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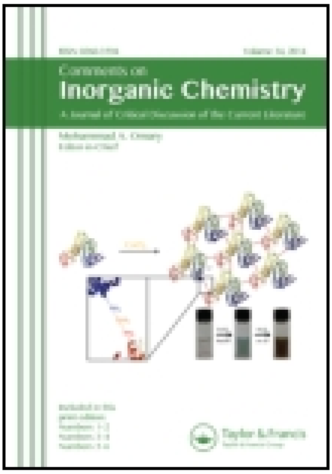

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Coordination Chemistry of Verdazyl Radicals

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Coordination Chemistry of Verdazyl Radicals

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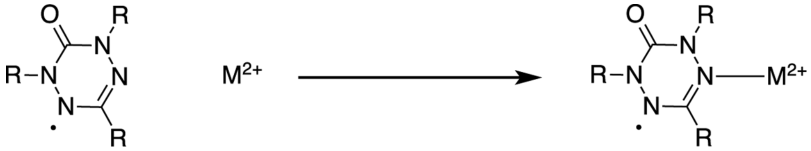

The past 17 years have seen the growth of the coordination chemistry of verdazyls—stable free radicals first reported in 1963. Though verdazyls are weakly basic ligands, the ability to synthesize derivatives with chelating substituents, along with the steric similarity of verdazyls to aromatic azine ligands, has resulted in a variety of coordination compounds. Coordination compounds have been reported with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{+}, Cu^{2+}, Zn^{2+}, Ru^{2+}, Ag^{+}, Cd^{2+}, Tb^{3+}, Dy^{3+}, Gd^{3+} and Hg^{2+}. These studies have resulted in observations of strong ferromagnetic exchange (up to $400\,cm^{-1}$), ligand-based redox processes, and non-innocent behavior. On the whole, verdazyls are weakly basic ligands in which the half-filled pi orbital can act as either an electron acceptor or an electron donor. The richness of the metal-verdazyl interaction, along with the structural diversity of verdazyls, provides many further opportunities for novel chemistry, as well as fertile ground for the introduction of undergraduates to research.

Keywords verdazyl, free radical, coordination chemistry

1. INTRODUCTION

The coordination chemistry of stable free radicals is an area that has seen much growth in the last 30 years. This is largely a result of interest in molecular magnetism and in understanding magnetic phenomena at a molecular

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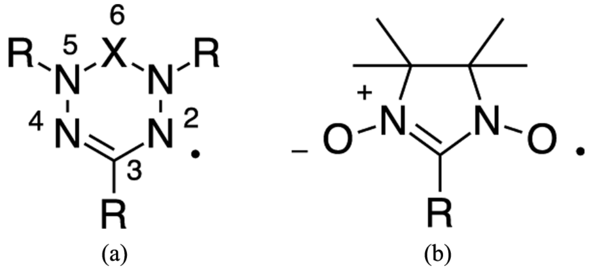


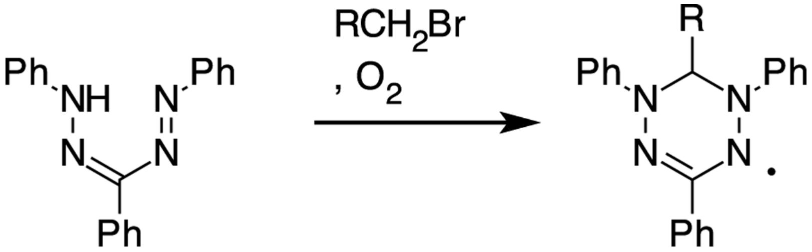
Figure 1: (a) General verdazyl structure and numbering scheme; (b) a nitronyl nitroxide for comparison.

level. Despite the increasing interest, radical ligands are few and far between, and most reported chemistry has utilized nitronyl nitroxides as spin-bearing ligands. Verdazyls (Figure 1) predate nitronyl nitroxides by five years[1] but, relatively speaking, have been neglected as ligands. Though the first coordination compounds of nitronyl nitroxides were reported in 1987,[2] it was 10 years later that we reported the first verdazyl coordination compound.[3] We provide here background on the verdazyl system and a review of the coordination chemistry of verdazyls reported by ourselves and others to the present day. We also comment on the contribution of undergraduate researchers to this interesting area.

Verdazyls were first reported by Kuhn and Trischmann in 1963 as products of alkylation and oxidation of formazans[1] (Scheme 1).

ESR shows nearly equal hyperfine coupling constants to all four nitrogen atoms in the ring, suggesting that all four resonance contributors shown in Figure 2 are nearly equally important. Molecular orbital calculations are also consistent with ESR with the unpaired electron occupying an orbital spanning all four nitrogen atoms but having a node at C3[4] (Figure 2). Because of this node, groups at C3 usually bear very little spin density, but it is the spin density on the imine nitrogen atoms at the 2 and 4 positions that makes verdazyls attractive as ligands for design of magnetic materials.

Though triphenyl verdazyls are remarkably stable, Kuhn noted in his intial reports that verdazyls are disproportionate at low pH (Scheme 2).[1,5]



Scheme 1: Synthesis of triaryl verdazyls.

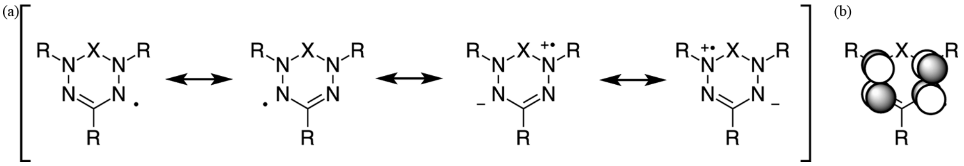
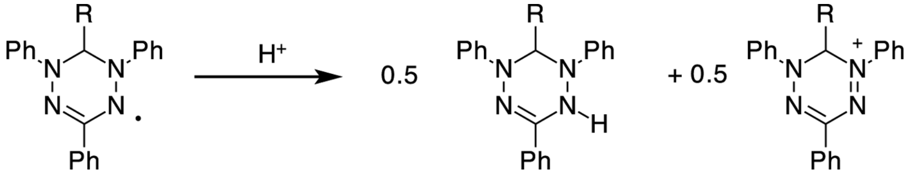
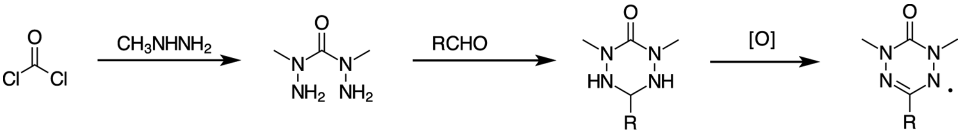


Figure 2: (a). Major resonance contributors to verdazyl structure; (b) shape of the verdazyl singly occupied molecular orbital (SOMO).



Scheme 2: Acid-induced disproportionation of triaryl verdazyls.



Scheme 3: Synthesis of 6-oxoverdazyls.

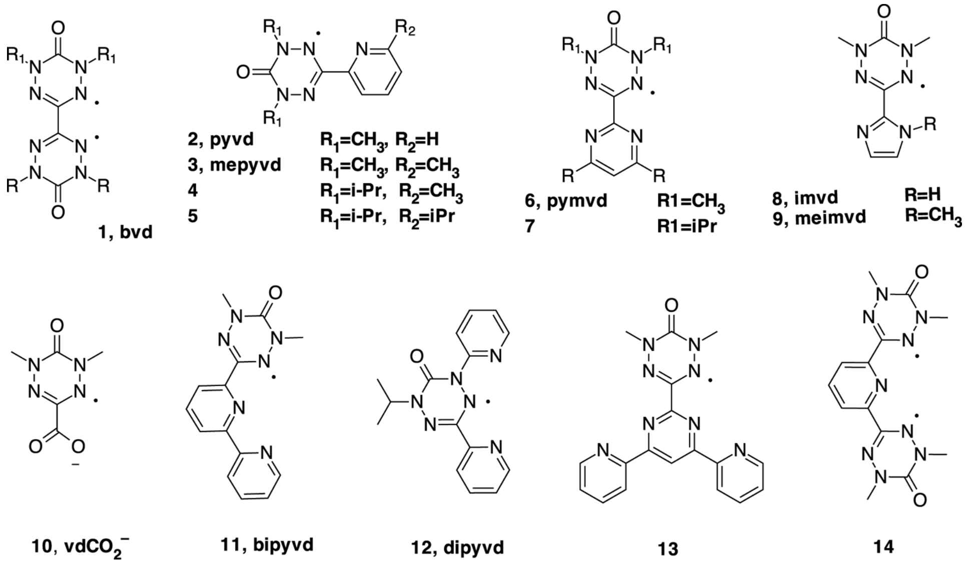


Figure 3: Structures of verdazyl ligands. Other chelating verdazyls are known(10) but coordination compounds of these have not been reported.

Thus, it is not too surprising that early attempts at coordination also resulted in disproportionation of the radical.[6,7] Much more recent electrochemical studies indicate that the electrode potentials for oxidation and reduction of these systems are relatively close,[8] facilitating this mode of decomposition. In 1980, Neugebauer reported the synthesis of 6-oxoverdazyls through reaction of alkylhydrazines with phosgene, followed by condensation with an aldehyde and subsequent oxidation to give the radical (Scheme 3).[9]

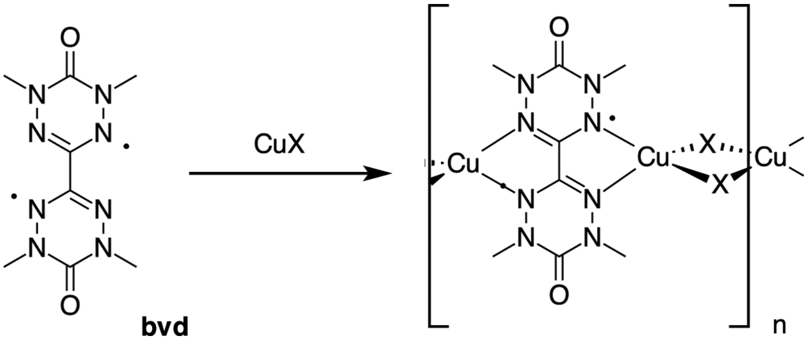
These radicals are significantly less prone to disproportionation; nevertheless, metal coordination compounds were not reported for another 17 years. Since our initial report, numerous verdazyl ligands have been reported. Structures of these are shown in Figure 3.

2. COPPER(I) COMPLEXES

The first metal complex of a verdazyl resulted from our combination of copper salts with the bis(6-oxoverdazyl) **(1, bvd)** reported by Neugebauer.[3] Though we initially tried combining **bvd** with several different transition metal salts, only copper gave coordination compounds in a straightforward manner. This illustrates a further point regarding 6-oxoverdazyls: they are not inherently very basic ligands. In any case, somewhat to our surprise, both copper(I) and copper(II) salts gave rise to copper(I) coordination polymers that typically precipitated as black, microcrystalline powders (Scheme 4).

The formation of only copper(I) complexes of **bvd** seems to be a result of oxidation of the verdazyl by Cu^{2+}. Using Cu^{2+} in methanol rather than Cu^{+}, polymer growth was sufficiently slowed such that single crystals of the bromide could be obtained, allowing a full structure determination (Figure 4).

Powder diffraction confirmed that the chloride was isostructural, while the iodide appears to have a similar structure but a distorted unit cell (from orthorhombic to monoclinic). The copper(I) systems provided an interesting start to verdazyl coordination; though copper(I) itself is diamagnetic, it has



Scheme 4: Coordination of **bvd** to copper(I) halides.

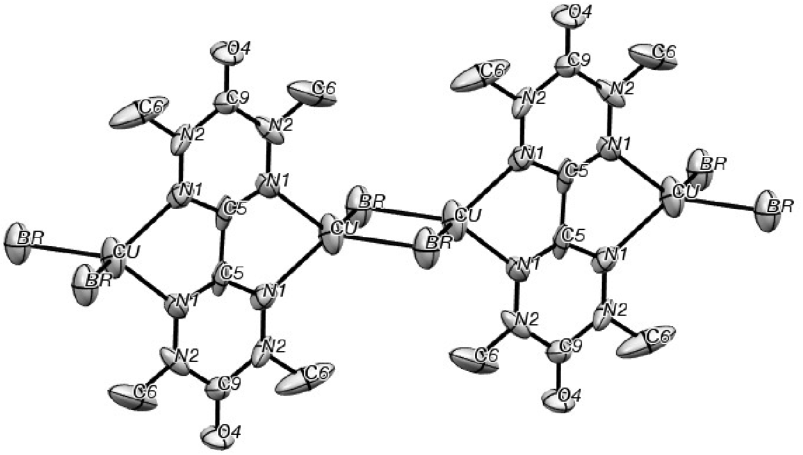


Figure 4: Thermal ellipsoid plot of a section of the (**bvd**)Cu_2Br_2 polymer.(3)

a significant impact on magnetic properties. In the free ligand, the radicals couple to give a singlet ground state, with an excited triplet 760 cm^{-1} above it.[11] Coordination to Cu(I) reduces this gap by providing an alternate ferromagnetic exchange pathway through the copper ion, dropping the intraligand exchange by $\sim$500 cm^{-1}. Coordination is also accompanied by a dramatic broadening of the ESR linewidth that may be associated with flexibility of the Cu(I) coordination geometry (*vide infra*) (Figure 5).

To better understand the metal ligand interaction, we looked for well-characterized discrete metal complexes to compare with the polymeric

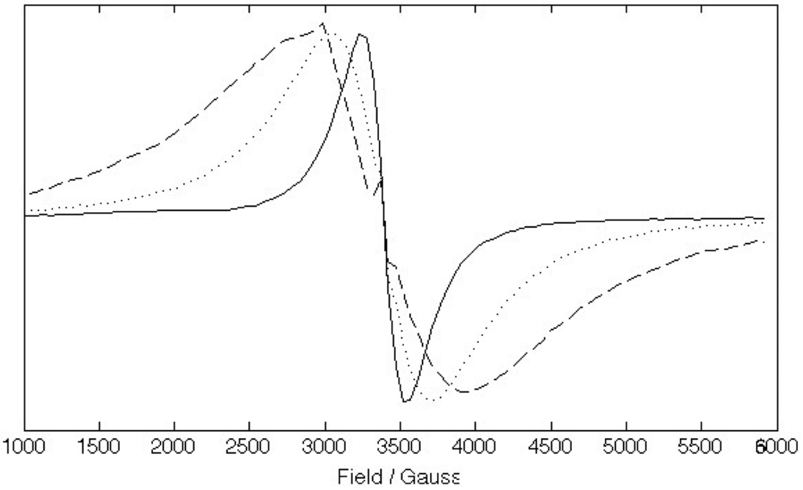


Figure 5: ESR spectra of Cu_2I_2(**bvd)** (solid line), Cu_2Br_2(**bvd)** (dotted line), and Cu_2Cl_2(**bvd)** (broken line), recorded as neat solid samples at 290 K.(3)

systems. In particular, the monoradical 3-(2′-pyridyl-1,5-dimethyl-6-oxoverdazyl) (**2, pyvd**) played an important role by removing the interfering radical-radical interaction. The synthesis of **pyvd** was first reported by Hicks,[12] while our group reported the coordination of Zn^{2+}, Cd^{2+}, and Hg^{2+} by **pyvd** in solution.[4] Both studies reported the rather unexpected result that, unlike other 6-oxoverdazyls, the ligand **pyvd** decomposes slowly at room temperature.[4,12] The reaction appears to be a disproportionation since one of the products is a leucoverdazyl, but the reason for the instability of this particular radical is still not clear.[12] Several approaches were used to get around the limited ligand stability. The most direct was to store the verdazyl at 77 K, but we also generated radical complexes by oxidation of the tetrazane in presence of a metal ion. In some cases, the metal ion also served as a catalyst for atmospheric oxidation of the tetrazane.[4,13] The Hicks group took an alternative approach, finding that oxidation of the tetrazane with benzoquinone gave a stable co-crystal with hydroquinone. The radical could be separated from this material by chromatography immediately before coordination experiments.[14] In any case, once coordinated to a metal center, the radical is significantly more stable.

Following up on our work with the bisverdazyl **bvd**, one of our first products with the **pyvd** ligand was a bromide bridged dimeric copper complex[13] (Figure 6).

This complex, while magnetically rather uninteresting, provides important evidence supporting our earlier assumption that magnetic exchange across the halogen bridge was weak. A second series of experiments involved the synthesis of mixed ligand verdazyl-copper(I)-phosphine complexes.[15] These species were not isolated, but could be characterized in solution by electrospray MS, UV-vis, and ESR. In particular, both ESR and UV-vis showed spectral changes that can be correlated with the phosphine structure. All of

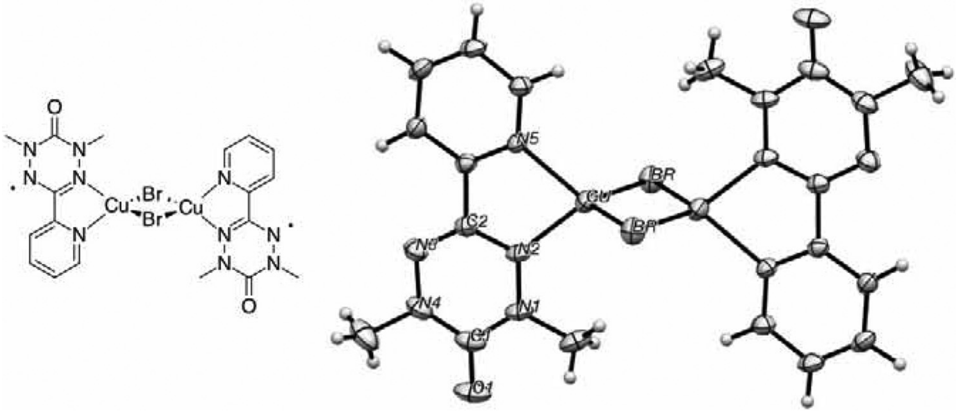


Figure 6: Structure and thermal ellipsoid plot for Cu_2(**pyvd**)$_2$$Br_2$.(13).

the species showed coupling to copper(I) and phosphorus atoms in the ESR, coupling being stronger with chelating and more electron-donating phosphines. These changes suggest a charge transfer interaction from the metal to the ligand SOMO that transfers spin density onto the metal.

The electronic spectra of 3-arylverdazyls typically show two overlapping bands in the visible region centered around 420 and 500 nm. Though we initially misidentified the latter, subsequent work indicated that the long wavelength band corresponds to transition of an electron into the radical SOMO.[4,16] Coordination of the verdazyl to the copper-phosphine unit is associated with a red shift in this band that correlates with the stronger hyperfine coupling to copper. Together this suggests that the verdazyl is acting as a pi acceptor and the long wavelength band is taking on some MLCT character depending upon the electron-donating ability of the phosphines (Figure 7).

With a half-empty pi orbital, verdazyls can also act as pi donors, and this was illustrated through the copper(I) complex of pyvd and triphenyl phosphite. This system has a relatively large spin density on copper by ESR, but the UV-vis is blue-shifted rather than red-shifted. In this case, we reasoned that the phosphite ligands increase the pi acidity of the copper(I) 4*p* orbital such that the charge transfer interaction is reversed; spin density is donated directly from the verdazyl SOMO into the empty copper(I) *p* orbital.

The homoleptic complex $[\mathrm{Cu}(\mathbf{pyvd})_2]^+$ has a UV spectrum very similar to that of the Cu(**pyvd**)(dppe) system (Figure 7), suggesting the former also has significant spin density on copper. This observation, combined with

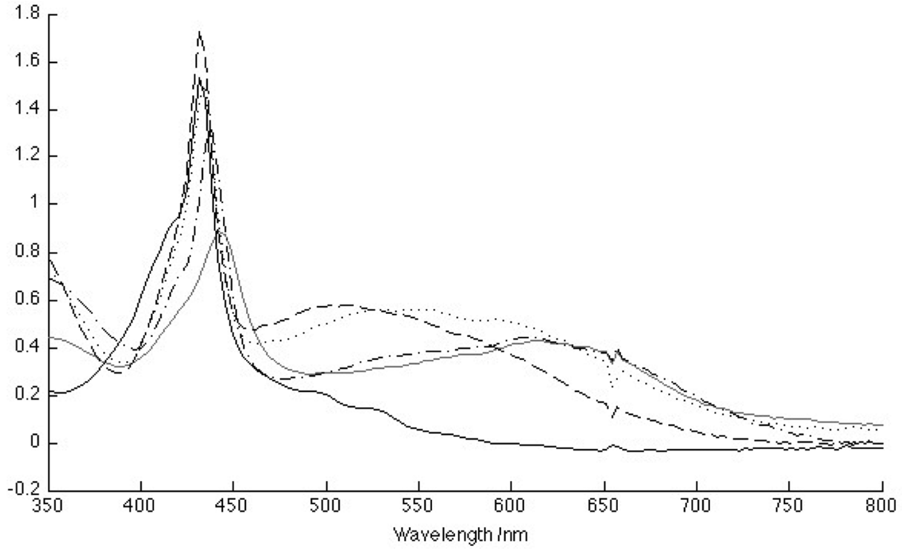


Figure 7: Visible spectra of Cu(**pyvd**)(phosphine) species, (approx 0.4 mM in acetonitrile): Cu(**pyvd**)$_2$ (grey), Cu(pyvd)(triphenyl phosphite)$_2$, (–), Cu(**pyvd**)(tri-*p*-tolylphosphine)$_2$ (—), Cu(**pyvd**)(dppb) (....), Cu(**pyvd**)(dppe) (-.-.).(15)

an established, metal-mediated, ferromagnetic exchange pathway in the case of the **bvd** complexes, and the existence of an analogous imino nitroxide that shows strong radical-radical exchange,[17] prompted us to expect strong inter-ligand magnetic exchange in [Cu(**pyvd**)$_2$]$^+$ and related systems. Surprisingly, however, that was not the case. Hicks and co-workers reported the homoleptic compound [Cu(**mepyvd**)$_2$]$^+$,[18] which shows a very small separation between singlet and triplet states, despite showing other spectroscopic signs of strong metal-radical interaction. These include the aforementioned strong red shift of the UV-vis spectrum, and severe broadening of the ESR line that was associated with metal coordination in **bvd.** The structure of the **mepyvd** system,

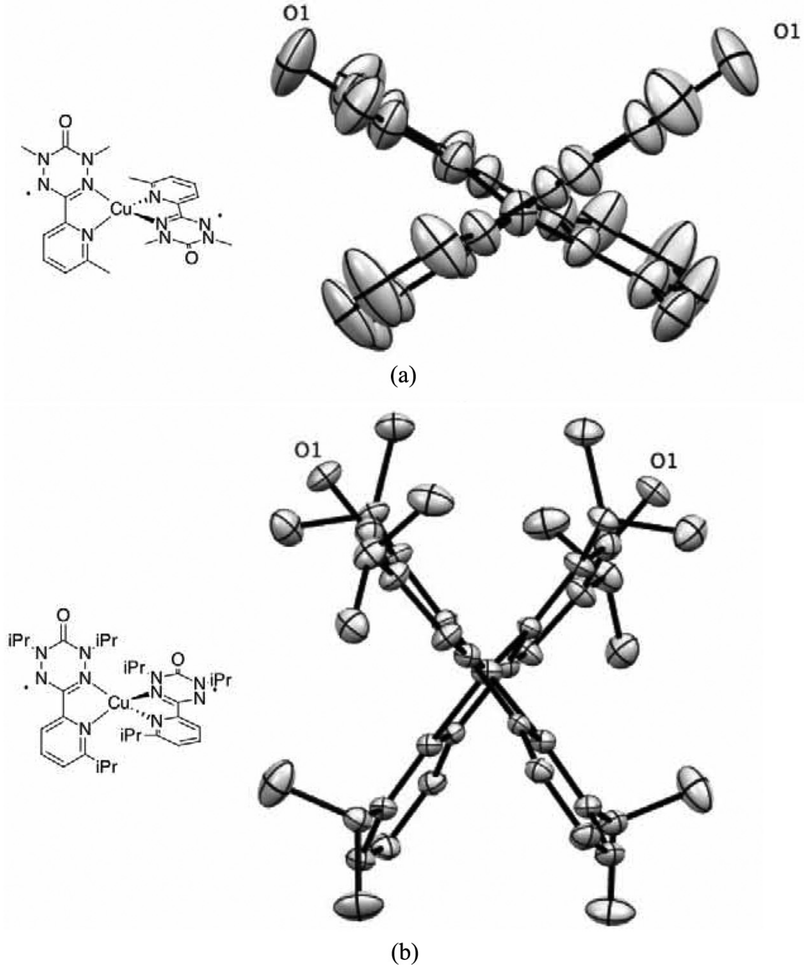


Figure 8: Cu(I) complexes of subtituted pyridylverdazyl ligands. (a) [Cu(**mepyvd**)$_2$]$^+$; dihedral angle between verdazyl rings 116°[18]; (b) [Cu(**5**)$_2$]$^+$; dihedral angle between verdazyl rings 75°.[21] The verdazyl oxygens have been labelled to clarify the difference in coordination geometry.

in particular, showed a flattening of the metal coordination tetrahedron (Figure 8a), which computational studies suggested might be associated with a weakened exchange.[19] As a $3d^{10}$ metal ion copper(I) has a flexible coordination geometry that can be manipulated with ligand-ligand interactions, so we set out to build a more sterically demanding verdazyl ligand. A more elaborate synthetic pathway[20] resulted in verdazyls substituted with isopropyl groups in the 1 and 5 positions, which we hoped, when combined with an isopropyl substituted pyridine ring (ligand **5**), would result in sufficient change in coordination geometry on copper to give ferromagnetic exchange between radicals.[21] Though we did achieve ferromagnetic exchange, the result was somewhat fortuitous because the resulting complex was still distorted from tetrahedral (Figure 8b), probably as a result of crystal packing forces. Nevertheless, the distortion brought the radicals closer together, rather than further apart, enhancing the ferromagnetic exchange. It appears that the exchange between radicals coordinated to copper(I) is sensitive to the dihedral angle between the ligands, and for the $[\mathrm{Cu}(\mathbf{mepyvd})_2]^+$ system, the angle in the crystal structure is coincidently close to the value that makes the singlet and triplet states degenerate.

As an added bonus, the new, isopropyl-substituted verdazyls were considerably more robust than their methyl counterparts[20]; consequently, more recent verdazyl studies tend to use the isopropyl-substituted systems such as **4, 5**, and **7**.

3. MAGNETISM

The majority of coordination studies on verdazyls are focused on the magnetic exchange between radical and metal. Many of these studies involve nickel and manganese as the metal ions. These metals are frequently the subject of magnetism studies since the unpaired electrons on Ni^{2+} are in the d_σ orbital set and would be expected to couple ferromagnetically with coordinated π radicals, while the half-filled d_π orbitals of high-spin Mn^{2+} generally give antiferromagnetic coupling. Most of these also feature hexafluoroacetylacetonate (hfac) ancillary ligands which boost the Lewis acidity of the metal center, allowing the weakly basic verdazyl to coordinate. For the bidentate and tridentate verdazyl ligands (**pyvd, pymvd, imvd, meimvd, $\mathbf{vdCO_2}^-$, bipyvd, dipyvd**) with these metals, the sign of the exchange fits theoretical predictions. Reported exchange magnitudes for Ni and Mn systems are listed in Table 1. Notably, the magnitude of verdazyl-metal exchange is remarkably high (as high as 350 cm^{-1}), especially for the nickel systems. For the ferromagnetic cases, this precludes accurate determination of the magnitude of exchange because the fit to magnetic susceptibility is not very sensitive. Consequently, these numbers should be considered approximate.

Table 1: Exchange parameters for Mn and Ni complexes of verdazyl ligands

Ligand	Ancillary ligands	Metal	$J_{M\text{-}vd}$ /cm^{-1}	Other exchange values/cm^{-1}	Reference
pyvd	hfac	Ni	>240		(14)
pyvd	hfac	Mn	−45		(14)
pymvd	hfac	Ni	+220		(35)
pymvd	hfac	Mn	−48		(35)
$vdCO_2^-$	H_2O	Ni	+188		(26)
bipyvd	–	Ni	+240	$J_{vd\text{-}vd} = -8$	(22, 23)
bipyvd	–	Mn	−93	$J_{vd\text{-}vd} = -10$	(23)
dipyvd	–	Ni	+250 to 350	$J_{vd\text{-}vd} = +510$ to $+100$	(25)
imvd	hfac	Ni	+190		(34)
imvd	hfac	Mn	−65		(34)

Though the exchange magnitude is high, changes in the ligand spectrum are, for the most part, small. Metal coordination is accompanied by a small but diagnostic increase in C=O stretching frequency, but with the exception of Cu(I) and Ru(II) systems, and complexes of ligand **dipyvd** (*vide infra*), the changes in the UV-vis spectra are relatively minor—typically a small red shift in the absorption spectrum of the verdazyl. For example, UV-vis spectra of a series of **bipyvd** complexes are shown in Figure 9.[4,22,23]

Train and co-workers used computational methods to understand the origin of the strong magnetic exchange in these systems.[24] They concluded that, to a large extent, the exchange results from ligand to metal charge transfer interactions from the ligand SOMO that transfers spin density onto the metal ion promoting the exchange. We invoked a similar mechanism to understand

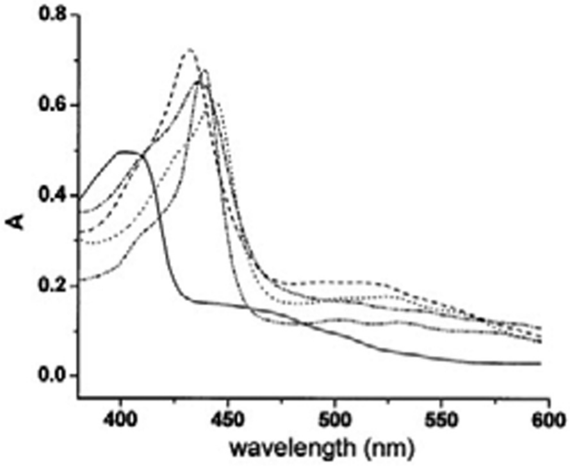


Figure 9: UV-vis spectra of **bipyvd** (—), and its coordination compounds with Mn^{2+}(. . .), Ni^{2+}(-..-), Cu^{2+}(-.-) and Zn^{2+}(—) (approx 0.14 mM in nitromethane).[23] © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reproduce must be obtained from the rightsholder.

the spectroscopic properties of verdazyl-copper-phosphite systems (*vide supra*).

Unlike the verdazyl systems described earlier, the tridentate ligand **dipyvd** is notable because of the unusually large exchange[25] (even for a verdazyl) and a drastically changed UV-vis spectrum (Figure 10; compare with the bipyvd spectra in Figure 9). These unique features are the subject of ongoing investigation by our research group but currently appear to be the result of the significantly shorter (by 0.2 Å) metal-radical bond length, which results, in turn, from the central placement of the verdazyl ring in the ligand and the lack of steric hindrance toward coordination.

Though magnetic exchange studies with Mn and Ni are the most numerous, there are other coordination compounds of verdazyls that have probed magnetic properties. Two coordination compounds have been reported with Co^{2+}; one with the verdazyl carboxylate **10, $vdCO_2^-$**[26] and the other with a polydentate verdazyl ligand **13**.[27] Both show high-spin Co(II), which appears to be ferromagnetically coupled to the verdazyl ($J = +68\,cm^{-1}$ for **10** $J = +20\,cm^{-1}$ for **13**), which is consistent with orbital overlap arguments used for the Ni^{2+} and Mn^{2+} systems; however, because of zero field splitting and other effects, neither system was fully magnetically characterized, so the magnitude of the exchange remains ambiguous. Two copper(II) systems have also been reported. Copper(II) was initially neglected in verdazyl complexes because, under some solvent conditions (particularly in acetonitrile), the ion is a sufficiently strong oxidant to oxidize the verdazyl to a verdazylium cation, and early attempts at Cu^{2+} complexes only gave Cu^+ species. Nevertheless,

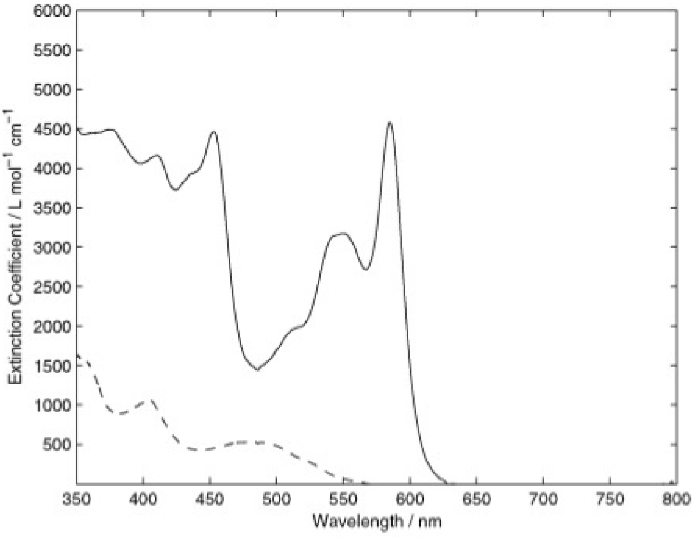


Figure 10: UV-vis spectra of **dipyvd (—)** and $(Ni(\textbf{dipyvd})_2)^{2+}$ (—). Contrast with the **bipyvd** spectra in Figure 9.

unambiguous Cu(II) systems have been reported with the tridentate ligand **bipyvd**[23]and the bidentate ligands **pyvd** and **meimvd**.[28] In the former, the copper(II)-verdazyl interaction was found to be weakly antiferromagnetic, in conflict with traditional orbital overlap arguments. For the latter, both hfac complexes and complexes with bridging chlorides were reported, with relatively distorted coordination geometries. Magnitudes of metal radical exchange varied from very weakly ferromagnetic to strongly antiferromagnetic, but on the whole consistent with coordination geometry and orbital overlap arguments.

The zinc complex of **bipyvd** was also reported by Hicks in order to study the metal-mediated exchange; however, the measured magnetic properties were dominated by intermolecular effects, suggesting that the radical-radical interaction itself was weak.[23] Two other studies have used heavier metals; one involved the formation of a coordination polymer of **pymvd** with Ag^+ that showed weak antiferromagnetic exchange[29] (Figure 11). The sign of the exchange contrasts with that observed with Cu^+ systems (*vide supra)*, especially since the ligands have a near perpendicular arrangement around the metal atom. Clearly, there is more to learn regarding exchange and ligand interaction in this area.

A final magnetic study by the same authors reported the coordination of a verdazyl (**imvd**) to the lanthanides Tb^{3+}, Dy^{3+} and Gd^{3+}.[30] This latter study is notable as the only reported example of a verdazyl coordinating through the carbonyl oxygen (as befits the rather hard nature of lanthanides). The complexes themselves are also coordination polymers, with the metal coordinating to the imidazolyl nitrogen (Figure 12). Fitting of magnetic susceptibility data for the Gd^{3+} system as an alternating chain gave two

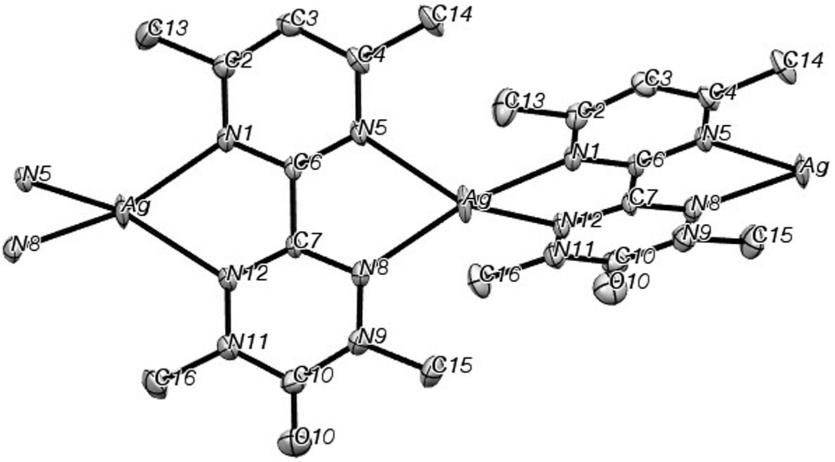


Figure 11: Section of the coordination polymer $\{(Ag(\textbf{pymvd}))^+\}_n$.(29)

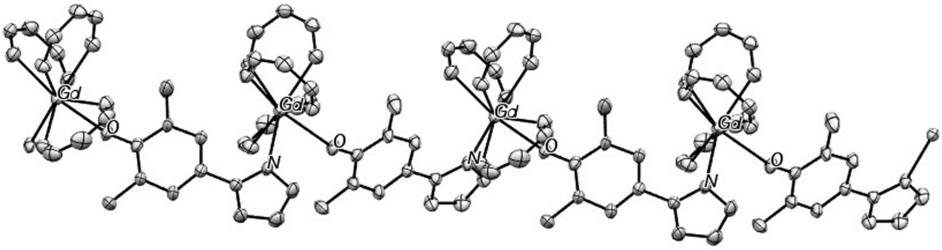


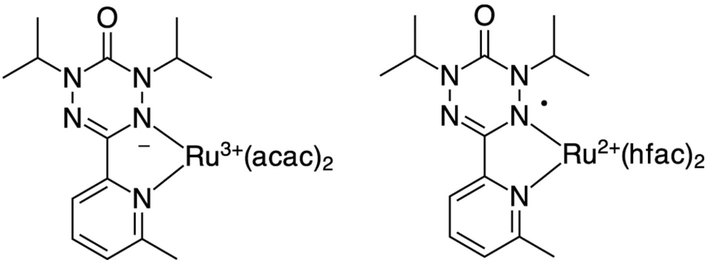
Figure 12: Section of the Gd(hfac)$_3$(**imvd**) polymer showing coordination through the C=O oxygen and imidazolyl nitrogen. Trifluoromethyl groups are not shown to improve clarity.(30)

antiferromagnetic exchange parameters, $J_1 = 1.6\,\text{cm}^{-1}$ and $J_2 = –0.43\,\text{cm}^{-1}$. Qualitatively similar behavior was observed for the Tb^{3+} and Dy^{3+} systems, but no modeling of the data was reported. The low value of the magnetic exchange in these systems contrasts dramatically with the values for the first-row elements. Though exchange is typically weaker for lanthanide systems, in this case it is compounded by the node in the verdazyl SOMO that runs through the C=O group and the verdazyl C3.

4. LIGAND-BASED ELECTROCHEMISTRY AND NON-INNOCENT BEHAVIOR

In addition to the presence of an unpaired electron, verdazyls are redox active. Most examples show reversible one electron oxidation and one electron reduction waves in cyclic voltammetry.[8] For the 6-oxo species, oxidation occurs near +0.6 V vs SCE and reduction occurs near −1.0 V vs SCE. The accessibility of these processes compared to typical transition metal redox potentials agrees with the observations noted earlier that coordinated verdazyls may also be redox active. Recently, Hicks reported the first electrochemical studies on coordinated verdazyls.[31] In these, the electrode potential for reduction of verdazyl **11** coordinated to Zn^{2+} increases from −1.35 V to −0.87 V, and the electrode potential for oxidation increases from +0.2 to +0.43 V (vs Ferrocene/Ferricinium) as a result of coordination. Similar effects are observed for ligand **14** but, in this case, oxidation of the ligand results in dissociation of the verdazyl rings, which then coordinate back to the metal center upon reduction.

With an appropriately matched redox active metal ion, non-innocent ligand behavior and valence tautomerism might be observed. In fact, the spin observed on the copper ion in copper(I) verdazyl complexes may be interpreted as arising from a small amount of Cu(II) character. More dramatic effects are seen with ruthenium verdazyl complexes; these systems show significant delocalization between verdazyl and ruthenium, dependent on the ancillary ligands on the metal center. With acetylacetonate (acac) ligands, the Ru center



Scheme 5: Electron distribution in Ru verdazyl complexes.

is electron-rich enough to donate a sizable fraction of one electron to the verdazyl, and the complex with ligand **4** is best described as a Ru^{3+} complex of a leucoverdazyl anion. The reduction of the verdazyl is clearly evident in the elongated bond lengths and distortion of the tetrazane ring. With hexafluoroacetylacetonate (hfac) ligands, the ruthenium is far less

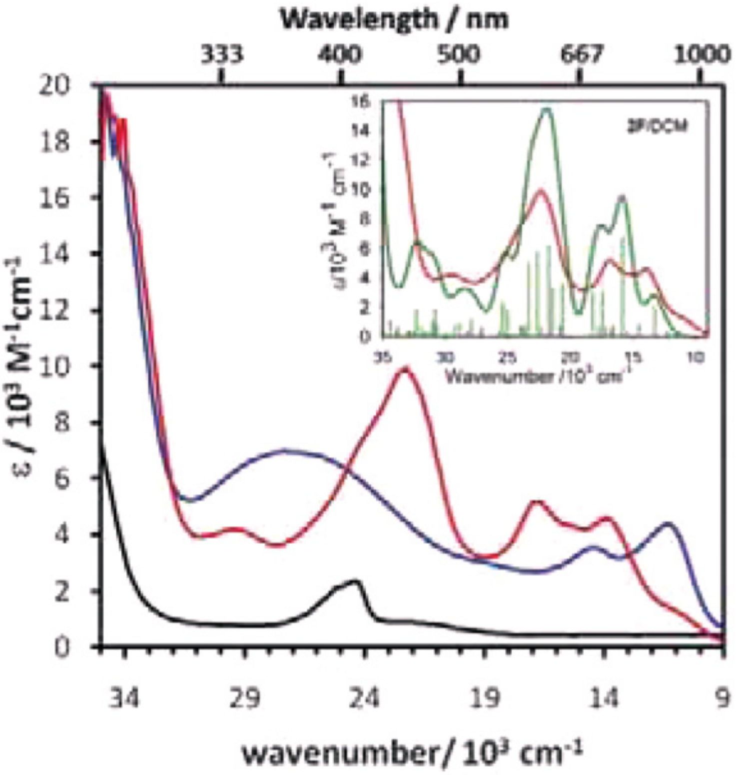
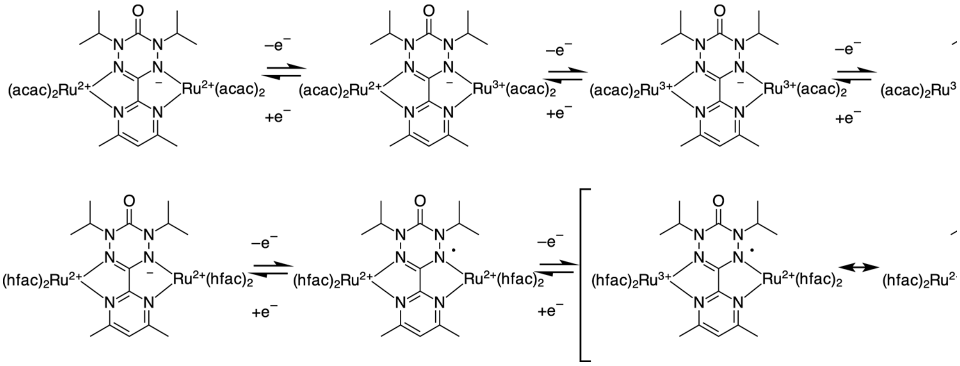


Figure 13: UV-vis spectra of ligand **4** (black), (Ru(acac)$_2$(**4**)) (blue), and (Ru(hfac)$_2$(**4**))(red). The inset shows predicted spectra computed using DFT methods.[(33)] © American Chemical Society. Reproduced by permission of American Chemical Society. Permission to reproduce must be obtained from the rightsholder.



Scheme 6: Electrochemical equilibria of ruthenium complexes of **7**.

electron-rich; consequently, the verdazyl has more radical character and the metal ion is appropriately described as Ru^{2+}[32] (Scheme 5).

The non-innocent nature of the ligand is evident in the UV-vis spectra, which are significantly changed from the free pyvd radical (Figure 13).

The non-innocent nature of verdazyls was further investigated with a pyrimidine-substituted verdazyl bridging two ruthenium ions. The same effects of hfac vs acac ancillary ligands were noted, especially in the electrochemistry.[33] With hfac ligands, the redox chemistry was largely based on the verdazyl, while with acac ligands, the verdazyl remained in the anionic form until both metal ions were oxidized to Ru^{3+} (Scheme 6).

5. SUMMARY OF LIGAND PROPERTIES AND FUTURE DIRECTIONS

Over the past 15 years, enough verdazyl metal complexes have been reported to demonstrate the typical properties of these radicals as ligands. Verdazyls are relatively weak basic ligands that typically require an additional chelating atom to give coordination. With transition metals, strong magnetic exchange is often observed, consistent with the orbital arguments that have been developed based on nitronyl nitroxides. The exchange tends to be stronger than observed with nitronyl nitroxides, and this can be attributed to the greater spin density on the coordinating atom. The other major difference between these systems and nitroxides, which was hinted at by early copper(I) studies and is much more manifest in the recent Ru systems, is that verdazyls can act as pi acceptors, with overlap between metal d orbitals and the ligand SOMO and a rich redox chemistry while coordinated to the metal center. Like the quinone/semiquinone/catecholate systems, the redox active orbitals may remain localized on the ligand, or there may be significant orbital mixing, resulting in a new series of mixed valence complexes. We may expect to find semiquinone-associated phenomena, such as valence tautomerism, also occuring with verdazyls. Furthermore, the accessible structural versatility associated with verdazyls holds the promise for many further metal complexes and materials with unusual electronic structure. Such properties may be useful in the development of molecular switches and devices and new electronic or magnetic materials.

Several research groups have made major contributions to verdazyl coordination chemistry over the past 15 years; however, I particularly would like to note the contributions of my own research group because, with few exceptions, they have been undergraduates. Coordination chemistry, such as the chemistry of verdazyls described here, can provide an excellent introduction to research for undergraduates because the projects can be conveniently broken up into small units, and the combination of esthetic (color changes) and unusual (the bizarreness of a stable free radical) provides an important hook to get students interested. Even though undergraduates are limited in available time and experience, it is clear that undergraduates can contribute to some outstanding research. Though the overall research timescale may be longer, I look forward to my students generating some fascinating and unique results to come.

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