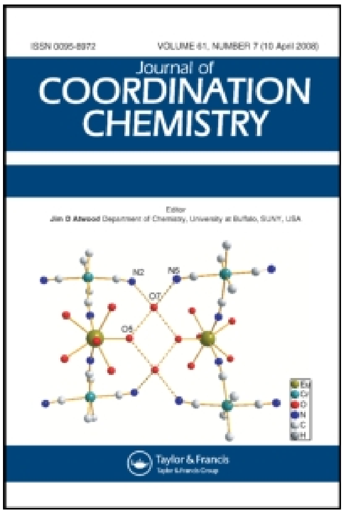

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Synthesis, characterization, and spectroscopic properties of binuclear copper(I) complexes with N^N-N^N, N^N^OH, N^C^N, and phosphine ligands

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Synthesis, characterization, and spectroscopic properties of binuclear copper(I) complexes with N^N-N^N, N^N^OH, N^C^N, and phosphine ligands[#]

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Three new binuclear copper(I) complexes, $[Cu_2(paa)(dppm)_2](BF_4)_2$ (**1**), $[Cu_2(N\hat{}N\hat{}O)(dppm)_2]BF_4$ (**2**), and $[Cu_2(N\hat{}C\hat{}N)(dppm)_2](BF_4)_2$ (**3**), were prepared with bridging or chelating pyridine-2-carbaldehyde azine (paa or N^N-N^N), 2,4-dimethyl-7-hydroxyl-1,8-naphthyridine (N^N^OH), 1-methyl-3,5-di(2-pyridyl)benzene (N^C^N), and bis(diphenylphosphino)methane (dppm) ligands and their structures were determined by X-ray crystal analysis. The structural analysis revealed that coppers in the complexes are three- and four-coordinate and N^N-N^N adopts *N,N* chelating and bridging coordination modes while N^N^OH, N^C^N and dppm afforded only a bridging model. The two metal centers approach closely with copper(I)–copper(I) distances of 2.7811–3.420 Å. Intense solid-state emission centered at 490 nm was observed for **1**.

Keywords: Dinuclear copper(I) complex; Multi-pyridine derivatives; Phosphine ligand; Crystal structures; Spectroscopy

1. Introduction

There has been considerable interest in metal complexes with (6-phenyl-2,2′-bipyridine) (HC^N^N) [1, 2], tripyridine [3, 4], or 1,3-di(2-pyridyl)benzene [5, 6] derivatives for their stability, multiform structures, and rich photoluminescent properties [7]. A series of cyclometalated platinum(II) complexes with HC^N^N exhibited potential applications in the fields of sensitive chemosensors [8–11], luminescent materials [12], and supramolecular chemistry [13]. Some ruthenium(II) and platinum(II) complexes with tripyridine ligands have also been applied in dye-sensitized solar cells [14–16]. Compared to the enormous number of publications about different aspects of ruthenium(II) and platinum(II) complexes [17, 18], reports on copper(I) complex have remained scarce [19]. Polynuclear zinc(II) [20, 21] and copper(I) [22–26] complexes

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[#] Dedicated to Prof Rudi van Eldik on the occasion of his 65th birthday.

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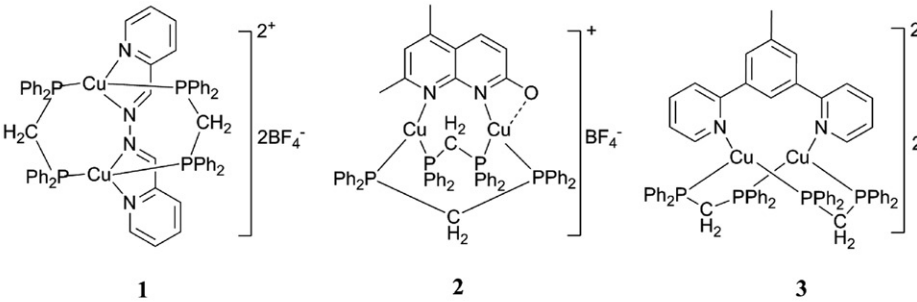


1 **2** **3**

Scheme 1. The chemical structures of **1–3**.

with substituted 1,8-naphthyridine derivatives or paa [27] and phosphine-bridged ligands were prepared, structurally characterized, and their spectroscopic properties reported. With the aim of further understanding coordination modes and properties of copper(I) complexes [28], reactions of pyridine-2-carbaldehyde azine [29], 2,4-dimethyl-7-hydroxyl-1,8-naphthyridine, 1-methyl-3,5-di(2-pyridyl)benzene with copper(I) metal salts were carried out. Herein, we report the synthesis, structures, and spectroscopic properties of new binuclear copper(I) complexes, $[Cu_2(paa)(dppm)_2](BF_4)_2$ (**1**), $[Cu_2(N^\wedge N^\wedge O)(dppm)_2]BF_4$ (**2**), and $[Cu_2(N^\wedge C^\wedge N)(dppm)_2](BF_4)_2$ (**3**) (scheme 1).

2. Experimental

2.1. *Materials and reagents*

All reactions were performed under a nitrogen atmosphere. 1,3-Dibromo-5-methylbenzene, chlorotrimethylstannane, lithium chloride, bis(triphenylphosphine)-palladium(II) chloride and bis(diphenylphosphino)methane were purchased from Acros Chemicals Inc. 2-(Tri-methylstannyl)pyridine [30], $[Cu(CH_3CN)_4]BF_4$ [31, 32], ligands paa [33], and $N^\wedge N^\wedge OH$ [34] were prepared by literature methods. Other reagents were of analytical grade and were used as received. All solvents were purified and distilled by standard procedures before use.

2.2. *Instrumentation*

^1H and ^{31}P NMR spectra were recorded on a Bruker AVANCE DPX-400 spectrometer at 298 K with chemical shifts (δ, ppm) relative to tetramethylsilane (Me_4Si) and 85% H_3PO_4, respectively. MALDI-TOF MS data were obtained on a Bruker Biflex III Model MALDI-TOF mass spectrograph. Elemental analyses were performed with an Elementar Vario EL (Germany) instrument. UV-Vis spectra were obtained using a HITACHI U-3010 spectrophotometer. Corrected emission spectra of solutions and solids were obtained on a HITACHI F-4500 fluorescence spectrophotometer adapted to a right-angle configuration at room temperature.

2.3. *Synthesis of 1-methyl-3,5-di(2-pyridyl)benzene (N^C^N)*

1,3-Dibromo-5-methylbenzene (0.50 g, 2.00 mmol) and 2-(tri-methylstannyl)pyridine (1.50 g, 6.20 mmol) were mixed in 50 mL toluene with stirring for 15 min at room temperature, then lithium chloride (1.05 g, 24.8 mmol) and bis(triphenylphosphine)-palladium(II) chloride (0.14 mg, 0.20 mmol) were added. The mixture was refluxed with stirring for 36 h under nitrogen, and the solution became black gradually. The resulting solution was then cooled to room temperature, after which a saturated aqueous solution of KF (10 mL) was added slowly. The precipitate was isolated by filtration and washed with toluene. Volatiles were removed under reduced pressure to give a crude product. The product was extracted into dichloromethane (150 mL) and washed with aqueous $NaHCO_3$ (5% by mass, 2×100 mL). The organic phase was dried over anhydrous K_2CO_3, filtered, and evaporated to dryness. The brown residue was purified by column chromatography on a silica gel column using diethyl ether as eluent to yield an off-white solid (0.22 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 2.34$ (s, 3H, $-CH_3$), 7.26 (m, 2H), 7.77 (m, 4H), 7.82 (m, 2H), 8.55 (s, 1H), 8.73 (d, $J = 5.6$ Hz, 2H); Ms: m/z: 246 (M^+); Anal. Calcd (%) for $C_{17}H_{14}N_2$: C 82.90, H 5.73; N 11.37; Found: C 82.83, H 5.77, N 11.34.

2.4. *Synthesis of [Cu₂(paa)(dppm)₂](BF₄)₂ (1)*

The procedure was similar to that for complex $[Cu_2(paa)(dcpm)_2](BF_4)_2$ except that dppm was used instead of dcpm (dcpm = bis(dicyclohexylphosphino)methane) [35]. Yield (72%); Ms: m/z: 1279 (M^+); Anal. Calcd (%) for $C_{62}H_{54}B_2Cu_2F_8N_4P_4$: C 58.19, H 4.25; N 4.38; Found : C 58.12, H 4.21, N 4.46.

2.5. *Synthesis of [Cu₂(N^N^O)(dppm)₂](BF₄)₂ (2)*

To a dichloromethane solution (20 mL) of N^N^OH (0.035 g, 0.20 mmol) was added solid $[Cu(CH_3CN)_4]BF_4$ (0.126 g, 0.4 mmol). The mixture was stirred for 6 h at room temperature under nitrogen, and then a solution of dppm (0.15 g, 0.40 mmol) in dichloromethane (10 mL) was added to the pale yellow solution. The resulting solution was stirred for another 3 h and then filtered. The filtrate was concentrated in vacuum and the crude product was recrystallized from CH_2Cl_2/diethyl ether to give orange crystals of **2** (0.143 g, 65%). Ms: m/z: 1155 (M^+); Anal. Calcd (%) for $C_{60}H_{53}BCu_2F_4N_2OP_4$: C 62.35, H 4.62, N 2.42; found: C 62.43, H 4.65, N 2.52.

2.6. *Synthesis of [Cu₂(N^C^N)(dppm)₂](BF₄)₂ (3)*

Complex **3** was synthesized by adding $[Cu(CH_3CN)_4]BF_4$ (0.13 g, 0.40 mmol) to a solution of N^C^N (0.05 g, 0.20 mmol) in dichloromethane (20 mL). The mixture was stirred for 4 h at room temperature under nitrogen and solution of dppm (0.15 g, 0.40 mmol) in dichloromethane (10 mL) was then added. The resulting solution was

Table 1. Selected crystallographic and data collection parameters for **1**–**3**.

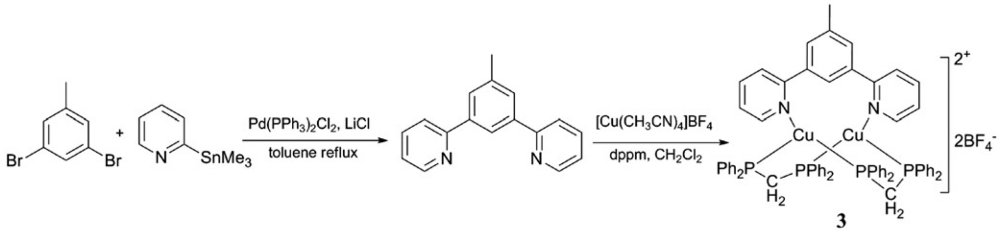
Complex	**1**	**2**	**3** $\cdot$ CH_2Cl_2
Formula	$C_{62}H_{54}B_2Cu_2F_8N_4P_4$	$C_{60}H_{53}BCu_2F_4N_2OP_4$	$C_{68}H_{60}B_2Cl_2Cu_2F_8N_2P_4$
Formula weight	1279.68	1155.81	1400.66
Temperature (K)	293(2)	298(2)	294(2)
Crystal size (mm^3)	0.70×0.60×0.20	0.31×0.26×0.13	0.40×0.18×0.16
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C2/c*	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	23.7669(4)	13.1904(18)	12.291(9)
b	11.5704(2)	14.400(2)	25.072(18)
c	23.9568(5)	18.160(2)	25.535(19)
α	90	111.254(3)	61.878(13)
β	118.5523(8)	90.692(2)	89.349(13)
γ	90	115.421(3)	88.744(14)
Volume (Å^3), Z	5786.72(18)	2845.4(7)	6938(9)
Z	8	2	2
Calculated density ($g\,cm^{-3}$)	1.469	1.349	1.341
$2\theta_{max}$ (°)	54.96	50.02	53.30
μ (mm^{-1})	0.916	0.914	0.844
Reflections collected/unique	51,316/6597	14,548/9827	39,870/28069
Parameters	374	667	1612
R_{int}	0.0846	0.0289	0.0431
Goodness of fit	1.019	1.000	0.892
R_1, $wR_2[I>2\sigma(I)]$[a]	0.0399, 0.0861	0.0451, 0.0929	0.0758, 0.1956
R_1, wR_2 (all data)	0.0942, 0.0942	0.0992, 0.1041	0.1800, 0.2301
Largest difference peak and hole (e Å^{-3})	0.618 and −0.317	0.751 and −0.336	1.073 and −0.642

[a] $R_1 = \sum \|F_o|-|F_c\| \sum|F_o|.wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

concentrated in vacuum to *ca* 5 mL, and then addition of diethyl ether afforded a crude product. Yellow crystals were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex (0.17 g, 65%). ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 2.49$ (s, 3H, CH_3), 3.37 (s, 4H, CH_2), 7.12 (t, $J = 7.2$ Hz, 16H), 7.26 (t, $J = 7.2$ Hz, 8H), 7.43 (broad, 18H), 7.89–8.07 (m, 6H), 8.71 (broad, 2H); ^{31}P NMR (DMSO-d_6, 161.96 MHz): $\delta = -11.21$. Ms: *m/z*: 1315 (M^+); Anal. Calcd (%) for $C_{67}H_{58}B_2Cu_2F_8N_2P_4$: C 61.16; H 4.44; N 2.13; Found (%): C 61.22, H 4.41, N 2.18.

2.7. *X-ray crystallography*

Crystals suitable for X-ray crystallography were obtained by vapor diffusion of diethyl ether into a solution of the complexes in dichloromethane. The details of the crystallographic data are listed in table 1. Diffraction data were collected on a KappaCCD or Bruker SMART X-Ray diffractometer using a graphite monochromator with Mo-Kα radiation ($\lambda = 0.071073$ nm) at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on all F^2 data (SHELX-97) [36]. The non-hydrogen atoms were refined anisotropically. All hydrogens were generated geometrically, assigned appropriate isotropic thermal parameters, and included in structure factor calculations.



3

Scheme 2. Synthesis of N^C^N and **3**.

Table 2. Selected bond lengths (Å) and angles (°) of **1**–**3**.

1			
Cu(1)–N(1)	2.138(2)	Cu(1)–N(2)	2.042(2)
Cu(1)–P(1)	2.577(7)	Cu(1)–P(2)#1	2.2343(7)
N(2)–C(30)	1.268(3)	N(2)–N(2)#1	1.399(4)
N(1)–Cu(1)–N(2)	77.30(8)	N(1)–Cu(1)–P(1)	114.42(6)
N(2)–Cu(1)–P(1)	115.74(6)	N(2)–Cu(1)–P(2)#1	114.98(6)
N(1)–Cu(1)–P(2)#1	114.88(6)	C(30)–N(2)–N(2)#1	121.9(2)
P(1)–Cu(1)–P(2)#1	114.45(3)		
2			
Cu(1)–N(1)	2.006(3)	Cu(1)–P(3)	2.259(1)
Cu(1)–P(1)	2.270(1)	Cu(2)–N(2)	2.042(3)
Cu(2)–P(4)	2.246(1)	Cu(2)–P(2)	2.273(1)
Cu(2)–O(1)	2.448(3)	Cu(1)–Cu(2)	2.7811(7)
N(1)–Cu(1)–P(3)	122.49(9)	N(1)–Cu(1)–P(1)	116.19(9)
P(3)–Cu(1)–P(1)	120.44(4)	N(1)–Cu(1)–Cu(2)	92.73(8)
P(3)–Cu(1)–Cu(2)	93.64(3)	N(2)–Cu(2)–P(4)	121.02(9)
P(4)–Cu(2)–P(2)	118.90(4)	N(2)–Cu(2)–O(1)	59.0(1)
P(4)–Cu(2)–O(1)	108.13(7)	N(2)–Cu(2)–Cu(1)	73.65(8)
P(2)–Cu(1)–Cu(2)	93.72(3)	O(1)–Cu(2)–Cu(1)	132.58(7)
3			
Cu(1)–N(1)	2.055(6)	Cu(1)–P(3)	2.239(2)
Cu(1)–P(1)	2.261(2)	Cu(2)–N(2)	2.046(6)
Cu(2)–P(4)	2.251(2)	Cu(2)–P(2)	2.256(2)
N(1)–Cu(1)–P(3)	115.0(2)	N(1)–Cu(1)–P(1)	107.0(2)
P(3)–Cu(1)–P(1)	132.48(8)	N(2)–Cu(2)–P(4)	112.6(2)
N(2)–Cu(2)–P(2)	112.2(2)	P(4)–Cu(2)–P(2)	131.58(7)

#1: $-x+1, y, -z+1/2$.

3. Results and discussion

3.1. *Synthesis and crystal structures*

Scheme 2 shows details of the synthetic strategy for N^C^N and **3**. Compared to the synthesis using $Pd(PPh_3)_4$ as a catalyst reported by Williams and co-workers [5], N^C^N was prepared readily in one step *via* $Pd(PPh_3)_2Cl_2$-catalyzed cross-coupling between 1,3-dibromo-5-methylbenzene and excess of 2-(tri-methylstannyl)pyridine in toluene.

All of the complexes reported here have been structurally characterized by X-ray crystal analysis. Selected bond lengths and angles are listed in table 2. A perspective view with atom numbering scheme of the cations is illustrated in figures 1–3.

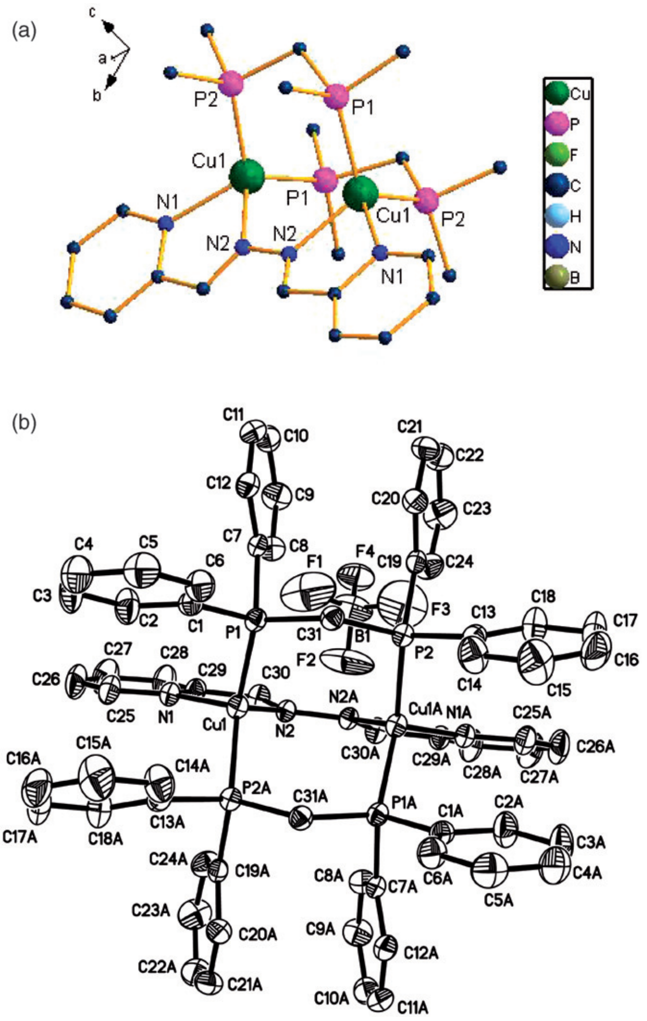


Figure 1. (a) The cation structure of **1**, the hydrogens and phenyl rings of dppm are omitted for clarity; (b) The cation structure of **1**, the hydrogens are omitted for clarity.

The structural investigations show a changeover of coordination number around copper(I) from 4 to 3, and Cu(I) $\cdots$ Cu(I) contact distances in the complexes follow the sequence (**1**) > (**3**) > (**2**). Complex **1** comprises a dicopper center and each copper(I) adopts a twisted tetrahedral coordination geometry (figure 1). The Cu–N and Cu–P distances fall into normal limits, and the Cu(1)–N(1) bond length of 2.138(2) Å is slightly longer than that of 2.042(2) Å for Cu(1)–N(2). Corresponding P(1)–Cu(1)–P(2A), N(1)–Cu(1)–N(2), and N(2)–Cu(1)–P(1) bond angles are 114.4(3)°, 77.30(8)°, and 114.42(6)°, respectively. In contrast to the similar $[Cu_2(paa)(dcpm)_2](BF_4)_2$ (dcpm = bis(dicyclohexylphosphino)methane) reported by our group [35], the two copper(I) of **1** are located at the same side of the paa in which four nitrogens are in the same plane. The intramolecular Cu $\cdots$ Cu distance is 3.420 Å. Additionally, the

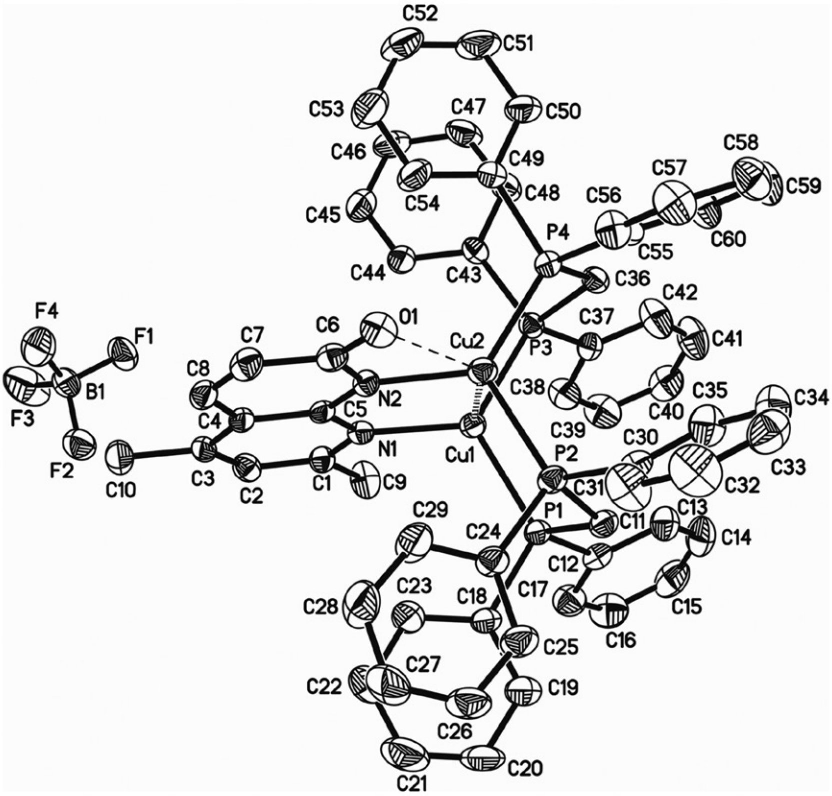


Figure 2. The cation structure of **2**, the hydrogens are omitted for clarity.

seven-membered bimetallacycle consisting of Cu(1), N(2), N(2A), Cu(1A), P(2), C(31), and P(1) with paa and dppm was found in the complex.

As shown in figure 2, **2** exhibits two different coordinated copper(I) centers. One features a trigonal planar configuration with copper bonded to one nitrogen from naphthyridine ring and two phosphorus atoms of dppm ligands, the N–Cu–P bond angles vary from 116.19(9)° to 122.49(9)°, and P–Cu–P bond angle is 120.44(4)°. The other is coordinated by phosphorus and nitrogen, finishing trigonal planar geometry at copper(I), with N(2)–Cu(2)–P(4), N(2)–Cu(2)–P(2), and P(4)–Cu(2)–P(2) bond angles of 121.02(9)°, 119.03(9)°, and 118.90(4)°, respectively. The interaction between Cu(2) and oxygen at the 9-position of the naphthyridine ligand was found. The non-bonded separations of Cu(2)···O(1) and Cu(1)···Cu(2) are 2.448(3) and 2.7811(7) Å, respectively [37].

X-ray crystal analysis showed that **3** contains two bimetallic 12-membered rings with N^C^N and dppm bridging two copper(I) metal centers *via* two N- and four P-donor sites. Copper–copper separation of 3.314 Å is observed. Perspective view of its cation is depicted in figure 3 and selected bond lengths and angles are listed in table 2. Compared with other observed copper(I) analogues [38], the structural data of **3** showed that each copper has a distorted trigonal planar coordination geometry with the average distances of Cu–N and Cu–P being 2.051(6) and 2.252(2) Å, respectively. The bond angles at the

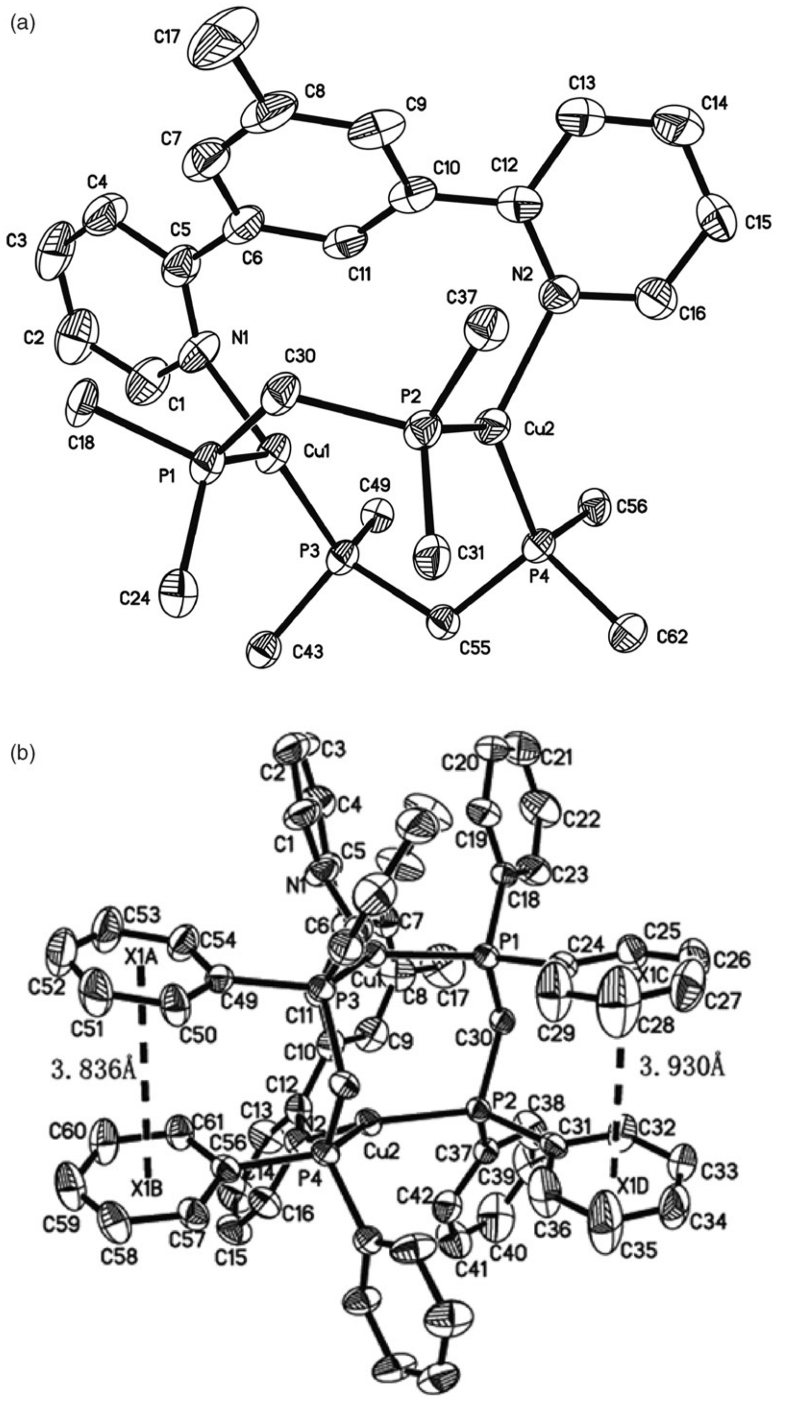


Figure 3. (a) The cation structure of **3**, the hydrogens and phenyl rings of dppm are omitted for clarity; (b) the intramolecular π–π interactions of **3**.

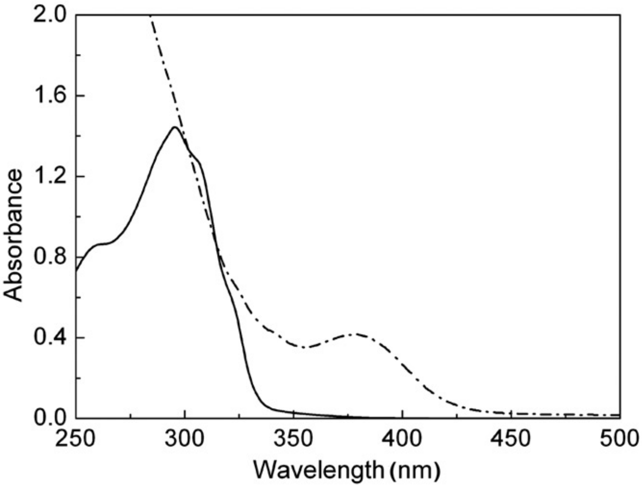


Figure 4. UV-Vis absorption spectra of **1** (–·–·) and paa (—) in acetonitrile at room temperature.

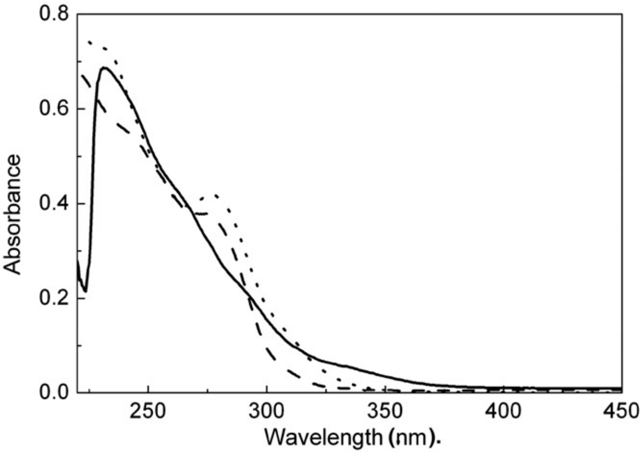


Figure 5. UV-Vis absorption spectra of **3** ($1.0 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$) in acetonitrile (– – – –), methanol (· · ·) and dichloromethane (—).

copper atoms vary from 112.2(2)° to 132.48(8)°. Three aromatic ring planes of the N^C^N ligand are not coplanar. Both phenol and pyridine with N1 plane are separated from each other by a dihedral angle of 37.0°, while the dihedral angle between phenol and N2 pyridine planes is 131.2°. There are intramolecular π–π interactions between phenol rings C49–C54 and C56–C61 as well as C24–C29 and C31–C36 in the two dppm ligands with interplanar separations of 3.836 and 3.930 Å, respectively (figure 3b).

3.2. *Absorption and emission spectra*

UV-Vis absorption spectra of **1** and **3** in different solvents are shown in figures 4 and 5. Complex **1** exhibits low-energy absorption centered at 375 nm in acetonitrile at

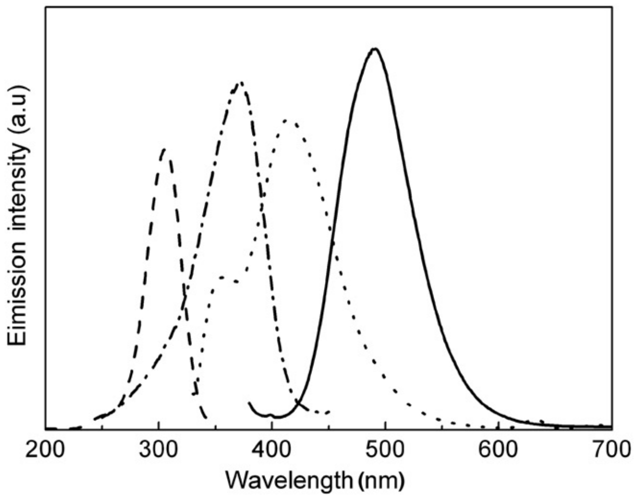


Figure 6. Emission and excitation spectra for **3** at room temperature. Emission (···) and excitation (– –) spectra in dichloromethane; emission (—), and excitation (–·–·) spectra in solid state.

room temperature. While the absorption spectra of **3** in CH_2Cl_2 was characterized by an absorption band at *ca* 340 nm with tails extending to 450 nm. The lower-energy absorptions can be tentatively assigned to a metal-to-ligand charge transfer (MLCT) d(Cu) $\rightarrow \pi^*$(NCN or paa). In comparison, the absorption at <320 nm was attributed to intraligand (IL) $\pi \rightarrow \pi^*$ transition [39–41].

Upon excitation at 310 nm, **3** exhibits a relatively intensive emission with λ_{max} at 415 nm in degassed dichloromethane solution at room temperature (figure 6), and the measured emission quantum yield is 0.153. Complex **1** has weak red solid-state luminescence with a λ_{max} at 675 nm at room temperature. In contrast, solid sample of **3** displays intense room-temperature emission centered at 490 nm upon excitation at 370 nm. We therefore assign the emissions to metal-to-ligand charge-transfer excited state [42].

4. Conclusions

Three binuclear complexes having three- and four-coordinate copper(I) centers have been prepared and characterized. X-ray crystal analysis revealed 7- to 12-membered bimetallacycle structures and showed that the complexes exhibit both *N,N*-chelating and *N*,*N*-/*P*,*P*-bridging coordination. Although obvious copper–copper interactions were not observed in the complexes, a close Cu ··· Cu distance of 2.7811(7) Å was found for **2**. Spectroscopic investigations suggest that room-temperature solid-state emission of **1** and **3** can be ascribed to ^{3}MLCT excited state.

Supplementary material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication

Nos. CCDC-762289 (**1**), CCDC-762287 (**2**), CCDC-762288 (**3**). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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