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# The preparation, crystal structure and properties of a mixed-ligand copper(I) complex [CuI(PPh<sub>3</sub>)(DPPZ)]·DMF

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#### Abstract

The mixed ligand mononuclear copper(I) complex of formula [CuI(PPh<sub>3</sub>)(DPPZ)]·DMF (DPPZ = dipyrido[3,2,-a:2',3'-c]phenazine) has been synthesized and has been characterized by single-crystal X-ray diffraction method, FT-IR spectrum, the electrospray ionization mass spectrum and the thermogravimetric analysis. The pairwise  $\pi - \pi$  stacking between DPPZ ligands exists through the crystal lattice.

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Keywords: Copper(I) complex; Crystal structure; Electrospray ionization mass spectrum; DPPZ

# 1. Introduction

Metal polypyridyl coordination compounds such as ruthenium polypyridyl complexes have been extensively studied in the past few years, as their unusual binding properties combined with their general photoactivity, make them suitable candidates as DNA secondary structure probes, photocleavers and antitumor drugs [1]. It is of note that despite the interesting properties and the large amount of work that has performed on complexes with dipyrido[3,2,-a:2',3'-c]phenazine (DPPZ) [2–20], there are relatively few reports on

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the crystal structure of these complexes [15-20]. To the best of our knowledge, no crystal structure of a copper(I) complex of this ligand has been reported. In the present paper, we report the preparation, X-ray crystal structure and properties of copper(I) complex [CuI(PPh<sub>3</sub>)(DPPZ)]·DMF.

# 2. Experimental

#### 2.1. Materials and measurements

All chemicals used were of analytical grade and used as received. The ligand DPPZ was prepared as described earlier [21] while 1,10-phenanthroline-5,6quinone was prepared according to the literature method [3]. Elemental analyses were performed with a Perkin–Elmer 240C instrument. IR spectrum was recorded on a Nicolet 170SX FT-IR

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spectrophotometer (range:  $400-4000 \text{ cm}^{-1}$ ) as KBr pellets. Electrospray ionization mass spectrum (ESI-MS) was recorded with a Finnigan mat APISSQ 710 mass spectrometer, with MeOH on the mobile phase, the flow rate of the mobile phase was  $0.75 \text{ cm}^3 \text{ min}^{-1}$ . The spray voltage was 4.5 kV and the capillary voltage was 38.0 V. The capillary temperature was 200 °C. Thermogravimetric and differential analyses were taken on a TA Inst 2100 thermal analyzer under flowing N<sub>2</sub> with a heating rate of  $10 \text{ °C min}^{-1}$ . Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrometer at room temperature (25 °C).

# 2.2. Preparation of [CuI(PPh<sub>3</sub>)(DPPZ)]·DMF

To 20 ml DMF was added 0.190 g (1 mmol) CuI, 0.520 g (2 mmol) PPh<sub>3</sub> and 0.262 g (1 mmol) DPPZ with stirring, the mixture was then stirred at room temperature for about 8 h, after which it was filtered. Orange-red single crystals of the complex suitable for X-ray diffraction were obtained by evaporating the filtrate in air for a few days. The yield of the compound is ca. 60%. Anal. Found: C, 58.22; H, 3.80; N, 8.57%; Calc. for  $C_{39}H_{32}N_5CuIPO$ : C, 57.96; H, 3.99; N, 8.67%. IR (KBr pellets)/cm<sup>-1</sup>: 1676(vs), 1577(m), 1482(vs), 1431(s), 1409(vs), 1381(m), 1354(s), 1089(s), 1069(vs), 996(m), 818(m), 738(s), 696(vs), 521(s), 498(m).

#### 2.3. X-ray crystallography

An orange-red block crystal of the new mixedligand complex, with the dimensions  $0.24 \times 0.23 \times 0.21 \text{ mm}^3$ , was selected for unit cell parameters determination and collection of intensity data at 293 K on an Euraf Nonius CAD4 diffractometer with graphite monochromated Mo Ka radiation ( $\lambda = 0.7103$  Å) using a  $\theta/2\theta$  scan mode. The data was corrected for Lorenz and polarization effects during data reduction. An empirical absorption correction based on  $\psi$  scans was applied. The structure was solved by the direct methods and refined by a full-matrix least-squares on  $F^2$  to  $R_1 = 0.0500 \quad (wR_2 = 0.1535)$  for 6194 reflections  $(I > 2\sigma(I))$  of 6510 reflections collected in the range  $1.81^\circ \le \theta \le 24.96^\circ$ . All non-hydrogen atoms Table 1

Crystal data and structure refinement parameters for the title complex

Empirical formula	C <sub>39</sub> H <sub>32</sub> CuIN <sub>5</sub> OP
Molecular weight	808.11
Crystal size (mm)	$0.24 \times 0.23 \times 0.21$
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	12.4424(12)
<i>b</i> (Å)	12.641(2)
c (Å)	13.9553(18)
$\alpha$ (deg)	64.426(11)
$\beta$ (deg)	65.656(10)
$\gamma(\text{deg})$	88.860(9)
$V(Å^3)$	1770.2(4)
Z	2
$D_{\text{Calc}} (\text{g cm}^{-3})$	1.516
$\mu (\mathrm{mm}^{-1})$	1.573
F(000)	812
$\theta$ Range for data	1.81-24.96
collection (deg)	
Index ranges	$0 \le h \le 14, -15 \le k \le 15,$
	$-15 \le l \le 16$
Reflections collected: total,	6510, 6194
independent	
R <sub>int</sub>	0.0463
Data/restraints/parameters	6194/8/409
Goodness-of-fit S on $F^2$	1.109
Final $R_1$ , $wR_2$ $[I > 2\sigma(I)]$	0.0500, 0.1535
All data	0.0719, 0.1788
Largest peak, hole (e $Å^{-3}$ )	1.437, -1.350

were refined anisotropically whereas the hydrogen atoms were generated geometrically. In the final difference map, the residual maxima and minima were 1.437 and  $-1.350 \text{ e} \text{ Å}^{-3}$ , respectively. The goodness of fit on  $F^2$  is 1.080. All calculations were performed on a PC-586 personal computer using SHELXTL-97 program. Details of crystal data, collection and refinement are listed in Table 1.

# 3. Results and discussion

#### 3.1. Description of the structure

The atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are listed in Table 2. Selected bond distances and angles are listed in Table 3. The structure of the title

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Table 2

Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å × 10<sup>3</sup>) for the title complex.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

Atom	x	У	z	$U_{\rm eq}$
Cu(1)	- 820(1)	2754(1)	4812(1)	41(1
I(1)	1131(1)	2484(1)	5063(1)	46(1
P(1)	-545(1)	3684(1)	2948(1)	38(1
N(1)	-6033(4)	-487(4)	9182(4)	44(1
N(2)	-5921(4)	1548(4)	9512(4)	41(1
N(3)	-2084(4)	1155(4)	5915(4)	41(1
N(4)	-1996(4)	3114(4)	6173(4)	39(1
C(1)	-1106(50)	2722(5)	2516(5)	42(1
C(2)	-453(6)	2578(6)	1518(6)	52(2
C(3)	-938(9)	1816(7)	1286(8)	73(2)
C(4)	-2081(10)	1154(7)	2028(10)	85(3)
C(5)	-2765(8)	1273(8)	3032(9)	82(3)
C(6)	-2286(6)	2062(6)	32,829(6)	59(2)
C(7)	-1285(5)	4960(5)	2569(5)	39(1)
C(8)	-1782(6)	5249(6)	1772(5)	50(1)
C(9)	-2330(6)	6200(6)	1538(6)	55(2)
C(10)	-2418(7)	6928(6)	2079(6)	59(2)
C(11)	-1914(7)	6661(7)	2864(6)	60(2)
C(12)	-1376(6)	5674(6)	3114(6)	50(2)
C(13)	1014(5)	4272(5)	1800(5)	38(1)
C(14)	1425(6)	5442(6)	877(5)	49(1)
C(15)	2595(6)	5850(6)	46(6)	60(2)
C(16)	3396(6)	5075(7)	104(6)	60(2)
C(17)	3026(6)	3924(7)	1017(60	57(2)
C(18)	1830(6)	3514(6)	1870(5)	48(1)
C(19)	-4056(5)	272(5)	7568(5)	37(1)
C(20)	-4036(6)	-755(5)	7409(6)	49(2)
C(21)	-3050(6)	-800(6)	6518(6)	54(2)
C(22)	-2094(6)	157(5)	5794(5)	50(2)
C(23)	-3061(4)	1190(4)	6804(4)	33(1)
C(24)	-3007(5)	2251(5)	6965(4)	35(1)
C(25)	-3951(5)	2347(5)	7904(5)	37(1)
C(26)	- 3810(6)	3354(6)	8051(6)	50(2)
C(27)	-2786(6)	4203(5)	7273(6)	54(2)
C(28)	- 1912(6)	4058(5)	6348(5)	49(1)
C(29)	-5076(5)	385(5)	8497(5)	36(1)
C(30)	-5021(5)	1413(5)	8673(4)	35(1)
C(31)	-6914(5)	665(5)	10,209(5)	42(1)
C(32)	-6967(5)	-356(5)	100,032(5)	43(1)
C(33)	- 7919(6)	775(6)	11,114(5)	53(2)
C(34)	- 8910(6)	-102(6)	11,820(5)	57(2)
C(35)	-8972(6)	-1126(7)	11,657(6)	61(2)
C(36)	-8023(6)	-1248(6)	10,791(6)	56(2)
N(5)	5102(8)	6962(8)	5400(8)	99(2)
C(38)	4484(14)	6431(13)	5009(13)	146(5)
C(39)	5694(13)	8157(11)	4696(13)	138(5)
C(37)	5089(16)	6459(15)	6534(12)	164(6)
O(1)	5687(18)	8531(17)	3668(17)	276(8)
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complex is shown in Fig. 1 and the unit cell is illustrated in Fig. 2.

The title complex crystallizes in space group P-1 and X-ray analysis shows that it is a mononuclear copper(I) complex.

The four-coordinated copper atom is surrounded by one iodide, one phosphorous and two nitrogen atoms to form a distorted tetrahedral geometry. The Cu-I distance is 2.5880(8) Å, which is 0.003 Å shorter than that of  $[CuI(PPh_3)(2,2'_{-})]$ bipy)] [22]. The Cu-P distance is 2.2146 Å, which is 0.0164 Å longer than that in  $[CuI(PPh_3)(2,2'-bipy)]$  [22] and about 0.05 Å shorter than that in  $\{[Cu(PPh_3)_2]_2BH_4\}ClO_4$  [23]. The Cu-N distances are 2.091(5) Å for Cu(1)-N(3) and 2.094(5) Å for Cu(1)-N(4), while in  $[CuI(PPh_3)(2,2'-bipy)]$  [22], the Cu-N distances are 2.070(3) and 2.082(4) Å. In [CuI(PPh<sub>3</sub>)(-DPPZ)]·DMF, the binding angle of the two coordinating nitrogens of the DPPZ ligand N(3)-Cu(1)-N(4) is 79.00(17)°, almost the same as in  $[CuI(PPh_3)(2,2'-bipy)]$  [22], which are in the range of the reported values 74.1-82.1° in dppz complexes [15–20].

The DPPZ ligand is essentially planar, similar to that in  $[RuO(dppz)(tpy)]^{2+}$  [16] and in  $[Co(en)_2(dppz)](ClO_4)_3 \cdot 0.5H_2O$  [18]. The dihedral angle between the two planes of the ligands is about 2.1°. A pairwise  $\pi$ -stacking interaction therefore exists throughout the crystal, as shown in Fig. 3. All previously reported structures containing the DPPZ ligand have shown crystal packing that appears to be driven by favorable  $\pi$ - $\pi$  interactions of the extended conjugated systems of the ligands. The distance between the ring planes of the two ligands is about 3.4 Å, about 0.1 Å shorter than the case in of  $[RuO(dppz)(tpy)]^{2+}$ [16] and  $[Co(en)_2($ dppz)](ClO<sub>4</sub>)<sub>3</sub>·0.5H<sub>2</sub>O [18], similar to the basepair stacking distance in DNA [24] and the intercalator-base pair stacking distance in crystal structure of oligonucleotide-intercalator complexes [25,26]. The same two-ring overlap pattern has been observed as in the case of  $[RuO(dppz)(tpy)]^{2+}$  [16], while in the case of  $[Co(en)_2(dppz)](ClO_4)_3 \cdot 0.5H_2O$  [18], the DPPZ ligands of adjacent molecules do not lie directly

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Table 3 Selected bond distances (Å) and bond angles (deg)

Cu(1)-N(3)	2.091(5)	Cu(1) - N(4)	2.094(5)
Cu(1)-P(1)	2.2146(16)	Cu(1)-I(1)	2.5880(8)
P(1)-C(7)	1.826(6)	P(1)-C(1)	1.828(6)
P(1)-C(13)	1.830(6)	N(1)-C(29)	1.323(7)
N(1)-C(32)	1.346(8)	N(2)-C(30)	1.319(7)
N(2)-C(31)	1.359(7)	N(3)-C(22)	1.344(7)
N(3)-C(23)	1.350(7)	N(4)-C(28)	1.332(7)
N(4)-C(24)	1.364(7)		
N(3)-Cu(1)-N(4)	79.00(17)	N(3)-Cu(1)-P(1)	115.80(14)
N(4)-Cu(1)-P(1)	124.83(14)	N(3)-Cu(1)-I(1)	110.47(14)
N(4)-Cu(1)-I(1)	106.40(13)	P(1)-Cu(1)-I(1)	114.97(5)
C(7) - P(1) - C(1)	103.2(3)	C(7)-P(1)-C(13)	103.7(3)
C(1) - P(1) - C(13)	102.5(3)	C(7) - P(1) - Cu(1)	116.08(18)
C(1) - P(1) - Cu(1)	113.26(19)	C(13) - P(1) - Cu(1)	116.40(19)

above each other but are displaced along the *b*-axis so that there is no overlap of any of the atoms of the ligands.

# assigned to $[Cu(PPh_3)(DPPZ)]^+$ . The peak at m/z 376.9 is probably due to $[Cu(DPPZ)]^+(CH_3OH)$ .

#### 3.3. Luminescent properties

The structure of the complex in solution was also studied by ESI-MS [27–29]. Fig. 4 displays a positive ion ESI mass spectrum of the title complex in the methanol solution. Three main peaks were observed. The peak at m/z 868.7 is assigned to [Cu(PPh<sub>3</sub>)<sub>2</sub>(DPPZ)]<sup>+</sup> and the peak at m/z 607.1 is

3.2. ESI-MS spectrum

Fig. 5 shows the emission spectrum of the title complex in solid state at room temperature. A broad peak at 620 nm was observed when the solid sample was excited at 350 nm. Barton et al. [14] reported the emission spectra of Ruthenium dipyridophenazine complex [Ru(phen)<sub>2</sub>(DPPZ)](PF<sub>6</sub>)<sub>2</sub> in CH<sub>3</sub>CN solution, where a maximum emission peak



Fig. 1. ORTEP diagram and atomic labeling system of [CuI(PPh<sub>3</sub>)(DPPZ)]. Hydrogen atoms are omitted for clarity.

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Fig. 2. Unit cell packing diagram of the title complex. DMF molecule is omitted for clarity.



Fig. 3. Pairwise  $\pi - \pi$  stacking diagram showing the two-ring overlap pattern in the title complex.

at 618 nm was observed, which was attributed to the metal-to-ligand charge transfer (MLCT). We assign the emission peak of 619 nm in the complex to the MLCT.

# 3.4. Thermogravimetric analysis

The title complex (4.70 mg) was heated in a nitrogen atmosphere from 25 to 600 °C at a heating rate of 10 °C min<sup>-1</sup>. Thermogravimetric analysis (TGA) shows that the decomposition starts at 110 °C, a significant mass loss at 125 °C corresponding to the loss of one DMF molecule per formula unit (observed 8.9%, calculated 9.0%). The second step of decomposition takes place between 213 and 260 °C



Fig. 4. Positive ion ESI mass spectrum of complex in methanol solution.

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Fig. 5. Emission spectrum of the title complex in solid state excited at 350 nm at room temperature.

probably corresponding to the loss of one DPPZ ligand (observed 34.8%, calculated 34.9%), and the last decomposition step is observed between 430 and 502  $^{\circ}$ C, and the residue was not detected.

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