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Geometric Control of Ground State Multiplicity in a Copper(I) Bis(verdazyl) Complex

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A copper(I) complex of a 3-(6′-isopropylpyridyl)-substituted verdazyl was synthesized and characterized by X-ray crystallography and magnetic susceptibility. The complex crystallizes in the monoclinic space group *C*2/*c* with cell dimensions $a = 22.544$ Å, $b = 11.576$ Å, $c = 17.157$ Å, $\beta = 123.907°$, $V = 3716.2$ Å^3. The coordination geometry at copper is distorted tetrahedral, with the two ligand planes separated by 75°. Magnetic susceptibility measurements indicate that the ground state of the diradical is a triplet at this geometry. Fitting to a simple Heisenberg Hamiltonian ($\mathbf{H} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$) gave $J = 47(1)$ cm^{-1}. The triplet ground state results from exchange mediated by the copper ion; in particular, the direction of the distortion from tetrahedral geometry appears to be essential to maintain the high-spin ground state.

Introduction

Magnetostructural correlation, that is the role that molecular structure plays in magnetic interaction, plays an important role in the design of magnetic materials and magnetic molecular devices. The basic principles behind prediction of the sign of magnetic exchange have been reasonably well elucidated,[1] and for some examples, detailed correlations between structural parameters and the sign and magnitude of magnetic exchange have been determined.[2−5] Most well understood systems involve the interactions of transition metal ions mediated by bridging ligands, and in these examples, the relatively localized nature and well-defined geometry of the magnetic orbitals simplify analysis. Other examples involving the interaction of free radicals (either through-space interactions or interactions mediated by covalent bonds) are more challenging because of the more complex shape of the magnetic orbitals involved and the relatively weak nature of the interaction. Covalent systems where one interaction dominates, such as the interaction of radicals "meta-through-benzene", are usually consistent with predictions, but even then, geometric distortion can give unexpected results.[6] Other interactions of particular interest are those associated with self-assembly, such as hydrogen bonding and metal coordination,[7] because the self-assembly of paramagnetic species may provide routes toward molecular magnetic devices. As an example of a radical interaction through a coordinated diamagnetic metal center that may form the basis for a self-assembled system, the two copper(I) complexes shown in Chart 1, [Cu(immeppy)$_2$]$^+$ (**1**) and [Cu(mepyvd)$_2$]$^+$ (**2**), are an interesting pair. The former, an iminonitroxide complex, has a triplet ground state and a pseudotetrahedral geometry at copper, with a near 90° angle between the ligand planes.[8,9] The latter, a verdazyl complex, appears to have near degenerate singlet and triplet states and in the solid state shows a distorted structure in which the angle between the two ligand planes is 116°.[10] Interpretation of the magnetic data for **2** is complicated by the poor fit of the data to a simple dimer model and the very small singlet−triplet splitting. DFT calculations predict a perpendicular geometry minimum and a triplet ground state for both species,[11] suggesting that the solid state distortion is a result of crystal packing. It is appealing to conclude that the difference in singlet−triplet separation is also due to this distortion, but the effects of subtle differences in the radical ligands cannot be easily

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[1] Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

[2] Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

[3] Leitch, A. A.; Yu, X.; Winter, S. M.; Secco, R. A.; Dube, P. A.; Oakley, R. T. *J. Am. Chem. Soc.* **2009**, *131*, 7112.

[4] Shultz, D. A.; Bodnar, S. H.; Lee, H.; Kampf, J. W.; Incarvito, C. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 10054.

[5] Rajca, A.; Mukherjee, S.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.* **2006**, *128*, 13497.

[6] Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

[7] Lehn, J. M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995.

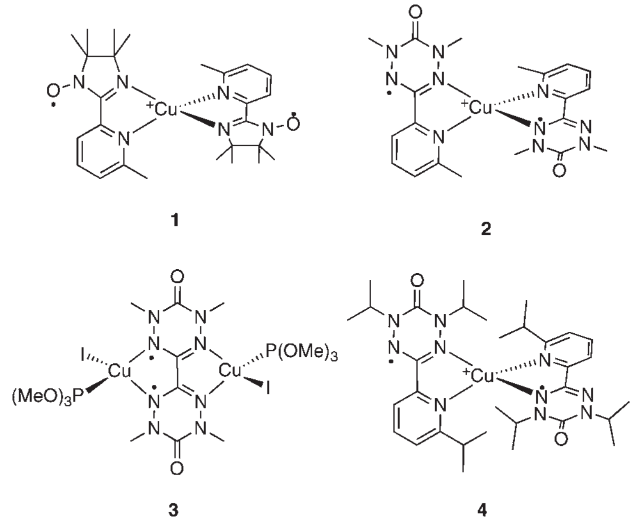
[8] Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T.; Ikoma, T.; Tero-Kubota, S. *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 47.

[9] Oshio, H.; Watanabe, T.; Ohto, A.; Ito, T.; Nagashima, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 670.

[10] Barclay, T. M.; Hicks, R. G.; Lemaire, M. T.; Thompson, L. K. *Inorg. Chem.* **2001**, *40*, 6521.

[11] Stevens, J. E.; Brook, D. J. R.; Abeyta, V. W. *Polyhedron* **2003**, *22*, 2241.

Chart 1. Copper(I) Radical Complexes **1**−**4**



eliminated. Neither complex has rigorously orthogonal radical SOMOs, and thus there is no particular reason to anticipate a ground-state triplet. Experimentally, both species show very rapid spin relaxation resulting in very broad ESR spectra even in frozen solution; consequently a reliable determination of magnetic exchange in solution (where the geometry should be less distorted) has not been possible. Adding to this picture is the copper (bisverdazyl) complex **3**, in which the copper ion appears to mediate ferromagnetic exchange between two coplanar verdazyls, though this is not enough to compete with the direct verdazyl−verdazyl interaction.[12]

We now report a copper(I) bis(verdazyl) complex **4** with otherwise identical electronic structure to **2** but with a change in ground-state geometry sufficient to give a triplet ground state, thus providing a key data point in understanding the sign and magnitude of exchange interactions mediated by copper(I).

Experimental Section

General. 2,4-Diisopropyl-carbonobishydrazide dihydrochloride was synthesized as reported previously.[13] 2-Bromo-6-isopropylpyridine was synthesized in five steps from 2-methyl-2-butanone, ethyl formate, and cyanoacetamide; however, after this project was begun, a shorter route to this compound was reported.[14] Details of our route are supplied in the Supporting Information.

6-Isopropylpyridine-2-carboxaldehyde (5). 2-Bromo-6-isopropyl pyridine (0.4 g, 2 mmol) was dissolved in 5 mL of dry THF under nitrogen. The solution was cooled to −78 °C in a dry ice/acetone bath, and 1.4 mL of a 1.6 M solution of 1-butyllithium in hexanes (2.2 mmol) was added dropwise via syringe to give an orange solution. After the mixture was stirred for 30 min, dry dimethylformamide (0.5 mL) was added via syringe, and stirring continued for another 30 min. The solution was then allowed to warm to room temperature and diluted with 2 mL of water and 3 mL of ethyl acetate. The organic layer was separated, dried, and evaporated to give the crude product. This was redissolved in dichloromethane and filtered through silica gel to give the product as a colorless oil (0.15 g, 50%) with ^{1}H NMR ($CDCl_3$) 10.04 (s, 1H), 7.79 (d, 2H, J = 4.5), 7.41 (t, 1H, J = 4.5), 3.17 (septet, 1H, J = 7), 1.36 (d, 6H, J = 7); ^{13}C NMR ($CDCl_3$) 194.2, 168.1, 152.2, 137.2, 125.0, 119.1, 36.2, 22.5; IR (NaCl plate) 3063, 2964, 2928, 2870, 1711 (C=O), 1589 (C=N), 1470, 1453, 1363, 1254, 1214, 1159, 1094, 992, 858, 809, 748, 640; MS (EI) m/z (abundance) 149 (19), 148 (23), 134 (100), 121 (13), 104 (22).

1,3-Diisopropyl-5-(6′-isopropylpyridyl)-tetrazane-2-one (6). 6-Isopropylpyridine-2-carboxaldehyde (53 mg, 0.35 mmol) and 2,4-diisopropylcarbonobis(hydrazide) bishydrochloride (88 mg, 0.35 mmol) were combined in methanol (1 mL) at room temperature. Sodium acetate (60 mg, 0.7 mmol) dissolved in water (0.5 mL) was added, and the solution was allowed to stand for 1 h. The methanol was evaporated under vacuum, and the tetrazane was separated as an oil that crystallized on standing (45 mg, 50%): mp 127−129 °C; ^{1}H NMR ($CDCl_3$) 7.64 (t, 1H, J = 7.5), 7.18 (d, 2H, J = 7.5), 4.68 (septet, 2H, J = 7), 4.40 (bs, 2H (NH)), 4.32 (bs, 1H (CH)), 3.04 (septet, 1H, J = 7), 1.29 (d, 6H, J = 7), 1.09 (d, 6H, J = 7), 1.08 (d, 6H, J = 7); ^{13}C NMR ($CDCl_3$) 167.5, 153.7, 153.2, 121.1, 120.8, 71.1, 47.7, 36.0, 22.5, 19.3, 18.4; IR (NaCl plate) 3227 (NH) 2964, 2929, 1617, 1453, 1415, 1360, 1129; MS (EI) m/z (abundance) 305, 232, 206, 190, 162, 149, 121.

Bis(1,5-diisopropyl-3-(6′-isopropyl-2′-pyridyl)-verdazyl)copper(I) Hexafluorophosphate (4). A solution containing 90 mg (0.3 mmol) of 2,4-diisopropyl-6-(6′-isopropyl-2′-pyridyl)-1,2,4,5-tetrazane-3-one, 45 mg of benzoquinone (0.45 mmol), and 55 mg (0.15 mmol) of tetrakis(acetonitrile)copper(I) hexafluorophosphate in 5 mL of acetonitrile was warmed on a hot plate for 5 h during which time the solution turned brown and then deep green. Evaporation of the solvent gave a black solid that was redissolved in dichloromethane (2 mL), and the solution was filtered. The copper complex was precipitated by slow diffusion of ether vapor into the solution giving dark green-brown crystals (49 mg, 50%): IR (NaCl plate) 2972, 2937, 2876 (C−H), 1694 (C=O), 842 cm^{-1} (PF_6); anal. calcd for $C_{32}H_{48}CuF_6N_{10}O_2P$, C 47.26, H 5.95, N 17.22; found, C 47.14, H 6.12, N 16.94; electronic absorption (CH_2Cl_2) λ_{max} = 612 nm (ε = 2590 L mol^{-1} cm^{-1}), 567 (2320), 532 (2170), 445 (6130); ESMS m/z 667.3 (100, CuL_2^+), 365 (100, CuL^+). A sample for crystallographic analysis was submitted through the Service Crystallography at Advanced Light Source (SCrALS) program at Lawrence Berkeley National Laboratory. Intensity data were collected at 150 K on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source using synchrotron radiation tuned to λ = 0.7749 Å. A series of 3 s frames measured at 0.2° increments of ω were collected to calculate a unit cell. For data collection, frames were measured for a duration of 3 s for low-angle data and 5 s for high-angle data at 0.3° intervals of ω with a maximum 2θ value of ~60°. The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for absorption and beam corrections based on the multiscan technique as implemented in SADABS. Details of data collection, solution, and refinement are given in Table 1 and in Supporting Information in CIF format.

Results

The tetrazane **6** was synthesized by established methods[13,15] from 2-bromo-6-isopropyl pyridine. The corresponding copper(I) complex **4** was synthesized by oxidation of the tetrazane with benzoquinone in the presence of Cu(I) (Scheme 1).

A single crystal grown from diffusion of ether into a dichloromethane solution was examined by X-ray crystallography.

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(12) Brook, D. J. R.; Lynch, V.; Conklin, B.; Fox, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 5155.

(13) Paré, E. C.; Brook, D. J. R.; Brieger, A.; Badik, M.; Schinke, M. *Org. Biomol. Chem.* **2005**, *3*, 4258.

(14) Gaillard, S.; Elmkaddem, M. K.; Fischmeister, C.; Thomas, C. M.; Renaud, J.-L. *Tetrahedron Lett.* **2008**, *49*, 3471.

(15) Barr, C. L.; Chase, P. A.; Hicks, R. G.; Lemaire, M. T.; Stevens, C. L. *J. Org. Chem.* **1999**, *64*, 8893.

Table 1. Crystal Data and Structure Refinement for **4**

empirical formula	$C_{64}H_{96}Cu_2F_{12}N_{20}O_4P_2$
formula weight	1626.62
temp	150(2) K
wavelength	0.7749 Å
cryst. syst.	monoclinic
space group	*C*2/*c*
unit cell dimensions	a = 22.54400(10) Å b = 11.57640(10) Å c = 17.1570(10) Å α = 90° β = 123.9070(10)° γ = 90°
volume	3716.2(2) Å^3
Z	2
density (calcd)	1.454 Mg/m^3
abs coeff	0.706 mm^{-1}
F(000)	1696
cryst. size	0.17 × 0.13 × 0.02 mm^3
θ range for data collection	2.26−29.16°.
index ranges	$-28 \leq h \leq 23$; $-14 \leq k \leq 14$; $0 \leq l \leq 21$
reflns collected	7432
completeness to θ = 29.16°	99.6%
refinement method	full-matrix least-squares on F^2
data/restraints/params	7432/0/237
GOF on F^2	0.971
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0579, wR_2 = 0.1503
R indices (all data)	R_1 = 0.0885, wR_2 = 0.1701
largest diff. peak and hole	0.765 and −0.786 e·Å^{-3}

Scheme 1. Synthesis of Complex **4**

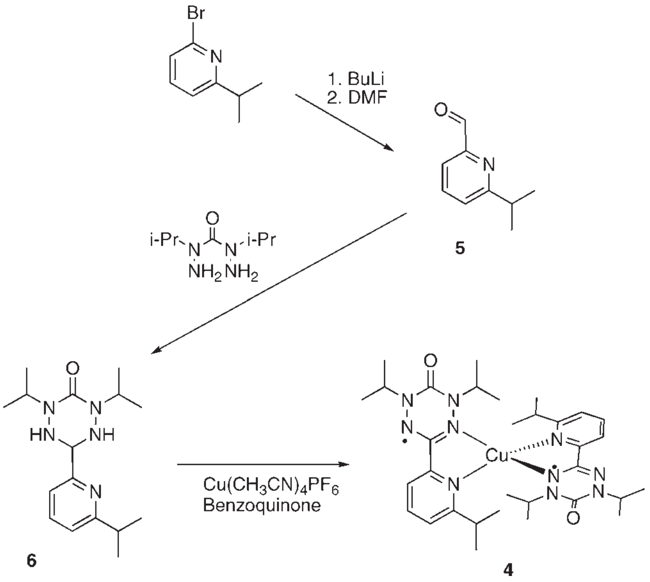

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4**

Cu(1)−N(2)	2.010(2)
Cu(1)−N(1)	2.070(2)
N(2)′−Cu(1)−N(2)	132.66(13)
N(2)−Cu(1)−N(1)	81.27(8)
N(2)−Cu(1)−N(1)′	128.61(9)
N(1)−Cu(1)−N(1)′	107.97(12)

Crystallographic details are summarized in Table 1, and important bond lengths and angles are given in Table 2. A thermal ellipsoid plot is shown in Figure 1. Full details of data collection and refinement are given in the Supporting Information in CIF format.

Examination of the structure shows that the two ligands are related by a 2-fold axis passing through the copper ion.

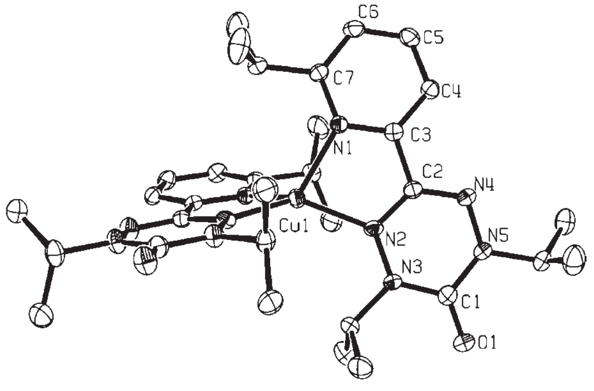

Figure 1. Thermal ellipsoid plot of **4**. In order to improve clarity, hydrogen atoms are not shown. Ellipsoids are plotted at the 50% level.

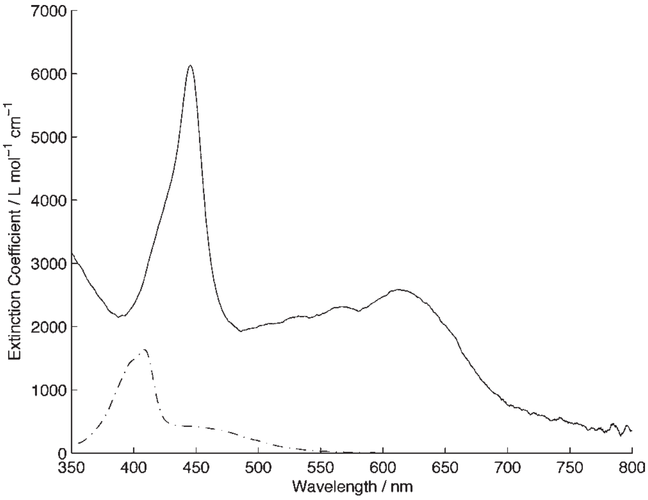

Figure 2. Electronic absorption spectrum of **4** in dichloromethane (solid line). The electronic absorption of 1,5-diisopropyl-3-(2′-pyridyl)verdazyl (broken line) is shown for comparison.

The ligands are almost planar; the angle between mean planes of the verdazyl and pyridine rings is 5.5°. The coordination geometry around copper is best described as distorted tetrahedral. The angle between the planes of the verdazyl rings is 75°, but the ligands are splayed outward at the verdazyl end; the distance between the verdazyl nitrogens is 3.68 Å, while that between the pyridyl nitrogens is 3.35 Å.

The electronic absorption spectrum in dichloromethane shows a significant increase in intensity and red shift compared with the pyridyl verdazyl[15,16] with a broad maximum at 617 nm along with a sharper peak at 445 nm (Figure 2). The spectrum is essentially indistinguishable from the spectrum of samples of **2**.

The magnetic properties of **4** were investigated from 5 to 300 K. The data were fitted to the spin Hamiltonian $\mathbf{H} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$ with the exchange parameter J, along with the diamagnetic correction and a simple intermolecular correction, zJ', as parameters. The exchange is clearly ferromagnetic with $J = +47(1)$ cm^{-1}. Data and the best fit are shown in Figure 3. X-ray powder diffraction was used to confirm that the sample used for susceptibility had the

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(16) Brook, D. J. R.; Fornell, S.; Stevens, J. E.; Noll, B.; Koch, T. H.; Eisfeld, W. *Inorg. Chem.* **2000**, *39*, 562.

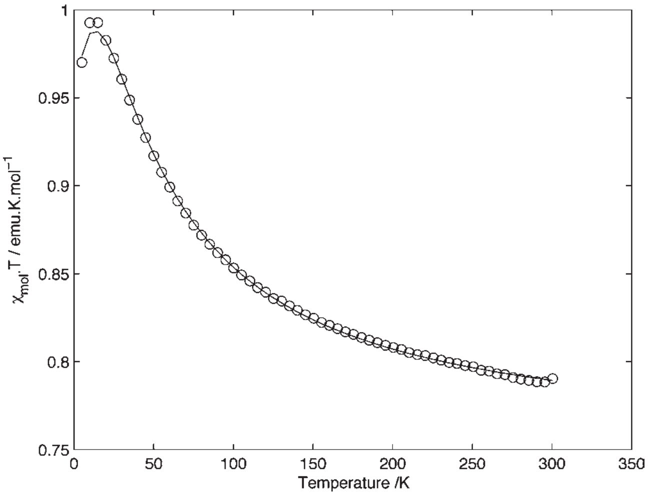

Figure 3. Plot of χT vs T for compound **4**. The solid line is the best fit to a dimer model with $J = +47(1)$ cm^{-1} and a mean field correction, $zJ' = -0.1$ cm^{-1} for intermolecular antiferromagnetic interaction at low temperature.

same structure as the single crystal used for crystallographic measurements.

Discussion

Computational results for pyridyl verdazyl copper complexes[11] suggest that in the absence of crystal packing forces, the ligands in these complexes are perpendicular and the ground state is a triplet; however, the X-ray structure of the previously reported complex, **2**, shows a distorted geometry with the planes of the two pyridyl verdazyl ligands separated by 116°.[10] Complex **4** is also distorted from the perpendicular geometry, and the distortion is of a similar magnitude, though opposite in direction. Despite this similarity, the two compounds differ markedly in their magnetic properties. Complex **2** shows very weak, if any, exchange interaction between the two radicals; though an antiferomagnetic interaction is apparent at low temperature, it could easily be intermolecular in origin.[10] In contrast, complex **4** shows a well-defined triplet ground state. Our goal is to understand how such apparently similar compounds can have such distinct magnetic properties. To approach this problem, it is convenient to use the active electron approximation and the "natural magnetic orbital" approach of Kahn.[1] In this approach the exchange interaction between magnetic orbitals (which depends upon the extent to which orbitals occupy the same space) tends to stabilize the triplet state. Overlap of the orbitals (which depends on the sign of the wave function) results in the formation of a bonding orbital and stabilizes the singlet state. Triplet ground states are thus expected when the magnetic orbitals containing the unpaired electrons occupy some space in common yet are prevented from overlap through symmetry or other fortuitous circumstances.

ESR measurements and computational studies indicate that the verdazyl singly occupied orbital (SOMO) is located on the four nitrogen atoms of the verdazyl ring.[13,16−18] Though this is the obvious initial choice for magnetic orbitals, a little inspection reveals that the two verdazyl SOMOs have some degree of overlap at any coordination geometry around the copper ion, and thus without any interaction with the metal, we would expect singlet ground states for all bis(verdazyl) copper complexes.

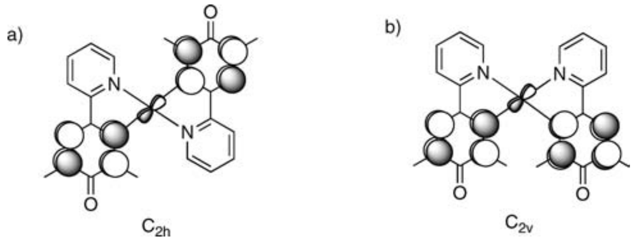

Figure 4. Orbital overlap in hypothetical C_{2h} (a) and C_{2v} (b) geometries for copper(I) pyridyl verdazyl compounds.

Clearly, to explain the triplet ground state in **4** and related systems, a more sophisticated model is required. Earlier ESR experiments with verdazyl−copper−phosphine mixed ligand systems indicate that overlap between the verdazyl SOMO and copper d orbitals results in a transfer of spin density onto copper.[19] The increase in intensity and red shift of the electronic absorption spectrum is also indicative of significant interaction between the metal and ligand orbitals, and in the case of the verdazyl−copper−phosphine systems was taken to indicate a charge transfer interaction from the filled metal d-orbitals to the verdazyl SOMO.[19] When we consider the calculated "vacuum" geometry described by Stevens et al.[11] and construct magnetic orbitals that include a contribution from a Cu d orbital, it is apparent that there is still overlap between magnetic orbitals, but because spin density from both verdazyls is transferred to the Cu(I) ion, the exchange interaction resulting from approach of the two electrons is also significantly increased.[1] If the calculations[11] are correct, this is sufficient to give a triplet ground state.

This perpendicular geometry, while consistent with the geometry and magnetic properties of the related iminonitroxide complex, does not correspond to the crystalline geometry of either complex **2** or **4**. In both latter cases, the two ligands, while still related by a 2-fold axis, are no longer perpendicular. The difference between the two structures is that in the case of **4** the distortion brings the verdazyl rings closer together, while in **2** it moves them further apart. To see how the energy of the triplet and singlet states vary with the distortion, it is useful to look at the hypothetical limit of the distortion; molecules with square planar geometries. Taken to extremes, the distortions in compounds **2** and **4** result in planar compounds with C_{2h} and C_{2v} point groups, respectively.

In the case of an idealized C_{2h} geometry, both ligand SOMOs are of the appropriate symmetry to overlap with the same d-orbital (Figure 4a); the overlap between magnetic orbitals would predict a singlet ground state. Conversely, in the C_{2v} geometry, the two ligand SOMOs interact with different d orbitals on copper, increasing the exchange interaction but not overlap between the SOMOs and predicting a stable triplet ground state (Figure 4b). A similar interaction results in the stabilization of the triplet state in copper(I) bis(verdazyl) complexes.[12] Passing from the C_{2v} geometry to the C_{2h} geometry by rotation of one ligand through a

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(17) Brook, D. J. R.; Fox, H. H.; Lynch, V.; Fox, M. A. *J. Phys. Chem.* **1996**, *100*, 2066.

(18) Chemistruck, V.; Chambers, D.; Brook, D. J. R. *J. Org. Chem.* **2009**, *74*, 1850.

(19) Brook, D. J. R.; Abeyta, V. *J. Chem. Soc., Dalton Trans.* **2002**, 4219.

pseudotetrahedral species should thus result in a smooth transition between triplet and singlet ground states, and at some point, the two states should be degenerate.

It appears from the previously published data and our data that this equivalence point corresponds quite closely to the geometry of complex **2**; the small singlet–triplet splitting is almost certainly not a result of weak interaction between the unpaired electrons. Furthermore, both the calculated geometry and the geometry of complex **4** are further in the C_{2v} direction than **2** and thus would be expected to have triplet ground states. The strong geometry dependence of the exchange interaction, combined with the geometric lability of the copper(I) center, also provides an explanation for the rapid relaxation observed in the ESR spectra of these compounds. Twisting of the two ligands with respect to each other modulates the singlet–triplet splitting and thus provides a rapid relaxation pathway for the excited spin.

Though the difference in geometry between complexes **2** and **4** seems largely fortuitous, it is reasonable to expect that the geometry of copper bis(diimine) complexes can be manipulated using peripheral ligand–ligand interactions. Consequently these bis-verdazyl compounds provide a route to novel molecules with a potentially switchable ground state through careful manipulation of ligand substitution.

Conclusion

We have synthesized a copper(I) bis(verdazyl) complex with a very similar electronic structure to an earlier copper(I) verdazyl system and a distorted tetrahedral coordination geometry in the crystal structure. Nevertheless, because the direction of distortion differs from the earlier system, the ground state remains a triplet, supporting earlier conclusions based on computational results and providing a possible avenue to manipulate the spin multiplicity of the ground state.

Acknowledgment. Funding for this project came in part from the Petroleum Research Fund (Grant 35178-GB3,1 to D.J.R.B.) and San José State University. The Advanced Light Source (ALS) is supported by the U.S. Department of Energy, Office of Energy Sciences Materials Sciences Division, under contract DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory.

Supporting Information Available: Details of the structure determination and refinement of complex **4** in CIF format, ^{1}H and ^{13}C spectra of aldehyde **5** and tetrazane **6**, and detailed experimental descriptions of the synthesis of 6-isopropyl-2-bromopyridine. This material is available free of charge via the Internet at http://pubs.acs.org.