© 2006 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 79, No. 3, 437–441 (2006)

Synthesis and Luminescence of New Cu(I) Complexes Containing a Binap Ligand and a Diimine Ligand

Ken Saito, Toshiaki Tsukuda, and Taro Tsubomura*

Department of Applied Chemistry, Seikei University, Kichijoji-Kitamachi, Musashino, Tokyo 180-8633

Received May 20, 2005; E-mail: tsubomura@st.seikei.ac.jp

A series of novel Cu(I) complexes with an *s*-binap ligand and a diimine ligand, [Cu(*s*-binap)(bpy)]PF_6, [Cu(*s*-binap)(phen)]PF_6, and [Cu(*s*-binap)(dmp)]PF_6, were synthesized, where bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dmp = 2,9-dimethyl-1,10-phenanthroline, and *s*-binap = (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. All three complexes show intense photoluminescence in the solid state, whereas [Cu(*s*-binap)(dmp)]PF_6 is a comparatively good emitter in CH_2Cl_2 solutions. These luminescence bands have been assigned to the emission from ^{3}MLCT states. The complexes [Cu(*s*-binap)(bpy)]PF_6 and [Cu(*s*-binap)(dmp)]PF_6 were characterized by X-ray structure analyses. Although the distorted tetrahedral structures around the central metals of the two complexes are similar, the photophysical properties of the dmp complex differ from those of the other complexes in solution. The structures and the photophysical properties of the three complexes have been discussed.

There has been increasing interest in the photophysics and photochemistry of Cu(I) complexes in the last few decades.[1–3] Mixed-ligand Cu(I) complexes containing diimine and diphosphine ligands represent an attractive class of compounds. We have been studying the synthesis and emissive properties of the mixed-ligand complexes, and found that the use of diphosphine chelates leads to the stabilization of the mixed-ligand compounds. Recently, McMillin and co-workers synthesized a Cu(I) complex with a diphosphine ligand, DPEphos (=bis[2-(diphenylphosphino)phenyl] ether). The complex shows strong luminescence and has a very long excited-state lifetime.[4] It suggests that using other diphosphine chelates is also effective to make strongly emissive compounds.

We reported that the complex [Pt(*s*-binap)$_2$] (*s*-binap = (*S*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) shows interesting photochemical and photophysical properties. The luminescent MLCT state based on the low-energy π^* orbitals of *s*-binap is characteristic of the [Pt(*s*-binap)$_2$] complex.[5–7] Since Cu(I) has the same d^{10} electronic arrangement as Pt(0), the photophysics of Cu(I) complexes containing an *s*-binap ligand are interesting.

We report here the synthesis and photophysical properties of three mixed-ligand Cu(I) complexes, [Cu(*s*-binap)(diimine)]$^+$. We use the term “diimine” to represent the ligands, bpy, phen, and dmp. In this paper, *s*-binap is used as the diphosphine ligand, which is abbreviated as binap.

Experimental

Materials. The preparation of the mixed-ligand complexes was conducted under an Ar atmosphere using standard Schlenk tube techniques. All reagents were obtained from commercial suppliers and used without further purification. The starting material, [Cu(MeCN)$_4$]PF_6, was prepared according to the published method.[8]

[Cu(binap)(dmp)]PF_6. [Cu(MeCN)$_4$]PF_6 (0.37 g, 1 mmol), dmp (2,9-dimethyl-1,10-phenanthroline) (0.22 g, 1 mmol), and (*S*)-(−)binap (0.62 g, 1 mmol) were dissolved in CH_2Cl_2 (15 mL). After stirring for 90 min at room temperature, the addition of diethyl ether to the solution of the complex gave a yellow powder of the mixed-ligand complex, [Cu(binap)(dmp)]PF_6. The complex was obtained by filtration, and dried in vacuo. Anal. Calcd for $C_{59}H_{46}CuF_6Cl_2N_2P_3$ ([Cu(binap)(dmp)]$PF_6 \cdot CH_2Cl_2$): C, 63.03; H, 4.12; N, 2.49%. Found: C, 63.34; H, 3.73; N, 2.95%.

Other mixed-ligand complexes were prepared from [Cu(MeCN)$_4$]PF_6, diimine and diphosphine in CH_2Cl_2 in a similar manner to that described above, where phen (1,10-phenanthroline) and bpy (2,2′-bipyridine) were used as diimine ligands.

[Cu(binap)(bpy)]PF_6: Anal. Calcd for $C_{54}H_{40}CuF_6N_2P_3$: C, 65.69; H, 4.08; N, 2.84%. Found: C, 65.34; H, 4.10; N, 2.65%.

[Cu(binap)(phen)]PF_6: Anal. Calcd for $C_{56}H_{42}CuF_6N_2P_3O$ ([Cu(binap)(phen)]$PF_6 \cdot H_2O$): C, 65.34; H, 4.11; N, 2.72%. Found: C, 65.53; H, 4.03; N, 2.73%.

Spectroscopic Measurement. The spectroscopic properties of the mixed-ligand complexes in the CH_2Cl_2 solution were measured using a quartz cell connected to a glass tube and a Teflon stop-cock. All samples were thoroughly deoxygenated by successive freeze–pump–thaw cycles. Absorption and luminescence spectra were measured with a Shimadzu UV-2100 spectrophotometer and a Shimadzu RF-5000 fluorometer, respectively. Luminescence decay-curves were measured on a laboratory-made apparatus; the sample was excited using a nitrogen laser (USHO AN-200) and the emission light was focused into a Jobin-Yvon H-20 monochromator equipped with a Hamamatsu R955 photomultiplier. The output of the photomultiplier was digitized by a HP 54510 digital oscilloscope and then downloaded to a PC.

Emission quantum yields, Φ, were measured in a deaerated (freeze–pump–thaw cycles) CH_2Cl_2 solution at 20 ± 1 °C with the use of [Ru(bpy)$_3$](PF$_6$)$_2$ in CH_3CN as a standard ($\Phi = 0.09$).[7] The emission spectra were corrected with a calibration function that was made with the use of *N*,*N*′-dimethyl-3-nitroaniline and 4-dimethylamino-4′-nitrostylbene as standard substances.[9]

Data Collection and Reduction for X-ray Crystallographic Analyses of [Cu(binap)(bpy)]PF_6 and [Cu(binap)(dmp)]$PF_6\cdot$

Published on the web March 8, 2006; DOI 10.1246/bcsj.79.437

$C_4H_{10}O$. Data were collected on an automated Rigaku AFC5S diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 23 °C. Three standard reflections were measured in every 150 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied. Calculations were carried out by using teXsan.[10] The single crystals for X-ray structural analysis were obtained by slow diffusion of hexane or ether for the bpy and dmp complexes, respectively, into the CH_2Cl_2 solution of the complexes. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-282440 for [Cu(binap)(bpy)]PF_6, CCDC-282439 for [Cu(binap)(dmp)]PF_6. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal Data of [Cu(binap)(bpy)]PF_6: $a = 16.461(3)$ Å, $b = 15.142(5)$ Å, $c = 22.371(3)$ Å, $\beta = 107.40(1)°$, $V = 5320(1)$ Å^3, space group = $P2_1$ (#4), $Z = 4$, $D_{\text{calcd}} = 1.250$ g cm^{-3}, $\omega - 2\theta$ scan method, No. of collected reflections = 16059, No. of unique reflections ($2\theta < 50.0°$) = 9741, $R_1 = 0.078$ ($I > 2\sigma(I)$), $wR_2 = 0.224$ (all data), GOF = 1.044, $\mu = 1.11$ mm^{-1}, highest peak and deepest hole in the last difference Fourier map were 0.66 and -0.42 e Å^{-3}, respectively.

Crystal Data of [Cu(binap)(dmp)]PF_6•$C_4H_{10}O$: $a = 11.944(1)$ Å, $b = 40.749(1)$ Å, $c = 10.561(1)$ Å, $V = 5140(7)$ Å^3, space group = $P2_12_12_1$ (#19), $Z = 4$, $D_{\text{calcd}} = 1.343$ g cm^{-3}, ω scan method, No. of collected reflections = 5554, No. of unique reflection ($2\theta < 60.0°$) = 5509, $R_1 = 0.0803$ ($I > 2\sigma(I)$), $wR_2 = 0.2425$ (all data), GOF = 0.975, $\mu = 0.58$ mm^{-1}, highest peak and deepest hole in the last difference Fourier map were 0.64 and -0.42 e Å^{-3}, respectively.

Structure Determination of [Cu(binap)(bpy)]PF_6 and [Cu(binap)(dmp)]PF_6. The structures were solved by a direct method and refined by full-matrix least-squares methods.[11] Hydrogen atoms were placed at the idealized positions, and the coordinates and the isotropic temperature factors were fixed. Anisotropic temperature factors were used for all non-hydrogen atoms except for the atoms shown below. The structure of [Cu(binap)(bpy)]PF_6 showed disorder in a phenyl group (C103–108 and C109–114). The phenyl carbon atoms were treated as rigid bodies. The occupancy ratio for both disordered phenyl groups was 50/50.

Results and Discussion

Crystal Structure Analysis of [Cu(binap)(bpy)]PF_6. The crystal of the complex consists of two [Cu(binap)(bpy)]$^+$ cations (Fig. 1) and two PF_6 anions in an asymmetric unit. The structures of the two complex ions are similar to each other. The coordination geometry of each of the Cu(I) atoms is best described as a distorted tetrahedron. The Cu–P distances (2.241(4), 2.232(5), 2.272(4), and 2.258(5) Å) are comparable to those found in other Cu(I) complexes containing diphosphine chelate ligands.[12,13] The Cu–N distances (2.07(1), 2.09(1), 2.05(1), and 2.03(2) Å) are also similar to other Cu(I) complexes containing diimine chelate ligands.[3,4,12,14,15] The two P–Cu–P angles of the binap chelate and the two N–Cu–N angles of the bpy chelate are (101.9(2) and 103.2(2)°) and (80.0(6) and 79.5(5)°), respectively. These values are typical for Cu(I) complexes containing diphosphine and/or diimine chelate ligand(s).[3,4,12–15] Other geometrical parameters around the Cu(I) atoms are listed in the caption of Fig. 1.

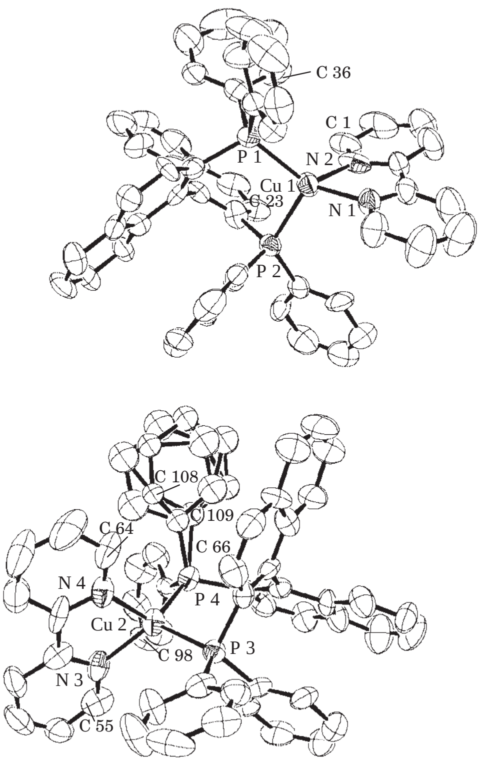

Fig. 1. Molecular structure of [Cu(binap)(bpy)]PF_6 (the counter ion and hydrogen atoms are omitted). Two crystallographically independent cations are shown. Selected bond lengths (Å) and angles (°): Cu1–P1 = 2.272(4), Cu1–P2 = 2.258(5), Cu1–N1 = 2.07(1), Cu1–N2 = 2.09(1), Cu2–P3 = 2.241(4), Cu2–P4 = 2.232(5), Cu2–N3 = 2.05(1), Cu2–N4 = 2.03(2); P1–Cu1–P2 = 101.9(2), N1–Cu1–N2 = 80.0(6), P3–Cu2–P4 = 103.2(2), N3–Cu2–N4 = 79.5(5).

Crystal Structure Analysis of [Cu(binap)(dmp)]PF_6. The structure is similar to that of [Cu(binap)(bpy)]PF_6. An asymmetric unit of the crystal of the complex consists of one [Cu(binap)(dmp)]$^+$ cation (Fig. 2), one $PF_6{}^-$ anion and one ether molecule. The Cu–P distances (2.292(4) and 2.290(4) Å) are slightly longer than those of [Cu(binap)(bpy)]$^+$, but comparable to those found in other Cu(I) complexes containing P, P chelate ligands, and the Cu–N distances (2.10(1) and 2.09(1) Å) compare well with other Cu(I) complexes containing diimine chelate ligands.[3,4,12–15] The P–Cu–P angles of the binap chelate and the N–Cu–N angles of the dmp chelate are 100.6(1) and 80.8(6)°, respectively. Other geometrical parameters around the Cu(I) atoms are listed in the caption of Fig. 2.

The non-bonding interactions are listed in Table 1. The table shows non-bonding C–C distances shorter than 3.90 Å. The carbon atoms C13 and C14 in the methyl group of dmp are close to some carbon atoms of the binap ligand. It is clear that the structure of [Cu(binap)(dmp)]$^+$ is more crowded around the copper atom of than [Cu(binap)(bpy)]$^+$. The long Cu–P distances in [Cu(binap)(dmp)]$^+$ compared with those in [Cu(binap)(bpy)]$^+$ may reflect the interaction.

Photophysical Properties. The UV spectra of the CH_2Cl_2 solution containing the [Cu(binap)(diimine)]$^+$ complexes are

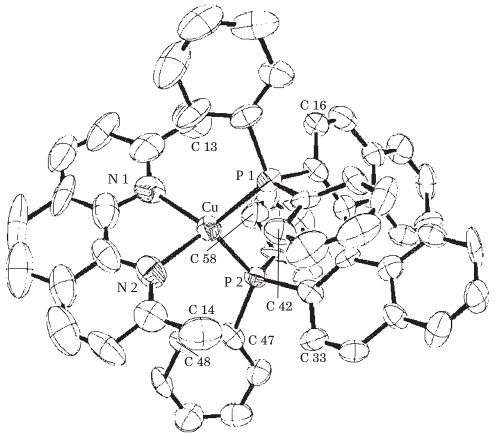

Fig. 2. Molecular structure of $[Cu(binap)(dmp)]PF_6$ (the counter ion and hydrogen atoms are omitted). Selected bond lengths (Å) and angles (°): Cu–P1 = 2.292(4), Cu–P2 = 2.290(4), Cu–N1 = 2.10(1), Cu–N2 = 2.09(1); P1–Cu–P2 = 100.6(1), N1–Cu–N2 = 80.8(6).

Table 1. Intramolecular Non-Bonding C–C Distances[a)]

Complex			
$[Cu(binap)(bpy)]PF_6$		$[Cu(binap)(dmp)]PF_6$	
Atoms	Distance/Å	Atoms	Distance/Å
C1–C36	3.35(3)	C13–C36	3.39(3)
C1–C23	3.58(3)	C13–C16	3.56(3)
C55–C98	3.69(3)	C13–C35	3.57(3)
C64–C108	3.51(3)	C13–C58	3.65(3)
C64–C66	3.55(3)	C14–C33	3.46(3)
C64–C109	3.87(4)	C14–C42	3.61(2)
		C14–C48	3.82(2)
		C14–C47	3.86(3)

a) Intramolecular non-bonding C–C distances shorter than 3.9 Å. The carbons shown in left of hyphen are those contained in the diimine ligand, and those shown in right of hyphen are contained in the binap ligand. C13 and C14 are the carbons of the methyl group in dmp.

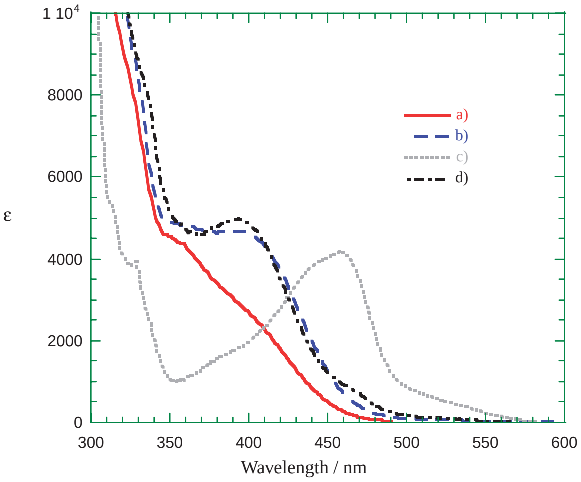

Fig. 3. Room-temperature electronic absorption spectra of a) = $[Cu(binap)(bpy)]PF_6$, b) = $[Cu(binap)(phen)]PF_6$, c) = $[Cu(dmp)_2]PF_6$, and d) = $[Cu(binap)(dmp)]PF_6$. These spectra are measured in degassed CH_2Cl_2.

presented in Fig. 3. A distinct absorption band at 393 nm with a small shoulder at 457 nm is found for $[Cu(binap)(dmp)]^+$. The absorption bands of $[Cu(diimine)_2]^+$ were extensively studied, and they are typically observed at 440–460 nm ($[Cu(phen)_2]^+$, 440 nm; $[Cu(dmp)_2]^+$, 457 nm; and $[Cu(tmbp)_2]^+$, 454 nm (tmbp = 4,4′,6,6′-tetramethyl-2,2′-bipyridine)). The bands have been assigned as MLCT (Cu(d) → diimine(π^*)) transitions. It has been reported that substitution of the diimine chelate by a phosphine ligand causes a blue shift of the MLCT band: e.g., 365 nm for $[Cu(phen)(PPh_3)_2]^+$, 383 nm for $[Cu(dmp)(DPEphos)]^+$, and 400 nm for $[Cu(dmp)(dppe)]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane).[3] The absorption maximum of $[Cu(binap)(dmp)]^+$ (393 nm) is blue-shifted from that of $[Cu(dmp)_2]^+$, and the intensity of the band ($\varepsilon = 5200$ $M^{-1}\,cm^{-1}$) is similar to those of the $[Cu(diimine)_2]^+$ complexes. Therefore, the absorption band presented at 393 nm is characterized as MLCT involving the π^* orbital of the dmp ligand of the mixed-ligand complex. For the complexes $[Cu(binap)(bpy)]^+$ and $[Cu(binap)(phen)]^+$, absorption bands of moderate intensities ($\varepsilon = 3000$–$5000\,M^{-1}\,cm^{-1}$) are observed in the region 350–450 nm, which are also assigned to the MLCT transitions.

The real species of the mixed-ligand complexes present in a CH_2Cl_2 solution would not be simple, because Cu(I) is known to be labile in the solution. Since CH_2Cl_2 cannot act as a ligand, simple ligand dissociation, i.e. substitution with a solvent molecule, seems unlikely. Therefore, the following disproportionation is the most probable reaction:

$$2[Cu(binap)(diimine)]^+ \rightleftharpoons [Cu(diimine)_2]^+ + [Cu(binap)_2]^+. \quad (1)$$

The formation of binuclear complexes is another possibility as shown in the other diphosphine complexes,[15,16] but binap is not likely to act as a bridging ligand. If the above disproportionation reaction occurs, an absorption band of $[Cu(diimine)_2]^+$ should be observed in the 450 nm region. However, the absorption spectra of the complexes all show very low absorption intensities at 450 nm. Therefore, the concentration of $[Cu(diimine)_2]^+$ should be significantly low when compared with that of the mixed-ligand complex. On the basis of the above consideration, we concluded that the major species present in each solution was the mononuclear mixed-ligand complex, $[Cu(binap)(diimine)]^+$.

The emission spectra of the solid-state $[Cu(binap)(diimine)]PF_6$ are presented in Fig. 4. In the solid state, all three complexes, $[Cu(binap)(dmp)]PF_6$, $[Cu(binap)(bpy)]PF_6$, and $[Cu(binap)(phen)]PF_6$, are strong emitters. The bpy and phen complexes exhibit a slightly higher intensity in the emission bands than the dmp complex. The emission maxima of the three complexes are 558, 594, and 572 nm, respectively.

Since the energies of the emission bands are comparable to those of $[Cu(dmp)(PPh_3)_2]^+$ (560 nm) and $[Cu(dmp)(dppe)]^+$ (630 nm),[3] and the emissive states of the latter two complexes were assigned to ^{3}MLCT, the emission of the binap complexes should originate from the ^{3}MLCT states.

The emission spectra of the CH_2Cl_2 solutions containing the $[Cu(binap)(dmp)]^+$ complexes (1×10^{-5} M) and $[Cu(binap)(bpy)]^+$ complexes (1×10^{-4} M) are presented in Fig. 5. In

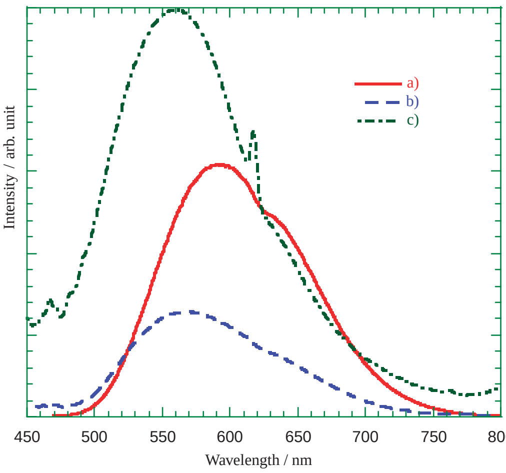

Fig. 4. Room-temperature solid-state emission spectra of a) = [Cu(binap)(bpy)]PF$_6$, b) = [Cu(binap)(phen)]PF$_6$, and c) = [Cu(binap)(dmp)]PF$_6$ ($\lambda_{ex} = 310$ nm).

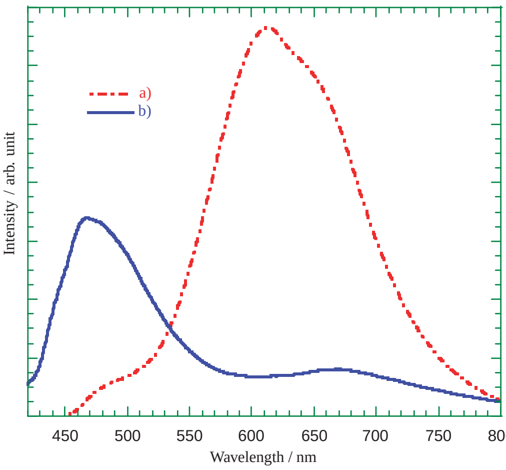

Fig. 5. Room-temperature solution-state emission spectra of a) [Cu(binap)(dmp)]$^+$ (1×10^{-5} M) and b) [Cu(binap)(bpy)]$^+$ (1×10^{-4} M) measured in degassed CH_2Cl_2 ($\lambda_{ex} = 370$ nm).

contrast to the solid-state spectra, the three complexes show completely different luminescence. [Cu(binap)(dmp)]$^+$ has a comparatively strong emission band centered at 613 nm. The emission maximum of [Cu(binap)(dmp)]$^+$ in the solution state is red-shifted ca. 50 nm from that of the solid state, and the band is blue-shifted from that of [Cu(dmp)$_2$]$^+$. The quantum yield (Φ) of luminescence of [Cu(binap)(dmp)]$^+$ is $1.0 \pm 0.2\%$ in the CH_2Cl_2 solution; the value is the same as the reported value for [Cu(dmp)(dppe)]$^+$.[4] The quantum yield is much larger than that of [Cu(dmp)(PPh$_3$)$_2$]$^+$. A single exponential decay ($\tau = 600$ ns) was observed for [Cu(binap)(dmp)]$^+$. The value indicates that the MLCT state has a triplet character.

The intensity of the luminescence of [Cu(binap)(bpy)]$^+$ and [Cu(binap)(phen)]$^+$ in a CH_2Cl_2 solution is very low when the concentrations of the complexes are low (1×10^{-5} M). In Fig. 5, we show the luminescence spectrum of the solution containing [Cu(binap)(bpy)]$^+$ in high concentration (1×10^{-4} M). The luminescence spectrum of the solution of [Cu(binap)(bpy)]$^+$ consists of two bands. The low-intensity band (670 nm) is assigned to the MLCT band of the mixed-ligand complex. In addition to the 670 nm band, there is an additional band at 467 nm. The emission maximum of [Cu(binap)(bpy)]$^+$ in the solution state is red-shifted from that of the [Cu(binap)(dmp)]$^+$, which is similar to that of the solid state. The high-energy emission is assigned to the π–π^* transition of the binap ligand.[17] These data show that some amounts of [Cu(binap)$_2$]$^+$ and/or free binap should be present in the solution of [Cu(binap)(bpy)]$^+$, although the dominate species must be the mixed-ligand complex, which has already been discussed above. Since the absorption intensity of the solution of [Cu(binap)(dmp)]$^+$ at 460 nm is not 0, existence of the binap ligand or [Cu(binap)$_2$]$^+$ is also suggested in the solution. However, the MLCT emission of the mixed-ligand complex, [Cu(binap)(dmp)]$^+$, is dominant in the luminescence spectra of the solution.

The spectrum of the MLCT luminescence in the solution of [Cu(binap)(phen)]$^+$, which is not shown in the figure, consists of bands similar to those observed for [Cu(binap)(bpy)]$^+$, and the intensities of the bands are also very weak. We could not get reliable data on the quantum yields of the emission of [Cu(binap)(bpy)]$^+$ and [Cu(binap)(phen)]$^+$, because of 1) low intensity of the emission and 2) presence of two emissive species in the spectrum.

The above results show that the MLCT emission is severely quenched for the bpy and phen complexes in solution. This is explained by a solvent-induced exciplex quenching. This quenching mechanism, which involves a transient increase in the coordination number of the copper center, is widely found for the CT excited state of copper(I) complexes.[18]

An important feature of [Cu(binap)(dmp)]$^+$ is that the diimine ligand has methyl groups at the 2,9-positions. The role of the substituents on the luminescence properties of the complexes has been discussed in detail.[1,2,18] The methyl groups at the 2,9-positions resist the structural distortion of the complex in the excited state. At the same time, the steric bulkiness around the metal-center becomes large because of the methyl groups at the 2,9-positions, and prevent [Cu(binap)(dmp)]$^+$ reactions with the solvent molecules. These effects should prevent the [Cu(binap)(dmp)]$^+$ complex from quenching of the luminescence.

In this work, we synthesized a series of [Cu(binap)(diimine)]$^+$ complexes, and an X-ray study clarified the steric crowdedness of the [Cu(binap)(dmp)]$^+$ complex. The dmp complex only shows relatively intense emission in solution, whereas all three complexes are good emitters in the solid state. The steric crowdedness of the dmp complex should also contribute to the photophysical properties of [Cu(binap)(dmp)]$^+$.

References

1 D. R. McMillin, K. M. McNett, *Chem. Rev.* **1998**, *98*, 1201.

2 D. R. McMillin, J. R. Kirchhoff, K. V. Goodwin, *Cood. Chem. Rev.* **1985**, *64*, 83.

3 D. G. Cuttell, S.-M. Kuang, P. E. Fanwick, D. R. McMillin, R. A. Walto, *J. Am. Chem. Soc.* **2002**, *124*, 6.

4 S.-M. Kuang, D. G. Cuttell, D. R. McMillin, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* **2002**, *41*, 3313.

5 H. Tominaga, K. Sakai, T. Tsubomura, *J. Chem. Soc., Chem. Commun.* **1995**, 2273.

6 T. Tsubomura, M. Abe, M. Tarutani, H. Yamada, T. Tsukuda, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 2151.

7 Z. A. Siddique, T. Ohno, K. Nozaki, T. Tsubomura, *Inorg. Chem.* **2004**, *43*, 663.

8 G. J. Kubas, *Inorg. Synth.* **1979**, *19*, 90.

9 E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger, W. Voss, *Z. Anal. Chem.* **1959**, *17*, 1.

10 *teXsan: Crystal Structure Analysis Package*, Molecular Structure Corporation, **1989** and **1992**.

11 G. M. Sheldrick, *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

12 T. Okubo, S. Kitagawa, M. Kondo, H. Matuzaka, T. Ishii, *Angew. Chem., Int. Ed.* **1999**, *38*, 931.

13 a) I. V. Kourkine, S. V. Maslennikov, R. Ditchfield, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, *Inorg. Chem.* **1996**, *35*, 6708. b) S. Kitagawa, M. Kondo, S. Kawata, S. Wada, M. Maekawa, M. Munakata, *Inorg. Chem.* **1995**, *34*, 1455. c) A. P. Gaughan, R. F. Ziolo, Z. Dori, *Inorg. Chem.* **1971**, *10*, 2776. d) P. Fiaschi, C. Floriani, M. Pasquali, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.* **1986**, *25*, 462. e) A. P. Gaughhan, K. S. Bowman, Z. Dori, *Inorg. Chem.* **1972**, *11*, 601. f) A. L. Airey, G. F. Swiegers, A. C. Willis, S. B. Wild, *Inorg. Chem.* **1997**, *36*, 1588. g) D. J. Darensbourg, C.-S. Chao, J. H. Reibenspies, C. J. Bischoff, *Inorg. Chem.* **1990**, *29*, 2153. h) G. Doyle, K. A. Eriksen, D. Van Engen, *J. Am. Chem. Soc.* **1985**, *107*, 7914. i) E. W. Ainscough, E. N. Baker, M. L. Brader, A. M. Brodie, S. L. Ingham, J. V. Hanna, P. C. Healy, *J. Chem. Soc., Dalton Trans.* **1991**, 1243. j) E. W. Ainscough, E. N. Baker, A. M. Brodie, C. A. Smith, *J. Chem. Soc., Dalton Trans.* **1989**, 2167. k) G. A. Abakumov, V. K. Cherkasov, A. V. Karashilina, I. L. Eremenko, S. E. Nefdov, *Russ. Chem. Bull.* **1998**, *47*, 2262. l) B. Mohr, E. E. Brooks, N. Rath, E. Deutsch, *Inorg. Chem.* **1991**, *30*, 4541.

14 a) E. W. Ainscough, E. N. Baker, M. L. Brader, A. M. Brodie, S. L. Ingham, J. V. Hanna, P. C. Healy, *J. Chem. Soc., Dalton Trans.* **1991**, 1243. b) S. Yao, X. Fang, K. A. Jørgensen, *Chem. Commun.* **1998**, 2547. c) P. Coppens, I. Vorontsov, T. Graber, A. Y. Kovalesky, Y. Chen, G. Wu, M. Gembicky, I. V. Novozhilova, *J. Am. Chem. Soc.* **2004**, *126*, 5981. d) T. Sato, H. Takeda, K. Sakai, T. Tsubomura, *Inorg. Chim. Acta* **1996**, *246*, 413. e) M. K. Eggleston, P. E. Fanwick, A. J. Pallenberg, D. R. McMillin, *Inorg. Chem.* **1997**, *36*, 4007. f) J. R. Kirchhoff, D. R. McMillin, W. R. Robinson, D. R. Powell, A. T. McKenzie, S. Chen, *Inorg. Chem.* **1985**, *24*, 3928.

15 T. Tsubomura, N. Takahashi, K. Saito, T. Tsukuda, *Chem. Lett.* **2004**, *33*, 678.

16 E. W. Ainscough, E. N. Baker, M. L. Brader, A. M. Brodie, S. L. Ingham, J. V. Hanna, P. C. Healy, *J. Chem. Soc., Dalton Trans.* **1991**, 1243.

17 Preliminary experiment shows that $[Cu(binap)_2]^+$ and free binap shows similar luminescence in solution.

18 a) M. K. Eggleston, D. R. McMillin, K. S. Koenig, A. J. Pallenberg, *Inorg. Chem.* **1997**, *36*, 172. b) C. E. A. Palmer, D. R. McMillin, *Inorg. Chem.* **1987**, *26*, 3837. c) D. J. Casadonte, Jr., D. R. McMillin, *Inorg. Chem.* **1987**, *26*, 3950.