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Structural variations and spectroscopic properties of copper(I) complexes with bis(schiff base) ligands

Xin-Hui Zhou, Tao Wu, Dan Li *

Department of Chemistry, Shantou University, Daxue Road, Shantou, Guangdong 515063, People's Republic of China

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Abstract

Six copper(I) complexes { $[Cu_2(L1)(PPh_3)_2I_2] \cdot 2CH_2Cl_2]_n$ (1), { $[Cu_2(L2)(PPh_3)_2]BF_4]_n$ (2), $[Cu_2(L3)(PPh_3)_4I_2] \cdot 2CH_2Cl_2$ (3), [$Cu_2(L4)(PPh_3)_4I_2]$ (4), [$Cu_2(L5)(PPh_3)_2I_2]$ (5) and [$Cu_2(L6)(PPh_3)_2I_2]$ (6) have been prepared by reactions of bis(schiff base) ligands: pyridine-4-carbaldehyde azine (L1), 1,2-bis(4'-pyridylmethyleneamino)ethane (L2), pyridine-3-carbaldehyde azine (L3), 1,2-bis(3'-pyridylmethyleneamino)ethane (L4), pyridine-2-carbaldehyde azine (L5), 1,2-bis(2'-pyridylmethyleneamino)ethane (L6) with PPh_3 and copper(I) salt, respectively. Ligand L1 or L2 links (PPh_3)_2Cu_2(\mu-I)_2 units to form an infinite coordination polymer chain. Ligand 3 or 4 acts as a monodentate ligand to coordinate two copper(I) atoms yielding a dimer. Ligand 5 or 6 chelates two copper(I) atoms using pyridyl nitrogen and imine nitrogen to form a dimer. Complexes 1–4 exhibit photoluminescence in the solid state at room temperature. The emission has been attributed to be intraligand π - π * transition mixed with MLCT characters. © 2005 Elsevier B.V. All rights reserved.

Keywords: Copper(I) complex; Crystal structures; Schiff base; Triphenylphosphine; Photoluminescence; Coordination polymer

1. Introduction

It is of great interest to learn about how molecular properties of ligands affect the evolving structures of complexes and their physical properties [1,2]. Many efforts have been devoted to the design and synthesis of pre-organized ligands that are able to control the structures and properties of the complexes [3,4]. Copper(I) complexes with various of N, S, P and halide donor ligands are of growing interest owing to their wide variation in structural format and rich photo-physical and chemical properties. Many of these complexes have been reported to be luminescent and their emission behavior varies with structures, identities of halides, and steric and electronic effects of used ligands [5–8]. In this type of complexes, N-donor ligands are mainly focused on pyridine-containing rigid ligands, such as pyridine, 2,2'-bipyridyl, 4,4'-bipyridyl and phenanthroline, etc. [6,9,10]. Complexes based on flexible pyridine-containing ligands were also employed in literatures [11-13]. In this context, we select a series of flexible pyridine-containing bis(schiff base) ligands (L1–L6) (Scheme 1) as N-donor ligands to explore the structures and spectroscopic properties of their complexes with copper(I). Differences in structures and rigidity of ligands L1–L6, namely different spacer and different position of N atom in pyridine, may have some unique influence on the structures and the spectroscopic properties of copper(I) complexes.

2. Experimental

2.1. General

All reagents for synthesis were commercially available and used as received. Infrared spectra from KBr pellets were collected on a Nicolet Avatar 360 FTIR spectrometer in the range 4000–400 cm⁻¹. Emission and excitation spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer. UV–Vis absorption spectra were recorded

^{*} Corresponding author. Tel.: +86 754 290 3154; fax: +86 754 290 2767. *E-mail address:* dli@stu.edu.cn (D. Li).

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on a Hewlett–Packard 8453 spectrophotometer. Elemental analyses of C, H and N were determined with a Perkin–Elmer 2400C Elemental Analyzer. Ligands L1–L6 were prepared using the reported procedures [14–17].

2.2. Synthesis of complexes

2.2.1. $\{[Cu_2(L1)(PPh_3)_2I_2] \cdot 2CH_2Cl_2\}_n$ (1)

To a solution of PPh₃ (104.9 mg, 0.4 mmol) in CH₂Cl₂ (10 ml) were added, with continuous stirring, CuI (38.1 mg, 0.2 mmol). The mixture was stirred for about 1 h to give a clear colorless solution. Then ligand L1 (21 mg, 0.1 mmol) was added with stirring at room temperature to give a clear yellowish solution. Yellowish single crystals (54%) suitable for X-ray diffraction were obtained by slow evaporation from the filtrate for several days. *Anal.* Calc. for C₅₀H₄₄Cl₄Cu₂I₂N₄P₂: C, 46.72; H, 3.45; N, 4.36. Found: C, 46.80; H, 3.38; N, 4.30%. IR (KBr)/cm⁻¹: 3048w, 1625w (C=N), 1602w, 1478m, 1432s, 742s, 694s, 517m.

2.2.2. $\{[Cu(L2)(PPh_3)_2]BF_4\}_n$ (2)

The complex was prepared similar to that for complex **1** except that **L1** was replaced by **L2**, CuI by $[Cu(CH_3CN)_4]BF_4$. Yellowish single crystals were obtained in 30% yield. *Anal*. Calc. for C₅₀H₄₄BCuF₄N₄P₂: C, 65.77; H, 4.86; N, 6.14. Found: C, 65.71; H, 4.89; N, 6.16%. IR (KBr)/cm⁻¹: 3044m, 1624s (C=N), 1592s, 1480m, 1437s, 1090m, 745m, 694s, 521vs.

2.2.3. $[Cu_2(L3)(PPh_3)_4I_2] \cdot 2CH_2Cl_2(3)$

The complex was prepared similar to that for complex 1 except that L1 was replaced by L3. Yellow single crystals were obtained in 60% yield. *Anal.* Calc. for $C_{86}H_{74}Cl_4Cu_2I_2N_4P_4$: C, 57.07; H, 4.12; N, 3.10. Found: C, 57.07; H, 4.19; N, 3.13%. IR (KBr)/cm⁻¹: 3048w, 1626m (C=N), 1584w, 1479m, 1432s, 741s, 694vs, 517m.

2.2.4. $[Cu_2(L4)(PPh_3)_4I_2]$ (4)

The complex was prepared similar to that for complex **1** except that **L1** was replaced by **L4**. Yellow single crystals were obtained in 52% yield. *Anal.* Calc. for $C_{86}H_{74}Cu_2I_2N_4P_4$: C, 61.92; H, 4.47; N, 3.36. Found: C, 61.85; H, 4.52; N, 3.41%. IR (KBr)/cm⁻¹: 3043m, 1625s (C=N), 1584m, 1479s, 1432m, 742s, 695m, 517m.

2.2.5. $[Cu_2(L5)(PPh_3)_2I_2]$ (5)

To a solution of PPh₃ (104.9 mg, 0.4 mmol) in CH₂Cl₂ (8 ml) were added, with continuous stirring, CuI (38.1 mg, 0.2 mmol). The solution was stirred for about 1 h to give a clear colorless solution. Then the solution was poured into a test tube, to which a solution of ligand L5 (20 mg, 0.1 mmol) in CH₃OH (5 ml) was added dropwise with care. Brown prism single crystals (20%) suitable for X-ray diffraction analysis were obtained after standing for several days. *Anal.* Calc. for C₄₈H₄₀Cu₂I₂N₄P₂: C, 51.68; H, 3.61; N, 5.02. Found: C, 51.74; H, 3.55; N, 4.95%. IR (KBr)/cm⁻¹: 3042m, 1625s (C=N), 1592s, 1476s, 1437m, 746m, 696m, 521vs.

2.2.6. $[Cu_2(L6)(PPh_3)_2I_2]$ (6)

The complex was prepared similar to that for complex **1** except that **L1** was replaced by **L6**. Dark red single crystals were obtained in 69% yield. *Anal.* Calc. for $C_{50}H_{44}Cu_2I_2N_4P_2$: C, 52.47; H, 3.85; N, 4.90. Found: C, 52.49; H, 3.92; N, 4.97%. IR (KBr)/cm⁻¹: 3049m, 1626s (C=N), 1592m, 1477m, 1436s, 744m, 694s, 521s.

2.3. Crystal structure determination

Crystallographic data for 1-6 were collected at 293(2) K with a Bruker-AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and Mo K α radiation ($\lambda = 0.71073$ A). Reflection intensities were integrated using SAINT software [18] and absorption correction was applied semi-empirically [19]. The structure were solved by the direct methods and refined by full-matrix least-squares refinement based on F^2 . All non-hydrogen atoms were anisotropically refined except for those of complex 3 and the hydrogen atoms were generated geometrically. Disordered CH₂Cl₂ molecules were observed in complex 3. The Cl atoms in CH₂Cl₂ were split into two groups with 50% site occupancy for each group. Atoms C(43), Cl(1), Cl(2), Cl(3) and Cl(4) of CH_2Cl_2 were refined isotropically. Structure solutions, refinements and graphics were performed with the SHELXL-97 package [20].

Table 1 Crystal data and structure refinement parameters for complexes **1–6**

Compound	1	2	3	4	5	6
Empirical formula	$C_{50}H_{44}Cl_4Cu_2I_2N_4P_2$	$C_{50}H_{44}BCuF_4N_4P_2$	$C_{86}H_{74}Cl_4Cu_2I_2N_4P_4$	$C_{86}H_{74}Cu_2I_2N_4P_4$	$C_{48}H_{40}Cu_2I_2N_4P_2$	$C_{50}H_{44}Cu_2I_2N_4P_2$
Formula mass	1285.51	913.18	1810.05	1668.25	1115.66	1143.71
Crystal system	triclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\overline{1}$	C2/c	$P\overline{1}$	P2(1)/n	$P\overline{1}$	P2(1)/n
a (Å)	9.915(3)	13.4414(10)	11.0924(9)	13.9744(7)	9.3952(11)	8.8070(5)
<i>b</i> (Å)	11.214(3)	24.6684(10)	13.1742(11)	17.8186(10)	10.7617(12)	17.1379(9)
<i>c</i> (Å)	13.049(4)	13.8239(10)	14.6867(12)	15.3126(8)	12.8199(14)	31.7579(17)
α (°)	77.275(5)	90.00	99.2890(10)	90.00	100.221(2)	90.00
β (°)	70.730(5)	96.796(5)	93.5350(10)	90.8490(10)	104.287(2)	91.7070(10)
γ (°)	76.875(5)	90.00	102.4750(10)	90.00	111.652(2)	90.00
$V(Å^3)$	1317.0(7)	4551.5(5)	2057.7(3)	3812.5(3)	1114.4(2)	4791.2(5)
Ζ	1	4	1	2	1	4
T (K)	293(2)	298(2)	293(2)	293(2)	293(2)	293(2)
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.621	1.333	1.461	1.453	1.662	1.586
$\mu (mm^{-1})$	2.280	0.606	1.520	1.499	2.449	2.281
Reflections collected	11 353	7292	18094	23937	5541	30033
Unique reflections	5866	3998	9368	8848	4483	11150
R _{int}	0.0223	0.0441	0.0243	0.0335	0.0141	0.0283
$R_1 [I \ge 2\sigma(I)]$	0.0640	0.0633	0.0646	0.0479	0.0530	0.0527
$wR_2 \ [I \ge 2\sigma(I)]$	0.1522	0.0990	0.1599	0.1002	0.1342	0.1253

Details of the crystal parameters, data collection and refinement for complexes 1-6 are listed in Table 1.

3. Results and discussion

The complexes 1, 3-6 were readily obtained by reactions of CuI and PPh₃ with the corresponding ligands in a molar ratio of 2:4:1 under mild conditions. When CuI and PPh₃ reacted with ligand L2 using the similar procedure for complex 1, yellowish crystals were obtained. However, the crystals are very unstable when exposed to air and fail to be characterized by X-ray crystallography. Instead, complex

2 was prepared in the similar way as the other complexes except that CuI was replaced by $[Cu(CH_3CN)_4]BF_4$. The elemental C, H and N analysis and X-ray crystal structure analysis confirmed the chemical formulation of these complexes.

3.1. Crystal structures

The structures of complexes **1–6** were determined by X-ray crystallography. Selected bond lengths and angles are listed in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for complexes 1-6

Sele	cted bond lengths	(A) and angles	(°) for complexes I-	-6				
1	Cu(1)–I(1) Cu(1) ^{#1} –I(1) Cu(1)–N(1)	2.6591(11) 2.6858(10) 2.068(5)	$Cu(1)-I(1)^{\#1}$ $Cu(1)-Cu(1)^{\#1}$ Cu(1)-P(1)	2.6858(10) 2.9864(16) 2.2298(16)	P(1)-Cu(1)-I(1) N(1)-Cu(1)-P(1) N(1)-Cu(1)-I(1)	111.23(5) 117.16(18) 105.6(2)	$\begin{array}{l} N(1) - Cu(1) - I(1)^{\#1} \\ P(1) - Cu(1) - I(1)^{\#1} \\ I(1) - Cu(1) - I(1)^{\#1} \end{array}$	100.88(18) 109.50(5) 112.06(3)
2	Cu(1)–N(1) Cu(1)–P(1)	2.120(3) 2.275(1)			$\begin{array}{l} N(1)-Cu(1)-P(1)^{\#2} \\ N(1)-Cu(1)-N(1)^{\#2} \end{array}$	117.2(1) 93.8(2)	N(1)-Cu(1)-P(1) P(1)-Cu(1)-P(1) ^{#2}	101.1(1) 123.2(1)
3	Cu(1)–N(1) Cu(1)–I(1) Cu(1)–P(2)	2.145(4) 2.6678(7) 2.2936(14)	Cu(1)–P(1)	2.2827(13)	P(2)-Cu(1)-P(1) N(1)-Cu(1)-P(2) N(1)-Cu(1)-P(1)	124.68(5) 101.75(12) 106.07(13)	P(2)-Cu(1)-I(1) P(1)-Cu(1)-I(1) N(1)-Cu(1)-I(1)	106.55(4) 111.27(4) 104.40(12)
4	Cu(1)–I(1) Cu(1)–N(1) Cu(1)–P(2)	2.6538(4) 2.116(3) 2.2830(9)	Cu(1)–P(1)	2.3058(9)	N(1)-Cu(1)-P(2) N(1)-Cu(1)-P(1) P(2)-Cu(1)-P(1)	107.41(8) 104.07(8) 123.19(3)	P(2)-Cu(1)-I(1) P(1)-Cu(1)-I(1) N(1)-Cu(1)-I(1)	105.85(3) 110.55(3) 104.25(7)
5	Cu(1)–I(1) Cu(1)–N(1) Cu(1)–N(2)	2.5928(8) 2.077(4) 2.116(4)	Cu(1)–P(1)	2.2033(14)	N(1)-Cu(1)-N(2) N(1)-Cu(1)-P(1) N(2)-Cu(1)-P(1)	78.24(16) 123.73(13) 114.54(12)	N(2)-Cu(1)-I(1) P(1)-Cu(1)-I(1) N(1)-Cu(1)-I(1)	98.84(12) 123.41(5) 106.33(12)
6	Cu(1)–I(1) Cu(1)–N(2) Cu(1)–P(1) Cu(1)–N(1) Cu(2)–P(2) Cu(2)–N(4)	2.5678(6) 2.063(4) 2.1849(12) 2.107(3) 2.1990(11) 2.091(3)	Cu(2)–N(3) Cu(2)–I(2)	2.103(4) 2.6015(6)	$\begin{array}{l} N(2)-Cu(1)-N(1) \\ N(2)-Cu(1)-P(1) \\ N(1)-Cu(1)-P(1) \\ N(2)-Cu(1)-I(1) \\ N(1)-Cu(1)-I(1) \\ P(1)-Cu(1)-I(1) \end{array}$	79.40(15) 125.25(11) 115.39(11) 99.95(11) 104.34(10) 123.11(4)	N(4)-Cu(2)-N(3) N(4)-Cu(2)-P(2) N(3)-Cu(2)-P(2) N(4)-Cu(2)-I(2) N(3)-Cu(2)-I(2) P(2)-Cu(2)-I(2)	78.82(14) 121.32(10) 124.72(11) 107.85(10) 93.97(11) 120.66(4)

Symmetry operators: ${}^{\#1}2 - x$, -y, -z; ${}^{\#2}1 - x$, +y, 0.5 - z.

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Crystallographic analysis indicates that the asymmetric unit of neutral complex { $[Cu_2(L1)(PPh_3)_2I_2] \cdot 2CH_2Cl_2$ } (1) consists of one copper(I) ion, one I^- anion, one PPh₃ molecule, one half of ligand L1 and a CH₂Cl₂ solvent molecule. The structure contains $(PPh_3)_2Cu_2(\mu-I)_2$ units (Fig. 1(a)) bridging by L1 to construct an infinite chain structure (Fig. 1(b)) as in 4,4'-bipyridine analogue [21]. Each copper(I) atom in 1 is coordinated by one N atom of a pyridyl unit from L1, one P atom from PPh₃ and two I atoms to complete a slightly distorted tetrahedral geometry with coordination angles ranging from 100.88(18)° (N1–Cu1–I1A) to 117.16(18)° (N1–Cu1–P1). The average Cu-I bond length is comparable with other previously reported I-bridged copper(I) complexes [5,22-24]. However, the Cu–I bond length (2.6725 Å) in complex 1 is significantly larger than that in complexes 3-6 due to double bridging coordination mode of iodine atom [25]. The Cu···Cu distance in the Cu₂I₂ fragment is 2.9864(16) Å, significantly shorter than that (3.143 Å) in its 4,4'-bipyridine analogue [21], implying weak Cu-.-Cu interactions. Typical values for Cu...Cu distances of this type were in the range 2.53-3.58 Å [26]. In 1, each L1 ligand, retaining the same conformation of the free ligand [27], is almost coplanar with a maximum deviation of 0.1246 Å at N2 and a mean deviation of 0.0598 Å from the best plane. The coplanar conformation implies conjugation throughout the π system. The CH₂Cl₂ molecule forms an intermolecular C-H···I hydrogen bond with a C–H···I angle of 155.5° and a H···I separation of 3.121 Å.

Ligand L2 with a longer spacer was employed in complex 2. Unfortunately, we can not determine the structure of the complex analogue to 1. Instead, a similar 1D infinite chain polymer 2 without double bridging iodide units was obtained. In 2, the coordination atoms around copper(I)atom are two pyridyl N atoms from two different L2 ligands and two P atoms from two different PPh₃ molecules (Fig. 2). The distorted copper(I) tetrahedral geometry bears coordination angles from 93.8(2)° (N1-Cu1-N1A) to 123.2(1)° (P1-Cu1-P1A). The distance of Cu-P coordination bonds in complex 2 is significantly longer than that of $[Cu(PPh_3)_4]^+$ due perhaps to a consequence of steric crowding around metal [28] and a second-order John-Teller distortion observed commonly for Cu(I)-aromatic ligand interaction [29,30]. Unlike that in the coplanar ligand L1 in 1, the dihedral angle between both terminal pyridyl rings in L2 is 47.5°. The insertion of -CH₂-CH₂between the N atoms of the azine group leads to the loss of conjugation and the increase of flexibility.

Alternation of the nitrogen position in pyridyl rings shows that the diversity of the nitrogen donor sites gives rise to the conformational features of the complexes. Reactions of L3 and L4 with CuI in the same conditions as those in syntheses of 1 and 2 result in two dinuclear complexes, respectively. Structures of complex 3 (Fig. 3) and complex 4 (Fig. 4) are very similar, in which each copper(I) is coordinated by one iodide, one N atom from the Schiff-base ligand and two P atoms from triphenylphosphine. Complex 3 contains a CH_2Cl_2 solvent molecule in each unit cell, in contrast, no solvent molecule exists in 4.

Two dinuclear chelate complexes were obtained when the ligands with the -N=C- group in *ortho*-position of pyridyl ring were used in the syntheses. Each copper(I) atom in



Fig. 1. 1D infinite chain structure (b) of $\{ [Cu_2(L1)(PPh_3)_2I_2] \cdot 2CH_2Cl_2 \}_n$ (1) with $(PPh_3)_2Cu_2(\mu-I)_2$ unit (a) (symmetry codes: A 2 - x, -y, -z; B 3 - x, 1 - y, -z).



Fig. 2. 1D chain structure of $\{ [Cu(L2)(PPh_3)_2]BF_4 \}_n$ (2) (symmetry code: 1 - x, +y, 0.5 - z).



Fig. 3. Crystal structure of $[Cu_2(L3)(PPh_3)_4I_2] \cdot 2CH_2Cl_2$ (3) (symmetry code: 1 - x, 2 - y, -z).



Fig. 4. Crystal structure of $[Cu_2(L4)(PPh_3)_4I_2]$ (4) (symmetry code: 2 - x, 1 - y, 1 - z).

the two complexes is chelated by two N atoms from pyridine and imine of a Schiff-base ligand arm to give a CuC_2N_2 five-membered chelating ring similar to those in other complexes of ligands L5 and L6 [31–39]. In 5 (Fig. 5), the five-membered ring is almost coplanar with a maximum deviation of 0.0076 Å at N1 from best plane defined by CuC_2N_2 five-membered ring. The dihedral angle



Fig. 5. Crystal structure of $[Cu_2(L5)(PPh_3)_2I_2]$ (5) (symmetry code: -x, 1 - y, -z).

between CuC_2N_2 five-membered ring and pyridyl ring of ligand **L5** is only 1.2°. In contrast, two copper(I) atoms in **6** (Fig. 6) have slightly different coordination environment. The values of the maximum deviation at N from best plane defined by CuC_2N_2 five-membered ring are 0.0853 and 0.0682 Å, respectively. The dihedral angle between CuC_2N_2 five-membered ring and pyridyl ring of ligand **L6** is 3.0° for Cu(1) and 2.5° for Cu(2), respectively. Ligand **L6** in **6** is not coplanar with the dihedral angle of two terminal pyridyl rings of 1.6°.

3.2. Spectroscopy properties

The UV–Vis absorption and emission spectroscopic data for complexes 1–6 and corresponding ligands are summarized in Table 3. In absorption spectra of the free ligands, the strong absorption peaks ($\varepsilon \sim 10^4$ dm³ mol⁻¹ cm⁻¹) are due to the π – π * transition of pyridyl and its conjugate system. In spectra of the complexes, however, these absorptions are overlapped by the stronger absorptions coming from the triphenylphosphine ligands ($\varepsilon \sim 10^5$ dm³ mol⁻¹ cm⁻¹), which were commonly found in the absorption spectra of triphenylphosphine complexes [40].

Ligands 1–6 exhibit photoluminescence in the solid state at room temperature. Many schiff-base ligands with heterocyclic groups have found to be photoluminescence. The emission was attributed to come from a (π, π^*) excited state. Complexes 1–4 show emission in the similar regions with those in free ligands as depicted in Fig. 7. It is reasonable to assign the emissions of the complexes to be from an intraligand transition [41,42]. Except for the higher energy emission, the emission curves of the complexes also show shoulder peaks at lower energy region (550–600 nm). In



Fig. 6. Crystal structure of $[Cu_2(L6)(PPh_3)_2I_2]$ (6).

Table 3 Spectroscopic data for complexes **1–6** and their corresponding ligands

	$\lambda_{max}^{abs}/nm \ (\epsilon/dm^3 \ mol^{-1} \ cm^{-1} imes 10^5)^a$	$\lambda_{\rm max}^{\rm em}/{\rm nm}^{\rm c}$
L1	286 (0.3)	459, 487, 530
1	252 (3.1), 273sh (2.6)	515, 590sh
L2	230 (0.4), 275sh (0.09)	465
2	227sh (1.0), 272sh (0.4)	474, 575sh
L3	284 (1.0)	460, 487, 533
3	250 (0.9), 276sh (0.8)	455, 487, 523, 560sh
L4	235 (0.3), 271sh (0.1)	473
4	245sh (0.7), 270sh (0.4)	448, 526, 570sh
L5	296 (0.5)	455, 531
5	b	d
L6	236 (0.2), 271sh (0.1)	467, 510
6	270sh (0.05)	d

sh, shoulder.

^a Absorption in CH₃CN.

^b Insoluble.

^c Emission in solid state.

^d No emission.



Fig. 7. Solid-state emission spectra (excited in 320–400 nm) of complexes 1–4 at room temperature.

comparison with the Cu(I)–PPh₃–bipyridine complexes, [(PPh₃)₂Cu₂(μ -I)₂(μ -4,4'-bipyridine)]_n with $\lambda^{em} = 535$ nm [21] and [(PPh₃)₂Cu₂(μ -Cl)₂(pyridine)₂] with $\lambda^{em} = 510$ nm [43], it seems likely that the lowest excited state of the shoulder emission can be ascribed to be a Cu(I) to schiff base ligand metal-to-ligand charge transfer (MLCT) excited state. Interestingly, complexes **5** and **6** do not emit at room temperature. In **5** and **6**, the lone pair electrons of imine nitrogen atoms are used for the coordination with copper(I) to form the thermodynamic preferential CuC₂N₂ five-membered ring, reducing the degree of delocalization through the π system, a consequence of the absence of intraligand π – π * emission.

4. Conclusion

Systematic experiments have been implemented using different pyridine-containing bis(schiff base) ligands to synthesize a series of mixed-ligand copper(I) complexes in examining the influence of ligands on the structures and spectroscopic properties of the complexes. It has been presented that the position of N atom in pyridyl ring of bis(schiff base) ligands determine the formation of coordination polymer or dimer with diverse spectroscopic properties. The Cu(I) bis(schiff base) complexes show solid state photoluminescence at room temperature, which is ascribed to be from intraligand π - π * transition mixed with MLCT characters. Ligands with -N=C- group in the *ortho*-position of pyridyl favor acting as a chelate ligand to form more stable complexes. However, the chelating mode results in the loss of π conjugate system reflecting on the loss of emission of complexes.

5. Supplementary material

Crystallographic data for the structural analysis of **1–6** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 285754–285759, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ ccdc.ac.uk or on the web www: http://www.ccdc. cam.ac.uk.

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