

# Articles

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## Comparative Studies of the Photophysical Properties of Copper Phenanthrolines: From $\text{Cu}(\text{dmp})_2^+$ to the Copper(I) Catenates

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Received April 5, 1989

Comparisons of solution and solid-state absorbance data reveal that  $\text{Cu}(\text{dpp})_2^+$  (where dpp denotes 2,9-diphenyl-1,10-phenanthroline) and the related copper(I) catenate  $\text{Cu}(\text{cat-30})^+$  adopt low-symmetry structures in solution that mimic those found in the solid state. Spectral changes occur in solution upon cooling, and these are tentatively ascribed to a narrowing of the distribution of torsion angles subtended by the phenyl substituents. The data for the more rigid catenate  $\text{Cu}(\text{cat-27})^+$  support this interpretation because the absorption spectrum is less temperature dependent. In dichloromethane at 25 °C the excited-state lifetime of  $\text{Cu}(\text{cat-30})^+$  is 190 ns compared with 250 ns for  $\text{Cu}(\text{dpp})_2^+$ . However, the relatively rigid  $\text{Cu}(\text{cat-27})^+$  system has a longer lifetime (280 ns). Although the novel topology and the encapsulating nature of the catenands stabilize the reduced, formally zerovalent copper complexes, the copper(I) catenates are weak photooxidants. The data suggest that reductive quenching is difficult to observe because the excited state is only mildly oxidizing ( $E_{1/2} \approx 0.4$  V vs SHE) and because there is a significant inner-sphere reorganizational energy barrier posed within the complex due to the change in the formal oxidation state of copper.

### Introduction

$\text{Cu}(\text{NN})_2^+$  complexes, where NN denotes a derivative of 1,10-phenanthroline, exhibit reasonably intense metal-to-ligand charge-transfer (CT) bands in the visible region. The photophysical properties of several systems, especially  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{dpp})_2^+$ , where dmp denotes 2,9-dimethyl-1,10-phenanthroline and dpp denotes 2,9-diphenyl-1,10-phenanthroline, have been extensively investigated,<sup>1-3</sup> and these studies have shown that substituents at the 2- and 9-positions of the ligand have a critical bearing on the properties of the excited state. For example, the intensity of the CT absorption is decreased for  $\text{Cu}(\text{dpp})_2^+$  because delocalization of the  $\pi^*$ -acceptor orbital over the phenyl substituents attenuates the transition dipole length.<sup>4</sup> On the other hand, the excited-state lifetime is significantly lengthened in the case of the dpp complex because bulky groups protect the metal center from associative quenching interactions involving the solvent.<sup>3,5</sup> The quenching reaction involves a transient increase in the coordination number of copper, and the question arises as to whether further structural elaboration and rigidification of the whole molecular system could result in even longer excited-state lifetimes. A series of topologically novel complexes, the catenates, have been synthesized by Sauvage and co-workers<sup>6-8</sup> and are of interest in this regard. These interlocked ligand systems are synthesized by taking advantage of the three-dimensional template effect wherein appropriately functionalized dpp ligands are first bound to a central metal ion and then cyclized. The cat-27 and cat-30 ligands and the corresponding catenate complexes are depicted in Figure 1. The complexes obtained are surprisingly inert toward decomplexation because the interlocked coordinating system provides a highly protected and rigid environment for the metal ion. For instance, the demetalation rate of  $\text{Cu}(\text{cat-30})^+$  by  $\text{CN}^-$  in solution is decreased by several orders of magnitude as compared to that of  $\text{Cu}(\text{dpp})_2^+$  or  $\text{Cu}(\text{dap})_2^+$  (dap denotes 2,9-dianisyl-1,10-phenanthroline; see Figure 1). Because decomplexation is slow, solutions of the reduced complex are also relatively stable against the deposition of copper metal.<sup>7</sup> In view of the novel ligand topology and the steric impediments protecting the central metal ion, we have investigated the photophysical properties of the catenates, and our findings are discussed below.

### Experimental Section

**Materials.** The dpp and dap ligands were synthesized as before.<sup>10-12</sup> The  $[\text{Cu}(\text{NN})_2]\text{BF}_4$  salts and the catenates were prepared by methods

described previously.<sup>1,6-8,13</sup> Spectral grade solvents were used for all physical studies. Hydroquinone was obtained from Baker Chemical Co. The sodium dithionite was purchased from Sigma.

**Apparatus.** Absorption measurements were made on a Cary 17D spectrophotometer. The emission spectra were obtained with either a Perkin-Elmer MPF-44B or an SLM Aminco SPF-500C fluorescence spectrophotometer, and lifetimes were measured with a Princeton Applied Research Model 2100  $\text{N}_2$ -pumped dye laser source and a data collection system, which have previously been described.<sup>14</sup> Low-temperature measurements were obtained with an Oxford Instruments Model DN-704 cryostat or a quartz finger Dewar flask. For the work around ambient temperature the temperature of the cuvette was controlled with a Lauda K-2/RD circulating water bath.

**Methods.** The low-temperature absorption data are from a 4:1 EtOH/MeOH glass, and all samples measured in the cryostat were allowed to equilibrate for at least 30 min after the sensor reached the desired reading. The solid-state sample of  $[\text{Cu}(\text{dpp})_2]\text{CuCl}_2 \cdot \frac{2}{3}\text{CH}_3\text{CN}$  was prepared as a KBr pellet. Room-temperature luminescence measurements were obtained with solutions that had been deoxygenated by repetitive freeze-pump-thaw cycles. Quantum yields were calculated by the method of Parker and Rees<sup>15</sup> with aqueous  $\text{Ru}(\text{bpy})_3^{2+}$  as the reference ( $\phi = 0.042$ ).<sup>16</sup> Luminescence lifetimes were secured from the

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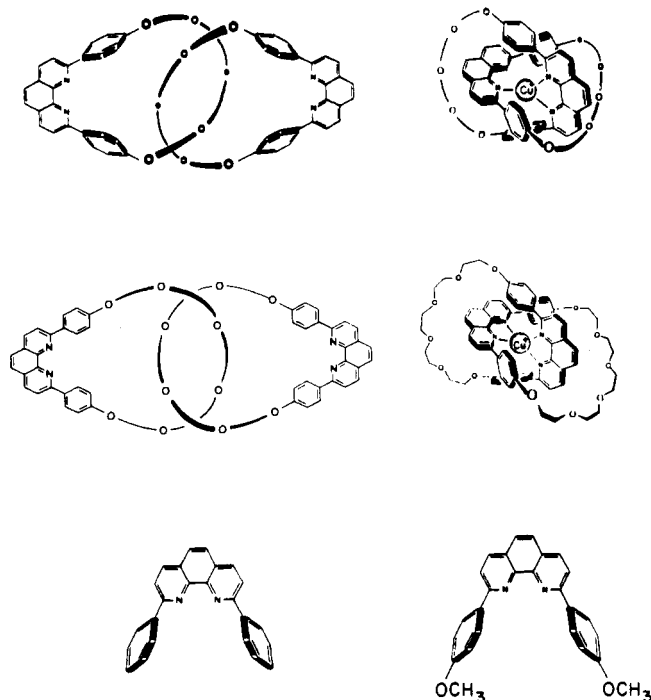


Figure 1. Molecules. Clockwise from the upper left: cat-27, Cu(cat-27)<sup>+</sup>, Cu(cat-30)<sup>+</sup>, dap, dpp, cat-30. Cu(cat-30)<sup>+</sup> and Cu(cat-27)<sup>+</sup> are depicted as idealized, high-symmetry structures.

Table I. Absorption Data

	298 K <sup>a</sup>		90 K <sup>b</sup>	
	$\lambda_{\max}$ , nm	$\epsilon$	$\lambda_{\max}$ , nm	$\epsilon^c$
Cu(dmp) <sub>2</sub> <sup>+</sup>	454	7950	390 <sup>d</sup>	4800
			440	10800
			460	16500
			510 (sh)	
Cu(dpp) <sub>2</sub> <sup>+</sup>	440	3200	413 <sup>d</sup>	3900
			560 (sh)	400
			560	3100
			600	2800
Cu(dap) <sub>2</sub> <sup>+</sup>	436	2310		
Cu(cat-30) <sup>+</sup>	440	2250	415	2500
			440	2480
			530	2040
			625	1900
Cu(cat-27) <sup>+</sup> <sup>e</sup>	430 (sh)	2080	410	3400
			515	1850
			520	3300
			610 (sh)	2400

<sup>a</sup>CH<sub>2</sub>Cl<sub>2</sub> is the solvent. <sup>b</sup>4:1 EtOH/MeOH is the solvent. <sup>c</sup>Uncorrected for solvent contraction. <sup>d</sup>Reference 5. <sup>e</sup>The low-temperature absorption spectrum was measured for this complex at 77 K in a quartz finger Dewar flask.

slopes of standard log plots. Attempts to observe reductive quenching with hydroquinone were carried out in a 2:3 mixture of MeOH and 0.025 M pH 8.95 tris buffer or in a 2:3 mixture of 0.05 M pH 9 ammonium acetate buffer and acetonitrile. The latter solvent system was used in the experiments involving dithionite as well. The quencher concentrations were 0.01 M for hydroquinone and 0.005 M for dithionite.

## Results

**Electronic Spectra.** All five complexes investigated exhibit intense CT absorption in the visible region; the absorption maxima and the apparent molar absorptivities are compiled in Table I. With the exception of Cu(cat-27)<sup>+</sup>, the room-temperature absorption is broad and maximizes between 430 and 440 nm with a shoulder toward the red region (Figure 2). The spectrum of the dpp complex has also been measured in the solid state, and similar results are obtained (Figure 2). When the temperature is lowered to 90 K, all spectra sharpen, and a series of partially

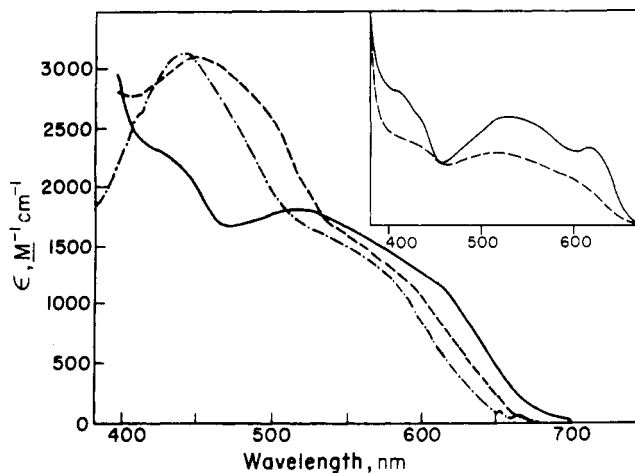


Figure 2. Absorption spectra of Cu(dpp)<sub>2</sub><sup>+</sup> (---) and Cu(cat-27)<sup>+</sup> (—) in CH<sub>2</sub>Cl<sub>2</sub> and [Cu(dpp)<sub>2</sub>]CuCl<sub>2</sub>·2/3CH<sub>3</sub>CN in a KBr pellet (— · —) at 20 °C. The absorption of the last material and those in the inset are depicted in arbitrary units. Inset: Absorption spectrum of Cu(cat-27)<sup>+</sup> at room temperature (—) and in 4:1 EtOH/MeOH at 77 K (---).

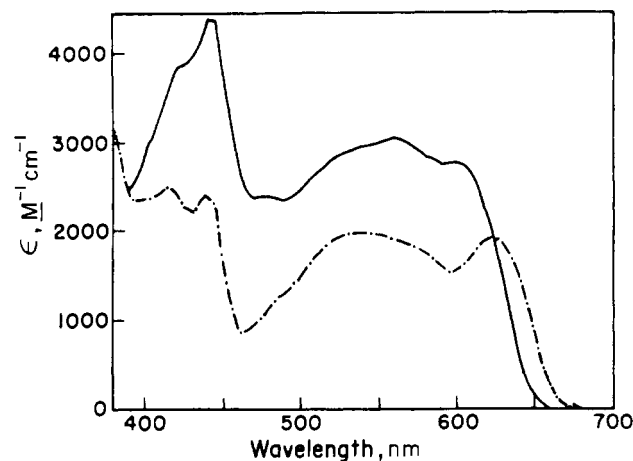


Figure 3. Absorption spectra of Cu(dpp)<sub>2</sub><sup>+</sup> (—) and Cu(cat-30)<sup>+</sup> (---) at 90 K in a 4:1 EtOH/MeOH glass.

Table II. Emission Properties in CH<sub>2</sub>Cl<sub>2</sub> at 298 K<sup>a</sup>

	$\lambda_{\max}$ , nm	$10^4\phi$	$\tau$ , ns
Cu(dmp) <sub>2</sub> <sup>+</sup>	750	2.7	90
Cu(dpp) <sub>2</sub> <sup>+</sup>	710	10.7	250
		100 <sup>b</sup>	
Cu(dap) <sub>2</sub> <sup>+</sup>	710	8.3	260
Cu(cat-30) <sup>+</sup>	730	8.1	190
Cu(cat-27) <sup>+</sup>	715	9.4	280

<sup>a</sup>Lifetimes were measured at a copper concentration of 50–100  $\mu$ M. <sup>b</sup>In 2:3 MeOH/0.025 M pH 8.95 Tris buffer.

resolved peaks appear in place of the shoulders observed at room temperature (Figure 3).

**Luminescence Data.** Each complex is photoluminescent in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, and the emission data are presented in Table II. The lifetime of Cu(cat-30)<sup>+</sup> is somewhat shorter than those of the other complexes with aryl substituents, but there is very little difference in the emission quantum yield. Although we sought to observe reductive quenching of the CT excited state, the presence of hydroquinone or sodium dithionite had no effect on the luminescence intensity of Cu(dpp)<sub>2</sub><sup>+</sup>.

## Discussion

**Structural Implications of Absorption Spectra.** As has been reported previously, the (CT) absorption spectrum of Cu(dmp)<sub>2</sub><sup>+</sup> can be assigned under the assumption of *D*<sub>2d</sub> symmetry.<sup>5</sup> However, Cu(dpp)<sub>2</sub><sup>+</sup> exhibits a very different spectrum that spans a much broader range of energies, and the same is true of the copper(I) catenates. In view of what is known about the structures in the

solid state, the spectral differences can be explained in terms of a change in the coordination geometry. In the crystalline state, the symmetry about the metal center in  $\text{Cu}(\text{dpp})_2^+$  and  $\text{Cu}(\text{cat-30})^+$  is strongly distorted from  $D_{2d}$ .<sup>17,18</sup> In each case the four donor nitrogens approximately define a trigonal pyramid. One reason for the distortion may be that it permits extensive *intramolecular* stacking interactions to occur between phenyl substituents on one of the phenanthroline rings and either the opposing phenanthroline ring or one of its phenyl substituents.<sup>17,18</sup> Since the dpp complex exhibits broad visible absorption in room-temperature solution as well as the solid state, the same low-symmetry structure probably also occurs in solution.

There is, however, evidence of fluxionality in the structures of these systems in solution.<sup>19</sup> For example, <sup>1</sup>H NMR measurements on  $\text{Cu}(\text{cat-30})^+$  show that the phenyl substituents rapidly rotate about the C–C bond to the phenanthroline core at room temperature. However, this rotational reorientation slows down and freezes out on the NMR time scale at lower temperatures.

The absorption spectra also indicate that some type of structural change occurs in solution upon cooling. Thus, the spectra of the dpp and the cat-30 complexes sharpen and become considerably better resolved at 90 K. In addition, the absorption bands that occur around 575 nm appear to intensify by comparison with the bands that fall around 440 nm. These changes can be understood if the complexes display a distribution of structures in room-temperature solution but freeze into their lowest energy conformation at lower temperatures. The spread in the angular distribution of the phenyl groups is likely to narrow upon cooling, and this could explain changes in the relative intensities of different absorption bands.<sup>4</sup>

In contrast to the above, the absorption spectrum of  $\text{Cu}(\text{cat-27})^+$  is relatively insensitive to temperature; see the inset to Figure 2. This suggests that the low-symmetry structure of this complex is favored at all temperatures. Flexibility is certainly limited because CPK models suggest that the copper ion can barely fit into the cat-27 ligand due to the short polyether linkage.<sup>13</sup> Consistent with these results, NMR data show that the pentakis(oxyethylene) chain is confined to the "hollow" regions on the back side of the phenanthroline moiety. The chain resides either in the region between C4 and C5 or that between C6 and C7 and does not readily exchange between these positions. As a result, the complex is chiral, and interconversion between enantiomers is not observed on the NMR time scale even at 160 °C.<sup>13</sup> The cat-27 complex is so rigid that demetalation is accompanied by a large proportion of ligand decomposition.<sup>13</sup>

**Structural Interpretation of Luminescence Data.** As can be seen in Table II, the emission quantum yields and the excited-state lifetimes of the copper(I) catenates compare with those of  $\text{Cu}(\text{dpp})_2^+$  and  $\text{Cu}(\text{dap})_2^+$ . In fact, the additional constraints imposed on the structure by interlocking the phenanthrolines have a variable effect on the excited-state lifetimes. In view of the shorter lifetime, solvent-induced quenching may even be more important for the  $\text{Cu}(\text{cat-30})^+$  system than for the dpp or the dap complexes. On the other hand, the more rigid  $\text{Cu}(\text{cat-27})^+$  system exhibits the longest lifetime in the series. The changes in lifetime are small, however, and the important conclusion is that simple aryl substituents in the 2- and 9-positions suffice to minimize solvent-induced quenching, at least in weakly donating media.

**Attempts to Observe Reductive Quenching.** In previous studies the CT states of  $\text{Cu}(\text{dpp})_2^+$  and  $\text{Cu}(\text{dmp})_2^+$  have been shown to be strong reducing agents that readily undergo oxidative quenching,<sup>1,14,20,21</sup> but there has been no indication to date that

these systems undergo reductive quenching.<sup>22</sup> Now that the reduction potential for the  $\text{Cu}(\text{cat-30})^{+/0}$  couple is available, we can analyze the reactivity—or rather the lack of reactivity—that these systems show with respect to reductive quenching in more detail. Since more data is available for the  $\text{Cu}(\text{dpp})_2^+$  complex, the discussion will focus on this ion. The reduction potential for the  $^*\text{Cu}(\text{dpp})_2^+/\text{Cu}(\text{dpp})_2$  couple is approximately given as

$$^*E_{1/2} = -1.6 + 2.0 = +0.4 \text{ V vs SHE} \quad (1)$$

where the zero-zero of the CT state is taken to be 2.0 V<sup>23</sup> and the corresponding ground-state potential is assumed to be equal (–1.6 V vs SHE) to that of the structurally similar  $\text{Cu}(\text{cat-30})^+$  complex.<sup>7</sup> Perhaps the main reason that reductive quenching has not been more evident is that the CT state is a rather weak oxidant in the thermodynamic sense.

Further analysis shows that there is a kinetic barrier that also inhibits reductive quenching. The hydroquinone data suffice to establish this point. Reductive quenching can be expected to occur at a rate *at least* as fast as that predicted for outer-sphere electron transfer quenching by the Marcus theory.<sup>24</sup> According to this theory, the rate of electron transfer from species *i* to the CT state can be expressed as

$$k_i = (k_{ii}k_{*}K_i)^{1/2} \quad (2)$$

where  $k_{ii}$  is the self-exchange rate for the quencher couple,  $k_{*}$  is the self-exchange rate for the  $^*\text{Cu}(\text{dpp})_2^+/\text{Cu}(\text{dpp})_2$  couple, and  $K_i$  is the equilibrium constant relating the two couples. When hydroquinone is the quencher, electron transfer can originate from the neutral molecule ( $\text{H}_2\text{Q}$ ) or one of the deprotonated forms ( $\text{HQ}^-$  or  $\text{Q}^{2-}$ ). With data from the literature,<sup>25,26</sup> it can be shown<sup>27</sup> that  $k_{*} < 10^9 \text{ M}^{-1} \text{ s}^{-1}$  if we assume that quenching could be detected with a rate even 10% as large as the natural decay rate.

By comparison, the self-exchange rate for oxidative quenching of the same CT state is estimated to be ca.  $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>14</sup> The reorganizational energy required for oxidation of the excited state is minimal because this process involves the depopulation of a  $\pi^*$  orbital that is essentially localized on the ligand. Fused-ring aromatic systems typically exhibit a low barrier to exchange of a  $\pi$  electron. On the other hand, reduction of the CT state requires the electronic configuration to change from  $d^9\pi^{*1}$  to  $d^{10}\pi^{*1}$ , i.e., formally conversion from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$ . Due to the distinct structural chemistry of the two oxidation states, there is a significant Franck–Condon barrier to electron-transfer. The literature reveals, for example, a self-exchange rate of  $2 \times 10^{-4} \text{ M s}^{-1}$  for the  $\text{Cu}^{2+}(\text{aq})/\text{Cu}^+(\text{aq})$  couple,<sup>28</sup>  $4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for the  $\text{Cu}(\text{dmp})_2^{2+/+}$  couple,<sup>28</sup> and  $10^5 \text{ M}^{-1} \text{ s}^{-1}$  for the  $\text{Cu}(\text{phen})_2^{2+/+}$  couple<sup>29</sup> where phen denotes 1,10-phenanthroline. A reviewer has pointed out that the bulkiness of the ligand could result in a reduced transmission coefficient for electron transfer and that this could also inhibit the self-exchange rate.

**Acknowledgment.** The Purdue research group was supported by National Science Foundation Grant No. CHE-8719538. The Strasbourg group acknowledges the financial support of the CNRS.

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