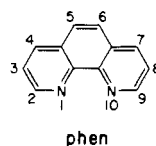
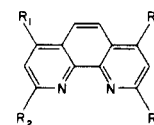
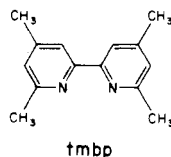


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**Registry No.** 1, 111059-89-3; NaPdCl<sub>4</sub>, 13820-53-6.

**Supplementary Material Available:** Tables of coordinates and isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters (2 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.



	R <sub>1</sub>	R <sub>2</sub>
dmp	H	CH <sub>3</sub>
bcp	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>
dpp	H	C <sub>6</sub> H <sub>5</sub>
dnp	H	1-naphthyl
tpp	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>

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### Charge-Transfer Absorption and Emission of Cu(NN)<sub>2</sub><sup>+</sup> Systems

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Luminescence from Cu(NN)<sub>2</sub><sup>+</sup> systems, where NN denotes a substituted 1,10-phenanthroline ligand, has been reported for pure solids,<sup>1</sup> as well as for complexes dissolved in fluid-solution<sup>2,3</sup> or in glassy media.<sup>4,5</sup> The emission originates from d-π\* metal-to-ligand charge-transfer (CT) excited states; more specifically, temperature-dependent emission studies have established that at least two different excited states are involved and that they differ in spin multiplicity.<sup>6</sup> The photophysical properties of Cu(NN)<sub>2</sub><sup>+</sup> systems have also been found to be strongly affected by substituent groups on the ligand moieties. Steric<sup>3,5</sup> and electronic<sup>7</sup> effects are involved, but the steric effects are very dramatic because the excited state is subject to a novel type of quenching wherein a Lewis base attacks the "Cu(II)" center, possibly forming a short-lived excited-state complex (exciplex).<sup>2,5,8</sup> Sterically active groups on the complex or the incoming nucleophile introduce "F-strain"<sup>9</sup> and inhibit exciplex quenching, thereby enhancing the excited-state lifetime.<sup>5,10</sup> Other aspects of the photochemistry and photophysics of these systems are also being pursued.<sup>3,11-20</sup> In order to characterize the electronic structures and the excited-state dynamics of these systems in more detail, we have carried out systematic studies of the absorption and emission properties of a number of complexes of NN ligands (Figure 1) in fluid solution and frozen matrices.

### Experimental Section

**Materials.** The [Cu(NN)<sub>2</sub>]BF<sub>4</sub> salts were prepared by a method previously described.<sup>21</sup> The dmp (2,9-dimethyl-1,10-phenanthroline) and bcp (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) ligands were obtained from Aldrich, while phen (1,10-phenanthroline) was purchased from G. F. Smith; each was used without purification. dpp (2,9-diphenyl-1,10-phenanthroline) and tpp (2,4,7,9-tetraphenyl-1,10-phenanthroline) were synthesized as before,<sup>22</sup> and dnp (2,9-bis(1-naphthyl)-1,10-phenanthroline) was prepared analogously.<sup>23</sup> tmbp (4,4',6,6'-tetramethyl-2,2'-bipyridine) was synthesized by the method of Linnell.<sup>24</sup> Spectral grade solvents were used for all the physical studies.

**Apparatus.** Absorption measurements were made on a Cary 17D spectrophotometer. The emission spectra were obtained with a Perkin-Elmer MPF-44B fluorescence spectrophotometer, while lifetimes were measured with a Princeton Applied Research Model 2100 N<sub>2</sub>-pumped dye laser source and a data-collection system that have previously been described.<sup>12</sup> Measurements in the glass were obtained with either a quartz finger Dewar or an Oxford Instruments DN-704 cryostat. For

Figure 1. NN ligands.

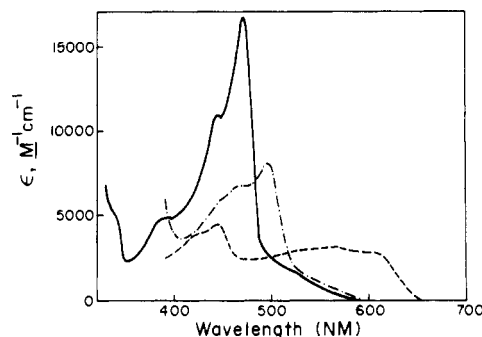


Figure 2. Absorption spectra at 90 K in 4:1 EtOH/MeOH glass of Cu(dmp)<sub>2</sub><sup>+</sup> (—), Cu(dnp)<sub>2</sub><sup>+</sup> (---), and Cu(dpp)<sub>2</sub><sup>+</sup> (· · ·).

Table I. Absorption Data for Cu(NN)<sub>2</sub><sup>+</sup> Systems in 4:1 EtOH/MeOH at 90 K

NN <sup>a</sup>	band	λ, nm	ε, <sup>b</sup> M <sup>-1</sup> cm <sup>-1</sup>
phen	I	500 (sh)	
	IIa	463	17 200
	IIb	435	12 500
dmp	III	380	8 100
	I	510 (sh)	
	IIa	460	16 500
bcp	IIb	440	10 800
	III	390	4 800
	I	540 (sh)	
dnp	IIa	495	31 600
	IIb	460	20 200
	III	425	10 700
tmbp	I	530 (sh)	
	IIa	485	8 100
	IIb	460	7 100
dpp	I	510 (sh)	
	IIa	477	13 770
	IIb	447	10 270
tpp	I	600	2 800
	IIa	560	3 100
	IIb	436	4 400
dnp	I	413	3 900
	I	590	9 800
tpp	I	460	10 300
	I	460	10 300

<sup>a</sup> See Figure 1 for abbreviations. <sup>b</sup> The ε values are not corrected for solvent contraction.

measurements in fluid solution, temperature control was achieved with a Lauda K-2/RD circulating water bath.

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Table II. Emission Data at 25 °C

	CH <sub>2</sub> Cl <sub>2</sub>			MeOH		
	$\lambda_{\max}$ , <sup>a</sup> nm	$10^4\Phi^b$	$\tau$ , <sup>b</sup> ns	$\lambda_{\max}$ , <sup>a</sup> nm	$10^4\Phi^b$	$\tau$ , <sup>b</sup> ns
Cu(phen) <sub>2</sub> <sup>+</sup>						
Cu(dmp) <sub>2</sub> <sup>+</sup>	750	2.7	90			
Cu(bcp) <sub>2</sub> <sup>+</sup>	770	3.2	80			
Cu(dnp) <sub>2</sub> <sup>+</sup>	715	12	250	720	5.6	120
Cu(tmbp) <sub>2</sub> <sup>+</sup>	775	0.7	18			
Cu(dpp) <sub>2</sub> <sup>+</sup>	710	11	250	735	4.8	180
Cu(tpp) <sub>2</sub> <sup>+</sup>	745	14.8	230	765	5.1	120

<sup>a</sup> From corrected spectra. <sup>b</sup> Estimated uncertainty is 10%.

**Methods.** For the low-temperature absorption data the samples were prepared as a 4:1 EtOH/MeOH glass, and all samples were allowed to equilibrate for at least 30 min once the cryostat sensor reached the desired reading (-183 ± 2 °C). Room-temperature luminescence samples were deoxygenated by repetitive freeze-pump-thaw cycles. Quantum yields were calculated by the method of Parker and Rees,<sup>25</sup> where Ru(bpy)<sub>3</sub><sup>2+</sup> was used as the standard.<sup>26,27</sup> Luminescence lifetimes were secured from the slopes of standard log plots.

## Results

Each complex exhibits intense CT absorbance in the visible region. In the low-temperature spectrum of Cu(dmp)<sub>2</sub><sup>+</sup> the main band is split into at least two components (Figure 2), and additional weaker absorption bands are evident to either side. The three distinct types of absorbances are labeled as bands I, II, and III in order of increasing energy in Table I. Analogous bands appear in the spectra of most of the other complexes (Table I and Figure 2), although in some cases, e.g., Cu(dnp)<sub>2</sub><sup>+</sup>, the onset of intraligand absorption obscures the near-UV region of the spectrum. However, the low-temperature absorption spectra of Cu(dpp)<sub>2</sub><sup>+</sup> and Cu(tpp)<sub>2</sub><sup>+</sup> conform to a very different pattern. While these systems exhibit absorption in the neighborhood of 450 nm, separate, more intense absorption occurs in the region of 600 nm.

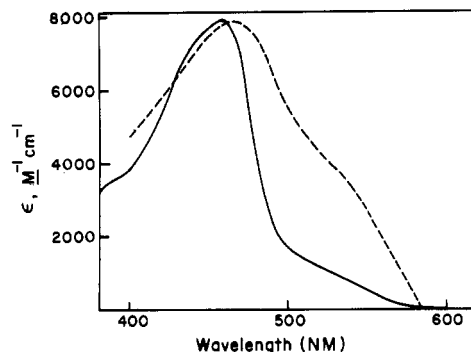


Figure 3. Absorption spectra of [Cu(dmp)<sub>2</sub>]BF<sub>4</sub> in methylene chloride solution (—) and in a KBr pellet (---) at 298 K. The solid-state absorbance is depicted in arbitrary units.

Except for Cu(phen)<sub>2</sub><sup>+</sup>, each complex also exhibits CT luminescence in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. In methanol, only those systems with bulky aromatic substituents in the 2,9-positions give detectable emission. Even then, the lifetimes and the quantum yields are decreased (Table II).

## Discussion

**CT Assignments in D<sub>2d</sub> Symmetry.** The highest available symmetry for a Cu(NN)<sub>2</sub><sup>+</sup> system is D<sub>2d</sub>, and the room-temperature MCD spectrum of Cu(phen)<sub>2</sub><sup>+</sup> has previously been analyzed in terms of this symmetry.<sup>28</sup> In particular, one of the transitions was attributed to an A term, which requires an orbital degeneracy not possible in a lower symmetry. On the other hand, Cu(phen)<sub>2</sub><sup>+</sup><sup>29</sup> and Cu(dmp)<sub>2</sub><sup>+</sup><sup>30</sup> have been shown to adopt a flattened structure in the solid state such that the dihedral angle between mean ligand planes is significantly smaller than 90°. However, the angle varies significantly with the counterion,<sup>30</sup> and the flattening distortion has been attributed to intermolecular stacking interactions among the heteroaromatic ligands.<sup>31</sup> According to this interpretation, the distortion would not necessarily persist in solution, and the differences between the shapes of the absorption spectra of Cu(dmp)<sub>2</sub><sup>+</sup> in solution and in the solid state suggest this may be the case (Figure 3). Therefore, except as noted, we will consider the band assignments in D<sub>2d</sub> symmetry, where the ligand-ligand repulsions would be minimized. Since the complexes with aryl substituents in the 2,9-positions appear to adopt a different geometry, they are considered in a subsequent section.

In D<sub>2d</sub> symmetry as many as seven CT transitions are formally symmetry allowed for a Cu(NN)<sub>2</sub><sup>+</sup> complex, where NN denotes a derivative of 1,10-phenanthroline,<sup>7</sup> including transitions to the ligand  $\psi^*$  and  $\chi^*$  orbitals.<sup>32</sup> Nevertheless, at most three absorption bands are resolved, consistent with a theoretical model that predicts that in D<sub>2d</sub> symmetry the oscillator strength occurs in but two of the dipole-allowed transitions<sup>7,33,34</sup> which are polarized along the line joining the metal and ligand centers.<sup>33</sup> If we call this the z axis, the relevant symmetry labels for the z-polarized, one-electron transitions of the D<sub>2d</sub> form of Cu(phen)<sub>2</sub><sup>+</sup> are  $e(xz, yz) \rightarrow e(\psi^*)$  and  $b_1(x^2 - y^2) \rightarrow a_2(\chi^*)$ .

The transition to  $e(\psi^*)$  can be unambiguously assigned to band II in Table I since, for the 1,10-phenanthroline derivatives, the intensity of the transition to  $\psi^*$  is expected to be 2–3 times as intense as the transition to  $\chi^*$ .<sup>7</sup> The other z-polarized transition can plausibly be assigned to band III since the band is missing in the spectrum of Cu(tmbp)<sub>2</sub><sup>+</sup>, where the  $\chi^*$  orbitals occur at

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considerably higher energies.<sup>35</sup> (Pure  $\chi^*$  and  $\psi^*$  excited states probably do not exist because some degree of configuration interaction is likely.) The relative energies of bands II and III are also in accord with the proposed assignments. Thus, the  $\psi^*$  and  $\chi^*$  orbitals have similar energies in the phenanthroline ligands, but calculations suggest that the  $e(xz, yz)$  orbitals occur at higher energy than  $b_1(x^2 - y^2)$  in a related  $\text{Cu}(\text{NN})_2^+$  system, where the ligand is 1,4-diazabutadiene.<sup>36</sup> Transition-state energies have also been calculated, and they reveal that the trend in orbital energies is generally a reliable indicator of excitation energies.<sup>36</sup>

The assignment of band I is more problematic. The possibility that band I is a spin-forbidden triplet CT transition can probably be ruled out because the spin-orbit coupling constant of copper is too small to account for the observed intensity. At least two other possible assignments exist for band I, however. If the assumption of  $D_{2d}$  symmetry is correct, band I must be attributed to a transition with  $x, y$  polarization. This assignment is plausible because various mechanisms exist that can impart oscillator strength to  $x, y$ -polarized transitions.<sup>7,34</sup> Indeed, perpendicularly polarized transitions have been assigned in the spectra of  $\text{W}(\text{C}-\text{O})_4(\text{NN})$ <sup>37</sup> and  $\text{Cu}(\text{dmp})\text{X}$ <sup>38</sup> systems, where X is a bridging anion. Other possibilities exist if the symmetry is lower than  $D_{2d}$ , and Crosby and co-workers have suggested that band I can be  $z$ -polarized if there is a low-symmetry distortion.<sup>39</sup> The spectra in Figure 3 may lend support to this interpretation.

**CT Spectra of  $\text{Cu}(\text{NN})_2^+$  Systems with 2,9-Di-aryl Substituents.** As can be seen in Figure 2, the low-temperature CT absorption spectrum of  $\text{Cu}(\text{dpp})_2^+$  spans an even broader range of energies than the solid-state spectrum of  $\text{Cu}(\text{dmp})_2^+$ . The CT spectrum of  $\text{Cu}(\text{tpp})_2^+$  is similar to that of  $\text{Cu}(\text{dpp})_2^+$ . Since extended Hückel calculations reveal that the presence of the phenyl substituents has little effect on the energy gap between the  $\psi^*$  and  $\chi^*$  orbitals, we attribute the spectral spread to enhanced splitting among the  $d_{x^2-y^2}$  and the  $d_{xz}$  and  $d_{yz}$  orbitals, presumably due to a low-symmetry distortion. In line with this reasoning, a related complex of a catenand ligand assumes a very distorted geometry in the solid state, where the coordination geometry is approximately trigonal pyramidal. Here the relative orientation of the ligands is probably determined, at least in part, by intramolecular interligand stacking interactions,<sup>40</sup> and these may persist in the fluid phase as well. Moreover, previous work has shown that lowering the symmetry gives rise to an intense, low-energy band in related nickel systems.<sup>44,45</sup>

In the limit of a large distortion the absorption intensity is spread over a number of transitions,<sup>7</sup> and clear resolution of transitions to the  $\chi^*$  and  $\psi^*$  orbitals is unlikely. The dnp complex also contains aromatic substituents in the 2,9-positions of the phenanthroline core; however, its CT absorption spectrum, albeit broadened, more nearly resembles that of  $\text{Cu}(\text{dmp})_2^+$  (Figure 2). This may indicate less distortion from  $D_{2d}$  symmetry.<sup>41</sup>

**Vibronic Structure.** Various CT bands in Figure 2 exhibit underlying structure. For example, band II generally consists of at least two overlapping components separated by 1000–1500  $\text{cm}^{-1}$ . In view of the magnitude of the energy separation and the splitting being essentially independent of the substituent, we attribute the structure to vibronic effects. The CT spectra of analogous  $\text{Cu}(\text{I})$  complexes of simple diazabutadiene ligands also exhibit vibrational structure, and the spacing is about 1500  $\text{cm}^{-1}$ , characteristic of

a stretching motion involving the  $\text{C}=\text{N}$  double bonds.<sup>36,42</sup> In all likelihood, the vibronic structure of the CT transitions studied herein reflects  $\text{C}=\text{N}$  stretching motion as well; however, more than one vibrational mode of the extended heteroaromatic ligands is apt to be involved.

**Emission Spectra.** Although it has been possible to identify the CT states that are involved in absorption, the assignment of the emitting state(s) is unclear because geometry changes can be expected to attend relaxation of the initially excited Franck-Condon state. This follows because a change in the formal oxidation state of the metal center attends CT excitation, and  $\text{Cu}(\text{II})$  and  $\text{Cu}(\text{I})$  centers usually assume quite different coordination geometries. As a result neither the relative energies nor the relative magnitudes of the transition probabilities necessarily correspond in the absorption and emission spectra. These complications notwithstanding, it can be noted that the magnitude of the radiative rate constant for the emitting singlet CT state of  $\text{Cu}(\text{dmp})_2^+$  is sensibly related to the molar extinction coefficient of band I in the absorption spectrum.<sup>6</sup>

At least qualitatively, the emission spectra reflect important structural effects. As can be seen from the results in Table II, only  $\text{Cu}(\text{NN})_2^+$  systems with bulky substituents in the 2,9-positions exhibit detectable luminescence in donor solvents such as methanol. We attribute this to a type of exciplex quenching that is inhibited when bulky ligands are bound to the copper center.<sup>5,8,10</sup> The correlation between the lifetime in methylene chloride and the size of the substituents in Table II suggests that even a weakly basic solvent is capable of inducing quenching. Also significant in this regard is that the above correlation is lost in a rigid matrix at 77 K, where exciplex quenching should be inhibited.<sup>43</sup>

It is intriguing to note that the  $\text{Cu}(\text{phen})_2^+$  system does not exhibit detectable luminescence even at 77 K. Since its absorption spectrum is similar to that of  $\text{Cu}(\text{dmp})_2^+$  and those of the other emitting systems, we attribute the lack of emission to efficient nonradiative decay rather than to an inefficient radiative process. Radiationless decay is enhanced if, on formation of the excited state, a large structural reorganization occurs such that the ground- and excited-state energy surfaces approach each other. This may be the case with  $\text{Cu}(\text{phen})_2^+$  because the minimal steric demands of the phen ligand would permit significant rearrangement within the coordination sphere; for example, recent studies have shown that packing forces induce a pronounced flattening distortion on the  $\text{Cu}(\text{phen})_2^+$  molecule in the solid state.<sup>29</sup> While a similar flattening occurs in complexes with bulky 2,9-substituents, these groups limit the degree of distortion.<sup>31</sup>

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#### Evidence for Differing Ion-Pair Precursor Structures in the Oxidation of Cobalt(II) Amine Derivatives by $[\text{Co}(\text{edta})]^-$

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Oxidation of racemic  $[\text{Co}(\text{en})_3]^{2+}$  by optically active  $[\Delta\text{-Co}(\text{edta})]^-$  results in formation<sup>1</sup> of an enantiomeric excess around 10% of  $[\Lambda\text{-Co}(\text{en})_3]^{3+}$ , a  $\Delta\Lambda$  interaction, in aqueous media at 25

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