Inorg. Chem. **1999,** *38,* 3061−3065

Controlling the Singlet−Triplet Splitting in Bisverdazyl Diradicals: Steps toward Magnetic Polymers

Michael T. Green*,† and Thomas A. McCormick

Department of Chemistry and James Franck Institute, The University of Chicago,
5735 South Ellis Avenue, Chicago, Illinois 60637

Received December 14, 1998

Density functional calculations were performed on 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-biverdazyl diradical (BVD) and BVD[CuI(PL_3)]$_2$ complexes (L = H, Me, OH, OMe, F) in order to investigate how Cu chelation affects the singlet−triplet splitting of the verdazyl system. It was found that donating ligands on Cu destabilize the singlet ground state. Size was also found to play a role, as smaller ligands allow for closer Cu−verdazyl contacts. Although a triplet ground state was not obtained for any of the molecules examined, a very small splitting of 40 cm^{-1} was calculated for the phosphine complex.

Introduction

There has been considerable interest recently in the rational design of "hybrid" magnetic materials. Research has been aimed at constructing extended systems, which consist of metal centers linked by closed shell,[1−3] or radical organic ligands.[4−6] The hope is that these hybrid materials will combine desirable properties from each of the components to generate magnetic materials which are lightweight, soluble in organic solvents, and optically transparent. In almost all of these materials it has been spins on the metal centers which investigators have sought to align. However, a molecule which seems to allow an interesting alternative to this approach has recently been used to construct extended networks.[7] 1,1′,5,5′-tetramethyl-6,6′-dioxo-3,3′-biverdazyl diradical (BVD) (Figure 1) was first synthesized by Neugebauer and Fischer.[8] This diradical has an unpaired electron on each ring, and these are known to couple antiferromagnetically, yielding a singlet ground state with a singlet−triplet splitting of 760 cm^{-1}.[9] Fox and co-workers have reported that the complex BVD[CuI(P(OMe)$_3$)]$_2$ (Figure 2) is formed by the addition of (trimethyl phosphite) copper(I) iodide to chloroform or dichloromethane solutions of BVD. This complex is also a singlet, but interestingly the singlet−triplet splitting has been reduced to 230 cm^{-1}.[7] This decrease of over 500 cm^{-1} is an encouraging result because it suggests that through the proper choice of metal and ligand, it may be possible to obtain a BVD complex with a triplet ground state. If this is the case the bridging ability of the BVD complex could provide us with a wealth of magnetic coordination polymers.

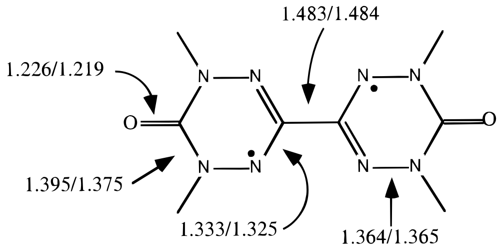

Figure 1. Calculated/experimental bond lengths for BVD. The crystal structure of BVD does not have D_{2h} symmetry. The experimental values given are averages, but differ only in the third decimal place from the actual values.

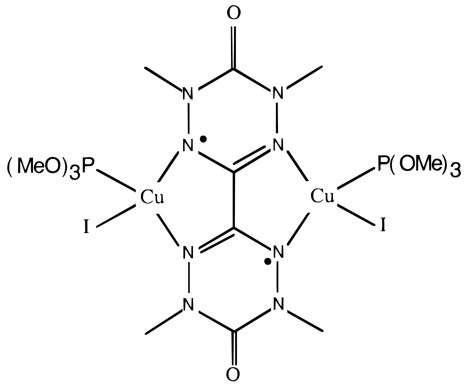

Figure 2. The BVD[CuI(P(OMe)$_3$)]$_2$ complex. The Cu coordination is tetrahedral, but the actual stereochemistry is unknown.

To understand the decrease in singlet−triplet splitting which accompanies the formation of the Cu−BVD complex, we have performed density functional calculations on a series of BVD-[CuI(PL_3)]$_2$ complexes. The ligands chosen for this investigation (L = Me, H, OMe, OH, F) run the spectrum of donating ability and should give an indication of the tunability of the verdazyl system. The results of this study should provide the insight necessary to guide the rational synthesis of high-spin BVD complexes.

[†] Current address: Department of Chemistry, California Institute of Technology, Pasadena, CA 91125. E-mail: green@wag.caltech.edu.

(1) Verdaguer, M.; Julve, M.; Michalowicz, A.; Khan, O. *Inorg. Chem.* **1983**, *22*, 2624.

(2) Pei, Y.; Verdaguer, M.; Khan, O.; Sletten, J.; Renard, J. P. *Inorg. Chem.* **1987**, *26*, 138.

(3) Coronado, E.; Drillon, M.; Fuertes, A.; Beltran, D.; Mosset, A.; Galy, J. *J. Am. Chem. Soc.* **1986**, *108*, 900.

(4) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.

(5) Zhao, H.; Heintz, R. A.; Dunbar, K. R. *J. Am. Chem. Soc.* **1996**, *118*, 12844.

(6) Caneschi, A.; Gatteschi, D.; Sessoli, R. *Acc. Chem. Res.* **1989**, *22*, 392.

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

(8) Neugenbauer, F. A.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 724.

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

10.1021/ic981424l CCC: $18.00

Computational Methods

Calculations were performed on BVD and the series of complexes BVD[CuI(PL$_3$)]$_2$ (L = H, OH, Me, OMe, F), using GAUSSIAN94 (Revision E.2).[10] The structures used in this study were obtained by optimizing each molecule in its restricted singlet state. These optimizations were performed using the B3LYP functional and employing the LANL2DZ effective core potentials,[11-13] and basis set for Cu, I, and P. The D95(d) basis set[14] was used for H, C, N, and O. L = H, Me (OH, OMe, F) were optimized using C_{2v} (C_2) symmetry. (The L = F compound could have been optimized using C_{2v} symmetry but was not. However, the symmetry of the geometry obtained is very near C_{2v}. The Cu−N distances differ by less than 0.003 Å.) Unrestricted calculations were then performed at the optimized geometries. The symmetry of the unrestricted states was broken so that localization could occur.

Results and Discussion

The optimized and experimentally determined bond distances for BVD are shown in Figure 1. Interestingly BVD was found to be planar not twisted, as AM-1 calculations have previously suggested. To confirm this result optimizations were performed with initial dihedral angles between the rings of 0°, 45°, and 90°. A local minimum was found at 90° but the total energy was 303 cm^{-1} higher than that of the planar geometry. Thus, the complexation of copper does not seem to require BVD to alter its structure. This result is somewhat surprising since other molecules such as biphenyl and 2,2′-bipyrimidine, which are also planar in the solid state, are known to be twisted in solution or gas phase.[15-17] As a test, geometry optimizations were carried out, at the same level of theory, on both biphenyl and 2,2′-bipyrimidine. Dihedral angles of 36.02° (biphenyl) and 41.93° (2,2′-bipyrimidine) were determined. These values, which are in reasonable agreement with experiment, indicate that our BVD findings are reliable.[13]

Previous investigations have shown that restricted AM-1 calculations are incapable of predicting the correct ground state for BVD ($E_s - E_t = 17\,000$ cm^{-1}), but that unrestricted AM-1 calculations predict the singlet state to lie 970 cm^{-1} below the triplet. Using the B3LYP functional, we also found it necessary to perform unrestricted calculations in order to obtain the proper ground state. These calculations gave a singlet−triplet splitting of 600 cm^{-1}, which compares well to the experimentally determined value of 760 cm^{-1}. The BVD[CuI(P(OMe)$_3$)]$_2$ complex is believed to exist in solution, and Fox and co-workers have reported its singlet−triplet separation to be 230 cm^{-1}. Using the B3LYP method with effective core potentials for Cu, I, and P, the singlet−triplet splitting of this molecule was calculated to be 261 cm^{-1}. To our knowledge, the other complexes examined in this study have not yet been synthesized, making comparison between experiment and calculation impossible. However, given the good agreement for BVD and BVD-[CuI(P(OMe)$_3$)]$_2$, it is reasonable to assume that reliable results were obtained for the other systems as well. The calculated singlet−triplet splittings for these molecules are shown in Table 1.

Table 1. Singlet−Triplet Splittings for BVD and BVD[CuI(PL$_3$)]$_2$

	$E_{\text{singlet}} - E_{\text{triplet}}$	
compd	calcd (cm^{-1})	exptl (cm^{-1})
BVD	−600	−760
L =		
H	−40	−
Me	−139	−
OH	−222	−
OMe	−261	−230
F	−282	−

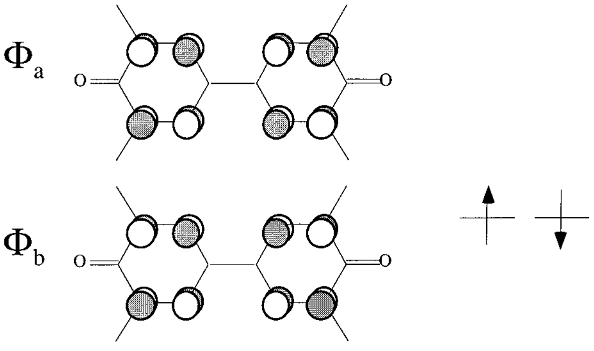

Figure 3. HOMO and LUMO of BVD, at the Hückel level they are degenerate.

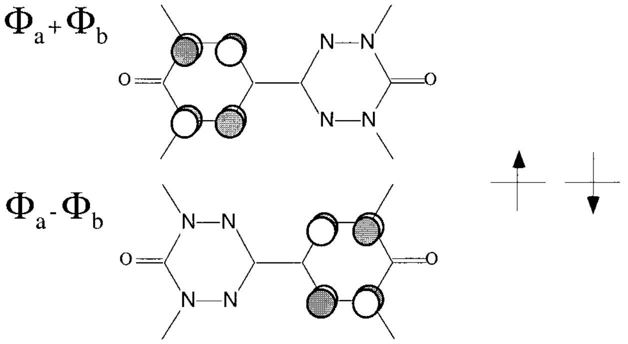

Figure 4. NMO's made from linear combinations of the orbitals in Figure 3.

The results indicate that it is indeed possible to control the singlet−triplet splitting of these complexes, and although none of the compounds studied possess a triplet ground state, the phosphine complex was found to have a very small splitting. If the relationship between ligand and singlet−triplet splitting shown in Table 1 can be understood, it may be possible to engineer molecules with a high-spin ground state.

Fox and co-workers have proposed a mechanism (in the spirit of Borden and Davidson's work on conjugated biradicals[18]) to explain the decrease in singlet−triplet splitting which accompanies the formation of the BVD[CuI(P(OMe)$_3$)]$_2$ complex. Their model, which is based on simple Hückel arguments, is centered around the mixing of Cu d orbitals with the π^* levels of the verdazyl system. Shown in Figure 3 are the π^* levels (the HOMO and LUMO) of BVD. At the Hückel level only nearest-neighbor interactions are included, making these two levels degenerate. As a result, one may take linear combinations of them to obtain new eigenfunctions, called natural magnetic orbitals (NMOs),[19] shown in Figure 4. The preferred spin state of the verdazyl system is determined by the overlap and proximity of these orbitals. If two orbitals are very close but have an overlap integral of zero (e.g. the d orbitals on a transition

---

(10) Frisch, M. J.; et al. *Gaussian 94*, Revision E.2; Gaussian, Inc.: Pittsburgh, PA, 1995.
(11) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
(12) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
(13) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
(14) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1976.
(15) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59.
(16) Fernholt, L.; Romming, C.; Samdal, S. *Acta Chem. Scand.* **1981**, A *35*, 707.
(17) Barone, V.; Cristinziano, P. *Chem. Phys. Lett.* **1993**, *215*, 40.
(18) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.
(19) Khan, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

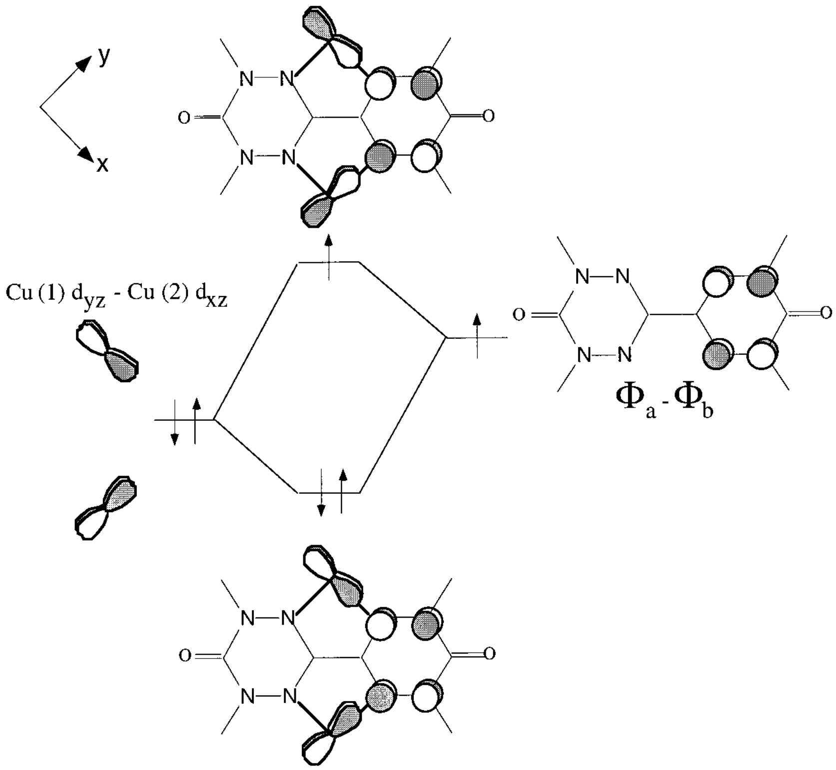

Figure 5. Interaction of Cu d orbitals with one of the NMO's of BVD.

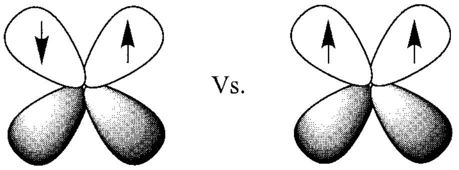

Figure 6. Electrons in orthogonal d orbitals on copper. When electrons have the same spin, exchange can lower the Coulombic energy associated with their interaction. This favors the triplet state.

metal, shown in Figure 6) then the system will be high-spin. If, however, a nonzero overlap integral exists (e.g. the atomic orbitals of H_2), this will favor spin pairing. Fox et. al. suggest that long-range overlap between the NMOs shown in Figure 4 results in a weak bonding interaction, which leads to a singlet ground state. When copper binds with BVD its d orbitals interact with the NMO's as shown in Figure 5, generating two new singly occupied orbitals. Because these new magnetic orbitals are orthogonal on nearest neighbors, Fox and co-workers argue that there is still no interaction. However, the electrons in these orbitals now spend time on the same atom, and as a result there is an increased Coulombic repulsion between them. This, according to Fox and co-workers, is the driving force which stabilizes the triplet state. These researchers argue that this stabilization, which is a result of exchange, should increase with the Cu character of the magnetic orbitals. Thus it appears possible to tune the singlet−triplet splitting by choosing the appropriate ligands. Donating ligands should push the Cu levels closer to the π^* orbitals of the verdazyl system, increasing Cu−verdazyl mixing and stabilizing the triplet.

While this mechanism works at the Hückel level, it fails at higher levels of theory. The first sign of this can be seen in Figures 7 and 8, which show the orbitals of the unrestricted singlet and triplet states of BVD. Notice the difference between these two sets of orbitals. The singlet orbitals are localized as Fox et al. have suggested, but the triplet orbitals are completely delocalized. This difference is a result of overlap between the NMOs of the two verdazyl rings. Since electrons are fermions, they must reside in orthogonal orbitals. For the singlet case the spatial overlap of the verdazyl NMOs is not a problem. The electrons have different spins and as a result their wave functions

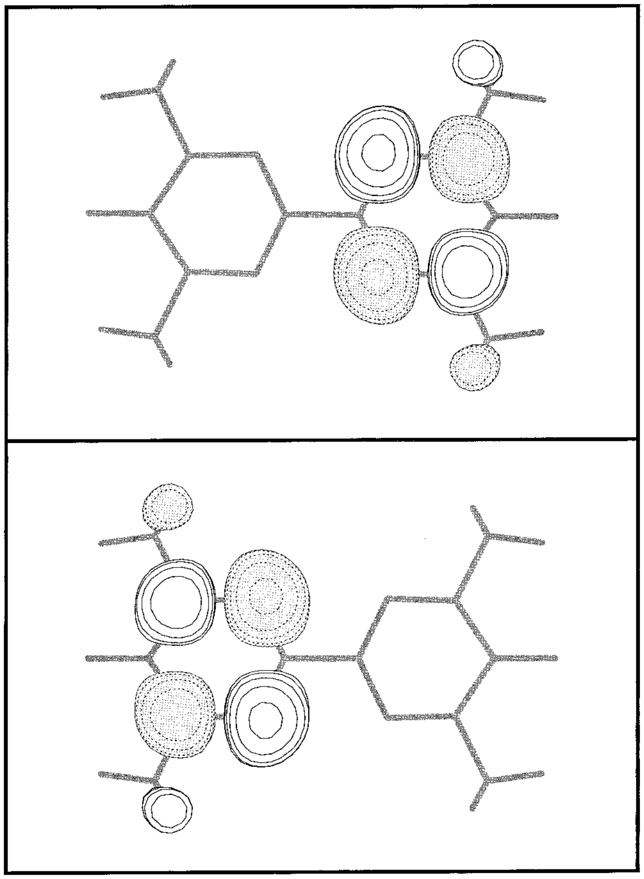

Figure 7. Up- and down-spin wave functions for the unrestricted singlet of BVD. One electron resides in each orbital.

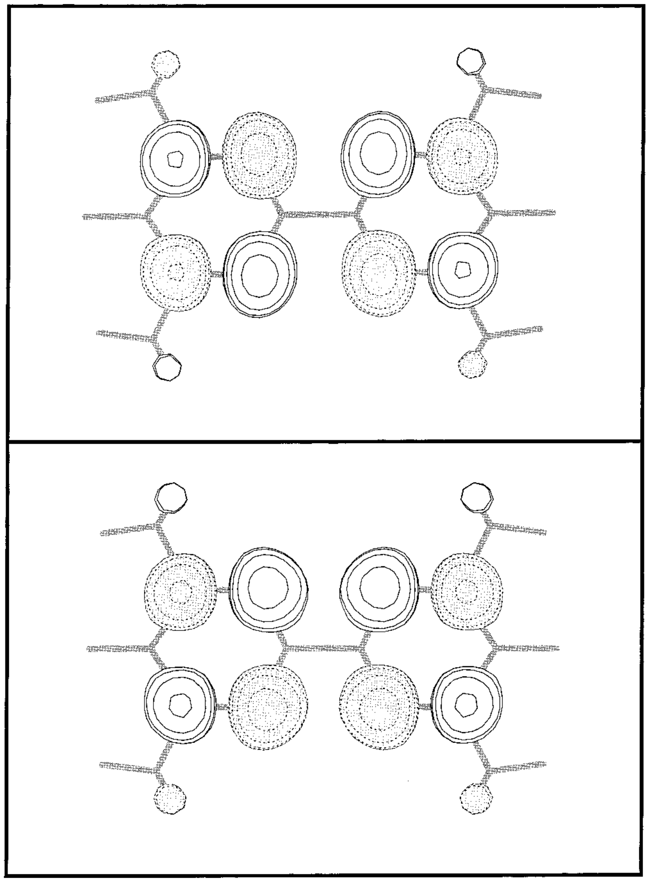

Figure 8. Up-spin wave functions for the triplet state of BVD. One electron resides in each orbital.

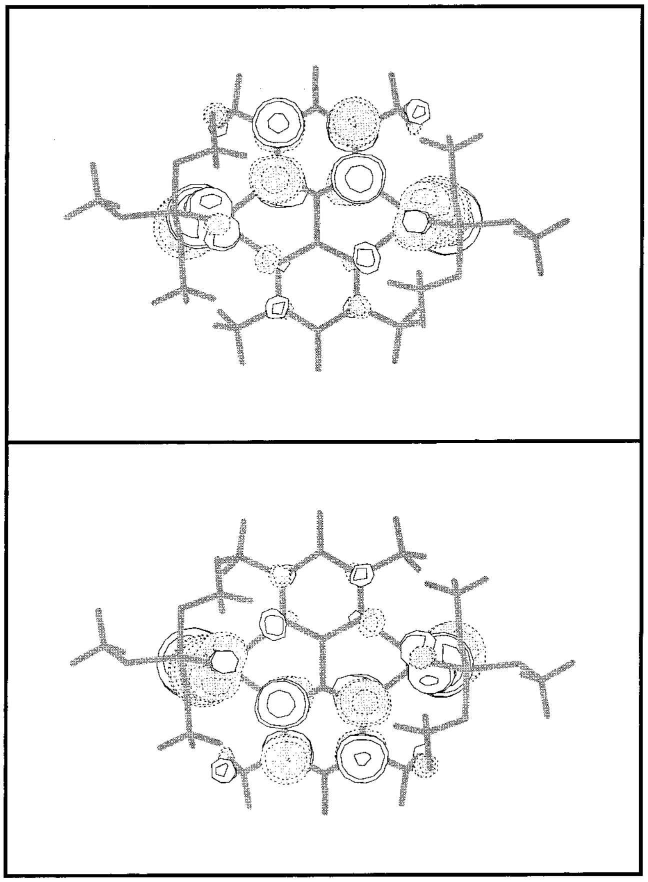

Figure 9. Up- and down-spin wave functions for the unrestricted singlet of BVD[CuI(P(OMe)$_3$)]$_2$. One electron resides in each orbital.

are orthogonal. This is obviously not true for the triplet case, and it is therefore necessary that these electrons reside in orbitals which are spatially orthogonal. It is, however, impossible to construct two localized orbitals (one on each ring) which retain the symmetry of the electron density and are orthogonal. As a result, the triplet orbitals must be delocalized.

Shown in Figures 9 and 10 are the unrestricted singlet and triplet orbitals of BVD[CuI(P(OMe)$_3$)]$_2$. The same pattern found for BVD can be seen here. The singlet orbitals are localized, while the triplet orbitals are delocalized. According to the mechanism proposed by Fox the triplet state is stabilized by the formation of the copper complex, because electrons are forced to spend more time in the same region of space. But looking at the results of the calculations on BVD and BVD[CuI(P(OMe)$_3$)]$_2$ reveals that in both of these compounds the triplet orbitals occupy the same region of space. The singlet orbitals, however, are a different story. These orbitals are more localized in BVD, with essentially one electron occupying each ring. When the copper complex is formed these orbitals mix with the d orbitals of Cu to make NMOs which are not as well localized, resulting in a good deal of spatial overlap and increased Coulomb interactions. Thus it appears that it is the singlet state which is destabilized, and not the triplet which is stabilized, upon complexation.

Although the actual mechanism which decreases the singlet–triplet splitting seems to be different than that proposed by Fox and co-workers, one still arrives at the same conclusion regarding which ligands will be likely candidates to produce a triplet ground state. The more delocalized the singlet orbitals are the more they will overlap and the more the singlet state will be destabilized relative to the triplet. The situation in these system is similar to that of molecular hydrogen. For larger internuclear distances it is possible to calculate an unrestricted singlet wave function which localizes one electron on each hydrogen atom. This singlet is lower in energy than the corresponding triplet state which, because there is overlap between the hydrogen orbitals, must be delocalized, leading to larger electron–electron repulsions. It is also possible to calculate a restricted singlet state for molecular hydrogen. Just as in the triplet, the orbitals of this species are delocalized, resulting in a large Coulombic interaction between the electrons. However in the triplet state the electrons have the same spin, and this allows for an exchange stabilization which is not present in restricted singlet. As a result the triplet state lies lower in energy than the restricted (but not the unrestricted) singlet state.

Both AM-1 and B3LYP calculations reveal this type of behavior for BVD. They show the energy of the triplet state to lie below that of the restricted singlet. Thus in a sense what we need our ligands to do is to drive the singlet solution from the unrestricted to the restricted regime, thereby creating a triplet ground state. It is clear then that we want ligands which, by causing the Cu d orbitals to interact strongly with the verdazyl π system, will delocalize the singlet orbitals. Ligands which are strongly donating should push the Cu levels closer to the ring orbitals and increase the mixing between them.

One would expect then that the singlet–triplet splitting could be made increasingly smaller by selecting ligands with increasingly larger donating ability. However, examination of Table 2 does not reveal this trend. This table, which shows the d orbital (HOMO) energies of the CuI(PL$_3$) fragments along with the calculated singlet triplet splittings, reveals that the most donating ligands do not necessarily result in the smallest singlet–triplet

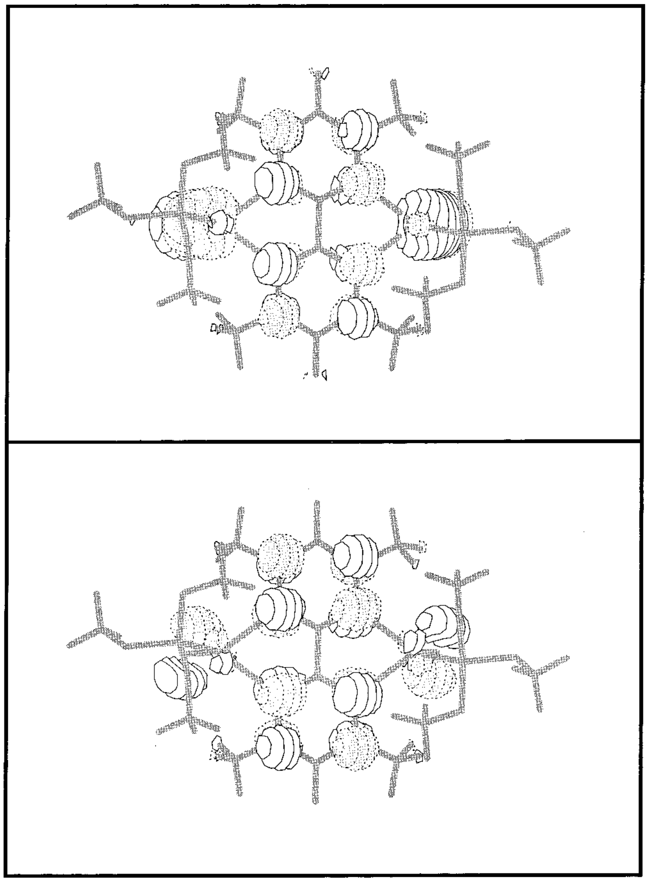

Figure 10. Up-spin wave functions for the triplet state of BVD[CuI(P(OMe)$_3$)]$_2$. One electron resides in each orbital.

Table 2. HOMO Energies for CuI(PL$_3$) Fragment and Singlet−Triplet Splittings of BVD[CuI(PL$_3$)]$_2$ Complex

ligand	HOMO energy (Ry)	$E_{\text{singlet}} - E_{\text{triplet}}$ (cm^{-1})
Me	−0.202	−139
H	−0.217	−49
OMe	−0.217	−261
OH	−0.237	−222
F	−0.246	−282

Table 3. Bond Lengths and Angles for BVD[CuI(PL$_3$)]$_2$

ligand	N−Cu$_{\text{avg}}$ (Å)	N−Cu−N (deg)	Cu−I (Å)	Cu−P (Å)	I−Cu−P (deg)
H	2.178	75.24	2.565	2.414	110.44
OH	2.175	75.29	2.636	2.303	101.68
F	2.165	75.78	2.545	2.313	107.10
Me	*2.206*	*73.89*	*2.620*	*2.337*	*114.09*
OMe	*2.221*	*73.48*	*2.608*	*2.315*	*124.74*

splittings. The singlet−triplet splitting should decrease in the order F > OH > OMe ≈ H > Me, but the order observed is F > OMe > OH > Me > H, indicating that factors other than pure donating ability are involved.

Insight into these other factors is obtained by looking at the geometrical properties of this series of molecules. Examination of the Cu−N bond lengths and N−Cu−N angles shows that these ligands can basically be divided into two groups, {Me, OMe} and {H, OH, F}. This division is a result of the size of the ligands, which determines how close the CuI(PL$_3$) fragment can get to the BVD molecule. Some selected bond lengths and angles for this series of compounds are shown in Table 3.

Table 4. Ordering of Complexes with Respect to Size and Donating Ability Reproduces Calculated Trends in Singlet−Triplet Splitting

ligand	CuIPL$_3$ HOMO (Ry)	θ	$E_{\text{sing}} - E_{\text{trip}}$
H	−0.217	40.0	−49
OH	−0.237	48.5	−222
F	−0.246	43.0	−282
Me	*−0.202*	*78.1*	*−139*
OMe	*−0.217*	*86.1*	*−261*

Table 5. Comparison of Results Obtained at Optimized Geometries with Results Obtained for a Model Compound

compound	HOMO (Ry)	N−Cu (Å)	N−Cu−N (deg)	$E_{\text{sing}} - E_{\text{trip}}$ (cm^{-1})
P(OH)$_3$	−0.237	2.156	101.68	−222
P(OMe)$_3$	−0.202	2.233	124.74	−261
model P(OH)$_3$	−0.223	2.233	124.74	−344

If one groups these molecules according to the size of the angle θ (which is centered at Cu and defined by the two widest nuclei of the PL$_3$ ligand) and then orders each group with respect to donating ability, the trends in singlet−triplet splitting within each group are reproduced (Table 4). Although we have chosen to use the nuclei to define the angle θ, we realize that atoms do vary in size. However, in almost all of the cases examined it is two hydrogen nuclei which define this angle, making comparison among these species justified, and certainly the variation in size between F and H (covalent radius + atomic radius = 1.29/1.11 Å, respectively) is not enough to make up for the differences shown in Table 4.

Thus it appears that donating ability and size of the ligand are two important factors which determine the singlet−triplet splittings of these molecules. To test this theory we performed a calculation on the following model compound. Taking the optimized structure of BVD[CuI(P(OMe)$_3$)]$_2$ we replaced the P(OMe)$_3$ ligand with the P(OH)$_3$ ligand taken from the BVD-[CuI(P(OH)$_3$)]$_2$ optimized structure. All other bond distances (including Cu−P) and angles were kept the same. Since P(OH)$_3$ is not as good a donor as P(OMe)$_3$, the singlet−triplet splitting for the P(OH)$_3$ compound should be greater than that found using P(OMe)$_3$. This was not the case for the optimized structures because the larger P(OMe)$_3$ unit did not allow Cu to get as close to the BVD molecule as the smaller P(OH)$_3$ ligand. The model compound, however, has the same geometry as the P(OMe)$_3$ compound. Thus the relative singlet−triplet splitting should be determined only by donating effects. Table 4 shows the results. As expected the model compound has a larger singlet−triplet splitting than the P(OMe)$_3$ complex.

Conclusion

It appears that one can control the singlet−triplet splitting of this unique molecule. The essential factors governing the splitting seem to be the donating ability and the size of the ligand. The more donating the ligand the more the Cu orbitals can mix with the verdazyl π system and destabilize the singlet by driving the system toward the restricted solution. However, how well the d orbitals on Cu can mix with the BVD π system is also governed by geometrical factors. The larger ligands do not allow Cu to get as close to the verdazyl rings and as a result there is less overlap between the copper orbitals and the verdazyl π system. Thus there is a trade off between donating ability and size. The small singlet−triplet splitting for phosphine (40 cm^{-1}) suggests that it may be possible to obtain a triplet ground state by using a small ligand which is strongly donating.

IC981424L