

# A Twist on the Copper Center in the Crystal Structure of [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub> and the Charge-Transfer Excited State? (dnpp = 2,9-Dineopentyl-1,10-phenanthroline)

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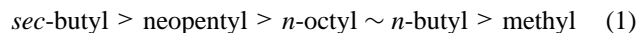
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The X-ray structure of [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>, where dnpp denotes 2,9-dineopentyl-1,10-phenanthroline, reveals a flattened tetrahedral copper complex with a dihedral angle between the least-squares planes of the ligands of only 63.4(1)°. Steric interactions involving  $\gamma$  methyl groups of the substituents have an important role in shaping the complex, but lattice forces are ultimately responsible for the flattened geometry. Crystal data: [Cu(C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub>, triclinic,  $P\bar{1}$ ,  $a = 10.2755(10)$  Å,  $b = 13.9750(12)$  Å,  $c = 16.4354(12)$  Å,  $\alpha = 79.376(7)^\circ$ ,  $\beta = 86.989(7)^\circ$ ,  $\gamma = 69.981(7)^\circ$ ,  $Z = 2$ . Spectral measurements involving four other Cu(NN)<sub>2</sub><sup>+</sup> systems, where NN denotes a 2,9-dialkyl-1,10-phenanthroline ligand, reveal that the room-temperature emission maxima fall at shorter wavelengths (20–50 nm) in the solid state as compared with fluid solution. The emission from Cu(dnpp)<sub>2</sub><sup>+</sup> is unique in that it maximizes at a slightly longer wavelength in the rigid solid (670 nm vs 665 nm in CH<sub>2</sub>Cl<sub>2</sub>). The spectral data support the following conclusions regarding structures in fluid solution: (1) The vibrationally relaxed excited state of Cu(dnpp)<sub>2</sub><sup>+</sup> adopts a structure similar to that observed in the solid. (2) However, the ground state assumes a less flattened, more tetrahedral geometry.

## Introduction

Derivatives of 1,10-phenanthroline (NN ligands) with moderately bulky substituents at the 2 and 9 positions are important in copper(I) chemistry. For example, 2,9-dimethyl-1,10-phenanthroline (dmp) is frequently the reagent of choice for the colorimetric analysis of copper(I) because of the selectivity for copper(I) and the strong visible absorbance of the Cu(dmp)<sub>2</sub><sup>+</sup> adduct.<sup>1,2</sup> This complex is stable in air because the steric requirements of the methyl substituents destabilize the flattened tetrahedral and five-coordinate geometries that copper(II) adopts in comparison to the pseudotetrahedral coordination geometry that is typical of copper(I).<sup>3–5</sup> Substituents also exert a profound influence on the lifetime and the reactivity of the metal-to-ligand charge-transfer (CT) excited state of the copper(I) system.<sup>6–9</sup> Thus, in weakly coordinating solvents like methylene chloride or in rigid glasses, bulky substituents in the 2,9 positions of the phenanthroline ligand enhance the energy and the lifetime of the CT excited state. The key effect is the inhibition of a flattening distortion in the CT excited state which formally involves a copper(II) center with a half-filled metal–ligand  $\sigma^*$  orbital.<sup>8–11</sup> Thus, Eggleston et al. have recently established that the emission energy and the excited-state lifetime increase with

the size of the substituent,<sup>12</sup> where the size order varies as follows:



Of course, sufficiently bulky substituents are likely to create strain in the ground state, and Cu(dnpp)<sub>2</sub><sup>+</sup> is a case in point, where dnpp denotes 2,9-dineopentyl-1,10-phenanthroline. In the coordinating solvent acetonitrile, the strain is such that Cu(dnpp)<sub>2</sub><sup>+</sup> tends to dissociate one of the chelating dnpp groups. Also, the dnpp complex exhibits its CT absorption maximum at 449 nm in methylene chloride, whereas the other members of the series all give absorption maxima at 456 ± 2 nm. To account for these properties, in particular, the position of the absorption maximum, Eggleston et al. proposed that steric effects cause elongation of the Cu–N bond lengths.<sup>12</sup> This was the impetus for the present investigation of the crystal structure of [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>. The results confirm that the Cu–N bond lengths are unusually long, but they also reveal a remarkable flattening distortion. Even if packing forces are responsible, the structure is worthy of note because spectral data suggest that the vibrationally relaxed CT excited state adopts a very similar structure in fluid solution.

## Experimental Section

**Materials and Methods.** The methylene chloride came from Scientific Products as a Burdick and Jackson, high-purity distilled in glass grade chemical. The laser dye, Coumarin 440, came from Laser Science, while the [Cu(NN)<sub>2</sub>]PF<sub>6</sub> salts were available from a previous study.<sup>12</sup> Additional ligand abbreviations: dop = 2,9-di-*n*-octyl-1,10-phenanthroline; dbp = 2,9-di-*n*-butyl-1,10-phenanthroline. For each solid, the sample holder was a Kimax-51 capillary tube. For the lifetime data the excitation wavelength was 440 nm, and a combination of 585

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**Table 1.** Crystallographic Data for  $[\text{Cu}(\text{C}_{22}\text{H}_{28}\text{N}_2)_2]\text{PF}_6$ 

$\text{CuPF}_6\text{N}_4\text{C}_{44}\text{H}_{56}$	formula wt 849.47
$a = 10.2755(10) \text{ \AA}$	space group $P\bar{1}$ (No. 2)
$b = 13.9750(12) \text{ \AA}$	$T = 296 \text{ K}$
$c = 16.4354(12) \text{ \AA}$	$\lambda = 1.54184 \text{ \AA}$
$\alpha = 79.376(7)^\circ$	$\rho_{\text{calc}} = 1.297 \text{ g cm}^{-3}$
$\beta = 86.989(7)^\circ$	$\mu = 1.548 \text{ mm}^{-1}$
$\gamma = 69.981(7)^\circ$	$R(F_o)^a = 0.051$
$V = 2179.4(4) \text{ \AA}^3$	$R_w(F_o^2)^b = 0.131$
$Z = 2$	

<sup>a</sup>  $R = \sum(|F_o| - |F_c|) / \sum|F_o|$  for  $F_o^2 > 2\sigma(F_o^2)$ . <sup>b</sup>  $R_w = [\sum w(|F_o^2| - |F_c^2|)^2 / \sum w|F_o^2|]^2$ .

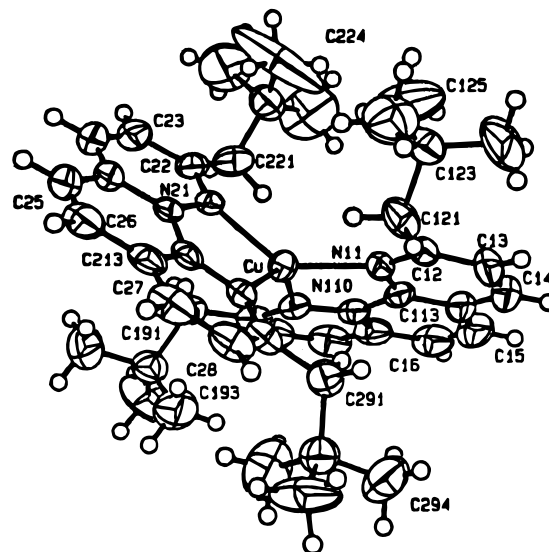
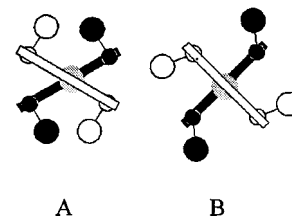
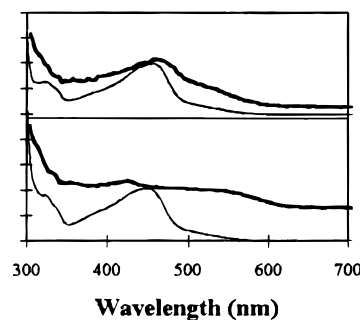
and 700 nm long-wave-pass filters served to isolate the luminescence signal. For the emission spectra, the excitation wavelength was also 440 nm, and the setup included a notch filter in the excitation beam in conjunction with a 510 nm long-pass filter in the emission beam. The excitation and emission bandpass settings were both 10 nm. The opal-glass method yielded the solid-state absorption spectra at room temperature.<sup>9,13</sup>

**Instrumentation.** A Perkin-Elmer Lambda 4C spectrophotometer provided the absorbance data, while the emission spectra came from an SLM/Aminco SPF-500C spectrofluorometer. The information about the lifetime apparatus is available in the literature.<sup>12</sup> The diffractometer was an Enraf/Nonius CAD4 computer-controlled,  $\kappa$ -axis device with a graphite-crystal, incident-beam monochromator.

**Crystal Structure Determination.** The crystal of  $[\text{Cu}(\text{dnpp})_2]\text{PF}_6$  used for the diffraction study was an orange, plate-like specimen of dimensions  $0.25 \times 0.25 \times 0.15 \text{ mm}$  produced by evaporation of a methanol/water solution. The diffractometer yielded 6884 unique reflections with  $2\theta \leq 124.6^\circ$ . The refinement treated the hydrogen atoms isotropically and allowed the  $\gamma$  methyl groups of one of the neopentyl substituents (at C22) to disorder over five, equal-weight positions. Similarly, the solution required 12 positions to model the fluorine atoms of the  $\text{PF}_6^-$  anion. Although the refinement took account of all reflections, the condition for inclusion in the calculation of  $R$  was  $F_o^2 > 2\sigma(F_o^2)$ . The solution came from an analysis of the Patterson function and a series of difference Fourier maps. The statistics were  $R(F) = 0.051$ ,  $R_w(F^2) = 0.131$ , and  $\text{GOF} = 1.007$ . Table 1 gives a summary of the crystal parameters and other details of refinement.

## Results

**Crystal Structure.** The crystal structure reveals a lattice of molecular ions; see Figure 1 for a view of the copper complex and the atom labels. The positional and thermal parameters as well as selected interatomic distances and angles appear in Tables 2 and 3. In crude terms the coordination geometry at copper is pseudotetrahedral, but there are significant deviations from tetrahedral symmetry. Thus, the average chelate-bite angle is only  $82.8^\circ$ , a typical value for such phenanthroline complexes.<sup>14,15</sup> In addition, the ligand planes are not orthogonal to each other;  $\theta_z$ , the dihedral angle between the  $\text{Cu}-\text{N}(11)-\text{N}(110)$  and the  $\text{Cu}-\text{N}(21)-\text{N}(210)$  planes, is only  $75.0(1)^\circ$ . The interplanar angle is even smaller ( $63.4(1)^\circ$ ) if the reference planes are the best least-squares planes through the phenanthroline moieties which actually exhibit small ruffling distortions. Figure 2A is a schematic representation of the flattened structure, and it shows how each substituent extends back away from the abutting neopentyl group on the opposite ligand. (The torsion angles between the  $\text{C}(\alpha)-\text{C}(\beta)$  vectors of the neopentyl substituents and the  $\text{N}(11)-\text{C}(12)$  or  $\text{N}(110)-\text{C}(19)$  vectors of the phenanthroline cores average around  $-125^\circ$  on one ligand and  $-106^\circ$  on the other.) However, this disposition of the

**Figure 1.** ORTEP drawing of  $\text{Cu}(\text{dnpp})_2^+$  with labeling scheme and 50% ellipsoids, except for the spheres shown for the hydrogen atoms.**Figure 2.** Schematic views of structures available to  $\text{Cu}(\text{dnpp})_2^+$  as seen down the short axes of the phenanthroline ligands. Structure A exists in the solid, complete with the clashing *tert*-butyl groups. The hypothetical, more extended structure B may be a closer facsimile of the structure in solution.**Figure 3.** Room-temperature absorbance spectra. Top panel:  $\text{Cu}(\text{dmp})_2^+$  in acetonitrile (thin line) and  $[\text{Cu}(\text{dmp})_2]\text{PF}_6$  in the solid state. Bottom panel:  $\text{Cu}(\text{dnpp})_2^+$  in acetonitrile (thin line) and  $[\text{Cu}(\text{dnpp})_2]\text{PF}_6$  in the solid state.

neopentyl groups produces additional steric contacts. Resulting interligand  $\gamma$ -methyl/ $\gamma$ -methyl interactions include a  $\text{C}(125)/\text{C}(226)$  contact at  $3.258(4) \text{ \AA}$  and a  $\text{C}(193)/\text{C}(293)$  interaction at  $3.421(4) \text{ \AA}$ . (The sum of the van der Waals radii of two methyl groups is nominally about  $4 \text{ \AA}$ .<sup>16</sup>) The packing diagram reveals a network of stacking interactions among the dnpp moieties, but the ligand–ligand overlap is modest. The closest intermolecular contacts among ring atoms are  $\text{C}(14)-\text{C}(14)$ ,  $3.5379(82) \text{ \AA}$ ;  $\text{C}(17)-\text{C}(17)$ ,  $3.5451(66) \text{ \AA}$ ;  $\text{C}(24)-\text{C}(24)$ ,  $3.6627(55) \text{ \AA}$ ; and  $\text{C}(27)-\text{C}(27)$ ,  $3.6377(155) \text{ \AA}$ .

**Absorption and Emission Data.** The extent of flattening is enough to have a significant impact on the spectral properties of the solid. For comparison, Figure 3 contains the absorption

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**Table 2.** Positional and Temperature Parameters (Å<sup>2</sup>) for [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>

atom	x	y	z	U (Å <sup>2</sup> )
Cu	0.26750(5)	0.25492(4)	0.24976(3)	0.04087(17)
N(11)	0.4157(2)	0.1590(2)	0.1841(2)	0.0398(10)
N(21)	0.2509(2)	0.3103(2)	0.35884(15)	0.0364(8)
N(110)	0.2703(3)	0.3661(2)	0.14806(15)	0.0392(10)
N(210)	0.1245(2)	0.1906(2)	0.3052(2)	0.0368(8)
C(12)	0.4738(3)	0.0560(3)	0.1995(2)	0.0488(12)
C(13)	0.5502(4)	0.0030(3)	0.1383(3)	0.0673(14)
C(14)	0.5739(4)	0.0569(4)	0.0642(3)	0.0748(18)
C(15)	0.5414(5)	0.2272(5)	-0.0279(3)	0.078(2)
C(16)	0.4848(5)	0.3302(5)	-0.0405(3)	0.077(2)
C(17)	0.3328(4)	0.4891(4)	0.0098(3)	0.0688(16)
C(18)	0.2450(4)	0.5320(3)	0.0676(2)	0.0629(16)
C(19)	0.2097(4)	0.4697(3)	0.1361(2)	0.0467(12)
C(22)	0.3030(4)	0.3783(3)	0.3799(2)	0.0467(12)
C(23)	0.2581(4)	0.4224(3)	0.4507(3)	0.0641(16)
C(24)	0.1643(4)	0.3928(4)	0.5016(3)	0.0706(14)
C(25)	0.0137(4)	0.2831(4)	0.5338(2)	0.0713(17)
C(26)	-0.0324(4)	0.2125(4)	0.5129(2)	0.0702(17)
C(27)	-0.0400(4)	0.1026(3)	0.4103(3)	0.0618(16)
C(28)	-0.0028(4)	0.0745(3)	0.3360(3)	0.0585(14)
C(29)	0.0756(3)	0.1225(2)	0.2812(2)	0.0461(12)
C(111)	0.4338(3)	0.2123(3)	0.1087(2)	0.0445(12)
C(112)	0.5179(4)	0.1647(4)	0.0473(2)	0.0595(14)
C(113)	0.3955(4)	0.3814(4)	0.0193(2)	0.0581(14)
C(114)	0.3637(3)	0.3236(3)	0.0917(2)	0.0420(12)
C(121)	0.4503(4)	-0.0018(3)	0.2824(3)	0.0606(14)
C(122)	0.5733(4)	-0.0636(3)	0.3402(3)	0.0680(16)
C(123)	0.6729(7)	-0.1532(6)	0.3051(4)	0.174(3)
C(124)	0.5177(6)	-0.1067(4)	0.4203(3)	0.104(3)
C(125)	0.6474(8)	0.0058(7)	0.3587(4)	0.143(4)
C(191)	0.1107(4)	0.5157(3)	0.1993(2)	0.0515(12)
C(192)	-0.0442(4)	0.5616(3)	0.1767(3)	0.0596(12)
C(193)	-0.0873(6)	0.4764(5)	0.1512(4)	0.103(3)
C(194)	-0.0791(6)	0.6551(5)	0.1085(4)	0.129(3)
C(195)	-0.1226(5)	0.5895(4)	0.2547(3)	0.091(2)
C(211)	0.1535(3)	0.2838(2)	0.4083(2)	0.0392(12)
C(212)	0.1104(4)	0.3202(3)	0.4825(2)	0.0538(12)
C(213)	0.0056(3)	0.1762(3)	0.4362(2)	0.0526(12)
C(214)	0.0930(3)	0.2147(2)	0.3823(2)	0.0398(12)
C(221)	0.4064(4)	0.4097(3)	0.3239(2)	0.0621(16)
C(222)	0.5581(4)	0.3698(3)	0.3529(3)	0.0670(16)
C(223)	0.6440(7)	0.3945(7)	0.2830(5)	0.160(5)
C(224)	0.6055(15)	0.2785(19)	0.4155(18)	0.243(16)
C(225)	0.575(2)	0.4598(17)	0.3948(15)	0.172(13)
C(226)	0.5909(11)	0.2508(9)	0.3542(9)	0.086(5)
C(227)	0.5815(15)	0.3900(14)	0.4327(10)	0.093(6)
C(291)	0.1125(4)	0.0958(3)	0.1970(2)	0.0555(14)
C(292)	-0.0016(4)	0.1248(3)	0.1307(3)	0.0629(16)
C(293)	-0.0771(8)	0.2398(5)	0.1169(4)	0.136(3)
C(294)	0.0698(6)	0.0968(5)	0.0510(3)	0.097(3)
C(295)	-0.1004(6)	0.0645(6)	0.1525(4)	0.124(3)
P	0.2629(2)	0.75322(9)	0.26068(8)	0.0782(5)
F(1A)	0.250(2)	0.6711(8)	0.3370(10)	0.141(7)
F(1B)	0.188(2)	0.6781(13)	0.3050(8)	0.124(7)
F(2A)	0.2470(18)	0.8249(14)	0.3274(13)	0.137(9)
F(2B)	0.172(3)	0.8431(10)	0.3020(13)	0.200(10)
F(3A)	0.369(2)	0.7129(17)	0.3326(8)	0.217(12)
F(3B)	0.4191(11)	0.7178(15)	0.2725(12)	0.187(8)
F(4A)	0.343(2)	0.6639(8)	0.2181(10)	0.137(6)
F(4B)	0.293(3)	0.6802(15)	0.1959(12)	0.178(11)
F(5A)	0.1074(10)	0.7893(18)	0.2562(10)	0.189(8)
F(5B)	0.1615(17)	0.7872(16)	0.1868(9)	0.192(8)
F(6A)	0.345(2)	0.8199(14)	0.2140(9)	0.142(10)
F(6B)	0.270(3)	0.8408(10)	0.1883(12)	0.164(8)

spectra of [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub> and [Cu(dmp)<sub>2</sub>]PF<sub>6</sub> in solution and the solid state. In solution the dmp complex exhibits a CT absorption maximum at 457 nm, whereas the dnpp complex gives its maximum at 445 nm. Both spectra have a shoulder at about 520 nm, on the long-wavelength side of the CT absorption maximum. In accord with the results of Shinozaki and Kaizu, who studied related salts,<sup>9</sup> the absorption spectrum of the dmp complex is very similar in solution and in the solid state. Here,

**Table 3.** Selected Interatomic Distances (Å) and Angles (deg) for [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>

Distances			
Cu—N(21)	2.057(2)	Cu—N(210)	2.064(2)
Cu—N(11)	2.059(2)	Cu—N(110)	2.068(3)
Angles			
N(21)—Cu—N(11)	138.88(10)	N(21)—Cu—N(110)	111.93(10)
N(21)—Cu—N(210)	82.74(10)	N(11)—Cu—N(110)	82.85(11)
N(11)—Cu—N(210)	113.59(10)	N(210)—Cu—N(110)	136.27(10)

**Table 4.** Room-Temperature Emission Data

system	$\lambda_{\max}$ (nm)	
	solid	CH <sub>2</sub> Cl <sub>2</sub> solution
[Cu(dspp) <sub>2</sub> ]PF <sub>6</sub>	628	650
[Cu(dnpp) <sub>2</sub> ]PF <sub>6</sub>	670	665
[Cu(dop) <sub>2</sub> ]PF <sub>6</sub>	645	673
[Cu(dbp) <sub>2</sub> ]PF <sub>6</sub>	620	670
[Cu(dmp) <sub>2</sub> ]PF <sub>6</sub>	665	690

the CT maximum occurs at a slightly longer wavelength in the solid-state spectrum. In contrast, the CT maximum of the dnpp complex shifts to around 425 nm in the solid-state spectrum. Even more dramatic is the increase in the relative intensity of the low-energy shoulder which also extends to much longer wavelengths. The solid-state emission data for the dnpp complex are also anomalous. Unlike any other member of the series, the dnpp complex exhibits a longer-wavelength emission maximum in the solid state than in solution (Table 4).

## Discussion

**Structure.** As anticipated, the structure reveals that the dnpp complex contains relatively long Cu—N bonds. However, the degree of flattening was a surprise because the conventional wisdom is that bulky substituents encourage the formation of a more nearly tetrahedral structure. On the other hand, for Cu—(NN)<sub>2</sub><sup>+</sup> systems with methyl substituents in the 2,9 positions, long Cu—N bond lengths tend to occur in flattened complexes.<sup>15</sup> The [Cu(dmp)<sub>2</sub>]NO<sub>3</sub> system, which represents one extreme, has an average Cu—N distance of 2.07 Å and an interligand dihedral angle of  $\theta_z = 72.4^\circ$ . This contrasts with [Cu(bcp)<sub>2</sub>]BF<sub>4</sub>·CH<sub>3</sub>OH, where the average Cu—N distance is 2.02 Å, and  $\theta_z = 87.6^\circ$ . (Here, bcp denotes the 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline ligand.) In line with this trend, the average Cu—N distance is 2.062 Å in [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>, and  $\theta_z = 75.0^\circ$ . Face-to-face contacts of ring substituents apparently account for the Cu—N bond elongation. In [Cu(dnpp)<sub>2</sub>]PF<sub>6</sub>, for example, the C(121)—C(291) and C(221)—C(191) distances between abutting methylene carbons are only 3.528(6) Å and 3.475(5) Å, respectively. As a calibration, recall that the nominal radius of a methyl group is about 2 Å.

In systems involving the Cu(dmp)<sub>2</sub><sup>+</sup> ion, the dihedral angle varies markedly with the counterion, because lattice forces, including stacking interactions, shape the conformation.<sup>15</sup> In the case of Cu(dnpp)<sub>2</sub><sup>+</sup>, intramolecular  $\gamma$ -methyl/ $\gamma$ -methyl interactions play an important role (see Figure 2). Even so, lattice forces appear to be ultimately responsible for the geometry because the complex adopts a more regular structure in solution, *vide infra*.

**Spectral Analysis.** The absorbance data from the solid, but not the solution, are consistent with a significantly flattened structure. As Parker and Crosby have pointed out, in *D*<sub>2d</sub> symmetry  $e(xz,yz) \rightarrow e(\text{NN})$ , HOMO-to-LUMO excitation of a Cu(NN)<sub>2</sub><sup>+</sup> system generates four singlet terms, but only one of the four possible spin-allowed transitions involved is likely to

exhibit significant absorption intensity.<sup>17</sup> The reason is that, ordinarily, only one component of the dipole moment operator provides significant oscillator strength, namely, the one that lies along the axis connecting the metal and ligand centers.<sup>18,19</sup> However, in the presence of a  $D_2$  flattening distortion, this component of the dipole moment operator connects other excited states to the ground state, and a shoulder with an identical polarization appears on the long-wavelength side of the principal CT transition.<sup>17</sup> As revealed in Figure 3, this “shoulder” actually dominates the visible spectrum of  $[\text{Cu}(\text{dnpp})_2]\text{PF}_6$  in the solid. Shinozaki and Kaizu have reported a similar effect on the solid-state absorption spectrum of  $[\text{Cu}(1,10\text{-phenanthroline})_2]\text{ClO}_4$  wherein the copper complex has similar low symmetry.<sup>9</sup> (See refs 8, 11, and 17 for detailed analyses of the absorption spectrum.) In contrast, the solution data provide barely any evidence for flattening of the dnpp complex as the free ion.

The emission data are also consistent with the existence of different ground-state structures in solution and the solid state. Indeed, the solid-state emission maxima in Table 4 show no correlation with the size of the substituent. Even more striking, the  $\text{Cu}(\text{dnpp})_2^+$  system exhibits almost the same emission maximum in the solid state and in solution. This unusual result suggests that the excited state has nearly the same structure in both phases.

## Conclusions

The crystal structure of  $[\text{Cu}(\text{dnpp})_2]\text{PF}_6$  reveals that the copper complex has a compact, flattened structure with an interligand dihedral angle of  $63.4(1)^\circ$ . Surprisingly, the dispositions of the neopentyl groups are such that each experiences steric interactions with *both* substituents of the opposite ligand. From spectral data, it is clear that lattice forces induce the flattening distortion and that this structure does not persist in solution. However, in light of the rigidity of the solid and the close match between the emission spectra from both phases, it is likely that the reported structure mimics the one that the vibrationally relaxed CT excited state adopts in fluid solution.

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**Supporting Information Available:** One X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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