Synthesis, crystal structures and spectroscopic investigation of new Cu/Schiff-base complexes

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ABSTRACT

Three novel Copper complexes, [Cu(L1)2][CuCl2] (1), [Cu(L2)Cl] (2) and [Cu2(L3)3Cl2] (3), have been prepared by reaction of CuCl with the Schiff-base ligands L1: N,N’-bis(thiophen-2-ylmethylene)-ethane-1,2-diamine, L2: N,N’-bis(1H-pyrrol-2-ylmethylene)ethane-1,2-diamine and L3: N,N’-bis(2-nitrobenzylidene)-ethane-1,2-diamine in acetonitrile. The solid-state structures of these complexes were determined by X-ray diffraction from single crystal data and characterized by 1H and 13C NMR, IR and UV/Vis spectroscopies. This study shows that (1) is an ionic complex with a Cu(I)-centered cation and an isolated linear dichlorocuprate(I) anion, (3) is a dinuclear neutral complex of Cu(I) while (2) is a mononuclear neutral complex of Cu(II). In the three complexes, Cu is tetracoordinated in different geometrical environments. The atomic arrangements and spectroscopic properties of the three complexes are reported. Complexes 1-3 exhibit, in the solid state at room temperature, photoluminescence between 320 and 550 nm.

Indexing terms/Keywords

bis(Schiff-base) ligands; Copper complexes; spectroscopic properties; X-ray crystal structures.

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3068 | P a g e   N o v e m b e r  1 3 ,  2 0 1 4
1. Introduction

Luminescent metal complexes have attracted an increasing attention in many areas of chemistry, biology, medical and material science [1-9]. Their uses as emitter material in luminescence devices and luminescent chemo sensor are particularly prominent [10-12]. One of simple strategy for designing luminescent coordination compounds is to organize d10 electronic configuration metal ions with chromophore ligand. The origins of emission arise from the transitions of π→→π* within ligand. This emission could be efficiently enhanced in coordination complex due to increasing of the rigidity of the ligand and reducing of energy loss by radiation less thermal vibrations [13, 14]. The design and synthesis of desired structure luminescent complex is a challenge because the assembly of metal ion with ligand is sensitive to the delicate synthetic conditions [15]. Schiff-bases become one of the research hotspots owing to their strong coordination capability, biological activities, photochromic characteristics, etc. [16]. Copper complexes with various bis(Schiff-base) halide donor ligands are of growing interest owing to their wide variation in structural format and rich photo-physical and chemical properties. The steric, electronic, and conformational effect imparted by the coordinated ligands play an important role in modifying the properties of the prepared metal complexes. Although structural reports on [Cu(N4)]+ complex cations are numerous [17-19], there are a limited number of studies on the copper(I) complexes with isolated linear dihalogenocuprate(I) anions [20-22]. In this work, we select three flexible aromatic bis(Schiff-base) ligands (L1-L3) as N-donor ligands to explore the structures, electronic and spectroscopic properties of their complexes with copper.

2. Experimental

2.1. Starting materials

All reagents were used as received from Sigma-Aldrich without further purification. Solvents used for the reactions were purified by literature methods [23].

2.2. Synthesis

All syntheses and preparations for spectroscopic were carried out under purified Ar atmosphere using Schlenk techniques.

2.3. Synthesis of Ligands

we synthesized and characterized the three ligands L1-L3 as described in our previous work [24].

2.4. Reaction of diimine ligands with copper chloride

The three complexes 1-3 were synthesized in accordance with a previously published procedure [25]. To a 100 mL Schlenk flask containing CH3CN (5 mL) and a stir bar were added (99 mg, 1.0 mmol, 1.0 equiv) of copper chloride and (1.0 mmol, 1.0 equiv) of the corresponding ligand (L1 or L2) and (198 mg, 2.0 mmol, 2.0 equiv) of copper chloride and (453 mg, 3.0 mmol, 3.0 equiv) of L3, each dissolved in 5 mL CH2Cl2 at room temperature. All starting materials dissolved to give a yellow solution. The flask was sealed, and the atmosphere was purified of dioxygen by evacuation argon. The reaction was allowed to stir for 20 minutes at room temperature. The solution was then cannula-filtered into a Schlenk flask containing diethyl ether (50 mL), and the yellow solid that precipitated was allowed to settle for 30 minutes. The supernatant was cannula filtered off, and the product was dried under dynamic vacuum, giving complex (1) (95%), complex (2) (96%) and complex (3) (95%).

2.5. Physical measurements

NMR spectra were obtained on a BRUKER AM, 300 MHz spectrometer in DMSO-d6. 1H and 13C chemical shifts δ are reported in part per million (ppm) relative to the non deuterated residual DMSO. Coupling constants are given in Hertz. IR spectra were determined as KBr pellets on a Perkin Elmer FT-IR Spectrometer BX I. The UV/Vis spectra were recorded on a 6705 UV/Vis spectrophotometer JENWAY with quartz cells (1 cm path length). Excitation and emission spectra were measured with a Perkin-Elmer LS55 Fluorimeter using solid samples at room temperature.

2.6. Crystallographic data collection and structure determination

Suitable single crystals of [Cu(L1)2][CuCl4] (1), [Cu(L2)Cl] (2) and [Cu2(L3)2Cl6] (3) were used for x-ray diffraction analysis. Diffraction data were collected at room temperature on an Enraf–Nonius Mach3 diffractometer using graphite-monochromated AgKα (λ = 0.56087 Å) radiation. The structures were solved by direct methods and refined by the full-matrix least- squares based on F2 using SHELXTL-97 program [26]. For the three compounds, the non-hydrogen atoms
were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for 1-3 are summarized in (Table 1).

**Table 1. Crystal data and structural refinement parameters for complexes 1-3.**

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{24}$H$</em>{24}$CuN$_4$S$_4$·Cl$_2$Cu</td>
<td>C$<em>{12}$H$</em>{12}$ClCuN$_4$</td>
<td>C$<em>{48}$H$</em>{42}$O$<em>2$Cu$<em>2$N$</em>{12}$O$</em>{12}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>694.69</td>
<td>312.25</td>
<td>1176.92</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.746 (3) Å</td>
<td>8.630 (2) Å</td>
<td>9.583 (3) Å</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.523 (2) Å</td>
<td>10.309 (3) Å</td>
<td>11.491 (4) Å</td>
</tr>
<tr>
<td>c (Å)</td>
<td>17.654 (4) Å</td>
<td>14.965 (4) Å</td>
<td>12.183 (2) Å</td>
</tr>
<tr>
<td>α (°)</td>
<td>90°</td>
<td>79.52 (3)°</td>
<td>101.74 (3)°</td>
</tr>
<tr>
<td>β (°)</td>
<td>93.97 (3)°</td>
<td>78.92 (4)°</td>
<td>105.13 (4)°</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90°</td>
<td>83.27 (2)°</td>
<td>91.87 (2)°</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>5785.1 (17)</td>
<td>1280.2 (6)</td>
<td>1262.7 (6)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>ρ$_{calc}$ (Mg m$^{-3}$)</td>
<td>1.595</td>
<td>1.620</td>
<td>1.548</td>
</tr>
<tr>
<td>μ (mm$^{-1}$)</td>
<td>1.02</td>
<td>1.00</td>
<td>0.54</td>
</tr>
<tr>
<td>F (0 0 0)</td>
<td>2816</td>
<td>636</td>
<td>602</td>
</tr>
<tr>
<td>λ (Ag Kα) (Å)</td>
<td>0.56087</td>
<td>0.56087</td>
<td>0.56087</td>
</tr>
<tr>
<td>Collected Reflections</td>
<td>23340</td>
<td>14386</td>
<td>13682</td>
</tr>
<tr>
<td>Independent Reflections</td>
<td>14170</td>
<td>12523</td>
<td>12326</td>
</tr>
<tr>
<td>reflections with I &gt; 2σ(I)</td>
<td>5936</td>
<td>5674</td>
<td>5781</td>
</tr>
<tr>
<td>parameters</td>
<td>302</td>
<td>325</td>
<td>343</td>
</tr>
<tr>
<td>R[F2 &gt; 2σ(F2)], wR(F2)</td>
<td>0.076, 0.236</td>
<td>0.077, 0.159</td>
<td>0.113, 0.310</td>
</tr>
<tr>
<td>Δρ max and min (e Å$^{-3}$)</td>
<td>0.84, −0.47</td>
<td>0.50, −0.46</td>
<td>0.64, −0.90</td>
</tr>
<tr>
<td>S</td>
<td>0.91</td>
<td>0.92</td>
<td>0.90</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Synthesis

The copper(I) complexes were prepared by reacting the copper(I) CuCl with bis(Schiff-bases), in a mixed acetonitrile-dichloromethane (1:1) solution. The synthesis of these complexes was carried out in an inert atmosphere. The stability of these complexes in solution depends on the solvent used.

In complex (1) (Fig. 1), central metal is surrounded by 4 nitrogen atoms from two bis-imine L1. In complex (2) (Fig. 1), the stereoechemistry (syn and anti) of the ligand allowed the copper to be chelated only by 3 nitrogen atoms belonging to the same bis-imine L2, the nitrogen atom of the second pyrrol in L2 was far from the zone of central attack of metal due to the Z configuration. Otherwise, in complex (3) (Fig. 1), the presence of the NO2 group in ortho position in the aromatic system could present a steric obstruction preventing the complexation of the metal with four nitrogen from two ligands L3, then one copper atom was chelated with two nitrogen atoms belonging to the first ligand L3 and with a third one from a second ligand L3. Finally, two copper atoms react with three ligands L3 to form binuclear Cu(I) complex 3.

Figure 1. Structure of Bis-Schiff bases ligands (L1-L3) and the corresponding complexes (1-3)

3.2. Structure elucidation

The structures of the obtained products were determined by X-ray diffraction and characterized by 1H and 13C NMR, IR, UV/Vis and photoluminescence.

3.2.1. X-ray diffraction

3.2.2. [Cu(L1)2][CuCl2] (1)

The molecular structure of the compound (1), along with the numbering scheme, is shown in (Fig. 2). The asymmetric unit of (1) is composed of two half [Cu(L1)2]⁺ cations and one dichlorocuprate(I) anion. The copper atom of [CuCl3]⁻ occupies a general position in an anion nearly linear with an angle Cl-Cu-Cl = 178.18(8)° whereas the copper atoms of [Cu(L1)2]⁺ groups are on special positions Cu1(0, y, ½) and Cu2(½, y, ½) in tetrahedral environments built up from four nitrogen atoms (N1, N1i, N2, N2i) and (N3, N3i, N4, N4i) of four L1 bidentate ligands [Symmetry codes: (i) =x, y, z; (ii) =x, y, z+2; (iii) =x, y, ½; (iv) =x, y, ½; (v) =x-1, y, ½; (vi) =x+1, y, ½; (vii) =x, y, z-2; (viii) =x, y, z+1; (ix) =x, y, z].
(ii) $-x + 1$, $y$, $-z + 3/2$. Around of Cu1 the two ligand molecules are independent while around of Cu2 they are symmetrical. The shortest Cu-Cu distance is of 6.20(1) Å. Geometrical analysis of the bond lengths and angles in both tetrahedra, Cu1N1N1iN2N2i and Cu2N3N3iiN4N4ii, shows that the coordination spheres around copper(I) are distorted by restricting bite angle of the chelating ligand. The average bite angles in Cu1N1N1iN2N2i and Cu2N3N3iiN4N4ii are 85.11(10)$^\circ$ and 84.88(14)$^\circ$, respectively. The Cu-N distances are 2.064(3) Å and 2.066(4) Å in the first tetrahedron and 2.075(3) Å and 2.083(3) Å in the second one.

Figure 2. Perspective view showing the coordination environments of Cu(I) atoms in [Cu(L1)$_2$][CuCl$_2$] (1).

Similar coordination geometry around the central atom has been observed in other Cu(I) complexes [22, 27]. It should be noted also that, in the crystal packing of (1), the [Cu(L1)$_2$]$^+$ cation forms a cluster where the two L1 molecules are connected by C-H···S (3.570(5) Å) intramolecular bonds (Fig. 3).
Figure 3. The crystal packing in [Cu(L1)2][CuCl2] (1), viewed along the a-axis, showing the C-H---Cl (green) and C-H ---\(\pi\) (red) interactions.

Additional intermolecular interactions, of types C-H---Cl and C-H---\(\pi\) associate these clusters into layers parallel to the bc plane (Fig. 3). These interactions involve the following methylene C-H, chlorine atoms and thiophen rings: C5-H5i---Cl2 (3.705(8) Å); C24-H24ii---Cl1 (3.852(3) Å); C6-H6Bi---\(\pi\) (3.508(2) Å) (to centroid of S4C21C22C23C24); C7-H7Bii---\(\pi\) (3.650(6) Å) (to centroid of S3C13C14C15C16); C13-H13iii---\(\pi\) (3.692(55) Å) (to centroid of S2C9C10C11C12); [Symmetry codes: (i) 0.5 - x, -0.5 + y, 1.5 - z; (ii) 1 - x, y, 1.5 - z; (iii) 0.5 - x, 0.5 + y, 1.5 - z; (iiii) -0.5 + x, 0.5 - y, -0.5 + z].

3.2.2.1. [Cu(L2)Cl] (2)

Single-crystal structural analysis of (2) shows that this material is a neutral mononuclear complex with two formula units in the asymmetric unit. An ORTEP [28] view of the basic structural unit with the corresponding numbering system is depicted in (Fig. 4). Each copper ion in this basic structural unit is bound to one chloride ion and three nitrogen atoms (comprised of one deprotonated pyrrole nitrogen donor, and two imine nitrogen donors) of the deprotonated tridentate ligand (L2), giving an ClN3 coordination sphere.
The charge balance and X-ray analysis demonstrate that, in this case where L2 is partially deprotonated, the copper is in the Cu(II) oxidation state. In fact, despite the absence of oxygen in the reaction medium, a redox reaction occurred between Cu(I) and H+ which results from the deprotonation of a pyrrolic nitrogen, to form the complex (2) and H2, which emerges. This is happened with L2 only due to the possible deprotonating of its secondary amine function. L1 and L3 do not present this possibility. The pyrrolic ring linked to copper(II) has an aromatic character similar to the cyclopentadienyl one in ferrocene. The calculation of bond valence sum, using an empirical formula of bond valence, $S = \exp[(R_o - R)/B]$ ($S$ = bond valence, $R_o$ = bond length) [29,30], indicates that the oxidation state of both Cu sites in the asymmetric unit of complex (2), was 2+ (2.013 and 2.030 valence units for Cu1 and Cu2 atoms respectively). This oxidation state is identical with the charge balance consideration. In the complex (2), the geometry of the coordination polyhedron around each copper(II) cation is square planar (with $\Sigma$ angles = 360.04° and 359.61° at Cu1 and Cu2, respectively). Bond lengths and angles between these four-coordinate atoms and the central copper(II) atoms are comparable. For the square-plane (Cu1N1N2N3C1): Cu1-Cl1 = 2.2308(13), Cu1-N ranging from 1.949(3) Å to 2.001(3) Å; N-Cu1-N ranging from 81.30(14)° to 162.78(14)° and N-Cu1-Cl1 ranging from 98.06(10)° to 179.36(11)°. For the square-plane (Cu2N5N6N7Cl2): Cu2-Cl2 = 2.2373(13) Å, Cu2-N ranging from 1.944(4) Å to 1.988(4) Å, and N-Cu2-N ranging from 81.30(14)° to 162.78(14)°, N-Cu2-Cl2 ranging from 98.06(10)° to 179.36(11)°. The metals are displaced by 0.0822(6) Å, and 0.0189(6) Å for Cu1 and Cu2, respectively, from their basal planes. The shortest Cu1-Cu2 distance is of 5.959(8) Å. In this atomic arrangement, intramolecular C20-H20---Cl2 (3.278(5) Å) and C8-H8A---Cl1 (3.300(4) Å) H-bonding interactions are observed (Fig. 5), between the skeletal methylene C-H of the ligand (L2) and the coordinated chloride of both independent entities C12H12ClCuN4. These latters are themselves connected by intermolecular bonds of types N8-H8i---Cl2 (3.234(6) Å) and N4-H4ii---Cl3 (3.247(4) Å) [Symmetry codes: (i) $-x+1$, $-y+2$, $-z$; (ii) $-x+1$, $-y+1$, $-z+1$ and C19-H19B---Cl3 (3.690(25) Å) [to centroid of C1C2C3C4] and C6-H6B---π (3.703(19) Å) [to centroid of N5C13C14C15C16] (Fig. 3), leading to the formation of a corrugated layer extended parallel to the bc plane.

Figure 4. Perspective view showing the coordination environments of Cu(II) atoms in [Cu(L2)Cl] (2).
3.2.2.2. [Cu₂(L₃)₂Cl₂] (3)

Single-crystal X-ray diffraction study of (3) shows that it consists of discrete neutral [Cu₂Cl₂(N,N'-bis(2-nitrobenzylidene)-ethane-1,2-diamine)₃] molecule (Fig. 6). It is a dinuclear complex, distributed across a center of inversion, so that the asymmetric unit consists of one Cu(I) cation, one chloride anion and one and half molecule of ligand L₃. Both copper(I) ions, symmetrically bridged by L₃ in a bis-monodentate fashion, are separated by 6.33(8) Å, comparable to that of 6.20(1) Å and 5.96(8) Å found in the (1) and (2) complexes, respectively.

The Copper(I) ion locates on a general position and is tetrahedrally coordinated by one chlorine atom and three imine nitrogen atoms of two bidentate ligands (L₃), giving an ClN₃ tetrahedral coordination environment. In the CuClN₃ tetrahedron, the bond distances Cu-N range from 1.979 (5) to 2.242 (5) Å, with a longer distance Cu—Cl (2.321(2) Å) and the angles range from 82.42(19) to 134.15 (19)°. This tetrahedron is less distorted compared to complex (1), case where Cu(I) is coordinated to four nitrogen atoms of two (L₁) ligands. The dinuclear molecules, stabilized by intramolecular C2-
H2i--C1 (3.482(8) Å) and C14-H14ii--C11 (3.627(9) Å) hydrogen bonds, are stacked into a polymeric molecular column along [001] in which the monomers are linked by intermolecular C10-H10--O3 (2.71(1) Å) and C20-H20--O2 (3.27(1) Å) interactions [Symmetry code: (i) x + 1, y, z ] (Fig. 7). The columns are held together by C19-H19i--O1 (3.57(7) Å) and C23-H23ii--O6 (3.30(4) Å) hydrogen bonds [Symmetry codes: (i) 2 - x, 1-y, 1-z; (ii) 1-x, 1-y, -z].

Figure 7. Projection of the crystal structure of [Cu2(L3)3Cl2] (3), along the a-axis, showing the C-H--Cl (green) and C-H --- O (red) Hydrogen-bonding.

3.2.2.3. Spectroscopic properties (IR and NMR)

The IR absorption bands for the imines in the Schiff-base ligands (CH=N stretching vibration) were observed at 1629 - 1637 cm\(^{-1}\). Once, the coordination is done, the frequency of the imine group decreases. This observation is attributable to the decrease in the sp\(^2\) character of the imine group by the donation of the π-electron.

The 1H NMR spectra data and peak assignments are presented in the experimental section for each complex. The sharp singlet at about 3.98-4.11 ppm is assigned to the CH\(_2\)--CH\(_2\) protons. 1H NMR chemical shifts and IR absorption bands of the copper complexes correlate with the basicity of the original Schiff-bases depending on the electronic characters of the Schiff-base.

The degree of donation of π-electrons in imine groups was evaluated from the difference between the IR absorption band and the 1H NMR chemical shifts, of the imine group in the free ligands and the corresponding complexes.

The δ ppm values from the 1H NMR spectroscopic data increased as the increase in the electron-donating ability (i.e. the Hammett’s σ \(\pi\) values) of the aromatic [31]. The shifts towards low magnetic fields agree with the cases of the coordination of the nitrogen ligand to metals [31, 32], as in the case of the protonation of amines [33] and imines [29], by which the electron densities of the nitrogen atoms decrease [33]. This shift towards low magnetic fields is attributable to the strong donation of the π-electron on the nitrogen atoms included in the conjugated π systems consisting of the aromatic rings and the conjugated diimines to copper atom.

3.2.2.4. Optical properties

The optical properties of the Schiff-base ligands (L1-L3) and their complexes (1-3) were explored using UV/Vis and phospholuminescence. Table 2 summarizes the absorption data for (1-3) dissolved in DMSO. The complexes (1-3) have
similar patterns with different characteristic bands. By comparing the absorption spectrum of each complex with that of the corresponding free ligand, the high intensity bands can be ascribed to $\pi-\pi^*$ and $\pi-\pi^*$ transitions [34].

Table 2. UV–Vis spectral data of complexes 1-3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>UV–Vis $\lambda$ max (nm) ($\varepsilon$ (M$^{-1}$ cm$^{-1}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu(L}_1\text{)}_2\text{][CuCl}_2]$ (1)</td>
<td>DMSO</td>
<td>286 (65 440)$^a$, 324 (56 924)$^d$</td>
</tr>
<tr>
<td>$[\text{Cu Cl(L}_2\text{)}]$ (2)</td>
<td>DMSO</td>
<td>239 (45 366)$^b$, 388 (54 302)$^e$</td>
</tr>
<tr>
<td>$[\text{Cu}_2\text{(L}_3\text{)}_3\text{Cl}_2]$ (3)</td>
<td>DMSO</td>
<td>285 (74 120)$^c$, 363 (55 036)$^f$</td>
</tr>
</tbody>
</table>

$^a$ c = 2.5 · 10$^{-5}$ M.
$^b$ c = 4 · 10$^{-5}$ M.
$^c$ c = 2.5 · 10$^{-5}$ M.
$^d$ c = 2.5 · 10$^{-4}$ M.
$^e$ c = 4 · 10$^{-4}$ M.
$^f$ c = 2.5 · 10$^{-4}$ M.

The luminescent properties of the free ligands and their complexes were investigated in the solid state at room temperature. This study constitutes an independent evidence of complexation between the ligands and the copper ions. Fig. 8 represents the comparison between the excitation and emission spectra of the free ligand L1 and the corresponding complex 1. The emission spectra of the free ligand (Fig. 8d) and that of the corresponding complex 1 (Fig. 8c) were obtained by excitation at similar wavelengths from their excitation spectra given in Figure 8a and Figure 8b, respectively. Ligand L1 and complexes 1, emit between 300 and 550 nm upon the UV excitations (Table 3). As shown in Fig. 8, under comparable excitation conditions, the complex 1, gave an emission spectrum similar to its corresponding ligand L1, which suggests that these emissions can be ascribed to the intra-ligand $\pi^*\rightarrow\pi$ and $\pi^*\rightarrow\pi$ transitions of Schiff-bases (ILCT) [35-37]. The lower energy bands were attributed to the transitions $\pi^*\rightarrow\pi$ and the highest energy one to the $\pi^*\rightarrow\pi$ charge transfer of Schiff-bases [37].

Figure 8. Comparison between solid-state excitation and emission spectra (excited in 280 – 286 nm) of the ligand L1 and the complex 1 at room temperature.
On the other hand, under comparable excitation conditions, the complexes 2 and 3 gave also emission spectra similar to those of their corresponding ligands L2 and L3 (Table 3).

### Table 3. Photoluminescence data for ligands L1-L3 and their corresponding complexes 1-3.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λ_{exc,max}/nm</th>
<th>λ_{em}/nm</th>
<th>λ_{em,max}/nm</th>
<th>λ_{exc}/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>233, 286</td>
<td>(405)</td>
<td>405, 419, 460, 482, 427</td>
<td>(286)</td>
</tr>
<tr>
<td>1</td>
<td>236, 300, 343</td>
<td>(405)</td>
<td>410, 422, 442, 484, 532</td>
<td>(286)</td>
</tr>
<tr>
<td>L2</td>
<td>235, 292, 299</td>
<td>(415)</td>
<td>404, 418, 482, 527</td>
<td>(299)</td>
</tr>
<tr>
<td>2</td>
<td>237, 262, 287, 301</td>
<td>(420)</td>
<td>420, 438, 473, 424</td>
<td>(299)</td>
</tr>
<tr>
<td>L3</td>
<td>232, 288</td>
<td>(408)</td>
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<td>(288)</td>
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<tr>
<td>3</td>
<td>234, 290, 299</td>
<td>(408)</td>
<td>410, 421, 440, 484, 532</td>
<td>(288)</td>
</tr>
</tbody>
</table>

The enhancement of the fluorescence of the complexes compared to their respective ligands appears to be related to the L-L π...π stacking interactions, which result in a decrease in the HOMO-LUMO energy gap of the complex [38]. In addition, the complexes 1 and 3 exhibit an emission shoulder at 442 and 441 nm, respectively that do not appear on the spectra of their corresponding ligands (L1 and L3). This emission can be ascribed to be a Cu(I) to Schiff-base ligand, i.e. metal-to-ligand, charge transfer (MLCT) [35].

### 4. Conclusion

The construction of supramolecular architectures is currently of great interest due to their intriguing network topologies and interesting electronic, magnetic, catalytic and optical properties. Three novel copper supramolecules with different structural motifs were prepared by reaction of CuCl with the Schiff-base ligands L1-L3 in acetonitrile. The structural motifs of these species depend mainly of the coordination geometry of the central atom and the flexibility and stereochemistry (syn and anti) of ligand molecules. In the complexes (1) and (3) the central atom is a copper(I) which has a d^10 diamagnetic configuration, while in (2) the central atom is a copper(II), which has a d^9 paramagnetic configuration. These two copper oxidation states commonly exhibit tetrahedral and square planar coordination geometries depending upon the nature of the ligand(s) L. Both geometries occur with a coordination number of four. Square planar is favoured when the Crystal Field Splitting Parameter (Δ) is large as this produces maximum electronic stabilization, whereas tetrahedral geometry is favoured for smaller values of Δ. The larger the value of Δ, the larger is the tendency for the d electrons to pair up in the lower lying orbitals, overcoming the repulsive pairing energy associated with two electrons occupying the same orbital. This has the effect that certain d^4 electron configurations favour certain geometries. The photoluminescence behavior of complexes 1-3 and their ligands L1-L3 respectively, could be of fundamental interest and also significant for different applications of photoactive materials.

### 5. Supplementary material

CCDC: 832196, 838322 and 837372 contain the supplementary crystallographic data for (1-3). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

### References