Structure and Luminescence of a Dinuclear Copper Complex Bridged by a Diphosphine Ligand

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A new dinuclear copper(I) complex containing two 2,9-dimethylphenanthroline ligands and a bridging diphosphine ligand has been prepared. The structure of the complex was characterized by X-ray crystallography. A considerable blue shift was observed for the solid-state photoluminescence and absorption spectra of the complex as compared with the mononuclear mixed-ligand complex.

Luminescent copper(I) complexes containing diimine ligands are of considerable interest because of rich photophysical and photochemical properties.[1] Potential applications of these complexes for photovoltaic cell or electroluminescent display have been explored.[2] Extensive studies reported by McMillin's group and other groups have made clear the properties and electronic structures of the luminescent metal-to-ligand charge transfer (MLCT) states of the copper(I) diimine complexes.[3]

Recently, remarkable luminescent properties of the mixed-ligand copper(I) complexes containing a diphosphine chelate and a dmp ligand have been reported. For example, the orange-colored $[Cu(dppe)(dmp)]^+$ complex (dppe = bis(diphenylphosphino)ethane, dmp = 2,9-dimethyl-1,10-phenanthroline) shows photoluminescence in CH_2Cl_2 solution with a quantum yield of 1%.[4] As a part of our study of luminescent metal complexes,[5] we have been studying the structure and photophysical properties of copper(I) complexes. We found that two types of the mixed-ligand complexes containing dppe and dmp ligands can be obtained when different solvents were used in the synthesis of the complexes. In this work, the structure and properties of the yellow-colored copper complex have been examined.

The mixed-ligand complexes were prepared as follows. To a solution of $[Cu(CH_3CN)_4]PF_6$ (0.5 mmol) in acetone (20 mL) were added dmp (0.5 mmol) and dppe (0.5 mmol). Stirring for 1 h at room temperature and concentration of the solution afforded $[Cu(dppe)(dmp)]PF_6$ (**1**) as orange crystals.[6] On the other hand, if the similar reaction was performed in acetonitrile, a yellow powder was obtained. Recrystallization of the yellow complex (**2**) from acetonitrile–diethyl ether gave yellow crystals.[7] The structure of **2** is shown in Figure 1.[8] The complex has a dinuclear structure in which a dppe ligand bridges the two copper(I) atoms. Although there are a number of crystallographic studies of copper(I) complexes containing dppe as a bridging ligand, this is the first example of the dinuclear copper complex containing dppe and diimine ligands. The complex has a center of inversion, which locates between the two methylene carbon atoms of the dppe ligand. Each of the two copper(I) atoms is coordinated by a bidentate dmp chelate, a bridged dppe ligand and an acetonitrile ligand. The coordination geometry of the copper(I) atom is a distorted tetrahedron. The N–Cu–N angle of the dmp chelate is 79.6(2)°, and N–Cu–P angles are in the range of 115.7–119.8°. The N (dmp)–Cu–N (acetonitrile) angles are near the ideal tetrahedral angle. The bond lengths of Cu–P and Cu–N (dmp) are 2.224(1) Å and 2.10 Å (the average of the two Cu–N bonds), respectively. These values are typical for Cu(I) complexes.[4] The Cu–N (acetonitrile) bond length (2.015(3) Å) is notably shorter than that of the Cu–N (dmp) bonds.[9] An intermolecular stacking interaction of dmp ligands is observed in the crystal. The nearest interatomic C···C distance between two dmp ligands is 3.410(7) Å. Similar intermolecular stacking of dmp ligands has been reported.[10] The interaction seems not to influence the photophysical properties of the copper complex.

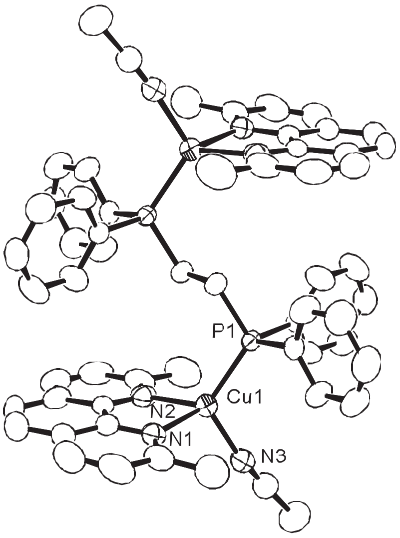

Figure 1. The structure of $[Cu_2(dmp)_2(dppe)(CH_3CN)_2]^{2+}$.

The solid-state photoluminescence spectra of the dinuclear complex **2** and the mononuclear complex **1** are shown in Figure 2. The dinuclear complex shows an emission maximum at 550 nm, whereas the monomer at 600 nm. The emission bands are reasonably assigned to MLCT transitions.[4] The diffusion reflectance spectra also show the 50-nm blue shift for the dinuclear complex. Phosphine ligands are known to give strong crystal field in metal complexes. The blue shift may be due to the weakened crystal field in the dinuclear complex (N_3P_1 coordination) compared with that in the mononuclear (N_2P_2 coordination) complex. The coordination of the acetonitril molecule causes a decrease in the energy of the higher-energy occupied d orbitals.

The absorption spectra of the **1** and **2** in solution are shown in Figure 3. Contrary to the above result, the absorption and emission spectra of the two complexes in CH_2Cl_2 solution are similar to each other. The bands centered at 400 nm are typical

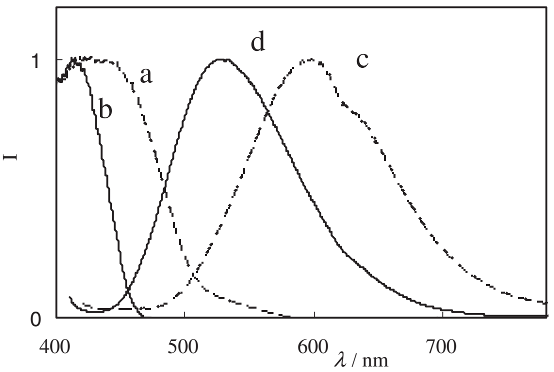

Figure 2. The absorption spectra of **1** (a) and **2** (b), and emission spectra of **1** (c) and **2** (d). All spectra were recorded in the solid state at room temperature. Absorption and emission intensities (I) are in arbitrary units. The absorption spectra were obtained by Kubelka–Munk transformation of the diffuse reflectance spectra of the powdered samples.

for the MLCT band of the [Cu(dmp)(diphosphine)]$^+$ complexes.[4] The shoulder found at 460 nm presumably shows the existence of [Cu(dmp)$_2$]$^+$ complex.[11]

The ^{31}P NMR spectrum (160 MHz) of **2** measured in CD_2Cl_2 consists of a broad singlet[12] centered at -8.1 ppm and a septet at -145 ppm which is attributable to the $PF_6{}^-$ ion. The ^{31}P NMR of **1** shows a broad singlet at the same chemical shift as observed for **2** associated with a very small and broad signal at 6.2 ppm. The results indicate that the dominant phosphine-containing species in the solutions of **1** and **2** are identical.

As a conclusion, the dinuclear complex shows a significant blue shift of the emission spectra compared with the mononuclear complex in the solid state. This work shows that the choice of solvents is important to the structure, nuclearity and photophysical properties of the copper complexes. Although the structure of the species in solution needs further study, the spectral data suggest that the emissive species in the CH_2Cl_2 solution of **2** is identical with the mixed-ligand mononuclear complex, **1**. Researches on the luminescence of the complexes containing a series of diphosphines as a bridge ligand are now in progress.

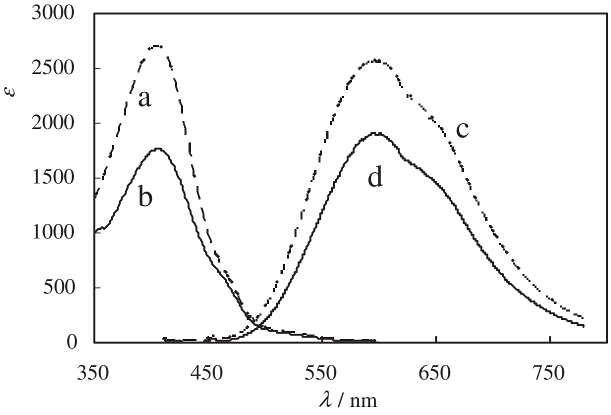

Figure 3. The absorption spectra of **1** (a) and **2** (b) in CH_2Cl_2. The emission spectra of the CH_2Cl_2 solution of **1** (c) and **2** (d). All spectra are measured at room temperature. Emission intensities (I) are in arbitrary units.

References and Notes

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6 Preliminary X-ray study shows that the orange complex has a mononuclear structure, [Cu(dppe)(dmp)]PF_6.

7 Anal. Found: C, 52.92; H, 4.12; N, 6.31. Calcd for [Cu_2(dmp)$_2$(dppe)(CH_3CN)$_2$](PF_6)$_2$: C, 53.01; H, 4.14; N, 6.40.

8 A yellow crystal ($C_{68}H_{66}N_8P_4F_{12}Cu_2$) recrystallized from an acetonitrile–benzene mixed solvent was investigated at 295 K on a Rigaku AFC-5S diffractometer ($\lambda = 0.71069$ Å). $a = 12.721(4)$ Å, $b = 13.501(4)$ Å, $c = 10.587(4)$ Å, $\alpha = 92.44(3)°$, $\beta = 92.29(3)°$, $\gamma = 108.06(2)°$, $V = 1724.4(9)$ Å^3. $D_{\text{calcd}} = 1.57$ g/cm^3, $Z = 1$, space group $= P\bar{1}$. Of the 8333 reflections which were collected, 7906 were unique ($R_{\text{int}} = 0.027$). $\mu = 7.9\,\text{cm}^{-1}$. The structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were fixed except those on methyl groups, which are refined using a riding model. The final cycle of full-matrix least-squares refinement was based on $|F|^2$ of all unique reflections and 428 variables. $R_1 = 0.1437$ (0.059 for $F_o > 4\sigma(F_o)$), $Rw_2 = 0.1539$, GOF $= 1.01$, Max.shift/esd $= 0.06$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 235471. Copies of the data can be obtained free of charge via 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; or deposit@ccdc.cam.ac.uk).

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