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Strong Ferromagnetic and Antiferromagnetic Exchange Coupling between Transition Metals and Coordinated Verdazyl Radicals

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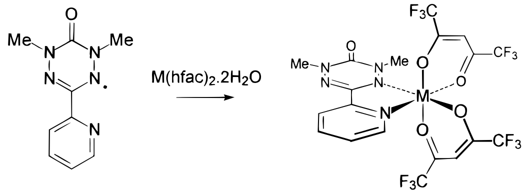
The design and synthesis of molecular-based magnetic materials is a major focus of molecular materials research.[1] One of the more promising strategies relies on direct exchange coupling between metal ions and coordinated open shell (i.e., radical-based) ligands in clusters or coordination polymers. Among the most heavily studied paramagnetic ligands in this context are nitroxide radicals (including nitronyl nitroxides and imino nitroxides),[2] and radical anions such as semiquinones[3] and TCNE[4] and TCNQ[5] radical anions. The nitrogen-rich framework of the stable verdazyl[6] radical represents an attractive alternative ligand system. However, there are currently very few examples of metal−verdazyl complexes, and all of these complexes are based on *diamagnetic* metal ions such as Cu(I) or group 12 M(II) ions.[7] The absence of metal-based free electrons in these systems precludes the possibility of verdazyl-metal magnetic exchange interactions. We describe herein the preparation of the first verdazyl radical complexes of open shell ions, namely Ni(II) and Mn(II), and demonstrate that the verdazyl-metal coupling is strong and ferromagnetic in the case of Ni(II). These results highlight the potential of creating new magnetic materials based on coordinated verdazyl radicals and paramagnetic transition metal ions.

Scheme 1



pyvd

1 M = Mn
2 M = Ni

Reactions of 1,5-dimethyl-3-(2-pyridyl)-6-oxoverdazyl (**pyvd**)[7b,8] with M(hfac)$_2$•2H$_2$O afforded **1** (M = Ni) and **2** (M = Mn) (Scheme 1) as air-stable complexes.[9] Preliminary X-ray crystallographic data[10] confirm the mononuclear, pseudo-octahedral nature of complexes **1** and **2**, both of which contain a fully planar, chelating **pyvd** ligand as depicted in Scheme 1. The UV−vis spectra (Figure 1) indicate that these are appropriately described as (**pyvd•**)M(II) complexes. The spectrum of the free radical contains two peaks at 409 nm ($\epsilon = 2 \times 10^3$ L•mol^{-1}•cm^{-1}) and 450 nm ($\epsilon = 0.8 \times 10^3$). The spectra of **1** and **2** are slightly red-shifted (λ_{max} = 425, 510 nm for **1** and 425, 513 nm for **2**) and more intensely absorbing ($\epsilon_{425} = 3.8 \times 10^3$ (**1**), 3.4×10^3 (**2**)) relative to free **pyvd**; the intensity of these electronic transitions completely mask any d−d transitions. Alternative formulations, for example (**pyvd**$^-$)M(III), can be ruled out also because the potentials at which Ni(II) complexes are oxidized to Ni(III) (generally >+1.0V vs SCE)[11] are incompatible with the reduction potential of **pyvd** (−1.25V vs SCE).[8]

The temperature dependence of the magnetic susceptibility of **1** and **2** (Figure 2) shows important differences in the magnetic behavior of these complexes.[12] The room-temperature value of χT for Mn complex **1** is 3.84 emu•K•mol^{-1}, less than expected for two noninteracting ($S_A = {}^1/_2$, $S_B = {}^5/_2$) spin systems. χT gradually decreases with temperature down to about 50 K, where it levels off and then decreases more sharply as T decreases further. These data are consistent with a model in which the verdazyl and manganese spins are antiferromagnetically coupled, with the following parameters: $g = 1.987$, $\theta = -0.8$ K, $J_{AB} = -45$ cm^{-1}.[13]

In contrast to **1**, the room-temperature value of χT for Ni complex **2** is 2.0 (which corresponds closely to the expected value for an $S = {}^3/_2$ system) and does not vary significantly with temperature above 80 K. The magnetic behavior of **2** is consistent with that of a ferromagnetically coupled $S_A = {}^1/_2$, $S_B = 1$ pair with the following parameters: $g = 2.1$, $\theta = -2.0$ K, $J_{AB} = +240$ cm^{-1}.[14] Further support for ferromagnetic coupling in **2** is provided by low temperature (3 K) magnetization studies: although **2** does not saturate at 5 T, its magnetization at this field

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(9) Synthesis of **1**: A heptane solution (60 mL) of Ni(hfac)$_2$•2H$_2$O (600 mg, 1.18 mmol) and a CH$_2$Cl$_2$ solution (15 mL)of **pyvd** (240 mg, 1.18 mmol) were combined and stirred for 1 h. After solvent removal, the residue was recrystallized from hexanes to yield **1** (463 mg, 58%). Anal. Calcd (found) for C$_{19}$H$_{12}$N$_5$O$_5$F$_{12}$Ni: C, 33.71 (33.78); H, 1.79 (1.87); N, 10.34 (10.19) %. MS (EI) = m/z 676 (M$^+$, 100%). Compound **2** was prepared in an analogous fashion from Mn(hfac)$_2$•2H$_2$O, yield 88%. Anal. Calcd (found) for C$_{19}$H$_{12}$N$_5$O$_5$F$_{12}$Mn: C, 33.90 (34.14); H, 1.80 (1.87); N, 10.40 (10.83) %. MS (EI) = m/z 673 (M$^+$, 100%).

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(12) Variable temperature magnetic data (2−300 K) were obtained with a Quantum Design MPMS5S Squid magnetometer operating at 0.1−0.5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with [H$_2$TMEN][CuCl$_4$] (Brown, D. S.; Crawford, V. H.; Hall, J. W.; Hatfield, W. E. *J. Phys. Chem.* **1977**, *81*, 1303.

(13) $\hat{H} = -JS_M S_{verd}$, where M = Mn (**1**) or Ni (**2**). $10^2R = 1.1$ (**1**) and 0.8 (**2**), where $R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2]^{1/2}$. The drop in χT at low temperatures for both **1** and **2** was modeled by incorporating a Weiss constant into the respective equations. The low-temperature behaviour could also arise from zero-field splitting, although the choice of model for the low-temperature behaviour has no effect on the high-temperature magnetic data fit.

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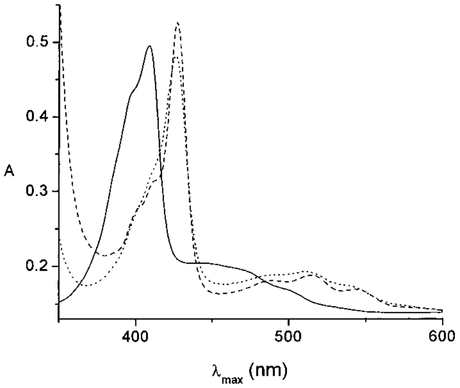


Figure 1. UV−vis spectra of **pyvd** (—), **1** (···), and **2** (- - -) in CH_2Cl_2.

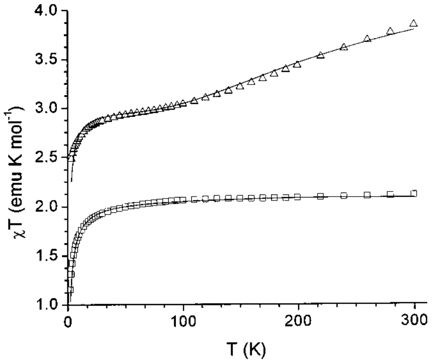
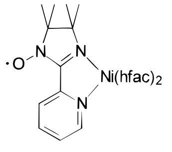


Figure 2. χT vs T for **1** (Δ) and **2** (□). The solid lines correspond to data fits using the data described in the text.

(2.3 Nβ) corresponds to a value larger than expected for an $S = 1$ system but smaller than expected for an $S = {}^3/_2$ species. The deviation from the expected $S = {}^3/_2$ value is ascribed to intermolecular antiferromagnetic interactions which predominate at 3 K (as is evident from the χT vs T data).[13]

The varying verdazyl-radical exchange coupling in **1** and **2** can be explained by orbital symmetry arguments.[15] The verdazyl magnetic orbital is a delocalized π symmetry molecular orbital spanning the four ring nitrogen atoms.[7a,8] The nickel's spins in **2** reside in the d_{z^2} and $d_{x^2-y^2}$ orbitals, both of which have σ symmetry with respect to the metal−verdazyl bond. Thus, all three magnetic orbitals are orthogonal; such an arrangement is predicted to produce ferromagnetic spin coupling. In contrast, in **1** there is nonzero (dπ-pπ) overlap between the verdazyl SOMO and one of the t_{2g} orbitals on Mn, which favors antiferromagnetic metal−radical coupling.

Intramolecular spin coupling in metal-nitroxide and nitronyl nitroxide complexes is usually antiferromagnetic because the nitroxide magnetic orbital is not orthogonal to the metal d orbitals.[2a,b] In rare cases the nitroxide−metal binding geometry enforces magnetic orbital orthogonality, thereby producing weak ferromagnetic coupling.[16] The strong ferromagnetic radical−Ni(II) exchange coupling in **2** is striking; only one other metal−radical complex with comparable intramolecular ferromagnetic coupling is known, a semiquinone−Ni(II) complex.[17] In both of these systems the orthogonality of magnetic orbitals favors ferromagnetic coupling, while the strength of the coupling (i.e., large J) arises from a coordinate bond in which both atoms bear large spin densities.[18,19] In comparison, the radical−nickel coupling in imino nitroxide complex **3**[20] is ferromagnetic but considerably weaker ($J = +95$ cm^{-1}) than that found in **2** because the imine nitrogen coordinated to the metal has a relatively small spin density associated with it.[21]



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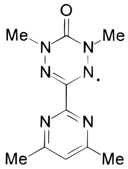

pmvd

We have prepared the first verdazyl complexes of paramagnetic metal ions and found that the **pyvd** radical is capable of engaging in strong intramolecular exchange interactions with metal-based spins. Exceptionally strong ferromagnetic coupling produces a high spin ($S = {}^3/_2$) molecule in the nickel complex **2**. These results highlight the great potential for the synthesis of new strongly magnetically coupled systems based on verdazyl−metal arrays. As an additional advantage, the design of new chelating verdazyls can be undertaken based on their structural similarities to oligopyridines and related nitrogen-based heterocyclic ligands. For example, the recently reported pyrimidine-substituted verdazyl **pmvd**[8] is a close structural mimic of 2,2′-bipyrimidine and as such is ideally suited for the assembly of binuclear or linear chain complexes. Efforts to this end are in progress.

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