

Syntheses, Crystal Structures, and Luminescence Properties of Co(II), Ni(II) and Zn(II) Complexes with 4'-(4-(Imidazol-1-yl)phenyl)-2,2':6',2''-Terpyridine¹

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Abstract—Three coordination complexes [Co(Imphpty)₂]Cl₂ · CHCl₃ · 3H₂O (I), [Ni(Imphpty)₂]Cl₂ · CHCl₃ · C₂H₅OH (II) and [Zn(Imphpty)]Cl₂ (III) (Imphpty = 4'-(4-(imidazol-1-yl)phenyl)2,2':6',2''-terpyridine) have been synthesized and characterized by IR, elemental analysis and X-ray single crystal diffraction (CIF files CCDC nos. 1012055 (I), 1011708 (II), 1011709 (III)). Complexes I and II are isomorphism except for some solvent molecules. In the crystal, both face-to-face interactions between pyridyl ring, imidazole rings and phenyl rings and hydrogen bonds facilitate the construction of 3D networks. There are no hydrogen bonds in III and the packing of discrete neutral molecules were ascribed to face-to-face interactions and van der Waals forces. The luminescence properties of three complexes have been investigated in the solid state at room temperature.

Keywords: 4'-(4-(imidazol-1-yl)phenyl)-2,2':6',2''-terpyridine, Co(II) complex, Ni(II) complex, Zn(II) complex, crystal structure, luminescence

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INTRODUCTION

In the past decades, coordination complexes based on substituted 2,2':6',2''-terpyridine with various groups have been widely investigated for their diverse structures and potential applications in luminescence [1, 2], magnetism [3, 4], catalysis [5, 6], dye-sensitized solar panel [7, 8] and nonlinear optical properties [9]. One of the most used strategies is to adopt ligands with coordination groups on 4' position of 2,2':6',2''-terpyridine [10–17]. Heterocyclic groups have been widely accepted and their influences on structures and properties have been well explored. Constable et al synthesized terpyridine ligands with substituted pyrazole or thiophene and the influence of these substitutes on the crystal structures were explored [18, 19]. Kharat et al synthesized a series of terpyridine complexes with thiophene as substitutes and their catalysis properties have been studied [20–24]. Terpyridine complexes with diphenylthiophen-2-amine substitutes were synthesized and their third order nonlinear optical properties have been studied by Tian [25]. Tian et al have also synthesized imidazole [17, 26, 27] or triazole [28–31] based terpyridine ligands and their fluorescence properties and ion probe potential have been studied. In [32–36], several terpyridine complexes with imid-

azole on 4' position of terpyridine have been synthesized and the DNA cleavage activities have been studied. Recently, terpyridine complexes with furan or thiophene substitutes have been studied for their potential applications as metallo-hydrogels in visual recognition [37]. Polyimidazole ligands have been accepted in constructing complexes with diverse structures and different properties for their coordination affinity [38–40]. In order to test the influence of imidazole substitutes on the crystal packing and properties of terpyridine complexes, a ligand combined by terpyridine and imidazole unit with benzene as bridge [41] was synthesized and three complexes with different metal ions, Co(II), Ni(II) and Zn(II), were synthesized and investigated with their fluorescence properties. Complexes I and II adopt a normally found homoleptic [M(Tpy)₂]²⁺ mode (Tpy = 2,2':6',2''-terpyridine) and they are isomorphism except for some solvent molecules. Complex III are single coordinated with only one ligand, 4'-(4-(imidazol-1-yl)phenyl)2,2':6',2''-terpyridine (Imphpty).

EXPERIMENTAL

Methods and materials. Imphpty ligand was synthesized by a literature method [42]. All the other reagents and solvents were commercially available and

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used as received. The infrared spectra of the complexes were recorded from KBr pellets in the range 4000–400 cm^{-1} on a shimadzu FTIR-8700 spectrometer. Elemental analyses of C, H and N were performed on an EA1110 CHNS-0 CE elemental analyzer. Photoluminescent analyses were performed on an Edinburgh EI920 fluorescence spectrometer with 450W xenon light.

Synthesis of complex I. A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.024 g, 0.1 mmol) in ethanol (10 mL) was layered onto a solution of imphtpy (0.038 g, 0.1 mmol) dissolved in chloroform (10 mL). After two weeks, brown crystalline blocks suitable for X-ray analysis were formed. The yield was 11.6%.

For $\text{C}_{49}\text{H}_{42}\text{N}_{10}\text{O}_{3.5}\text{Cl}_5\text{Co}$

Anal. calcd., %: C, 55.36; H, 3.98; N, 13.18.

Found, %: C, 54.94; H, 4.45; N, 12.86.

IR (KBr; ν , cm^{-1}): 3552.88 w, 3057.17 w, 1600.92 s, 1527.62 s, 1471.69 s, 1409.96 m, 1307.74 m, 1244.08 m, 1124.50 w, 1060.85 m, 1014.56 m, 962.48 m, 833.25 m, 790.81 s, 731.02 m, 655.80 m, 524.64 w.

Synthesis of complex II was carried out by similar to that of I except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.024 g, 0.1 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Slight blue crystalline blocks suitable for X-ray analysis were formed. The yield was 13%.

For $\text{C}_{52}\text{H}_{48}\text{N}_{10}\text{O}_{3.5}\text{Cl}_5\text{Ni}$

Anal. calcd., %: C, 56.52; H, 4.38; N, 12.68.

Found, %: C, 55.23; H, 4.70; N, 13.57.

IR (KBr; ν , cm^{-1}): 3392.79 m, 3078.39 w, 1600.92 v.s, 1527.62 s, 1471.69 v.s, 1409.96 s, 1303.88 m, 1244.08 m, 1055.06 m, 1014.56 m, 960.55 m, 904.61 w, 835.18 m, 794.67 s, 752.24 w, 657.72 m, 516.92 w, 418.55 m.

Synthesis of complex III was carried out by similar to that of I except that ZnCl_2 (0.014 g, 0.1 mmol) was used instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Slight yellow crystalline blocks suitable for X-ray analysis were formed. The yield was 8.7%.

For $\text{C}_{24}\text{H}_{25}\text{N}_5\text{O}_4\text{Cl}_2\text{Zn}$

Anal. calcd., %: C, 49.38; H, 4.32; N, 12.00.

Found, %: C, 48.11; H, 3.11; N, 11.30.

IR (KBr; ν , cm^{-1}): 3588 s, 352 (), 3109 m, 3074 m, 1614 v.s, 1600 v.s, 1570 s, 1545 s, 1487 s, 1475 s, 1458 s, 1431 s, 1383 m, 1304 w, 1252 m, 1230 m, 1090 v.s, 1014 v.s, 928 m, 883 m, 833 m, 793 s, 758 m, 744 s, 729 s, 685 m, 623 s, 584 m, 474 m, 447 m, 407 m.

X-ray structure determination. Crystals of I–III were mounted on a Bruker SMART APEX II CCD

diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K for I and II and CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) at 296(2) K for III. Empirical absorption corrections were applied by using the SADABS program. The structures were solved by direct methods and refined by full-matrix least squares on F^2 via SHELXL-97 program [43]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms in structure II and partly in I were generated geometrically. In structure I, some H atoms are refined isotropically. In complex III, the disordered benzyl group was modeled by splitting it into two parts. Crystallographic data and structural refinement parameters for complexes I–III are listed in Table 1. Selected bond lengths and angles are presented in Table 2. PLATON/SQUEEZE estimated the solvent-accessible region void to contain (11 + 11), (23 + 9 + 9 + 23 + 9 + 9) and (80 + 80) electrons for 1, 2 and 3, respectively. The electron densities were tentatively modeled as two water ($z = 4$; half H_2O molecule per asymmetric unit) for I, two ethanol and four H_2O molecules ($z = 4$; half ethanol and one H_2O molecules per asymmetric unit) for II and 16 H_2O molecules ($z = 4$; four H_2O molecules per asymmetric unit) for III. The final chemical formula of I–III were calculated from the SQUEEZE results combined with the elemental analyses data.

Supplementary crystallographic information for I–III has been deposited with Cambridge Crystallographic Data Center (CCDC nos. 1012055 (I), 1011708 (II), 1011709 (III); deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

RESULTS AND DISCUSSION

The asymmetric unit of I contains one Co(II) cation, two imphtpy ligands, two chlorine anions, one chloroform molecule and three and one half water molecules. Co(II) is coordinated by six N atoms from two imphtpy ligands. The distances between Co and N atoms from central pyridines (Co(1)–N(4) and Co(1)–N(7)) are 1.918(5) and 1.883(5) Å which are slightly shorter than that between Co and N atoms from outer pyridines (Co–N(6), Co–N(8), Co–N(3) and Co–N(5)), 2.013(3), 2.030(5), 2.113(5) and 2.119(5) Å). There are fifteen NCoN bond angles, which can be divided into two parts. Three are transoid angles ranged from $157.27(18)^\circ$ to $177.3(2)^\circ$ and the other twelve are cisoid ranged from $78.5(2)^\circ$ to $104.15(19)^\circ$. Both the differences of bond lengths and bond angles show a distorted octahedral geometry which are common for terpyridine coordinated complexes [44, 45]. The angles between imidazole ring and phenyl rings planes are 28.8° and 30.2° which suggest some twist relationships between these rings. The angles between phenyl ring and terpyridine ring are 41.8° and 35.9° which also suggest some twist relationships. The angle between two terpyridine rings is 86.1° .

Table 1. Crystallographic data and structure refinement parameters for **I–III***

Parameter	Value		
	I	II	III
Empirical formula	C ₄₉ H ₄₂ N ₁₀ O _{3.5} Cl ₅ Co	C ₅₂ H ₄₈ N ₁₀ O _{3.5} Cl ₅ Ni	C ₂₄ H ₂₅ N ₅ O ₄ Cl ₂ Zn
Formula mass	1063.12	1104.96	583.80
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>	<i>C</i> ₂ / <i>c</i>
<i>a</i> , Å	16.434(9)	16.3543(10)	11.067(2)
<i>b</i> , Å	15.553(8)	15.5876(13)	21.911(5)
<i>c</i> , Å	25.782(10)	26.0154(15)	11.3337(18)
β, deg	127.39(2)	127.819(4)	103.818(14)
<i>V</i> , Å ³	5236(4)	5238.9(6)	2668.9(9)
<i>Z</i>	4	4	4
ρ _{calcd} , g/cm ³	1.337	1.349	1.273
μ, mm ⁻¹	0.633	0.675	3.268
<i>F</i> (000)	2164	2192	1040
θ Range, deg	2.04–25.01	2.37–25.00	5.70–65.00
Reflections collected	32532	19704	6309
Unique reflections	9193	9233	2245
Reflections with <i>I</i> > 2σ(<i>I</i>)	5263	5542	1011
<i>R</i> _{int}	0.0785	0.0438	0.1176
GOOF on <i>F</i> ²	1.016	1.093	1.162
Restraints/parameters	105/624	14/629	26/155
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0936, 0.2521	0.0766/0.2267	0.0950/0.1984
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1425, 0.2947	0.1216, 0.2613	0.1793/0.2332
Largest diff. peak and hole, e Å ⁻³	0.527 and -0.674	1.221 and -0.666	0.675 and -0.774

$$*R = \sum(|F_o| - |F_c|) / \sum|F_o|, wR = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2 F_c^2)]^{1/2}.$$

Eleven hydrogen bonds, four with O–H⋯Cl type, two with C–H⋯N type, three with C–H⋯O type, and others with C–H⋯Cl type, link the individual components of **I** into three dimensional network which have been shown in Fig. 1b and listed in Table 3. Cl(1) atom is a triple acceptor linked with hydrogen H(1A), H(2A) and H(49) which are attached with O(1), O(2) and C(47). Cl(2) atom is also a triple acceptor linked with hydrogen H(1B), H(3A) and H(32) which are attached with O(1), O(3) and C(32). O(1) is a double acceptor linked with hydrogen H(28) and H(38) which are attached with C(28) and C(38). The most shortest hydrogen bonds is 2.0(2) Å for H(3A)⋯Cl(2). The other moderate hydrogen bond is 2.34(11) Å for H(1B)⋯Cl(2)^{#1}, 2.45(9) Å for H(2A)⋯Cl(1), 2.47 Å for H(25)⋯N(10)^{#4}, 2.49 Å for H(49)⋯Cl(1)^{#7} (symmetry codes are shown in Table 3). All the other hydrogen bond lengths are longer than 2.5 Å and they are weak hydrogen bonds. In addition, there exist three kinds of offset face-to-face interactions between pyridine,

imidazole and benzene rings as that shown in Fig. 1c. The distances between centroids of outer pyridine rings and pendant imidazole rings are 3.912 and 3.953 Å which are slightly shorter than that between two phenyl rings, 3.749 Å. These three almost parallel interactions link the [M(Imphpty)₂]²⁺ cations into one dimensional chains.

The asymmetric unit of **II** contains one Ni²⁺ cation, two Imphpty ligands, two chlorine anions, one ethanol molecule and one water molecule. The Ni²⁺ cation is coordinated by six N atoms from two Imphpty ligands. The distances between Ni and N from central pyridines (Ni–N(1) and Ni–N(6)) are 1.983(3) and 1.988(3) Å which are slightly shorter than that between Ni and N from outer pyridines (Ni–N(8), Ni–N(2), Ni–N(3) and Ni–N(7)), 2.109(4), 2.106(4), 2.106(3) and 2.098(3) Å. Among fifteen N–Ni–N bond angles, three transoid angles are 155.13(14)°–177.88(13)° and other twelve are cisoid angles ranged from 77.44(14)° to 103.12(13)°. All these

Table 2. Selected bond lengths and angles for **I–III**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
I					
Co(1)–N(4)	1.918(5)	Co(1)–N(5)	2.119(5)	Co(1)–N(6)	2.013(3)
Co(1)–N(7)	1.886(4)	Co(1)–N(3)	2.113(5)	Co(1)–N(8)	2.030(5)
II					
Ni(1)–N(1)	1.983(3)	Ni(1)–N(2)	2.106(4)	Ni(1)–N(3)	2.106(3)
Ni(1)–N(6)	1.988(3)	Ni(1)–N(7)	2.098(3)	Ni(1)–N(8)	2.109(4)
III					
N(1)–Zn(1)	2.150(3)	N(2)–Zn(1)	2.075(4)	Zn(1)–Cl(1)	2.2518(13)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
I					
N(4)Co(1)N(5)	78.5(2)	N(4)Co(1)N(3)	78.77(19)	N(4)Co(1)N(6)	99.12(17)
N(4)Co(1)N(8)	100.47(19)	N(3)Co(1)N(5)	157.27(18)	N(7)Co(1)N(4)	177.3(2)
N(7)Co(1)N(5)	104.15(19)	N(7)Co(1)N(3)	98.55(18)	N(7)Co(1)N(6)	80.43(17)
N(7)Co(1)N(8)	80.07(19)	N(8)Co(1)N(3)	92.91(19)	N(6)Co(1)N(3)	92.30(19)
N(6)Co(1)N(8)	160.36(16)	N(8)Co(1)N(5)	89.77(19)	N(6)Co(1)N(5)	92.70(18)
II					
N(1)Ni(1)N(2)	77.71(13)	N(1)Ni(1)N(3)	77.77(13)	N(1)Ni(1)N(6)	177.88(13)
N(1)Ni(1)N(7)	100.33(13)	N(1)Ni(1)N(8)	89.77(13)	N(2)Ni(1)N(8)	94.10(14)
N(3)Ni(1)N(2)	155.37(13)	N(3)Ni(1)N(8)	89.77(13)	N(6)Ni(1)N(2)	101.47(13)
N(6)Ni(1)N(3)	103.12(13)	N(6)Ni(1)N(7)	77.71(13)	N(6)Ni(1)N(8)	77.44(14)
N(7)Ni(1)N(2)	91.93(14)	N(7)Ni(1)N(3)	94.71(14)	N(7)Ni(1)N(8)	155.13(14)
III					
N(2)Zn(1)N(1) ^{#1}	74.97(9)	N(2)Zn(1)N(1)	74.97(9)	N(1) ^{#1} Zn(1)N(1)	149.94(18)
N(2)Zn(1)Cl(1) ^{#1}	121.48(4)	N(1) ^{#1} Zn(1)Cl(1)	98.37(8)	N(1)Zn(1)Cl(1) ^{#1}	97.20(8)
N(2)Zn(1)Cl(1)	121.48(4)	N(1) ^{#1} Zn(1)Cl(1)	97.20(8)	N(1)Zn(1)Cl(1)	98.36(8)
Cl(1) ^{#1} Zn(1)Cl(1)	117.03(7)				

* Symmetry codes: ^{#1} $-x, y, -z + 3/2$.

fifteen bond angles are similar with that in **I**. Both the differences of bond lengths and bond angles show a distorted octahedral geometry in **II** like **I** and other terpyridine coordinated complexes [44, 45]. The angles between imidazole ring and phenyl rings planes are 29.9° and 30.9° which suggest some twist [46] relationship between these rings. The angles between phenyl ring and terpyridine ring are 40.4° and 34.7° which also suggest some twist relationship. The angle between two terpyridine rings is 85.0°. Nine hydrogen bonds, one with O–H···O type, two with O–H···Cl type, two with C–H···O type, two with C–H···Cl type and others with C–H···N type, link the individual components of **II** into three dimensional network which have been shown in Fig. 2b and listed in Table 3. Cl(1) atom is a triple acceptor linked with hydrogen H(2A), H(2B) and H(3) which are attached with O(2) and C(3). The most shortest hydrogen bonds is 2.03 Å for H(1A)···O(2)^{#1}. The other moderate hydrogen

bond is 2.38 Å for H(46)···O(1)^{#5}, 2.41 Å for H(2)···O(2), 2.42 Å for H(15)···N(5)^{#3}, 2.48 Å both for H(25)···N(10)^{#4} and H(49)···Cl(2) (symmetry codes are shown in Table 3). All the other hydrogen bond lengths are longer than 2.5 Å and they are weak hydrogen bonds. In addition, there also exist three kinds of offset face-to-face interactions between pyridine and benzene rings like **I** as that shown in Fig. 2c. The distances between centroids of outer pyridine rings and pendant imidazole rings are 3.863 and 3.867 Å which are slightly shorter than that between two phenyl rings, 3.685 Å. These three shorter interactions than that in **I** are almost parallel too, and they link the [M(Imphpty)₂]²⁺ cations into one dimensional chains as that in **I**.

The asymmetric unit of **III** contains one Zn²⁺ cation, one Imphpty ligands, two perchlorate anions. The Zn²⁺ cation is coordinated by three N atoms from one Imphpty ligands, two Cl[−] anions. The distance

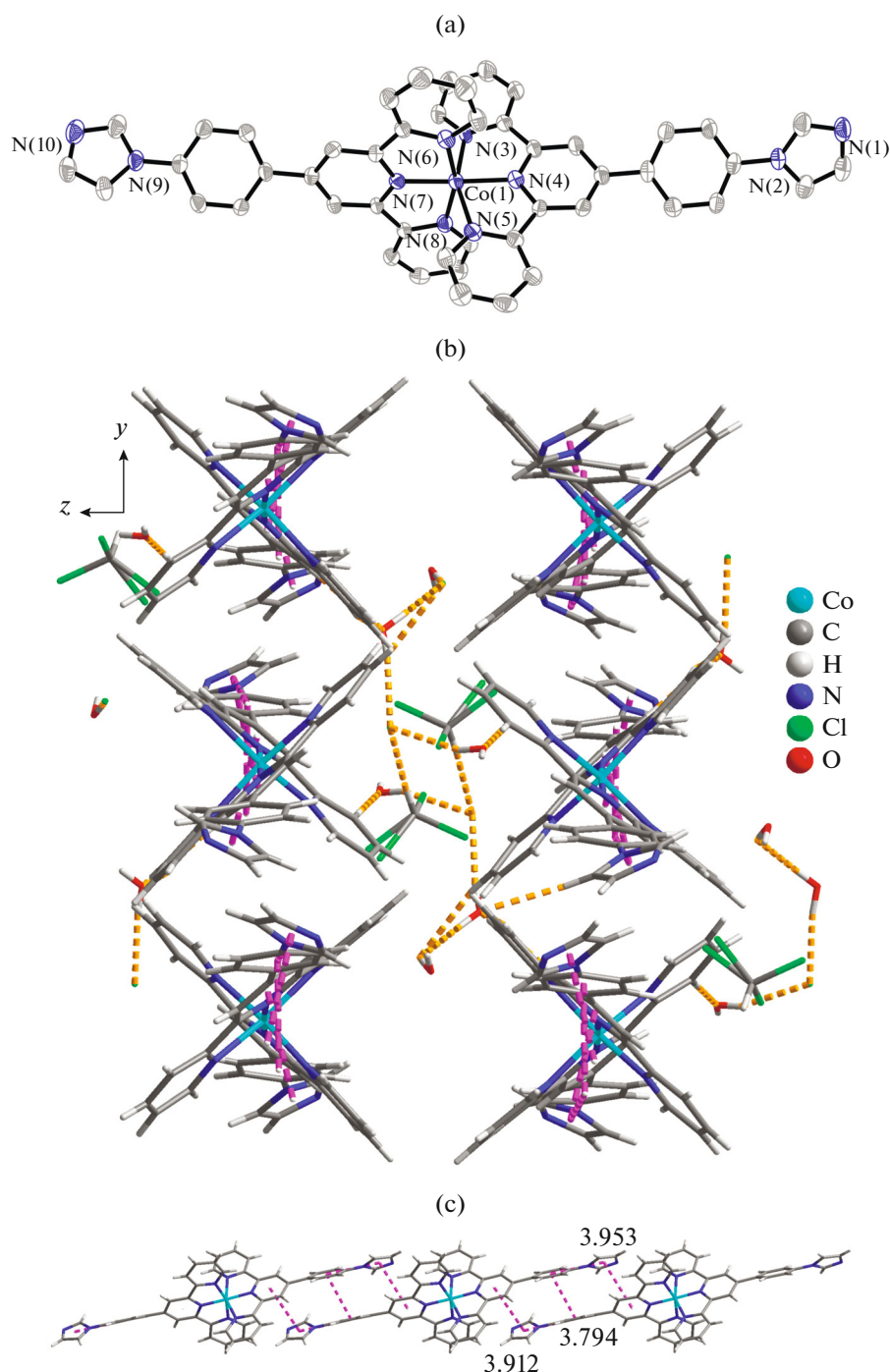


Fig. 1. The ORTEP view of $[\text{Co}(\text{Imphpty})_2]^{2+}$ in **I** with thermal ellipsoids at 30% probability level (a); the 3D supramolecular network of **I** formed through hydrogen bonds and the face-to-face π – π interactions (shown in dashed lines with different colors in electric print) (b); the face-to-face π – π interactions between two adjacent $[\text{Co}(\text{Imphpty})_2]^{2+}$ motifs (c).

between Zn and N from central pyridine (Zn–N(2)) are 2.075(4) Å, which are slightly shorter than that between Zn and N from outer pyridines (Zn–N(1)), 2.150(3) Å. The distance between Zn and Cl atom is 2.2518(13) Å which are similar with other chlorine coordinated terpyridine complexes [46, 47]. There are

ten bond angles around Zn²⁺ cation, which can be divided into two parts. One is transoid angle with N(1)^{#1}Zn(1)N(1), 149.94(18)° and the other nine are cisoid ranged from 74.97(9)° to 121.48(4)°. The angles between imidazole ring and phenyl rings are 13.5° or 29.2° and the angles between phenyl rings and terpyri-

Table 3. Geometric parameters of hydrogen bonds for **I–II***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
I				
O(1)–H(1A)···Cl(1)	0.84(5)	2.19(6)	3.026(7)	172(14)
O(1)–H(1B)···Cl(2) ^{#1}	0.85(10)	2.34(11)	3.129(9)	155(11)
O(2)–H(2A)···Cl(1)	0.85(11)	2.45(9)	3.252(10)	160(14)
O(3)–H(3A)···Cl(2)	0.85(19)	2.0(2)	2.802(14)	156(10)
C(1)–H(1)···N(1) ^{#2}	0.93	2.59	3.410(13)	147
C(12)–H(12)···O(2) ^{#3}	0.93	2.54	3.470(15)	177
C(25)–H(25)···N(10) ^{#4}	0.93	2.47	3.270(12)	145
C(28)–H(28)···O(1) ^{#5}	0.93	2.54	3.463(11)	170
C(32)–H(32)···Cl(2) ^{#6}	0.93	2.75	3.666(8)	169
C(38)–H(38)···O(1) ^{#5}	0.93	2.56	3.492(9)	176
C(49)–H(49)···Cl(1) ^{#7}	0.98	2.49	3.47(2)	175
Symmetry code: ^{#1} $-x + 1, -y - 1, -z$; ^{#2} $x - 1, y, z$; ^{#3} $-x + 1, -y, -z$; ^{#4} $x + 1, y, z$; ^{#5} $-x, y + 3/2, -z + 1/2$; ^{#6} $-x + 1, y + 3/2, -z + 3/2$; ^{#7} $-x + 1, y + 1/2, -z + 1/2$.				
II				
O(1)–H(1A)···O(2) ^{#1}	0.90	2.03	2.91(2)	163
O(2)–H(2A)···Cl(1) ^{#2}	0.85	2.79	3.176(19)	110
O(2)–H(2B)···Cl(1) ^{#2}	0.85	2.82	3.176(19)	107
C(2)–H(2)···O(2)	0.93	2.41	3.214(17)	145
C(3)–H(3)···Cl(1) ^{#2}	0.93	2.68	3.593(7)	166
C(15)–H(15)···N(5) ^{#3}	0.93	2.42	3.251(12)	149
C(25)–H(25)···N(10) ^{#4}	0.93	2.48	3.282(11)	144
C(46)–H(46)···O(1) ^{#5}	0.93	2.38	3.306(9)	173
C(49)–H(49)···Cl(2)	0.98	2.48	3.452(17)	174
Symmetry code: ^{#1} $-x + 2, -y, z - 2$; ^{#2} $x, -y + 1/2, z + 1/2$; ^{#3} $x + 1, y, z$; ^{#4} $x - 1, y, z$; ^{#5} $-x + 2, y + 3/2, -z - 1/2$.				

* According to platon calculation, no classic hydrogen bonds were found for complex **III**.

dine ring planes are 18.7° or 24.0° just as there are disordered C atoms on phenyl rings. These relatively small dihedral angles suggest fine coplanar properties. In the crystal, as that shown in Fig. 3b, all the terpyridine planes are almost parallel with each other by van der Waals forces or two kinds of π – π interactions, one between imidazole ring and outer pyridine ring and the other between outer pyridine ring and central pyridine ring which are occasionally found in some complexes [48–51].

The solid-state luminescence of the ligand Imphpty (**L**¹) and complexes **I–III** were measured at room temperature. In comparison to the emission of **L**¹ (454 nm, excited at 360 nm), **I** and **II** show almost same fluorescent peaks at 458 nm (excited at 360 nm) and 458 nm (excited at 360 nm) with a slight red-shift of 4 nm, accompanied by a higher intensity for **I** and

lower intensity for **II** (Fig 4). Although Co(II) and Ni(II) have d^7 or d^8 configurations, these emissions were attributed to intraligand (ILCT) rather than metal to ligand or ligand to metal charge transfer for their similarities. In comparison to the emission of **L**¹, **III** shows a peak at 530 nm (excited at 360 nm) with a bathochromic shift of 76 nm and similar intensity which would be also attributed to Zn(II) influenced ILCT and this obvious red-shift of maximum wavelength were commonly found in terpyridine Zn(II) complexes [2, 52–54]. Compounds **L**¹, **I** and **II** may be used as blue luminescence materials and **III** maybe used as green luminescence materials.

Thus, three 4'-(4-(imidazol-1-yl)phenyl)-2,2':6',2''-terpyridine complexes, two with $[M(\text{Tpy})_2]^{2+}$ type and one with $[M(\text{Tpy})]^{2+}$ type have been synthesized and investigated for their crystal structures and fluo-

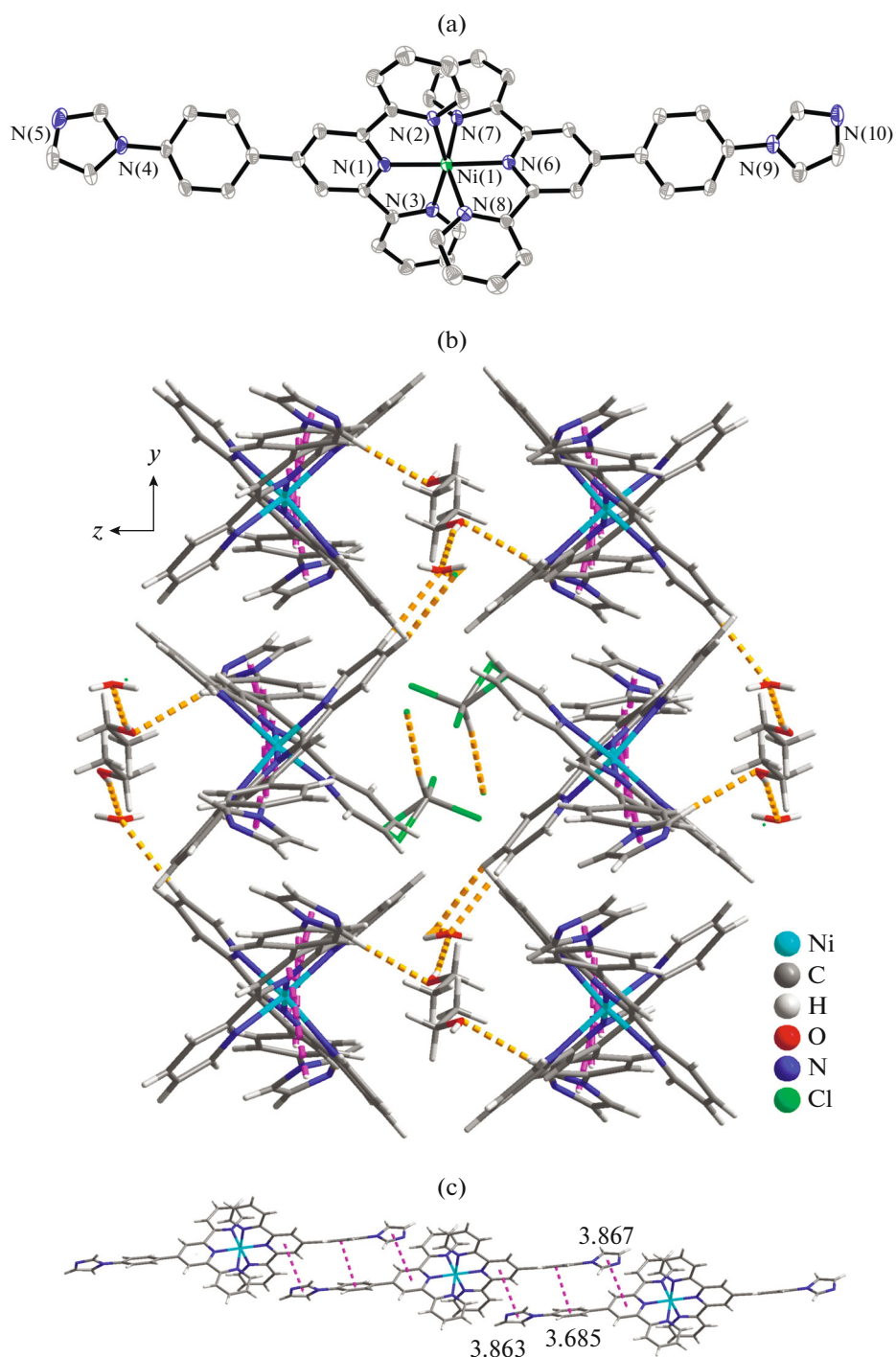


Fig. 2. The ORTEP view of $[\text{Ni}(\text{imphpty})_2]^{2+}$ in **II** with thermal ellipsoids at 30% probability level (a); the 3D supramolecular network of **II** formed through hydrogen bonds and the face-to-face π - π interactions (shown in dashed lines with different colors in electric print) (b); the face-to-face π - π interactions between two adjacent $[\text{Ni}(\text{Imphpty})_2]^{2+}$ motifs (c).

rescence properties. Different hydrogen bonds and π - π interactions between aromatic rings resulted in different crystal packing patterns in these complexes. Complexes **I** and **II** are isomorphs except for some solvent molecules and rarely found three parallel π - π

interactions link the $[\text{Mn}(\text{Tpy})_2]^{2+}$ motifs into 1D chain. In contrast, parallel planes of $[\text{M}(\text{Tpy})]^{2+}$ were found in **III** formed by two π - π interactions. The similar intensities and different fluorescence peaks of three complexes and Imphpty ligand were found and

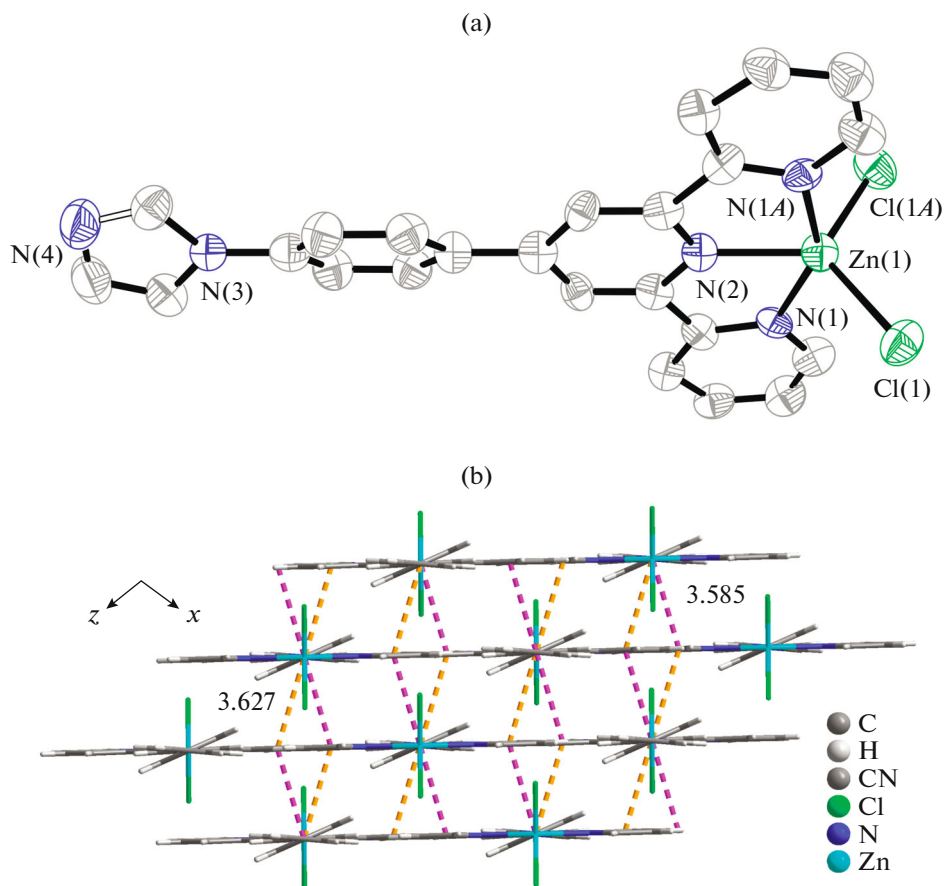


Fig. 3. The ORTEP view of $[\text{Cu}(\text{meophpty})_2]^{2+}$ in **III** with thermal ellipsoids at 30% probability level (a); the face-to-face π – π interactions between adjacent $[\text{Zn}(\text{Imphpty})]\text{Cl}_2$ motifs (b).

they could be used as potential luminescent materials with blue or green light emissions.

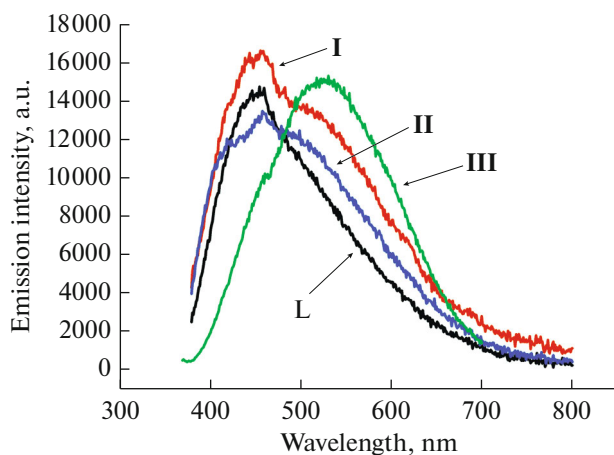


Fig. 4. Emission spectra of the complexes **I–III** and free ligands Imphpty (L^1).

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