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Luminescence of Copper(I) Dinuclear Complexes Bridged by Diphosphine Ligands

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Mixed-ligand dinuclear Cu(I) complexes containing both diimine and diphosphine ligands have demonstrated interesting photophyisical properties; the complexes are emissive in solution at room temperature, even with 1,10-phenanthroline (phen) lacking a 2,9-substituted group.

Much attention has been paid to emissive copper(I) complexes containing polypyridine and/or phenanthroline ligands.[1] They have been considered for the practical components of chemical sensors, display devices, and solar-energy conversion schemes.[2] Extensive studies on the photophysical properties of the complexes have been reported by McMillin and other groups,[3,4] and theoretical interpretation of $[Cu(diimine)_2]^+$ (In this paper, "diimine" shows the chelate ligand containing the diimine moiety, e.g. phenanthroline.) type complexes have also been studied.[5] Recently, some mixed-ligand Cu(I) complexes involving both imines and phosphines have been reported as candidates for good emitters.[3] $[Cu(dmp)(DPEphos)]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline and DPEphos = bis[2-(diphenylphosphino)phenyl]ether) exhibits on unprecedented high quantum yield and long lifetime in CH_2Cl_2 at room temperature.[4]

The luminescence of Cu(I) complexes with 1,10-phenanthroline (phen) is generally weak, e.g. luminescence of $[Cu(phen)_2]^+$ is not observed, even in low temperature glass.[2a] Only a small number of luminescent Cu(I) complexes of phen have been reported. It is well-known that 2,9-substitution on the phen ligand is very effective to suppress emission quenching since introduction of steric bulkiness prevents geometric relaxation in solution and/or solvent attack in donor media. Actually, the emission yield for $[Cu(dmp)(PPh_3)_2]^+$ ($\Phi = 0.14\%$) is ca. fifty times stronger than that of $[Cu(phen)(PPh_3)_2]^+$ ($\Phi = 0.003\%$) in methanol.[3]

Some mixed-ligand dinuclear Cu(I) complexes bridged by diphosphine have been reported.[6–8] $[\{Cu(phen)\}_2(\mu\text{-dppm})_2](PF_6)_2$ (dppm = bis(diphenylphosphino)methane), prepared by Kitagawa et al.,[6] has a similar coordination environment around the metal to that of mononuclear mixed-ligand complexes. However, the luminescence of such Cu(I) dinuclear complexes has not been studied. We report here the luminescence of the dinuclear complex and a new, structurally similar complex with bis(diphenylphosphino)amine (dppa) in solution.

Treatment of $[Cu(CH_3CN)_4]PF_6$ with equimolar amounts of 1,10-phenanthroline and dppm in acetone readily gave the dinuclear copper complex, $[\{Cu(phen)\}_2(\mu\text{-dppm})_2](PF_6)_2$ (**1**). The use of 2,2′-bipyridine (bpy) and 4,7-dimethyl-1,10-phenanthroline (4,7-dmp) instead of phen gave the corresponding complexes $[\{Cu(bpy)\}_2(\mu\text{-dppm})_2](PF_6)_2$ (**2**) and $[\{Cu(4,7\text{-dmp})\}_2(\mu\text{-dppm})_2](PF_6)_2$ (**3**). $[\{Cu(phen)\}_2(\mu\text{-dppa})_2](PF_6)_2$ (**4**) can be obtained by a similar method. Elemental analysis supports the formation of the mixed-ligand complexes. Since dppm or dppa has only one methylene or aza group between the two phosphorus donors, bridging coordination by the ligands is favored rather than chelate coordination. Attempts to prepare similar complexes by using dmp or 2,2′-biquinoline as diimine ligands were unsuccessful.

X-ray analysis of the pale yellow crystals of **4** is shown in Fig. 1. An inversion center is located at the center of the dinuclear complex. Each copper atom was coordinated by a phen chelate and two phosphorus atoms of the bridging dppa ligands. The coordination geometry around the copper atoms is described as a distorted tetrahedron donated by two phosphorus and two nitrogen atoms. This structure is similar to that of **1**.[6] Selected bond distances and angles are summarized in Table 1. The Cu–P and Cu–N distances are almost similar to those of generally reported copper(I) complexes containing phosphine and diimine.[3,4,6–8] The angle of P(1)–Cu–P(2)* is 131.68(5)°, which is considerably larger than that of the corresponding mononuclear complex, $[Cu(phen)(PPh_3)_2]^+$ (115.44(4)°),[3c] but similar to that of **1** (134.34(9)°).[6] One notable difference between **1** and **4** is that the Cu···Cu distance of **4** (4.04 Å) is much shorter than that of **1** (4.74 Å). The shortening is accompanied by a more staggered conformation of the Cu–dppa framework

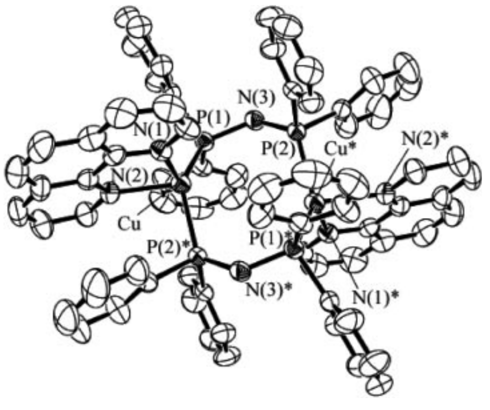

Fig. 1. An ORTEP structure of the dinuclear complex cation, $[\{Cu(phen)\}_2(\mu\text{-dppa})_2]^{2+}$.

Table 1. Selected Bond Lengths (Å) and Angles (°) for $[\{Cu(phen)\}_2(\mu\text{-dppa})_2]^{2+}$

Cu–P(1)	2.238(1)	Cu–P(2)*	2.282(1)
Cu–N(1)	2.080(3)	Cu–N(2)	2.137(3)
P(1)–Cu–P(2)*	131.68(5)	N(1)–Cu–N(2)	79.8(1)
P(1)–Cu–N(1)	116.3(1)	P(1)–Cu–N(2)	111.6(1)
P(2)*–Cu–N(1)	106.7(1)	P(2)*–Cu–N(2)	96.1(1)
P(1)–N(3)–P(2)	128.2(2)		

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for **4**; the torsion angle of P(1)–Cu···Cu*–P(2) is 65° for **4**, which is considerably larger than that for **1** (25°). The structural difference between the complexes may be governed by a delicate balance between the electronic effect of metal or donor ligands and the steric requirements of the bulky ligands.[7] It is expected that such a short Cu···Cu distance of these dinuclear complexes bridged by dppm or dppa causes an increase of steric hindrance between the diphenylphosphino groups and the phenanthroline ligands. This may be the reason why a similar complex can not be prepared using dmp.

In the ^{1}H NMR spectrum of **4**, the signals of the phen moiety were shifted to a higher field when compared with the free phen ligand. Especially, an upfield shift of 2,9-H by 0.65 ppm was observed. It suggests that the phen ligand undergoes a ring current effect of the coordinated dppa. Since the phenyl protons also undergo the same effect due to the phen ligands, upfield shifts by ca. 0.1 ppm were observed. As previously reported, this interaction is characteristic of the dimeric structure.[6]

The photophysical properties of the copper dinuclear complexes in dichloromethane are shown in Fig. 2 and Table 2. There are absorption bands of moderate intensity ($\varepsilon = 5 \times 10^3$ mol^{-1} dm^3 cm^{-1}) in the UV region. Each spectrum has an absorption maximum or a shoulder band at ca. 360 nm, except for the bpy complex (ca. 340 nm). The Cu–diimine MLCT bands are known to be in the region 400–360 nm for mononuclear Cu–P_2N_2 complexes.[3,4] The absorption bands are shifted to higher energies in the dinuclear complexes, since considerably large P–Cu–P angles lead to an increase of d–σ^* interactions in these complexes and enhancement of the CT excitation energy.[9]

All dinuclear Cu–P_2N_2 complexes effectively emit luminescence in CH_2Cl_2 solution even though they have only phen ligands with no 2,9-substituents. The emission maxima of **1**–**3** range from 610 to 630 nm. The emission maximum of **4** is shifted to a higher energy (565 nm) than that of **1** though MLCT absorption bands for both complexes are similar. The difference in the Stokes shifts between **1** and **4** shows the greater structural rigidity of **4**, arisen from a shorter Cu···Cu length. The smaller Stokes shift observed for **4** suggests that the geometric relaxation[10] in the excited states resulting from tetragonal fluttering motion is more effectively inhibited due to the steric requirement of the dinuclear structure.

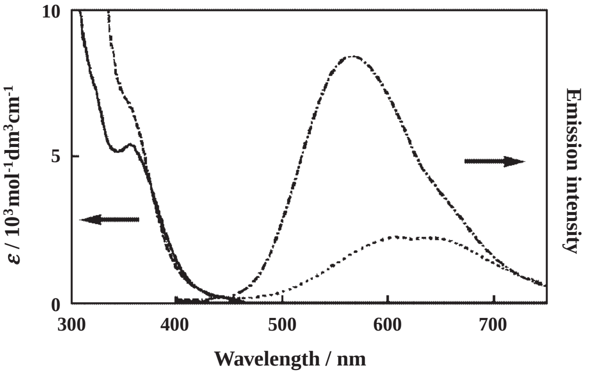

Fig. 2. Absorption spectra of **1** (solid line) and **4** (broken line), and emission spectra of **1** (dotted line) and **4** (dash-dotted line).

Table 2. Photophysical Properties for Copper Dinuclear Complexes

Complex	λ_{abs}/nm (ε/10^3 mol^{-1} dm^3 cm^{-1})	λ_{em}/nm	τ/µs	Φ/10^{-3}
1	355 (5.0)	613, 644	0.36	1.3
2	338 (sh, 4.9)	604, 644	0.14	0.31
3	354 (sh, 6.2)	617	0.71	2.1
4	355 (sh, 6.8)	565	0.43	1.4

The emission lifetime of **1** in CH_2Cl_2 is 0.36 µs, which is longer than that of [Cu(phen)(PPh$_3$)$_2$]$^+$ (0.22 µs). The quantum yield of **1** is 1.3×10^{-3}, which is comparable to that of [Cu(phen)(DPEphos)]$^+$.[3a] These properties of **1** are superior to **2** because of the high rigidity of the phen ligand compared to bpy. **4** shows the same extent of lifetime and quantum yield compared to **1**. In **3**, the longest lifetime (0.71 µs) and the highest quantum yield ($\Phi = 2.1 \times 10^{-3}$) of all complexes are shown. In Cu–diimine complexes, it has already been shown that the electronic effect of methyl-substituted groups results in slightly higher quantum yield and longer emission lifetime.[11]

The emissive properties of the complexes show that solvent-induced exciplex quenching is fairly suppressed due to the large P–Cu–P angles, even without 2,9-substituted groups. In addition, the introduction of electron-rich phosphines suppresses exciplex quenching by reducing the effective charge on the copper center, as described by Sakaki et al.[12] This result may give important information for designing new luminescent metal complexes.

Experimental

[{Cu(phen)}$_2$(μ-dppa)$_2$](PF$_6$)$_2$ was prepared by a similar method to that of [{Cu(phen)}$_2$(μ-dppm)$_2$](PF$_6$)$_2$.[6] 1,10-Phenanthroline monohydrate (99 mg, 0.5 mmol) and bis(diphenylphosphino)amine (193 mg, 0.5 mmol) were dissolved in 20 mL of acetone. Tetrakis(acetonitrile)copper(I) hexafluorophosphate (186 mg, 0.5 mmol) was then gradually added to the solution. The obtained yellow orange solution was stirred for 1 h. Addition of diethylether (30 mL) to the solution gave a pale yellow powder. Yield 310 mg (80%). ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.47 (d, 2H, 2,9-H), 8.31 (d, 2H, 4,7-H), 8.00 (s, 2H, 5,6-H), 7.34–7.11 (m, 22H, 3,8-H and phenyl-H of dppa), 6.54 (s, 1H, NH); ^{31}P NMR (acetone-d_6, 161.92 MHz) δ −5.61 (br); Elemental Anal. calcd for $C_{72}H_{58}N_6P_6F_{12}Cu_2$: C, 55.86; H, 3.78; N, 5.43%. Found: C, 55.31; H, 3.68; N, 5.40%.

Crystallographic Details. Orange single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of diethyl ether in $(C_2H_5)_2CO$ solution. An X-ray measurement was made on a Rigaku AFC5S with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 296 K. The structure could be solved reasonably by using direct method (SIR92 programs[13]) and was refined by full-matrix least-squares procedure (SHELXL97[14]). Crystallographic data for [(phen)Cu(μ-dppa)$_2$Cu(phen)](PF$_6$)$_2$·2(C$_2$H$_5$)$_2$CO are as follows: $C_{41}H_{39}N_3OPF_6Cu$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.454(2)$ Å, $b = 14.339(2)$ Å, $c = 12.825(2)$ Å, $\alpha = 115.59(1)°$, $\beta = 104.62(1)°$, $\gamma = 65.65(1)°$, $V = 2024.8(5)$ Å^3, $Z = 2$. $R1 = 0.061$ ($Rw = 0.153$) for 5089 ($I > 2.0\sigma(I)$) reflections. All calculations were carried out by using teXsan software.[15] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-

286764 for $[\{Cu(phen)\}_2(\mu\text{-dppa})_2](PF_6)_2$. 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).

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