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# Free radical complexes of copper(I): geometry and ground state

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## Abstract

DFT calculations were performed on the singlet and triplet states of a series of copper(I)–bis(radical) complexes. For a copper(I)–bis(iminonitroxide) complex, the results are consistent with experimental data, predicting a triplet ground state and an excited singlet at 38.7 $cm^{-1}$. For two related copper(I)–bis(verdazyl) complexes, the calculations predict a triplet ground state and singlet excited states at 58.6 and 34.9 $cm^{-1}$, respectively; however both the minimized structure and singlet–triplet separation are inconsistent with experimental data. We suggest that the difference between theory and experiment is a result of intermolecular interactions within the crystal lattice.

*Keywords:* DFT calculation; Copper; Verdazyl; Singlet–triplet separation

## 1. Introduction

The electronic structure of diradicals, and in particular, the ground state multiplicity of these species, is an important area of study in molecular magnetism. Models with varying degrees of complexity have been used to predict ground state, and while some of the simple models perform qualitatively well, geometrical flexibility can be a complicating factor. This has been demonstrated with a variety of organic systems, both theoretically and experimentally. For example, *m*-phenylene linked diradicals are generally accepted to have triplet ground states, though rotation about the phenylene-radical single bond can change the ground state from triplet to singlet [1–3]. In one particular case, conformers with differing ground state multiplicity were observed simply by changing the measurement matrix [4]. In organometallic systems changes in multiplicity of a metal center induced by ligand orientation effects have been reported [5], but the effects of coordination geometry upon the interaction of radicals linked through a diamagnetic metal is less well studied. An interesting case is that of N-donor radicals coordinated to copper(I). The copper(I)–bis(iminonitroxide) ion, **1** (see Fig. 1) reported by Oshio et al. [6,7], features strong charge transfer bands in the visible spectrum, two nitroxide radical ligands in an almost perpendicular arrangement, and a triplet ground state with a singlet excited state at 55 $cm^{-1}$. By comparison, the copper(I)–bis(verdazyl) complex **2** (Fig. 1) reported by Hicks and coworkers [8] also features strong visible charge transfer bands, but the coordination geometry is severely distorted with the two verdazyl ligands at an angle of 65°, and the singlet and triplet states are almost degenerate, with the singlet apparently the ground state. These observations lead to the following questions: (1) what is the origin of the distortion in the verdazyl complex? and (2) is the difference in ground state multiplicity between **1** and **2** a result of the change in coordination geometry?

Verdazyl radicals and related diradicals have recently been the subject of a number of computational studies

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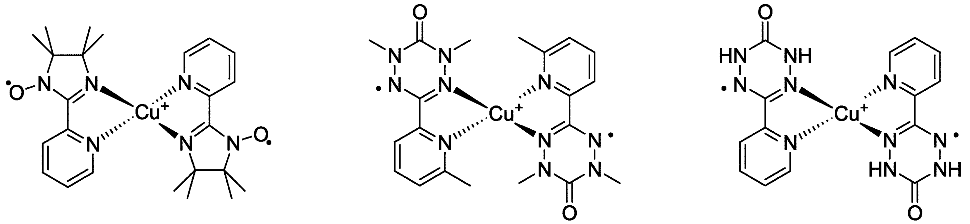

**1** **2** **3**

Fig. 1. Structures of **1**–**3**.

[9–13]. However, aside from the work of Green and McCormick [12], no theoretical/computational studies have yet examined verdazyl-metal or iminonitroxide radical complexes. Such calculations may directly address the questions of geometry and spin multiplicity noted above. To elucidate existing experimental data on copper(I)–verdazyl complexes and provide information that may lead to answers to these questions, we have performed density functional calculations on complexes **1** and **2** in singlet and triplet electronic states. In addition, to investigate any possible role of the methyl substituents upon coordination geometry we have performed calculations on the hypothetical demethylated species **3**. The method of these computations is detailed in Section 2. Results are presented in Section 3. Comparisons of the results to experimental data and a discussion of their possible significance appear in Section 4.

## 2. Computational methods

The geometry of all copper–radical complexes were optimized on singlet and triplet potential energy surfaces using the B3LYP [14,15] hybrid density functional method. Unrestricted wavefunctions (UB3LYP) were used in both triplet and singlet state computations. A 6–31G basis was used for all carbon and hydrogen atoms; nitrogen and oxygen atoms were also assigned a 6–31G basis with additional d polarization functions. (6–31G(d)). For copper atoms, the Los Alamos [16] effective core potential was used with the accompanying double-zeta basis set. All computations are gas-phase, i.e., no solvent modeling is included in the calculation. Calculation of geometrical parameters (e.g. least squares planes) was performed with the computational package Octave (http://www.octave.org).

## 3. Results

Initially, UB3LYP single-point calculations were made at the reported experimental geometries of **1** and **2**. For the copper–iminonitroxide ion **1**, computations at Oshio's reported geometry determine that the triplet state is lower in energy; the vertical excitation to the singlet state is 172.5 kcal $mol^{-1}$ (60 344.4 $cm^{-1}$). A similar calculation for the copper–bis verdazyl complex **2** again show that the triplet is the more stable state; the singlet appears at a vertical excitation energy of 22.0 kcal $mol^{-1}$ (7711.3 $cm^{-1}$).

The singlet–triplet gap for both species decreases appreciably upon optimization. Optimized triplet and singlet structures of **1** are shown in Fig. 2; the structures are notably similar to one another and to the experimental geometry. The triplet structure is the more stable, with the singlet minimum located at 38.7 $cm^{-1}$ relative to the triplet. This compares favorably with the experimental value of 55.1 $cm^{-1}$ [7].

As shown in Fig. 2, geometric parameters for the singlet and triplet minima of **1** are very similar. The complex belongs to the $C_2$ point group in both singlet and triplet states, and there are two unique Cu–N bond lengths and four unique N–Cu–N bond angles. Both structures show a tetrahedral arrangement of bonds about the Cu atom; Cu–N bond lengths and bond angles for the two are nearly identical. Both singlet and triplet show a perpendicular arrangement of ligands; the angle between the planes defined by the copper and coordinating nitrogens of each ligand are 94.0° for the singlet and 93.9° for the triplet. Other structural parameters compare well with experiment. Table 1 summarizes some structural data for the triplet and singlet complexes, with experimental data provided for comparison.

Fig. 3 displays the optimized singlet and triplet minima of **2**. The triplet state is the ground state, with the singlet located at an energy of 58.6 $cm^{-1}$ relative to the triplet. These results are distinctly different from those reported by Hicks and coworkers, who find that the singlet is the lower energy state, with the triplet at an energy of 2 $cm^{-1}$ relative to the singlet.

Optimized triplet and singlet complexes both belong to the $C_2$ point group. The geometry again shows tetrahedral coordination to the copper atoms and a perpendicular arrangement of ligands. The angle between the least squares planes defined by the Cu–N–C–C–N chelate rings of each ligand are 91.0° for the singlet

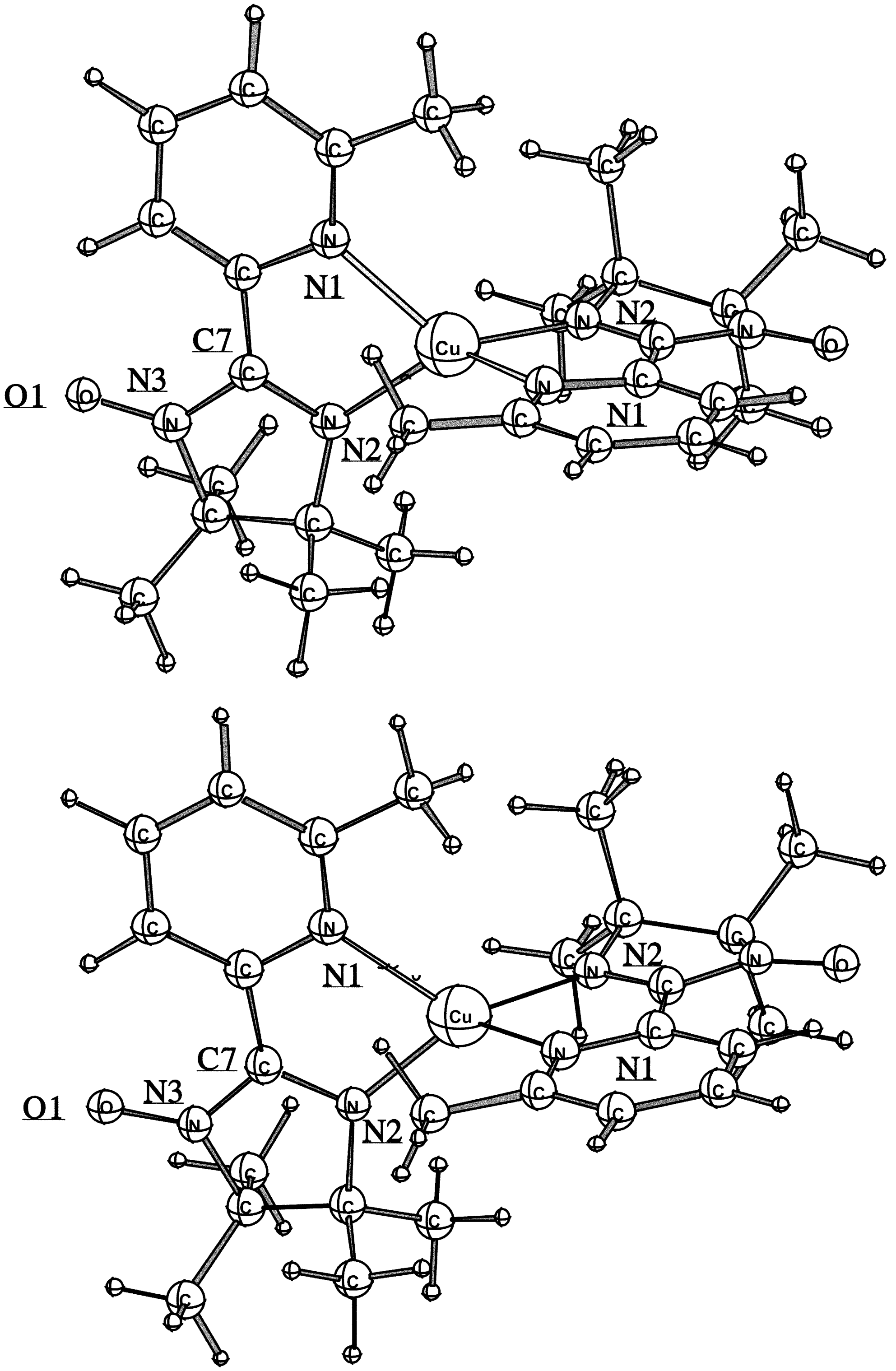

Fig. 2. Optimized triplet (top) and singlet (bottom) structures of **1**. The atomic numbering scheme corresponds to that of Oshio et al. [7].

and 90.5° for the triplet. The triplet and singlet optimized structures are nearly identical; however, they differ from the reported experimental structure in two notable ways. Firstly, as previously noted, in the experimental structure the ligand planes are significantly distorted from a perpendicular orientation. A more subtle deviation is observed in the orientation of the methyl groups. Our gas-phase UB3LYP calculation shows a methyl group adjacent to the carbonyl oxygen rotated so that a hydrogen atom is in proximity to an O

Table 1
Optimized structural parameters for the triplet and singlet minima of **1**

| | Triplet minimum | Singlet minimum | Experiment [7] |
|---|---|---|---|
| *Distances* | | | |
| Cu–N1 | 2.1816 | 2.1819 | 2.081 |
| Cu–N2 | 2.0483 | 2.0504 | 1.953 |
| O1–N3 | 1.263 | 1.263 | 1.273 |
| N2–C7 | 1.3103 | 1.3098 | 1.271 |
| N3–C7 | 1.3891 | 1.3898 | 1.374 |
| *Angles* | | | |
| N1–Cu–N1 | 118.4 | 118.5 | 116.8 |
| N2–Cu–N2 | 130.3 | 130.3 | 131.2 |
| N1–Cu–N2 | 79.4 | 79.4 | 81.1 |
| N1–Cu–N2 [a] | 127.8 | 127.9 | 126.0 |
| N2–C7–N3 | 112.9 | 112.9 | 112.5 |
| O1–N3–C7 | 127.3 | 127.3 | 126.1 |

Experimental data is provided for comparison. All lengths are in angstroms and angles are in degrees

[a] Bridging from one iminonitroxide radical to the other.

atom in what is apparently a weak hydrogen-bonding interaction. Table 2 displays additional structural data for both singlet and triplet complexes, with experimental data included for comparison.

In the case of **3**, optimizations of triplet and singlet minima (see Fig. 4) again find a more stable triplet state, with the singlet minimum appearing at an energy of 34.9 $\mathrm{cm}^{-1}$ relative to the triplet minimum. Tetrahedral coordination of the Cu atom and a perpendicular arrangement of the verdazyl ligands is again observed; the angle between the ligand planes being 90.5° for the singlet and 91.2° for the triplet.

## 4. Discussion

Orbital overlap arguments are often used to predict, qualitatively, the ground state multiplicities of organic and organometallic polyradical species. The predicted ground state depends upon the symmetry of the ligand orbitals and the coordination geometry around the metal center. In the case of four coordinate, diamagnetic metal ions with $\pi$ centered radical ligands, at one extreme a square planar geometry allows overlap of both ligand SOMOs with the metal $\pi$ orbitals, giving a singlet ground state; in a pseudotetrahedral geometry such overlap is not possible and a triplet ground state should result [17]. Consequently we initially suspected that the steric requirements of the iminonitroxide ligand enforced a pseudotetrahedral geometry and a triplet ground state, while the less sterically demanding verdazyl ligand could adopt a distorted structure resulting in a more stable singlet ground state.

Our initial computational results on the experimentally determined structure of complex **1** were somewhat disappointing; however, two factors contribute to the poor result. Firstly, the crystal structure is a weighted average of singlet and triplet structures and thus may not correspond well to the ideal geometry of either state. Secondly, because the value in question (the singlet–triplet separation) is so small, it is more appropriate to use computationally optimized structures, whereby errors in the calculation on both singlet and triplet potential energy surfaces may cancel out. Upon optimization, though the geometry change is small, the calculated singlet–triplet splitting becomes very close to the experimental value. As a result we are confident that the optimized geometry calculated for the bis verdazyl complexes, which feature near perpendicular ligand planes, are representative of the actual structure of this ion in solution. Our data thus strongly suggest that the distorted structure observed for **2** in the crystal is a result of crystal packing forces rather than the electronic structure of the radical. This is consistent with other copper(I)–imine complexes such as $\mathrm{Cu(phen)_2^+}$ which are also known to distort from a perpendicular to a flattened geometry upon crystallization [18,19]. Interestingly, McMillin and coworkers have reported evidence that some $\mathrm{Cu(phen)_2^+}$ type complexes *do* retain a distorted structure in solution, but that this results from pi-stacking interactions between arms of the ligand [18].

In addition to the distinction between solution and solid state structures, our calculations also suggest that the perpendicular orientation of the copper(I)–bis(verdazyl) complex should exhibit a triplet ground state, and singlet–triplet separation similar to that observed for the iminonitroxide complex **1**. Furthermore, computations at the flattened geometry observed in the crystal structure give a triplet ground state, though because we could not optimize the structure at this geometry the singlet–triplet separation is unreliable. The question then, is why is the measured singlet triplet separation in

Table 2
Optimized structural parameters for the triplet and singlet minima of **2**

| | Triplet minimum | Singlet minimum | Experiment [8] |
|---|---|---|---|
| *Distances* | | | |
| Cu–N1 | 2.1132 | 2.1171 | 2.0434 |
| Cu–N5 | 2.0990 | 2.0982 | 2.0164 |
| N1–N2 | 1.3632 | 1.3629 | 1.3625 |
| N3–N4 | 1.3498 | 1.3498 | 1.3626 |
| N1–C4 | 1.3488 | 1.3484 | 1.3266 |
| N4–C4 | 1.3297 | 1.3301 | 1.3246 |
| *Angles* | | | |
| N1–Cu–N1 | 124.2 | 123.9 | 130.6 |
| N5–Cu–N5 | 129.5 | 129.7 | 140.2 |
| N1–Cu–N5 | 79.4 | 79.4 | 81.0 |
| Cu–N1–C4 | 113.7 | 113.6 | 113.2 |

Experimental data is provided for comparison. All lengths are in angstroms and angles are in degrees.

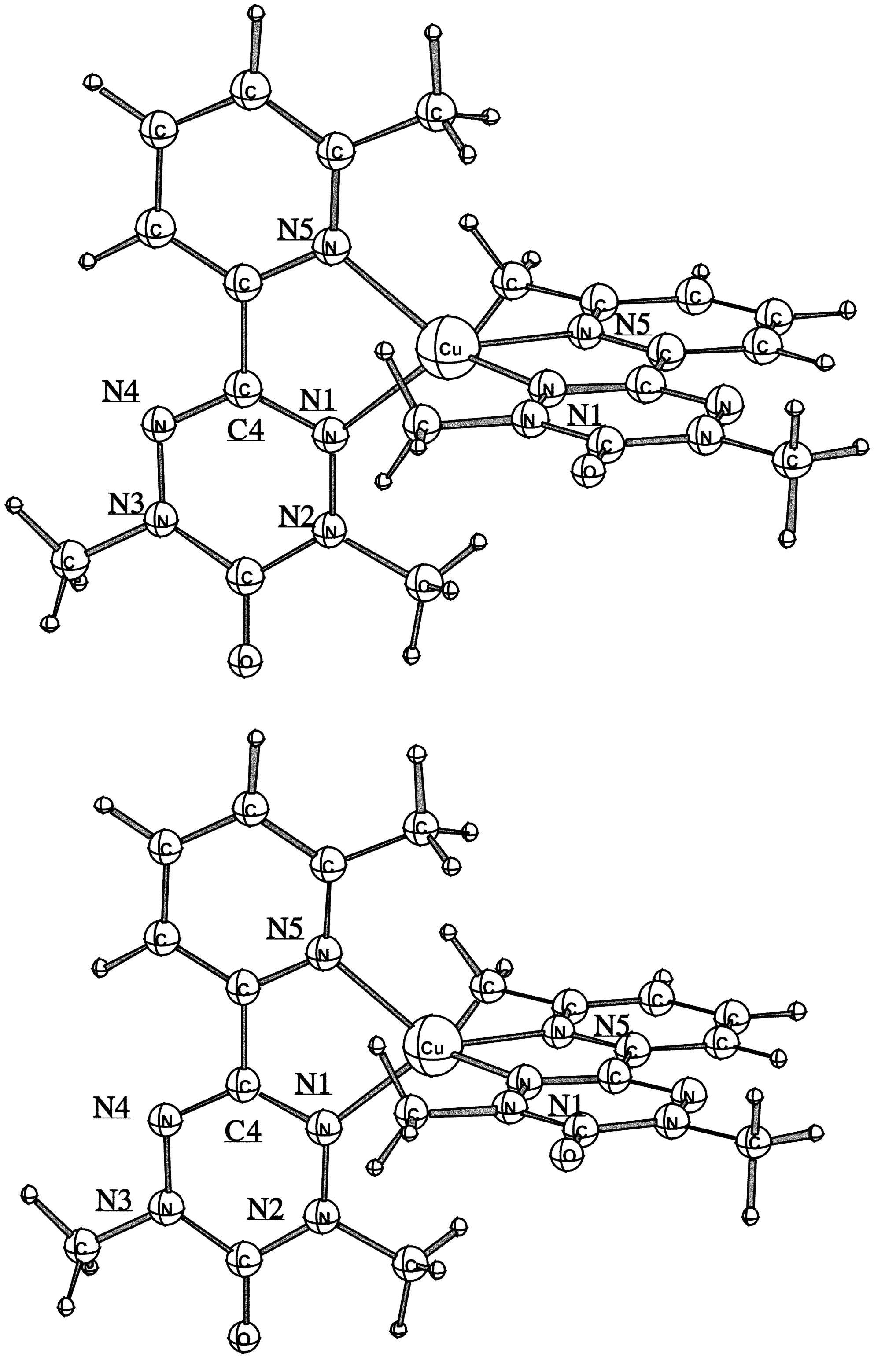

Fig. 3. Optimized triplet (top) and singlet (bottom) structures of **2**. The atomic numbering scheme corresponds to that of Barclay et al. [8].

this species so small? A hint comes from careful inspection of the experimental data, which does not fit the Bleany–Bowers equation for a diradical without inclusion of a term to include intermolecular interactions [8]. Since our calculations suggest that the crystalline geometry is a result of *inter*molecular forces, it is probable that there is significant *inter*molecular magnetic exchange in the crystal structure, complicating analysis of magnetic data and possibly resulting in the deceptively weak magnetic interactions.

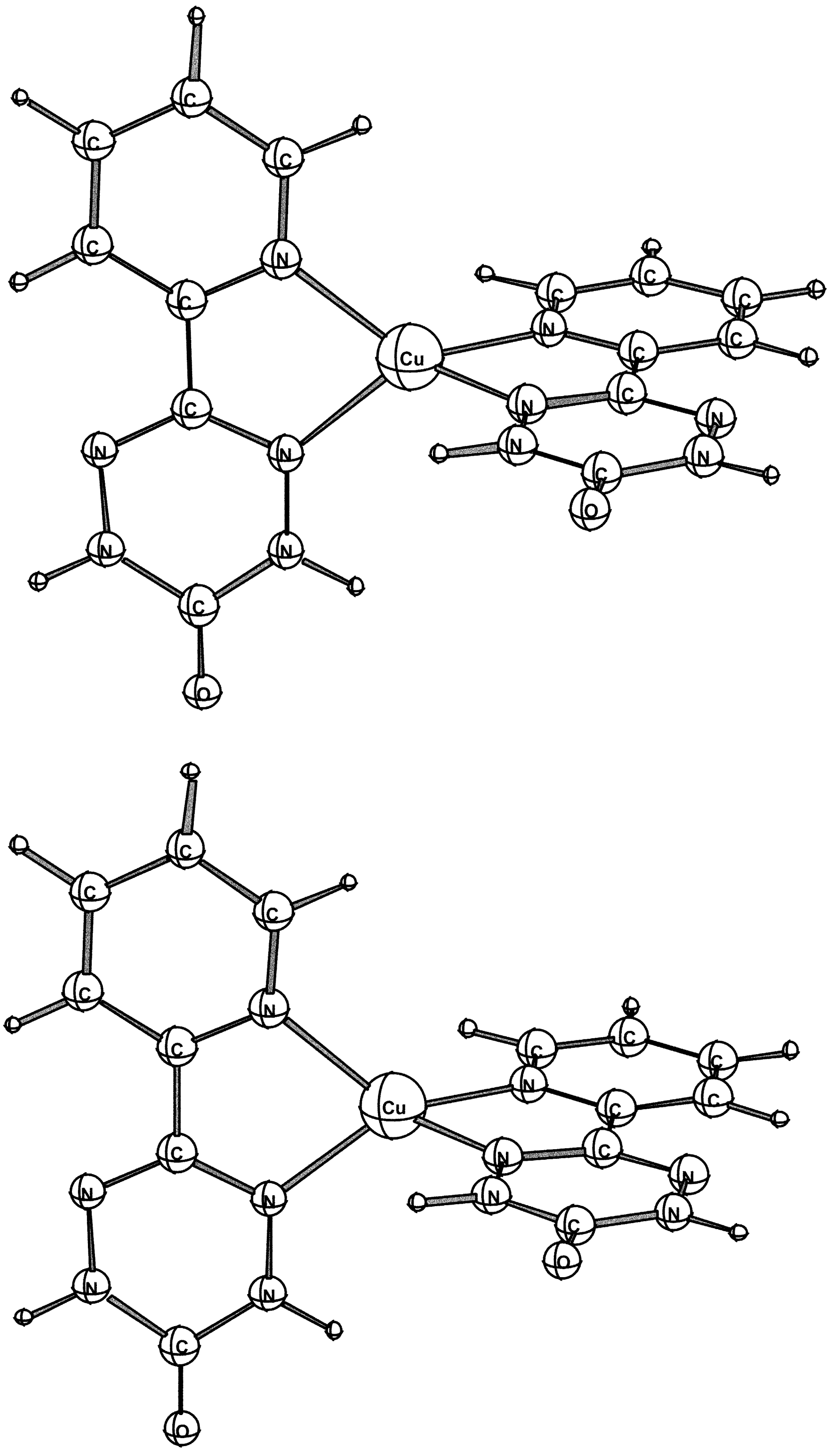

Fig. 4. Optimized triplet (top) and singlet (bottom) structures of **3**.

It is noteworthy that experimentally, the singlet triplet splitting of both the verdazyl and iminonitroxide complexes have not been measured by ESR in frozen solution. The problem arises because the ESR spectra show very broad linewidths that prevent resolution of a clear triplet signal [7]. This phenomenon is believed to be due to a rapid relaxation mechanism. A similar phenomenon was observed in copper(I)–halide complexes of **bvd**, where the relaxation rate appeared to show a weak thermal activation [20]. Our calculations may provide some insight into this phenomenon; the singlet and triplet minima of both species differ so little geometrically that there is likely to be an intersection of the singlet and triplet surfaces near to both minima.

The barrier to intersystem crossing is consequently liable to be very small, allowing rapid conversion between singlet and triplet even at low temperatures.

## 5. Conclusion

As with other purely organic species, our results suggest that geometry may play an important role in the ground state of metal-radical species, and that in the case of conformationally flexible species such as those of Copper(I), care must be taken to ensure this geometry is maintained, if these substances are to be used in materials and devices. We are currently developing the synthesis of verdazyl radicals with more controlled coordination geometry. Furthermore, our successful calculation of the singlet triplet splitting of the copper–iminonitroxide species, confirms that ab initio computational studies have an important role to play in the design and synthesis of magnetic materials.

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## References

[1] S. Fang, M.S. Lee, D.A. Hrovat, W.T. Borden, J. Am. Chem. Soc. 117 (1995) 6727.

[2] W. Adam, C. van Barneveld, S.E. Bottle, H. Engert, G.R. Hanson, H.M. Harrer, C. Heim, W.M. Nau, D.M. Wang, J. Am. Chem. Soc. 118 (1996) 3974.

[3] K. Okada, T. Imakura, M. Oda, H. Murai, M. Baumgarten, J. Am. Chem. Soc. 118 (1996) 3047.

[4] D.A. Shultz, A.K. Boal, G.T. Farmer, J. Am. Chem. Soc. 119 (1997) 3846.

[5] E.D. Brady, J.S. Overby, M.B. Meredith, A.B. Mussman, M.A. Cohn, T.P. Hanusa, G.T. Yee, M. Pink, J. Am. Chem. Soc. 124 (2002) 9556.

[6] H. Oshio, T. Watanabe, A. Ohto, T. Ito, U. Nagashima, Angew. Chem. Int. Ed. Engl. 33 (1994) 670.

[7] H. Oshio, T. Watanabe, A. Ohto, T. Ito, T. Ikoma, S. Tero-Kubota, Inorg. Chem. 36 (1997) 3014.

[8] T.M. Barclay, R.G. Hicks, M.T. Lemaire, L.K. Thompson, Inorg. Chem. 40 (2001) 6521.

[9] G. Chung, D. Lee, Chem. Phys. Lett. 350 (2001) 339.

[10] R.G. Hicks, L. Ohrstrom, G.W. Patenaude, Inorg. Chem. 40 (2001) 1865.

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

[12] M.T. Green, T.A. McCormick, Inorg. Chem. 38 (1999) 3061.

[13] V. Barone, A. Bencini, I. Ciofini, C. Daul, J. Phys. Chem. A. 103 (1999) 4275.

[14] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[15] A.D. Becke, J. Chem. Phys. 96 (1992) 2155.

[16] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.

[17] C.W. Lange, B.J. Conklin, C.G. Pierpont, Inorg. Chem 33 (1994) 1276.

[18] C.T. Cunningham, J.J. Moore, K.L.H. Cunningham, P. Fanwick, D.R. McMillin, Inorg. Chem. 39 (2000) 3638.

[19] M.K. Eggleston, D.R. McMillin, K.S. Koenig, A.J. Pallenberg, Inorg. Chem. 36 (1997) 172.

[20] D.J.R. Brook, B. Conklin, V. Lynch, M.A. Fox, J. Am. Chem. Soc. 119 (1997) 5155.