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Structures of the Copper(I) and Copper(II) Complexes of 2,9-Diphenyl-1,10-phenanthroline: Implications for Excited-State Structural Distortion

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The syntheses, crystal structures, and electronic absorption spectra of the copper(I) and copper(II) complexes of 2,9-diphenyl-1,10-phenanthroline (dpp) are reported. The complex $[Cu(dpp)_2](PF_6)$ (**1**) crystallizes in space group $P2_1/c$ with $a = 11.081(4)$ Å, $b = 25.491(8)$ Å, $c = 14.263(5)$ Å, $\beta = 92.84(3)°$, $Z = 4$, and $V = 4024(2)$ Å^3. For 4813 unique data with $F > 4.0\sigma(F)$, $R = 5.41\%$ and $R_w = 6.43\%$. The coordination geometry about the copper(I) center in $[Cu(dpp)_2]^+$ is best described as distorted tetrahedral with approximate C_2 symmetry. The structure of $[Cu(dpp)_2]^+$ is largely determined by interligand π-stacking interactions that occur between the phenyl groups of one ligand and the phenanthroline moiety of the other ligand. Solution-state absorption and ^{1}H NMR spectra indicate that the $[Cu(dpp)_2]^+$ complex is fluxional in solution, rocking between two enantiomeric structures of C_2 molecular symmetry through an intermediate of C_s symmetry. The complex $[Cu(dpp)_2](ClO_4)_2$ (**2**) crystallizes in space group $P\bar{1}$ with $a = 7.809(3)$ Å, $b = 13.027(6)$ Å, $c = 20.344(10)$ Å, $\alpha = 87.68(4)°$, $\beta = 89.16(4)°$, $\gamma = 79.26(4)°$, $Z = 2$, and $V = 2032(1)$ Å^3. For 4943 unique data with $F > 4.0\sigma(F)$, $R = 5.22\%$ and $R_w = 5.37\%$. The coordination geometry about the copper(II) center in $[Cu(dpp)_2]^{2+}$ is best described as flattened tetrahedral with approximate D_2 symmetry. There are no interligand π-stacking interactions in the structure of $[Cu(dpp)_2]^{2+}$. The four-coordinate geometry in $[Cu(dpp)_2]^{2+}$ persists in solution on the basis of solution-state and solid-state absorption spectroscopy. Structural distortion in the metal-to-ligand charge-transfer excited state of $[Cu(dpp)_2]^+$ is discussed on the basis of the structures of **1** and **2**.

Introduction

In the past two decades, the field of inorganic photochemistry has focused on molecular systems that possess low-lying metal-to-ligand charge-transfer (MLCT) excited states capable of electron and energy transfer. Although complexes of ruthenium(II), osmium(II), and rhenium(I) have been the most studied in this area, certain copper(I) polypyridine complexes also display these photophysical characteristics.[1−3] In 1980, Blaskie and McMillin first demonstrated the room-temperature luminescence of $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) in dichloromethane upon excitation into the visible MLCT band.[4] After that study, the structural requirements for emission in homoleptic copper(I) polypyridine complexes were investigated. Since the complex $[Cu(phen)_2]^+$ (phen = 1,10-phenanthroline) shows no detectable emission even at 77 K, substituents at the 2- and 9-positions of the phenanthroline have been shown to be necessary for luminescence.[5] The complex of 4,4′,6,6′-tetramethyl-2,2′-bipyridine (tmbp) is emissive; however the lifetime in CH_2Cl_2 is significantly shorter than that of the dmp complex: $[Cu(tmbp)_2]^+$, $\tau = 18$ ns; $[Cu(dmp)_2]^+$, $\tau = 90$ ns.[6] Thus, the majority of copper(I) photochemical research has focused on the complexes of 2,9-disubstituted phenanthrolines.[4−31]

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One area of emphasis in inorganic photochemistry has been the investigation of the ligand structural requirements that are necessary for long-lived excited states in fluid solution. Since complexes with longer luminescent lifetimes are more useful for photoinduced electron and energy transfer, the factors that control lifetimes are of interest. In this context, a significant achievement in the study of copper(I) polypyridine complexes came in 1983 when Sauvage and McMillin showed that the complex of 2,9-diphenyl-1,10-phenanthroline ($[Cu(dpp)_2]^+$) has a lifetime in CH_2Cl_2 at room temperature of 310 ns.[7] This lifetime has subsequently been reported to be 250 ns in CH_2Cl_2,[5,13,31] and is slightly concentration dependent.[14] Relative to $[Cu(dmp)_2]^+$, there is an increase in lifetime by about a factor of 3. There is also an increase in quantum yield by about a factor of 4 for the dpp complex over the dmp complex (CH_2Cl_2).[5,13] Sauvage and McMillin also showed that, unlike $[Cu(dmp)_2]^+$, $[Cu(dpp)_2]^+$ is emissive in donor solvents such as methanol ($\tau = 180$ ns).[5,7] For the dmp complex, quenching of the excited state occurs in methanol, ethanol, and acetonitrile.[4] The quenching of $^*[Cu(dmp)_2]^+$ by these solvents has been explained by McMillin and co-workers in terms of an exciplex model. This model depicts the formation of a five-coordinate adduct in the excited state that decays very rapidly.[1,12,15] In the localized extreme, the MLCT excited state can be viewed as a copper(II) species: $[Cu^{II}(L^{\bullet -})(L)]$[32,33] (recent results indicate that the excited electron may be delocalized over both phenanthrolines[34]). Therefore, the exciplex model is consistent with the tendency for copper(II) to be five- (or six-) coordinate.[35] Since $[Cu(dpp)_2]^+$ is emissive in donor solvents, the phenyl groups are thought to protect the metal center from the solution environment and prevent the formation of a five-coordinate exciplex.[7]

With these systems, excited-state structural information can be obtained from crystal structures of the copper(II) complexes. In the case of the copper(II) complex of dmp, a five-coordinate structure has been observed in the solid state ($[Cu(dmp)_2(ONO_2)]^+$), demonstrating the tendency for the copper(II) ion to bind a fifth ligand.[36] Although considerable research has focused on the photochemistry of the $[Cu(dpp)_2]^+$ complex[5,8,12,13,19,21,30,31] and copper(I) bis(phenanthroline) complexes with 2,9-diaryl substituents,[24−28] no structural information about the copper(II) complex of dpp or related ligands has been published.

This paper describes our investigation of the solid-state and solution-state structure of $[Cu(dpp)_2]^{2+}$. The crystal structure of this molecule represents the first definitive example of a four-coordinate copper(II) phenanthroline complex in the solid state. Although a structure of the copper(I) complex of dpp has been reported,[16] we have determined the crystal structure of $[Cu(dpp)_2]^+$ with a different anion and present that structure. The analysis and comparison of the $[Cu(dpp)_2]^+$ and $[Cu(dpp)_2]^{2+}$ complexes provide insight into the structural distortion that occurs in the excited states of copper(I) polypyridine complexes. Since excited-state structural information is relevant to energy-transfer and electron-transfer quenching processes,[19,31] it is important to understand the stereochemical preferences of the copper(I) and copper(II) ions.

Experimental Section

General Procedures. All chemicals used were reagent grade unless otherwise specified. Acetonitrile and dichloromethane were Burdick and Jackson high-purity grade and were used as received. The compounds $[Cu(CH_3CN)_4](PF_6)$[37] and 2,9-diphenyl-1,10-phenanthroline (dpp)[38] were synthesized as previously reported. Elemental analyses were performed by Desert Analytics, Tucson, AZ. Proton NMR spectra were recorded with a General Electric QE300 spectrometer. Absorption spectra were recorded with a Hewlett-Packard 8452A diode array spectrophotometer.

$[Cu(dpp)_2](PF_6)$ (1). This procedure is based on one previously published.[31] A solution of dpp (500 mg; 1.50 mmol) in 100 mL of degassed CH_3CN was added with stirring to a flask charged with $[Cu(CH_3CN)_4](PF_6)$ (280 mg; 0.75 mmol) under Ar. The red solution was stirred for 10 min and taken to dryness, and the residue was redissolved in CH_2Cl_2. Layering of the solution with Et_2O yielded large, air-stable red-brown crystals. UV−vis [λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))]: CH_2Cl_2, 440 (3800); CH_3CN, 440 (3300); CH_3CN/H_2O (50/50), 440 (3550). ^1H NMR (dmso-d_6), δ: 6.52 (t, 8H, phenyl *meta*), 6.78 (t, 4H, phenyl *para*), 7.43 (d, 8H, phenyl *ortho*), 8.05 (d, 4H, $H_{3,8}$), 8.20 (s, 4H, $H_{5,6}$), 8.74 (d, 4H, $H_{4,7}$). Anal. Calc (found) for $CuC_{48}H_{32}N_4PF_6$: C, 66.02 (65.47); H, 3.69 (3.67); N, 6.42 (6.30).

$[Cu(dpp)_2](ClO_4)_2$ (2). To a suspension of dpp (42 mg; 0.13 mmol) in 15 mL of MeOH was added $[Cu(ClO_4)_2]\cdot 6H_2O$ (25 mg; 0.067 mmol). The blue solution was stirred at room temperature for 2 h, resulting in the deposition of a blue-black crystalline material. The solution was placed in a freezer overnight, and the air-stable crystals were collected. Frozen-solution EPR spectra of **2** in CH_2Cl_2 (158 K) were collected: $g_\perp = 2.07$, $g_\parallel = 2.37$, $A_\parallel = 177$ G. UV−vis [λ_{max} (nm) (ϵ ($M^{-1}cm^{-1}$))]: CH_2Cl_2, 582 (620); CH_3CN, 572 (610); CH_3CN/H_2O (50/50), 572 (580). Anal. Calc (found) for $CuC_{48}H_{32}N_4Cl_2O_8$: C, 62.18 (61.43); H, 3.48 (3.39); N, 6.04 (5.78). *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive.[39]

Crystal Structure Determinations. For the structure determinations of **1** and **2**, a Siemens R3m/V four-circle diffractometer was used to collect the data using Mo Kα radiation. Data collection and crystal parameters are reported in Table 1. No absorption corrections were applied. Each of the structures was solved by direct methods (SHELXTL PLUS). All non-hydrogen atoms were refined anisotropically, while the hydrogens were calculated and fixed in idealized positions (d(C−H) = 0.96 Å). Tables of positional parameters, bond lengths, bond angles, and anisotropic thermal parameters and unit-cell packing diagrams are available in the Supporting Information.

Results and Discussion

Solid-State Structure of $[Cu(dpp)_2]^+$. The structure of the PF_6^- salt determined here (**1**) is very similar to the structure previously reported by McMillin and Sauvage for the $CuCl_2^-$ salt;[16] however, the present structure has a higher degree of accuracy (Tables 1 and 2). A stereoview of the complex cation is shown in Figure 1, and selected bond angles and distances are presented in Table 2. Although the coordination geometry of $[Cu(dpp)_2]^+$ in the $CuCl_2^-$ salt was described as trigonal

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Table 1. Crystallographic Data for **1** and **2**

	$[Cu(dpp)_2](PF_6)$ (**1**)	$[Cu(dpp)_2](ClO_4)_2$ (**2**)
formula	$CuC_{48}H_{32}F_6N_4P$	$CuC_{48}H_{32}Cl_2N_4O_8$
color; habit	red-brown prisms	blue-black blocks
crystal size (mm)	0.5 × 0.7 × 0.2	0.3 × 0.3 × 0.4
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	11.081(4)	7.809(3)
b (Å)	25.491(8)	13.027(6)
c (Å)	14.263(5)	20.344(10)
α (deg)		87.68(4)
β (deg)	92.84(3)	89.16(4)
γ (deg)		79.26(4)
V (Å^3)	4024(2)	2032(1)
Z	4	2
fw	873.3	927.2
temp (K)	295	188
2θ range (deg)	3.0−50.0	3.0−50.0
no. of reflns collected	10580	7400
no. of indep reflns	7099	7177
no. of obsd reflns ($F > 4.0\sigma(F)$)	4813	4943
final R indices (obs data) (%): R, R_w	5.41, 6.43	5.22, 5.37
R indices (all data) (%): R, R_w	8.01, 10.72	7.92, 7.27
goodness of fit	1.31	1.66
data-to-parameter ratio	8.9:1	8.9:1

Table 2. Selected Structural Data for **1** and **2**

	$[Cu(dpp)_2](PF_6)$ (**1**)	$[Cu(dpp)_2](ClO_4)_2$ (**2**)
Distances (Å)		
Cu−N1A	2.112(3)	1.993(4)
Cu−N2A	2.019(3)	1.997(4)
Cu−N1B	2.082(3)	1.980(4)
Cu−N2B	2.032(3)	1.994(4)
Angles (deg)		
N1A−Cu−N2A	82.5	85.0
N2B−Cu−N1A	121.4	110.5
N1B−Cu−N1A	98.9	139.5
N2B−Cu−N2A	142.4	140.2
N1B−Cu−N2A	124.7	107.5
N1B−Cu−N2B	82.8	84.6
θ_x	104.6	91.2
θ_y	69.7	88.8
θ_z	100.2	118.9
Phenanthroline−Phenyl Dihedral Angles (deg)		
A−C	61.4	39.9
A−D	50.2	40.1
B−E	55.1	43.3
B−F	42.6	39.9
Angles between Planes Involved in π-Stacking (deg)		
A−E	12.5	
B−C	7.5	

pyramidal, the geometry around the copper in **1** is best described as distorted tetrahedral with approximate C_2 symmetry. The C_2 symmetry is indicated by the six N−Cu−N bond angles and the fact that there are two long Cu−N bonds (to N1A and N1B) and two short Cu−N bonds (to N2A and N2B) (Table 2). The C_2 axis bisects the N1B−Cu−N1A angle, thus relating the two phenanthroline ligands and resulting in approximate molecular C_2 symmetry. A significant feature of the structure is the π-stacking interactions at 3.4 Å between phenanthrolines A and B and phenyl groups E and C, respectively (Figure 1). These interactions were also observed in the $CuCl_2^-$ structure.[16] The remaining phenyl groups (D and F, Figure 1) are involved in an edge-to-face interaction. The two longer Cu−N bonds are adjacent to the phenyl groups that are involved in π-stacking. In addition, intermolecular phenanthroline−phenanthroline π-stacking interactions at 3.4 Å are present, resulting in phenyl−phenanthroline−phenanthroline−phenyl π-stacks in the unit cell (see the Supporting Information).

Copper(I) bis(phenanthroline) complexes generally display distorted tetrahedral geometries. The distortion from D_{2d} symmetry can be described in terms of the angles θ_x, θ_y, and θ_z (Table 2).[40] These θ values describe the interligand angles based on the CuN_4 core of the complex. For a molecule that possesses D_{2d} symmetry, $\theta_x = \theta_y = \theta_z = 90°$.[40] The θ_z value is similar to the dihedral angle between the ligand planes. Deviation of θ_z from 90° indicates a flattening distortion of the molecule that lowers the symmetry to D_2. The θ_x and θ_y values indicate the degree of a "rocking" distortion. The observed θ_z of 100.2° in **1** is similar to that observed for related copper(I) compounds.[16,40] The large deviations from 90° for the θ_x and θ_y values are due to the π-stacking interactions which cause considerable distortion from D_{2d} symmetry.

The dihedral angles between the phenanthroline moieties and their phenyl substituents in **1** range from 43 to 61° (Table 2). The phenyl groups (C and E) that engage in interligand π-stacking are observed to have the largest dihedral angles. Thus, it appears that these dihedral angles are larger to allow π-stacking interactions; however, in the absence of π-stacking, the angles are lower to increase π-conjugation in the ligand.

Solid-State Structure of $[Cu(dpp)_2]^{2+}$. A stereoview of the four-coordinate complex cation is shown in Figure 1, and selected bond angles and distances are presented in Table 2. The coordination geometry around the copper in **2** is best described as flattened tetrahedral, and the molecular symmetry is almost perfectly D_2. Unlike what is seen in the copper(I) complex, there are no intermolecular or intramolecular π-stacking interactions observed in the copper(II) complex. As expected, the Cu−N bond lengths decrease with the increase in oxidation state (Table 2). Although these shorter bonds may lead to the loss of the π-stacking interactions, it is more likely that the angular requirements of the copper(II) ion do not allow interligand π-stacking. The lack of π-stacking interactions results in phenanthroline−phenyl dihedral angles of 40−43° that allow for increased π-conjugation in the ligands (Table 2).

The value of θ_z increases with the increase in oxidation state: 100.2° in **1** to 118.9° in **2** (Table 2). The value of θ_z will approach 180° (or 0°) as the coordination geometry

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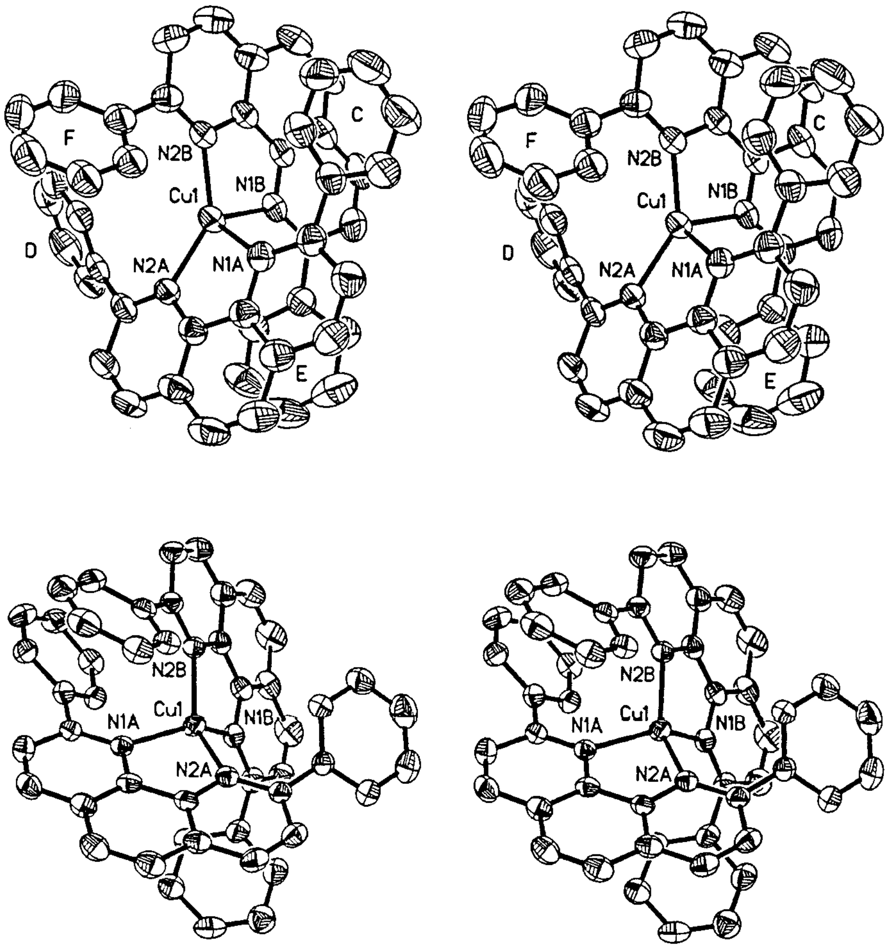

Figure 1. ORTEP stereoviews of $[Cu(dpp)_2]^+$ (top) and $[Cu(dpp)_2]^{2+}$ (bottom). Ellipsoids are shown at the 50% probability level.

approaches "square planar" with D_{2h} symmetry. Thus, relative to those of **1**, the phenanthroline ligands in **2** are flattened toward a D_{2h} geometry. This is expected since copper(II) prefers a square planar geometry with neutral N ligands, as shown by the structures of $[Cu(en)_2]^{2+}$ and $[Cu(pn)_2]^{2+}$ (pn = 1,3-diaminopropane).[41−44] Also, the θ_x and θ_y values in **2** are much closer to 90° (Table 2), reflective of the D_2 symmetry of $[Cu(dpp)_2]^{2+}$.

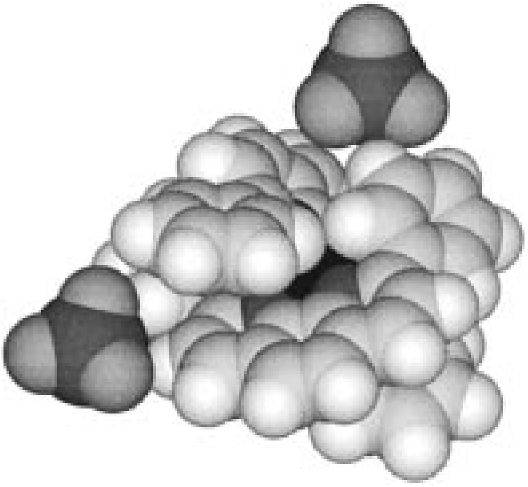

Figure 2. Space-filling view of $[Cu(dpp)_2]^{2+}$ and the two ClO_4^- counterions.

Four-coordinate structures of copper(II) are not typical. Copper(II) complexes with diimine ligands almost exclusively form five- or six-coordinate complexes in the solid state (and in solution; vide infra). Of the 62 structures in the Cambridge Structural Database containing the $[Cu^{II}(phen)_2]$ moiety (with or without ligand substituents), only $[Cu(phen)_2](PF_6)_2$ is four-coordinate.[45] Coordination at the fifth and/or sixth position usually occurs from H_2O, CH_3COO^-, ClO_4^-, or BF_4^-. In the structure of $[Cu(phen)_2](PF_6)_2$, a Cu−F distance of 2.75 Å is observed, indicating a secondary interaction.[45] The tendency for copper(II) bis(diimine) complexes to be five-coordinate is further demonstrated by the structures of $[Cu(tmbp)_2](ClO_4)_2$ and $[Cu(tmbp)_2](ClO_4)_2{\cdot}2H_2O$ (tmbp = 4,4′,6,6′-tetramethyl-2,2′-bipyridine), both of which are five-coordinate with ClO_4^- and H_2O coordination, respectively.[46] The methyl groups at the 6- and 6′-positions of the bipyridine ligands in these complexes do not provide sufficient steric shielding of the copper center to prevent coordination by solvent or counterions. In the structure of **2**, however, the shortest $Cu{-}OClO_3$ distance is 6.19 Å, clearly indicating no interaction. The phenyl groups in $[Cu(dpp)_2]^{2+}$ are very effective at shielding the copper(II)

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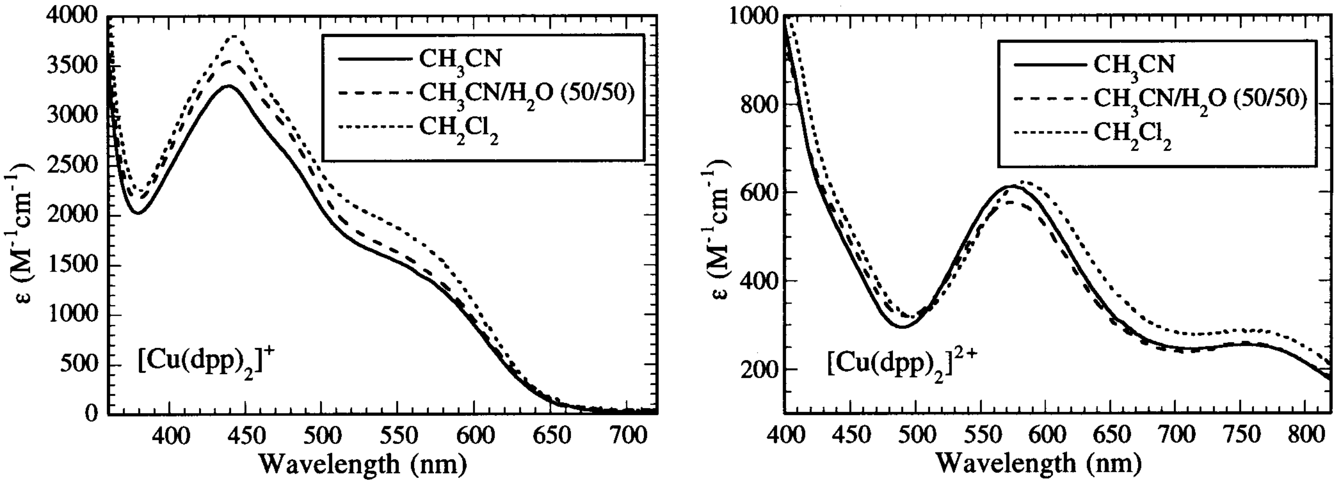

Figure 3. Electronic absorption spectra of [Cu(dpp)$_2$](PF$_6$) (left) and [Cu(dpp)$_2$](ClO$_4$)$_2$ (right) at room temperature.

center. A space-filling view of [Cu(dpp)$_2$]$^{2+}$ and the perchlorate anions is shown in Figure 2. It is also apparent from Figure 2 that the orientation of the phenyl groups relative to the phenanthroline planes (i.e., with approximate 40° dihedral angles) results in more effective shielding of the metal center than if the phenyl groups were perpendicular to the phenanthroline planes.

Solution-State Structure of [Cu(dpp)$_2$]$^+$. An interesting aspect of the visible spectrum of [Cu(dpp)$_2$]$^+$ is the large spread of the MLCT bands over the range 400−650 nm.[5,13] This is in contrast to what is observed in the visible spectrum of [Cu(dmp)$_2$]$^+$, which has a sharper band centered at 454 nm (CH$_2$Cl$_2$).[13] McMillin and Sauvage have shown that the solid-state absorption spectrum of [Cu(dpp)$_2$]$^+$ is essentially the same as the solution-state spectrum, and these authors have interpreted the data to reflect a low-symmetry structure for [Cu(dpp)$_2$]$^+$ in solution.[13] The room-temperature ^{1}H NMR spectrum of [Cu(dpp)$_2$]$^+$,[47] however, demonstrates that the four phenyl groups are equivalent (see Experimental Section). These results indicate that the molecule is fluxional in solution. On the basis of the solid-state structure of **1**, the molecular motion is assigned to a rocking between two enantiomeric C_2-symmetric structures via an intermediate of C_s symmetry (neglecting the phenyl substituents). The structure shown in Figure 1 represents one of the C_2 enantiomers. Two π-stacking interactions occur in the C_2 structures. One of these interactions is not possible in the intermediate, and thus the C_s structure would likely be of higher energy. An averaging mechanism through an intermediate of D_2 or D_{2d} symmetry is also possible; however, in these cases, no π-stacking interactions would occur in the intermediate (vide supra). The absorption spectra of [Cu(dpp)$_2$]$^+$ in Figure 3 demonstrate that the solution-state structure is not solvent dependent.

Solution-State Structure of [Cu(dpp)$_2$]$^{2+}$. As noted above, there is a great tendency for [Cu(NN)$_2$]$^{2+}$ (where NN represents a chelating diimine ligand) species to bind a fifth ligand. It was therefore of interest to investigate whether the [Cu(dpp)$_2$]$^{2+}$ species retains its four-coordinate structure in solution and in donating solvents. The absorption spectra of [Cu(dpp)$_2$]$^{2+}$ in three solvent systems are shown in Figure 3. The low-energy shoulder at 750 nm is assigned to a d−d transition, and the 575 nm band, to an LMCT transition.[48] These bands are expected to be highly sensitive to the coordination environment. In different coordinating solvents, the energies and extinction coefficients of the visible bands of [Cu(dmp)$_2$]$^{2+}$ vary significantly, since this cation is five-coordinate in solution.[49] In CH$_2$Cl$_2$ and in the solid state (KBr pellet; data not shown), the energies of the visible bands of [Cu(dpp)$_2$]$^{2+}$ do not change. In addition, the visible spectra of [Cu(dpp)$_2$]$^{2+}$ are nearly identical in CH$_2$Cl$_2$, CH$_3$CN, and CH$_3$CN/H$_2$O (50/50) (Figure 3). Thus, the cation remains four-coordinate in each of these cases.

Conclusions

As outlined in the Introduction, the principal impetus for this work was to determine the structural changes that occur in the [Cu(dpp)$_2$]$^+$ complex upon oxidation to copper(II) and relate these changes to the MLCT excited state of [Cu(dpp)$_2$]$^+$. The structure of **2** demonstrates that the shielding effects of the phenyl groups result in a rarely seen four-coordinate copper(II) species for [Cu(dpp)$_2$]$^{2+}$ in the solid state that is shown to persist in solution. This is consistent with the fact that [Cu(dpp)$_2$]$^+$ emits at room temperature in donating solvents such as methanol and acetonitrile. Thus, exciplex quenching does not readily occur in the MLCT excited state of [Cu(dpp)$_2$]$^+$.

Although there is no change in coordination number, there are substantial structural differences between the coordination geometries of [Cu(dpp)$_2$]$^+$ and [Cu(dpp)$_2$]$^{2+}$. An overlay of the cores of the complexes is shown in Figure 4. Immediately after excitation into the MLCT state of [Cu(dpp)$_2$]$^+$, the copper ion will retain the geometry of the ground-state copper(I) complex.[50] Subsequent evolution to the lowest energy excited state will lead to a geometry that closely resembles the structure of [Cu(dpp)$_2$]$^{2+}$. The structures shown in Figure 4 indicate that a significant rotation of the phenanthroline ligands is expected in the lowest energy excited state. Such a large distortion would be expected to lead to fast nonradiative decay from the excited state[51] and may play an important role in limiting the excited-state lifetimes in these systems.

An additional point of interest concerns the stereochemical preferences of the copper(I) and copper(II) ions in the structures

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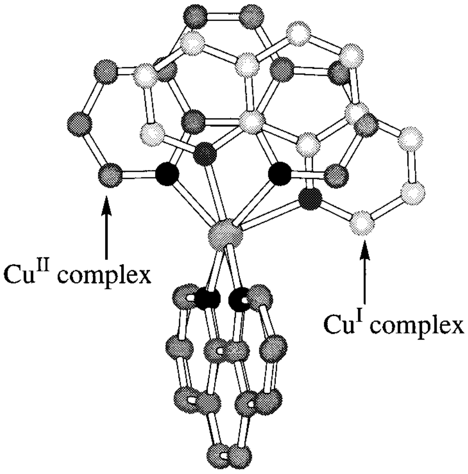

Figure 4. View of the cores of $[Cu(dpp)_2]^+$ and $[Cu(dpp)_2]^{2+}$. One phenanthroline moiety of each of the complex cations was overlaid to show the relative orientation of the other ligand. The phenyl groups at the 2- and 9-positions of the ligands have been omitted for clarity.

of **1** and **2**. As discussed above, the structure of $[Cu(dpp)_2]^+$ is largely determined by π-stacking interactions, whereas these interactions are not observed in $[Cu(dpp)_2]^{2+}$. Solution-state data indicate that significant fluxionality occurs with the d^{10} ion, which permits the phenanthroline ligands to "rock" back and forth to maximize π-stacking. In contrast, the d^9 ion constrains the phenanthroline ligands closer to a square planar geometry in which π-stacking interactions are not possible.

An important goal in inorganic photochemistry is to determine ways to maximize excited-state lifetimes since complexes with longer lifetimes are more useful for photoinduced electron and energy transfer. Reducing the amount of structural distortion in the excited state has been shown to significantly extend lifetimes in Ru^{II} and Os^{II} polypyridine complexes.[52-55] To reduce excited-state distortion in copper(I) photochemistry will necessitate the design of systems in which the geometries around the copper(I) and copper(II) ions are similar. These complexes will thus require significant steric constraint to prevent the excited-state flattening distortion.

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Supporting Information Available: Tables of positional parameters, bond lengths, bond angles, and anisotropic thermal parameters and unit-cell packing diagrams for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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