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Note

Synthesis, crystal structures and spectroscopic properties of copper(I) complexes containing β-dialdiminato supporting ligands

Xiaowei Li [a,b,c], Junqiao Ding [b,c], Weiqun Jin [a], Yanxiang Cheng [b,c,*]

[a] Department of Chemistry, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[c] Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

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Dedicated to Professor Michael F. Lappert

Abstract

Two mononuclear neutral copper(I) complexes, Cu(L^1)PPh$_3$ (**1**), Cu(L^2)(PPh$_3$)$_2$ (**2**) ($[L^1]^- = [\{N(C_6H_3{}^iPr_2\text{-}2,6)C(H)\}_2CPh]^-$; $[L^2]^- = [\{N(C_6H_5)C(H)\}_2CPh]^-$) have been synthesized and structurally characterized by X-ray crystallography. In complex **1**, the copper(I) atom is in a distorted three-coordinate trigonal planar environment, whereas in complex **2** with the less sterically hindered β-dialdiminato ligand, the copper(I) atom is the centre of a four-coordinate distorted tetrahedron. At room temperature complexes **1** and **2** in a film of PMMA exhibit green emission at 543 and 549 nm with lifetimes of 5.28 and 5.32 ns, respectively.

Keywords: Copper(I) complexes; Crystal structures; β-Dialdiminatoes; Triphenylphosphine; Photoluminescence

1. Introduction

Luminescent Cu(I) complexes are currently receiving much attention mainly due to their potential applications in organic light-emitting diodes (OLEDs) [1–6] and photochemistry [7–10]. Most efforts have focused on the synthesis and photophysical properties of these complexes supported by pyridine-type ligands, such as bipyridine and phenanthroline [11,12]. However, the utilization of those ligands results in the formation of ionic Cu(I) complexes, which have a long response time in light-emitting devices with the distribution of counter ions [13,14].

β-Diketiminates are widely used as chelating ligands in coordination chemistry due to their strong binding ability to metals, and readily tunable steric and electronic properties by means of changing the substituents [15]. Many of their Cu(I) complexes have been prepared and studied mainly as models for active sites of metalloenzymes [16–18], but less attention has focused on photoluminescence (PL). β-Dialdiminato ligands in monoanionic form are generally π-delocalized conjugated systems with the conjugation often extending to the aromatic substituent in γ–position and of the ligand to chelating N atoms as in a phenanthroline ligand [19,20]. These facts afford the possibility to synthesize neutral Cu(I) complexes exhibiting photoluminescence. In this paper, we present the syntheses and characterization of two new photoluminescent Cu(I) complexes of β-dialdinimine (Chart 1) and PPh$_3$ ligands.

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[*] Corresponding author. Address: State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China. Tel.: +86 431 85262106; fax: +86 431 85684937.
E-mail address: yanxiang@ciac.jl.cn (Y. Cheng).

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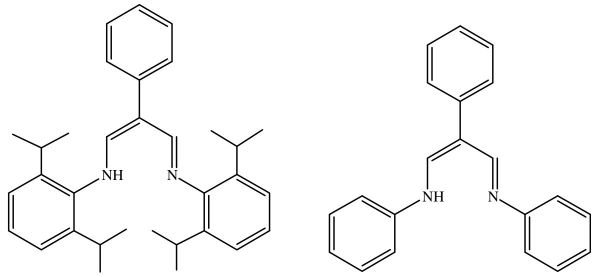

HL^1 HL^2

Chart 1.

2. Experimental

2.1. Materials and methods

All manipulations were performed under nitrogen using standard Schlenk techniques. The solvents THF, toluene and diethyl ether were distilled from Na/benzophenone. Pentane was distilled from CaH_2 under nitrogen. The Cu(I) starting materials: $(PPh_3)_3CuCl$ [21] and $[Cu(CH_3CN)_4]BF_4$ [22] were prepared according to the literature procedures. Ligand precursors HL^1 and HL^2 were synthesized using the reported procedures [23].

NMR data were recorded on a Bruker Avance 300 spectrometer (300 MHz) with TMS as internal standard. Elemental analyses (C, H and N) were determined using a Bio-Rad elemental analysis system. UV–Vis absorption and emission spectra were recorded on a Perkin–Elmer Lambda 35 UV–Vis spectrophotometer and a Perkin–Elmer LS 50B fluorescence spectrophotometer, respectively. Thermal gravimetric analysis (TGA) was carried out using the Perkin–Elmer-TGA7 instrument under a nitrogen atmosphere at a heating rate of 20 °C min^{-1}. Emission lifetime measurements were recorded by a system equipped with a Quanty-Ray DCR-2 pulsed Nd:YAG laser with a THG 355 nm output and ca. 3 ns pulse width. Melting points were taken in sealed capillaries and are uncorrected.

2.2. Synthesis of complexes

2.2.1. Synthesis of Cu(L$_1$)(PPh$_3$) (**1**)

Under an N_2 atmosphere, nBuLi (0.75 ml, 1.6 M) was added dropwise to a stirred solution of HL^1 (460 mg, 1.0 mmol) in 10 ml THF at room temperature. After stirring for 1 h, the above solution was added to a slurry of $(PPh_3)_3CuCl$ (850 mg, 1.0 mmol) in 10 ml THF to give a light yellow-green solution and the mixture was allowed to stir for 6 h. The solvent was then removed under reduced pressure to yield a yellow solid which was extracted into pentane (10 ml)/diethyl ether (40 ml). The resulting mixture was filtered and the filtrate was stored at −20 °C to afford light yellow crystals (508 mg, 64%). M.p. 142–157 °C. *Anal.* Calc. for $C_{51}H_{56}CuN_2P$: C, 77.4; H, 7.1; N, 3.5. Found: C, 77.5; H, 7.2; N, 3.7%. ^{1}H NMR (C_6D_6, 300 MHz, ppm): δ 7.83 (s, 2H), 7.27–7.04 (m, 20H), 6.79–6.75 (m, 6H), 3.41 (septet, $J = 6.8$ Hz, 4H), 1.16 (d, $J = 6.8$ Hz, 12H), 0.71 (d, $J = 6.8$ Hz, 12H).

2.2.2. Synthesis of Cu(L$_2$)(PPh$_3$)$_2$ (**2**)

Under an N_2 atmosphere nBuLi (0.5 ml, 1.6 M) was added dropwise to a stirred solution of HL^2 (150 mg, 0.5 mmol) in 10 ml THF at room temperature. After stirring for 1 h, the above solution was added to a slurry of $[Cu(CH_3CN)_4][BF_4]$ (160 mg, 0.5 mmol) in 10 ml THF. After stirring for 4 h, PPh_3 (350 mg, 1.3 mmol) was added to give a yellow-green solution and the mixture was allowed to stir for 12 h. The solvent was then removed under reduced pressure to yield a yellow residue which was extracted into pentane (20 ml)/toluene (40 ml). The resulting mixture was filtered. The filtrate was stored at −20 °C overnight to afford orange-red crystals (466 mg, 95%). M.p. 105–106 °C. *Anal.* Calc. for $C_{64}H_{55}CuN_2P_2$: C, 78.6; H, 5.7; N, 2.9. Found: C, 78.4; H, 5.7; N, 3.0%. ^{1}H NMR (C_6D_6, 300 MHz, ppm): δ 8.21 (s, 2H), 7.45–7.17 (m, 40H), 7.04–6.92 (m, 10H), 2.40 (s, 3H).

2.3. X-ray crystallography

Intensity data for **1** and **2** were collected at 293(2) K on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares refinement based on F^2 using the SHELXL package [24]. The hydrogen atoms were placed in idealized positions and refined as riding atoms, except the disordered toluene molecule in complex **2**. Further details of the structural analyses are summarized in Table 1. Selected bond lengths and bond angles are shown in Table 2.

3. Results and discussion

3.1. Syntheses

Complex **1** was obtained by the reaction of $(PPh_3)_3CuCl$ and LiL^1 in a 1:1 molar ratio under a nitrogen atmosphere. However, complex **2** was not obtained by this procedure. Instead, its synthesis was achieved by the reaction of $[Cu(CH_3CN)_4][BF_4]$, LiL^2 and 2 equiv. of PPh_3. Both complexes were fully characterized by ^{1}H NMR, elemental analysis, thermal gravimetric analysis (TGA) and found to be air-stable in the solid state at room temperature. TGA data revealed that the two complexes are thermally stable; their decomposition temperature (T_d) was 184 °C for **1** and 202 °C for **2**.[1]

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[1] The crystals of complex **2** start to decompose at 103 °C due to the loss of the solvent toluene molecular.

Table 1
Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	$C_{51}H_{56}CuN_2P$	$C_{64}H_{55}CuN_2P_2$
Molecular weight	791.49	977.58
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	21.5472(9)	24.216(3)
b (Å)	11.4189(5)	14.0411(17)
c (Å)	17.8966(8)	17.525(2)
β (°)	101.5640(10)	117.743(2)
V (Å^3)	4314.0(3)	5273.7(11)
Z	4	4
D_{calc} (g/cm^3)	1.219	1.128
$F(000)$	1680	1876
Absorption coefficient (mm^{-1})	0.580	0.511
θ range (°)	1.93–26.03	1.73–26.03
Crystal size (mm)	$0.21 \times 0.17 \times 0.11$	$0.21 \times 0.18 \times 0.11$
Reflections collected	23916	15037
Independent reflections (R_{int})	8465(0.0557)	5195(0.0777)
Goodness-of-fit on F^2	1.016	1.020
Final R indices [$I > 2\sigma(I)$], R_1, wR_2	0.0546, 0.1144	0.0546, 0.1041
R indices (all data) R_1, wR_2	0.0885, 0.1303	0.1017, 0.1131

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**		Complex **2**	
Cu–N1	1.954(2)	Cu–N	2.053(3)
Cu–N2	1.956(2)	Cu–P	2.2917(10)
Cu–P	2.1645(8)	C1–N	1.320(4)
C1–N1	1.319(4)	C1–C2	1.403(4)
C1–C2	1.399(4)	C2–C3	1.484(6)
C2–C3	1.405(4)	C7–N	1.421(4)
C3–N2	1.313(3)	P–C13	1.823(4)
C2–C4	1.497(4)	P–C19	1.831(4)
N1–C10	1.432(4)	P–C25	1.836(3)
N2–C22	1.442(4)		
P–C34	1.825(3)		
P–C40	1.830(3)		
P–C46	1.824(3)		
N1–Cu–N2	96.16(10)	N–Cu–N0A	93.13(15)
N1–Cu–P	132.50(8)	N–Cu–P	106.85(8)
N2–Cu–P	130.97(7)	N–Cu–P0A	113.90(8)
		P–Cu–P0A	119.27(5)

Symmetry transformations to generate equivalents atoms for **2**: 0A $-x$, y, $-z + 3/2$.

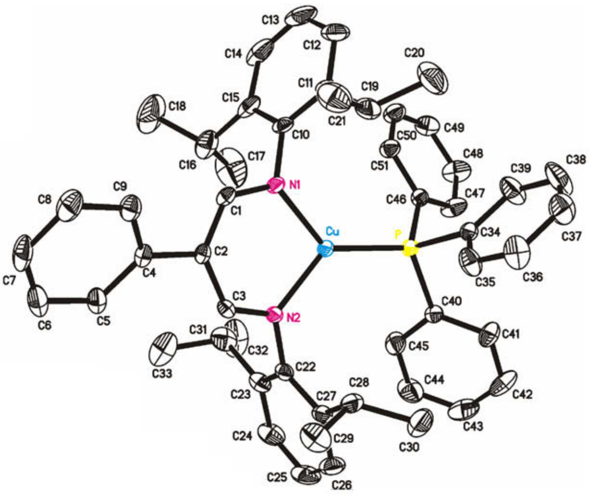

Fig. 1. Molecular structure of complex **1** with hydrogen atoms omitted for clarity.

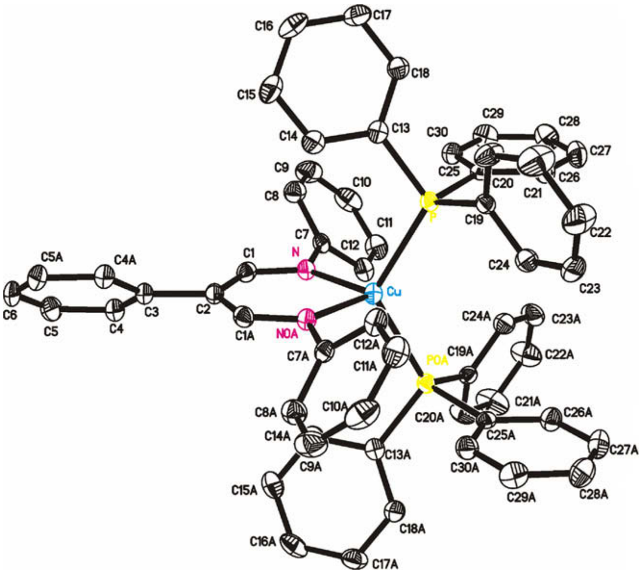

Fig. 2. Molecular structure of complex **2** with hydrogen atoms and the solvent toluene molecular omitted for clarity.

3.2. Crystal structures

The molecular structures of complexes **1** and **2** were determined by X-ray crystallography and are shown in Figs. 1 and 2, respectively. The Cu(I) atom in complex **1** is coordinated by two N-donor atoms from the bidentate ligand L^1 and the P atom from PPh_3 to form a three-coordinate environment, which is similar to that found in $Me_2L^{ipr2}Cu(PPh_3)$ ($Me_2L^{ipr2} = [\{N(C_6H_3{}^iPr_2\text{-}2,6)C(CH_3)\}_2\text{-}C(H)]$) [25] and $Me_2L^{ipr,SMe}Cu(PPh_3)$($Me_2L^{ipr,SMe} = [N(C_6H_3{}^iPr_2\text{-}2,6)\,C(CH_3)C(H)C(CH_3)N\,(C_6H_3{}^iPr_2\text{-}2)(SMe\text{-}6)]$) [18]. The bond distances Cu–N [1.954(2) and 1.956(2) Å] and Cu–P [2.1645(8) Å] in **1** are much closer to those in $Me_2L^{ipr,SMe}Cu(PPh_3)$ [Cu–N 1.956(3) and 1.950(3); Cu–P 2.1687(11) Å] and shorter than those in $Me_2L^{ipr2}Cu(PPh_3)$ [Cu–N 1.9683(19) and 1.975(2) Å; Cu–P 2.1813(7) Å]. Interestingly, the Cu(I) atom in complex **2** exhibits a distorted tetrahedral coordination geometry, being bonded to the two N atoms from L^2 and two P atoms from the two triphenylphosphine ligands. The bond lengths Cu–N and Cu–P are 2.053(3) and 2.2917(10) Å, respectively, which are longer than those in complex **1** due to the more crowded coordination environment around Cu(I) in **2**.

The mean deviations of the CuNCCCN six-membered-ring plane [19] are 0.0469 Å in complex **1** and 0.0124 Å in **2**. The torsion angles are 74.8° [C1, N1, C10 and C11],

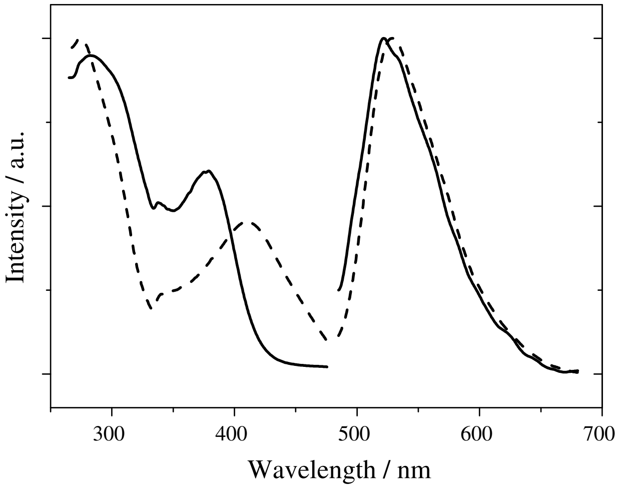

Fig. 3. Absorption and emission spectra of complexes Cu(L$_1$)PPh$_3$ (**1**, solid line) and Cu(L$_2$)(PPh$_3$)$_2$ (**2**, dashed line) in THF at room temperature.

90.5° [C3, N2, C22 and C23] in **1** and 43.7° [C1, N, C7 and C8] in **2**, respectively, which indicate that complex **2** is more strongly conjugated than complex **1**, although the torsion angles are 37.0° [C1, C2, C4 and C5] in **1** and 39.4° [C1, C2, C3 and C4] in **2**, respectively.

3.3. Spectroscopic properties

The UV–Vis absorption and emission spectra for complexes **1** and **2** are shown in Fig. 3. Both complexes **1** and **2** exhibit two absorption bands with maxima at 282 ($\varepsilon = 1.99 \times 10^4$) and 379 ($\varepsilon = 1.29 \times 10^4$ dm^3 mol^{-1} cm^{-1}) nm for complex **1**, 274 ($\varepsilon = 2.61 \times 10^4$) and 411 ($\varepsilon = 1.18 \times 10^4$ dm^3 mol^{-1} cm^{-1}) nm for complex **2**. These are attributed to π–π^* transition from phenyl rings and NCCCN units. The low energy bands are somewhat red-shifted relative to those observed in the spectra of the free ligands (361 nm for HL^1 and 404 nm for HL^2) indicating the increasing of conjugation in the central NCCCN units of ligands as anion. The wider absorption bands may indicate some MLCT character, which is confirmed by the relatively large Stokes shift. Both **1** and **2** show photoluminescence with the emission peak at 543 and 549 nm, respectively, in the PMMA [poly(methyl methacrylate)] film while no emission was observed from the free ligands. These emission peaks are tentatively assigned as metal-to-ligand charge transfer (MLCT) due to their short excited state lifetimes.

Complexes **1** and **2** also show photoluminescence in THF at room temperature with the emission peak at 522 and 528 nm, respectively, when excited with 350 nm UV light. The excited-state lifetimes [6.82 ns for **1** and 7.88 ns for **2**, respectively] in THF solution are longer than those in PMMA films, and the emission wavelengths in solution exhibit a smaller blue-shift than those in PMMA films.

4. Conclusion

Two neutral luminescent copper(I) complexes were synthesized by using β-dialdiminato ligands, which exhibit green emission in the solid state at room temperature. They are air and thermally stable and might be used as emitter in light-emitting devices.

5. Supplementary material

CCDC 629129 and 6219130 contain the supplementary crystallographic data for **1** and **2**. These 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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