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Weak Magnetic Coupling of Coordinated Verdazyl Radicals through Diamagnetic Metal Ions. Synthesis, Structure, and Magnetism of a Homoleptic Copper(I) Complex

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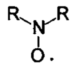
Introduction

The properties of transition-metal complexes containing coordinated radicals have received a great deal of attention.[1−3] One of the main themes in contemporary metal−radical research is the design, synthesis, and study of molecular-based magnetic materials based on metal−radical assemblies. Much work has been devoted to the study of discrete and polymeric complexes of nitroxide-type radicals **1**−**3**,[4−6] and the radical-anion-based ligands such as the semiquinones[7−10] and radical anions of tetracyanoethylene (TCNE)[11−13] and 7,7,8,8-tetracyanoquinodimethane (TCNQ)[14] have also been explored. In recent years, the coordination chemistry of other radicals has been pursued, particularly complexes containing the coordinated verdazyl radicals (**4**). Specifically, verdazyls possessing a chelating environment (e.g., **5**) are capable of coordinating to metal ions,[15−17] and metal−radical magnetic-exchange interactions can be very strong in some cases.[18,19] However, the nature of radical−radical exchange in verdazyl complexes containing at least two radicals bound to the same metal atom has not yet been addressed. To date, only one metal complex has been reported containing two bound verdazyls, and in this system, the radical−radical interactions could not be ascertained because of the dominance of strong metal−radical coupling in determining the observed magnetic behavior.[19] In this paper, we report the synthesis of a new verdazyl derivative (**6**) and its homoleptic copper(I) complex. The diamagnetic nature of the copper ion now permits for the assessment of the intramolecular radical−radical magnetic interactions in the complex.



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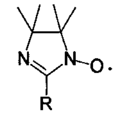

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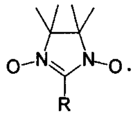

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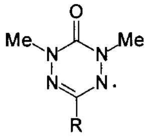

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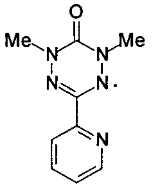

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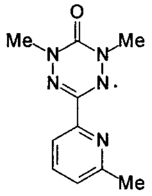

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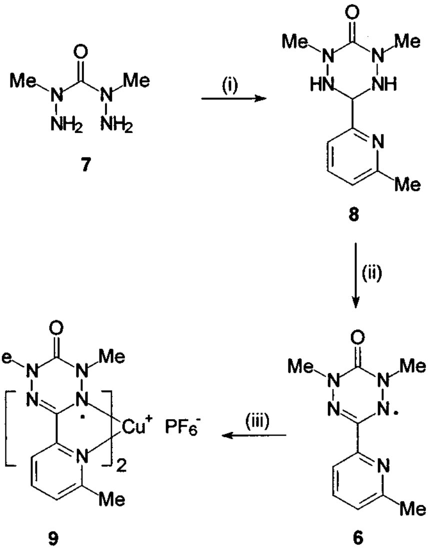
Synthesis and Structure of the Complex

Scheme 1. Reagents (i) 6-Methyl-2-pyridinecarboxaldehyde, (ii) 1,4-Benzoquinone, and (iii) $[Cu(NCCH_3)_4]^+$ PF_6^-



The preparation of verdazyl radical **6** and its copper complex **9** are shown in Scheme 1. The radical was prepared according to our established procedures used to make **5**.[20] Thus, the bis(1-methylhydrazide) of carbonic acid (**7**) was condensed with 6-methyl-2-pyridinecarboxaldehyde to afford tetrazane **8**. The

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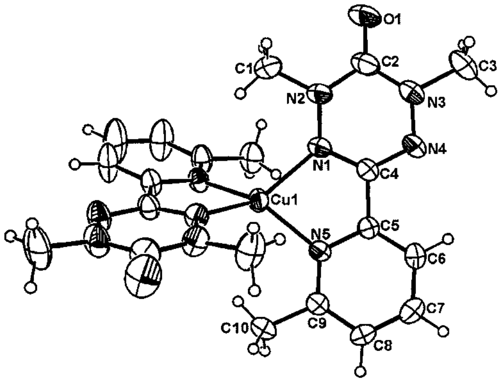


Figure 1. Molecular structure of the cation of **9**. Selected bond lengths (Å) and angles (deg): Cu1−N1 = 2.043(4), Cu1−N5 = 2.016(4), N1−N2 = 1.362(5), N3−N4 = 1.362(6), N1−C4 = 1.326(6), N4−C4 = 1.324(6), N2−C2 = 1.376 (6), N3−C2 = 1.372(7), C2−O1 = 1.212(6), C4−C5 = 1.467(6); N1−Cu1−N5 = 81.01(14), N1−Cu1−N1^1 = 130.6(2), N5−Cu1−N5^1 = 140.2(2), Cu1−N1−C4 = 113.2(3), N2−N1−C4 = 115.8(4), N3−N4−C4 = 114.9(4), N1−C4−N4 = 127.0(4), N2−C2−N3 = 115.0(4), N1−C4−C5 = 116.8(4), N5−C5−C4 = 115.2(4).

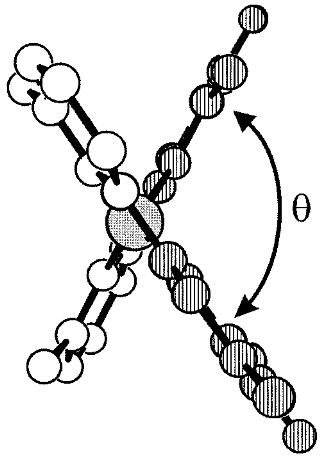


Figure 2. Ball and stick representation of the cation of **9**, illustrating the distortion from tetrahedral geometry and the interplanar angle θ between the two verdazyl rings [gray shading = copper, vertical stripes = verdazyl-ring atoms, and colorless = pyridine-ring atoms].

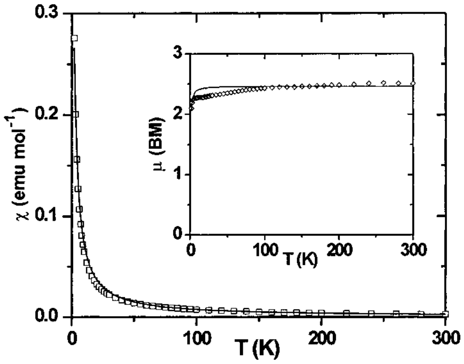
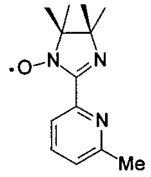


Figure 3. Magnetic moment (μ) versus T for **9**. The solid line represents the data fit using a dimer model, and the dashed line represents a fit using a modified dimer model. The parameters and equation for the modified dimer model are given in the text.

tetrazane was then oxidized with benzoquinone to afford radical **6**, which was isolated and stored as its hydroquinone adduct (similarly to **5**). The radical can be liberated from the hydroquinone by flash chromatography. The addition of freshly purified **6** to a solution of [Cu(MeCN)$_4$]$^+$PF$_6^-$ led to the immediate formation of a dark-green solution, which on evaporation and recrystallization afforded dark-green crystals of **9**.

The molecular structure of the Cu(**6**)$_2$ cation of **9** is shown in Figure 1. Crystals of the complex belong to the tetragonal space group I_1/acd. The copper ion resides on a high-symmetry site, and the two-coordinated radicals are crystallographically equivalent. The Cu1−N1 bond to the verdazyl ring (2.043(4) Å) is only slightly longer than the Cu1−N5 pyridine bond (2.016(4) Å); both of these bond lengths are within the typical range for pyridine−Cu(I) complexes as well as related copper−verdazyl coordination complexes.[15,16] The internal structural features of the coordinated verdazyl radical are quite similar to those of other coordinated verdazyls, and in fact, the heterocyclic bond lengths do not change significantly in comparison to those of the structures of noncoordinated verdazyl radicals.[21−23]

The geometry at the copper ion is best described as flattened-pseudotetrahedral. The dihedral angle between the two-coordinated verdazyl rings ligands (see Figure 2) about the copper ion is 115.8°. In a related copper complex of an imino nitroxide radical **10**, the interligand angle is 88.7°,[24] and the interligand dihedral angle varies substantially among copper(I) bis(α,α′-diimine) complexes.[25−29] The reasons behind the flexible stereochemistry in pseudotetrahedral Cu(I) complexes are not understood; crystal packing forces may be a factor in addition to the lack of a strong geometric preference by the d^{10} copper(I) ion.



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Magnetic Properties

Variable-temperature magnetic-susceptibility measurements were carried out on a microcrystalline sample of **9**. The temperature dependencies of both the susceptibility (χ) and the magnetic moment (μ) are shown in Figure 3. The room-temperature moment of 2.51 μ_B is close to the value predicted for two noninteracting $S = {}^1/_2$ spin systems. From room temperature down to 100 K, the moment is essentially temperature independent, and then, on further cooling, the moment decreases only very gradually, reaching a value of 2.25 μ_B at 5 K before a sharper decrease begins to occur at extremely low temperatures. Qualitatively, it is evident that the magnetic exchange between the radicals is very weak. However, attempts to model the data to a simple dimer model gave poor visual

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fits (in the μ vs T plot) at very low temperatures. The parameters for the fit shown in Figure 3 (solid line) are $J = -2$ cm^{-1}, temperature-independent paramagnetism (TIP) = 0, and ρ (fraction of $s = {}^{1}/_{2}$ impurity spins) = 0.01 ($R = 0.055$; $R = [\sum(\chi_{obs} - \chi_{calcd})^2/\sum\chi_{obs}{}^2]^{1/2}$). A modified dimer model[30] was employed in attempts to account for the possibility of intermolecular interactions contributing to the low-temperature behavior. These models proved no better than the simple-dimer model described above. Clearly, the details of the low-temperature magnetic behavior are fairly complex and likely involve several intermolecular exchange interactions. However, all of these interactions must be very small ($\ll$10 cm^{-1}) and do not alter the general conclusions regarding the general nature of the radical−radical exchange: the exchange coupling both *between* molecules and, most importantly, *within* individual molecules is extremely weak.

Discussion

Intramolecular magnetic interactions between coordinated radicals have been studied in complexes bearing at least two semiquinones[31−34] or nitroxides,[24,35−37] and a wide range of magnetic behavior has been observed. The previously mentioned copper(I) complex of imino nitroxide **10** bears the strongest qualitative structural resemblance to the title compound. However, in the imino nitroxide complex, the two radicals are strongly ferromagnetically coupled ($J = +56$ cm^{-1}), while in **9** the coupling between the two verdazyls is weak and antiferromagnetic. In the imino nitroxide complex, the coupling was ascribed to Cu(I)−radical charge transfer (CT) interactions, a proposal that is supported by the observation of charge-transfer bands in the solution UV−visible spectrum.[36] The green color of **9** also arises from a CT band at 623 nm, although this complex does not exhibit strong ferromagnetic coupling. This may simply reflect the fact that the two radicals being compared (imino nitroxide vs verdazyl) do not have the same frontier orbitals; there is no a priori reason for the magnetic behavior of the two complexes to be similar. In addition, we have described stereochemical differences between the two complexes. If magnetic coupling between two radicals involves the metal, then the relative orientation of the radical- and metal-based orbitals will be a prime factor in determining the sign and magnitude of the intramolecular radical−radical coupling. To gain further insight into the possible mechanism for magnetic coupling between coordinated radicals, a larger array of metal complexes is required. Such studies are underway and will be reported in due course.

Experimental Section

General Considerations. All of the reactions were carried out under an argon atmosphere using standard Schlenk-line or glovebox techniques. Solvents were distilled using standard agents (CaH_2 for CH_2Cl_2; sodium/benzophenone for benzene, toluene, and THF). All of the reagents were purchased from Aldrich and used as received. Nuclear magnetic resonance spectra were recorded on 360 or 250 MHz instruments. Infrared spectra were recorded as Nujol mulls on KBr plates or as KBr pressed pellets. Elemental analyses were carried out by Canadian Microanalytical Services Ltd., Vancouver, British Columbia. 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 $[H_2TMEN][CuCl_4]$.[38]

Table 1. Crystallographic Data for **9**

formula	$C_{20}H_{24}CuF_6N_{10}O_2P$
fw	645.00
space group	I_1/acd
V, Å^3	11 524(2)
Z	16
D_{calcd}, g/cm^3	1.49
a, Å	27.269(3)
c, Å	15.498(2)
T, K	293
μ(MoKα), mm^{-1}	0.89
wavelength, Å	0.710 73
R$_F{}^a$, wR^b	0.054, 0.152

[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 of the reflections.

Synthesis of 1,5-Dimethyl-3-(6-methyl-2-pyridyl)-1,2,4,5-tetrazane 6-Oxide (8). A solution of 6-methyl-2-pyridinecarboxaldehyde (1.3 g, 11 mmol) in 200 mL of methanol was added dropwise to a refluxing solution of carbonic acid bis(1-methylhydrazide)[20] (**7**; 1.3 g, 11 mmol) in 30 mL of methanol. After the addition was complete, the solution was refluxed for 18 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure, yielding an off-white solid. The crude product was recrystallized from hot ethyl acetate (∼20 mL) to afford colorless blocks of **1**, yield 2.09 g (86%). Mp: 137−138 °C. ^{1}H NMR ($CDCl_3$): δ 7.58 (t, 1H, J = 8.1 Hz), 7.20 (d, 1H, J = 7.4 Hz), 7.12 (d, 1H, J = 8.1 Hz), 4.95 (br s, 2H), 4.78 (s, 1H), 3.14 (s, 6H), 2.49 (s, 3H) ppm.^{13}C NMR ($CDCl_3$): δ 158.8, 154.4, 152.7, 137.4, 123.8, 120.5, 69.3, 38.1, 24.2 ppm. IR (KBr disk): ν(NH) 3249(s), 3215(s); ν(CO) 1627(s br) cm^{-1}. MS (CI methane): m/z 222 (M + 1, 100%). Anal. Calcd for $C_{10}H_{15}N_5O$: C, 54.28; H, 6.83; N, 31.65. Found: C, 54.29; H, 6.98; N, 31.37.

Synthesis of 1,5-Dimethyl-3-(6-methyl-2-pyridyl)-6-oxoverdazyl (6) (as a Hydroquinone Adduct). 1,4-Benzoquinone (347 mg, 3.21 mmol) was added to a solution of **8** (474 mg, 2.14 mmol) in 10 mL of benzene. The solution immediately turned yellow-orange and then gradually turned darker red. The reaction was stirred for 2 h at 50 °C during which time a dark red-brown solid precipitated out of a deep-red solution. The benzene was removed under reduced pressure, affording a dark-red solid, yield 675 mg (95%). The product was recrystallized from a 3:1 toluene/ethyl acetate mixture to afford red-brown needles. Mp: 115−117 °C. IR (KBr): ν(OH) 3288(br m); ν(CO) 1692(s) cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 410 nm (ϵ = 1600). MS (CI methane): m/z 329 $(M + C_6H_6O_2)^+$, 219 $(M + 1)^+$, 111 $(C_6H_6O_2 + 1)^+$. Anal. Calcd for $C_{10}H_{12}N_5O{\cdot}C_6H_6O_2$: C, 58.53; H, 5.52; N, 21.33. Found: C, 58.45; H, 5.51; N, 21.34.

Synthesis of a Copper Complex of Radical 6 (9). A solution of **6** (freshly separated from hydroquinone by flash chromatography; 229 mg, 1.05 mmol) in 3 mL of methanol was added in one portion to a solution of $[Cu(CH_3CN)_4]PF_6$ (196 mg, 0.53 mmol) in 3 mL of methanol. Immediately, the reaction mixture turned forest-green. After being stirred for 15 min, the solvent was removed in vacuo, affording a forest-green powder, yield 200 mg (60%). Single crystals were grown by solvent diffusion of diethyl ether into an acetone solution of **9**. IR (KBr): ν(CO) 1698(s); ν(PF) 839(s) cm^{-1}. UV−vis (acetone): λ_{max} 443 nm (ϵ = 8500), 623 (ϵ = 4200). MS (FAB positive mode): m/z 499.1 ($(M - PF_6)^+$, 100%), 281 ($(M^+ - \mathbf{6})^+$, 90), 219 ($(\mathbf{6} + 1)^+$, 100).

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Anal. Calcd for $C_{20}H_{24}N_{10}O_2CuPF_6$: C, 37.31; H, 4.02; N, 20.72. Found: C, 37.84; H, 3.99; N, 20.73.

X-ray Crystallography. Relevant crystallographic information is presented in Table 1. Dark green-black needles were mounted on a glass fiber with silicone grease. Data were collected on a Smart 1000 diffractometer (Mo Kα, graphite-monochromated radiation (λ = 0.710 73 Å). Data were collected for $4 < 2\theta < 50°$. A total of 29 078 reflections were measured of which 2554 were independent and 1554 were used in the refinement of 199 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 = 0.054 ($I > 2\sigma(I)$) and wR2 = 0.152; min/max residual electron density = −0.28/+0.59 e Å^2. Complete crystallographic data for **9** have been deposited as Supporting Information.

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Supporting Information Available: X-ray crystallographic files for **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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