the references in [2]).



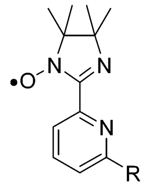
Scheme 1 General structures of nitroxide (a), imino nitroxide (b), and nitronyl nitroxide (c) free radicals.

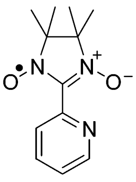
These efforts are directed toward the preparation of molecular magnetic materials by the linking of the paramagnetic N–O moiety with paramagnetic transition-metal centers. It was discovered that the N–O moiety is π-basic and can bind strongly Lewis acidic metal centers [5a,b]. Metal-bis(1,1,1,5,5,5-hexafluoroacetylacetonate) [M(hfac)$_2$] units were thus chosen as the metal anchors to coordinate these radicals, and a wide variety of zero-, one-, two-, and three-dimensional crystalline materials have been prepared and documented in a series of beautiful reports [2a–i,l,n]. A bounty of information regarding the coordination modes of nitroxide radicals, the strength and direction of metal-nitroxide magnetic exchange, and the factors that govern magnetic ordering in these complexes have been garnered from these studies [2f]. However, the inherent weakness of *interchain* magnetic interactions in these complexes, coupled with the low critical temperatures (T_c) for magnetic ordering that have thus far been observed, have provided a driving force for the design of new structural paradigms in nitroxide coordination chemistry. This leads to our first topic: Coordination chemistry of chelating nitroxide radicals.

Chelating nitroxide radicals

The coordination chemistry of chelating nitroxide radicals was first documented in the early 1990s. These ligands typically feature substituents bearing donor atoms in the 2 position of the nitronyl or imino nitroxide ring [6a,b]. Chelating nitroxide radicals can coordinate to weaker Lewis acidic metal sites in a multidentate fashion through the spin density rich oxyl group and the donor substituent; efforts in this regard have focused on using these more effective ligands to bind metal centers that are free of ancillary ligands (like hfac). This opens up the potential for coordination of up to three bidentate radicals per metal ion, for example, and coordination polymers with strong metal-radical interactions in three spatial directions. Chelating radicals also introduce important stereochemical constraints concerning the overlap of magnetic orbitals [7a–d.] In fact, rare ferromagnetic metal-nitroxide interactions have been observed for a number of these systems because of strict orthogonality of the magnetic orbitals, imposed directly because of the chelation [6a,7a–d]. A huge number of metal complexes with different chelating nitroxide ligands have been reported and the structural and magnetic behavior of the metal-nitroxide chelate is now well understood. With respect to potential magnetic materials, the following represents the most significant work published from 1997 to the present.

Oshio has reported the coordination chemistry of imino nitroxide ligands bearing *N*-heterocyclic substituents, like pyridine (**1** and **2**) [8]. When two equivalents of **1** were reacted with [Cu(CH$_3$CN)$_4$]PF$_6$, the tetrahedrally coordinated homoleptic complex Cu(**1**)$_2^+$ was obtained in which the magnetic coupling between imino nitroxides through the copper center was strongly ferromagnetic ($J = +55$ cm^{-1}). An interesting charge-transfer mechanism was described to explain the stabilization of the triplet state. A silver complex containing two equivalents of bidentate **2** has also been reported, but the magnetic interactions were much weaker. Other coordination complexes of **2**, having the general structural formula M^{II}Cl$_2$(**2**)$_2$ (M = Mn, Co, Ni, Zn), have been reported by Kaizaki [9]. The nickel or cobalt complexes exhibited ferromagnetic metal-radical exchange interactions ($J_{\text{M-rad}}$ = +95 and +14.9 cm^{-1} for the nickel and cobalt complexes, respectively), and antiferromagnetic coupling is observed with the manganese complex ($J_{\text{M-rad}}$ = –23.8 cm^{-1}). The spins of the coordinated radicals experience weak antiferromagnetic coupling through the central metal ion ($J_{\text{rad-rad}}$ = –9 cm^{-1}).


R = Me **1**
H **2**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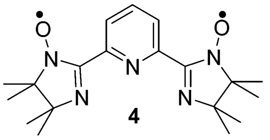
Other imino nitroxide radicals, including biradicals **4** and **5** have been reported by Oshio [10a–d]. A number of transition-metal complexes with these ligands have been structurally and magnetically characterized. These include nickel, copper, and zinc complexes of the general formula M^{II}(**4**)Cl (M = Cu, Zn), or [M^{II}(**4**)$(\text{H}_2\text{O})_2$Cl]Cl (M = Ni), as well as some unusual silver complexes with ligand **5**. In general, **4** coordinates as a tridentate ligand, and strong ferromagnetic metal-radical exchange interactions are observed in the copper and nickel complexes ($J_{\text{M-rad}}$ = +120 and +165 cm^{-1} for nickel and copper complexes with **4**, respectively).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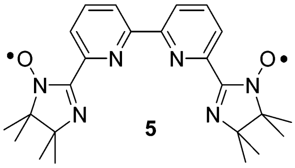
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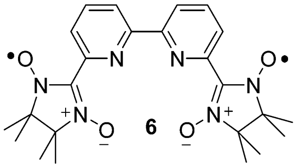
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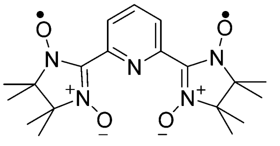
Ziessel and Luneau have reported a number of complexes containing the interesting tetradentate nitronyl nitroxide biradical **6** [7c,d]. Manganese, iron, cobalt, nickel, copper, and zinc(II) complexes with **6** have been crystallographically characterized. In each structure, the four equatorial coordination sites of the metal are occupied by ligand **6**; axial coordination positions are occupied by counterions (generally ClO_4^-), or water molecules, affording octahedrally coordinated metal complexes. The sign and magnitude of the metal-radical exchange coupling in these complexes is dependent on the planarity of the O–N–C–N–O unit with respect to the equatorial plane of the metal. For example, in a nickel complex with **6**, both ferro- and antiferromagnetic nickel-radical couplings were observed due to orthogonality of one radical unit with the nickel center, and overlap with the other ($J_{\text{M-rad}}$ = +39.6 and –48.7 cm^{-1}).

Other recently reported chelating nitronyl or imino nitroxide ligands include **7**, **8**, and **9** [11a,b]. Biradical **7** behaves as a tridentate ligand, and when reacted with metal perchlorates, generated a series of metal complexes of the general formula [M^{II}(**7**)$_2$]$(\text{ClO}_4)_2$· × S (M = Mn, Co, Ni, Cu, Zn), in which four nitroxide units are directly bound to each metal center. To decipher the observed magnetic behavior of these complexes, the authors incorporated two intramolecular exchange terms in the Hamiltonian. In addition to the strong metal-radical magnetic interactions, the exchange coupling between radicals through the central pyridine ring of **7** is also significant.

Ligands **8** and **9** were the first reported examples of radical-substituted 2,2′:6′,2″-terpyridine ligands. Reaction of tridentate **8** or **9** with $\text{M}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ afforded coordination complexes of the general formula [M(**8**)$_2$]$(\text{ClO}_4)_2$· × S (M = Ni, Cu, Zn for **8** and Ni, Zn for **9**). Considering the long distance between the spin carriers in these complexes, rather strong metal-radical exchange couplings were observed (e.g., $J_{\text{M-rad}} = -7.9$ cm^{-1} for the copper complex with **8**). The intervening orbitals of the ligand's central pyridine ring are thought to mediate the coupling.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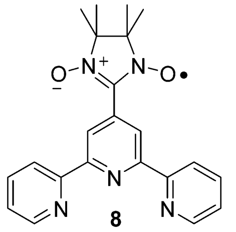
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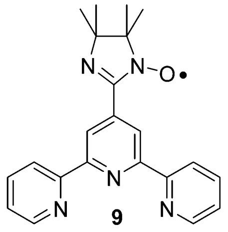
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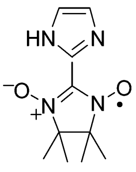
Other metal-nitroxide chelating strategies have been implemented rather successfully by Luneau and Rey using imidazole-substituted nitroxide ligands **10** (NITImH) and **11** (NITBzImH) [2i,j,12].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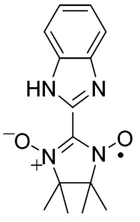
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Reaction of three equivalents of **10**, for example, with $M^{II}(ClO_4)_2 \cdot 6H_2O$ (M^{II} = Ni, Mn, and Zn) produced the first ever metal-nitronyl nitroxide homoleptic complexes having the formula [M(**10** or **11**)$_3$](ClO$_4$)$_2$. In all cases, the first coordination sphere of the metal contained only chelated radical ligands, exhibiting strongly antiferromagnetic metal-radical interactions ($-111 < J < -53$ cm^{-1}). Subsequent investigations have focused on using ligands **10** and **11** to generate coordination polymers. Deprotonation of the imidazole substituent of NITImH radical and subsequent coordination to a manganese(II) center, for example, has led to one-dimensional coordination polymers, such as [Mn(NITIm)(NITImH)]ClO$_4$ **12**, that magnetically order at 5 K (Fig. 1). Furthermore, the coordination sphere of **12** offered a metal-free protonated NITImH radical, and **12** represented a one-dimensional precursor to a two-dimensional array by deprotonation and coordination of the unionized pendant ligand.

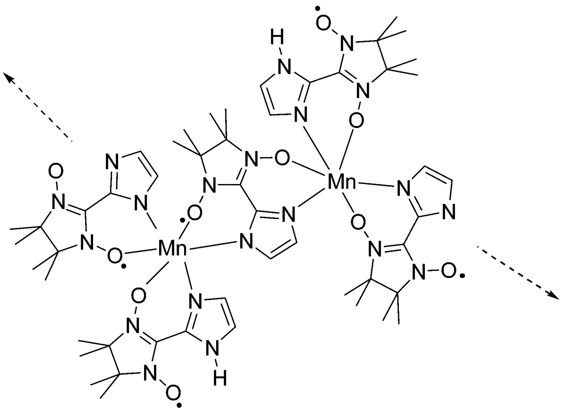


Fig. 1 Schematic of a fragment of the one-dimensional chain **12**.

Rey and Luneau have subsequently reported the preparation of the two-dimensional complexes $[Mn_2(NITIm)_3]ClO_4$ **13** and $[Mn_2(NITBzIm)_3]ClO_4$ **14**. The solid-state structure of **13** consists of two-dimensional honeycomb-like layers that are separated from each other by 10.32 Å (Fig. 2); the structure of **14** has not yet been reported (**13** and **14** are presumed to be isostructural). Ferromagnetic ordering in both complexes was indicated by magnetization experiments, but at significantly different temperatures (below 1.4 and 40 K for **13** and **14**, respectively); the result of slight structural differences between **13** and **14**. Nonetheless, the high T_c's generated by these complexes have demonstrated the utility of metal-radical coordination chemistry toward magnetic materials. Whether these values will be improved with other complexes containing current nitroxide structural motifs is unclear.

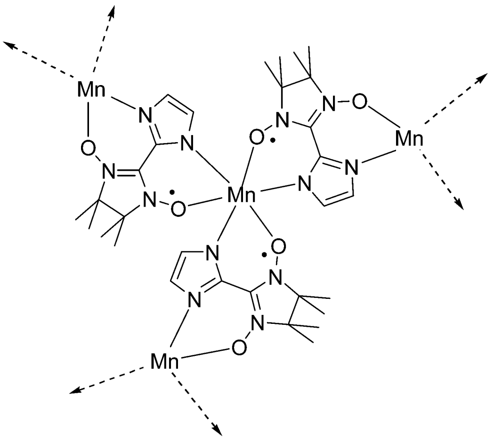


Fig. 2 Schematic of a unit of the two-dimensional layered structure of **13**.

Optical investigations of metal-nitroxide complexes

Photoinduced magnetization in iron-cobalt cyanide complexes, the control of intramolecular magnetic exchange coupling in diarylethene-substituted nitroxide biradicals by photoswitching, and the LIESST effect in iron(II) spin crossover materials are a few of the elegant studies from the research groups of Sato, Irie, and Real among others, which illustrate the enormous potential for creating materials with novel magnetic and optical properties [13a–h]. These materials offer themselves as potential precursors to more advanced molecular materials that may one day have practical applications for data storage, for example. Metal-radical complexes are another class of magnetic molecules that are just beginning to be investigated for their optical properties. Stable free-radical ligands usually exhibit distinct visible absorption bands (resulting in highly colored molecules), and these absorptions tend to remain intact in the resulting metal complexes. In addition, transition-metal and lanthanide complexes of closed-shell ligands have very well-known optical properties due to metal-centered d-d or f-f electronic transition as well as charge-transfer absorptions. It is, therefore, rather surprising that so few accounts focused on optical studies of metal-radical complexes have been reported. The following contributions from the groups of primarily Kaizaki, Luneau, and Reber represent the current state of spectroscopic investigations of metal-radical complexes.

Kaizaki has reported the spectroscopic behavior of discrete complexes consisting of bis(β-diketonato)chromium(III) or nickel(II) centers and chelated nitronyl nitroxide radicals in detail [14a–c]. This research has focused on attempting to quantify a Hammett-type correlation between the substituents on the β-diketone ancillary ligands with the magnitude of the antiferromagnetic intramolecular exchange coupling and with the changes in the intensity of spin-forbidden d-d transitions in the absorption spectra of the complexes. They have since expanded these investigations to lanthanide complexes of pyridine-substituted imino **2** and nitronyl nitroxide radicals **3** [15]. These complexes are of the form

[Ln(hfac)$_3$(**2** or **3**)], where Ln = Y, Nd-Lu, and contain a chelated molecule of **2** or **3**. The UV–visible spectra of these complexes featured a red-shifted absorption band (n-π*) that is also more intense and more structured relative to the uncoordinated radical **2**. Excitation into the f-f absorption bands of europium(III) and terbium(III) complexes with nonradical ligands generally results in sharp luminescence [16]. However, emission from the europium(III) and terbium(III) tris(hfac) complexes with **2** following excitation into their f-f absorption bands was completely quenched as a result of overlap between the Ln(III) excited energy levels with the nitroxide-centered n-π* level. On the other hand, a sharp emission centered at approximately 615 nm was observed from the europium(III)-**2** complex [but not from the analogous terbium(III) complex] upon excitation into a presumably hfac-based charge-transfer absorption band centered at 222 nm. Evidently, the excited levels of europium(III) and the ground-state energy levels of **2** do not overlap in energy as they do in the other complex in which the emission was quenched.

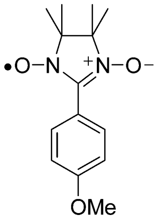
Reber and Luneau have investigated other lanthanide complexes of nitronyl nitroxide radicals [17a,b]. For example, benzimidazole-substituted nitroxide radical **11** complexes of formula Ln(III)(**11**)$_2$(NO$_3$)$_3$ [Ln(III) = La, Gd, Eu] were prepared and photophysically investigated. In the free ligand, luminescence at approximately 720 nm was observed at 50 and 5 K using excitation wavelengths between 300 to 400 nm. In all three lanthanide complexes of **11**, luminescence was observed that was slightly red-shifted, more intense, and more resolved than in the free ligand. The luminescence of the lanthanide complexes also occurred in an energy range approximately similar to the free ligand, and so was described by the authors as ligand-centered, in contrast to the lanthanide-centered luminescence observed by Kaizaki that was described previously. The changes in the position, intensity, and structure of the emission band upon coordination were ascribed to the influences of metal-ligand bonding in the complexes relative to the free ligand.

Revisiting one-dimensional metal-nitroxide chain complexes

Nitronyl nitroxide radicals contain two π-basic N–O groups in their structure. These moieties act as anchors for metal coordination, and can in fact bridge together two metal centers. A number of one-dimensional chain complexes have been prepared by combination of M(hfac)$_2$ with a variety of different nitronyl nitroxide radicals—these chains afforded the first examples of magnetically ordered materials obtained by metal-radical coordination chemistry [2a,c–d]. However, interchain magnetic interactions tend to be very weak appearing only at cryogenic temperatures and T_c's are generally very low. As a result, the focus of metal-nitronyl nitroxide coordination chemistry through the 1990s shifted away from one-dimensional materials. These efforts have very recently been "revived" with the publication of several studies investigating very interesting magnetic and magneto-chiral properties that are a *direct result* of the one-dimensional nature of these complexes; these reports are summarized below.

As early as 1963, Glauber pointed out that one-dimensional Ising ferri- or ferromagnetic materials could exhibit slow relaxation of their magnetization, provided the material was truly one-dimensional in the sense that magnetic interactions within the chain were much stronger than those between chains [18]. Reorientation of the magnetization becomes more difficult with decreasing temperature because parallel spin alignment is favored by spin correlation along the chains, and accordingly, the height of the barrier to magnetization reversal should scale with the nearest-neighbor exchange coupling. Gatteschi has recently discovered a chain complex containing Co(hfac)$_2$ and nitronyl nitroxide **15** that for the first time experimentally confirmed Glauber's prediction [19]. The structure is similar to other reported M(hfac)$_2$-nitronyl nitroxide complexes, consisting of alternating Co(hfac)$_2$ and radical units assembled together in a one-dimensional helix resulting from the trigonal crystallographic symmetry. The magnetic susceptibility of this chain complex is highly anisotropic (g_{Co} = 7.4) below 50 K and measurements in the ac mode confirmed Glauber's early prediction: Slow magnetization relaxation as well as hysteresis effects are observed that are not the result of three-dimensional magnetic ordering [20]. The barrier to magnetization reversal was calculated to be 154(2) K, very close to the cobalt-radical exchange coupling ($J = 220$ K) obtained by modeling the susceptibility vs. temperature data. These results highlight the potential that one-dimensional chain complexes may hold as "molecular magnetic nanowires" for information storage on the molecular level.

The combination of chirality and magnetism in other helical one-dimensional metal-nitroxide complexes has been investigated very recently by Luneau, Veciana, and Inoue [21a–c]. These studies involve the preparation of fully chiral molecular magnetic materials by, for example, incorporation of an asymmetric center into the structure of the radical ligand. Investigations like these are fueled by the quest for new magneto-chiral materials that could exhibit novel properties that result from the interaction of chirality and magnetism. For example, Inoue prepared chiral bisnitroxide radical **16**, which assembles into a one-dimensional chain when mixed with Mn(hfac)$_2$. Two oxygen atoms from the aminooxyl substituents from two different molecules of **16** (the asymmetric carbon is in the *S*-configuration) are bound in *trans* sites to the octahedrally coordinated Mn(hfac)$_2$ unit forming the chain structure, which has a chiral *R*-helical structure. Solutions of this complex exhibited optical activity, and the low-temperature solid-state magnetic properties suggested a field-induced transition to a ferromagnetic state (metamagnetic behavior) below 5.4 K.



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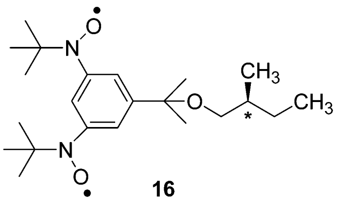

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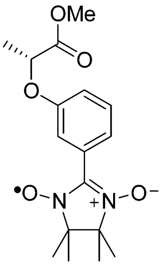
Luneau and Veciana have reported the structure and unusual magnetic behavior of a fully chiral metal-nitronyl nitroxide complex, containing the chiral radical ligand **17**. When coordinated to Mn(hfac)$_2$, a one-dimensional chain is generated in which each N–O unit from a single molecule of **17** is bound in a *cis* configuration to different molecules of Mn(hfac)$_2$ (the complex crystallizes in the chiral space group $P2_12_12_1$). Results from solid-state circular dichroism studies on samples of the complex and free ligand were similar, but the complex displayed a strong positive cotton effect at 460 nm, which the author's suggested could potentially be interesting for the observation of magneto-chiral phenomenon. Magnetization experiments confirmed the transition to a ferromagnetically ordered state at 3 K, below which very unusual dynamic magnetic behavior occurred, and an unusually strong uniaxially anisotropy that could be consistent with the special symmetry resulting from this magnet's chirality.



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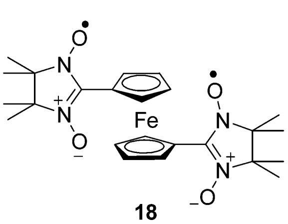

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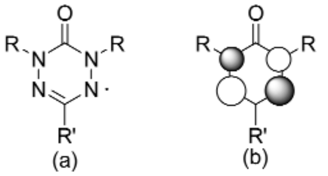
A method to generate chiral magnetic materials without having an asymmetric center anywhere in the molecule is through spontaneous resolution of the enantiopure complex upon crystallization. Veciana has observed just this behavior in a Mn(hfac)$_2$ coordination polymer with ferrocene-substituted bisnitronyl nitroxide radical **18**. The structure of this complex consists of octahedrally coordinated units of Mn(hfac)$_2$, each containing two *cis*-bound N–O units from different molecules of **18** forming a one-dimensional chain—of note, both enantiomorphous structures of this complex each contain seven sources of chirality! Undoubtedly painstaking and admittedly tedious separation of the enantiomorphous crystals, followed by measuring the circular dichroism spectrum of the hand-picked crystals (which contained the same enantiomorphic configuration at the manganese centers), proved the spontaneous resolution.

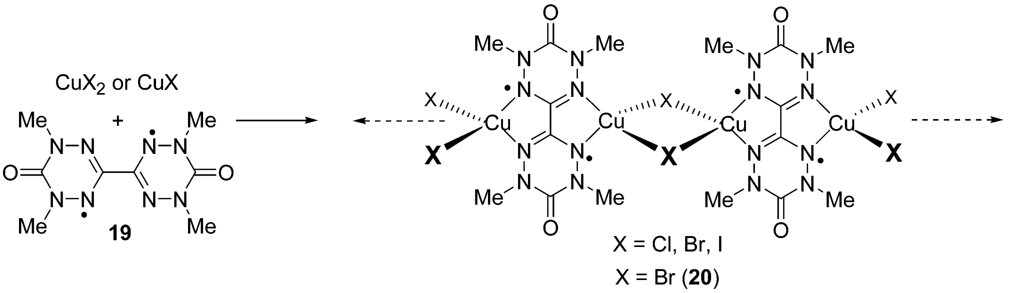
NEW "SPIN" ON AN OLD FAMILY OF RADICALS: COORDINATION CHEMISTRY OF VERDAZYL RADICALS

The first reports of verdazyl radicals appeared in 1963; a serendipitous discovery by Kuhn and Trischmann in an attempt to alkylate formazans [22]. Having a structure rich in donor atoms (Scheme 2), verdazyl radicals are π-radicals, and are stabilized mainly through delocalization of the spin over the four ring nitrogen atoms; R groups appended to the 1,5 positions of the verdazyl ring also contribute steric protection. A number of investigations that have been reported since these initial accounts have focused on the synthesis, electronic, and magnetic properties of these unusually stable free radicals [23a–j]. Despite offering a wealth of donor atoms amenable to metal coordination, as well as having a generally well-documented synthetic methodology, surprisingly, no reported transition-metal coordination complexes of verdazyl radicals had been published prior to 1997.



Scheme 2 General structure (a) and π-SOMO of a 6-oxo-verdazyl radical.

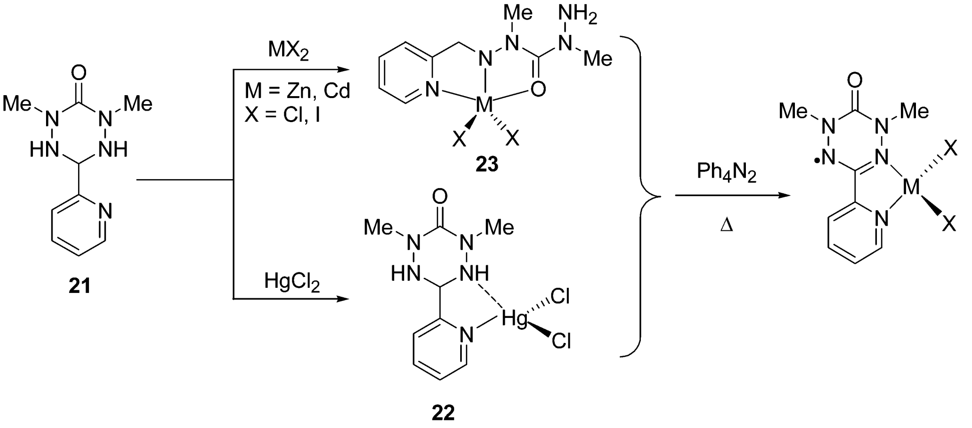
The first transition-metal complex of a verdazyl radical was reported in 1997 [24]. The group of Fox et al. presented the structures and electronic properties of a series of coordination complexes obtained by reaction of bisverdazyl **19** with copper(I) or (II) halides (Scheme 3). The bromide complex **20** was structurally characterized and found to consist of infinite one-dimensional chains made up of bisbidentate molecules of **19**, each with two copper(I) centers coordinated, and these units are linked together by bromide bridges. The chloride and iodide complexes were demonstrated by X-ray powder diffraction to share similar unit cell parameters as **20**, and in concert with other structural data, these complexes were presumed to share similar one-dimensional structures.



Scheme 3 Preparation of one-dimensional polymers of **19** with copper halides.

Variable-temperature magnetic susceptibility profiles for the three coordination polymers each contained broad features consistent with low-dimensional antiferromagnetic interactions. The data in each case was successfully reproduced with a one-dimensional alternating antiferromagnetic chain model with two exchange parameters J_1 and J_2. The strongest interaction in all cases J_1 was between spins on the same ligand. The unit cell packing of bromide-bridged complex **20** indicated substantial π-overlap between verdazyl rings from adjacent chains, and another exchange parameter between chains (J_2) was incorporated. Interactions between verdazyls through the Cu–Br–Cu bridges were presumed to be negligible and ignored. Intraligand J_1 was strongest for the iodide complex (–271 cm^{-1}), and comparable for the other two polymers (–190 and –200 cm^{-1} for the chloride and bromide, respectively). Exchange between stacked verdazyls was also strongest for the iodide complex (–200 cm^{-1}), and weaker for both the chloride (–116 cm^{-1}) and bromide complexes (–110 cm^{-1}).

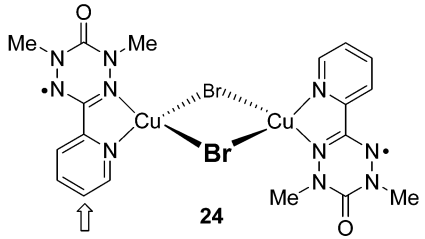
Brook has subsequently reported the coordination chemistry of pyridine-substituted verdazyl precursor **21** with group **12** halides [25]. Combination of **21** with mercuric chloride (Scheme 4) resulted in complex **22**, which was structurally characterized. When reacted with cadmium or zinc(II) halides, ring-opening of **21** was observed, and a cadmium complex of hydrazone **23** was structurally characterized (Scheme 4). In an attempt to prepare the analogous radical complexes, **21** was combined with tetraphenylhydrazine in an electron paramagnetic resonance (EPR) tube, followed by addition of the particular group **12** metal halide; alternatively, complexes **22** or **23** were treated with tetraphenylhydrazine. Metal coordination of the verdazyl radical was suggested in all cases by UV–visible and EPR spectroscopies, however, none of the complexes could be isolated for structural or magnetic characterization.



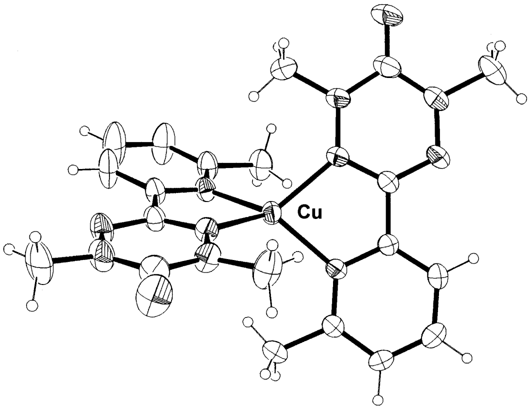
Scheme 4 Reaction of **21** with group 12 metal halides, and subsequent oxidation with tetraphenylhydrazine to generate metal-radical complexes.

In another report by Brook, combination of verdazyl precursor **21** with CuBr resulted in precipitation of a dimeric bromide-bridged copper(I) complex **24** containing a pyridine-substituted verdazyl [26]. Oxidation of the tetrazane was apparently aided by the presence of a transition-metal source. This is probably accomplished by metal coordination, oxidation by aerial O_2, and then precipitation of the copper-verdazyl complex. Exchange coupling through the bromide bridges was assumed to be negligible, and the magnetic data from **24** was fitted to an antiferromagnetic chain model with $J = -5\ \text{cm}^{-1}$; the use of a chain model was justified on the basis of overlap between pyridine and verdazyl rings from adjacent molecules of **25** observed in the crystal packing.

Recent work by Brook has focused on EPR studies of the spin distribution in copper(I) phosphine or phosphite complexes with verdazyl **25** [27]. Molecular orbital arguments were used to explain a correlation between the donor strength of the ancillary ligands with the magnitude of spin density trans-



ferred to the copper nuclei: Strong phosphine donors, or small bite angle chelating diphospines generated orbital interactions involving filled copper d-orbitals, while weak donor ancillary ligands resulted in interactions through an empty copper p-orbital—however, each mechanism resulted in larger copper(I) hyperfine coupling constants. In other copper(I)-verdazyl coordination chemistry, Hicks has reported the exchange coupling between coordinated verdazyl radicals **26** through a diamagnetic copper(I) center (Fig. 3) [28]. Variable-temperature magnetic susceptibility data indicated very weak antiferromagnetic exchange is mediated by the metal in this complex (J_{vdvd} = –2 cm^{-1}), in contrast to the analogous iminonitroxide complex describe in an earlier section of this review. In a recent article by Brook, DFT calculations suggested a triplet ground state (J = +56 cm^{-1}) for Cu(**26**)$_2$$^+$; the discrepancy between theory and experiment was ascribed to strong intermolecular interactions [29].

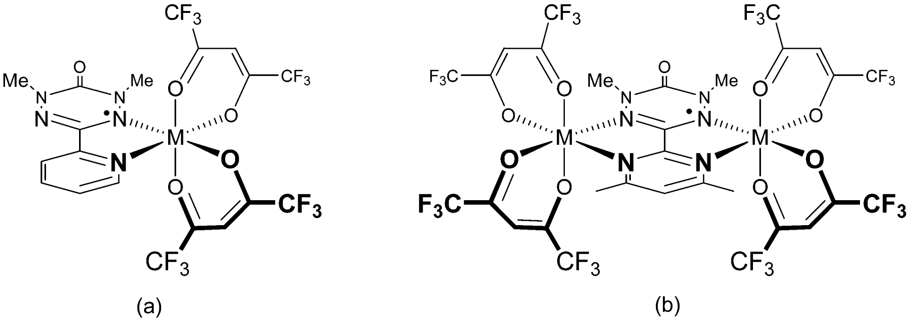


(26)

Fig. 3 Molecular structure of a copper(I) complex containing verdazyl **26**.

While the preceding compounds marked the first reported metal-verdazyl complexes, the metal centers were in all cases diamagnetic, and this precluded any *metal-verdazyl* exchange interactions. With regard to the preparation of magnetic materials, we were interested in the study of discrete coordination complexes of verdazyl ligands with *paramagnetic* transition-metal centers so that we could elucidate the type and strength of any metal-verdazyl exchange.

The first reported verdazyl complexes with paramagnetic transition-metal ions were the M^{II}(hfac)$_2$ (M = Mn, Ni) complexes with ligand **25** (Scheme 5) reported by Hicks [30]. Preliminary X-ray crystallography confirmed the structures as molecular *cis*-pseudooctahedral complexes containing one chelating molecule of **25**. Of note, the verdazyl binding configuration in these complexes is structurally analogous to 2,2′-bipyridine coordination—in this regard, **25** is a structural mimic of bipyridine. The demonstrated richness and diversity of bipyridine coordination chemistry augurs well for the metal binding abilities of **25**. Variable-temperature magnetic susceptibility studies of these complexes



Scheme 5 M(hfac)$_2$ (M = Mn,Ni) complexes with verdazyl **25** (a), and bimetallic complexes with verdazyl **27** (b).

indicated very strong ferromagnetic nickel-verdazyl exchange coupling ($J_{\text{Ni-vd}}$ ~ ≥ +240 cm^{-1})—a lower limit had to be imposed on the exchange coupling constant because thermal population of only the ferromagnetically coupled state (S = 3/2) is observed down to 80 K. The manganese complex exhibited weaker antiferromagnetic exchange ($J_{\text{Mn-vd}}$ = –45 cm^{-1}). Strong ferromagnetic nickel-verdazyl exchange is likely the result of the large amount of spin density on the coordinating verdazyl nitrogen atom (a_{N} = 6.5 G), combined with magnetic orbital orthogonality: Formally d$_z$2 and d$_{x}$2$_{-y}$2 for octahedral nickel, and the verdazyl π-system. Antiferromagnetic manganese-verdazyl exchange results from dπ-pπ overlap between manganese based t$_{2g}$ orbitals and the verdazyl π orbital.

Hicks has extended these studies and reported the preparation of bimetallic complexes containing pyrimidine-substituted verdazyl **27** [31]. In each case, two molecules of M$^{\text{II}}$(hfac)$_2$ (M = Mn, Ni) were coordinated to the bisbidentate ligand, generating the bimetallic complexes. The molecular structure of the manganese complex is shown in Fig. 4, the gross structural features of which are similar to those observed in the analogous monometallic complex. The magnetic properties of these complexes were also similar to the mononuclear congeners: Nickel-verdazyl exchange was strongly ferromagnetic ($J_{\text{Ni-vd}}$ ~ ≥ +240 cm^{-1}), and exchange coupling in the manganese complex was weaker and antiferromagnetic ($J_{\text{Mn-vd}}$ = –45 cm^{-1}).

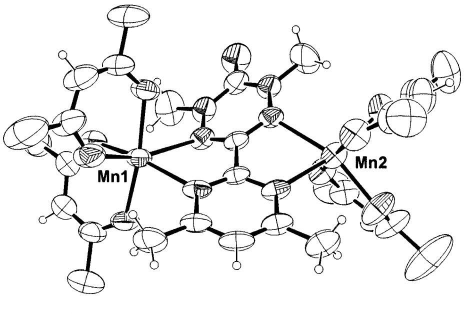
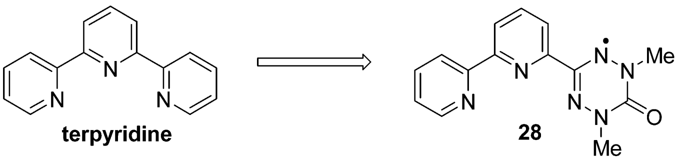


Fig. 4 Molecular structure of (hfac)$_2$Mn**27**Mn(hfac)$_2$.

Recent reports by Hicks have focused on investigating this apparent structural analogy between chelating verdazyl radicals and oligopyridine ligands [32a,b]. Verdazyl **28**, bearing a bipyridine substituent, was synthesized, and as such is a structural mimic of 2,2′:6′,6″-terpyridine (Scheme 6).



Scheme 6 Structural relationship between verdazyl **28** and terpyridine.

A series of monometallic coordination complexes of the form [M(**28**)$_2$](X$^-$)$_2$ [M(II) = Mn, Ni, Cu, Zn; X$^-$ = PF$_6$, ClO$_4$] were prepared and were all structurally characterized. In each case, pseudo-octahedral complexes were obtained containing two tridentate molecules of **28** bound in a meridonal geometry, nearly perpendicular to one another (the molecular structure of nickel complex is shown in Fig. 5)—these complexes are structurally analogous to reported metal-terpyridine systems [33]. In line with the magnetic behavior of previous nickel- or manganese-verdazyl coordination complexes, Ni(**28**)$_2^{2+}$ exhibited strong nickel-verdazyl ferromagnetic exchange (J = +240 cm^{-1}), while the metal-verdazyl exchange in the manganese analog was again antiferromagnetic (J = –93 cm^{-1}). The magnitude of the exchange between coordinated verdazyls through the diamagnetic zinc center was weakly antiferromagnetic. Of note, in contrast to predictions using magnetic orbital symmetry rules, copper(II)-verdazyl exchange coupling in complex Cu(**28**)$_2^{2+}$ is weakly antiferromagnetic! Structural analysis of Cu(**28**)$_2^{2+}$ indicated long coordinate bonds between the copper center and the verdazyl ring (2.347 and 2.330 Å; approximately 0.05 to 0.1 Å longer than those in the other three complexes), which could be a contributing factor for the weakened exchange interaction relative to the other complexes. Clearly, other copper(II)-verdazyl coordination complexes should be investigated in order to better understand this unusual magnetochemistry.

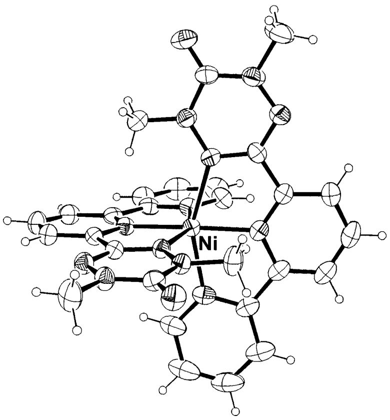


Fig. 5 Molecular structure of Ni(**28**)$_2^{2+}$.

Another interesting verdazyl ligand prepared in the Hicks' laboratory is carboxylic acid substituted verdazyl **29** [34]. The coordination chemistry of **29** was investigated in aqueous solution and two complexes have so far been reported. Charge neutral nickel or cobalt(II) complexes were generated by combining MCl$_2$•6H$_2$O with the verdazyl radical precursor in aerated aqueous solutions, as observed by Brook in the preparation of complex **20**. Complexes Ni(**29**)$_2$ and Co(**29**)$_2$ are structurally analogous and consist of two molecules of **29** bound *trans*, in an *anti* configuration around the metal's equatorial plane (Fig. 6). Two molecules of water occupy the axial coordination positions, filling out the remainder of the metal's coordination sphere.

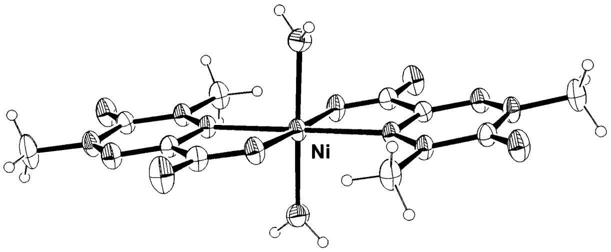
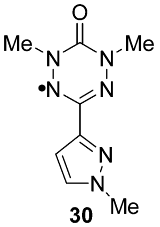


Fig. 6 Molecular structure of Ni(**29**)$_2$(H$_2$O)$_2$.

The magnetic properties of these complexes were also reported, with Ni(**29**)$_2$ exhibiting strong nickel-verdazyl exchange coupling (J = +94 cm^{-1}). The magnetochemistry of cobalt(II) complexes is difficult to elucidate as a result of unquenched orbital angular momentum in the $^4T_{2g}$ ground state, not to mention the added complexity of exchange coupling in cobalt-radical complexes. However, Hicks' preliminary data fitting indicated ferromagnetic cobalt-verdazyl interactions are operative in Co(**29**)$_2$ (J = +34 cm^{-1}); but this analysis is admittedly topical, and further investigation is needed in this regard. Data modeling for each complex also suggested rather strong interradical exchange coupling through the coordinated metal [$J_{\text{vd-vd}}$ = –21 in Ni(**29**)$_2$ and –19 cm^{-1} in Co(**29**)$_2$], a feature that is not shared by other verdazyl complexes. It is apparent that extended coordination architectures should be achievable, under the correct conditions, with verdazyl **29**, and efforts toward those ends are no doubt currently rearing fruit in the Hicks' research group.

The only other reported metal-verdazyl coordination compound is a Ru^{II}(bipy)$_2$ complex containing a methylated pyrazole-substituted verdazyl **30**, recently reported by Bouwman et al. [35]. Of interest, this complex exhibited a strong ^{1}MLCT absorption band in the visible spectrum (441 nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}), typical for [Ru(bipy)$_2$(NN)]$^{2+}$ complexes. Excitation into this absorption band did not, however, result in any emission, suggesting that the lowest-energy excited state has mostly verdazyl character.



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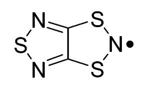
NEW STRUCTURAL MOTIFS IN STABLE RADICAL DESIGN AND FUTURE PROSPECTS

It is apparent that to advance the state of metal-radical coordination chemistry, it is absolutely necessary for the synthetic chemist to create new radical ligand structural types. Along this front, several researchers have reported new variations of known stable radicals, or other families of radicals whose coordination chemistry was hitherto unknown. Several metal coordination studies of these novel systems have also been initiated to investigate the feasibility of these radicals as ligands. These include Awaga's Cu(hfac)$_2$ polymeric complex with thiazyl radical **31**, in which both ferromagnetic and antiferromagnetic copper-radical couplings are observed as a result of differential binding of two **31** moieties to the copper center [36]. An orthogonal copper-thiazyl arrangement generates the ferromagnetic interaction, with an antiferromagnetic coupling between the other coordinated radical, which is tilted toward the Cu(hfac)$_2$ plane. Other π-radicals that have been investigated include Rubin's 2-azaphenalenyl radical

32, which can be extended to the 2,5-di- and 2,5,8-triaza derivatives by replacement of a –CH fragment with an isolobal –N atom—a strategy to engineer two- and three-dimensional metal-radical interactions [37]. Thus far, attempts to coordinate **32** to Cu(hfac)$_2$ have reportedly only led to the isolation of a complex containing the diamagnetic σ-dimer of **32** chelated to the metal center. Plater has prepared a series of 4,5-diazafluorene derivatives of Koelsch's free radical (**33**), and subsequent reaction with CuCl$_2$ has reportedly generated analytically pure metal-radical complexes, but which have not yet been structurally or magnetically characterized [38].



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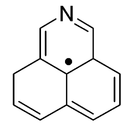

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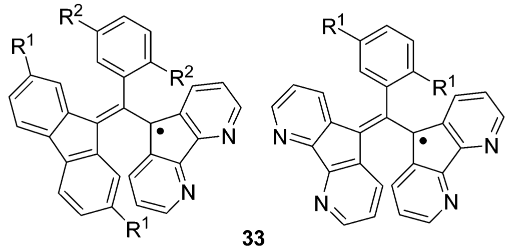

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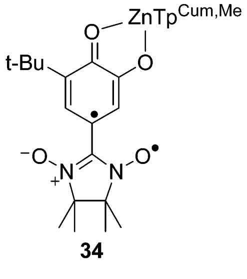
The synthesis and coordination chemistry of *spin diverse* ligands, those containing two or more different kinds of spin carriers per molecule, is another area of investigation underway in the group of David Shultz [39a–c]. In particular, the nitronyl nitroxide/semiquinone hybrid biradicals **34** and **35** prepared in Shultz's research group exhibited very strong intraligand ferromagnetic exchange coupling [$J_{\text{NN-SQ}}$ = > +300 and +100 cm^{-1}, for **34** and **35**, respectively; note that in these biradicals the semiquinone is stabilized by coordination to ZnTp$^{\text{Cum,Me}}$, where Tp$^{\text{Cum,Me}}$ = hydro-tris(3-cumenyl-5-methylpyrazolyl)-borate]: The coupling is so strong, in fact, that these systems may be treated as single $S = 1$ units. A series of coordination complexes were prepared and structurally characterized in which M(II)Tp$^{\text{Cum,Me}}$ (M = Mn, Co, Ni, Cu) groups were coordinated to the catechol fragments (the nitronyl nitroxide is uncoordinated), and aerial oxidation afforded the metal complexes of the semiquinone/nitronyl nitroxide biradical. The reported metal-radical exchange interactions were determined by variable temperature magnetic susceptibility experiments. The assembly of these interesting coordination complexes into chain structures by coordination of the nitronyl nitroxide end to M(hfac)$_2$ is an active area of investigation in the Shultz group. It should be noted that Weyhermüller has prepared other phenolate-substituted nitronyl nitroxide radicals and investigated their coordination chemistry [40]. All complexes yet reported with these ligands, however, exist only in the nitroxide-phenolate oxidation state, and are, therefore, not heterospin systems.



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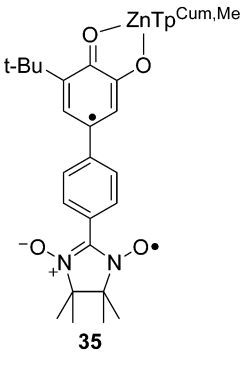

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An enormous amount of time and effort has been expended on the coordination chemistry of stable free-radical ligands. These investigations have provided a wealth of information regarding the structural and magnetic properties of these complexes, and magnetochemistry in general. Unfortunately, the number of stable radical families is limited in scope; however, versatile chemists, armed with keen imaginations and the tools of synthetic chemistry, will no doubt produce new radicals and improve on existing designs as they work toward functional magnetic materials.

ACKNOWLEDGMENTS

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