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# Synthesis, spectral characterization and crystal structure of *N*-2-hydroxy-4-methoxybenzaldehyde-*N*'-4-nitrobenzoyl hydrazone and its square planar Cu(II) complex

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# 1. Introduction

Schiff bases derived from the condensation of salicylaldehyde and its derivatives with alkyl and aroyl hydrazones play a very important role in coordination chemistry [1-5]. They display biological activity, play an important role in biological systems [6-10] and are considered to be suitable models for pyridoxal, and in general B<sub>6</sub>, vitamins. Adducts of nontransition, early transition, and f metals with o-hydroxy Schiff bases have been widely studied [11–13]. Furthermore, abilities of arovl hydrazones to coordinate to metals either in keto or enol tautomeric form make them attractive as ligands. As the salicylaldehyde aroyl hydrazone Schiff base is concerned, it can act as a tridentate ligand both in the monoanionic and dianionic forms and hence can form very stable chelates with metal ions. Salen-based metal complexes also play an important role in the SHG efficiency [14]. Thompson et al. in 1991 reported the first salen based NLO metal complex of the tetradentate salen [*N*,*N*'-bis(salicylaldeminato) ethylene] ligand. Compared to organic molecules, they can offer a large variety of molecular structures, the possibility of high thermal and environmental stability and a diversity of electronic properties by the virtue of coordinated metal atom.

# ABSTRACT

A new aroyl hydrazone, *N*-2-hydroxy-4-methoxybenzaldehyde-*N*'-4-nitrobenzoyl hydrazone (H<sub>2</sub>L) and its mixed ligand Cu(II) complex [CuLpy] [py, pyridine] have been prepared. The ligand is characterized by elemental analysis, electronic, infrared and NMR spectral studies and the complex by electronic, infrared, EPR spectral studies and the magnetic susceptibility data. The structures of the compounds were determined by single crystal X-ray diffraction studies. Both the ligand and the Cu complex crystallize into a triclinic lattice with a space group of *P*I. From the crystal studies, it is concluded that the ligand molecule exits in the keto form in the solid state, while at the time of complexation, it tautomerises into the enol form. The complex is formed by the double deprotonation of the ligand molecule—both the phenolic and the enolic protons.

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Aroyl hydrazones are potential multidentate ligands in coordination chemistry. As the part of our work for the search of new ligands which can form nonlinear optical active coordination complexes [15,16], we herein report the synthesis, spectral characterization and crystal structure of a new aroyl hydrazone, *N*-2-hydroxy-4-methoxybenzaldehyde-*N*'-4-nitrobenzoyl hydrazone (Scheme 1) and one of its square planar Cu(II) complex.

# 2. Experimental

# 2.1. Reagents

The solvents used for synthesis were purchased from Merck and used without further purification. 2-Hydroxy-4-methoxybenzaldehyde, 4-nitrobenzoyl hydrazine and copper(II) acetate were purchased from Sigma–Aldrich. Spectrograde solvents were used for spectral recording.

# 2.2. Physical measurements

Analysis of C, H and N were done on Elementar Vario EL III CHNOS Elemental Analyzer. IR spectra were recorded as KBr discs on SHIMADZU IR Spectrophotometer. Electronic spectra were carried out in UVWIN 5.0 Spectro UV–vis double beam UVD 3500 Spectrophotometer in the region 250–900 nm by using DMF as solvent. The <sup>1</sup>H NMR, <sup>13</sup>C NMR, COSY and

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Scheme 1. Structure of compound H<sub>2</sub>L.

HSQC spectra were recorded on a Brucker DRX500 using DMSO- $d_6$  as solvent and TMS as standard. EPR spectral measurements were carried out on a Varian E-112 X-band spectrometer using TCNE as standard at the Sophisticated Analytical Instruments Facility, Indian Institute of Technology, Mumbai, India.

# 2.3. Crystallography

Single crystal X-ray diffraction experiments were performed on a 'Bruker Smart Apex CCD Diffractometer' using graphitemonochromated MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) (all crystallographic data are deposited with the Cambridge Crystallographic data centre). Ligand crystal with dimensions 0.16 mm × 0.10 mm × 0.07 mm and complex crystal with dimensions 0.22 mm × 0.14 mm × 0.10 mm were used and the data collected at 293(2) K is shown in Table 1. The structure was solved by direct and refined by full matrix least squares on  $F^2$  with SHELXL-97 program [17]. The graphical tool used was DIAMOND version 3.1d [18]. All non-hydrogen atoms were refined anisotropically. Selected bond lengths and bond angles of the compounds are listed in Table 2.

# 2.4. Synthesis

The ligand was prepared by adding 2-hydroxy-4-methoxybenzaldehyde (0.761 g, 5 mmol) and 4-nitrobenzoyl hydrazine

#### Table 1

Crystal data and structure refinement for the ligand and the complex

#### Table 2

Selected bond lengths and bond angles of the ligand and the complex

Ligand	Complex	
N1-C8 1.278(2) N1-N2 1.384(1) N2-C9 1.338(2) C12-C11 1.376(2) C12-C13 1.379(2) O3-C9 1.232(2)	N1-C8 1.287(3) N1-N2 1.413(3) N2-C9 1.312(3) C11-C12 1.367(4) C12-C13 1.369(4) O3-C9 1.300(3)	
O2–C6 1.350(2)	O2-C6 1.318(3) Cu1-O2 1.892(1) Cu1-N1 1.921(2) Cu1-O3 1.932(1) Cu1-N4 2.000(2)	
C8-N1-N2 114.95(15) C9-N2-N1 120.59(15) C11-C12-C13 118.43(16) O4-N3-C13 117.62(15) O3-C9-N2 124.66(15) O3 - C9 - C10 120.47(15) N2-C9-C10 114.87(15)	C8-N1-N2 116.9(2) C9-N2-N1 108.0(2) C11-C12-C13 119.8(3) O4-N3-C13 118.6(2) O3-C9-N2 124.6(2) O3-C9-C10 117.7(2) N2-C9-C10 117.7(2)	
C14–C15–C10 120.53(15)	C14-C15-C10 120.8(2) O2-Cu1-N1 93.55(9) O2-Cu1-O3 174.32(7) N1-Cu1-O3 80.96(9) O2-Cu1-N4 92.46(9) N1-Cu1-N4 172.65(8) O3-Cu1-N4 93.13(9)	

(0.905 g, 5 mmol) to 10 mL of DMF (Scheme 2). The solution was heated to boiling for 5 min, cooled to room temperature and then poured into 40 mL of water containing crushed ice and 1 mL of concentrated sulphuric acid. The product formed was filtered, washed repeatedly with water, finally with a little ether and recrystallized from DMF (m.p. 228–230 °C, yield 85%). Yellow plate-like crystals suitable for single crystal X-ray diffraction studies were obtained by the slow evaporation of its solution in DMF. Anal. Calcd. for  $C_{15}H_{13}N_3O_5$ .<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O (%): C, 55.56; H, 4.35; N, 12.96. Found: C, 55.12; H, 4.52; N, 12.76.

	Ligand	Complex
Empirical formula	C <sub>15</sub> H <sub>15</sub> N <sub>3</sub> O <sub>6</sub>	C <sub>20</sub> H <sub>16</sub> CuN <sub>4</sub> O <sub>5</sub>
Formula weight	333.30	455.91
Temperature	293(2)K	293(2)K
Wavelength	0.71073 A	0.71073 A
Crystal system	Triclinic	Triclinic
Space group	ΡĪ	PĪ
Unit cell dimensions	a=6.721(6)Å	a = 6.400(4) Å
	b = 7.009(6) Å	b=10.082(6) Å
	c = 16.839(14)Å	<i>c</i> = 15.206(9) Å
	$\alpha = 78.103(13)^{\circ}$	$\alpha = 97.936(9)^{\circ}$
	$\beta = 80.585(13)^{\circ}$	$\beta = 91.940(9)^{\circ}$
	$\gamma = 78.125(13)^{\circ}$	$\gamma = 107.864(9)^{\circ}$
Volume, Z	753.5(11)Å <sup>3</sup> , 2	921.9(10) Å <sup>3</sup> , 2
Calculated density	$1.469  \text{mg/m}^3$	$1.642 \text{ mg/m}^3$
Absorption coefficient	$0.116 \mathrm{mm^{-1}}$	$1.228 \mathrm{mm^{-1}}$
F(000)	348	466
Crystal size	$0.16mm\times0.10mm\times0.07mm$	$0.22mm\times0.14mm\times0.10mm$
heta Range for data collection	1.25–28.48°	2.15–28.33°
Index ranges	$-8 \le h \le 8, -9 \le k \le 9, -22 \le l \le 22$	$-8 \le h \le 8, -13 \le k \le 13, -19 \le l \le 19$
Reflections collected/unique	6316/3357 [R(int)=0.0174]	7468/4015 [R(int)=0.0239]
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3357/0/277	4015/0/335
Goodness-of-fit on F <sup>2</sup>	1.025	1.065
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0483, wR_2 = 0.1279$	$R_1 = 0.0423$ , $wR_2 = 0.1022$
R indices (all data)	$R_1 = 0.0582, wR_2 = 0.1386$	$R_1 = 0.0520, wR_2 = 0.1068$
Largest difference peak and hole	0.269 and -0.181 eÅ <sup>-3</sup>	0.664 and -0.252 eÅ <sup>-3</sup>





For the preparation of the Cu(II) complex, a method was adapted to prepare the binuclear precursor according to the reported procedures [19] for the synthesis of similar complexes and then convert it to the mononuclear analogue. To a boiling solution of the ligand (0.1575 g, 0.5 mmol) in a 1:1 mixture of ethanol and DMF, an ethanolic solution of copper(II) acetate (0.0998 g, 0.5 mmol) was added and refluxed continuously for about four hours (Scheme 3) The brown colored product obtained was filtered and washed with a 1:1 mixture of ethanol/DMF and recrystallized from DMF (yield 78%). Anal. Calcd. for Cu<sub>2</sub>C<sub>30</sub>H<sub>22</sub>N<sub>6</sub>O<sub>10</sub> (%): C, 46.16; H, 3.23; N, 10.77. Found: C, 45.98; H, 2.75; N, 10.81.

About 200 mg of the dimeric Cu(II) complex was dissolved in about 10 mL of boiling pyridine and refluxed for about 5 min. A dark red colored product was obtained by the addition of water to this solution (Scheme 4). It was filtered, washed several times with water, finally with a little diethyl ether and dried (yield 86%). Dark yellow plate-like crystals of Cu(II) complex suitable for single crystal X-ray diffraction studies were obtained by the slow evaporation of its solution in pyridine. Anal. Calcd. for  $CuC_{20}H_{16}N_4O_5$  (%): C, 52.69; H, 3.54; N, 12.29. Found: C, 52.70; H, 3.28; N, 12.19.

# 3. Results and discussion

#### 3.1. Electronic spectrum

The electronic spectra of the compounds were recorded in solution state by dissolving in DMF. The ligand spectrum shows

two well-defined bands in the UV region and weak absorption in the visible region. The strong bands are at 270–319 nm and 320–380 nm. The former is assigned to the  $\pi \rightarrow \pi^*$  electronic transitions of the p-substituted benzene and the azomethine bonds. The latter one is due to  $n \rightarrow \pi^*$  transitions of carbonyl and nitro chromophores. A weak absorption is also observed in the visible region at 440–580 nm range due to the much extended electron delocalization from one to other end of the overall molecule.

In the case of square planar copper complexes, three allowed transitions are expected in the visible region, but often these theoretical expectations are overlooked in practice, and these bands usually appear overlapped due to the very small energy difference between the d levels [20]. The molecule reveals  $\pi \to \pi^*$  and  $n \to \pi^*$  transitions of the pyridyl and principal ligand functions as a very broad band in the region 268–343 nm. The charge transfer transitions are observed as two bands in the region 424–448 nm and 440–517 nm. The broad band appeared at 588–722 nm, when the spectrum was recorded high concentrations in the visible region as a continuation to the charge transfer band is due to the d–d transitions.

### 3.2. IR spectra

The IR spectra of the compounds were recorded as KBr discs in the range 4000–400 cm<sup>-1</sup>. Hydrazones can exist in the keto or in the enol tautomeric form in the solid state. In the present lig-



Scheme 4.

and, the absorption due to  $\nu$ (C=O) observed at 1655 cm<sup>-1</sup> confirms that the compound is in the keto form in the solid state. There are two well-defined infrared absorptions at 1655 and  $1599 \,\mathrm{cm}^{-1}$ , which were assigned to the amide I and amide II bands, respectively. These bands are shifted to the low frequency region than the theoretical values due to the conjugation of the amide groups with the aromatic group. Because of conjugation, the double bond nature of C=O decreases and hence the bond order decreases, which causes a shift to the lower frequency region. Amide II band seen at 1599 cm<sup>-1</sup> points out to the secondary amide exists in the trans conformation, which is confirmed by the crystal structure. A very broad band observed in the region 3000–3500 cm<sup>-1</sup> comprising of both the -OH and -NH- stretching absorptions. Two bands at 1512 and 1472 cm<sup>-1</sup> are due to the aromatic C=C stretching absorptions. It is very difficult to differentiate the bands in the fingerprint region, but a well-defined band at 1221 cm<sup>-1</sup> may be due to phenolic C–O stretching vibration. The characteristic  $\nu$ (C=N) absorptions of Schiff bases come in the region 1689–1471 cm<sup>-1</sup>. In the present case, it appears as a shoulder to the amide II band nearly at 1550 cm<sup>-1</sup>.

The IR spectrum of the complex was compared with that of the ligand and remarkable differences are noticed between them. The  $\nu$ (O–H) broad band at 3000–3500 cm<sup>-1</sup> for the ligand disappears in the complex, suggesting coordination through deprotonated phenolic oxygen. It also substantiates the enolization of the ligand at the time of complexation. The absence of strong band at 1655 cm<sup>-1</sup> due to  $\nu$ (C=O) (amide I), which was present in the ligand spectrum, in the complex spectrum bears out the deprotonation of the enolised hydrazone tautomer. The band due to  $\nu$ (C=N) (amide II) at 1599 cm<sup>-1</sup> is shifted to 1512 cm<sup>-1</sup> in the complex indicates coordination of the azomethine nitrogen to the metal atom. In the far IR region, the band at 272 nm confirms the coordination of the pyridine nitrogen to copper [21].

# 3.3. <sup>1</sup>H NMR and <sup>1</sup>H $^{-1}$ H COSY data of the ligand

The <sup>1</sup>H NMR spectrum of the compound  $H_2L$  and its assignments are shown in Fig. 1. There are two sharp singlets at the very down-field region of the spectrum i.e., at 12.24 and 11.43 ppm are assigned



to OH and NH protons, respectively. These hydrogen resonances are seen in the high  $\delta$  values because they are attached to highly electronegative atoms oxygen and nitrogen, respectively, and hence in a low electron density environment. This assignment can be confirmed by the deuteriated proton spectra in which the intensity of these bands is considerably decreased. Position of these peaks in the downfield region suggests the possibility of considerable extent of hydrogen bonding involved by them. Hydrogen bonding decreases the electron density around the proton and thus moves the proton absorption to lower field. The doublets observed at 8.15 and 8.37 ppm are assigned to the equivalent protons at C11 and C15 and C12 and C14, respectively. Protons at C12 and C14 resonate at more downfield compared to those at C11 and C15 because of the presence of electron withdrawing nitro group at its *ortho* position. The singlet with an area integral of one at  $\delta$  8.57 ppm is due to the





Fig. 3. <sup>13</sup>C-<sup>1</sup>H HSQC spectrum of the ligand.

resonance of the proton at C8. The peak at  $\delta$  7.47 ppm is the C4 proton resonance, is a doublet due to the presence of a neighboring proton at C3. Peaks generated by C3 and C7 are very close to each other because of their nearly same electron environment. C7 gives a singlet at 6.49 ppm and C3 gives a doublet due to the presence of neighboring proton C4 at 6.53 ppm. The singlet at 3.77 ppm, having an area integral of three is assigned to the methoxy protons.

The above assignments of the proton NMR spectrum are also confirmed by  ${}^{1}\text{H}{-}{}^{1}\text{H}$  correlation spectroscopy. The COSY spectrum is shown in Fig. 2. There is no correlation for the peaks at  $\delta$  3.77, 8.57, 11.43 and 12.24 in the COSY spectrum, which confirms the above assignments. Correlation patterns are observed in the aromatic region only. Peaks at  $\delta$  8.15, 8.37, 6.53 and 7.47 ppm make good contours in the COSY spectrum and peak at  $\delta$  6.49 ppm makes only a small correlation. Horizontal and vertical straight lines drawn from  $\delta$  8.15 ppm in the diagonal of COSY spectrum will meet the contours at  $\delta$  8.37 ppm, confirms the correlation between C11 and C15 protons with C12 and C14 protons. Similarly lines from  $\delta$  6.53 meet at  $\delta$  7.47, confirming the aforesaid assignments of the peaks. Small contour made by  $\delta$  6.49 peak with  $\delta$  6.53 peak suggests the small extent of correlation with the proton at the *meta* position.

# 3.4. ${}^{13}C$ NMR and ${}^{13}C-{}^{1}H$ HSQC spectra of the ligand

The <sup>13</sup>C spectrum and <sup>13</sup>C–<sup>1</sup>H correlation HSQC spectrum of the compound were also recorded in DMSO- $d_6$  and the HSQC spectrum is shown in Fig. 3. The correct assignment of the <sup>13</sup>C peaks can be done with the help of HSQC. The <sup>13</sup>C peaks at  $\delta$  162.6,111.88, 159.2, 169.8, 138.8 and 149.82 do not make any correlation pattern in HSQC suggesting that these peaks are made by nonprotonated carbons and are assigned as C2 (162.2), C5 (111.88), C6 (159.2), C9 (169.8) C10 (138.8) and C13 (149.82). The peak due to the carbonyl carbon C9 at  $\delta$  169.8 ppm is very weak and is difficult to distinguish from the noise. This may be due to the following reasons. Firstly, in the solution state, there may be considerable extent of keto–enol tautomerism so that the resonance frequency of carbonyl carbon changes continuously and the peaks are difficult

to locate due to the poor solubility of the compound. Secondly, the common spin-lattice relaxation mechanism for <sup>13</sup>C results from dipole–dipole interaction with directly attached protons. Thus, nonprotonated carbon atoms often have longer relaxation times





Fig. 4. The EPR spectra of the copper complex in polycrystalline state at 298 K and in DMF at 77 K.



Fig. 5. Molecular structure of  $H_2L$ . Intramolecular hydrogen bonds are shown as dotted lines. Ellipsoids are drawn with 50% probability.

and give small peaks. Hence carbonyl carbon will give only small peaks and at low concentrated solutions, it may not be detected. Peaks at  $\delta$  55.58, 106.87, 131.32, 101.31, 149.54, 129.24 and 123.91 make contours at <sup>1</sup>H  $\delta$  values corresponding to 3.77, 6.53, 7.47, 6.49, 8.57, 8.15 and 8.37 ppm, respectively, and are assigned as C1 (55.58), C3 (106.87), C4 (131.32), C7 (101.31), C8 (149.54), C11 and C15 (129.24), C12 and C14 (123.91).

#### 3.5. EPR specrum of the copper complex

The EPR spectra of the complex in the polycrystalline state at 298 K and in DMF at 77 K are shown in Fig. 4. Both the spectra are axial. The first one has *g* values  $g_{||} = 2.2041$  and  $g_{\perp} = 2.0536$  and the later one with *g* values of  $g_{||} = 2.195$  and  $g_{\perp} = 2.0937$ . Since the lowest *g* value is less than 2.04, the complex may have an axial symmetry with all the principal axes aligned parallel, which supports the square planar nature of the complex. The *f* value ( $f = g_{||}/A_{||}$ ), which reveals the extent of tetragonal distortion, is equal to 107.07 for the complex. The *f* values are reported to be in the range of 105–135 cm for square planar complexes [22]. Also, the trend  $g_e < g_\perp < g_{||}$  observed for the complex shows that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital of the copper(II) ions and the spectral features are characteristics of axial symmetry.

#### 3.6. Crystal structure of the ligand

The molecule crystallizes in the triclinic crystal system with a space group of  $P\overline{I}$ . The crystal structure of the compound with atom numbering scheme showing 50% displacement ellipsoids is shown in Fig. 5.



Fig. 7. Molecular structure of CuLpy. Ellipsoids are drawn with 50% probability.

The molecule exists in the keto tautomeric form and the configuration of C8-N1 bond is E. The molecule exists mainly in two planes. One plane corresponding to the phenyl ring of the nitrophenyl moiety and the other to the remaining part of the molecule. This twisting may be to relieve the steric interactions between the hydrogen atoms N2-H and C11-H. The three bond angles around C9 atom are not equal to 120° each. It is seen that the N2–C9–O3 bond angle is considerably greater than N2-C9-C10 angle. This observation is similar to the structures of hydrazones reported earlier, which is explained in order to decrease the repulsion between the lone pairs present in N2 and O3 atoms. The central part of the molecule adopts a completely extended double bonded conformation. It can be confirmed by the C9–O3 bond length (1.2324(23)Å), which is considerably longer than the standard C=O bond length 1.21 Å and N2-C9 bond length (1.3380(25) Å), which is shorter than standard N-C single bond length (1.47 Å). Similar observation was reported in the case of early published crystal structures of hydrazone molecules

The packing of the molecules (Fig. 6) in the crystal is effected by a wide network of intermolecular hydrogen bonds involving water. In the crystal lattice, the molecules are arranged parallel to each other, but in a zigzag fashion such that the nitrobenzoyl fragment of one molecule is just above the methoxy phenyl fragment of second one. The molecules are thus stalked together by a wide network of hydrogen bonds, Cg–Cg interactions and C–H··· $\pi$  interactions. Each water molecule forms three intermolecular hydrogen bonds in the packing pattern. They are O6···H(2A)–O2 and O6–H(62)···O3 with



Fig. 6. Packing diagram of the compound H<sub>2</sub>L. Intra and intermolecular hydrogen bonds are shown as dotted lines.



Fig. 8. Packing diagram of the compound CuLpy.

a molecule in the same plane and O6–H(61)…O1 with a molecule of adjacent plane arranged in an opposite fashion with it. In addition to this, there are two intramolecular H-bonding present viz., O2–H(2A)…N1 and N2–H1…O6. Cg–Cg interactions also have considerable influence in the packing pattern. There is a C–H… $\pi$  is also present between C8–H8 and Cg1 comprising of C2, C3, C4, C5, C6 and C7 with an H…Cg distance 3.357(21)Å.

## 3.7. Crystal structure of the complex

The structure of the Cu(II) complex together with the atom numbering scheme is shown in Fig. 7. In this complex the dinegative N-2-hydroxy-4-methoxy benzaldehyde-N'-4-nitrobenzoyl hydrazone is coordinated to Cu(II) through the deprotonated phenolic oxygen O2, azomethine nitrogen N1 and deprotonated enolate oxygen O3 forming five and six membered chelate rings. The fourth site is occupied by the pyridyl nitrogen N4. The C8-N1 and N1-N2 bonds of the ligand are found to be slightly increased and N2-C9 bond is found to be slightly decreased after coordination confirming the proposed mode of coordination. The complex is almost planar with a slight distortion. The distortion from the regular square planar structure is determined from the departure of the bong angles around Cu(II) [O2-Cu1-N1 (93.55(9)), N1-Cu1-O3 (80.96(9)), O2-Cu1-N4 (92.46(9)), O3-Cu1-N4 (93.13(9))] from 90°. The found distortion may be due to the rigidity of the chelate rings formed. The structures reported here are more or less similar to the compounds reported earlier [23,24]. The C9–O3 bond length is 1.300(3)Å is considerably greater than the C=O bond length, which confirms the enolization of the ligand at the time of coordination. In the crystal lattice (Fig. 8), the packing is effected by a wide network of  $\pi$ - $\pi$  staking interactions. No classic hydrogen bonds are found in the lattice, but a weak C–H $\cdots$  $\pi$  interactions are found between the hydrogen in the aromatic rings with the oxygen atoms of the neighboring molecules. Additional Y–X  $\cdots \pi$  ring interactions are found between N3-O4 and Cg1, where the centroid Cg1 consists of Cu1, O3, C9, N2, N1 having the Y...Cg distance 3.585 Å.

# 4. Supplementary data

CCDC 654105 and 654106 contain the supplementary crystallographic data for [CuLpy] and  $H_2L$  of this paper. These data

can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html [or from Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

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