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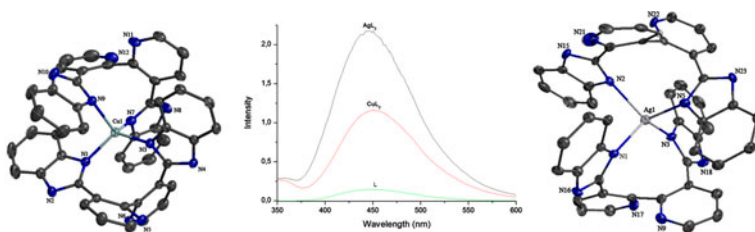
Spectroscopic and structural properties of complexes of 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine with copper(I) and silver(I)

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The pseudo-tetrahedral complexes [CuL₂]PF₆·7H₂O·CH₃OH (**1**) and [AgL₂]CF₃SO₃·H₂O (**2**) (L = 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine) have been synthesized and characterized through crystal structure analyses, electrochemistry, and spectroscopic methods. X-ray structural analyses of **1** and **2** indicate that sterically constrained N₄ ligands L are *cis* and behave as bidentate chelates to a single metal ion in a pseudo-tetrahedral fashion through the benzimidazole. As two benzimidazolyl rings exhibit considerable steric hindrance, the bipyridine unit of L remains uncoordinated. The pseudo-tetrahedral cation [CuL₂]⁺ shows a quasi-reversible Cu^I/Cu^{II} oxidation–reduction wave in the CV in DMF (counter-ion PF₆[−]). The fluorescence titration of L with copper(I), silver(I), and also with pH have been conducted to examine the selectivity. The ligand shows remarkably high selectivity and sensitivity for Ag(I).

Keywords: Benzimidazole; Bipyridine; N₄-ligand; Copper; Silver; X-ray structures

1. Introduction

Sterically hindered ligands which can impose a pseudo-tetrahedral geometry on metal ions are of interest for selective metal-ion extraction [1], models for mononuclear copper proteins [2–5], and study of the relationship between structure and properties of transition-metal complexes [6–13]. Copper(I), with the d¹⁰ electronic configuration, prefers tetrahedral

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coordination, whereas Cu(II), with d^9 electronic configuration, adopts five- or six-coordination [14]. Thus, upon oxidation of Cu(I) to Cu(II), a large structural change occurs; consequently, imposition of a particular geometry on the metal allows control of the copper(I)–copper(II) redox couple [15]. Systems for which this process does not occur [10, 11, 13, 16] are very rare [14].

Among the tetrahedrally enforcing ligands, 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine (**L**) [17] incorporating two benzimidazole units linked together through 2,2'-bipyridine is an optimal choice for achieving a tetrahedral environment. Through intramolecular rotations around the single bond joining the pyridine rings, the ligand readily provides a pseudo-tetrahedral coordination geometry as revealed by complexes with Co(II) [12], Zn(II) [18], and Cu(II) [17]. Co(II) and Cu(II) form 1:1 complexes, whereas Zn(II) forms a 1:2 complex akin to those formed by 2,2'-bis(2-imidazolyl)biphenyl with Cu(I, II), Ni(II), Co(II), and Zn(II) [10]. The present study reports another example for a nearly tetrahedral $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}\text{N}_4$ redox pair containing the same ligands. In order to make a comparison with the reported metal complexes, the complexes of the ligand with Cu(I), $[\text{CuL}_2]\text{PF}_6 \cdot 7\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (**1**) and Ag(I), $[\text{AgL}_2]\text{OTf} \cdot \text{H}_2\text{O}$ (**2**) were prepared and crystallographically characterized; electrochemical and spectroscopic studies were also performed.

2. Experimental

2.1. Materials and instruments

All chemicals were obtained from commercial sources and used without purification, unless otherwise stated. Solvents were freshly distilled over appropriate drying reagents under dry N_2 atmosphere. All experiments were carried out under dry nitrogen using standard Schlenk techniques, unless otherwise stated. Melting points were recorded on a Bushi Melting Points B-540 apparatus. CHN microanalyses were performed with a Heraeus Rapid CHNO elemental analyzer. The electrospray ionization mass spectral (ESI-MS) measurements were carried out on a LCQ (Finnegan MAT, USA) using acetonitrile as the mobile phase. The samples for ESI-MS measurements were prepared by redissolving the final isolated compounds in acetonitrile or methanol as appropriate. Solutions containing **1** and **2** in acetonitrile (1.2×10^{-4} M) were injected into the mass spectrometer source with a syringe pump at a flow rate of 10 $\mu\text{L}/\text{min}$. ^1H NMR spectra were measured in $\text{DMSO}-d_6$ with a Bruker AC300 300 MHz spectrometer at room temperature. Chemical shifts are given in parts per million with reference to TMS. Spectrophotometric titrations were performed with a Shimadzu UV-1601 UV–vis spectrophotometer connected to an external computer. In a typical experiment, 50 mL of **L** in acetonitrile (1.05×10^{-5} M) was titrated with a 2.6×10^{-3} M solution of the appropriate metal salt in acetonitrile. Each addition (0.01 mL increments of the salt solution at 5 min intervals) was carried out using a precision micropipette at 25 °C. The absorbance at 10 different wavelengths was recorded using a 1-cm quartz cell and transferred to the computer. Excitation and emission spectra were recorded on an AMINCO Browman Series 2 Luminescence Spectrometer. Cyclic voltammetry was performed using a Princeton Applied Research EG&G Model 283 Potentiostat/Galvanostat with a scan rate of 100 mVs^{-1} . The electrolytic cell used was a conventional three-compartment cell, in which a glassy carbon working electrode (surface of the glassy carbon working electrode was polished with a micro-cloth pad using alumina polishing powder (0.1 μm) and washed with distilled water before each experiment), a Pt counter electrode, and a Ag/AgCl reference

electrode were employed. The CV measurements were performed at room temperature using 0.10 M tetraethylammonium perchlorate as the supporting electrolyte and anhydrous DMF as the best solvent to obtain homogeneous solution, since the compounds are slightly soluble in acetonitrile. The acetonitrile, as a solvent for electrochemical study of similar compounds, was speculated to compete with the ligand for complexation to Cu(I) [19]. The ferrocenium/ferrocene couple was used as the internal standard ($E_0 = 0.45$ V).

2.2. Crystal structure determination

Single-crystal X-ray diffraction data were recorded with a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Data for **1** and **2** were collected at 293 and 150 K, respectively. The structures were solved by direct methods using SHELXS-97 [20] and refined by full-matrix least squares using the program olex2.refine [21]. All non-hydrogen atoms were refined anisotropically, whereas hydrogens were placed in geometrically calculated positions for non-water molecules. Water hydrogens in **1** were not modeled owing to disorder within the water of crystallization confounding their location. Water hydrogens in **2** were located by electron density and then freely refined. Crystal data and structure-refinement parameters for all compounds are summarized in table 1, while selected bond lengths and angles are given in table 2 and hydrogen-bonding parameters are given in table 3. Simple bond angles and lengths were calculated using Olex2 [21], while dihedral angles and torsion angles were calculated using Mercury [22]. Hydrogen bonding geometries were calculated using Platon [23].

Table 1. Structure solution and refinement information for **1** and **2**.

Compound	1	2
Empirical formula	C ₄₉ H ₄₈ N ₁₂ CuPF ₆ O ₇	C ₄₉ H ₃₈ N ₁₂ O ₄ F ₃ SAg
Formula weight	1113.42	1055.84
Temperature (K)	293	150.15
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P-1$
<i>a</i> (Å)	15.6905(8)	11.4669(18)
<i>b</i> (Å)	16.8156(8)	19.881(3)
<i>c</i> (Å)	20.4852(11)	19.984(3)
α (°)	90	91.067(3)
β (°)	107.051(1)	95.908(3)
γ (°)	90	92.518(3)
Volume (Å ³)	5167.3(5)	4526.0(12)
<i>Z</i>	4	4
ρ_{Calcd} (mg/mm ³)	1.4311	1.55
m/mm ⁻¹	0.538	0.566
<i>F</i> (0 0 0)	2275	2152
Crystal size (mm ³)	0.57 × 0.37 × 0.2	0.24 × 0.21 × 0.2
Radiation	Mo K_α ($\lambda = 0.71073$)	Mo K_α ($\lambda = 0.71073$)
2 θ range for data collection	5.94°–50.06°	5.868°–50.052°
Index ranges	–20 ≤ <i>h</i> ≤ 19, 0 ≤ <i>k</i> ≤ 21, 0 ≤ <i>l</i> ≤ 26	–15 ≤ <i>h</i> ≤ 15, –25 ≤ <i>k</i> ≤ 25, 0 ≤ <i>l</i> ≤ 26
Reflections collected	11,797	28,590
Independent reflections	9096 [$R_{\text{int}} = 0.0000$, $R_{\text{sigma}} = 0.0778$]	15,755 [$R_{\text{int}} = 0.0604$, $R_{\text{sigma}} = 0.1729$]
Data/restraints/parameters	9096/0/695	15,755/17/1277
Goodness-of-fit on F^2	1.024	0.665
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0588$, $wR_2 = 0.1739$	$R_1 = 0.0385$, $wR_2 = 0.0582$
Final <i>R</i> indexes [all data]	$R_1 = 0.0849$, $wR_2 = 0.1880$	$R_1 = 0.0841$, $wR_2 = 0.0652$
Largest diff. peak/hole (e Å ⁻³)	2.08/–0.82	0.58/–0.58

Table 2. Selected bond lengths for **1** and **2**.

Compound	Atom 1	Atom 2	Length (Å)
1	Cu1	N1	2.060(3)
	Cu1	N3	2.038(3)
	Cu1	N7	2.063(3)
	Cu1	N9	2.077(3)
2	Ag1	N1	2.323(3)
	Ag1	N4	2.347(4)
	Ag1	N7	2.253(3)
	Ag1	N10	2.306(3)
	Ag2	N13	2.518(3)
	Ag2	N16	2.261(3)
	Ag2	N19	2.263(3)
	Ag2	N22	2.324(4)

Table 3. Hydrogen-bonding geometries.

Compound	D	H	A	Symmetry	D–H	H···A	D···A
2	O(1)	h(1)	N(12)	i	0.82(3)	2.06(3)	2.875(5)
	N(2)	h(2)	O(2)		0.860(5)	1.956(5)	2.805(5)
	N(4)	h(4)	N(5)	ii	0.860(5)	2.025(5)	2.885(5)
	N(8)	h(8)	F(5)	iii	0.861(5)	2.257(5)	2.985(5)
	N(10)	h(10)	O(1A)	iv	0.860(5)	1.975(5)	2.829(5)
	C(9)	h(9)	O(7)	v	0.932(7)	2.439(10)	3.311(10)
	O(1)	h(1A)	O(8)	vi	0.97(3)	1.97(3)	2.923(5)
	O(1)	h(1B)	O(5)	vii	0.98(3)	1.91(3)	2.866(5)
	N(2)	h(2)	O(1)		0.88	1.95	2.811(4)
	N(5)	h(5)	N(3)	viii	0.88	2.03	2.877(5)
1	O(5)	h(5B)	O(4)	iv	0.97(4)	1.94(4)	2.902(5)
	O(5)	h(5C)	N(24)		0.98(4)	2.08(3)	3.042(5)
	N(8)	h(8)	N(12)	x	0.88	1.99	2.833(5)
	N(14)	h(14)	O(8)	viii	0.88	2.07	2.895(4)
	N(17)	h(17)	N(21)	xi	0.88	2.07	2.919(5)
	N(23)	h(23A)	N(15)	xii	0.88	2.03	2.854(5)
	C(12)	h(12)	O(7)	viii	0.95	2.57	3.480(5)
	C(27)	h(27)	F(4)		0.95	2.48	3.251(5)
	C(35)	h(35)	O(2)	x	0.95	2.52	3.270(6)
	C(38)	h(38)	O(2)	xiii	0.95	2.47	3.336(6)
	C(53)	h(53)	F(6)	viii	0.95	2.54	3.487(5)
	C(59)	h(59)	O(3)		0.95	2.34	3.287(5)
	C(64)	h(64)	O(3)	xii	0.95	2.4	3.255(5)

Note: Symmetry operations: (i) $1/2 - x, -1/2 + y, 1/2 - z$; (ii) $-x, 3 - y, 1 - z$; (iii) $-1 + x, y, z$; (iv) $1/2 - x, 1/2 + y, 1/2 - z$; (v) $1 - x, 3 - y, 1 - z$; (vi) $1 - x, -y, -z$; (vii) $1 + x, y, z$; (viii) $-x, -y, -z$; (ix) $-1 + x, y, z$; (x) $-x, -y, 1 - z$; (xi) $-x, -1 - y, -z$; (xii) $-x, -1 - y, 1 - z$; (xiii) $1 - x, -y, 1 - z$.

2.3. Synthesis of 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine (**L**)

The ligand, 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine (**L**) was prepared by a similar method as reported previously [24].

2.4. Synthesis of the copper(I) complex $[\text{CuL}_2]\text{PF}_6 \cdot 7\text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (**1**)

A solution of **L** (0.58 g, 1.5 mM) in dry, deoxygenated methanol (50 cm^3) was treated with $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ (0.48 g, 1.3 mM) in acetonitrile (20 cm^3) under dry nitrogen. The mixture was refluxed with vigorous stirring for 3 h. The resulting yellow solution was concentrated under vacuum to yield yellow powder. Crystallization from acetonitrile by

slow evaporation at room temperature afforded yellow crystals suitable for X-ray diffraction. 1.07 g (85%). Anal. Calcd for $C_{48}H_{32}N_{12}CuPF_6$: C, 58.51; H, 3.27; N, 17.06. Found: C, 58.5; H, 3.2; N, 17.1%. ESI-MS, m/z 839.0 $[CuL_2]^+$ (100%), 451.4 $[CuL]^+$ (10%) (figure S1, see online supplementary material at <http://dx.doi.org/10.1080/00958972.2014.943201>). FT-IR (KBr pellet) ν/cm^{-1} 3629w, 3389v, 3056w, 1622s, 1588 m, 1567vs, 1536w, 1441vs, 1409vs, 1366s, 1316s, 1276 m, 1223 m, 1145w, 1117w, 1093w, 1039w, 964w, 842vs, 794s, 740vs, 636s, 558vs, 427 m. λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) (acetonitrile) 292 (3590). 1H NMR (300 MHz, DMSO- d_6 , δ_{ppm}): 13.27 (1H, s, NH), 8.35 (1H, d, $J=4.02$ Hz), 7.43 (1H, d, $J=8.10$ Hz), 7.32 (1H, m), 7.10 (2H, t, $J=7.10$ Hz), 6.57 (1H, m), 5.96 (1H, m) (figure S2). ^{13}C NMR (300 MHz, DMSO- d_6 , δ_{ppm}): 158.1, 150.5, 149.0, 141.8, 137.3, 133.2, 125.8, 122.8, 122.6, 121.9, 118.9, 111.4 (figure S3).

2.5. Synthesis of the silver(I) complex $[AgL_2]CF_3SO_3 \cdot H_2O$ (2)

A solution of **L** (0.194 g, 0.5 mM) in dry, deoxygenated methanol (25 cm^3) was added to a solution of $AgCF_3SO_3$ (AgOTf) (0.128 g, 0.5 mM) in methanol (25 cm^3) under dry nitrogen in the dark (the flask was covered with aluminum foil) and stirred at room temperature for 2 h. The mixture was then set to reflux for a further 2 h to complete dissolution of the ligand. The homogenous solution was filtered and allowed to stand at room temperature in the dark to yield off-white precipitate. Crystallization from acetonitrile–methanol mixture afforded tan-white single crystals suitable for X-ray diffraction. 0.46 g (90%). Anal. Calcd for $C_{49}H_{32}N_{12}SO_3F_3Ag$: C, 56.92; H, 3.12; N, 16.26. Found: C, 56.5; H, 3.6; N, 16.2%. ESI-MS, m/z 883.1 $[AgL_2]^+$ (100%), 1272.7 $[AgL_3]^+$ (30%), 495.3 $[AgL_2]^{2+}$ (5%) (figure S4). FT-IR (KBr pellet) ν/cm^{-1} 3458w, 3057w, 1623s, 1564 m, 1469vs, 1440vs, 1410vs, 1366s, 1280 m, 1249 m, 1225 m, 1167w, 1059w, 1029w, 967w, 814vs, 638s, 558vs, 576 m. λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) (acetonitrile) 290 (3520). 1H NMR (300 MHz, DMSO- d_6 , δ_{ppm}): 13.36 (1H, s, NH), 8.42 (1H, d, $J=4.74$ Hz), 7.49 (2H, d, $J=8.04$ Hz), 7.25 (1H, m), 7.15 (1H, t, $J=7.67$ Hz), 6.74 (1H, m), 6.72 (1H, m) (figure S5). ^{13}C NMR (300 MHz, DMSO- d_6 , δ_{ppm}): 157.6, 151.5, 150.4, 149.1, 141.9, 138.0, 133.5, 126.6, 122.8, 122.0, 118.4, 111.6 (figure S6).

3. Results and discussion

3.1. Crystal structure of 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine

The single-crystal X-ray structure of **L** was previously reported [17]. The molecular structure of **L**, as shown in figure 1, adopts the *trans* conformation in the crystalline state with the two benzimidazole (bim, hereafter) fragments on opposite sides of the 2,2'-bipyridine backbone [17], which is similar to that of other geometrically constrained ligands such as bis(2-benzimidazolyl)biphenyl [25]. Two molecules of **L** form symmetry-related intermolecular H-bonds through bim of one **L** as hydrogen donor and pyridine of the adjacent **L** as hydrogen acceptor, $N(2)-H(2) \cdots N(6)^i$ as depicted in figure 2 (table 3). The dihedral angle between the bim planes is 81.26°.

3.2. Crystal structures of 1 and 2

Figures 3 and 4 show ORTEP drawings of **1** and **2**, respectively. The structure of **1** consists of a $[CuL_2]^+$, PF_6^- , one CH_3OH , and a number of water molecules (for which hydrogens

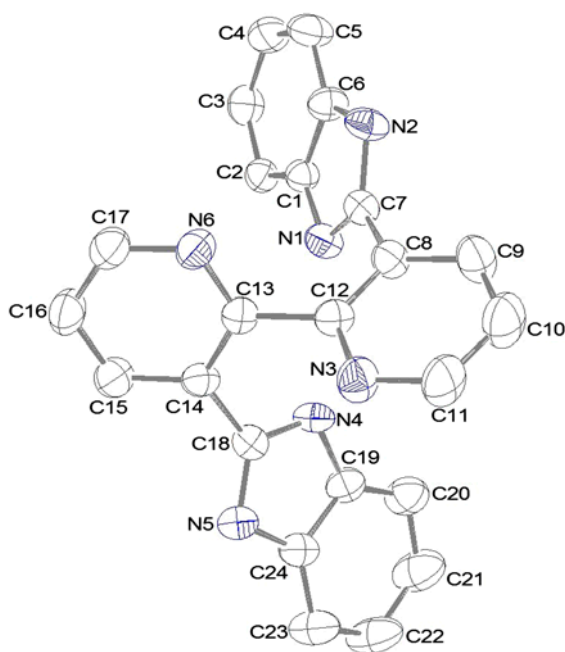


Figure 1. Molecular structure of **L** with the atom numbering and 50% probability displacement.

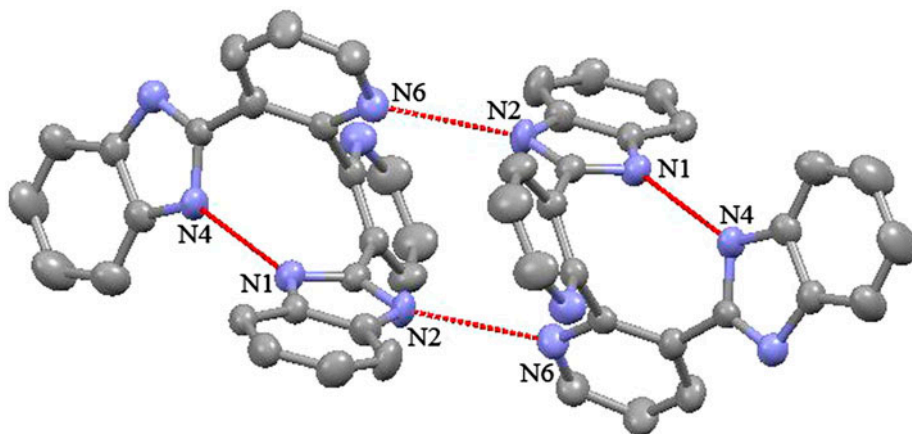


Figure 2. Stabilization of **L** by intermolecular N–H...N bonding.

could not be located). The coordination environment around the metal center is a slightly distorted tetrahedron coordinating two ligands through four benzimidazole nitrogens (N_{bim}). Deviations from T_d symmetry are very small as evident by the intra-ligand angles in the nine-membered rings in **1** and **2**. The coordination angles N(3)–Cu(1)–N(1) and N(7)–Cu(1)–N(9) are $115.80(11)^\circ$ and $113.66(11)^\circ$, respectively, for **1**. The structure of **2** contains two molecules in the asymmetric unit and the corresponding coordination angles, N(4)–Ag(1)–N(1) and N(5)–Ag(1)–N(2), are $121.00(12)^\circ$ and $113.58(12)^\circ$, respectively, for the first

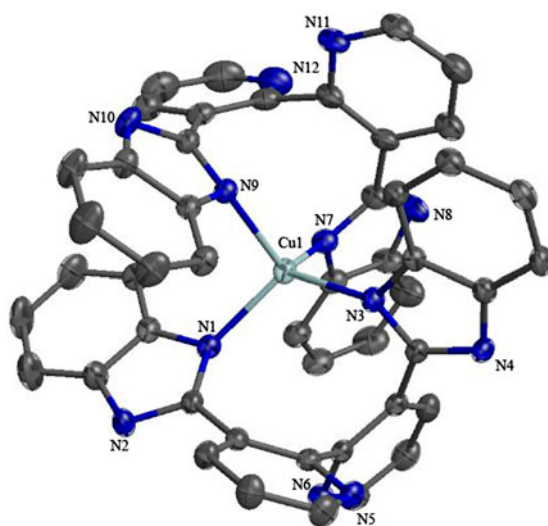


Figure 3. Molecular structure of **1** showing ideal tetrahedral geometry around the metal center.

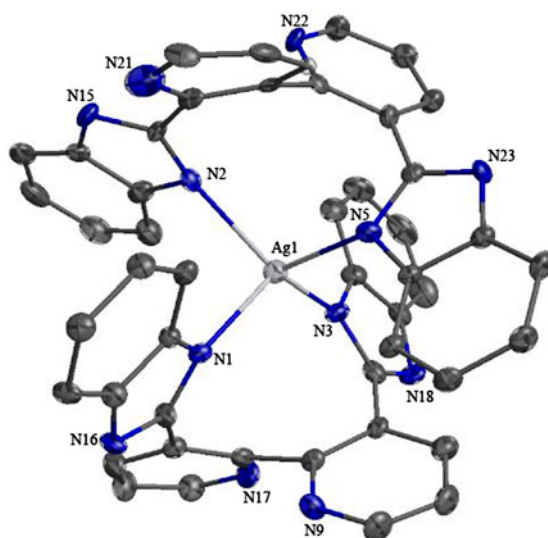


Figure 4. Molecular structure of **2** showing ideal tetrahedral geometry around the metal center.

molecule and N(10)–Ag(2)–N(14) and N(12)–Ag(2)–N(7) are $122.05(12)^\circ$ and $109.22(11)^\circ$, respectively, for the second. These angles are comparable to those observed in the slightly distorted tetrahedral Zn(II) complex, $[\text{ZnL}_2](\text{ClO}_4)_2 \cdot 2\text{DMF} \cdot 4\text{H}_2\text{O}$ [18], and Co(II) complex, $[\text{Co}(\text{L})\text{Cl}_2] \cdot 2\text{C}_3\text{H}_7\text{NO}$ [12], in which the corresponding angles are $116.38(6)^\circ$ and $118.13(18)^\circ$, respectively. The intra-ligand angles in all complexes are very close to the tetrahedral value. The coordination angle in the 1 : 1 Cu(II) complex is $139.06(12)^\circ$ [17]. Thus, D_{2d} flattening in Cu(II) is evidently due to Jahn–Teller distortion attributed to additional ligand

field effects compared to complexes of Co(II), Zn(II), Cu(I), and Ag(I), which typically form tetrahedral complexes. The geometry of the free ligands does not change significantly upon coordination to the Cu(I) ion, since the dihedral angles between the pyridyl (py) planes in the bipyridine backbone are 70.45° and 75.18° , very close to that of 71.96° in **L**, but larger than that of the angles 53.10° – 58.92° in **2**, and are comparable to those observed in the related complexes. The dihedral angles between the bim planes in **1** are 72.91° and 80.94° in each bound **L**, again very close to that of 80.86° in free **L**, and slightly different than those in **2**. Very similar dihedral angles between the py–py, py–bim and bim–bim planes in all complexes of **L** clearly indicate the preference of the ligand for tetrahedral geometry. Invariably, the ligand requires tetrahedral geometry not only with d^{10} metal ions, such as Cu(I), Ag(I) and Zn(II) [18], but also with d^7 ion, such as Co(II) [12], and with d^9 ion, such as Cu(II) [17], with comparatively larger intra-ligand angle due to flattening of the MN_4 unit akin to those of structurally similar 1 : 2 complexes of 2,2'-bis(2-imidazolyl) biphenyl [12]. The Cu–N_{bim} distances, Cu(1)–N(3) 2.038(3) Å, Cu(1)–N(1) 2.060(3) Å, Cu(1)–N(7) 2.063(3) Å, and Cu(1)–N(9) 2.077(3) Å, are typical for tetrahedral Cu(I) complexes [3, 10]. The Ag–N_{bim} distances are in the expected range, Ag(1)–N(7) 2.253(3) Å, Ag(1)–N(10) 2.306(3) Å, Ag(1)–N(1) 2.323(3) Å, and Ag(1)–N(4) 2.347(3) Å, and are larger than those in **1**, consistent for pseudo-tetrahedral geometries [13]. The differences in M – N distances are attributable primarily to difference in ionic radii of the metals.

The molecular structure of **2** may also be stabilized by intramolecular interactions between py and bim rings with center-to-center distances of 4.37 and 4.81 Å, resembling those in **1** (figures 5 and 6). As with **1**, the py and bim planes within each molecule are not parallel to each other, deviating from planarity with torsion angles over the range 41.36° – 50.82° , due to steric puckering of the bim rings coordinated to metal center. The structure of **2** consists of $[AgL_2]^+$, $CF_3SO_3^-$, and one water of crystallization. There are extensive H-bonding between the mononuclear units via symmetry-related bim and py

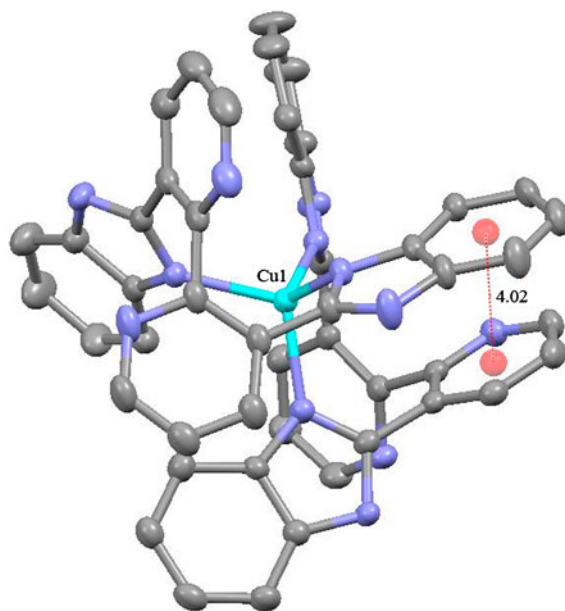


Figure 5. The intermolecular π - π stacking interactions in **1**.

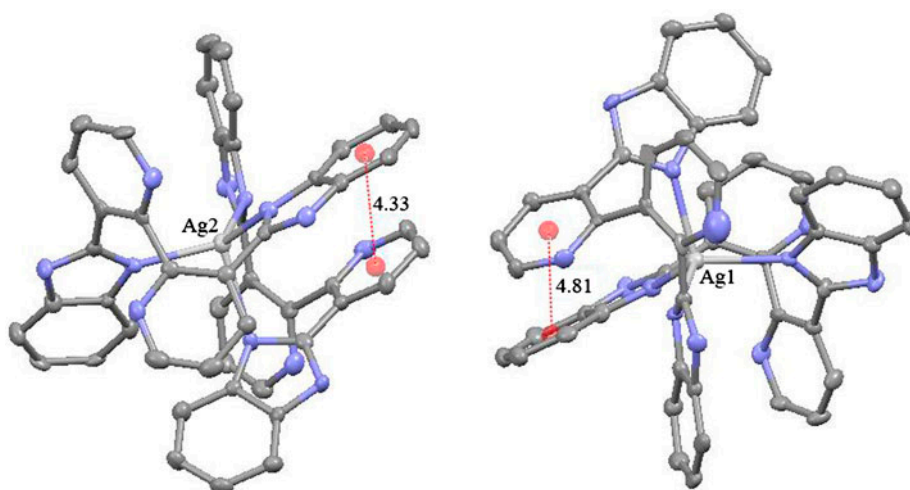


Figure 6. The intermolecular π - π stacking interactions in **2**.

through N(6)–H(6)···N(11), N(18)–H(18)···N(17), N(8)–H(8)···N(19), and N(15)–H(15)···N(22) as depicted in figure S7. Each molecular unit also forms H-bonds with the water molecule through N(13)–H(13)···O_w(8) and N(23)–H(23)···O_w(1). The triflates form intermolecular H-bonding with the water molecules, O(1)–H(1)···O(8)_{OTf} and adjacent unit via N(13)–H(13)···O(6)_{OTf} (table 3). The molecular units stack along the *a*-axis and are interlocked by N–H···N H bonding along the *b*-axis, and stabilized by N–H···O H bonding with water and triflate to result in a 2-D network.

3.3. Cyclic voltammetry

Cyclic voltammetry of **1** in dry and de-oxygenated DMF shows a quasi-reversible one-electron oxidation–reduction wave associated with the Cu(I)/Cu(II) couple as depicted in figure 7.

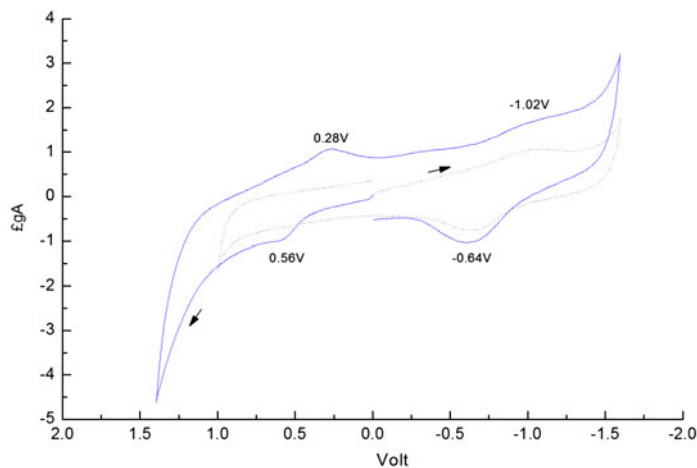


Figure 7. Cyclic voltammetry of **1** measured in dry and de-oxygenated DMF.

The oxidation potential of **1** is $E_{1/2} = -0.84$ V versus Fc^+/Fc ; the redox wave exhibits $I_{\text{pa}}/I_{\text{pc}} = 1.15$ and $E_{\text{pp}} = 100$ mV, $I_{\text{pa}}/I_{\text{pc}} = 1.07$ and $E_{\text{pp}} = 80$ mV, and $I_{\text{pa}}/I_{\text{pc}} = 0.92$ and $E_{\text{pp}} = 60$ mV, consistent with quasi-reversible one-electron oxidation process. $I_{\text{pc}} - I_{\text{pa}} = 100$ mV; -0.51 V in DMF. As shown in figure 7, the potential of the $\text{Cu}^{\text{I}}-\text{Cu}^{\text{II}}$ couples are at rather anodic potentials compared to those of the parent unsubstituted ligands due to steric hindrance in the ligand, imposing a tetrahedral geometry on the metal, and from the electrochemistry results, **L** confers similar properties on the metal center to ligands, such as 2,9-dimethyl-1,10-phenanthroline [26], 6,6'-disubstituted-2,2'-bipyridine [27], and related compounds [3]. This type of ligands tend to stabilize pseudo-tetrahedral Cu^{I} and to destabilize planar Cu^{II} complexes [13], consistent with the intra-ligand angles for the complexes of **L** with $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ [17]. These results obviously show that sterically hindered ligands, such as **L**, stabilize the tetrahedral geometry in the solid state and also in solution. Complex **1** is very stable in the solid state and in solution at room temperature.

3.4. Luminescence behavior

The photoluminescence behaviors of the free ligand, **1**, and **2** are examined in acetonitrile solutions. The UV-vis spectra of the ligand and of **1** and **2** are depicted in figure S8a and b, respectively. The UV-vis spectrophotometric titration of the ligand solution in methanol with acids, such as HPF_6 (pH range 8–2.5) (figure S9), and with base, such as TBAOH (pH range 8–12.9) (figure S10), at room temperature results in thermodynamic ground-state pK_a values $\text{pK}_1 = 3.71$, $\text{pK}_2 = 9.55$, and $\text{pK}_3 = 12.43$, whereas by luminescence titrations, excited-state pK_a values are $\text{pK}_1 = 3.62$, $\text{pK}_2 = 9.12$, and $\text{pK}_3 = 12.15$, respectively (figures S8 and S9). Figure 8 shows the emission spectra of **L**, **1**, and **2**. **L**, **1**, and **2**, upon photo-excitation at same wavelength (320 nm), show the same emission maximum band at 450 nm, but the highest intensity for $\text{Ag}(\text{I})$ complex and the lower intensity for copper(I) complex. This enhancement in luminescence intensity is very similar to the $\text{Zn}(\text{II})$ complex

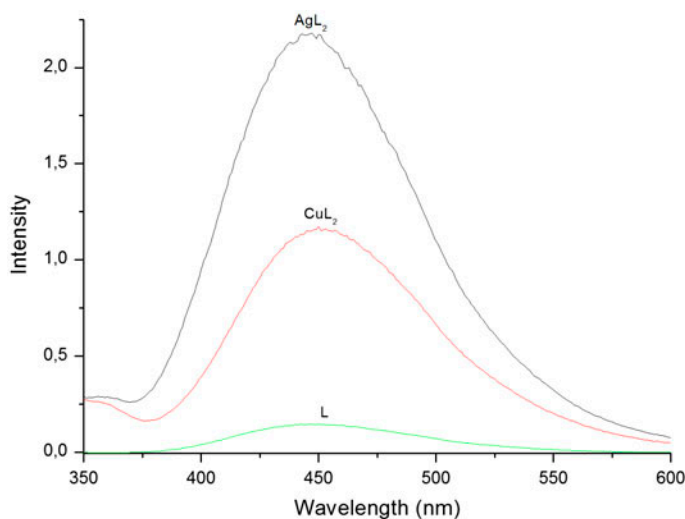


Figure 8. The photoluminescence of **L**, **1** and **2** measured in acetonitrile. The ligand shows the greatest sensing for silver(I).

[18]. The enhanced luminescence may be attributed to the coordination to metal ion, which increases the rigidity of the ligand and reduces the non-radiative decay through vibration in the excited state [18, 28, 29]. This is consistent with the X-ray structures of **1** and **2**, which show that the ligand forms the most stable complex with metal ion having preference for solely tetrahedral geometry. This is very similar to a benzimidazole ligand which shows a very significant change in emission in the presence of Hg^{2+} among other metal ions, due to its better coordination in the open cleft involving amides and benzimidazole rings [28]. In this complex, the increase in the quantum yield of the receptor was accounted for by steric features of the ligand that play a crucial role in the orientation of the benzimidazoles due to which the cavity selectively prefers Hg^{2+} . Usually, the increased fluorescence intensity is attributed to metal ion which strongly binds to the ligand as revealed in the present case [30].

4. Conclusion

We report the single-crystal X-ray structures of pseudo-tetrahedral complexes with copper(I) and silver(I) with 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine, which indicate that this sterically hindered ligand stabilizes metal ions with a strong preference for tetrahedral geometry. This is supported by the cyclic voltammetry measurements of the ligand and copper(I) complex in DMF. The luminescence titrations showed that, upon addition of metal ion, the luminescence intensity increases for the silver(I) ion and to a lesser extent for the copper(I) ion. This indicates that 3,3'-bis(2-benzimidazolyl)-2,2'-bipyridine shows relatively higher sensitivity to silver(I) in solution in comparison with Cu(I) under the same experimental conditions.

Supplementary material

Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC 992414 and CCDC 992415, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/deposit>).

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