donation from the Schiff base ligand and a higher energy d_{z^2} orbital. More electron transfer and a lower ν_{O-O} is expected for the Schiff base. The electron-withdrawing acetyl groups result in less electron density being placed on the cobalt; a weaker metal–O_2 adduct is predicted to form, and a higher O–O stretching frequency would result.

The largest differences in ν_{O-O} are observed when one compares the O_2 adducts of the free four-coordinate cobalt complex with those of the five-coordinate complexes. In solution, O_2 adducts of the four-coordinate complexes do not form at room temperature. In the Co(J-en) series,[32b] for Co(J-en)·O_2 in a matrix occurs at 1260 cm^{-1} while that for the pyridine adduct occurs at 1143 cm^{-1}. The ν_{O-O} for Co(TPP)·O_2 occurs at 1278 cm^{-1} and the pyridine adduct has a ν_{O-O} value of 1144 cm^{-1}. A significant fact has been overlooked[32] in the interpretation of these results. The ground state for many square-planar cobalt(II) complexes has the unpaired electron in the d_{xz}, d_{yz} set. Spin pairing of this electron with the π-antibonding electrons of O_2 results in a weaker interaction since the four-coordinate complexes do not readily form O_2 adducts in solution. Alternatively, if promotion of the electron to a largely d_{z^2} orbital is required for spin pairing, this energy must come from the Co–O_2 bond for there is no axial base to provide this energy. A higher O–O stretch is expected to accompany the weaker binding of O_2 to many four-coordinate Schiff base complexes.

Clearly, the spin-pairing model provides a valuable tool for correlating a wide variety of results on O_2 binding. If the formal positive charge on the metal is reduced, stronger O_2 binding, more electron transfer into O_2, and a lower O–O stretch result in a fashion readily understood by qualitative molecular orbital arguments.

Registry No. 1-MeIm, 616-47-7; py, 110-86-1; THTP, 110-01-0; H$_2$-4,6-CH$_3$Osal-4-CF$_3$oph, 107960-11-2; Co(4,6-CH$_3$Osal-4-CF$_3$oph), 106904-68-1; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·pip·O$_2$, 108007-43-8; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·1-MeIm·O$_2$, 108007-44-9; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·py·O$_2$, 108007-45-0; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·THTP·O$_2$, 108007-46-1; Me$_2$SO, 67-68-5; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·1-MeIm, 108007-42-7; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·py, 107985-21-7; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·THTP, 107985-22-8; O$_2$, 7782-44-7; Co(4,6-CH$_3$Osal-4-CF$_3$oph)·Me$_2$SO, 107985-23-9; 3,4-diaminobenzotrifluoride, 368-71-8; 4,6-dimethoxysalicylaldehyde, 708-76-9; 4-amino-3-nitro-benzotrifluoride, 400-98-6.

Supplementary Material Available: Tables of data pertaining to the physical measurements involved in this work including magnetic susceptibility data (Table A1), ^{19}F NMR data (Tables A2 and A3), UV–vis spectrophotometric data (Tables A4–A6), and spectrophotometric titration data (Tables A7–A9) (10 pages). Ordering information is given on any current masthead page.

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Absorption, Emission, and Photophysical Properties of Copper(I) Pyrazole Complexes and Their Carbonyl Adducts

Thomas N. Sorrell*[1] and A. S. Borovik

This work examines the electronic and photophysical properties of copper(I) pyrazole complexes. All two-, three-, and four-coordinate copper(I) pyrazole complexes investigated have strong MLCT electronic transitions in the UV region, and these transitions are affected by the ligand environment around the metal ion. Excitation at 77 K into the MLCT transitions produces visible emissions that are from ^{3}d-π^* excited states. Copper(I) pyrazole complexes with a phenolate donor have lower energy MLCT absorption and emission transitions relative to those of Cu(N)$_x^+$ complexes. The binding of carbon monoxide to the three-coordinate and phenolate complexes shifts the electronic transitions to higher energy while the emission (from a ^{3}d-π^* excited state) is found at lower energy. This has been explained by proposing that the Cu(I)–CO complexes have a low-energy electronic transition that is so weak it cannot be clearly resolved in the absorption spectrum. The intense absorption transitions resulting from the aromatic amino acid side chains will severely limit the possibility of observing MLCT transitions for most copper(I) proteins; nevertheless, such transitions are present and this work suggests that they may be useful for probing the metal ion site properties in those proteins. This is illustrated in comparing the present results with the spectroscopic properties of carbonylhemocyanin (HcCO).

The importance of copper(I) centers at the active sites of a number of proteins is well documented,[2] but investigations of those sites have been hindered because the d^{10} Cu(I) ion is invisible to many spectroscopic methods used to study metalloproteins. Excited-state properties associated with the metal ion may provide a way to circumvent the problem, since at least three copper proteins display luminescent emission when irradiated at around 300 nm: hemocyanin,[3] tyrosinase,[4] and metallothionein (MT).[5]

Corequisite with investigating the spectroscopic properties of copper(I) sites in proteins is the need to study the analogous properties in well-defined synthetic copper(I) complexes. Although such complexes exhibit no ligand field transitions that are usually found in the visible spectra of transition-metal complexes, there are a large number of systems with intensely absorbing Cu(I) chromophores. Recent studies have revealed many aspects of copper(I) photochemistry and photophysics, which include emission from intraligand or metal-to-ligand charge-transfer excited states,[6,7] dual emission occurring from two distinct excited

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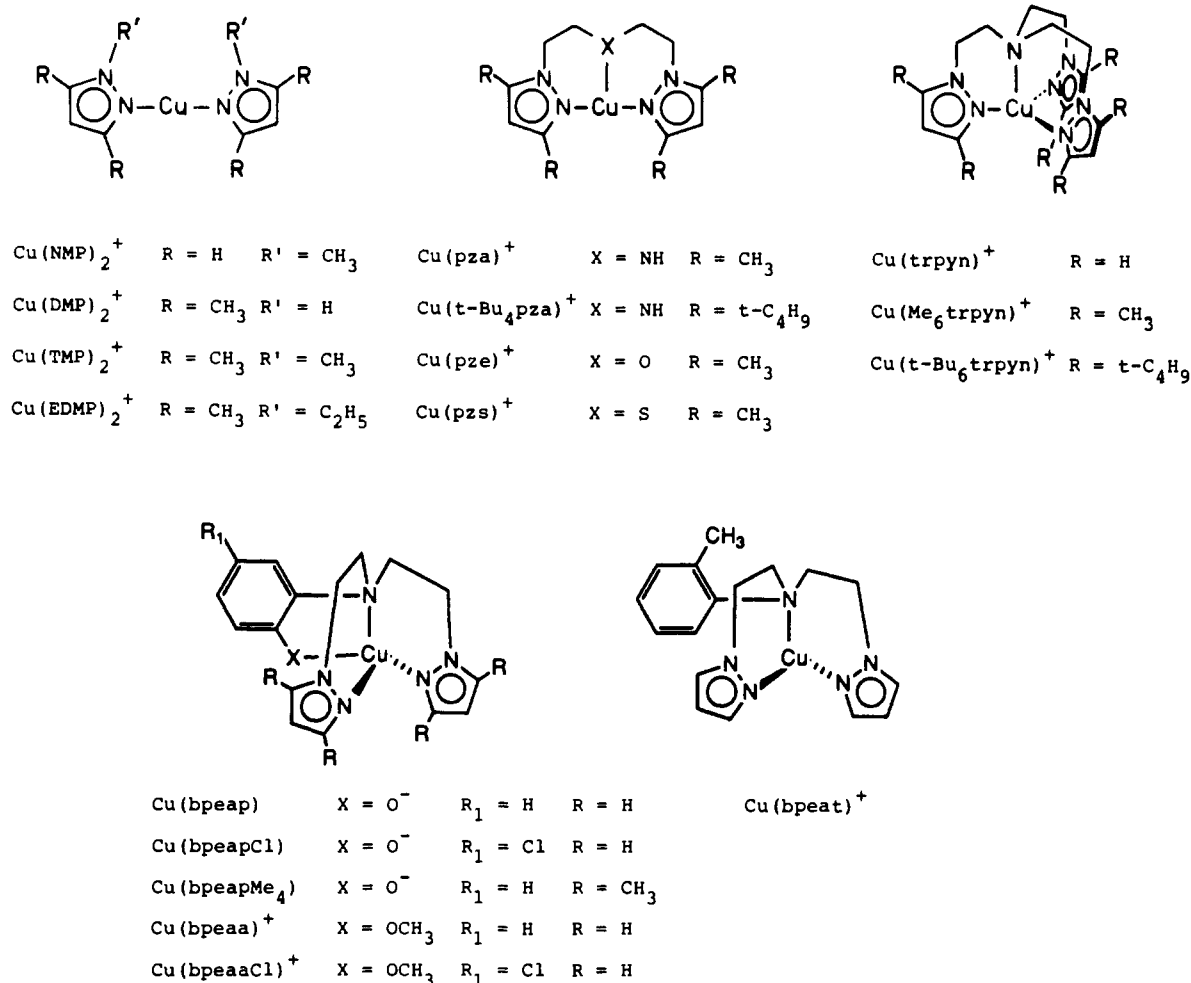
Figure 1. Structure and abbreviations for copper(I) complexes. For ionic complexes, the anion is BF_4^-.

states within one copper(I) complex,[8,9] production of hydrated electrons,[10,11] and photoassisted transformation of organic molecules.[12,13]

This paper reports the spectroscopic properties for a series of copper(I) complexes with various ligand sets (Figure 1). The aim of this work is to understand the origins of observed electronic and photophysical transitions and to determine how changes in the coordination environment around the copper(I) ion affect these transitions.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. The following solvents were distilled and stored under nitrogen: tetrahydrofuran (THF), from sodium–benzophenone ketyl under argon; methanol, from $Mg(OCH_3)_2$ under nitrogen; hexane, from CaH_2 under nitrogen. The 3,5-di-*tert*-butylpyrazole and two-, three-, and four-coordinate copper(I) complexes were synthesized as previously described.[14-17] The phenolate– and an-

isole–copper(I) complexes were synthesized by the literature methods.[18,19] Microanalysis were performed by MicAnal Laboratory, Inc., Tucson, AZ.

^{1}H NMR spectra were recorded on an IBM 200-MHz instrument with $CDCl_3$ as the solvent. All chemical shifts are reported in parts per million (ppm) relative to an internal standard of Me_4Si.

Bis[2-(3,5-di-*tert*-butyl-1-pyrazolyl)ethyl]amine. Under a nitrogen atmosphere, 5.25 g (29 mmol) of 3,5-di-*tert*-butylpyrazole was added dropwise to 1.75 g (73 mmol) of sodium hydride in 125 mL of DMF. After 2 h of heating at 50°C, a solution of 2.55 g (14 mmol) of bis(2-chloroethyl)amine hydrochloride in 25 mL of DMF was added to the sodium 3,5-di-*tert*-butyl-1-pyrazolate solution. Forty-eight hours later, the reaction was quenched with 10 mL of H_2O. Volatiles were removed under reduced pressure, and 50 mL of H_2O was added to the residue. The product was extracted with three 30-mL portions of methylene chloride. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated. Flash chromatography with ethyl acetate as the eluent afforded a yellow oil of pure product. ^{1}H NMR: δ 1.27 (9 H, s), 1.33 (9 H, s), 3.08 (4 H, t, $J = 10$ Hz), 4.23 (4 H, t, $J = 10$ Hz), 5.80 (2 H, s).

[Bis[2-(3,5-di-*tert*-butyl-1-pyrazolyl)ethyl]amine]copper(I) Tetrafluoroborate. This compound was prepared by the method described in ref 16. The complex was crystallized by slow diffusion of hexane into a THF solution of the complex under an inert atmosphere. Anal. Calcd for $C_{26}H_{47}BCuF_4N_5$: C, 53.84; H, 8.17; N, 12.07. Found: C, 53.39; H, 8.05; N, 12.19.

[Tris[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine]silver(I) Tetrafluoroborate. This compound was prepared by the method described in ref 17 using $AgBF_4$ as the silver(I) precursor. The complex was crystallized by slow diffusion of THF into a methanolic solution of the complex under an inert atmosphere. Anal. Calcd for $C_{21}H_{33}BAgF_4N_7$: C, 43.54; H,

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5.75; N, 16.92. Found: C, 43.66; H, 5.89; N, 17.24.

[Bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine]silver(I) Tetrafluoroborate. This compound was prepared by the method described in ref 16 and crystallized in the dark by slow diffusion of THF into a methanolic solution of the complex under an inert atmosphere. Anal. Calcd for $C_{14}H_{22}AgBF_4N_5$: C, 36.95; H, 4.87; N, 15.39. Found: C, 35.98; H, 4.89; N, 14.52.

Bis(1-methylpyrazole)silver(I) Tetrafluoroborate. This compound was prepared by the method described in ref 15 and crystallized in the dark by slow diffusion of THF into a methanolic solution of the complex under an inert atmosphere. Anal. Calcd for $C_8H_{12}AgBF_4N_4$: C, 26.77; H, 3.03; N, 15.60. Found: C, 26.82; H, 3.08; N, 15.73.

Spectroscopic Studies. For lifetime, emission, quantum yields, and absorption experiments, high-purity methanol and THF (without stabilizers), from Burdick-Jackson Laboratories, and absolute ethanol were used. The alcohols were further purified by distillation under nitrogen from their respective magnesium alkoxides and stored under nitrogen. THF was used without further purification and was stored under nitrogen. All samples were prepared under an inert atmosphere (<1 ppm of oxygen and H_2O) unless noted otherwise. Carbon monoxide was purified by successive passage of the gas through an acidic chromium(II) solution, concentrated H_2SO_4, NaOH pellets, and Drierite.

Absorption Measurements. Absorption spectra for all complexes were obtained in methanol by using a Hewlett-Packard 8540A diode array spectrophotometer. A 0.005 cm path length Suprasil cell was used to minimize absorption by the solvent. Carbon monoxide was added to the atmosphere above the samples by slow passage of the gas through a syringe needle for 5–10 min. Infrared spectra were obtained by using a NaCl cell with a path length of 0.1 mm on a Nicolet DX-20 FTIR spectrometer.

Emission Studies. Emission spectra were obtained on a SLM 8000 photon-counting spectrofluorimeter and were corrected for detector sensitivity with use of data and programs supplied by the manufacturer. Low-temperature (77 K) emission spectra of the complexes in absolute ethanol or 1:4 methanol:ethanol glasses were obtained by using a cylindrical quartz tip flask. Samples were prepared in quartz tubes that were sealed under nitrogen. All room-temperature emission spectra were taken of THF solutions unless otherwise noted. Excitation spectra were corrected for lamp intensity deviations ratiometrically with a concentrated solution of Rhodamine 6G as the standard. The standard was housed in a triangular Suprasil cell to prevent self-absorption.

Lifetimes. Emission lifetimes were determined by laser flash photolysis with the defocused 266-nm output (fourth harmonic) of a pulsed Quanta-Ray Nd:YAG laser as the excitation source (pulse width ca. 4 ns). Emission intensity, as a function of time following excitation, was monitored at right angles to the excitation pulse with an EMI Genocem Model RFI/S housing attached to a Bausch & Lomb 33-86-02 monochromator. The current output from the photomultiplier was dropped across a 50-Ω resistor. The voltage vs. time signal was acquired with a Tektronix 7623A oscilloscope, and the waveform was photographed by a Polaroid camera. The data used for lifetimes were the average result of approximately 200 decay traces. The average decay traces were digitized on a Commodore 8032 computer using a Hewlett-Packard (09872-60066) fiber optic digitizer. Lifetimes were obtained by least-squares analyses of the first-order decay plots of ln I vs. time (I = intensity).

Samples for lifetime measurements were prepared and sealed under a nitrogen atmosphere as described above for the emission spectra. No observable differences in the lifetimes were found when freeze–pump–thaw-degassed samples were used.

Radiative Quantum Yields. Radiative quantum yields were obtained in freeze–pump–thaw-degassed THF solutions at 25 ± 1 °C by the method outlined by Demas and Crosby.[20] Quinine sulfate in 1 N H_2SO_4 (φ = 0.546 at 25 °C) was used as the standard with excitation for all samples occurring at 254 nm.[20] The corrected emission spectra were integrated by using numerical integration. Corrections were made for the differing refractive indices of the solvents by using the relationship

$$\varphi_{rad} = \varphi_r^{obsd}(n^2/n_{H_2SO_4}^2) \qquad (1)$$

where φ_r^{obsd} is the uncorrected quantum yield, n is the refractive index of THF, and $n_{H_2SO_4}$ is the refractive index of H_2SO_4.

Results and Discussion

Absorption Studies for $Cu(N)_x^+$ (x = 2, 3, 4). Representative spectra for the series $Cu(N)_2^+$, $Cu(N)_3^+$, and $Cu(N)_4^+$ are shown in Figure 2, and complete data for several copper(I) pyrazole complexes are summarized in Table I. The spectra for all of these
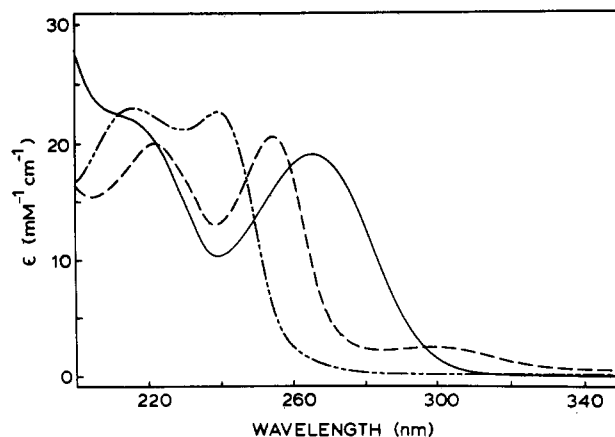
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Figure 2. Absorption spectra of $Cu(Me_6trpyn)^+$ (—), $Cu(pza)^+$ (– –), and $Cu(EDMP)^+$ (– - – -) in methanol solution at room temperature.

Table I. Absorption Data for the $Cu(N)_x^+$ Complexes and Ligands[a]

complex	λ_{max}^b (ϵ^c)	ligand	λ_{max}^b (ϵ^c)
	Two-Coordinate		
$Cu(DMP)_2^+$	209 (20.8)	DMP	214 (6.4)
	234 (24.8)		
$Cu(TMP)_2^+$	215 (23.5)	TMP	220 (7.8)
	239 (23.1)		
$Cu(EDMP)_2^+$	215 (23.4)	EDMP	220 (7.7)
	239 (23.0)		
$Ag(NMP)_2^+$	217 (13.4)	NMP	216 (6.5)
	Three-Coordinate		
$Cu(pza)^+$	222 (20.0)	pza	220 (13.2)
	231 (sh)		
	254 (20.6)		
	298 (2.61)		
$Cu(t\text{-}Bu_4pza)^+$	222 (23.0)	$t\text{-}Bu_4pza$	221 (18.0)
	242 (21.2)		
	303 (3.4)		
$Cu(pze)^+$	220 (20.5)	pze	220 (16.1)
	231 (20.0)		
	246 (21.8)		
$Cu(pzs)^+$	217 (20.9)	pzs	220 (15.5)
	236 (18.6)		
$Ag(pza)^+$	220 (16.5)		
	Four-Coordinate		
$Cu(trpyn)^+$	215 (17.2)	trpyn	216 (19.8)
	261 (16.5)		
$Cu(Me_6trpyn)^+$	218 (21.4)	Me_6trpyn	220 (25.1)
	265 (19.1)		
$Cu(t\text{-}Bu_6trpyn)^+$	223 (27.6)	$t\text{-}Bu_6trpyn$	221 (27.2)
	248 (16.4)		
$Ag(Me_6trpyn)^+$	217 (34.3)		

[a] In methanol. [b] nm. [c] mM^{-1} cm^{-1}; sh = shoulder.

complexes are characterized by intense absorptions in the UV region of the spectrum. The highest energy absorption bands are due to the $\pi \rightarrow \pi^*$ transitions associated with the pyrazole ligands. The lower energy bands, which are not present for the free ligands or Cu(I) precursor, are assigned as Cu(I)-to-pyrazole charge-transfer transitions (vide infra).

The spectra in Figure 2 were obtained on complexes that constitute the series having $(N)_2$, $(N)_3$, and $(N)_4$ donor sets in which at least two of the donors are trisubstituted pyrazoles. The results show that changes in the coordination environment have pronounced effects on the energy of the MLCT transitions. The observed decrease in energy for the $d\pi \rightarrow \pi^*$ transition (vide infra) in going from two- to four-coordination is most likely caused by an increase in the ligand field splitting associated with the copper(I) ion. In the two-coordinate complexes a broad, asymmetric peak is seen at approximately 240 nm, which corresponds to both the $d\sigma^* \rightarrow \pi^*$ and $d\pi \rightarrow \pi^*$ transitions.

The three-coordinate copper(I) pyrazole complexes exhibit intense absorption bands between 240 and 255 nm, which we
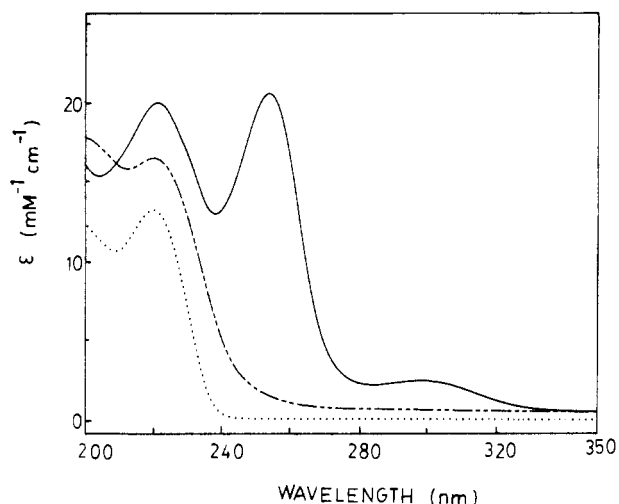
Figure 3. Absorption spectra of Ag(pza)$^+$ (— — —), Cu(pza)$^+$ (—), and pza (···) in methanol solution at room temperature.

assign as the $d\pi \rightarrow \pi^*$ transitions. Also found for these complexes are lower energy bands, which are the $d\sigma^* \rightarrow \pi^*$ transitions; for Cu(pza)$^+$ the latter appear as weak bands centered at 305 nm. The existence of well-defined but weak absorption bands for the $d\sigma^* \rightarrow \pi^*$ transitions in the three-coordinate complexes is due, in part, to the planar geometry of these complexes. In this geometry there will be substantial splitting between the $d\sigma^*$ and $d\pi$ orbitals of the copper(I) ion relative to that found for the two- and four-coordinate compounds. This allows the two types of transitions to be resolved. The small overlap between the $d\sigma^*$ orbitals of the copper ion and the π orbitals of the pyrazole rings accounts for the weak intensity of these low-energy absorption bands.

The four-coordinate copper(I) complexes have a broad, intense absorption peak that comprises both the $d\pi \rightarrow \pi^*$ and $d\sigma^* \rightarrow \pi^*$ transitions. These are at significantly higher energy than the reported MLCT transitions for the related copper(I) polypyridyl complexes.[21] The difference in energies of the MLCT transitions in these four-coordinate copper(I) complexes is related to the fact that the π^* orbitals of pyrazole are at higher energies relative to those of 2,2'-bipyridine and 1,10-phenanthroline.

To corroborate the assignment of the MLCT character of the absorption transitions in these copper(I) pyrazole complexes, the silver(I) analogue of each type of complex was synthesized. The reasons for making the silver(I) complexes are twofold: (1) Ag(I) and Cu(I) ions have similar coordination chemistries, which allows the synthesis of analogous two-, three-, and four-coordinate complexes;[22] (2) silver(I) ions are harder to oxidize than copper(I) ions; hence, the MLCT transitions should be shifted to higher energy for the case of Ag(I). Figure 3 compares the absorption spectra for Cu(pza)$^+$, Ag(pza)$^+$, and the free ligand; and the results for the remaining silver(I) complexes are found in Table I. In all cases the MLCT transitions shift to higher energy as expected.

Absorption Studies for Cu(N₃X) (X = ArO⁻, ArOCH₃, Ar). These complexes were synthesized in order to investigate systematically the effect of a bound phenolate on the MLCT transitions of copper(I) complexes. The results for this series of complexes are found in Table II. Figure 4 shows the absorption spectra for the complexes Cu(bpeap), Cu(bpeaa)$^+$, and Cu-(bpeat)$^+$. There are a number of similarities between the absorption properties of these complexes and those of the Cu(N)$_x$$^+$ type. Cu(bpeap) has an intense band at 244 nm and a broad shoulder at 300 nm, which corresponds to the Cu(I) $\rightarrow$ pyrazole MLCT transitions. The effect of binding a phenolate ion is seen in the broadening toward lower energy of the absorption band at

Table II. Absorption Data for the Cu(N₃X) Complexes and Ligands[a]

complex	λ_{max}[b] (ϵ^c)	ligand	λ_{max}[b] (ϵ^c)
Cu(bpeap)	244 (14.1)	Hbpeap	212 (26.9)
	300 (sh)		281 (3.68)
Cu(bpeapCl)	253 (20.2)	HbpeapCl	217 (28.0)
	282 (sh)		258 (sh)
	315 (sh)		293 (3.8)
Cu(bpeapMe₄)	243 (16.2)	HbpeapMe₄	213 (29.5)
	293 (sh)		254 (sh)
			282 (3.6)
Cu(bpeaa)$^+$	212 (26.0)	bpeaa	213 (37.0)
	246 (15.8)		254 (8.82)
	275 (sh)		286 (sh)
Cu(bpeaaCl)$^+$	217 (28.2)	bpeaaCl	219 (34.7)
	246 (16.8)		259 (8.0)
	283 (sh)		295 (4.3)
Cu(bpeat)$^+$	208 (33.7)	bpeat	208 (14.6)
	240 (18.0)		246 (3.2)
	274 (sh)		

[a]In methanol. [b]nm. [c]mM^{-1} cm^{-1}; sh = shoulder.

Table III. Photophysical Data for the Cu(N)₄$^+$ Complexes at Room Temperature[a]

complex	λ_{em},[b] nm	λ_{ex},[c] nm	τ, 10^{-6} s	φ
Cu(*t*-Bu₆trpyn)$^+$	482	250	5.0	0.068
Cu(Me₆trpyn)$^+$	473	268	5.2	0.023

[a]In THF. [b]Emission. [c]Excitation.

Figure 4. Absorption spectra of Cu(bpeap) (—), Cu(bpeaa)$^+$ (—·—), and Cu(bpeat)$^+$ (— — —) in methanol solution at room temperature.

300 nm (the broadness on the high-energy side of the band is a result of ligand-localized transitions of the phenolate moiety). The low-energy broadening is expected since phenolate has better σ-donating ability than pyrazole, which will destabilize the $d\sigma^*$ orbitals of the copper(I) ion and lower the energy of the corresponding MLCT transitions.

While there are intense, higher energy MLCT absorption transitions for Cu(bpeaa)$^+$ and Cu(bpeat)$^+$, the low-energy MLCT transitions that are found for the copper(I) phenolate complexes are not resolved. For Cu(bpeaa)$^+$ the ligand-localized transitions occur at lower energy than the MLCT transitions. The shoulder at 275 nm in the absorption spectrum of Cu(bpeaa)$^+$ is from intraligand transitions that are associated with the methoxyaryl moiety (see Table II).

Emission Studies in Fluid Solution. No emission is observed for any of the Cu(I) complexes in protic solvents such as methanol. The complexes in the Cu(N)$_x$$^+$ series did have observable emission signals in THF.[23] Table III summarizes the photophysical results
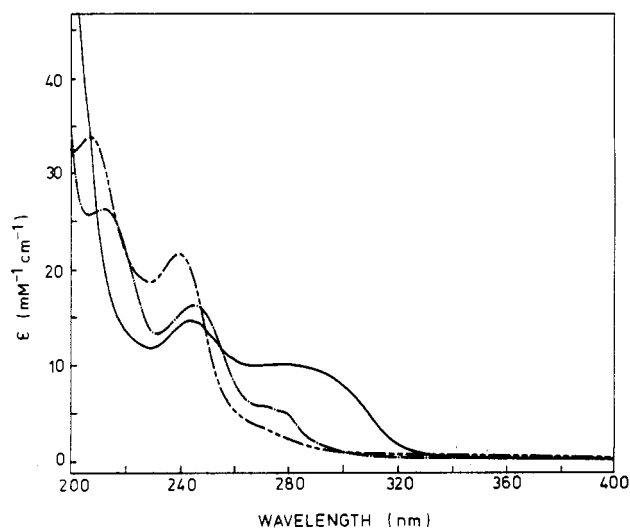
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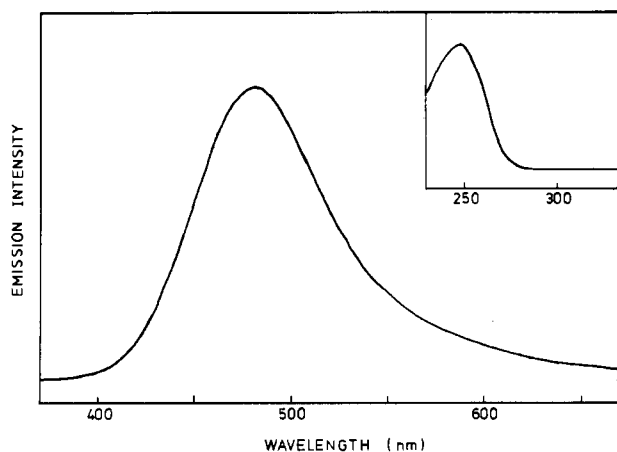
Figure 5. Corrected emission spectrum of Cu(t-Bu$_6$trpyn)$^+$ in a THF solution at room temperature with excitation between 280 and 310 nm. The insert is the corrected excitation spectrum.

Table IV. Photophysical Data for the Cu(N)$_x^+$ Complexes at 77 K[a]

complex	λ_{em},[b] nm	λ_{ex},[c] nm	τ, 10^{-6} s
Two-Coordinate			
Cu(TMP)$_2^+$	420	248	268
Cu(EDMP)$_2^+$	430	248	470
Cu(DMP)$_2^+$	430	239	441
		270 (sh)	
Three-Coordinate			
Cu(pza)$^+$	463	263	113
		310 (sh)	
Cu(t-Bu$_4$pza)$^+$	442	247	133
		313	
Cu(pze)$^+$	440	250	186
Cu(pzs)$^+$	415	250	264
Four-Coordinate			
Cu(trpyn)$^+$	453	268	81.3
Cu(Me$_6$trpyn)$^+$	450	273	125
Cu(t-Bu$_6$trpyn)$^+$	433	255	247

[a] In an ethanol glass. [b] Emission. [c] Excitation; sh = shoulder.

for the four-coordinate Cu(I) complexes in this series. The corrected emission and excitation spectra for Cu(t-Bu$_6$trpyn)$^+$ are shown in Figure 5. Both Cu(t-Bu$_6$trpyn)$^+$ and Cu(Me$_6$trpyn)$^+$ have broad unstructured emission spectra, with corresponding excitation spectra matching their room-temperature absorption spectra.[24] The long lifetime associated with the emission suggests that the excited state from which the radiative process originates is predominantly triplet in character (vide infra).

The photophysical results for these four-coordinate Cu(I) complexes are substantially different from those found by McMillin for related Cu(I) complexes.[25] In comparison to those for the four-coordinate copper(I) polypyridyl complexes, the excited-state lifetimes and radiative quantum yields for Cu(t-Bu$_6$trpyn)$^+$ and Cu(Me$_6$trpyn)$^+$ are larger.[26] The major reason for these differences is the shielding effect that the tripodal ligands create around the Cu(I) center.[27] The six *tert*-butyl substituents

Figure 6. Corrected emission spectra of (A) Cu(Me$_6$trpyn)$^+$, (B) Cu(pza)$^+$, and (C) Cu(EDMP)$^+$ in an ethanol glass at 77 K with excitation between 280 and 310 nm. The inserts are the corrected excitation spectra.

attached to the t-Bu$_6$trpyn ligand form a protective pocket around the copper(I) ion, which prevents metal ion–solvent interactions. The same effect occurs in Cu(Me$_6$trpyn)$^+$ but to a lesser extent as reflected in its lower radiative quantum yield (vide infra).

Emission Studies of the Cu(N)$_x^+$ Systems in a Rigid Environment. Figure 6 shows the corrected emission and excitation spectra at 77 K for Cu(Me$_6$trpyn)$^+$, Cu(pza)$^+$, and Cu(EDMP)$^+$; and

(23) All of the complexes in the series Cu(N)$_x^+$ luminesce in THF at room temperature. The emission energies for the two- and three-coordinate Cu(I) complexes are strongly Stokes shifted, concentration dependent, and weak (φ >0.0001). These results suggest that these coordinatively unsaturated Cu(I) complexes are binding other ligands during the radiative process (they are either binding solvent molecules or are forming polymeric species). Hence, the exact nature of the species that is causing the emission is unknown. The four-coordinate complexes also had emission in methylene chloride but were unstable upon exposure to UV light.

(24) No photophysical data were obtained for Cu(trypn)$^+$.

(25) McMillin, D. R.; Kirchoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83.

(26) For Cu(dmp)$^+$ (where dmp is 2,9-dimethyl-1,10-phenanthroline): λ_{em} = 670 nm; φ_{rad} = 0.00015; τ = 90 ns (Del Paggio, A. A.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 691).
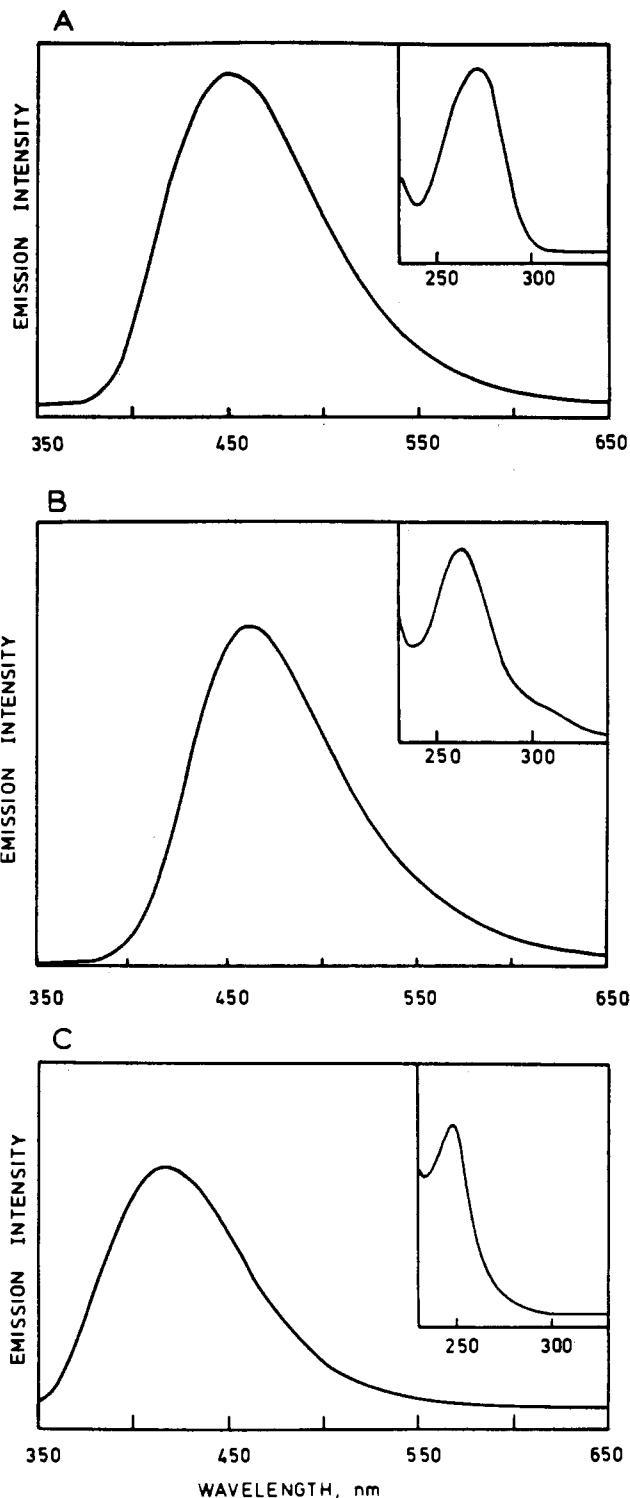
(27) One reviewer pointed out that the energy gap law also favors the pyrazole systems. See: Caspar, J. V.; Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 630.

Table IV contains the photophysical results for all remaining complexes that have been examined. All three types of complexes (two-, three-, and four-coordinate) exhibit broad, structureless emission signals with lifetimes in the microsecond range. The bands present in the excitation spectra are similar to, but not identical with, the MLCT transitions found in the room-temperature absorption spectra. For the series $Cu(N)_2^+$, $Cu(N)_3^+$, and $Cu(N)_4^+$, the results show that changes in the coordination number also have an effect on the energy of emission. The emission energy for the complexes decreases in the order two- > four- > three-coordinate, which is expected from the absorption and excitation spectra. Recall that $Cu(pza)^+$ has the lowest energy MLCT transitions in this series.

While the excitation processes in these complexes clearly involve metal-to-ligand charge-transfer excited states, the assignment of the excited state(s) from which the emission originates is not so straightforward. The basic types of electronic transitions that can produce excited states for copper(I) complexes are ligand-centered, metal-centered, and metal-to-ligand charge-transfer transitions.[7] For these complexes it is unlikely that the emission is a ligand-centered process. Such emissions from transition-metal complexes are generally shifted only slightly to lower energy (<1000 cm^{-1}) compared to the emission from the uncoordinated ligand.[28-30] The emissions for all copper(I) complexes reported here are substantially shifted to lower energy (>6500 cm^{-1}) compared to those of the free pyrazole ligands.[31]

Neither is it likely that the emission observed for the copper(I) complexes originates from metal-centered excited states, although these excited states have recently been proposed to be involved in the emission from other d^{10} metal systems.[32] The emitting species in those systems are believed to be three-coordinate Pd(0), Pt(0), and Ni(0) complexes ligated by phosphines, phosphites, and arsines. The excited states are assigned as metal centered (d-p) on the basis of extended Hückel calculations and the fact that the observed emission energy is invariant on the basis of the ligands bound to the metal ion. For the present two- and three-coordinate complexes, *small changes* in the ligands bound to the Cu(I) ion have a *large effect* on photophysical properties of these complexes (see Table IV). For example, $Cu(pza)^+$ and $Cu(t\text{-}Bu_4pza)^+$ (which differ only by the substituents on the pyrazole rings) have a difference in emission energies that is >1000 cm^{-1}.

The final possibility is that the emission originates from metal-to-ligand charge-transfer excited states. Such excited states have been implicated in the radiative processes from four-coordinate copper(I) polypyridyl complexes.[7,25] For copper(I) complexes, emission from MLCT excited states at 77 K is characterized by broad, structureless transitions with the lifetime of the emitting state in the microsecond range. Emission from charge-transfer states is also sensitive to the ligand environment about the metal ion. The electron acceptor ability of the ligands has an important role in the radiative process since the energy of the excited state depends on the electronic properties of both the metal ion and the ligand. Additionally, in the excited state, the copper ion is formally a Cu(II) (d^9) metal center; hence, significant distortions can occur around the metal ion in the excited state relative to the ground state. The flexibility of the ligands and their ability to shield the metal ion from the solvent environment are important factors that can influence the energy of emission.[33]

(28) Ziolo, F.; Lipton, S.; Dori, Z. *J. Chem. Soc., Chem. Commun.* **1967**, 1124.
(29) Carsten, D. H. W.; Crosby, G. A. *J. Mol. Spectrosc.* **1970**, *34*, 113.
(30) Watts, R. J.; Crosby, G. A.; Sansregret, J. L. *Inorg. Chem.* **1972**, *11*, 1474.
(31) The free pyrazole ligands have excitation bands that were too blue-shifted for the light source of our spectrometer; hence, it was difficult to obtain accurate values for emission and lifetime measurements. The lifetimes are long; therefore, the ligands are phosphorescent.
(32) Caspar, J. V. *J. Am. Chem. Soc.* **1985**, *107*, 6718.
(33) Consistent with this argument is the room-temperature results for the four-coordinate complexes. The emission from these complexes is also assigned as originating from a ^3d-π^* excited state.

Table V. Photophysical Data for the $Cu(N_3X)$ Complexes at 77 K[a]

complex	λ_{em},[b] nm	λ_{ex},[c] nm	τ, 10^{-6} s
Cu(bpeap)	510	252	41.4
		284	
Cu(bpeapCl)	510	254	30.9
		281	
Cu(bpeapMe₄)	475	250	70.5
		282	
Cu(bpeaa)⁺	390	255	
		274 (sh)	
		282	
Cu(bpeaaCl)⁺	395	252	
		285	
		294	
Cu(bpeat)⁺	425	251	71.9
		285 (sh)	

[a] In an ethanol glass. [b] Emission. [c] Excitation; sh = shoulder.

Table VI. Absorption Data for the Copper(I) Carbonyl Complexes[a]

complex	λ_{max}, nm	ϵ[b]	ν_{CO},[c] cm^{-1}
Cu(pza)CO⁺	219	37.9	2089
	281	6.3	
Cu(t-Bu₄pza)CO⁺	222	25.0	2096
	243	sh	
	293	3.7	
Cu(pze)CO⁺	220	23.4	2105
	231	sh	
	246	20.8	
	290	sh	
Cu(pzs)CO⁺	217	23.5	2123
	236	sh	
	281	2.5	
Cu(bpeap)CO	220	sh	2074
	239	sh	
	292	8.9	
Cu(bpeapCl)CO	246	22.4	2077
	309	sh	
Cu(bpeapMe₄)CO	224	36.3	2066
	292	11.3	
Cu(bpeaa)CO⁺	207	36.6	2098
	246	sh	
	275	6.6	
Cu(bpeaaCl)CO⁺	216	39.4	2098
	246	sh	
	286	6.8	
Cu(bpeat)CO⁺	274	sh	2102

[a] In methanol. [b] mM^{-1} cm^{-1}; sh = shoulder. [c] In methylene chloride.

On the basis of the above discussion and the long lifetimes observed for all of the copper(I) complexes, the excited states involved in the radiative process are most plausibly assigned as being predominantly triplet metal-to-ligand charge transfer in character (^3d-π^*). While previous studies have shown that triplet charge-transfer states are important in the emission from the four-coordinate Cu(I) complexes,[7] these are the first examples in which MLCT excited states are involved in emission from two- and three-coordinate copper(I) complexes.

Emission Studies of $Cu(N_3X)$ ($X = ArO^-$, $ArOCH_3$, Ar) in a Rigid Environment. The results of the photophysical studies for this series of complexes are found in Table V. The emission from the copper(I) phenolate complexes occurs at the lowest energies: 475 and 510 nm for Cu(bpeapMe₄) and Cu(bpeap), respectively. As previously determined for the $Cu(N)_x^+$ complexes, the emission from the copper(I) phenolate complexes is most reasonably assigned to a MLCT excited state (copper(I) pyrazole excited state). On the other hand, the copper(I) ether complexes [Cu(bpeaa)⁺ and Cu(bpeaaCl)⁺], have the highest observed emission energy for any copper(I) complex that was studied.[34] The assignment of the radiative excited state is uncertain, but two possibilities include a purely ligand-localized state or some mixture of ligand-centered and MLCT excited states.

(34) The excited-state lifetime for the Cu(I)–ArOCH₃ complexes could not be measured.

Table VII. Photophysical Data for the Copper(I) Carbonyl Complexes at 77 K[a]

complex	λ_{em},[b] nm	λ_{ex},[c] nm	τ, 10^{-6} s
Cu(pza)CO[+]	525	290	45.6
		270	
Cu(t-Bu4pza)CO[+]	513	280	45.3
Cu(pze)CO[+]	483	280	24.0
		255 (sh)	
Cu(pzs)CO[+]	500	279	35.4
		253	
Cu(bpeap)CO	550	289	50.2
Cu(bpeapCl)CO	546	248	54.4
		290	
Cu(bpeapMe4)CO	548	290	38.6
Cu(bpeaa)CO[+]	520	277	52.2
		295 (sh)	
Cu(bpeaaCl)CO[+]	512	245	56.4
		285	
Cu(bpeat)CO[+]	497	250	29.1
		274	

[a] In an ethanol glass. [b] Emission. [c] Excitation; sh = shoulder.
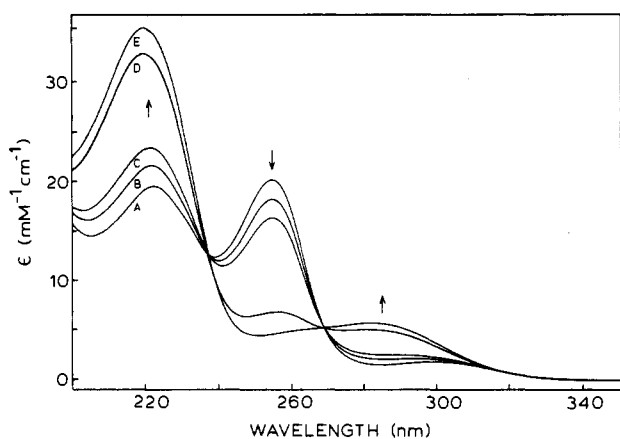

Figure 7. Absorption spectra of Cu(pza)[+] (A) under increasing partial pressures of carbon monoxide (B–E) in methanol solution at room temperature.

Spectroscopic Properties of Copper(I) Carbonyl Complexes.

Tables VI and VII contain the room-temperature absorption measurements and the results of the photophysical studies at 77 K for several copper(I) carbonyl complexes. All three-coordinate complexes as well as tripod complexes with N_3X (but not N_4) donor sets bind CO in solution as determined by observation of a strong band in the infrared spectrum between 2070 and 2150 cm^{-1}, indicative of the terminal carbonyl group. As illustrated in Figure 7 for Cu(pza)[+], the binding of CO has a significant effect on the absorption properties of the three-coordinate complexes. The MLCT transition (d$\pi \rightarrow \pi^*$) at 254 nm is shifted to higher energy where it overlaps with the ligand $\pi \rightarrow \pi^*$ band at 220 nm to yield a single, more intense peak at 217 nm. The lower energy MLCT transition (d$\sigma \rightarrow \pi^*$) is also shifted to higher energy upon the addition of CO (300 vs. 282 nm). Similar results were found for the copper(I) phenolate carbonyls also, as shown for Cu(bpeap)CO in Figure 8.

The corrected emission and excitation spectra for Cu(pza)CO[+] and Cu(bpeap)CO are presented in Figures 9 and 10, respectively. For all of the complexes the emission shifts to *lower energy* and the lifetime of the excited state decreases after the binding of CO.[35] The carbonyl adducts of the copper(I) phenolate complexes have the lowest energy of emission among the Cu(I)–CO species (ca. 550 nm), consistent with the earlier investigation (vide supra). By analogy to the previous luminescence results and the long lifetimes associated with the emission, the radiative process of the Cu(I)–CO complexes is assigned to a triplet, MLCT excited state
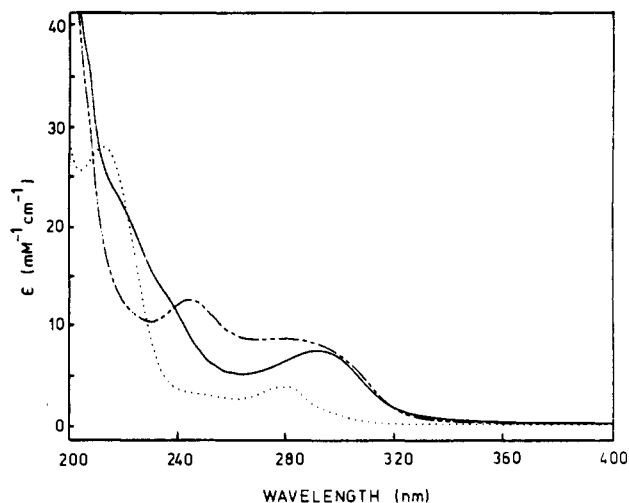
(35) The lifetimes for the copper(I) phenolate carbonyl complexes were slightly longer than for the corresponding copper(I) phenolate complexes.

Figure 8. Absorption spectra of Cu(bpeap) (—), Cu(bpeap)CO (----), and bpeap (···) in methanol solution at room temperature.
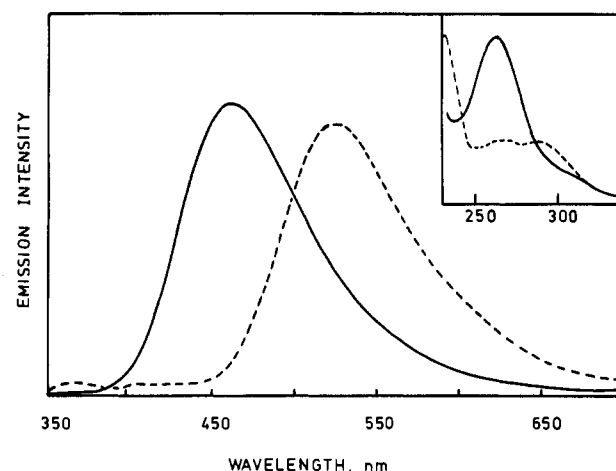

Figure 9. Corrected emission spectra of Cu(pza)[+] (—) and Cu(pza)CO[+] (---) in an ethanol glass at 77 K with excitation between 280 and 310 nm. The insert shows the corresponding corrected excitation spectra.
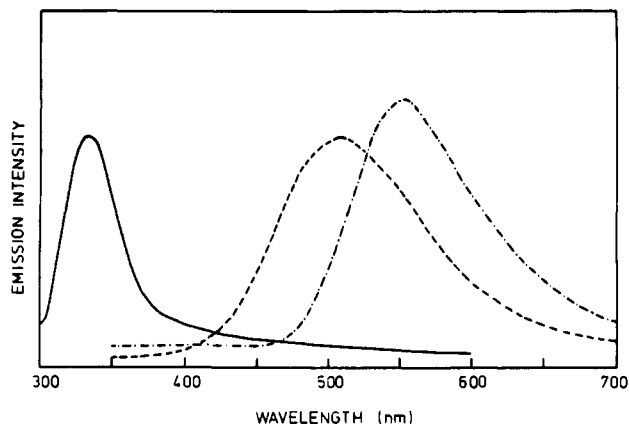

Figure 10. Corrected emission spectra of Cu(bpeap) (---), Cu(bpeap)CO (-·-), and bpeap (—) in an ethanol glass at 77 K with excitation between 280 and 310 nm.

[^{3}d-π^*(pyrazole)]. These complexes are the first to clearly demonstrate that Cu(I)–CO complexes have well-defined photophysical properties.

An unexpected result is that the emission shifts to lower energy upon binding CO while the absorption transitions shift to higher energy. To explain this conflicting evidence, we postulate the existence of a very weak low-energy absorption transition for the carbonyl complexes. In the three-coordinate complexes, the molecules are T-shaped.[16,36] If we assume that their atoms lie

in the xy plane, this leaves the $d_{x^2-y^2}$ orbital (with $d\sigma^*$ character) highest in energy. As CO binds along the z axis, forming a four-coordinate complex, the orientation of the d orbitals of the metal is affected as follows: the π-acid CO will stabilize the $d\pi$ orbitals, causing the observed increase in the corresponding $d\pi \rightarrow \pi^*$ MLCT transitions in the absorption spectrum. The d_{z^2} orbital, which is now involved in σ-bonding, will be raised in energy, making it the highest lying metal d orbital in the carbonyl complex. As the T-shaped geometry around the copper(I) ion relaxes to form a pseudotetrahedral molecule, the flexible tridenate ligand will move out of the xy plane, causing the $d_{x^2-y^2}$ orbital to be lowered in energy and allowing it to have greater overlap with the pyrazole π^* orbitals. This accounts for the shift to higher energy and greater intensity observed for the $d\sigma^* \rightarrow \pi^*$ transition in the absorption spectra for the Cu(I)–CO complexes (vide supra). An additional result of this change in geometry is that the d_{z^2} orbital will have little overlap with the π^* orbitals of the pyrazole rings. Since the intensity of an optical transition is proportional to the amount of overlap between the donor and acceptor orbitals, the $d_{z^2} \rightarrow \pi^*$ electronic transition should be very weak. We have attempted to examine this low-energy transition in a concentrated solution of Cu(pza)CO$^+$ ($>$0.01 M). While a resolvable band was not observed, a small increase in intensity was found on the low-energy end of the MLCT transition (ca. 360 nm) relative to the corresponding uncarbonylated complex, Cu(pza)$^+$. This is consistent with the above hypothesis, suggesting that the copper(I) carbonyl complexes possess low-energy absorption transitions.

Summary and Conclusions. The purpose of this work was to examine the electronic and photophysical properties of copper(I) complexes. All two-, three-, and four-coordinate copper(I) pyrazole complexes investigated have strong MLCT electronic transitions in the UV region, and these transitions are affected by the ligand environment around the metal ion. Excitation at 77 K into these MLCT transitions produces visible emissions that are from ^{3}d-π^* excited states. The copper(I) phenolate complexes have both absorption and emission transitions from MLCT excited states at lower energies relative to those for the Cu(N)$_x^+$ complexes. The binding of carbon monoxide to the three-coordinate and phenolate complexes shifts the electronic transitions to higher energy while the emission (from a ^{3}d-π^* excited state) is found at lower energy. This has been explained by proposing that the Cu(I)–CO complexes have a low-energy electronic transition that is so weak it cannot be clearly resolved in the absorption spectrum.

The intense absorption transitions resulting from the aromatic amino acid side chains will severely limit the possibility of observing MLCT transitions for most copper(I) proteins. Nevertheless, such transitions are present and this work suggests that

they may be useful for probing the metal ion site properties in these proteins. This is illustrated in comparing the present results with the spectroscopic properties of carbonylhemocyanin (HcCO). Finazzi-Agro and co-workers have shown that HcCO has a strong emission at 550 nm when excited at 310 nm.[4] The above findings for synthetic copper(I) carbonyl complexes suggest that the emission is from a ^{3}d-π^* (MLCT) excited state. As observed for the synthetic complexes, the lifetime of the emission in HcCO is also in the microsecond range. Since it is known that there are histidines bound to the copper(I) ions in deoxyHc,[37,38] an imidazole is the most likely candidate for the role as π^* acceptor.

Additionally, since the emission from HcCO is observed in fluid solution, there is most likely a conformational change about the active site after the binding of CO, which allows the Cu(I)–CO moiety to be shielded from the external environment (i.e. solvent). In the excited state the d^9 copper(II) ion is able to coordinate other ligands, which can quench the radiative process.[7] If the metal ion center is shielded from possible ligands (i.e. solvent molecules), preventing further coordination at the metal ion center, the emission from the ^{3}d-π^* excited state will be enhanced. This explains why all of the synthetic copper(I) complexes described above luminesce in rigid environments where the possibility of solvent coordination is diminished, yet only the four-coordinate complexes with bulky ligands have well-defined photophysical properties at room temperature.

Although the copper(I) phenolate carbonyl complexes luminesce at an energy similar to that observed for HcCO (ca. 550 nm), caution must be taken in suggesting that a phenolate is bound to the copper(I) ion in the active site of HcCO. All the complexes examined utilize pyrazole instead of the biologically important imidazole as the heteroaromatic donor. While the two heterocycles are structurally similar, their electronic properties are different, and the $\pi \rightarrow \pi^*$ transitions of imidazole occur at higher energy than those of pyrazole.[39] Copper(I) imidazole complexes and the related phenoxide and carbonyl complexes need to be synthesized and their electronic and photophysical properties examined before conclusions can be made about the structure of the Cu(I)–CO moiety in HcCO. We have communicated a preliminary account of such work, and additional experiments are in progress.[40]

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