Polyhedron 29 (2010) 2862–2866

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Syntheses, structures, and luminescent properties of copper(II) complexes based on 2,6-bis(imino)pyridyl ligands

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ARTICLE INFO

Article history:
Received 17 March 2010
Accepted 14 July 2010
Available online 11 August 2010

Keywords:
Complexes
Luminescence
Bis(imino)pyridine ligands
X-ray diffraction

ABSTRACT

A series of five-coordinated 2,6-bis(imino)pyridyl Cu(II) complexes, [2,6-$(ArN{=}CMe)_2C_5H_3N$-$CuCl_2 \cdot nCH_3CN$] (Ar = 4-MeC_6H_4, $n = 0.5$, **Cu1**; Ar = 2,6-$Et_2C_6H_3$, $n = 1$, **Cu2**; Ar = 2,4,6-$Me_3C_6H_2$, $n = 1$, **Cu3**; Ar = 2,6-$Me_2C_6H_3$, $n = 0$, **Cu4**; Ar = 2-MeC_6H_4, $n = 1$, **Cu5**), were synthesized in acetonitrile by reactions of the corresponding bis(imino)pyridine ligands with $CuCl_2 \cdot 2H_2O$, respectively. The structures of five complexes were determined by single-crystal X-ray diffraction. In all complexes, the metal center is tridentately chelated by ligand and further coordinated by two chlorine atoms, resulting in distorted trigonal-bipyramidal geometry for **Cu1**, **Cu3**, **Cu4**, and **Cu5**, respectively, and approximately square-pyramidal geometry for **Cu2**. At 298 K in dichloromethane solution, all complexes exhibit blue-green luminescent emissions at about 478–499 nm, which could be attributed to ligand-centered $\pi^* \rightarrow \pi$ transitions. However, fluorescent emission of complexes **Cu1**–**Cu5** is significantly weaker than those of ligands, which could be attributed to fluorophore-quencher interactions *via* paramagnetic Cu(II) center.

1. Introduction

Luminescent coordination compounds with nitrogen-containing ligands have attracted much attention recently due to their good performance in sensor technologies and electroluminescent devices [1–13]. With the development of supramolecular chemistry, self-assembly *via* intermolecular hydrogen bonding and/or aromatic π–π interactions has provided an effective approach to construct functional coordination frameworks [8–11]. It has been found that, for a given complex, the size of π-conjugated system of the ligand and the electronic effect of substituents on the ligand are important factors for modulating its luminescent properties [3,4]. In the past decade, iron and cobalt complexes with bulky aryl substituted bis(imino)pyridyl ligands were reported by Gibson and Brookhart et al. [14,15]. These iron and cobalt complexes exhibit high activity for olefin polymerization. In 2009, Jurca et al. have reported one new 2,6-bis(imino)pyridyl indium complex and revealed a unique monomeric In(I) species with a surprisingly long metal–ligand bond [16]. In recent years, we have devoted efforts toward the synthesis of bis(imino)pyridine complexes with luminescent properties [12,13]. To our knowledge, the syntheses and luminescent properties of copper(II) complexes with aryl substituted bis(imino)pyridyl ligands have not been reported. A few fluorescent molecules which exhibit luminescence enhancement in the presence of Cu(II) ion are reported [17]. Many fluorescent molecules are often efficiently quenched by paramagnetic Cu(II) ion, and design and synthesis of efficiently luminescent chelating Cu(II) complexes is also of importance for detection of Cu(II), as copper and its derivatives are toxic contaminants for environment [17]. In this work, we report the syntheses, structures, and blue-green luminescent properties of new five Cu(II) complexes with bis(imino)pyridyl ligands.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out under nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Elemental analyses were performed with a Perkin–Elmer 240c element analyzer. IR spectra were obtained with a Nicolet Impact 410 FTIR spectrometer using KBr pellets. NMR spectra were recorded with a Varian Mercury 400 MHz spectrometer. UV–Vis spectra were obtained with a Perkin–Elmer Lambda 20 spectrometer. Luminescence spectra were measured with a Perkin–Elmer LS55 Luminescence spectrometer at room temperature. 4-Methylaniline, 2,6-diethylaniline, 2,4,6-trimethylaniline, 2,6-dimethylaniline, and 2-methylaniline were purchased from Aldrich Chemical Co., and used as received. Solvents were refluxed in the presence of an appropriate drying agent, and distilled and degassed prior to use. For methanol, Mg ribbon was used as drying agent, whereas acetonitrile and dichloromethane were dried with calcium hydride. 2,6-Diacetylpyridine was prepared according to a published procedure [19].

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doi:10.1016/j.poly.2010.07.012

*2.2. Syntheses of complexes **Cu1**–**Cu5***

*2.2.1. Synthesis of 2,6-bis[1-(4-methylphenylimino)ethyl] pyridine$CuCl_2\cdot 0.5CH_3CN$ (**Cu1**)*

A mixture of L^1 (170 mg, 0.50 mmol) and $CuCl_2\cdot 2H_2O$ (84 mg, 0.50 mmol) in acetonitrile (45 mL) was stirred under nitrogen at room temperature for 8 h. Evaporation of the solvent gave the crude product as yellow powder. Pure product **Cu1** was obtained in 77% yield (191 mg) by recrystallization from CH_3CN/THF (2:1). IR (KBr, cm^{-1}): ν 3415 (vs), 3063 (m), 3025 (m), 2915 (m), 2849 (w), 1624 (m), 1578 (m), 1503 (vs), 1419 (m), 1397 (m), 1376 (s), 1268 (s), 1227 (m), 1107 (m), 1014 (w), 849 (m), 808 (m), 745 (w), 707 (w), 663 (w), 554 (w), 518 (w), 477 (w). *Anal.* Calc. for $C_{23}H_{23}N_3CuCl_2\cdot 0.5CH_3CN$: C, 58.07; H, 4.97; N, 9.88. Found: C, 57.89; H, 4.66; N, 9.98%.

*2.2.2. Synthesis of 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine $CuCl_2\cdot CH_3CN$ (**Cu2**)*

The procedure is similar to that described for the preparation of **Cu1**, except L^2 was used in place of L^1 to obtain yellow crystals of **Cu2**. Yield 80%. IR (KBr, cm^{-1}): ν 3412 (s), 3062 (m), 3010 (m), 2964 (s), 2932 (m), 2874 (m), 1615 (s), 1582 (vs), 1446 (vs), 1368 (vs), 1264 (vs), 1219 (s), 1109 (w), 1037 (m), 874 (w), 809 (s), 783 (s), 653 (w), 556 (w), 432 (w). *Anal.* Calc. for $C_{29}H_{35}N_3CuCl_2\cdot CH_3CN$: C, 61.94; H, 6.37; N, 9.32. Found: C, 62.07; H, 6.22, N, 9.21%.

*2.2.3. Synthesis of 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl] pyridine$CuCl_2\cdot CH_3CN$ (**Cu3**)*

The procedure is similar to that described for the preparation of **Cu1**, except L^3 was used in place of L^1 to obtain yellow crystals of **Cu3**. Yield 70%. IR (KBr, cm^{-1}): ν 3083 (w), 2947 (w), 2920 (m), 1644 (s), 1581 (s), 1433 (s), 1365 (m), 1249 (s), 1215 (vs), 1161 (w), 1092 (w), 1017 (m), 860 (s), 813 (s), 738 (w), 635 (w), 567 (w). *Anal.* Calc. for $C_{27}H_{31}N_3CuCl_2\cdot CH_3CN$: C, 60.78; H, 5.98; N, 9.78. Found: C, 60.98; H, 5.81; N, 9.86%.

*2.2.4. Synthesis of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl] pyridine$CuCl_2$ (**Cu4**)*

The procedure is similar to that described for the preparation of **Cu1**, except L^4 was used in place of L^1 to obtain yellow crystals of **Cu4**. Yield 76%. IR (KBr, cm^{-1}): ν 3447 (m), 3074 (m), 3019 (w), 2942 (m), 2908 (m), 2866 (w), 1618 (s), 1584 (vs), 1556 (m), 1540 (m), 1501 (m), 1471 (vs), 1373 (s), 1266 (vs), 1223 (vs), 1162 (w), 1101 (m), 1036 (m), 981 (w), 827 (m), 814 (s), 785 (m), 769 (s), 740 (m), 641 (w), 592 (w), 515 (w), 427 (m). *Anal.* Calc. for $C_{25}H_{27}N_3CuCl_2$: C, 59.59; H, 5.40; N, 8.34. Found: C, 59.36; H, 5.19; N, 8.39%.

*2.2.5. Synthesis of 2,6-bis[1-(2-methylphenylimino)ethyl] pyridine$CuCl_2\cdot CH_3CN$ (**Cu5**)*

The procedure is similar to that described for the preparation of **Cu1**, except L^5 was used in place of L^1 to obtain yellow crystals of **Cu5**. Yield 81%. IR (KBr, cm^{-1}): ν 3438 (s), 3068 (m), 3016 (w), 2958 (w), 2912 (m), 2251 (w), 1621 (s), 1582 (vs), 1478 (s), 1459 (m), 1374 (s), 1271 (s), 1232 (m), 1199 (w), 1115 (w), 1037 (m), 992 (w), 815 (m), 757 (s), 718 (m), 660 (w), 601 (w), 556 (w), 445 (m). *Anal.* Calc. for $C_{23}H_{23}N_3CuCl_2\cdot CH_3CN$: C, 58.09; H, 5.07; N, 10.84. Found: C, 58.32; H, 4.98; N,10.64%.

2.3. X-ray crystallography

The data were collected with a Rigaku R-AXIS RAPID IP or a Siemens SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package [20]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in idealized position. Crystallographic data are given in Table 1 (for **Cu1**–**Cu5**).

3. Results and discussion

3.1. Synthesis and characterization

2,6-Bis[1-(4-methylphenylimino)ethyl]pyridine(L^1), 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine(L^2), 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine(L^3), 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridine(L^4), and 2,6-bis[1-(2-methylphenylimino) ethyl]pyridine(L^5) were synthesized according to modified published procedures in good yield by condensation of 2,6-diacetyl-

Table 1
Crystal data and structure refinement for **Cu1**–**Cu5**.

Data	**Cu1**	**Cu2**	**Cu3**	**Cu4**	**Cu5**
Formula	$C_{24}H_{24.5}N_{3.5}Cl_2Cu$	$C_{31}H_{38}N_4Cl_2Cu$	$C_{29}H_{34}N_4Cl_2Cu$	$C_{25}H_{27}N_3Cl_2Cu$	$C_{25}H_{26}N_4Cl_2Cu$
Formula weight	496.41	601.09	573.04	503.94	516.94
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	8.227(2)	12.988(1)	14.447(3)	12.689(3)	13.109(8)
b (Å)	13.995(3)	15.093(1)	15.025(3)	11.745(2)	14.783(9)
c (Å)	22.307(5)	16.467(1)	14.530(3)	16.560(3)	13.475(8)
α (°)					
β (°)	93.30(3)	101.635(1)	113.54(3)	97.92(3)	107.523(9)
γ (°)					
Volume (Å^3)	2564.1(9)	3161.6(3)	2891.5(10)	2444.4(8)	2490(3)
Z	4	4	4	4	4
D_{calc} (g cm^{-3})	1.286	1.263	1.316	1.369	1.379
μ (mm^{-1})	1.076	0.885	0.964	1.129	1.111
$F(0\,0\,0)$	1024	1260	1196	1044	1068
θ Range for data collection	1.72–27.48°	1.60–26.03°	3.06–27.47°	2.37–27.48°	1.90–26.04°
Limiting indices	$0 \leqslant h \leqslant 10$	$-15 \leqslant h \leqslant 16$	$-17 \leqslant h \leqslant 18$	$0 \leqslant h \leqslant 16$	$-15 \leqslant h \leqslant 16$
	$0 \leqslant k \leqslant 18$	$-18 \leqslant k \leqslant 18$	$-19 \leqslant k \leqslant 19$	$0 \leqslant k \leqslant 15$	$-16 \leqslant k \leqslant 8$
	$-28 \leqslant l \leqslant 28$	$-19 \leqslant l \leqslant 20$	$-18 \leqslant l \leqslant 18$	$-21 \leqslant l \leqslant 21$	$-16 \leqslant l \leqslant 13$
Absorption correction	Semi-empirical				
Data/restraints/parameters	5342/11/289	5640/36/345	6519/0/326	5584/42/280	4850/31/289
Goodness-of-fit on F^2	1.062	0.975	1.020	1.013	0.939
R_1[a]	0.0619	0.0552	0.0504	0.0520	0.0776
Largest difference in peak and hole (e Å^{-3})	0.792/−0.383	1.231/−0.468	0.819/−0.465	0.960/−0.468	0.866/−0.427

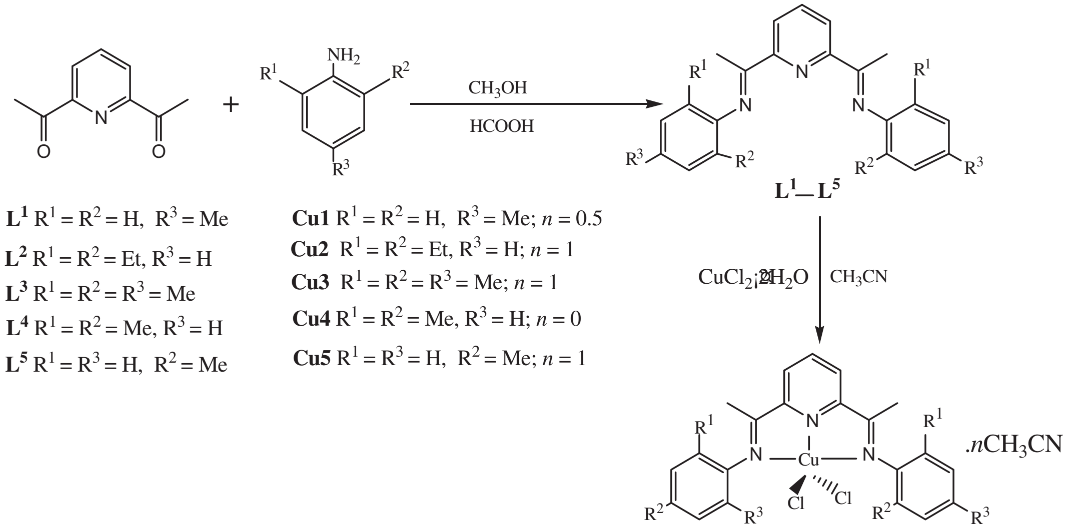
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

pyridine with the corresponding aniline in refluxing absolute methanol in the presence of a catalytic amount of formic acid (Scheme 1) [12–15]. Complexes **Cu1**–**Cu5** were prepared in good yields (>70%) as yellow crystalline solids by reaction of $CuCl_2 \cdot 2H_2O$, with corresponding equivalent free 2,6-bis(imino)pyridine ligands in acetonitrile. Upon exposure to air, all complexes are stable in the solid state and in solution such as CH_2Cl_2, CH_3CN, DMSO, and DMF. All the complexes were characterized by elemental analysis, IR, and UV–Vis spectroscopy.

3.2. Description of structures

The molecular structures of the complexes **Cu1**–**Cu5** were determined by X-ray crystallographic analysis. Single crystals of complexes **Cu1**–**Cu5** suitable for X-ray structural determination were grown from a solution of acetonitrile/tetrahydrofuran (2:1, v/v). Complexes **Cu1**–**Cu4** are similar symmetry, therefore, only the molecular structure of **Cu1** is shown in Fig. 1. The molecular structure of **Cu5** is shown in Fig. 2. Selected bond lengths and angles are summarized in Table 2.

Complexes **Cu1**–**Cu4** are approximate C_s symmetry about a plane bisecting the central pyridine ring and containing the copper atom and two chlorine atoms, while complex **Cu5** adopts C_2 symmetry. The central copper atom in complexes **Cu1**–**Cu5** is coordinated to five groups and the geometry about the copper atom is described as a distorted trigonal-bipyramid, with the equatorial plane defined by the N(2)(pyridine), two chloride atoms [Cl(1) and Cl(2)] and two nitrogen atoms [N(1) and N(3)(imino)] in the axial positions. Complexes **Cu2**, **Cu3**, and **Cu5** crystallize with an independent molecule and an acetonitrile molecule in unit cell, and complex **Cu1** crystallizes with an independent molecule and half acetonitrile molecule in the asymmetric unit. The mean deviation of the copper atoms in **Cu1**–**Cu5** from the equatorial planes is 0.007, 0.023, 0.003, 0.013, and 0.002 Å, respectively, and the axial Cu–N(imino) bonds subtend angles of 155.9(3)°, 136.43(13)°, 154.32(11)°, 151.35(12)°, and 155.4(2)°, respectively. The copper atoms in **Cu1**–**Cu5** deviate by 0.026, 0.361, 0.092, 0.314, and 0.002 Å, respectively, from the coordinated plane. The Cu–N(pyridine) bonds in **Cu1**–**Cu5** were in the range 1.944(6)–2.313(3) Å, while the distances between the copper atom and the imino nitrogen atoms in the five complexes are almost the same [2.078(6) and 2.082(6) Å] in **Cu1**, [2.416(4) and 2.426(3) Å] in **Cu2**, [2.137(3) and 2.149(3) Å] in **Cu3**, [2.099(3) and 2.118(3) Å] in **Cu4**, and [2.091(5) and 2.093(6) Å] in **Cu5**. According to Addison's geometric parame-



Scheme 1.

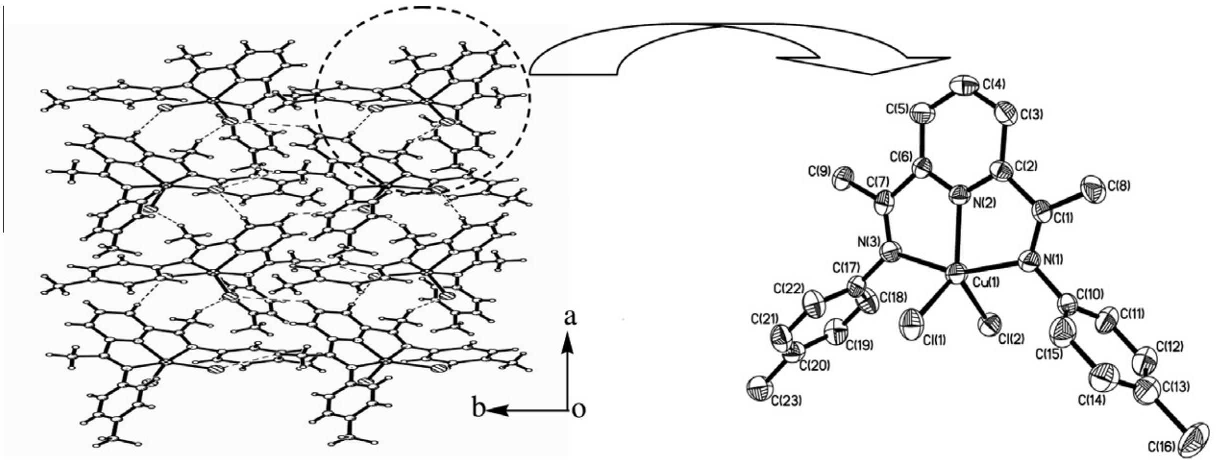


Fig. 1. Right: molecular structure of complex **Cu1** (The $0.5CH_3CN$ molecule has been omitted for clarity). Left: packing diagram of the complex **Cu1** along the *c*-axis. Hydrogen bonds are indicated by dashed lines.

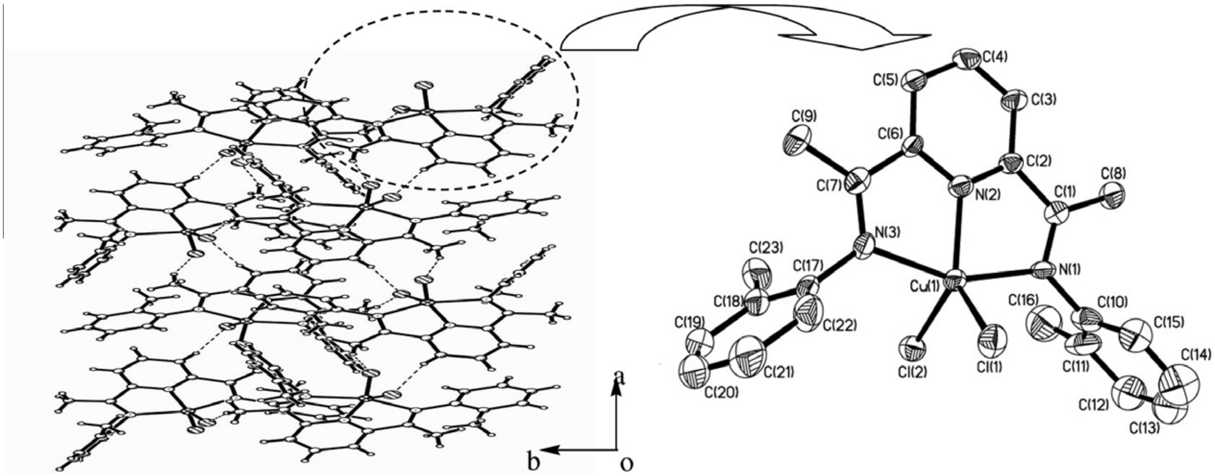


Fig. 2. Right: molecular structure of complex **Cu5** (The CH_3CN molecule has been omitted for clarity). Left: packing diagram of the complex **Cu5** along the *c*-axis. Hydrogen bonds are indicated by dashed lines.

Table 2
Selected bond lengths (Å) and angles (°) for **Cu1**–**Cu5**.

	Cu1	Cu2	Cu3	Cu4	Cu5
Cu–N(2)	1.965(6)	2.313(3)	1.960(3)	1.953(3)	1.944(6)
Cu–N(1)	2.078(6)	2.426(3)	2.149(3)	2.099(3)	2.093(6)
Cu–Cl(1)	2.326(3)	2.428(2)	2.377(2)	2.429(2)	2.286(2)
Cu–N(3)	2.082(6)	2.416(4)	2.137(3)	2.118(3)	2.091(5)
Cu–Cl(2)	2.277(3)	2.427(2)	2.246(1)	2.217(2)	2.332(3)
N(1)–C(1)	1.257(9)	1.294(6)	1.280(4)	1.277(5)	1.293(8)
N(3)–C(7)	1.293(10)	1.281(6)	1.274(5)	1.289(4)	1.295(9)
N(2)–Cu–N(1)	77.9(3)	68.7(1)	77.5(1)	77.4(1)	77.5(2)
N(2)–Cu–Cl(1)	119.5(2)	106.2(1)	115.8(1)	99.2(1)	126.1(2)
N(1)–Cu–Cl(1)	95.7(2)	100.7(1)	95.4(1)	100.1(1)	97.9(2)
N(2)–Cu–N(3)	78.1(3)	69.2(1)	77.2(1)	77.3(1)	77.8(2)
N(1)–Cu–N(3)	155.9(3)	136.4(1)	154.3(1)	151.4(1)	155.4(2)
Cl(1)–Cu–N(3)	97.1(2)	101.3(1)	98.9(1)	97.0(1)	96.6(2)
N(2)–Cu–Cl(2)	127.8(2)	138.8(1)	140.1(1)	158.8(1)	123.8(2)
N(1)–Cu–Cl(2)	97.1(2)	101.0(1)	99.8(1)	97.9(1)	96.2(2)
Cl(1)–Cu–Cl(2)	112.7(1)	115.0(1)	104.2(1)	102.0(1)	110.0(1)
N(3)–Cu–Cl(2)	96.7(2)	103.0(1)	97.2(1)	100.8(1)	97.4(2)

ter τ for metal-center five coordinate system [21], N(2) of complex **Cu1**–**Cu5** was chosen as the axial coordinate atom based on Cu atom center. The bond angles of Cl(1)–Cu–Cl(2) is close to 120° as α, and then β is the greater of the basal angles, N(1)–Cu–N(3). Therefore, the geometric parameters $\tau = (\beta - \alpha)/60$ were defined to 0.72, 0.36, 0.84, 0.82, 0.76 for **Cu1**–**Cu5**, respectively, in which the coordinate structures of **Cu1**–**Cu5** based on Cu-center show trigonal–bipyramidal geometry except **Cu2**. The geometric parameter τ for **Cu2** is smaller than the others, which **Cu2** exhibits approximately square-pyramidal geometry. The planes of the phenyl rings in **Cu1**–**Cu3** and **Cu5** are oriented essentially orthogonal to the coordination plane [with dihedral angles ranging between 79.74(28)° and 89.09(26)°]. However, dihedral angles between the phenyl rings and the plane formed by three coordinated nitrogen atoms in **Cu4** [68.08(14)° and 79.57(18)°, respectively] are smaller than those of **Cu1**–**Cu3** and **Cu5**. In each complex the Cu–N(pyridine) bond is significantly shorter than the Cu–N(imino) bonds, with the formal double-bond character of the imino linkages N(1)–C(1) and N(3)–C(7) being retained [C=N distances in the range 1.257(9)–1.295(9) Å]. There are no intermolecular packing features in five complexes. However, the structures of five complexes are stabilized by the hydrogen bonds between the Cl atom and aromatic C–H hydrogen atoms of the adjacent complexes (Figs. 1 and 2 left), as indicated by the distances of Cl···C, 3.479–3.799 Å, and the bond angles of Cl···H–C, 124–171°, respectively, which are similar to those reported in the literature [18].

3.3. Luminescent properties

Table 3 presents the absorption and emission data for all the complexes in dichloromethane solution at room temperature. The electronic absorption spectra of Cu(II) complexes show one main absorption band at *ca.* 425–445 nm, attributed to ligand-centered $\pi \rightarrow \pi^*$ transitions. The electronic absorption spectra of the Cu(II) complexes are also red-shift relative to the ligands due to metal perturbed intra-ligand $\pi \rightarrow \pi^*$ transition of the bis(imino)pyridyl unit [12,13]. The energy trend of this band for the series of complexes **Cu1**–**Cu5** is found to follow the order: **Cu3**, **Cu1** < **Cu4** < **Cu2** < **Cu5**. It is very interesting that the electron-donating ability of the alkyl group (2,4,6-trimethylphenyl ⩾ 2,6-dimethylphenyl ⩾ 2,6-diethylphenyl ⩾ 2-methylphenyl [4,13]) is in the line with the energy trend except for complex **Cu1**. The complex **Cu1** shows that the lowest absorption energy attributable to lower steric hindrance on the *p*-methyl-substituted phenyl ring of the bis(imino)pyridyl metal complex leads to a highly coplanar situation and an absorption energy red shift. Five complexes have blue-green emission in CH_2Cl_2 solution (concentration: $[M] \approx 10^{-5}$) at room temperature, with $\lambda_{max} = 499$ (**Cu1**), 486 (**Cu2**), 497 (**Cu3**), 494 (**Cu4**), and 478 (**Cu5**) nm, respectively (Fig. 3). Similar to the electronic absorption data for complexes **Cu1**–**Cu5**, emission energy trends in the orders **Cu1** < **Cu3** < **Cu4** < **Cu2** < **Cu5** are observed, respectively. Their emission energies are found to depend on the electron-donating ability of the alkyl substituents on the aryl rings of the bis(imino)pyridyl ligand and steric effect. The quantum yields of all compounds have been determined in solution (Table 3). The quantum yields were determined to be 0.003, 0.002, 0.003, 0.003, and 0.002 for complexes **Cu1**–**Cu5** and 0.008, 0.009, 0.012, 0.009, and 0.008 for ligand $\mathbf{L^1}$–$\mathbf{L^5}$ [13]. The fluorescent quantum yields of complexes **Cu1**–**Cu5**

Table 3
Photoluminescent data for **Cu1**–**Cu5**[a].

Compound	Absorption (nm) ε/dm^3 mol^{-1} cm^{-1}	Emission (λ_{max}, nm)	Quantum yields (Φ)[b]	Conditions
Cu1	445 (2670)	499	0.003	CH_2Cl_2, 298 K
Cu2	430 (2658)	486	0.002	CH_2Cl_2, 298 K
Cu3	445 (2645)	497	0.003	CH_2Cl_2, 298 K
Cu4	440 (2633)	494	0.003	CH_2Cl_2, 298 K
Cu5	425 (2227)	478	0.002	CH_2Cl_2, 298 K

[a] Concentration: $[M] = 1 \times 10^{-5}$ M.
[b] Determined using quinine sulfate in 0.1 M sulphuric acid as a standard.

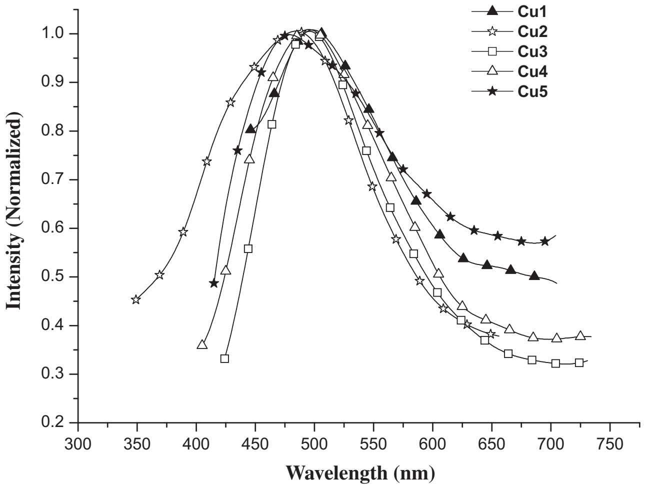


Fig. 3. Emission spectra of complexes **Cu1**–**Cu5** in CH_2Cl_2 solution at room temperature.

is significantly weaker than that of the corresponding ligands, which can be attributed to fluorophore-quencher interactions *via* paramagnetic Cu(II) center. However, in the solid state at room temperature no fluorescence emission bands have been found for the five copper complexes. These results can be easily understood considering the following factors: first, the paramagnetic Cu(II) cation can quench the fluorescence emission and result in luminescence disappearance. On the other hand the fluorescence emission of metal complexes in the solid state generally is lower than that in solution due to concentration quench [17].

4. Conclusions

A series of Cu(II) complexes with 2,6-bis(imino)pyridyl ligands have been synthesized and characterized. Complexes **Cu1**–**Cu5** were self-assembled through hydrogen bonding interactions to form a three-dimensional (3-D) supramolecular structure. Five complexes have blue-green fluorescent emission at 478–499 nm in dichloromethane solution at room temperature. In the solid state at room temperature no fluorescence emission bands have been found for the five copper complexes.

6. Supplementary data

CCDC 734358, 734359, 734360, 734361, and 734362 contains the supplementary crystallographic data for **Cu1**–**Cu5**. 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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 20771030, 20671025, 20971031, and 60778019), the Science Innovation Special Foundation of Harbin City in China (2010RFQXG017), and the Research Fund for the Doctoral Program of Higher Education (20070213005).

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