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Structure and emission properties of mixed-ligand Cu(I) complexes containing phosphinesulfide ligands

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ABSTRACT

Mixed-ligand Cu(I) complexes containing phosphinesulfide ligands were synthesized, and the structure and emission properties were studied for the Cu(I) complexes. X-ray crystallographic study showed that a chelating phosphinesulfide and diimine are coordinated to Cu(I) center. Coordination geometry around Cu(I) center of each complex is described as a distorted tetrahedron. Some of the complexes show photoluminescence in the solid state.

1. Introduction

Much attention has been paid to emissive copper(I) complexes containing diimine (polypyridine or phenanthroline) ligands in view of practical applications for chemical sensors, display devices and solar-energy conversion schemes [1]. Among the studies, the photophysical properties of the mixed-ligand Cu(I) complexes involving both diimines and diphosphines are notable, and thus extensive studies of the complexes have been reported [2–4]. $[Cu(dmp)(DPEphos)]^+$(dmp = 2,9-dimethyl-1,10-phenanthroline; DPEphos = bis[2-(diphenylphosphino)phenyl]ether) and $[Cu(dbp)(DPEphos)]^+$(dbp = 2,9-dibutyl-1,10-phenanthroline) exhibit high quantum yield and a long lifetime in CH_2Cl_2 at room temperature [2,3a]. We have been also studying the emissive properties of mixed-ligand copper(I) complexes with a diimine-type ligand such as dmp and a diphosphine ligand [4]. However, phosphine derivatives have a disadvantage when they are used in emitting devices. Since they have soft and strong σ-donor character of trivalent phosphorus atoms, they are easily oxidized in air or with light in the presence of air, even though triaryl phosphines are relatively stable on coordination with metal complexes (see Scheme 1).

Unlike phosphines, phosphine sulfides have pentavalent phosphorus atoms, so that they are stable for oxidation. In addition, sulfur atoms can function as soft donors, so phosphinesulfide can be used as the alternatives of phosphine ligands (Fig. 1). Several Cu(I) complexes with phosphine sulfides have been reported [5,6]. Reigle et al. reported the luminescence of $[Cu(dmp)(S{=}PPh_3)_2]BF_4$ and $[Cu_2(dmp)_2(dppbS_2)_2]BF_4$($dppbS_2$ = 1,2-bis-(diphenylphosphino)butanedisulfide) only at 77 K [7]. However, most of the studies about Cu(I) complexes with phosphine sulfides are limited to the structural aspects.

In this study, photophysical properties of the Cu(I) mixed-ligand complexes containing phosphinesulfides and diimines have been examined. They are the analogies of our previously reported mixed-ligand Cu(I) complexes containing phosphines [4].

2. Experimental

2.1. General procedures

All reactions were carried out under argon atmosphere using Schlenk techniques although the products are air-stable. 2,9-Dimethyl-1,10-phenanthroline (dmp) were purchased from TCI Co. Ltd. $[Cu(CH_3CN)]PF_6$ [8], 2,9-diphenyl-1,10-phenanthroline (dpp) [9], $dppmS_2$ and $dppaS_2^-$ [10] were synthesized by the literature methods. Elemental analyses of the complexes were performed on the Perkin–Elmer model 2400 CHN Analyser. NMR spectra were obtained using a JEOL Λ-400 spectrometer, in which chemical shifts are referenced to tetramethylsilane (^1H; as internal) or 85% H_3PO_4 ($^{31}P\{^1H\}$; as external). Absorption and luminescence spectra were measured with an Agilent 8453 spectrometer and a Shimadzu RF-5000 fluorometer, respectively.

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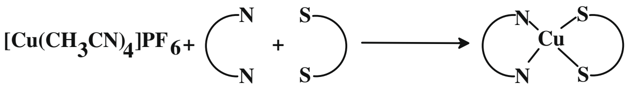

Scheme 1. Synthesis of mixed-ligand complexes.

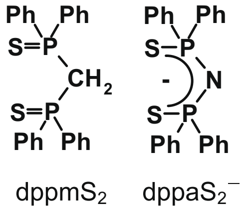

Fig. 1. Phosphinesulfide ligands.

2.2. X-ray measurements

X-ray crystallographic measurements were made on a Rigaku Saturn 70 CCD area detector with graphite-monochromated Mo Kα radiation. The crystal-to-detector distance was 54.90 mm. The data were collected at a temperature of −150 ± 1 °C to a maximum 2θ value of 57.5°. 1800 oscillation images were collected and the data were processed by using the CrystalClear software [11]. Absorption corrections were made by the numerical method for complex **1** and **2**, and by the spherical method for complex **3**. The intensity of the diffraction for complex **3** was weaker than that of the others, so complex **3** gave relatively high refinement residuals. The structure was solved by direct methods (SIR-92 [12]) and was refined by full matrix least squares procedures (SHELX-97 [13]). The non-hydrogen atoms are refined anisotropically and the positions of all hydrogen atoms were fixed at calculated positions. All calculations were performed by using the CrystalStructure crystallographic software package [14].

2.3. Synthesis of mixed-ligand Cu(I) complexes

2.3.1. [Cu(dmp)(dppmS$_2$)]PF$_6$ (**1**)

dmp (0.11 g, 0.50 mmol) and dppmS2 (0.22 g, 0.50 mmol) were dissolved in 10 ml of acetone. [Cu(CH$_3$CN)$_4$]PF$_6$ (0.19 g, 0.50 mmol) was then gradually added to the solution. After the solution was stirred for 2 h at room temperature, addition of diethylether (20 ml) to the solution gave orange crystals, which are collected by filtration. Yield 0.33 g (76%). *Anal.* Calc. for [Cu(C$_{14}$H$_{12}$N$_2$)-(C$_{25}$H$_{22}$P$_2$S$_2$)]PF6: C, 54.13; H, 3.96; N, 3.24. Found: C, 54.26; H, 4.14; N, 2.75%. ^{31}P NMR (acetone-d_6, 25 °C): δ 35.0.

2.3.2. [Cu(dmp)(dppaS$_2$$^-$)] (**2**)

dmp (0.11 g, 0.5 mmol) and K(dppaS$_2$$^-$) (0.24 g, 0.5 mmol) were dissolved in 10 ml of acetone. [Cu(CH$_3$CN)$_4$]PF$_6$ (0.19 g, 0.5 mmol) was then gradually added to the solution. The solution was stirred for 2 h at room temperature and an orange powder was obtained. Recrystallization of the powder from acetone/diethylether gave orange crystals. Yield 0.31 g (85%). *Anal.* Calc. for [Cu(C$_{14}$H$_{12}$N$_2$)-(C$_{24}$H$_{20}$NP$_2$S$_2$)]: C, 63.36; H, 4.48; N, 5.83. Found: C, 63.18; H, 4.21; N, 5.69%. ^{31}P NMR (acetone-d_6, 25 °C): δ 31.8.

2.3.3. [Cu(dpp)(dppaS$_2$$^-$)] (**3**)

This complex was prepared by a similar method used for the preparation of complex **3**; use of dpp (0.17 g, 0.5 mmol) instead of dmp gave purple crystals. Yield 0.29 g (71%). *Anal.* Calc. for [Cu(C$_{24}$H$_{16}$N$_2$)(C$_{24}$H$_{20}$NP$_2$S$_2$)]: C, 68.27; H, 4.30; N, 4.98. Found: C, 67.84; H, 4.09; N, 5.01%. ^{31}P NMR (acetone-d_6, 25 °C): δ 31.2.

3. Result and discussion

3.1. Synthesis and crystal structures

Treatment of [Cu(CH$_3$CN)$_4$]PF$_6$ with equimolar amount of dmp and dppmS$_2$ in acetone gave the mixed-ligand complex **1**. Attempt to prepare a similar complex to complex **1** by using dppaS$_2$ instead of dppmS$_2$ gave complex **2** containing dppaS$_2$$^-$ in which a proton on an amine moiety is eliminated from dppaS$_2$. Use of KdppaS$_2$ and dmp also led complex **2** readily. Treatment of KdppaS$_2$ and [Cu(CH$_3$CN)$_4$]$^+$ with dpp instead of dmp gave complex **3**.

The single crystals with X-ray quality of **1–3** were obtained by gradual addition of diethylether into the reaction solution. Structural data are summarized in Table 1. The structure of complex cation **1** is shown in Fig. 2. It was found that the complex has the tetrahedral structure in which each copper center is coordinated by dmp and dppmS$_2$ chelate ligands. Selected bond lengths, bond angles and torsion angles of **1** are shown in Table 2. The S–P bond lengths of **1** in dppmS$_2$ are 1.9670(7) and 1.9784(7) Å. Since it has been reported that P–S single-bond distance is 2.14 Å and P=S double-bond distance ranges from 1.916 to 1.959 Å, the P–S bond length in **1** shows the bonds almost have double-bond character [15]. The bond angle of S–Cu–S is 108.10(2)°, which is similar to that in the ideal tetrahedral structure. The chelate ring made of Cu-dppmS$_2$ moiety is like a twist boat, as deduced from the torsion angles within the chelate ring ranging from 14.6(2)° to 75.38(12)°.

Table 1
Crystallographic data for complex **1**, **2** and **3**.

Complex name	Complex **1**·acetone	Complex **2** (2 molecules)	Complex **3**
Formula	$H_{40}CuF_6N_2P_3S_2C_{42}O$	$C_{76}H_{64}Cu_2N_6P_4S_4$	$C_{48}H_{36}CuN_3P_2S_2$
Crystal size (mm)	0.25 × 0.25 × 0.20	0.40 × 0.20 × 0.10	0.20 × 0.16 × 0.12
Lattice type	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a (Å)	10.996(2)	10.649(6)	10.111(4)
b (Å)	11.249(2)	19.599(10)	21.340(8)
c (Å)	17.783(3)	32.222(17)	17.981(7)
α (°)	98.444(3)	90	90
β (°)	92.604(2)	92.990(3)	95.231(2)
γ (°)	107.468(3)	90	90
V (Å ^{3})	2066.1(7)	6716.1(60)	3863.8(25)
Z	2	4	4
D_{calcd} (g cm^{-3})	1.484	1.425	1.452
μ (Mo Kα) (cm^{-1})	8.09	9.03	7.97
R_1	0.033	0.052	0.079
wR_2	0.080	0.099	0.219