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Structures and Properties of Copper(II) and Copper(I) Complexes Containing an Ethane-Bridged Dimeric Phenanthroline Ligand

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The structures of $[Cu(Diphen)(H_2O)](ClO_4)_2$ (**1**) and $[Cu(Diphen)]_2(ClO_4)_2$ (**2**), where Diphen is 1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane, have been determined by single-crystal X-ray diffraction. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 12.075$ (2) Å, $b = 14.340$ (2) Å, $c = 16.201$ (2) Å, $\beta = 103.27$ (1)°, $Z = 4$, and $D_{calcd} = 1.692$ g cm^{-3}. Of the 3514 unique reflections (Mo Kα, $3.5° \leq 2\theta \leq 45°$), 2431 reflections with $F_o > 4\sigma(F_o)$ were used in full-matrix least-squares refinement. Final residuals were $R(F) = 0.0434$ and $R_w(F) = 0.0428$. The copper cation is in a trigonal bipyramidal environment with four sites occupied by nitrogen donor atoms from the L_2 ligand and the fifth site occupied by a water molecule. The cation exhibited dd transitions in the 600–900-nm range and a Cu(II/I) half-wave potential near 0.25 V vs SSCE. Both the energy of the dd transitions and the $E_{1/2}$-value depend on solvent donor number. ESR parameters were $g_\perp = 2.18$, $A_\perp = 89.5 \times 10^{-4}$ cm^{-1} and $g_\parallel = 2.01$, $A_\parallel = 80.7 \times 10^{-4}$ cm^{-1}. The dinuclear complex **2** crystallized in the monoclinic space group $C2/c$ with cell dimensions of $a = 24.445$ (11) Å, $b = 16.119$ (9) Å, $c = 17.270$ (9) Å, $\beta = 118.75$ (4)°, $Z = 8$, and $D_{calcd} = 1.560$ g cm^{-3}. Of the 3921 unique reflections (Mo Kα, $3.5° \leq 2\theta \leq 45°$), 2685 reflections with $F_o > 4\sigma(F_o)$ were used in full-matrix least-squares refinement. Final residuals were $R(F) = 0.0557$ and $R_w(F) = 0.0677$. Complex **2** forms a double-helicate structure with the two copper ions in distorted tetrahedral environments. The Cu···Cu separation is 5.729 Å. The bimetallic complex displayed an optical transition in the 450-nm region of the visible spectrum. Broad, featureless emission ($\lambda_{ex} = 450$ nm) located over the 600–800-nm region was observed at 77 K. A Cu(II/I) redox couple is found near 0.70 V vs SSCE. The unusual difference between redox couples of complex **1** and complex **2** is rationalized on the basis of slow structure changes which occur between the Cu(II) and Cu(I) complexes.

Introduction

The search for solar energy photocatalysts has involved studies of excited-state properties of ruthenium(II),[1] rhenium(I),[1] iridium(III),[2] rhodium(III),[2] platinum(II),[3-14] and copper(I)[15] complexes. The copper(I) complexes were based on derivatives of the 1,10-phenanthroline ligand with alkyl or aryl substituents in the 2,9-positions. McMillin and co-workers[15] found these complexes to luminesce in fluid solution at room temperature and to be capable of undergoing excited-state electron-tranfser events.

In our own work with ruthenium(I) polypyridyl complexes,[16] we have found that the photophysics of complexes can be enhanced with rigid, planar polypyridyl ligands. Thus, we embarked on a project to tie two 2,9-dimethyl-1,10-phenanthroline (dmp) ligands together according to the procedures outlined by Lehn and co-workers[17] and then prepare the copper(I) complex. We postulated that this new copper(I) complex would have enhanced photophysical properties. Recently, Lehn and co-workers[18] reported copper(I), cobalt(II), and iron(III) complexes containing the proposed tetradentate ligand and some of their properties. Here we provide details about the crystal structures of the copper(I) and copper(II) complexes and details about their visible/UV properties, redox properties, luminescence properties, and magnetic properties.

Experimental Section

Materials. Neocuproine (2,9-dimethyl-1,10-phenanthroline) was purchased commercially and was dried under vacuum at room temperature for 24 h. Tetrahydrofuran (THF) was dried by distillation over sodium benzophenone. Diisopropylamine was dried by distillation over CaH_2. Butyronitrile was dried by distillation over P_2O_5. Dimethyl sulfoxide, propylene carbonate, nitromethane, and nitrobenzene were dried over

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4-Å molecular sieves before use in electrochemistry and visible-UV spectral measurements. 1,2-Dibromomethane was purchased from Aldrich as gold label grade. *n*-Butylithium was purchased from Aldrich as a 2.5 M solution in hexane and was used without further purification. Tetrabutylammonium hexafluorophosphate (TBAH) was purchased commercially as electrometric grade from Southwestern Analytical Chemicals, Inc., Austin, TX, and dried in a vacuum oven at room temperature before use. All other materials, unless previously indicated, were purchased as reagent grade or HPLC grade and used without further purification.

Preparation of Compounds. 1,2-Bis(9-methyl-1,10-phenanthrolin-2-yl)ethane. The method followed the one previously reported by Lehn and Ziessel.[17] The yield was 20%. Mp > 260 °C. ^{1}H NMR: δ 8.19 (d, J = 8.1 Hz, 2 H, H-C_4 or H-C_7), 8.16 (d, J = 7.8 Hz, 2 H, H-C_4 or H-C_7), 7.75 (s, 4 H, H-C_5, H-C_6), 7.71 (d, J = 8.4 Hz, 2 H, H-C_3 or H-C_8), 7.53 (d, J = 8.1 Hz, 2 H, H-C_3 or H-C_8), 3.77 (s, $2CH_2$), 2.93 (s, $2CH_3$).

$[Cu(Diphen)(H_2O)](ClO_4)_2$ (1) (Diphen = 1,2-Bis(9-methyl-1,10-phenanthrolin-2-yl)ethane). A solution containing 0.045 g (0.228 mmol) of cupric acetate monohydrate dissolved in 15 mL of warm CH_3OH was added dropwise over a 10-min period to a stirring solution containing 0.10 g (0.228 mmol) of diphen dissolved in 40 mL of warm CH_3OH and 5 mL of CH_2Cl_2. A yellow-green solution resulted which was allowed to stir for an additional $1^1/_2$ h. An aqueous solution containing $NaClO_4$ was then added dropwise until precipitation of the complex was complete. The green precipitate was collected by vacuum filtration and washed with cold ethanol and then diethyl ether. The yield was about 70%. Anal. Calcd for $[Cu(Diphen)H_2O](ClO_4)_2$: C, 48.39; H, 3.48; N, 8.06; Cl, 10.20. Found: C, 48.21; H, 3.47; N, 8.05; Cl, 10.29. *Caution! Perchlorate salts are potentially explosive!*

$[Cu(Diphen)]_2(ClO_4)_2 \cdot {}^4/_3H_2O$ (2). A 0.1-g sample (0.144 mmol) of $[Cu(Diphen)(H_2O)](ClO_4)_2$ was dissolved in 12 mL of argon-purged acetonitrile. Under argon, a solution containing 0.051 g (0.228 mmol) of L(+)-ascorbic acid dissolved in 20 mL of argon-purged CH_3OH was added dropwise to the solution containing $[Cu(Diphen)H_2O]^{2+}$. During addition, the color of the solution changed from green to brick red. The solution was allowed to stir for an additional $^1/_2$ h, and the resulting copper(I) complex was precipitated as the perchlorate salt upon addition of ether. The precipitate was isolated by vacuum filtration, redissolved in acetonitrile, and reprecipitated by addition of diethyl ether. The yield was 0.06 g (60%). Anal. Calcd for $[Cu(Diphen)]_2(ClO_4)_2 \cdot {}^4/_3H_2O$: C, 56.69; H, 4.04; N, 9.44; Cl, 5.98. Found: C, 56.68; H, 3.69; N, 9.42; Cl, 6.00. ^{1}H NMR (CD_3CN): δ 8.60 (d, J = 8.1 Hz, 2 H, H-C_4), 8.09 (d, J = 8.7 Hz, 2 H, H-C_4), 7.83 (d, J = 7.5 Hz, 2 H, H-C_6), 7.80 (d, J = 6.9 Hz, 2 H, H-C_3), 7.57 (d, J = 8.4 Hz, 2 H, H-C_7), 6.77 (d, J = 8.4 Hz, 2 H, H-C_8), 2.89 (ABCD m, 4 H, CH_2), 2.34 (s, 6 H, CH_3). *Caution! Perchlorate salts are potentially explosive!*

Physical Measurements. Visible–UV spectra were recorded with Perkin-Elmer Lambda Array and Cary 14 spectrophotometers. Cyclic voltammograms were obtained using a three-electrode system consisting of a Pt disk working electrode, a Pt wire counter electrode, and a saturated sodium chloride calomel standard electrode (SSCE). Electrochemistry was carried out with a PAR 173 potentiostat in conjunction with a PAR 175 programmer. Cyclic voltammograms were recorded with a YEW 3022-A4 x-y recorder. NMR spectra were recorded in deuterated chloroform with a 300-MHz General Electric QE-300 NMR spectrometer. EPR spectra were recorded with an X-band JEOL Model JES-PE spectrometer and calibrated with DPPH (g = 2.0037). Corrected luminescence spectra were recorded with a SPEX Fluorolog 212 spectrometer. Excited-state lifetimes were determined with a PRA LN1000 pulsed nitrogen laser coupled with a PRA LN102 tunable dye head as the excitation source. The analog signal from the photomultiplier tube located at right angles to the excitation source was digitized with a LeCroy transient digitizer system. The LeCroy was interfaced to an IBM PS/2 Model 60 computer and controlled by "Catalyst" software supplied by LeCroy. Computations of time-dependent emission decays were performed with an algorithm designed to fit the data to a single exponential decay.

Beer's law studies were carried out by serial dilution for determining absorption coefficients. Samples for electrochemistry were prepared in various solvents containing 0.10 M TBAH, placed in a conventional H-cell, and purged with N_2 before measurements were effected. Samples for emission experiments were prepared in 10-mm-diameter Suprasil fused silica tubes as optically dilute solutions (~10^{-5} M) in 4:1 (v/v) ethanol/methanol and were freeze–pump–thaw degassed for four cycles using the system described previously.[19] Samples were filtered through 0.4-μm syringe filters (Millipore) prior to optical measurements.

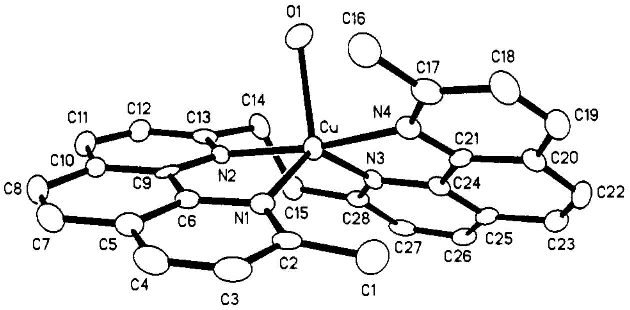

Figure 1. ORTEP drawing of the $[Cu(Diphen)(H_2O)]^{2+}$ cation.

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

formula	$[C_{28}H_{24}N_4OCu]$-$(ClO_4)_2$	$[C_{56}H_{44}N_8Cu_2](ClO_4)_2 \cdot 3CH_2Cl_2$
fw	695.0	1409.93
space group	$P2_1/c$	$C2/c$
a (Å)	12.075 (2)	24.445 (11)
b (Å)	14.340 (2)	16.119 (9)
c (Å)	16.201 (2)	17.270 (9)
β (deg)	103.270 (10)	118.75 (4)
V (Å^3)	2730.4 (8)	5966 (5)
Z	4	4
D_{calc} (g/cm^3)	1.69	1.57
radiation (λ (Å))	Mo Kα (0.7103)	
temp (°C)	−130	
μ (cm^{-1})	10.6	11.4
$R(F)/R_w(F)$ (%)[a]	4.34/4.28	5.59/6.77

[a] $R(F) = \sum\|F_o| - |F_c\|/\sum|F_o|$.

Collection and Reduction of X-ray Data. Green prismatic crystals of **1** were grown from CH_3CN, and reddish orange prismatic crystals of **2** were grown from CH_2Cl_2. Diffraction data for both crystals were collected on a Siemens R3mV diffractometer equipped with a LT2 low-temperature accessory. For each data set collected, three standard reflections were monitored every 97 reflections and showed no significant variation during the collection. The data were corrected for Lorentz and polarization effects but were not corrected for absorption.

Both structures were solved with the SHELXTL PLUS structure solution pacakage[20] by using the Patterson heavy-atom method. Non-hydrogen atoms were located in successive Fourier difference maps. During the last stages of refinement, hydrogen atoms were included at their calculated positions (C–H = 0.96 Å) and were not refined. Full-matrix least-squares refinements converged to the residuals listed in Table I.

Complex **2** crystallized with three solvent molecules of crystallization, $[Cu_2(L_2)_2](ClO_4)_2 \cdot 3CH_2Cl_2$. The asymmetric unit consisted of one-half of the dinuclear cation, which resided on a crystallographic 2-fold axis, one and one-half molecules of CH_2Cl_2, and one ClO_4^- ion. The one-half molecule of CH_2Cl_2 was located on a crystallographic 2-fold axis with the carbon atom located at the special position 0, y, $^1/_4$. The ClO_4^- ion is disordered such that two main orientations were identified from successive Fourier maps. One orientation had a C_3 axis canted approximately 31° to the C_3 axis of the other orientation with the Cl position common to both orientations. By assignment of reasonable isotropic thermal parameters to the perchlorate atoms, the site occupation factors for those atoms were refined and the model that was finally adopted included these two orientations in an approximately 57:43 occupation ratio.

Results

Structure of Aqua[1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)ethane]copper(II) Diperchlorate (1). The structure of the cation of **1** (Figure 1) contains a CuN_4O core in an approximate trigonal bipyramidal geometry. Atomic coordinates and selected bond distances and angles are given in Tables II and III, respectively. Each phen unit from the L_2 ligand provides an

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Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1**

	x	*y*	*z*	*U*(eq)[a]
Cu	2227 (1)	2034 (1)	3834 (1)	18 (1)
N(1)	1394 (4)	3280 (3)	3991 (3)	18 (2)
N(2)	661 (4)	1549 (3)	3585 (3)	16 (2)
N(3)	3106 (4)	1055 (3)	4695 (3)	16 (2)
N(4)	3784 (4)	2527 (3)	3916 (3)	19 (2)
O(1)	2246 (3)	1459 (3)	2580 (2)	26 (2)
C(1)	2951 (5)	4251 (4)	4789 (4)	35 (3)
C(2)	1746 (5)	4127 (4)	4299 (4)	21 (2)
C(3)	995 (6)	4893 (4)	4200 (4)	29 (3)
C(4)	−130 (6)	4777 (4)	3819 (4)	29 (3)
C(5)	−535 (5)	3894 (4)	3544 (4)	21 (2)
C(6)	258 (5)	3171 (4)	3648 (3)	19 (2)
C(7)	−1721 (5)	3703 (5)	3185 (4)	29 (3)
C(8)	−2077 (5)	2823 (5)	2967 (4)	29 (3)
C(9)	−135 (5)	2231 (4)	3427 (3)	18 (2)
C(10)	−1293 (5)	2065 (5)	3087 (3)	21 (2)
C(11)	−1611 (5)	1126 (4)	2902 (4)	24 (2)
C(12)	−799 (5)	439 (4)	3094 (4)	23 (2)
C(13)	332 (5)	663 (4)	3442 (4)	21 (2)
C(14)	1223 (5)	−76 (4)	3703 (4)	22 (2)
C(15)	1627 (5)	−138 (4)	4676 (3)	21 (2)
C(16)	3278 (5)	3606 (4)	2709 (4)	30 (2)
C(17)	4119 (5)	3208 (4)	3461 (4)	23 (2)
C(18)	5245 (5)	3541 (4)	3675 (4)	29 (3)
C(19)	6004 (5)	3197 (4)	4363 (4)	30 (3)
C(20)	5678 (5)	2474 (4)	4847 (4)	21 (2)
C(21)	4559 (5)	2150 (4)	4582 (3)	19 (2)
C(22)	6423 (5)	2078 (5)	5571 (4)	27 (2)
C(23)	6061 (5)	1358 (4)	5985 (4)	26 (2)
C(24)	4186 (5)	1386 (4)	5005 (4)	17 (2)
C(25)	4940 (5)	981 (4)	5708 (4)	20 (2)
C(26)	4550 (5)	197 (4)	6090 (4)	22 (2)
C(27)	3486 (5)	−133 (4)	5755 (4)	22 (2)
C(28)	2775 (5)	295 (4)	5044 (3)	17 (2)
Cl(1)	4873 (1)	3714 (1)	6883 (1)	24 (1)
O(2)	5575 (4)	4161 (3)	6397 (3)	43 (2)
O(3)	5555 (4)	3431 (3)	7692 (3)	39 (2)
O(4)	4018 (3)	4386 (3)	7029 (2)	24 (2)
O(5)	4310 (3)	2924 (3)	6440 (3)	35 (2)
Cl(2)	245 (1)	2614 (1)	891 (1)	28 (1)
O(6)	−852 (4)	2336 (4)	448 (4)	77 (3)
O(7)	553 (5)	3420 (3)	494 (3)	58 (2)
O(8)	274 (5)	2817 (4)	1756 (3)	66 (2)
O(9)	1040 (4)	1871 (3)	861 (3)	44 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

	Distances		
Cu–N(1)	2.094 (5)	Cu–N(4)	1.984 (5)
Cu–N(2)	1.967 (5)	Cu–O(1)	2.198 (4)
Cu–N(3)	2.089 (4)		
	Angles		
N(1)–Cu–N(2)	82.0 (2)	N(3)–Cu–N(4)	82.3 (2)
N(1)–Cu–N(3)	132.6 (2)	N(1)–Cu–O(1)	122.6 (2)
N(2)–Cu–N(3)	102.5 (2)	N(2)–Cu–O(1)	83.7 (2)
N(1)–Cu–N(4)	99.3 (2)	N(3)–Cu–O(1)	104.7 (2)
N(2)–Cu–N(4)	172.2 (2)	N(4)–Cu–O(1)	89.2 (2)

equatorial and an axial nitrogen donor atom. The fifth coordination site is occupied by a water molecule. Interestingly, nitrogen atoms that are chemically equivalent in the free ligand L_2 do not occupy equivalent sites in **1**. Of the two sets of chemically equivalent nitrogen atoms in L_2, one nitrogen atom from each set occupies an equatorial site and one occupies an axial site in **1**; thus, each phen unit provides an axial and an equatorial nitrogen donor atom. The axial distances are 1.967 (5) Å for Cu–N(2) and 1.984 (5) Å for Cu–N(4). The equatorial Cu–N distances are slightly longer at 2.094 (5) and 2.089 Å for Cu–N(1) and Cu–N(3), respectively. The oxygen atom from the water molecule occupies the third equatorial position with a Cu–O distance of 2.198 (4) Å. The axial angle of N(2)–Cu–N(4) is 172.2 (2)°. The N_{ax}–Cu–L_{eq} angles are within 10° of the ideal 90°; however, the deviation from ideal values is greater for equatorial angles. These deviations must be attributed in part to geometric restrictions of the ligand, crystal packing forces, and the presence of a unique oxygen in the equatorial plane.

The mean deviations from the least-squares planes of the phen rings and their substituent carbon atoms are only 0.0559 and 0.0652 Å, which demonstrates the near planarity of these units. The dihedral angle for the two least-squares planes containing the phen units is 48.6°. The trigonal bipyramidal geometry of **1** is in contrast to the square pyramidal geometry more commonly found for the related ternary copper(II) complexes of 2,2′-bipyridyl (bpy).[21] This difference is probably due in part to the steric and structural requirements of L_2 that result from the methyl substituent and the ethane bridge.

Structure of Bis[1,2-bis(9-methyl-1,10-phenanthrolin-2-yl)-ethane]dicopper(I) Diperchlorate (2). The atomic coordinates for **2** are given in Table IV. Selected bond distances and angles for the dinuclear cation of **2** are given in Table V, and the structure of the dication is shown in Figure 2. The structure is analogous to that of bis[1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane]dicopper(I) diperchlorate (**3**) reported recently.[18] The cation of **2** contains the CuN_4 core in a distorted tetrahedral arrangement. The CuN_4 core contains two nitrogen atoms from a phen unit of one L_2 molecule and two nitrogen atoms from a phen unit of a second L_2 molecule.

The mean deviations from the least-squares planes derived from the phen rings and their carbon substituents are 0.0716 Å for the plane that contains N(1) and N(2) and 0.0309 Å for the plane that contains N(3) and N(4). The dihedral angle for the two planes deviates from the ideal value of 90° by 9°. Also, the N(1)–Cu–N(2) and N(3)–Cu–N(4) angles are 82.5 and 82.6°, respectively. These less-than-ideal tetrahedral angles result from the restricted bite size of the phen units. The four Cu–N bond distances vary slightly from the shortest Cu–N(1) of 1.992 (7) Å to a Cu–N(2) distance of 2.081 (6). The Cu···Cu separation is 5.729 Å, a somewhat shorter distance than that found in the analogous bpy compound.[18]

Visible–UV Spectra. The visible–UV spectra were examined for $[Cu(Diphen)(H_2O)]^{2+}$ and $[Cu(Diphen)]_2^{2+}$ in the solid state and in various solvents. The data are summarized in Table VI. Absorptions for $[Cu(Diphen)(H_2O)]^{2+}$ were characterized by low-energy transitions located over the 9000–18 000-cm^{-1} region and high-energy transitions located in the UV region related to intraligand $\pi \rightarrow \pi^*$ transitions. The dd transitions were lost in $[Cu(Diphen)]_2^{2+}$ and replaced by ones of higher energy located near 22 575 cm^{-1}. These transitions are assigned as metal-to-ligand charge-transfer (MLCT) transitions on the basis of the analogy to other copper(I) heterocycles such as $[Cu(OBPY)]^{2+}$ [22] and $[Cu(dmp)_2]^{2+}$,[23] where OBPY = 1,2-bis(2,2′-bipyridyl-6-yl)ethane.

The dd absorption spectrum of $[Cu(Diphen)(H_2O)]^{2+}$ was examined in the solid state and in various solvents which differed in donor numbers.[24] The spectrum in the solid state consisted of

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Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*(eq)[a]
Cu	4375 (1)	2387 (1)	5608 (1)	30 (1)
N(1)	4828 (2)	1843 (3)	5046 (3)	23 (2)
N(2)	5151 (3)	3164 (3)	6128 (4)	31 (3)
N(3)	4009 (3)	2004 (3)	6379 (3)	28 (3)
N(4)	3598 (3)	3109 (3)	5062 (4)	32 (3)
C(1)	4061 (3)	763 (5)	4309 (5)	37 (3)
C(2)	4660 (3)	1190 (4)	4509 (4)	29 (3)
C(3)	5017 (3)	920 (5)	4123 (5)	44 (4)
C(4)	5556 (3)	1318 (5)	4303 (5)	39 (4)
C(5)	5757 (3)	2003 (5)	4870 (4)	28 (3)
C(6)	1371 (3)	2243 (4)	5222 (4)	24 (3)
C(7)	6305 (3)	2459 (5)	5088 (5)	38 (3)
C(8)	6468 (3)	3127 (5)	5623 (5)	34 (3)
C(9)	6093 (3)	3397 (4)	6004 (5)	31 (3)
C(10)	6228 (3)	4081 (5)	6563 (5)	42 (4)
C(11)	5833 (4)	4291 (5)	6884 (5)	51 (4)
C(12)	5294 (4)	3827 (6)	6647 (5)	48 (4)
C(13)	5540 (3)	2955 (4)	5796 (4)	27 (3)
C(14)	4693 (3)	813 (4)	7059 (4)	35 (3)
C(15)	4201 (3)	1419 (4)	6999 (5)	32 (3)
C(16)	3936 (4)	1326 (5)	7561 (5)	39 (4)
C(17)	3465 (4)	1834 (5)	7472 (5)	47 (4)
C(18)	3235 (3)	2449 (5)	6799 (5)	36 (3)
C(19)	3519 (3)	2498 (4)	6261 (4)	30 (3)
C(20)	2731 (4)	2984 (5)	6629 (6)	45 (4)
C(21)	2526 (3)	3542 (5)	5968 (6)	49 (4)
C(22)	2794 (3)	3605 (5)	5395 (5)	41 (4)
C(23)	2602 (4)	4167 (5)	4695 (6)	50 (4)
C(24)	2897 (4)	4186 (5)	4182 (6)	47 (4)
C(25)	3388 (3)	3645 (4)	4380 (5)	35 (3)
C(26)	3306 (3)	3088 (4)	5556 (5)	30 (3)
C(27)	3731 (4)	3635 (5)	3855 (5)	52 (4)
C(28)	4850 (4)	4017 (6)	7009 (5)	63 (4)
Cl	1714 (1)	6258 (1)	3130 (1)	34 (1)
O(1)	1318 (6)	5591 (8)	3076 (8)	60 (3)
O(2)	2141 (5)	6034 (8)	2847 (7)	45 (3)
O(3)	2048 (5)	6622 (7)	4006 (7)	32 (3)
O(4)	1338 (6)	6941 (8)	2631 (8)	63 (3)
O(1A)	2033 (6)	6294 (9)	4082 (8)	30 (4)
O(2A)	2082 (6)	5676 (9)	2881 (8)	29 (3)
O(3A)	1102 (7)	5929 (10)	2777 (1)	54 (4)
O(4A)	1680 (8)	6983 (10)	2611 (10)	58 (4)
C(30)	7233 (4)	3693 (6)	3837 (6)	56 (4)
Cl(2)	7619 (1)	4347 (2)	3450 (2)	65 (1)
Cl(3)	6546 (1)	4117 (2)	3719 (2)	66 (1)
C(31)	0	8001 (9)	2500	81 (9)
Cl(4)	−24 (1)	8595 (2)	3320 (2)	80 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Distances (Å) and Bond Angles (deg) for **2**

	Distances		
Cu–N(1)	1.992 (7)	Cu–N(3)	2.026 (7)
Cu–N(2)	2.081 (6)	Cu–N(4)	2.034 (6)
	Angles		
N(1)–Cu–N(2)	82.6 (2)	N(2)–Cu–N(3)	119.9 (2)
N(1)–Cu–N(3)	135.4 (2)	N(2)–Cu–N(4)	108.1 (2)
N(1)–Cu–N(4)	129.8 (2)	N(3)–Cu–N(4)	82.5 (2)

two peaks in accord with other systems characterized as trigonal bipyramidal. In solvents of low donor number two maxima were also observed. The maxima gradually merged into one maximum as the solvent donor number increased. As typical of trigonal bipyramidal copper(II) complexes, a shoulder was located on the high-energy side.[25-27] The dd absorption spectrum of [Cu(Diphen)(H_2O)]$^{2+}$ in nitromethane is illustrated in Figure 3A. Also illustrated is the deconvolution of the spectrum into three transitions by Gaussian line-shape analysis. The spectra obtained in other solvents were deconvoluted similarly, and as shown in Figure 3B, the three maxima decreased as the solvent donor number increased. This trend is in accord with solvent interaction with the complex resulting in a structure change from "distorted square pyramidal" ("trigonal bipyramidal") toward tetragonal geometry.

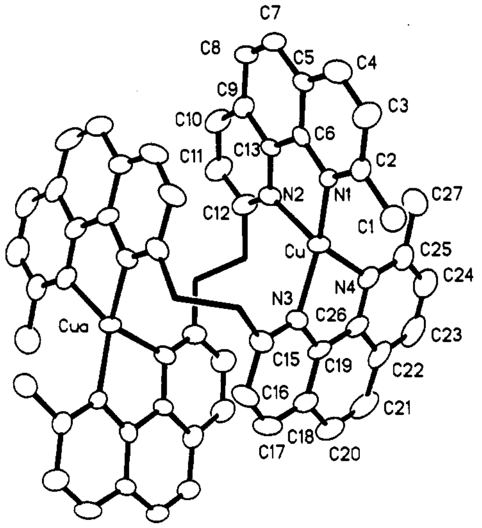

Figure 2. ORTEP drawing of the [Cu(Diphen)]$_2^{2+}$ cation.

Electrochemistry. Redox processes were investigated by cyclic voltammetry and are summarized in Table VII. The $E_{1/2}$-values were determined by averaging the anodic and cathodic peak potentials, $E_{1/2} = (E_{p,ox} + E_{p,red})/2$ relative to an internal standard. For the [Cu(Diphen)(H_2O)]$^{2+/+}$ couple, the internal standard was 1,1′-diacetylferrocene ($E_{1/2}$ = 0.790 V vs SSCE);[28] for the Cu(II/I) couple of [Cu(Diphen)]$_2^{2+}$, ferrocene ($E_{1/2}$ = 0.315 V vs SSCE) served as the standard.[29] The $E_{1/2}$-values of the Cu(II/I) couples ranged from 0.091 to 0.25 V vs SSCE for [Cu(Diphen)(H_2O)]$^{2+}$ in various solvents and from 0.55 to 0.92 V vs SSCE for [Cu(Diphen)]$_2^{2+}$ in the same solvents. These changes correlated with solvent donor number as illustrated in Figure 4. The sensitivity to solvent is greater for [Cu(Diphen)]$_2^{2+}$ than for [Cu(Diphen)(H_2O)]$^{2+}$.

For both complexes, the Cu(II/I) couples exhibited quasireversible behavior. The i_c/i_a ratio varied from 1.5 to 6, while ΔE_p, where $\Delta E_p = E_{p,ox} - E_{p,red}$, ranged from 45 to 325 mV. The 45-mV separation approached the 56/*n* mV separation expected for a reversible, one electron transfer process; the 325-mV separation in DMSO could best be described as quasireversible.[30]

The cyclic voltammograms for [Cu(Diphen)(H_2O)]$^{2+}$ and [Cu(Diphen)]$_2^{2+}$ are illustrated in Figure 5. The one for [Cu(Diphen)]$_2^{2+}$ consists of an oxidation and a reduction wave. Further, bulk electrolysis 0.1 V more positive than the $E_{1/2}$-value for [Cu(Diphen)]$_2^{2+}$ in acetone gave an *n*-value of 2, which is in agreement with the results of Lehn and co-workers.[18] The conclusion reached is that both copper(I) centers in the dimer are equivalent on the cyclic voltammetry time scale as has been observed with other copper(I) bimetallic complexes.[18] As noted in Figure 5, reduction of [Cu(Diphen)(H_2O)]$_2^{2+}$ resulted in the appearance of a redox couple in the 0.61–0.92-V region; oxidation of [Cu(Diphen)]$_2^{2+}$ resulted in the appearance of a redox couple in the 0.091–0.25-V vs SSCE region. Further, the initially generated [Cu(Diphen)(H_2O)]$^+$ species is more unstable than [Cu(Diphen)]$_2^{4+}$. We interpret these results as structure change variations which occur between the +2 and +1 oxidation states, where the d^9 electronic configuration favors distorted square pyramidal to an octahedral coordination, while the d^{10} electronic

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Table VI. Visible/UV Spectral Data for $[Cu(Diphen)(H_2O)]^{2+}$ and $[Cu(Diphen)]_2^{2+}$ in the Solid State and/or Various Sovlents[a]

complex	solvent	d → d (ε)	dπ → π* (ε × 10^{-3})	π → π* (ε × 10^{-4})	π → π* (ε × 10^{-4})	DN[b]
I	solid	759, 678				
II						
I	nitromethane	768 (191), 648 (179)		*c*	*c*	2.7
II			443 (8.0)	*c*	*c*	
I	nitrobenzene	800 (229), 687 (sh)		*c*	*c*	4.4
II			467 (2.8)	*c*	*c*	
I	acetonitrile	793 (181), 708 (sh)		275 (4.6)	227 (6.4)	14.1
II			443 (4.6)	278 (5.6)	230 (7.6)	
I	propylene carbonate	801 (216), 686 (sh)		279 (5.2)	237 (4.9)	15.1
II			444 (6.5)	278 (5.2)	234 (1.0)	
I	acetone	795 (215)		*c*	*c*	17.0
II			443 (5.2)	*c*	*c*	
I	dimethylformamide	818 (193), 722 (sh)		278 (1.1)	*c*	24.0
II			444 (7.0)	274 (8.6)	*c*	
I	dimethyl sulfoxide	835 (224)		279 (3.9)	*c*	29.8
II			447 (7.9)	279 (3.4)	*c*	
I	methylene chloride					
II			446 (4.9)	278 (4.7)	236 (4.5)	
Diphen	methylene chloride			274 (5.3)	234 (5.7)	

[a] λ_{max} in nm (±1 nm), ε in parentheses (±1 in last digit). [b] From ref 24. [c] Masked by solvent. [d] Not determined.

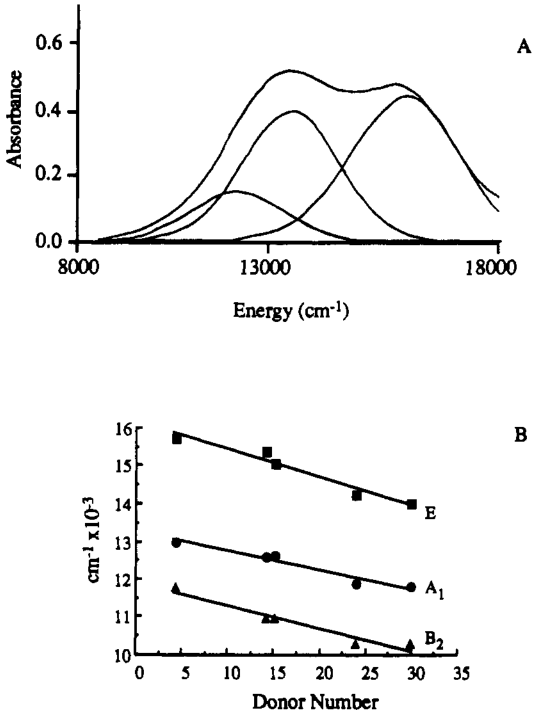

Figure 3. (A) Visible absorption spectrum of $[Cu(Diphen)(H_2O)]^{2+}$ in nitromethane. The three bands below the experimental spectrum were obtained by Gaussian line-shape analysis and added together to give the experimental line. (B) Dependence of the deconvoluted absorption maximum in cm^{-1} as a function of the donor number of the solvent: (1) lowest energy transition (B_2) (slope = 60 cm^{-1}/donor number; corr coeff = 0.97); (2) intermediate energy transition (A_1) (slope = −51 cm^{-1}/donor number; corr coeff = 0.98); (3) highest energy transition (E) (slope = −74 cm^{-1}/donor number; corr coeff = 0.96).

configuration favors a tetrahedral geometry. Similar configurational changes have been reported in related systems.[18,31]

Electron Spin Resonance Spectra. The *g*-value of the electron spin resonance spectrum of a polycrystalline sample of $[Cu(Diphen)(H_2O)](ClO_4)_2$ was 2.07. The spectrum was not split into $g_\perp$ and $g_\parallel$ components. The pure solid was presumably not magnetically dilute enough to yield an ESR spectrum that was indicative of solid-state stereochemistry.

The ESR spectrum of $[Cu(Diphen)(H_2O)](ClO_4)_2$ was obtained in fluid solution and in a glass at 77 K. The spectrum

Table VII. Polorographic Half-Wave Potentials of the Copper(I) and Copper(II) Diphen Complexes in Various Solvents[a]

solvent	$[Cu(Diphen)(H_2O)]^{2+/+}$ [b]	$[Cu(Diphen)]_2^{4+/2+}$ [c]	DN
nitromethane	0.22 (81)	0.80 (150)	2.7
nitrobenzene	0.22 (122)	0.77 (115)	4.4
acetonitrile	0.19 (120)	0.64 (45)	14.1
propylene carbonate	0.22 (180)	0.65 (190)	15.1
acetone	0.18 (111)	0.65 (80)	17.0
methanol[d]	0.11 (90)	0.61 (170)	20.0
DMF	0.091 (122)	0.55 (180)	24.0
DMSO	0.12 (182)	0.76 (325)	29.8
methylene chloride		0.92 (170)	

[a] $E_{1/2}$, V vs SSCE; 0.1 M Et_4NClO_4/solvent; sweep rate = 500 mV/s; error = ±0.02 V; value in parentheses is E_p in mV, where $E_p = E_{p,ox} - E_{p,red}$; Pt working electrode. [b] Internal standard, 1,1′-diacetylferrocene. [c] Internal standard, ferrocene. [d] Glassy-carbon electrode. Linear correlation: slope = 0.85, correlation coefficient = 0.99 excluding DMSO.

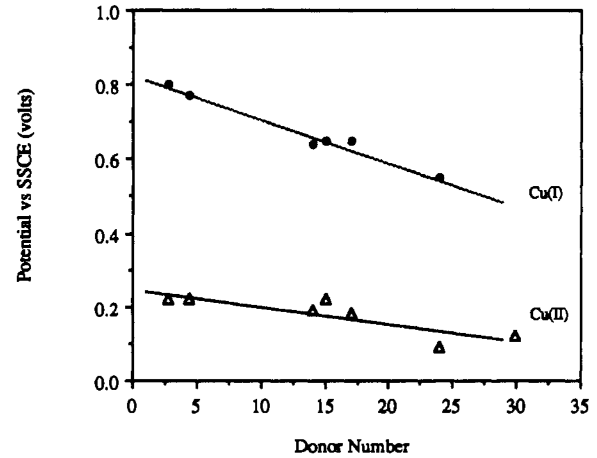

Figure 4. Dependence of $E_{1/2}$ for Cu(II/I) redox couples as a function of the donor number of the solvent: $[Cu(Diphen)(H_2O)]^{2+}$ (slope = −0.005 V/donor number; corr coeff = 0.83); $[Cu(Diphen)]_2^{2+}$ (slope = −0.011 V/donor number; corr coeff = 0.99).

obtained in solution (60:40 (v/v) MeTHF/DMF) at room temperature resulted in g_{iso} = 2.11. The spectrum obtained in the 60:40 (v/v) MeTHF/DMF glass is shown in Figure 6. It contained two identifiable magnetic *g* values along with the corresponding copper ($I = {}^3/_2$) hyperfine splitting constants. Their values were as follows: $g_\perp$ = 2.18, $A_\perp$ = 89.5 × 10^{-4} cm^{-1}; $g_\parallel$ = 2.01, $A_\parallel$ = 80.7 × 10^{-4} cm^{-1}. The *g*- and *A*-values were consistent with all reported cases of trigonal bipyramidal copper(II)

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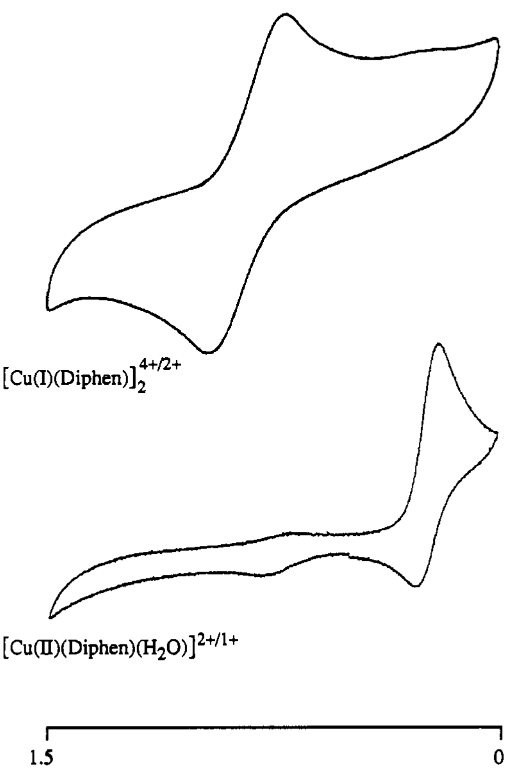

Figure 5. Cyclic voltammograms for $[Cu(Diphen)(H_2O)]^{2+}$ and $[Cu(Diphen)]_2^{2+}$ in acetonitrile containing 0.1 M TBAH.

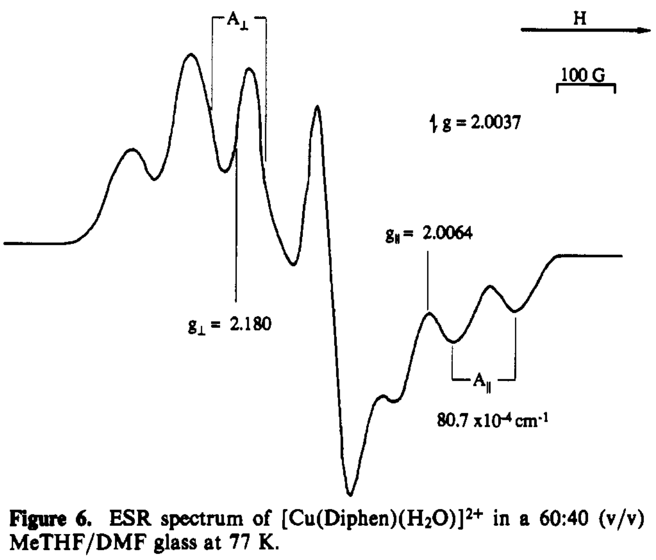

Figure 6. ESR spectrum of $[Cu(Diphen)(H_2O)]^{2+}$ in a 60:40 (v/v) MeTHF/DMF glass at 77 K.

complexes which have $g_\parallel \sim g_e < g_\perp$ and $50 \times 10^{-4}\ \text{cm}^{-1} < A_\parallel < A_\perp < 100 \times 10^{-4}\ \text{cm}^{-1}$.[32-35]

Emission Properties. Excitation of $[Cu(Diphen)]_2^{2+}$ at 450 nm in a 4:1 (v/v) EtOH/MeOH glass at 77 K resulted in the broad, featureless emission spectrum shown in Figure 7. The emission had a lifetime of 1.6 μs at its maximum (692 nm). No emission is observed at room temperature. It should be noted that many recrystallizations of the product were required after chromatographic separation to get rid of interfering impurity emissions.

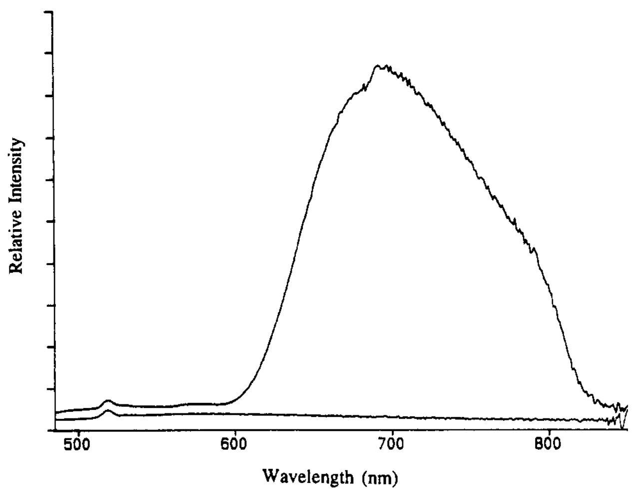

Figure 7. Corrected emission spectrum of $[Cu(Diphen)]_2^{2+}$ at 77 K and λ_{ex} = 450 nm. The lower spectrum was taken at 298 K. The band at 520 nm is due to solvent Raman.

Discussion

Preparations. The compounds were prepared by reacting copper(II) acetate with the ligand, Diphen, in methanol and precipitating the generated cation by addition of $NaClO_4$. The product, $[Cu(Diphen)(H_2O)](ClO_4)_2$, was then dissolved in acetonitrile and reduced to the copper(I) complex, $[Cu(Diphen)]_2(ClO_4)_2$, by addition of ascorbic acid. The ligand rearrangement that occurs upon reduction gives predominately the copper(I) binuclear complex rather than mononuclear or polynuclear product.

Copper(II) Complex. The copper(II) complex, $[Cu(Diphen)(H_2O)](ClO_4)_2$, crystallized in the $P2_1/c$ space group. The cation had a CuN_4O core in an approximate trigonal bipyramidal environment. The Cu–N axial bond lengths were 1.984 and 1.967 Å, but the Cu–N equatorial bond lengths were longer, 2.094 and 2.089 Å. The equatorial Cu–O bond length was the longest, 2.198 Å. There are a number of trigonal bipyramidal copper(II) complexes reported in the literature[32-35,37-39] but none with a copper(II)–water bond. The closest comparisons are $[Cu(bpy)_2(NH_3)][BF_4]_2$[38] and $[Cu(bpy)_2Cl]Cl{\cdot}6H_2O$,[39] where bpy is 2,2′-bipyridine. $[Cu(bpy)_2(NH_3)](BF_4)_2$ crystallized in the space group $P2_1/c$. The Cu–N axial bond distances were 1.985 and 1.959 Å; the equatorial Cu–N bond distances were 2.115 and 2.080 Å. The remaining Cu–N(NH_3) equatorial bond distance was 2.048 Å. $[Cu(bpy)_2Cl]Cl{\cdot}6H_2O$ crystallized in the space group *Pnan*. The axial Cu–N bond distances were 1.97 and 2.00 Å. The equatorial Cu–N distances were longer, 2.09 and 2.08 Å. The Cu–Cl equatorial bond distance was 2.36 Å. The structures all show shorter Cu–N axial bond distances than those in the equatorial positions. The remaining Cu–L bond distances (L = H_2O, Cl^-, NH_3) are not equal to the equatorial Cu–N bond distances. Thus, the complexes cannot be described as rigorously trigonal bipyramidal but more closely resemble a distorted square pyramid.

The structure of $[Cu(Diphen)(H_2O)]^{2+}$ can be contrasted to the one recently reported for $[Cu(OBPY)]^{2+}$,[22] where the OBPY ligand differs from Diphen in the lack of methyl substituents attached to the carbon atoms α to the nitrogen atoms in the

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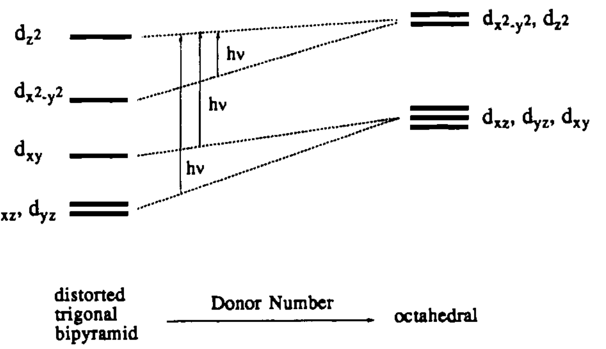

Figure 8. Crystal field model representing the conversion from a "distorted" trigonal bipyramidal structure to an octahedral structure for $[Cu(Diphen)(H_2O)]^{2+}$.

heterocyclic ring. Thus, the $[Cu(OBPY)]^{2+}$ cation assumes a distorted square planar geometry with two equivalent Cu–N bond distances of 1.99 and 2.02 Å. The presence of the methyl substituents in Diphen gives rise to steric effects which cause copper(II) to alter its geometry to one closely resembling a trigonal bipyramid.

The d-orbital splittings of copper(II) complexes in a trigonal bipyramidal configuration have been examined by polarized single-crystal studies.[31,36] The dz^2 orbital was assigned as the highest energy d-orbital, but various sequences of one-electron orbitals were proposed, depending on the point group associated with the cation. The sequence that is consistent with the physical properties of $[Cu(Diphen)(H_2O)]^{2+}$ is illustrated in Figure 8. The $g_\parallel$ value of 2.01 is in agreement with assigning the dz^2 orbital as the highest energy d-orbital. The shift to lower redox potential for the Cu(II/I) couple and the shift of the d–d transitions to the red as the donor number of the solvent increased are in agreement with the crystal field changes outlined in Figure 8. The slopes of the lines (E_{dd} vs DN (donor number) in Figure 3 and $E_{1/2}$ vs DN in Figure 4) were negative. Thus, as the solvent interacts more strongly, the energy of the dz^2 orbital is raised causing $E_{1/2}$ to become more negative. The red-shift of the dd-transitions outlined in Figure 3 would be greater for the $(dx^2 - y^2) \rightarrow dz^2$ (lowest energy) and the $dxz,dyz \rightarrow dz^2$ (highest energy) transitions than for the $dxy \rightarrow dz^2$ transition. Figure 8 is in agreement with these observations.

The relationship between absorption and redox processes with donor numbers appears related to outer-sphere effects and not to lability of the water molecule. The complex that crystallized from acetonitrile is the aquo derivative, rather than the acetonitrile species. The redox behavior also is inconsistent with replacement of water by solvent since the ligands with the stronger ligand field strengths would shift the $E_{1/2}$-value more negative than those with weaker ones. Such is not observed in the solvent series investigated.

Copper(I) Complex. $[Cu(Diphen)]_2^{2+}$ has the double-helicate structure observed for $[Cu(Dibpy)]_2^{2+}$ (**3**), where Dibpy is 1,2-bis(6′-methyl-2,2′-bipyridin-6-yl)ethane, and other complexes that contain bpy units linked by CH_2OCCH_2 bridges.[23] The Cu–N distances in these complexes are similar, 2.03 Å. Some subtle differences in the solid-state structures of dicopper complex **3** with the ethane-bridged bpy units and **2** with the ethane-bridged phen units appear to be due to the greater flexibility of the bpy subunits. In **3** each ligand contains a bipyridine subunit that is twisted about the ring junction by an average of 17°. Because of the rigidity of the phen units, such distortion from planarity is not possible; thus, unlike **3**, **2** has a molecular C_2 axis that corresponds to the crystallographic 2-fold axis.

Photophysics. The emission observed for $[Cu(Diphen)]_2^{2+}$ at 77 K is fairly typical for copper(I) polypyridyl complexes.[15f] The broad, featureless emission is readily assigned to a ^{3}MLCT state by comparison to that reported for other $[Cu(N\text{-}N)_2]^+$ species, such as the case when N-N = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, 4,4′,6,6′-tetramethyl-2,2′-bipyridine, and 2,9-dimethyl-1,10-phenanthroline (dmp).[15] At room temperature, however, $[Cu(Diphen)]_2^{2+}$ is emission silent. This is in sharp contrast to the other $[Cu(N\text{-}N)_2]^+$ complexes, such as $[Cu(dmp)_2]^+$,[15] which shows an increase in emission intensity with increasing temperature. Even in solvents with low dielectric constants, such as CH_2Cl_2, no ambient emission was observed. This loss of emission may be due to enhanced spin–orbit coupling facilitated nonradiative relaxation (heavy-atom effect) since numerous examples exist where diminished luminescence has been observed for bimetallic complexes compared to monometallic analogoues.[36] Alternatively, it is possible that ligand rearrangement is responsible for the facile room-temperature relaxation. Upon excitation, the metastable ^{3}MLCT state is formally Cu(II) and is coordinatively unsaturated. Intra- and interligand repulsion within the Cu dimer may result in large amplitude distortions that mix the ground and excited states. Another possibility is exiplex quenching from the ion pair state previously observed by Everly and McMillin in $[Cu(N\text{-}N)_2]^+$ systems.[42] We are currently investigating the nature of the relaxation coordinate and the nature of the complex ligand rearrangements that accompany monomer $\rightleftarrows$ dimer (Cu(I) $\rightleftarrows$ Cu(II)) interconversion.[43]

Copper(II) and Copper(I) Redox Behavior. Perhaps the most interesting property exhibited by $[Cu(Diphen)(H_2O)]^{2+}$ and $[Cu(Diphen)]_2^{2+}$ is their redox behavior. The complexes exhibit different Cu(II/I) redox potentials but appear to undergo a monomer–dimer interconversion process that can be controlled by the oxidation state of the metal. A similar process was noted for $[Cu(pQP)]_2^{2+}$,[31] where pQP is 5,5′,3″,5‴-tetramethyl-2,2′:6′,2″:6″,2‴-quaterpyridine. For $[Cu(pQP)]_2^{2+}$, controlled oxidation led to a Cu(I)–Cu(II) mixed-valence species. In contrast, $[Cu(Diphen)]_2^{2+}$ did not undergo stepwise oxidation. Rather it was converted from Cu(I)–Cu(I) to Cu(II)–Cu(II) in two closely spaced one-electron transfer processes.

Apparently, the presence of the sterically hindering methyl groups next to the nitrogen donor atoms of the ethane bridged bpy and phen derivatives triggers the monomer–dimer equilibrium process. The copper(II) and copper(I) complexes containing the OBPY ligand where the methyl groups are absent exhibited only one redox couple.[22] Currently, we are examining the kinetics of the monomer–dimer interconversion for $[Cu(Diphen)(H_2O)]^{2+} \leftrightarrow [Cu(Diphen)]_2^{2+}$. We anticipate trapping copper(II) and copper(I) intermediates in unusual coordination environments.

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Supplementary Material Available: Tables giving crystal data and details of the structure determinations, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (8 pages). Ordering information is given on any current masthead page.

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