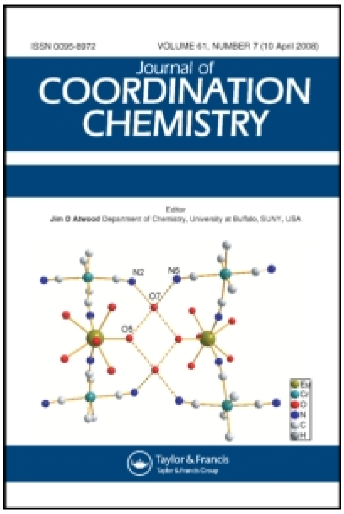

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Syntheses, crystal structures and luminescence of 2,6- <i>bis</i> - (5-phenyl-1H-pyrazol-3-yl)pyridine and its d^{10} metal complexes

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Syntheses, crystal structures and luminescence of 2,6-*bis*-(5-phenyl-1H-pyrazol-3-yl)pyridine and its d^{10} metal complexes

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A new *bis*-pyrazole derivative, 2,6-*bis*-(5-phenyl-1H-pyrazol-3-yl) pyridine (H_2BPPP), and two d^{10} metal complexes $[Zn(H_2BPPP)Cl_2](DMF)_2$ (**1**), $[Cd(H_2BPPP)Cl_2](DMF)_2$ (**2**) have been synthesized and characterized. There is a tautomeric equilibrium of the *bis*-pyrazole compound in solution and the H atom of pyrazolyl NH can transfer to the adjacent N atoms. X-ray structure analyses reveal the H atom is on the 2-position of pyrazolyl ring in donor solvents, while the H atom is on the 1-position of pyrazolyl ring in metal complexes. The luminescence of the ligand and complexes have been investigated.

Keywords: *Bis*-pyrazole ligand; Crystal structures; Proton transfer; Luminescence

1. Introduction

Coordination chemistry of pyrazole-derived ligands has been vigorously developed [1], since pyrazole derivatives are an important class of organic photochromic compounds. Fluorescent properties of multipyrazole compounds draw attention in the field of organic light emitting diodes (OLEDs) [2–5]; among organic luminophores pyrazoloquinoline (PQ, 1*H*-pyrazolo[3, 4–*b*] quinoline) and its derivatives have emerged as one of the most promising dopants for efficient electroluminescence applications [6–8]. Herein, we report the synthesis and characterization of a new *bis*-pyrazole compound, 2,6-bis-(5-phenyl-1H-pyrazol-3-yl) pyridine (H_2BPPP), and $[Zn(H_2BPPP)Cl_2](DMF)_2$ (**1**) and $[Cd(H_2BPPP)Cl_2](DMF)_2$ (**2**).

2. Experimental

2.1. *Reagents and physical measurements*

2,6-*Bis*(3-oxo-3-phenylpropionyl) pyridine (H_2BOPP) was synthesized according to the literature [9–11]. Other reagents and solvents were purchased from commercial sources

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and used without purification. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. IR spectra were recorded as KBr pellets from 4000–400 cm^{-1} with a Bruker EQUINOX-55 spectrometer. ^{1}H NMR spectra were recorded on an INOVA-400 Varian 400 MHz spectrometer at room temperature. Fluorescence spectra were measured at room temperature on a Hitachi F-4500 fluorescence spectrophotometer.

2.2. *Syntheses*

2.2.1. 2,6-*Bis*-(5-phenyl-1H-pyrazol-3-yl) pyridine (H_2BPPP). To a solution of H_2BOPP (1.85 g, 5 mmol) in THF (40 mL) was dropwisely added 80% aqueous hydrazine (0.85 g, 10 mmol) in ethanol (5 mL). The reaction mixture was refluxed for 2 h, the solvent was removed and the residue was recrystallized from ethanol to give colorless crystals. Yield: 1.51 g, 60%. Anal. Calcd for $C_{23}H_{18}N_5$ (364): C, 75.80; H, 4.98; N, 19.22%. Found: C, 75.78; H, 4.99; N, 19.23%. IR (KBr): $\nu = 3195$, 1598, 1456, 1285, 1189, 1069, 963, 806, 762, 687 cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ 13.60 s (2, H–N=N–H), 8.04 d (1, H-pyridyl), 7.93 d (4, H-pyridyl and aromatic), 7.84 t (2, H-aromatic), 7.54 s (2, H-pyrazolyl), 7.47 t (4, H-aromatic), 7.35 t (2, H–aromatic).

2.2.2. [Zn(H_2BPPP)Cl_2](DMF)$_2$ (1). $ZnCl_2$ (0.027 g, 0.2 mmol) and H_2BPPP (0.074 g, 0.2 mmol) were dissolved in DMF (7.5 mL) and ethanol (2.5 mL). Carefully layering the resulting colorless solution with ethyl ether, colorless needles were obtained after a few days. Yield: 0.048 g, 43%. Anal. Calcd for $C_{29}H_{31}Cl_2N_7O_2Zn$: C, 53.94; H, 4.82; N, 15.17%. Found: C, 53.91; H, 4.80; N, 15.21%. IR (KBr): $\nu = 3428$, 3201, 1614, 1576, 1449, 1286, 1080, 1011, 810, 768, 691 cm^{-1}.

2.2.3. [Cd(H_2BPPP)Cl_2](DMF)$_2$ (2). Complex **2** was obtained using a procedure similar to that for **1** except that $CdCl_2 \cdot 2.5H_2O$ (0.045 g, 0.2 mmol) was used instead of $ZnCl_2$. Yield: 0.068 g, 57%. Anal. Calcd for $C_{29}H_{31}CdCl_2N_7O_2$: C, 50.24; H, 4.53; N, 14.18%. Found: C, 50.27; H, 4.51; N, 14.16%. IR (KBr): $\nu = 3528$, 3120, 2927, 1656, 1611, 1577, 1448, 1282, 1213, 1165, 1102, 1011, 978, 955, 918, 812, 765, 691, 666, 515, 451 cm^{-1}.

2.3. *X-ray crystallography*

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Empirical absorption corrections were applied by the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 [12, 13]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined as riding models. Crystal data and structural refinement parameters for H_2BPPP, **1** and **2** are summarized in table 1 and selected bond distances and angles are listed in table 2.

Table 1. Crystal data and structural refinement parameters for H_2BPPP, **1** and **2**.

Complex	H_2BPPP	**1**	**2**
Empirical formula	$C_{25}H_{23}N_5O$	$C_{29}H_{31}Cl_2N_7O_2Zn$	$C_{29}H_{31}CdCl_2N_7O_2$
Formula weight	409.48	645.88	692.91
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
Unit cell dimensions (Å, °)			
a	9.727(4)	20.51(1)	21.115(8)
b	30.84(1)	13.53(1)	13.113(5)
c	7.225(3)	11.42(1)	11.396(4)
α	90	90	90
β	91.932(8)	94.94(2)	90.709(6)
γ	90	90	90
V (Å^3)	2166(2)	3155(5)	3155(2)
Z	4	4	4
Crystal size (mm^3)	$0.24 \times 0.13 \times 0.11$	$0.12 \times 0.10 \times 0.08$	$0.18 \times 0.16 \times 0.10$
D_{Calcd} (g cm^{-3})	1.256	1.360	1.459
μ (mm^{-1})	0.080	0.985	0.899
F(000)	864	1336	1408
λ (Mo-Kα) (Å)	0.71073	0.71073	0.71073
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Reflections collected	10911	7875	15671
Unique reflections	3831	2788	5585
Parameters	283	190	374
S on F^2	0.980	1.008	0.917
R_{int}	0.0395	0.0611	0.0773
R_1, wR_2 [$I > 2\sigma(I)$]	0.0423, 0.0928	0.0532, 0.1111	0.0492 and 0.0896
R_1, wR_2 (all data)	0.0924, 0.1029	0.1194, 0.1397	0.1382 and 0.1194
$\Delta\rho_{\mathrm{min\ and\ max}}$ (e Å^{-3})	0.160 and −0.133	0.307 and −0.236	0.519 and −0.571

$R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$ for $F_o \geq 4\sigma(F_o)$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°).

H_2BPPP			
N1–C7	1.345(2)	N1–N2	1.351(2)
N2–C9	1.352(2)	N3–C10	1.340(2)
N3–C14	1.344(2)	N4–N5	1.348(2)
N5–C17	1.335(2)	N4–C15	1.351(2)
C7–N1–N2	104.8(2)	N1–N2–C9	113.0(2)
N5–N4–C15	113.5(2)	C17–N5–N4	104.3(2)
1			
Zn(1)–N(1)	2.108(5)	Zn(1)–N(2)	2.244(4)
Zn(1)–Cl(1)	2.239(2)		
Cl(1)–Zn(1)–N(2)	98.2(1)	N(1)–Zn(1)–Cl(1)#1	120.89(5)
Cl(1)#1–Zn(1)–Cl(1)	118.2(1)	N(1)–Zn(1)–N(2)#1	74.0(1)
N(2)–Zn(1)–N(2)#1	148.0(2)	Cl(1)#1–Zn(1)–N(2)	98.1(1)
2			
Cd(1)–Cl(1)	2.437(2)	Cd(1)–Cl(2)	2.414(2)
Cd(1)–N(4)	2.406(5)	Cd(1)–N(2)	2.384(5)
Cd(1)–N(3)	2.320(4)		
N(3)–Cd(1)–Cl(2)	124.7(1)	N(4)–Cd(1)–Cl(2)	100.1(1)
N(3)–Cd(1)–Cl(1)	118.8(1)	N(2)–Cd(1)–N(4)	138.0(2)
N(2)–Cd(1)–Cl(1)	103.5(1)	N(4)–Cd(1)–Cl(1)	96.7(1)
Cl(2)–Cd(1)–Cl(1)	116.24(7)		

Symmetric code for **1**, #1: $-x, y, -z + 3/2$.

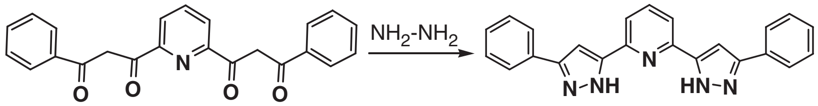
3. Results and discussion

3.1. *Syntheses*

Pyrazole derivatives can be prepared by reaction of 1,3-diketone with hydrazine through an isolable intermediate into a stable product [14, 15]. The *bis*(pyrazole) ligand, 2,6-*bis*-(5-phenyl-1H-pyrazol-3-yl) pyridine (H_2BPPP), was synthesized by reaction of the *bis*(1, 3-diketone) precursor, H_2BOPP with aqueous hydrazine (scheme 1). The H_2BOPP reacted with two equivalents of hydrazine in THF to form two pyrazolyl rings, and the product H_2BPPP was obtained and characterized by elemental analysis, IR and ^{1}H NMR. The molecular structure was confirmed by single crystal X-ray diffraction.

3.2. *Crystal structures*

3.2.1. H_2BPPP. The ligand crystallized in the monoclinic system with $P2_1/c$ space group. The asymmetric unit contains one H_2BPPP molecule and one ethanol. As shown in figure 1, the molecular structure is composed of one pyridyl ring bearing two phenyl pyrazolyl groups to form an arc structure. The central pyridyl and two pyrazolyl rings are almost coplanar with mean deviation of 0.092 Å. Two side phenyl rings are twisted to the least-squares plane (central pyridyl and pyrazolyl rings) in the opposite direction with dihedral angles of 35.33 and 38.31°, respectively. The pyrazolyl N–N bond lengths of 1.351(2) and 1.348(2) Å are in the normal range of pyrazolyl N–N bond distances reported [16, 17]. Two H_2BPPP molecules and two ethanol molecules assemble into a dimer by hydrogen bonding interactions (N2–H2A $\cdots$ O1, 2.918 Å, 153.0°;



Scheme 1. The synthesis of the H_2BPPP ligand.

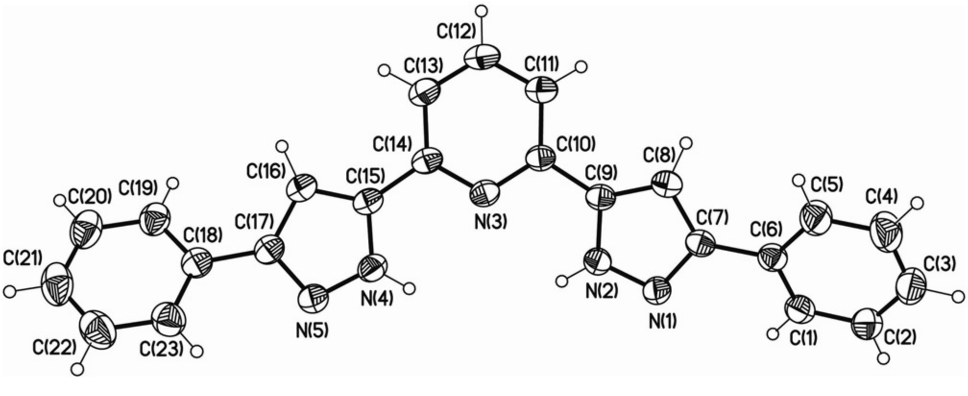


Figure 1. Perspective view of H_2BPPP with atomic numbering scheme (ellipsoids at the 30% level).

N4–H4A ⋯ O1, 2.963 Å, 169.9°; O1–H1A ⋯ N1B, 2.798 Å, 169.5°, symmetric code B: $-x+1, -y+2, -z+1$) (figure 2).

3.2.2. [Zn(H_2BPPP)Cl_2](DMF)$_2$ (1). Complex **1** is crystallized in the monoclinic system with $C2/c$ space group. The asymmetric unit contains half one Zn^{II} atom, half one H_2BPPP molecule, one chloride atom and one DMF. As shown in figure 3, the Zn^{II} is five-coordinate with a distorted trigonal bipyramidal geometry and is coordinated by three N atoms from H_2BPPP and two chlorides. The Zn–N bond lengths are 2.108(5) Å and 2.244(4) Å, respectively. The Zn–Cl bond length is 2.239(2) Å. The bond angles around Zn^{II} range from 73.99(10) to 148.0(2)°, similar to the reported values in [Zn((R, R)-et-pybox)Cl_2] ((R, R)-et-pybox is 2,6-*bis*[4′-(R)-ethoxyoxazolin-2′-yl]pyridine, the bond lengths Zn–N: 2.132(5) ~ 2.340(5), Zn–Cl: 2.217(18), 2.232(18);

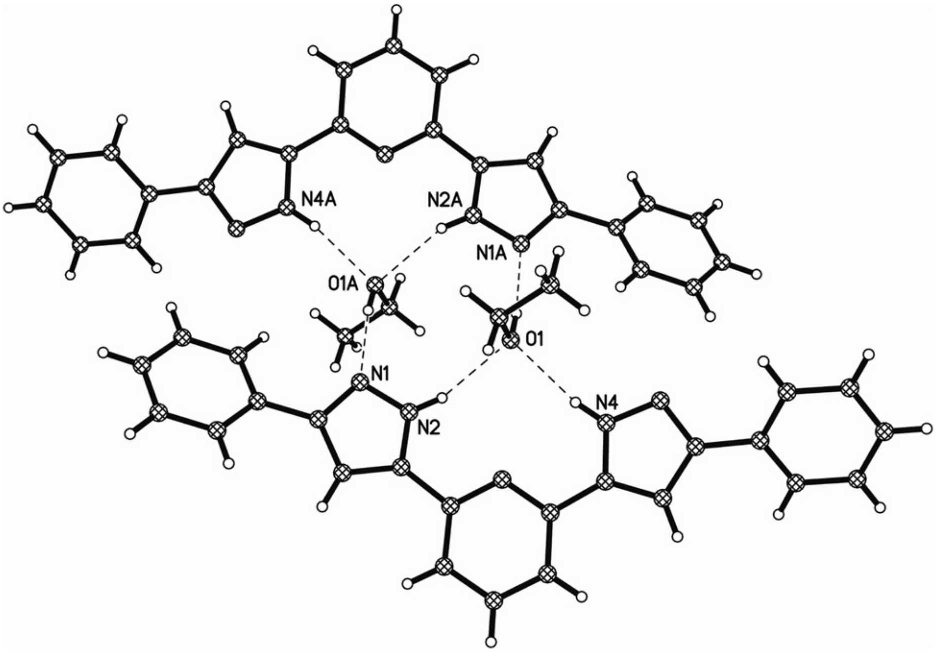


Figure 2. The hydrogen bonding interactions between H_2BPPP and ethanol.

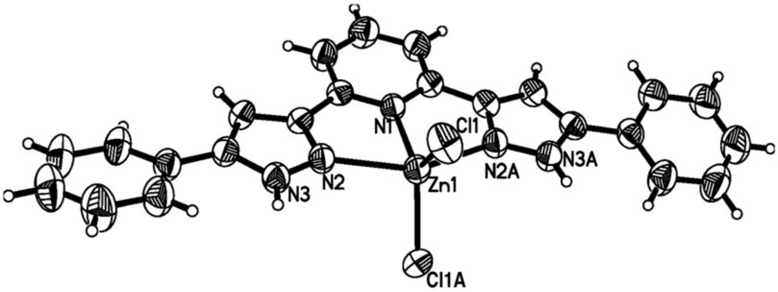


Figure 3. Perspective view of **1** with atomic numbering scheme (ellipsoids at the 50% level).

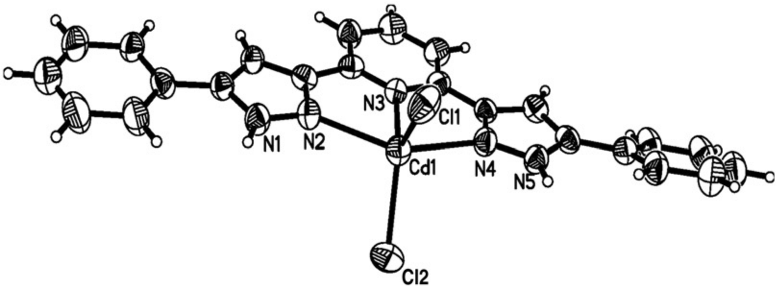


Figure 4. Perspective view of **2** with atom numbering scheme (ellipsoids at the 30% level).

the bond angle: $72.5 \sim 146.81^\circ$) [18]. The central pyridyl and two pyrazolyl rings are almost coplanar with mean deviation of 0.023 Å. Two side phenyl rings are twisted to the least-squares plane (central pyridyl and pyrazolyl rings) in the opposite direction with dihedral angle of 14.80°. A hydrogen bond is formed between the pyrazolyl NH and DMF [N3–H3 $\cdots$ O1A, 2.746(7) Å, 172.1°, symmetric code A: $(-x+1/2, -y+3/2, -z+1)$].

3.2.3. [Cd(L)Cl$_2$](DMF)$_2$ (2). Complex **2** is crystallized in the monoclinic system with $P2_1/c$ space group. The asymmetric unit contains one Cd^{II} atom, one H$_2$BPPP molecule, two chlorides and two DMF molecules. The molecular structure of **2** is similar to that of **1** (figure 4). The coordination geometry of Cd^{II} atom is best described as distorted trigonal bipyramidal with Cl1, Cl2 and N3 in the equatorial plane and N2 and N4 in axial sites. The Cd–N bond lengths range from 2.320(4) to 2.406(5) Å and Cd–Cl bond lengths are 2.414(2) and 2.437(2) Å. The bond angles around Cd^{II} range from 68.74(18) to 137.96(18)°, similar to reported values in [Cd(bbp)Cl$_2$] $\cdot$ DMF (bbp is 2,6-*bis*(benzimidazolyl)pyridine, the bond lengths Cd–N: 2.341(3)~2.383(3), Cd–Cl: 2.464(1) and 2.411(1); the bond angle: $68.7(1) \sim 138.3(1)^\circ$ [19]. The central pyridyl and two pyrazolyl rings are almost coplanar with mean deviation of 0.052 Å. The two phenyl rings are twisted to the least-squares plane (central pyridyl and pyrazolyl rings) in the opposite directions with dihedral angles of 5.62 and 22.75°, respectively. Hydrogen bonds are formed between the pyrazolyl NH and DMF [N1–H1 $\cdots$ O1C, 2.695(8) Å, 169.2°; N5–H5 $\cdots$ O2D, 2.740(7) Å, 173.7°; symmetric code C: $(x, -y+1/2, z+1/2)$; D: $(-x+1, -y, -z+1)$]. Although **1** and **2** have similar molecular structures, they adopt different molecular packing (figures 5 and 6) because the radius of Cd^{II} is larger than that of Zn^{II} atom.

3.3. *Proton transfer*

There are two adjacent nitrogens in the pyrazolyl ring and the H atom can be on either. So, there is a tautomeric equilibrium in the solution of H$_2$BPPP (scheme 2). Which tautomer is dominant could depend on the nature of the solvent [20–22]. In donor solvents such as MeCN, alcohols, pyridine or DMF, a strong hydrogen bond is formed between the pyrazolyl NH and the donor solvent. The H atoms are on the 2-positions of the pyrazolyl rings, confirmed by crystal structure of H$_2$BPPP. When metal cation

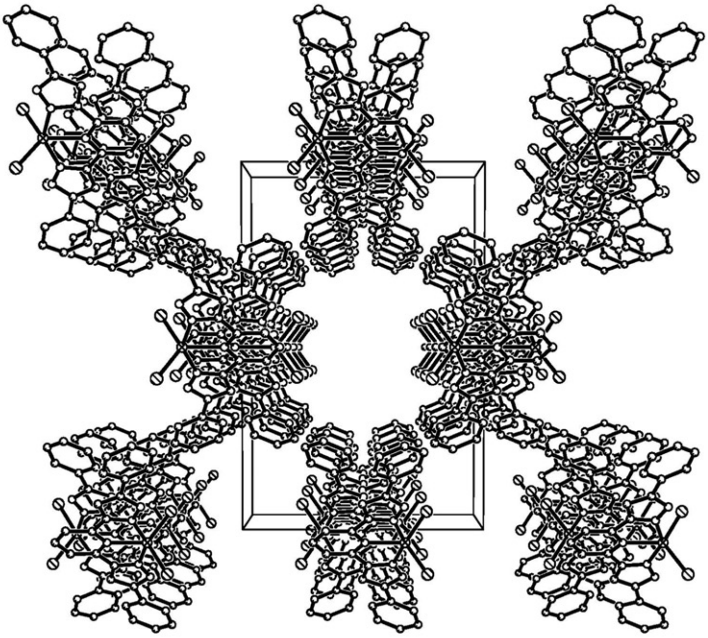


Figure 5. The packing diagram for **1** along the *c* axis.

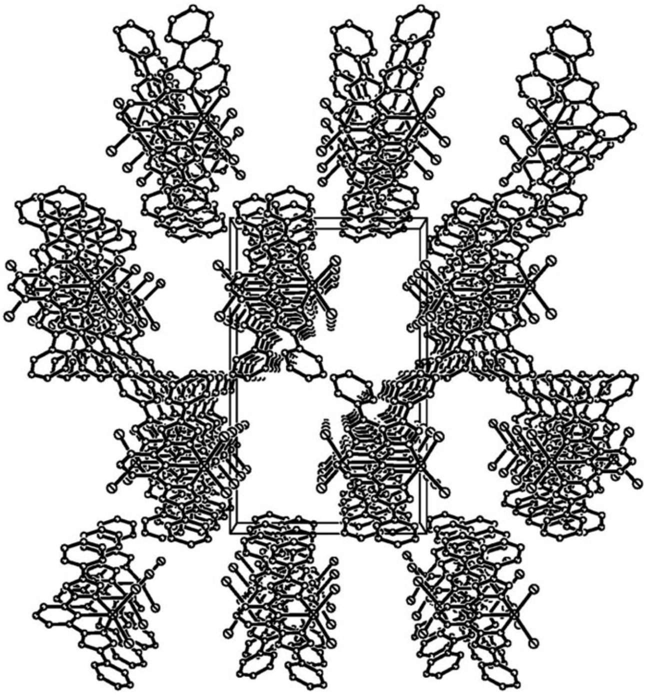
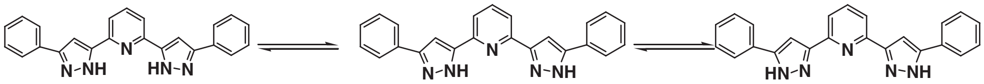


Figure 6. The packing diagram for **2** along the *c* axis.



Scheme 2. The tautomeric equilibrium of H_2BPPP in the solution.

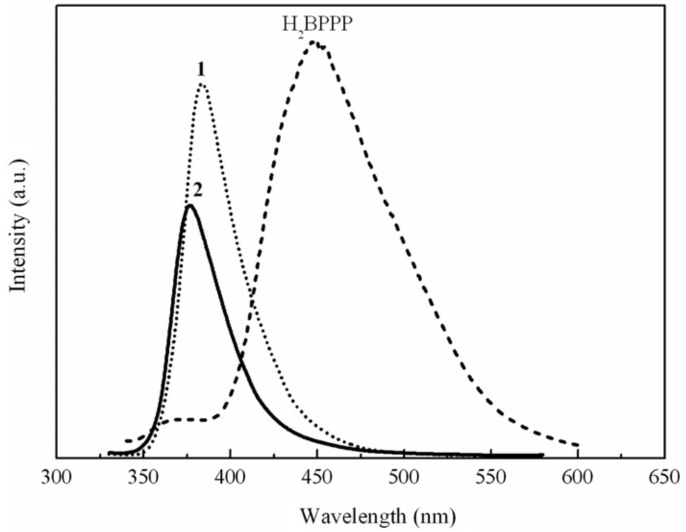


Figure 7. The emission spectra of H_2BPPP, **1** and **2** in the solid state at room temperature.

reacts with H_2BPPP, the N atoms of the 2-positions coordinate to the metal cation due to chelating effect. The H atoms of the pyrazolyl NH rings are on the 1-positions, confirmed by crystal structure of **1** and **2**.

3.4. *Luminescent properties*

The emission spectra of H_2BPPP, **1** and **2** were examined at room temperature, depicted in figure 7. H_2BPPP shows a strong and broad emission band at 448 nm upon excitation 320 nm, which originates from the π–π^* transition. Complex **1** displays a strong emission band at 383 nm upon excitation at 320 nm, a blue shift of about 65 nm relative to that of the H_2BPPP ligand. Similar to **1**, **2** also exhibits an intense emission peak at 377 nm upon excitation at 320 nm, a blue shift of 71 nm relative to that of H_2BPPP. We tentatively assign them to MLCT (metal to ligand charge transfer) transitions [23–25].

4. Conclusion

In summary, we have synthesized a new *bis*-pyrazole ligand, 2,6-*bis*-(5-phenyl-1H-pyrazol-3-yl)pyridine (H_2BPPP), and two d^{10} metal complexes. There is a tautomeric equilibrium of the *bis*-pyrazole compound in solution with the H atom of pyrazolyl NH group transferred to the adjacent N atoms. X-ray structure analyses reveal the H atom is on the 2-position of pyrazolyl in donor solvents, while the H atom is on the 1-position of pyrazolyl ring in the metal complexes. Moreover, the luminescence of the ligand and complexes have been examined.

Supplementary data

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC numbers are 635288, 681687 and 681688 for H_2BPPP, **1** and **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB 1EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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