



The syntheses, characterizations, X-ray crystal structures and properties of Cu(I) complexes of a bis-bidentate schiff base ligand

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ARTICLE INFO

Article history:

Received 7 August 2009

Received in revised form 25 November 2009

Accepted 4 December 2009

Available online 4 January 2010

Keywords:

Schiff bases

Bis-bidentate ligands

N-donor ligands

Copper(I) complex

Crystal structure

Electrochemistry

Photophysics

ABSTRACT

Bis-bidentate Schiff base ligand **L** and its two mononuclear complexes $[\text{CuL}(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**) and $[\text{CuL}(\text{PPh}_3)_2]\text{ClO}_4$ (**2**) have been prepared and thoroughly characterized by elemental analyses, IR, UV–Vis, NMR spectroscopy and X-ray diffraction analysis. In both the complexes the metal ion auxiliaries adopt tetrahedral coordination environment. Their reactivity, electrochemical and photophysical behavior have been studied. Complex **1** shows reversible $\text{Cu}^{\text{II/I}}$ couple with potential 0.74 V versus Ag/AgCl in CH_2Cl_2 . At room temperature **L** is weakly fluorescent in CH_2Cl_2 , however in Cu(I) complexes **1** and **2** the emission is quenched.

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1. Introduction

Schiff bases are significant class of compounds which can be used in a variety of studies, such as organic synthesis, catalyst and drug design [1–3] and models for active sites of metalloenzymes [4]. They are the most versatile group of chelators for facile preparation of metal–organic hybrid materials [5–10], single molecule based magnets [11–16], highly porous materials [17,18], optoelectronic devices [19–21], and sensors [22–24]. Rational design of organic ligand plays a vital role in assembling diverse architectures in the area of supramolecular chemistry [25–27]. Polydentate diazine ligands containing N–N bridge fragments can produce a variety of structural types, such as helices, polygons, polyhedra and oligomers [28–32,5] due to the free rotation of the metal–coordination planes around the N–N single bond. Polyvinyl chloride membrane electrode based on zinc complex of butane-2,3-dione bis(salicylhydrazine) are widely used as thiocyanate sensor. This can further be used in the titration of thiocyanate in saliva and urine sample [33,34]. The continued interest in coordination chemistry of Cu(I) is due to the fact that copper(I) complexes of polydentate ligands are the model compounds that can mimic or even ideally duplicate some of the important physical

and chemical properties of Cu(I) containing proteins and also because of their diverse structural and physicochemical properties [35]. Cu(I) salts catalyses many organic transformations like aryl guanidinylation [36], amination [37], photocycloaddition [38], oxidation of adrenaline [39], ferrocyclochrome *c* oxidation [40] and also olefin cyclopropanation [41].

Herein we report the synthesis of a flexible bis-bidentate ligand butane-2,3-dione bis(salicylhydrazine), **L** along with two of its Cu(I) complexes **1** and **2** (Scheme 1). The complexes have been characterized by various spectroscopic as well as with single crystal X-ray diffraction method. The reactivity, electrochemical and photophysical properties of the complexes **1** and **2** have also been studied.

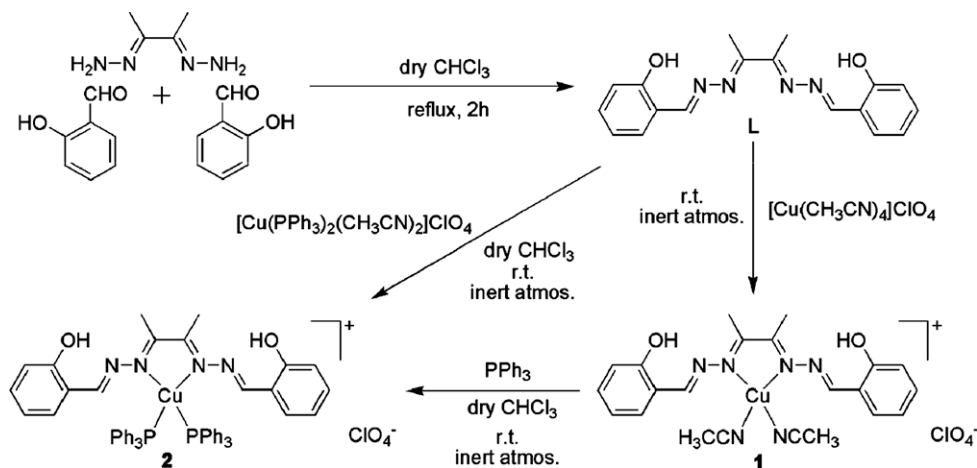
2. Experimental

2.1. General procedures

2,3-Butane dihydrazine and $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ were synthesized by reported procedures [42,43]. All other reagents were procured commercially and used without further purification. Copper was estimated gravimetrically as CuSCN . Microanalyses were carried out using a Perkin–Elmer 2400II elemental analyzer. The melting point was determined by an Electrothermal IA9000 series digital melting point apparatus and is uncorrected.

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Scheme 1. Synthesis of ligand and copper(I) complexes.

Fourier transform infrared (FTIR) and solution electronic spectra were recorded on Nicolet Magna-IR (Series II) and Shimadzu UV-160A spectrophotometers, respectively. ^1H NMR and Electrospray ionization mass (ESI-MS) measurements were made using a Bruker Advance 400 MHz and Finnigan LCQ Decap MAX mass spectrometer, respectively. Fluorescence spectra were recorded on a Perkin-Elmer LS50B spectrophotometer. All electrochemical measurements were made in dichloromethane on a BAS (Epsilon model) having a three-electrode setup consisting of a glassy carbon (polished with alumina before measurement) working, platinum wire auxiliary and a Ag/AgCl reference electrodes. Oxygen was rigorously removed from the dichloromethane solutions of the samples by purging with dry argon gas of high purity. Under the experimental conditions employed here, the ferrocene–ferrocenium couple appears at 0.42 V versus Ag/AgCl in 1 M KCl with an ΔE_p of 110 mV at a scan rate of 50 mV s^{-1} .

2.2. Synthesis of butane-2,3-dione bis(salicylhydrazone) (**L**)

2,3-Butane dihydrazone (0.57 g, 5 mmol) was dissolved in 50 mL of anhydrous chloroform. To this solution, 1.22 g (10 mmol) of freshly distilled salicylaldehyde was added. The resulting bright yellowish mixture was refluxed for 2 h, maintaining a dry atmosphere. Within 30 min of reflux orange yellow solid started separating out. After 2 h, the reaction mixture was cooled to room temperature and the product was collected by filtration. Crystals suitable for X-ray analysis were obtained by slow evaporation of chloroform solution. Yield, 1.44 (90%); mp > 250 °C. ^1H NMR (200 MHz, CDCl_3 , TMS): δ 11.81 (s, 2H), 8.68 (s, 2H), 7.39 (m, 4H), 7.10 (d, 2H), 6.90 (t, 2H), 2.43 (s, 6H). FTIR/ cm^{-1} (KBr): 506(s), 562(w), 647(m), 713(s), 757(vs), 790(m), 896(w), 981(w), 1019(s), 1040(s), 1123(m), 1160(m), 1209(s), 1271(vs), 1361(s), 1406(m), 1447(m), 1497(m), 1547(s), 1581(m), 1612(vs), 1626(vs), 2407(w), 2779(w), 2851(m), 2945(w), 3431(wb). ESI MS: 323.2 (LH^+ , 100%). UV–VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (CH_2Cl_2): 238 (15 080); 307 (21 450); 366 (10 970). Anal. Calc. for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$: C, 67.05; H, 5.63; N, 17.39. Found: C, 67.07; H, 5.69; N, 17.32%.

2.3. Synthesis of $[\text{CuL}(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**)

0.161 g (0.5 mmol) of **L** was dissolved in 75 mL of dry chloroform. Argon was purged through the solution for 15 min and to this orange yellowish solution 0.165 g (0.5 mmol) of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ was added at a time. The reddish brown reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Then the

reddish brown clear solution was cooled under argon. Reddish brown crystals suitable for X-ray analysis separated out, which were filtered out, and dried *in vacuo* over fused CaCl_2 . Yield, 0.185 g (65%). ^1H NMR (200 MHz, CDCl_3 , TMS): δ 11.1 (s, 2H), 8.74 (s, 2H), 7.40 (m, 6H), 6.95 (d, 2H), 2.43 (s, 6H), 2.18 (s, 6H), 2.04 (s, 6H). FTIR/ cm^{-1} (KBr): 636(s), 765(s), 905(m), 1091(vs), 1121(vs), 1160(m), 1209(m), 1227(vs), 1315(s), 1375(m), 1470(vs), 1553(vs), 1608(s), 1642(vs), 2235(s), 2931(w), 3435(wb). UV–VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (CH_2Cl_2): 322 (18 050); 432 (7500). Elemental analysis of the powdered material was performed. Anal. Calc. for $\text{C}_{22}\text{H}_{24}\text{N}_6\text{CuClO}_6$: C, 46.54; H, 4.26; N, 14.81; Cu, 11.20. Found: C, 46.56; H, 4.35; N, 14.88; Cu, 11.27%.

2.4. Synthesis of $[\text{CuL}(\text{PPh}_3)_2]\text{ClO}_4$ (**2**)

0.161 g (0.5 mmol) of **L** was dissolved in 75 mL of dry chloroform. Argon was purged through the solution for 15 min. Then to this orange yellow solution 0.365 g (0.5 mmol) of $[\text{Cu}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]\text{ClO}_4$ was added with stirring. The color of the reaction mixture gradually changed from yellow to red. The red reaction mixture was stirred at room temperature for 2 h under argon atmosphere. Red solid separated out. It was filtered off, washed with little amount of chloroform and dried *in vacuo* over fused CaCl_2 . Yield, 0.388 g (76%). Red crystals suitable for X-ray analysis were grown by slow evaporation of its methanol solution. ^1H NMR (200 MHz, CDCl_3 , TMS): δ 8.72 (s, 2H), 7.49 (m, 4H), 7.44–7.39 (m, 30H), 6.89 (t, 4H), 2.43 (s, 6H). FTIR/ cm^{-1} (KBr): 506(s), 518(vs), 526(s), 549(vs), 620(s), 645(s), 667(s), 695(s), 725(s), 744(s), 761(s), 805(s), 890(m), 958(m), 995(vs), 1028(vs), 1070(s), 1089(vs), 1129(vs), 1158(vs), 1125(vs), 1276(s), 1312(m), 1329(m), 1434(vs), 1451(vs), 1461(m), 1478(s), 1508(m), 1564(vs), 1583(m), 1609(vs), 1627(vs), 1649(vs), 2925(m), 3080(s), 3227(w), 3432(wb). UV–VIS $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) (CH_2Cl_2): 312 (10 500); 443 (8250). Anal. Calc. for $\text{C}_{54}\text{H}_{48}\text{N}_4\text{P}_2\text{CuClO}_6$: C, 64.20; H, 4.79; N, 5.55; Cu, 6.30. Found: C, 64.28; H, 4.88; N, 5.63; Cu, 6.36%.

2.5. X-ray crystallography

X-ray diffraction data for crystalline samples of **1**, **2** and **L** were collected using Mo $\text{K}\alpha$ radiation (0.71073 Å) on a Bruker KAPPA APEX II diffractometer. The SMART [44] program was used for collecting frames of data, indexing the reflections, and determination of lattice parameters; SAINT [44] program for integration of the intensity of reflections and scaling; SADABS [45] program for absorption correction. The structures were solved by direct methods (SHEL-

xs-97) and standard Fourier techniques, and refined on F^2 using full matrix least squares procedures (SHELXL-97) using the SHELX-97 package [46] incorporated in WINGX [47]. All non-hydrogen atoms were refined anisotropically except for the oxygen atom in the partially occupying water molecules in **1** which are in a disordered state. The hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atoms to which they were attached.

3. Results and discussion

3.1. Synthesis of ligand and copper(I) complexes

Syntheses of the copper(I) complexes **1** and **2** were achieved by reaction of ligand **L** with appropriate Cu(I) precursor complexes in equimolar ratio under inert atmosphere at room temperature. Reaction of **L** with $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ in anhydrous chloroform under argon atmosphere in 1:1 ligand-to-metal ratio yielded $[\text{Cu}(\text{L})(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**) as reddish brown blocks. The solid is fairly stable in air, but its CHCl_3 and CH_2Cl_2 solution were stable in air only for about 24 h. Treatment of $[\text{Cu}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2]\text{ClO}_4$ with **L** in dry chloroform under argon at room temperature with an equimolar amount resulted in the formation of a red solid. From its methanol solution red crystals $[\text{Cu}(\text{L})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**) were obtained. Complex **2** can also be obtained by replacing the CH_3CN in **1** with PPh_3 in 2:1 M ratio. The solubility of complex **2** is higher in common organic solvents compared to complex **1**. The relative stability of the complexes in solution is also higher in the case of complex **2**. Ligand **L** was earlier utilized to synthesize Zn(II) complexes for thiocyanate ion-selective PVC based membrane electrode [33]. However, the complex was not structurally characterized. From their physicochemical characterization Ardakani et al. [33] inferred that N, O donor atoms in the ligand moiety are disposed in a convergent manner, however as observed from the X-ray crystal structural studies (*vide infra*) in the present study the N, O donors in the ligand moiety as well as in the copper(I) complexes are disposed in a divergent fashion.

3.2. IR and NMR spectroscopy

The mononuclear Cu(I) complexes **1** and **2** under study show characteristic peaks due to the ligation of the ligand **L** to the metal center in the KBr-phase IR spectra. In the IR spectrum of ligand **L**, characteristic band at 1626 cm^{-1} is assigned to the imine ($\text{C}=\text{N}$) stretching frequency. This band due to $\text{C}=\text{N}$ stretching is shifted to lower energy and appear at around 1642 cm^{-1} and 1649 cm^{-1} in the complexes **1** and **2**, respectively. A sharp band observed at 2235 cm^{-1} in complex **1** indicates the existence of $\text{C}\equiv\text{N}$, which is absent in the IR spectra of **L** and **2**. The weak and broad band around 3431 cm^{-1} in the IR spectrum of **L** is assigned to be due to O–H stretching. There is not much shift of this band in the complexes **1** and **2** indicating the non-involvement of this group in coordination with the metal ion. The strong bands around 1435 , 744 , 695 and 506 cm^{-1} are due to the presence of PPh_3 group in the complex **2**. The typical strong bands due to the stretching vibrations of the non-coordinated ClO_4^- ions in **1** and **2** appear at the expected regions; 1091 and 636 cm^{-1} (for **1**); 1089 and 620 cm^{-1} (for **2**).

The ^1H NMR spectra of the ligand **L** in CDCl_3 shows a singlet at δ 8.68 ppm due to ($\text{HC}=\text{N}$) moiety. The downfield shift of the peak to around δ 8.74 and δ 8.72 ppm in case of **1** and **2**, respectively, indicates the coordination of the ligand **L** to the metal center. However, no significant shift compared to ligand **L** is observed for the outlying methyl protons in the complexes **1** and **2** and appears at around δ 2.43 ppm. The –OH proton resonates at δ 11.81 and δ 11.10 ppm

for **L** and **1**, respectively. The phenyl protons of PPh_3 in **3** resonate at δ 7.44–7.39 ppm.

3.3. UV–Vis and photophysical data

The absorption spectra of **L** (in dichloromethane) shows intra-ligand charge transfer bands at 238 nm (ϵ , $15\,080\text{ M}^{-1}\text{ cm}^{-1}$), 307 nm (ϵ , $21\,450\text{ M}^{-1}\text{ cm}^{-1}$) and 366 nm (ϵ , $10\,970\text{ M}^{-1}\text{ cm}^{-1}$), 274 nm (ϵ , $28\,100\text{ M}^{-1}\text{ cm}^{-1}$), respectively. These charge transfer bands appear at 322 nm (ϵ , $18\,050\text{ M}^{-1}\text{ cm}^{-1}$) and 312 nm (ϵ , $10\,500\text{ M}^{-1}\text{ cm}^{-1}$) for **1** and **2**, respectively. The Cu(I) complexes **1** and **2** display broad unstructured band at 432 nm (ϵ , $7500\text{ M}^{-1}\text{ cm}^{-1}$) and 443 nm (ϵ , $8250\text{ M}^{-1}\text{ cm}^{-1}$), respectively, which is supposed to be MLCT in origin, and these bands are responsible for characteristic color in complexes **1** and **2**.

Upon excitation at 315 nm (within the charge transfer envelope) at room temperature at dichloromethane the ligand **L** shows a weak emission band with maxima around 425 nm (Fig. 1). The emission quantum yield (ϕ) is determined to be 8.2×10^{-5} , against quinine sulfate in $0.1\text{ N H}_2\text{SO}_4$ [48]. The emission can be tentatively assigned to the intra-ligand fluorescent emission, which is related to the energy gap between the π – π^* molecular orbital of the π -conjugation of the ligand system. It has been found that the emission is quenched in both the complexes **1** and **2**. Quenching of fluorescence by paramagnetic and diamagnetic metal ions is well documented [49,50]. This might be due to the electron transfer by heavy atom.

3.4. Electrochemistry

The electrochemical properties of the copper(I) complexes $[\text{Cu}(\text{L})(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**) and $[\text{Cu}(\text{L})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**) have been studied by cyclic voltammetry in dichloromethane at glassy carbon electrode under dry argon atmosphere. The complex **1** shows a reversible voltammogram with single $\text{Cu}^{\text{I}}\text{--Cu}^{\text{II}}$ couple, occurring at $E_{1/2} = 0.74\text{ V}$ (versus Ag/AgCl in 1 M KCl , scan rate 50 mV s^{-1}) (Fig. 2). The ΔE_p value is 160 mV at 50 mV s^{-1} scan rate and it increases as the scan rate is increased. The electrode process is described by the Eq. (1) (where $\text{X} = \text{CH}_3\text{CN}$). However, under the similar conditions the complex **2** does not show a well defined voltammogram.

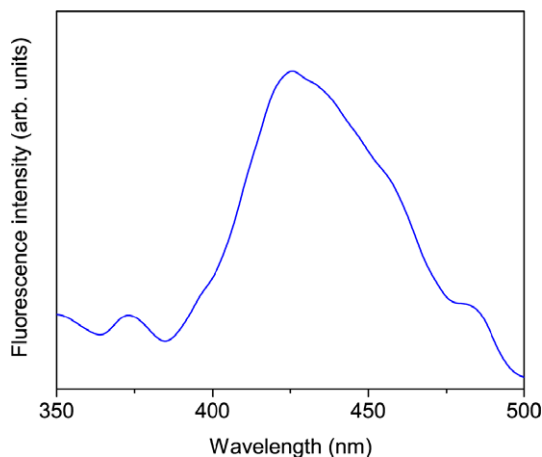
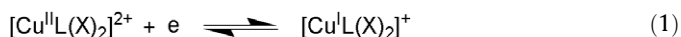


Fig. 1. Emission spectra of **L** in dichloromethane at room temperature on excitation at 315 nm .

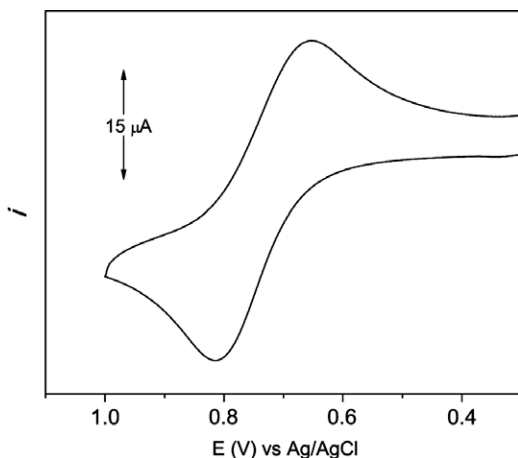


Fig. 2. Cyclic voltammogram for $[\text{CuL}(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**) in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NClO}_4$ at the scan rate of 50 mV s^{-1} .

Table 1
Crystallographic data and refinement parameters for **1**, **2** and **L**.

	1	2	L
Formula ^a	$\text{C}_{22}\text{H}_{33}\text{N}_6\text{O}_{11.5}\text{ClCu}$	$\text{C}_{54}\text{H}_{46}\text{N}_4\text{O}_6\text{P}_2\text{ClCu}$	$\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$
Formula weight (g mol^{-1}) ^a	664.53	1007.88	322.36
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	$P\bar{1}$	$P2_1/n$
<i>T</i> (K)	293(2)	140(8)	293(2)
<i>a</i> (Å)	23.365(4)	10.9575(2)	18.054(4)
<i>b</i> (Å)	18.523(4)	14.9373(3)	4.6824(10)
<i>c</i> (Å)	14.332(2)	15.5481(3)	19.780(4)
α (°)	90	80.0210(10)	90
β (°)	94.549(3)	86.906(2)	101.051(5)
γ (°)	90	84.6800(10)	90
<i>V</i> (Å ³)	6183.3(18)	2493.68(8)	1641.1(6)
<i>Z</i>	4	2	4
ρ_{calcd} (g cm^{-3})	1.404	1.342	1.305
μ (mm^{-1})	0.856	0.610	0.088
Collected reflections	29 014	20 736	6177
Unique reflections	5421	11 239	1026
<i>R</i> _{int}	0.0360	0.0371	0.0575
Goodness of fit (GOF) on <i>F</i> ²	1.152	1.024	1.074
Final <i>R</i> ₁ ^b , <i>wR</i> ₂ ^c (<i>I</i> ≥ 2 σ)	0.0820, 0.2573	0.0473, 0.1051	0.0353, 0.0900
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1059, 0.2904	0.0809, 0.1233	0.0504, 0.0995

^a Including solvate molecules.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ with P is $[2F_c^2 + \text{Max}(F_o^2, 0)] / 3$.

3.5. Reactivity

In our preliminary attempt to prepare heteroleptic (mixed ligands) complexes of **L**, and to compare the Lewis basicity of **L** to other two bispyridyl ligands $[\text{NC}_5\text{H}_4\text{CH}=\text{N}-\text{N}=\text{CHC}_5\text{H}_4\text{N}]$ (**A**) and $[\text{NC}_5\text{H}_4\text{CH}=\text{N}-\text{N}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{N}-\text{N}=\text{CHC}_5\text{H}_4\text{N}]$ (**B**), we reacted complex **1** with (**A**) and (**B**) in equimolar proportion under inert atmosphere, expecting that the two-*cis* oriented labile CH_3CN molecules in **1** will be replaced by **A** or **B**. But we have seen both the bispyridyl ligands **A** and **B** form stable homoleptic Cu(I) complexes, **3** and **4**, completely removing the ligand **L** as well as the CH_3CN molecules. The products **3** and **4** were characterized by multinuclear NMR spectroscopy and elemental analyses [**3**: ^1H NMR (200 MHz, $\text{DMSO}-d_6$, TMS); δ 8.69 (8H), 8.53 (4H), 7.73 (8H). Elemental analysis: C, 49.45; H, 3.51; N, 19.17%. **4**: ^1H NMR (200 MHz, $\text{DMSO}-d_6$, TMS); δ 8.61 (8H), 8.43 (4H), 7.86 (8H), 7.56–7.30 (20H). Elemental analysis: C, 62.75; H, 4.12; N, 16.78%]. This observation supports that the ligand **L** has less Lewis basicity compared to **A** and **B**.

3.6. Structural description

The structures of the ligand **L** and the complexes **1** and **2** were determined by single crystal X-ray diffraction. The crystallographic data and refinement parameters are presented in Table 1. A structural representation for the free ligand **L** is shown Fig. 3. It is characterized by an extended conformation with an *anti* conformation about the central C–C bond. Upon reaction with tetrahedral $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ complex, the ligand **L** adopts a *syn* conformation in complex **1** (Fig. 4) in order to optimize the tetrahedral coordination environment of copper(I) center. The distorted tetrahedral coordination geometry of copper(I) center in **1** is completed by the two N atoms of two different diazine fragments of the ligand **L** and two acetonitrile molecules. The corresponding Cu–N bond

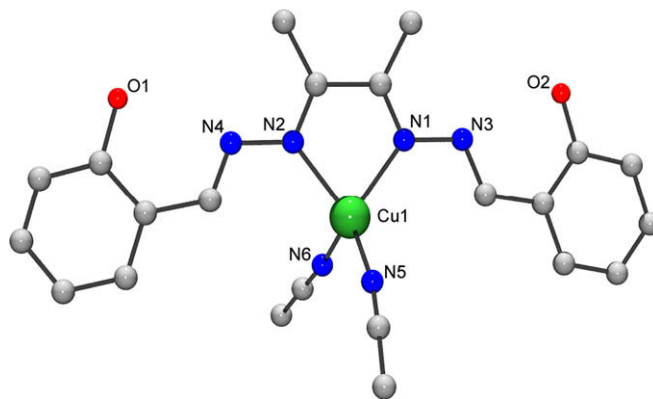


Fig. 4. Molecular representation of $[\text{CuL}(\text{CH}_3\text{CN})_2]\text{ClO}_4$ (**1**). Hydrogen atoms were omitted for clarity.

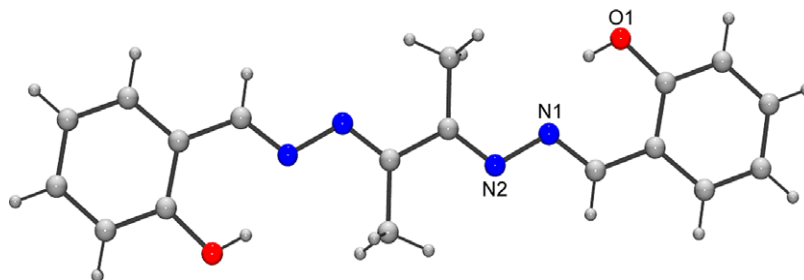


Fig. 3. Molecular representation of butane-2,3-dione bis(salicylhydrazone), **L**.

Table 2
Selected bond distances (Å) and angles for **1**, **2**.

Complex 1					
Cu(1)–N(1)	2.056(4)	Cu(1)–N(2)	2.058(4)	Cu(1)–N(5)	1.939(5)
Cu(1)–N(6)	1.971(6)	N(1)–N(3)	1.399(5)	N(2)–N(4)	1.401(5)
N(5)–Cu(1)–N(6)	105.1(2)	N(5)–Cu(1)–N(1)	120.12(18)		
N(6)–Cu(1)–N(1)	118.77(16)	N(5)–Cu(1)–N(2)	121.74(18)		
N(6)–Cu(1)–N(2)	112.12(17)	N(1)–Cu(1)–N(2)	77.81(15)		
Complex 2					
Cu(1)–N(1)	2.098(2)	Cu(1)–N(2)	2.070(2)	Cu(1)–P(1)	2.281(8)
Cu(1)–P(2)	2.255(8)	N(1)–N(3)	1.402(3)	N(2)–N(4)	1.402(3)
N(2)–Cu(1)–N(1)	76.34(9)	N(2)–Cu(1)–P(2)	114.18(7)		
N(1)–Cu(1)–P(2)	116.09(7)	N(2)–Cu(1)–P(1)	107.30(7)		
N(1)–Cu(1)–P(1)	109.58(7)	P(2)–Cu(1)–P(1)	123.48(3)		

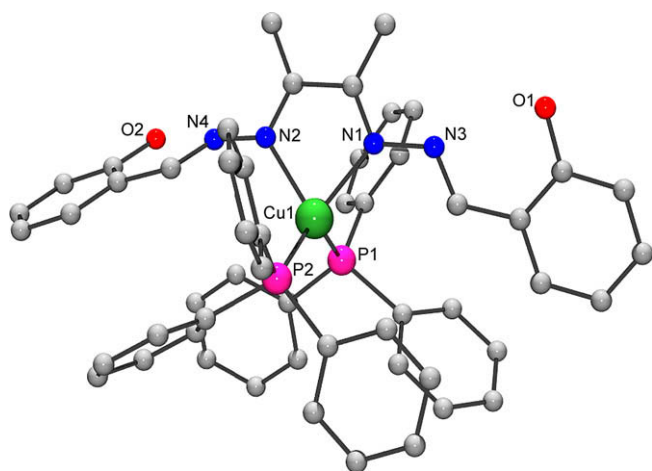


Fig. 5. Molecular representation of $[\text{CuL}(\text{PPh}_3)_2]\text{ClO}_4$ (**2**). Hydrogen atoms were omitted for clarity.

distances (Table 2) are Cu–N(imine), 2.056(4) and 2.058(4) Å, and Cu–N(acetonitrile), 1.939(5) and 1.971(6) Å and are consistent with literature values [5]. The N–Cu–N angles ranges from 77.80(2) to 121.70(2).

The structure of the complex **2** is shown in Fig. 5, and important bond distances and angles are included in Table 1. The complex **2** has identical conformational features with **1** having a distorted tetrahedral copper(I) as the central metal atom. Each copper atom coordinates simultaneously to two nitrogen atoms of the two different N–N diazine moieties of ligand **L** with two PPh_3 molecules completing the tetrahedral geometry. The Cu–N and Cu–P distances are typical [5] and ranges from 2.070(2) to 2.098(2) and 2.255(8) to 2.281(8), respectively. The increased crowding at the copper center forces one of the phenyl rings to deviate from planarity in complex **2**. The two phenyl rings make dihedral angle of 80.2° with each other. This is in contrast to the observation in complex **1** where the two outlying phenyl rings are coplanar with each other with N–C–C–N torsion angle being 180°.

4. Conclusions

In a search of new metal ion complexes of Cu(I) with interesting features we have synthesized two new Cu(I) complexes **1** and **2** using flexible polydentate diazine ligand **L** and investigated their structural, photophysical, electrochemical properties and reactivities. In the present study it was observed that the phenolate oxygens didn't coordinate to the metal ion. The non-involvement of phenoxide ion in the coordination with Cu(I) center is contrary to the usual binding modes observed in similar type of salen ligands with metal ions [51,52]. The phenolate oxygens did not take

part in metal-coordination because of the incompatibility of soft Cu(I) ion with hard O^- ion and also due to the free rotation of N–N bond, the N, O donor atoms in the ligand moiety are disposed in a divergent fashion. Moreover it should be taken in account that as the Cu(I) complexes were synthesized in an aprotic solvent and in the absence of any base, the deprotonation of ligand **L** (which is pre-requisite for coordination) is hindered.

Acknowledgement

G.K.P. thanks the Department of Science and Technology, Government of India, New Delhi for financial support.

Appendix A. Supplementary data

CCDC 738343, 738344 and 738345 contain the supplementary crystallographic data for the ligand **L** and the Cu(I) complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.12.009.

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