Synthesis, Structure, and Magnetism of Bimetallic Manganese or Nickel Complexes of a Bridging Verdazyl Radical

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Two binuclear metal−radical complexes, formed by the reaction of M(hfac)$_2$·2H$_2$O (M = Mn or Ni; hfac = hexafluoroacetylacetonate) with the 1,5-dimethyl-3-(4,6-dimethylpyrimidin-2-yl)-6-oxoverdazyl radical (**3**), were synthesized. The binuclear Mn complex **5** (i.e., **3**[Mn(hfac)$_2$]$_2$) crystallizes in the monoclinic space group $C2/c$: $C_{30}H_{17}N_6O_9F_{24}Mn_2$, $a = 29.947(3)$, $b = 17.143(3)$, $c = 16.276(3)$ Å, $\beta = 123.748(3)°$, $Z = 4$. The compound consists of two pseudo-octahedral Mn(II) ions, both bearing two hfac ancillary ligands, bridged by the bis(bidentate) radical **3**. The temperature dependence of the magnetic susceptibility of **5** reveals moderate antiferromagnetic exchange between each of the Mn(II) ions and the verdazyl radical ($J = -48$ cm^{-1}). The $S = 9/2$ ground spin state of the complex was corroborated by low-temperature magnetization versus field measurements. In contrast, the magnetic susceptibility versus temperature behavior of **6** (whose molecular structure is presumed to be analogous to that of **5**) indicates that the two Ni(II) ions are strongly ferromagnetically coupled to the verdazyl radical ($J = +220$ cm^{-1}). The magnetization versus field behavior of **5** is consistent with an $S = 5/2$ ground-state species.

Introduction

The design and construction of new magnetic materials from molecular components is a major contemporary theme in materials research.[1−4] Among the many approaches to molecule-based magnets, hybrid materials comprised of paramagnetic metal ions and stable radicals offer several advantages.[5,6] Direct metal−radical exchange interactions are possible, and the use of bridging radical-based ligands allows for the creation of extended metal−radical structures with cooperative magnetic properties. In the latter context, most work in this area has been carried out with bridging nitroxide radicals and diradicals.[7−12] Complexes containing coordinated radical anions, for example, cyanocarbons such as TCNE or TCNQ[13−15] or the semiquinones,[16−22] have also received attention. However, the paucity of high T_c magnets in these systems highlights the continued need to explore alternative metal−radical assemblies.

We[23,24] and others[25−27] have recently demonstrated that judiciously substituted verdazyl radicals chelate to metals with structural features reminiscent of chelating oligopyridines. Thus, mononuclear Ni(II) and Mn(II) complexes of pyridine-substituted verdazyl **1** and related derivatives have been shown to

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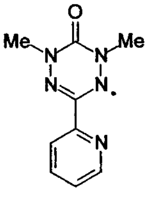
possess strong metal−verdazyl magnetic exchange interactions, while bis(verdazyl) **2** has been incorporated into one-dimensional chains with Cu(I) halides. However, to create metal−radical assemblies with macroscopic magnetic ordering, there is a need to explore the efficacy of paramagnetic metal ions in conjunction with bridging verdazyls, in particular metal−radical exchange phenomena in bridged systems. As a first step toward creating extended arrays of transition metals and bridging verdazyls, we present herein the synthesis and characterization of two model binuclear compounds containing the bridging ligand 1,5-dimethyl-3-(4,6-dimethyl-2-pyrimidinyl)-6-oxoverdazyl radical, **3**, a structural mimic of 2,2′-bipyrimidine, **4**.



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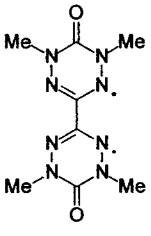

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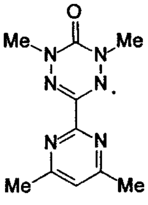

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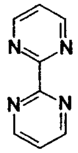

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Experimental Section

General Considerations. All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques. Solvents were dried and distilled under argon prior to use. All reagents were purchased from Aldrich and used as received. Verdazyl radical **3**,[28] $Mn(hfac)_2{\cdot}2H_2O$,[29] and $Ni(hfac)_2{\cdot}2H_2O$[30] were prepared according to literature procedures. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, B. C.

Synthesis of Binuclear Mn Complex 5. A solution of **3** (240 mg, 1.03 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a gently refluxing solution of $Mn(hfac)_2{\cdot}2H_2O$ (1.04 g, 2.06 mmol) in 60 mL of heptane. The dark purple reaction mixture was refluxed for 1 h, cooled to room temperature, and then filtered. The solvent was removed in vacuo, affording a dark brown solid which was recrystallized from hexanes to afford **1**, yield 600 mg (50%). Mp 147−149 °C. IR (KBr): 3137(vw), 2952(vw), 1653(s), 1646(s), 1616(m), 1560(m), 1534(m), 1483(m br), 1352(w), 1257(s), 1206(s), 1144(s), 1099(w sh), 1034(vw), 974(vw), 948(vw), 873(w), 800(m), 769(w), 740(w), 713(w), 663(s), 583(m), 537(w), 48(w) cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 434 nm (ϵ = 3408 L mol^{-1} cm^{-1}). MS (FAB negative ion mode): *m/z* 1170.9 $(M-H)^-$, 675.9 $(Mnhfac_3)^-$, 207 $(hfac)^-$. Anal. Calcd for $C_{30}H_{17}N_6O_9F_{24}Mn_2$: C, 30.76; H, 1.46; N, 7.17%. Found: C, 30.79; H, 1.48; N, 7.19%.

Synthesis of Binuclear Ni Complex 6. This compound was prepared in an analogous manner from **3** and $Ni(hfac)_2{\cdot}2H_2O$ in CH_2Cl_2 solution, yield 21%. Mp 210 °C (dec). IR (KBr): 2963 + 2935(w doublet), 1734(w), 1644(s), 1619 + 1605(w sh), 1558(w), 1530(m), 1485(m), 1351(w), 1258(s), 1202(s), 1144(s), 1107(m sh), 797(m), 744(w), 674(s), 587(m) cm^{-1}. UV−vis λ_{max} (CH_2Cl_2): 440 nm (ϵ = 3450 L mol^{-1} cm^{-1}). MS (FAB negative ion mode): *m/z* 1177 $(M-H)^-$, 678.9 $(Nihfac_3 - H)^-$, 471.9 $(Nihfac2 - H)^-$, 207 $(hfac)^-$. Anal. Calcd for $C_{30}H_{17}N_6O_9F_{24}Ni_2$: C, 30.57; H, 1.45; N, 7.13%. Found: C, 31.23; H, 1.71; N, 7.21%.

Structure Determination of 5. Crystal data and details of data collection are given in Table 1. Extremely thin, brown rodlike crystals were mounted on a glass fiber with silicone glue. Data were collected on a Smart 1000 diffractometer (Mo Kα, graphite monochromated radiation (λ = 0.71073 Å). Data were collected for $4 < 2\theta < 50°$. Total of 12256 reflections were measured, of which 4125 were independent, and 2341 were used in the refinement of 323 parameters ($I > 2.0\sigma(I)$). An empirical absorption correction (SADABS) was applied. The structure was solved by direct methods (SHELXS-97), and the hydrogen atoms were placed at idealized positions and refined according to the riding model. The structure was refined according to the full-matrix least-squares method on F^2 (SHELXL-97). At convergence $R1 = 0.067$ ($I > 2\sigma(I)$) and $wR2 = 0.217$; min/max residual electron density = −0.32/+0.48 e Å^2. The difference maps indicated that the disorder in the structure arises from the CF_3 groups, but attempts to model the disorder did not yield satisfactory results. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-157917.

Table 1. Crystallographic Data for Complex **5**

empirical formula	$C_{30}H_{17}F_{24}Mn_2N_6O_9$
formula weight	1171.38
space group	*C*2/*c*
V, Å^3	460.7(13)
Z	4
D_{calc}, g/cm^3	1.67
a, Å	29.947(3)
b, Å	17.143(3)
c, Å	16.276(3)
β, deg	123.748(3)
T, K	293
μ(Mo Kα), μm^{-1}	0.692
wavelength, Å	0.71073
R_F ($F > 2\sigma(F)$)[a]	0.067
R_W (F^2, all reflns)[b]	0.217

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ for reflections with $F > 2\sigma(F)$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$ for all reflections.

Magnetic Measurements. Variable temperature magnetic data (2−300 K) were obtained with a Quantum Design MPMS5S SQUID magnetometer operating at 0.1−5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with $[H_2TMEN][CuCl_4]$.[31]

Results

Synthesis and Structure of Complexes 5 and 6. The pyrimidine-substituted verdazyl **3**[28] was reacted with $M(hfac)_2{\cdot}2H_2O$ to afford binuclear complexes **5** (M = Mn) and **6** (M = Ni) (Scheme 1) as air-stable solids The solution UV−vis spectra of both complexes are fully consistent with previous data on manganese− and nickel−verdazyl complexes,[23,24] and indicate that **5** and **6** are appropriately described as M(II) complexes of a neutral radical. Unfortunately, despite repeated efforts, crystals of **6** suitable for X-ray crystallographic studies could not be grown, due primarily to the slow decomposition of the compound in solution. However, the general molecular structure of **6** is presumed to be analogous to that of the Mn complex, **5**, based on the spectroscopic, analytical, and magnetic characterization of both systems. In particular, the striking similarities of both the visible and FTIR spectra of both complexes (see Experimental Section and Supporting Information) lend support to analogous molecular structures.

The X-ray crystal structure of Mn complex **5** is shown in Figure 1. Molecules of **5** lie on a crystallographic two-fold rotation axis passing through the long axis of the verdazyl ligand. As anticipated, **3** simultaneously chelates to two pseudo-octahedral $Mn(hfac)_2$ moieties, and the verdazyl−Mn bonds are slightly longer (2.326 Å) than the pyrimidine−Mn bonds (2.28 Å). The verdazyl and pyrimidine rings of **3** are twisted relative to one another by 24°. This results in a slight pyramidalization at the coordinating verdazyl nitrogen atom (sum of angles at N2 = 352.2°), while the geometry at the coordinated pyrimidine

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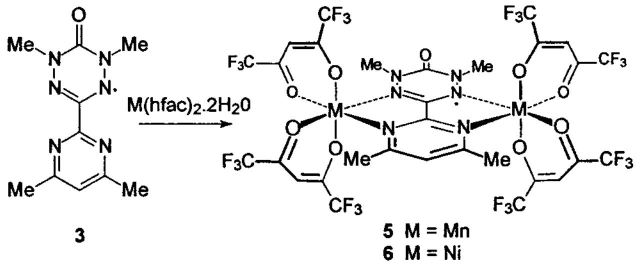
Scheme 1



nitrogen remains flat (Σ(N1) = 360°). The origins of this twisting are not clear but may be related to steric interactions between the methyl groups of **3** and neighboring CF_3 groups. In related Cu(I) complexes of **2**, the angle between the two verdazyl rings is zero.[25] However, the distortion from coplanarity in **5** is significantly lower than the inter-ring angle of 55° found in the related binuclear Mn(hfac)$_2$ complex of a bis(nitronyl nitroxide).[32] The spin density of verdazyl radicals in general, and in particular, pyrimidine derivative **3**, is known to be confined to the four nitrogen atoms of the verdazyl heterocyclic ring;[28] very little spin density leaks onto the aromatic substituents at C3. The slight twisting of the two rings is, therefore, not anticipated to have major consequences for the magnetic properties.

Magnetic Properties of 5 and 6. The temperature dependence of the magnetic susceptibility of **5** and **6** is presented in Figure 2 as χT versus T plots. For **5**, the χT value at room temperature is 9.3 emu K^{-1} mol^{-1}, close to the expected value of 9.12 for the three isolated spin centers (two $S = 5/2$ Mn ions and one $S = 1/2$ radical). Upon lowering the temperature, χT decreases slightly, reaching a minimum value of 9.2 at 240 K, then increases steadily on further cooling, reaching a plateau value of 12.35 at about 5 K. Below 5 K, χT increases again slightly, which we ascribe to very weak ferromagnetic intermolecular interactions (modeled by introducing a Weiss constant θ into the equation). The magnetic data were modeled as a linear three-spin system ($\mathbf{H} = -J(2\mathbf{S}_{\mathrm{Mn}}\mathbf{S}_{\mathrm{rad}})$), and the best fit yielded the following parameters: $J_{\mathrm{Mn-verd}} = -48$ cm^{-1}, $g = 2.00$, $\theta = +0.05$K, ρ(fraction of uncoupled spins as impurities) = 0.004, TIP(temperature independent paramagnetism) = 0.0001 (R = 0.009, where $R = [\Sigma(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2/\Sigma(\chi_{\mathrm{obs}})^2]^{1/2}$). The manganese−verdazyl exchange interaction $J_{\mathrm{Mn-verd}}$ determined for **5** is virtually identical to that found in a mononuclear Mn(hfac)2 complex of **1**.[23] However, in **5** the antiferromagnetic interactions between the verdazyl and both Mn ions aligns all of the Mn spins in a ferrimagnetic manner, leading to an $S = 9/2$ ground state. This is supported by the low temperature χT value of 12.35 and the magnetization versus temperature behavior at 2 K (see Supporting Information), both of which are in excellent agreement with theoretical predictions. The spin system in **5** (two $S = 5/2$ Mn centers sandwiched around an $S = 1/2$ radical) is the same as that of a previously reported linear Mn(II)−Cu(II)−Mn(II) complex. [33,34] The magnetic energy levels for this system were determined to possess an irregular spin structure; that is, the spin states S do not increase or decrease monotonically with energy. In fact, all of the qualitative features of the χT versus T plot for **5** (the broad minimum at high temperature, followed by a steady increase in χT as T is lowered, plateauing at cryogenic temperatures at 12.35 emu K mol^{-1}) are also seen in the MnCuMn system.

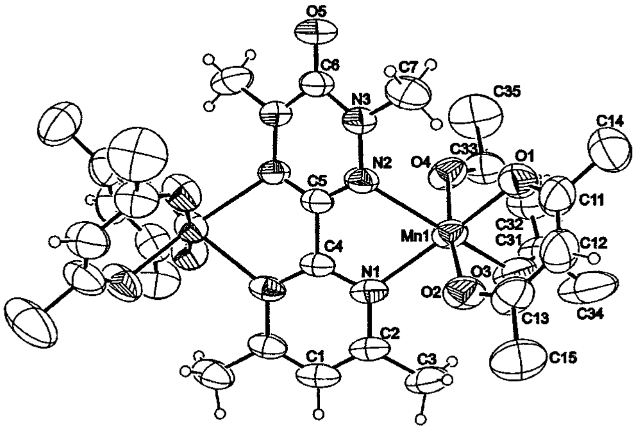


Figure 1. ORTEP drawing of **5**. Ellipsoids drawn at 30% probability level. Fluorine atoms are removed for clarity. Selected bond lengths [Å] and angles [deg]: Mn1−N1 2.281(4), Mn1−N2 2.326(4), Mn1−O1 2.124(5), Mn1−O2 2.108(4), Mn1−O3 2.110(4), Mn1−O4 2.133(3), C1−C2 1.365(6), C2−N1 1.363(6), N1−C4 1.321(5), C4−C5 1.485(8), C5−N2 1.305(5), N2−N3 1.361(5), N3−C6 1.376(6), C6−O5 1.175(8); N1−Mn1−N2 71.60(14), C4−N1−Mn1 115.8(3), C5−N2−Mn1 112.2(3), C5−N2−N3 115.0(4), N2−N3−C6 124.3(5), N2^1−C5−N2 127.8(6), N2−C5−C4 116.1(3), N3^1−C6−N3 113.3(6). Symmetry Code: $^1 = -x, y, -z + 3/2$.

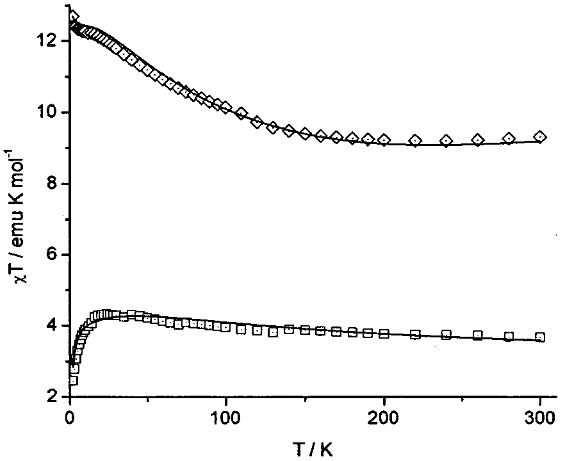


Figure 2. χT versus T plots for **5** (◇) and **6** (□). The solid lines represent fits of the data to models for the susceptibility as described in the text.

For the bimetallic Ni complex **6**, the room-temperature value of χT is 3.67 emu K^{-1} mol^{-1}, significantly higher than the anticipated value of 2.375 for the three isolated spin centers (two $S = 1$ Ni(II) ions and the $S = 1/2$ radical). Upon cooling, χT increases steadily to reach a maximum value of 4.31 at 22 K before decreasing at cryogenic temperatures. The data for **6** were fit using a spin Hamiltonian similar to the one employed for **5** ($\mathbf{H} = -J(2\mathbf{S}_{\mathrm{Ni}}\mathbf{S}_{\mathrm{rad}})$), yielding $J_{\mathrm{Ni-verd}} = +220$ cm^{-1}, $g = 2.03$, $\theta = -1$K,[35] $\rho = 0.02$, TIP = 0.0002 ($R = 0.012$). As has been observed for other Ni(II) verdazyl complexes, the coupling between the metal- and ligand-based spins, $J_{\mathrm{Ni-verd}}$, is ferromagnetic and extremely strong in **6**, a result of the orthogonality between the nickel magnetic orbitals (the $d_{x^2-y^2}$ and d_{z^2} orbitals)

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(35) The low-temperature magnetic behavior of **2** was modeled using a Weiss constant θ; an alternative approach would be to incorporate a zero-field splitting term D arising from the high-spin ground state. The choice of model for the low-temperature regime has no bearing on the other parameters included in the fit.

and the verdazyl SOMO (a delocalized π orbital).[23,24] In **6** the ferromagnetic alignment between two $S = 1$ Ni(II) ions and an $S = {}^1/_2$ verdazyl radical produces an $S = 5/2$ ground-state molecule. This is corroborated by the low-temperature value of χT which is close to the predicted value (4.38). Magnetization versus field data (see Supporting Information) at 2 K show that the system approaches an $S = 5/2$ ground state although it is not fully saturated at 5 T.

Discussion

The 2,2′-bipyrimidine ligand **4** has received considerable attention as a building block for the assembly of coordination polymers with cooperative magnetic properties.[36−41] However, metal−metal exchange interactions mediated by **4** are antiferromagnetic and, with the exception of selected Cu(II) systems, generally very weak ($|J| \leq 2$ cm^{-1}). By incorporating verdazyl derivative **3** as a spin-containing analogue of **4**, the structural utility of this ligand framework is maintained but with fundamentally different magnetic properties; nearest-neighbor magnetic coupling is now determined by metal−radical (as opposed to metal−metal) exchange. Regardless of the nature (ferro- versus antiferromagnetic) of the metal−verdazyl coupling, the metal−radical−metal topology guarantees that all metal-based spins are aligned with the same spin (this is analogous to ferrimagnetic interactions in bimetallic systems). Our demonstration that the coordination chemistry of **3** structurally mimics that of **4**, coupled with the novel magnetic properties exhibited by complexes of the former, makes metal−verdazyl complexes very attractive as building blocks for magnetic materials, particularly when coordination polymers are targeted. Efforts to prepare such structures are in progress.

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Supporting Information Available: Magnetization versus field plots, visible spectra, and FTIR spectra for **5** and **6**; X-ray crystallographic files for **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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