# Inorganica Chimica Acta 398 (2013) 98-105

Contents lists available at SciVerse ScienceDirect

# Inorganica Chimica Acta



journal homepage: www.elsevier.com/locate/ica

# Mononuclear and binuclear Cu(II) complexes of some tridentate aroyl hydrazones. X-ray crystal structures of a mononuclear and a binuclear complex

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# ARTICLE INFO

Article history Received 22 August 2012 Received in revised form 28 November 2012 Accepted 1 December 2012 Available online 29 December 2012

Keywords: Mononuclear Cu(II) complexes Binuclear Cu(II) complexes (µ-Cl)<sub>2</sub>-Bridge Pyridine-2-carbaldehyde hydrazone 2-Acetylpyridine hydrazone X-ray crystal structure

# ABSTRACT

Cu(II) complexes of eight N,N,O-donor hydrazone ligands, obtained by condensation of pyridine-2-carbaldehyde and 2-acetylpyridine with four aroyl hydrazides, are reported. Reactions of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with the pyridine-2-carbaldehyde hydrazones ( $L_1H$ ,  $L_2H$ ,  $L_3H$ ,  $L_4H$ ) in presence of Et<sub>3</sub>N, in 1:2:2 molar ratio, lead to isolation of mononuclear octahedral Cu(II) complexes of formula  $[Cu(L)_2]$  (L =  $L_1^-, L_2^-, L_3^-, L_4^-)$ . However, for the 2-acetylpyridine hydrazones (L<sub>5</sub>H, L<sub>6</sub>H, L<sub>7</sub>H, L<sub>8</sub>H) reactions under similar conditions yield dichloro bridged complexes of the type  $[Cu_2(\mu-Cl)_2(L')_2]$   $[L' = L_5^-, L_6^-, L_7^-, L_8^-)$ , where each Cu(II) ion is in a square-pyramidal geometry, the chloride ions coming from the in situ reduction of perchlorate by the 2-acetylpyridine hydrazones. The X-ray crystal structures of  $[Cu(L_1)_2]$  and  $[Cu_2(\mu-Cl)_2(L_5)_2]$  are reported. The spectroscopic and electrochemical behaviors of the complexes are also reported.

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# 1. Introduction

Interest in the metal complexes of Schiff base ligands remains unwavering because of their applications in varied fields such as catalysis [1-3], synthesis of compounds possessing designed and controllable magnetic properties [4,5], spin-crossover materials [6], biological activities including radical scavenging ability [7], synthons for crystal engineering and materials chemistry [8-14]. Aroyl hydrazones are an important class of Schiff base ligands, coordinating through protonated/deprotonated amide oxygen and the imine nitrogen of hydrazone moiety: very often an additional donor site (usually N or O) is provided by the aldehyde or ketone forming the hydrazone Schiff base. Aroylhydrazones have proved to be strong chelating agents for transition metals [10-12,15–17] and lanthanides [18,19] as well as main group elements [20,21]. In our laboratory we have been investigating the structural diversity of aroylhydrazone complexes along with their redox and magneto-structural properties [10-12,15,16]. In this paper we report mononuclear and binuclear complexes of Cu(II) with tridentate hydrazone ligands obtained by the condensation of four aroylhydrazides with pyridine-2-carbaldehyde and 2-acetyl pyridine (Scheme 1).

# 2. Experimental

# 2.1. Materials and methods

The hydrazone ligands were prepared following procedure described in literature [15,22-25]. CuCl<sub>2</sub>·2H<sub>2</sub>O, Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were obtained from Aldrich. The solvents for synthesis were of AR grade obtained from SRL (India) or Spectrochem (India) and used without purification, while solvents for spectroscopic and electrochemical work were of HPLC grade from Aldrich or SRL (India). Elemental analyses were performed on a Perkin-Elmer 2400 C, H, N analyzer. Infrared spectra were recorded as KBr pellets on a JASCO FT-IR-460 spectrophotometer. UV-Vis spectra were recorded using a JASCO V-530 spectrophotometer. Cyclic voltammograms were recorded in DMF solutions (for compounds 1-4) or DMSO solution (for compounds 5-8), containing 0.1 (M) TEAP as supporting electrolyte, using a CH1120A potentiostat, with Pt disc/glassy carbon working electrode, Pt wire as counter electrode and Ag,AgCl/saturated KCl as reference electrode. The ferrocene/ ferrocenium couple was observed at  $E^{0}(\Delta E_{p}) = 0.48 \text{ V} (100 \text{ mV}) \text{ un-}$ der our experimental conditions.



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Scheme 1. Ligands used in this work.

## 2.2. Synthesis of the complexes

## 2.2.1. Mononuclear Cu(II) complexes

 $[Cu(L_1)_2]$  (1): To a vigorously stirred methanolic solution (15 ml) of the hydrazone ligand (L<sub>1</sub>H) (482 mg, 2 mmol), Et<sub>3</sub>N (202 mg, 2 mmol) was added, when a clear yellow solution was obtained. A solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (369 mg, 1 mmol) in methanol (10 ml) was added drop wise to the above solution. The solution turned deep yellow to greenish brown. The mixture was stirred at room temperature for three hours and then filtered. The yellow-green residue was washed with methanol and then dried over

fused calcium chloride. The filtrate was allowed to evaporate slowly at room temperature when greenish red colored square shaped shiny crystals of complex  $[Cu(L_1)_2]$  (1), suitable for X-ray diffraction studies, appeared after 4 days.

The other three mononuclear Cu(II) complexes  $[Cu(L_2)_2]$  (**2**),  $[Cu(L_3)_2]$  (**3**),  $[Cu(L_4)_2]$  (**4**) were synthesized using a similar procedure as that for **1**, using appropriate ligands (Scheme 2).

[ $Cu(L_1)_2$ ] (**1**): Yield: 230 mg (42%). *Anal.* Calc. for  $C_{26}H_{20}N_6O_4Cu$ : C, 57.40; H, 3.71; N, 15.45. Found: C, 57.35; H, 3.65; N, 15.47%. Electronic spectrum in DMF solution  $\lambda_{max}/nm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 440(2400), 380(3744), 272(2625). Selected IR bands (cm<sup>-1</sup>): 3440br( $\nu_{OH}$ ), 1599( $\nu_{C=N}$ ).

[ $Cu(L_2)_2$ ] (**2**): Yield: 210 mg (41%). *Anal.* Calc. for  $C_{26}H_{20}N_6O_2Cu$ : C, 60.99; H, 3.94; N, 16.42. Found: C, 60.94; H, 3.88; N, 16.48%. Electronic spectrum in DMF solution  $\lambda_{max}/nm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 708(86), 382(2323), 296(1780), 270(1882). Selected IR band (cm<sup>-1</sup>): 1595( $\nu_{C=N}$ ).

[ $Cu(L_3)_2$ ] (**3**): Yield: 224 mg (41%). *Anal.* Calc. for  $C_{26}H_{22}N_8O_2Cu$ : C, 57.62; H, 4.09; N, 20.68. Found: C, 57.55; H, 3.9; N, 20.72%. Electronic spectrum in DMF solution  $\lambda_{max}/nm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 417(2555), 380(2525), 356(2040), 272(2558). Selected IR band (cm<sup>-1</sup>): 1605( $\nu_{C=N}$ ).

[*Cu*(*L*<sub>4</sub>)<sub>2</sub>] (**4**): Yield: 254 mg (49%). *Anal.* Calc. for C<sub>24</sub>H<sub>18</sub>N<sub>8</sub>O<sub>2</sub>Cu: C, 56.08; H, 3.50; N, 21.81. Found: C, 56.01; H, 3.43; N, 21.86%. Electronic spectrum in DMF solution  $\lambda_{max}/nm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 702(66), 379(2175), 290(1334), 272(1448). Selected IR band (cm<sup>-1</sup>): 1573( $\nu_{c=N}$ ).

## 2.2.2. Binuclear Cu (II) complexes

 $[Cu_2(L_5)_2(\mu-Cl)_2]$  (**5**) To a vigorously stirred methanolic solution (15 ml) of the hydrazone ligand (L<sub>5</sub>H) (510 mg, 2 mmol) containing Et<sub>3</sub>N (202 mg, 2 mmol) a solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (369 mg, 1 mmol) in methanol (10 ml), was added drop wise. The solution turned light yellow to deep green. The mixture was stirred at room temperature for three hours and then filtered. The green residue was washed in methanol and then dried over fused calcium chloride. The filtrate was allowed to evaporate slowly at room temperature, when green colored square shaped shiny crystals of complex **5**, suitable for X-ray diffraction studies, appeared after 4 days. The other three Cu (II) complexes [Cu<sub>2</sub>(L<sub>6</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**6**), [Cu<sub>2</sub>(L<sub>7</sub>)<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>]



Scheme 2. Schematic representation of the synthesis of the mono- and binuclear complexes.

(7),  $[Cu_2(L_8)_2(\mu-Cl)_2]$  (8) were synthesized using similar procedure as that for 5, using appropriate ligands (Scheme 2).

[ $Cu_2(L_5)_2(\mu$ - $Cl)_2$ ] (**5**): Yield: 343 mg (48%). Anal. Calc. for  $C_{28}H_{24}N_6Cl_2O_4Cu_2$ : C, 47.60; H, 3.42; N, 11.90. Found: C, 47.2; H, 3.32; N, 11.35%. Electronic spectrum in DMSO solution  $\lambda_{max}/mm$  ( $\varepsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 950(157), 818(159), 740(166), 610(151), 367(1492). Selected IR bands (cm<sup>-1</sup>): 3443br( $\nu_{OH}$ ), 1594( $\nu_{C=N}$ ).

 $[Cu_2(L_6)_2(\mu-Cl)_2] \quad \textbf{(6)}: \text{ Yield: } 321 \text{ mg } (48\%). \ \textit{Anal. Calc. for} \\ C_{28}H_{24}N_6Cl_2O_2Cu_2: C, 49.85; H, 3.59; N, 12.46. Found: C, 49.79; \\ H, 3.51; N, 12.52\%. Electronic spectrum in DMSO solution <math display="inline">\lambda_{max}/mn(\epsilon_{max}/M^{-1} \text{ cm}^{-1}): 709(63), 378(2338), 360(1938)\text{sh}, 290(1242). \\ \text{Selected IR band } (\text{cm}^{-1}): 1590(\nu_{C=N}).$ 

 $[Cu_2(L_7)_2(\mu-Cl)_2]$  (7): Yield: 336 mg (48%). Anal. Calc. for  $C_{28}H_{26}N_8Cl_2O_2Cu_2$ : C, 47.72; H, 3.72; N, 15.90. Found: C, 47.60; H, 3.61; N, 15.99%. Electronic spectrum in DMSO solution  $\lambda_{max}/$  nm  $(\epsilon_{max}/M^{-1}\ cm^{-1})$ : 686(124), 398(2667)sh, 290(1608). Selected IR bands (cm^{-1}): 1610( $\nu_{C=N}).$ 

 $[Cu_2(L_8)_2(\mu-Cl)_2]$  (**8**): Yield: 357 mg (53%). Anal. Calc. for C<sub>26</sub>H<sub>22</sub>N<sub>8</sub> O<sub>2</sub>Cl<sub>2</sub>Cu<sub>2</sub>: C, 46.15; H, 3.28; N, 16.56. Found: C, 46.19; H, 3.35; N, 16.50%. Electronic spectrum in DMSO solution  $\lambda_{max}/$  nm ( $\epsilon_{max}/M^{-1}$  cm<sup>-1</sup>): 732(102), 379(2399), 290(1253). Selected IR band (cm<sup>-1</sup>): 1609( $\nu_{C=N}$ ).

## 2.3. X-ray crystallography

For **1** data were collected on a Bruker smart CCD area diffractometer at 100(2) K, using Mo K $\alpha$  radiation (0.71073 Å). Data were corrected for absorption effects using the numerical method (sADABS). The ratio of minimum to maximum apparent transmission was 0.822. For **5** data were collected from a single crystal at room temperature on an APEX II CCD detector system using a Bruker FR-591 rotating copper radiation source with X-ray mirrors. An entire hemisphere of data was collected in multi-run mode with both phi and omega as the rotation axis. The APEX2 software package (Bruker AXS) was used for collecting data frames, indexing of reflections, and determination of lattice parameters. The data was solved by direct methods and refined by full matrix least squares on  $F^2$  using SHELX-97 [26]. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and refined as riding atoms using isotropic

#### Table 1

Compounds	1	5
Formula	$C_{26}H_{20}CuN_6O_4$	C28H24Cl2Cu2N6O4
Formula weight	544.02	706.51
Crystal size (mm)	$0.15 \times 0.34 \times 0.35$	$0.1 \times 0.06 \times 0.03$
Temperature (K)	100(2)	296(2)
Crystal system	orthorhombic	triclinic
Space group	Aba2	ΡĪ
a (Å)	12.57600(10)	8.3000(4)
b (Å)	17.82970(10)	9.1116(4)
<i>c</i> (Å)	10.76320(10)	10.8269(5)
α (°)	90	71.369(2)
β(°)	90	74.335(2)
γ (°)	90	68.143(2)
$d_{\rm calc} ({ m g}{ m cm}^{-3})$	1.497	1.654
$\mu$ (mm <sup>-1</sup> )	0.951	3.98
F(000)	1116	358
Total reflections	41115	11597
Unique reflections	2564	2394
Observed data $[I > 2\sigma(I)]$	2501	2280
R <sub>int</sub>	0.0340	0.0392
$R_1$ , $wR_2$ (all data)	0.0288, 0.0882	0.0349, 0.0951
Data/restraints/parameters	2564/1/197	2394/0/192
Goodness-of-fit (GOF) on F <sup>2</sup>	0.836	1.062
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.455, -0.584	0.392, -0.560

displacement parameters. A summary of the crystallographic data is presented in Table 1.

## 3. Results and discussion

## 3.1. Synthesis

The Cu(II) complexes reported here were obtained by reaction of  $Cu(ClO_4)_2$ · $GH_2O$  with the appropriate ligand, in presence of Et<sub>3</sub>N in 1:2:2 molar ratio. For the pyridine-2-carbaldehyde Schiff base ligands (L<sub>1</sub>H, L<sub>2</sub>H, L<sub>3</sub>H, L<sub>4</sub>H), mononuclear complexes, containing two tridentate monoanionic ligands were obtained. Surprisingly, under similar conditions, the Schiff bases of 2-acetylpyridine (L<sub>5</sub>H, L<sub>6</sub>H, L<sub>7</sub>H, L<sub>8</sub>H) reduced perchlorate to chloride and we got chloro-bridged binuclear complexes, where each Cu(II) ion is coordinated to only one monoanioinic tridentate ligand. Perchlorates are known to be explosively reduced by organic compounds, though the reaction rate is often sluggish at room temperature [27]. However, in our present work we find that the 2-acetylpyridine aroyl hydrazone ligands smoothly convert perchlorate to chloride even at room temperature, whereas the corresponding Schiff bases of pyridine-2-aldehyde cannot do so. Cyclic voltammetry experiments show (vide infra) that the salicyloyl hydrazone of pyridine-2-aldehyde (L<sub>1</sub>H) and 2-acetylpyridine (L<sub>5</sub>H) undergo oxidations at almost similar potential, in both protonated form as well as deprotonated form (generated *in situ* by addition of tetrabuty) ammonium hydroxide in the electrochemical cell) and thus there is not much difference in their reductive power. In spite of this, the fact that perchlorate is reduced to chloride by 2-acetylpyridine hydrazones but not by pyridine-2-aldehyde hydrazones, probably indicates a favorable kinetic factor for the reduction of perchlorate by 2-acetylpyridine hydrazones in presence of Cu<sup>2+</sup>. Semiemperical ZINDO/1 calculations, performed using a Window based Hyperchem program [28], using default parameters of the program, suggest that for both pyridine-2-aldehyde as well as 2-acetylpyridine hydrazone ligands the bis(hydrazone) octahedral Cu(II) complexes like **1–4** are much less stable than the binuclear complexes of the type 5–8 (see Table S1 in Supplementary material). However, Pal et al. have shown [29,30] that for pyridine-2-aldehyde aroyl hydrazone ligands, both mononuclear bis-(hydrazone) or dichlorobridged binuclear Cu(II) complexes can be obtained, by varying metal: ligand stoichiometry from 1:2 to 1:1. Thus the formation of the bis(hydrazone)Cu(II) complexes seemed to be kinetically governed and it is the major product when metal: ligand stoichiometry is 1:2 or more. So, it was thought, that if  $Cu(ClO_4)_2 \cdot 6H_2O$ is reacted with excess of a 2-acetylpyridine hydrazone ligand, we may get the corresponding bis(hydrazone) complex similar to 1-**4**, as even after a part of the ligand is used up for reduction of perchlorate to chloride, still sufficient ligand will be present in the reaction medium for formation of the bis(hydrazone) complex. In fact, it was found that when Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O was reacted with  $L_5H$  and  $Et_3N$  in 1:3:3 molar ratio we get the complex  $[Cu(L_5)_2]$ ; the same product was also obtained by reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O or CuBr<sub>2</sub>·2H<sub>2</sub>O with L<sub>5</sub>H and Et<sub>3</sub>N in 1:2:2 molar ratio. Unfortunately, we could not get single crystals of any bis-(hydrazone) complex of 2-acetylpyridine hydrazone ligands, so we have reported characterization data of only the  $[Cu(L_5)_2]$  complex in the supplementary material. Dang et al. were able to get single crystals of the same compound by diffusion of solution of L<sub>5</sub>H (0.1 mmol) and Et<sub>3</sub>N (0.1 mmol) in methanol to a solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1 mmol)in DMF [31]; however, except for X-ray single crystal structure no other characterization data was reported for the compound. Koo et al. isolated the complex  $[Cu(L_6)_2]$  by reaction of  $Cu(OAc)_2$ . ·H<sub>2</sub>O with L<sub>6</sub>H in 1:2 molar ratio, but they also could not obtain single crystals of the complex [32]. Sastry and Rao reported reaction



Fig. 1. ORTEP diagram for 1. H-atoms are omitted for clarity (Atoms with label 'A' refers to symmetry code i).

of CuCl<sub>2</sub>·2H<sub>2</sub>O with L<sub>8</sub>H in presence of KOH in 1:1:1 molar ratio, but they probably wrongly formulated the compound as  $[Cu(L_8-$ H)Cl<sub>2</sub>(H<sub>2</sub>O)] [33]. Synthesis and X-ray crystal structures of complexes 2 and 4 have been published by two groups in each case, using  $Cu(OAc)_2 \cdot H_2O$  or  $Cu(ClO_4)_2 \cdot GH_2O$  as starting materials [29,34,9,17]. However the detailed electrochemical study over both positive and negative sides of the reference electrode were lacking in these reports. Nardelli and co-workers reported crystal structure of  $[Cu(L_1)(L_1H)]ClO_4$ ·EtOH, prepared by reaction of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with L<sub>1</sub>H in 1:2 molar ratio, without addition of any base [35]. Similarly, the synthesis and X-ray crystal structure of **6**, obtained by reacting CuCl<sub>2</sub>·2H<sub>2</sub>O and L<sub>6</sub>H in 1:1 molar proportion was reported [25], however, the electrochemical data reported in the paper needs reexamination, as it appears, from the cyclic voltammogram given in the paper, that it has been obtained starting from a negative potential of -1.0 V, where the reduced complex may undergo appreciable decomposition and these secondary products may be responsible for some of the electrochemical responses reported therein.

## 3.2. Description of X-ray crystal structure

The ORTEP diagram along with atom numbering scheme for **1** is given in Fig. 1, while important bond distances and angles for **1** as well as **5** are collected in Table 2. In the structure of **1**, Cu(II) is in a distorted octahedral coordination environment, being coordinated by two monoanioinic tridentate ligands through pyridine nitrogen, azomethine nitrogen and enolate oxygen. The two ligands are equivalent and related by a C<sub>2</sub> axis passing through the copper center. The metal–ligand bond distances follow the order Cu–N(azomethine) < Cu–O  $\approx$  Cu–N(py), which is similar to that observed for the Ni(II) complex of the same ligand, which follow the order Ni–N(azomethine) < Ni–O < Ni–N(py) [36]. The ligands are planar, with the dihedral angle between two five membered chelate rings formed by the same ligand being 2.99°, while the dihedral angles between the chelate rings formed by two different ligands vary between 83.51° and 86.06°.The N(2)–N(3) (1.367(2) Å), C(7)–N(3)

Table 2								
Selected bond distances	(Å)	and	bond	angles	(°)	for 1	and	5.

1		5	
Cu1-N2	1.9889(15)	Cu1-N2	1.9352 (19)
Cu1-N1	2.1054(16)	Cu1-N1	2.0102 (19)
Cu1-02	2.1017(16)	Cu1-01	1.9722 (17)
		Cu1-Cl1	2.2505 (6)
		N3-C8	1.337 (3)
N2-C6	1.285(3)	N2-C6	1.290 (3)
N3-C7	1.345(2)		
02-C7	1.277(2)	01-C8	1.277 (3)
01-C9	1.351(2)	O2-C10	1.343(4)
N2-N3	1.367(2)	N2-N3	1.367 (3)
N2 <sup>i</sup> -Cu1-N2	173.48(10)	N2-Cu1-O1	79.45 (7)
N2-Cu1-O2	76.69(6)	N2-Cu1-N1	80.22 (8)
N2-Cu1-O2 <sup>i</sup>	98.65(6)	01-Cu1-N1	159.51 (8)
02-Cu1-N1 <sup>i</sup>	96.90(6)	N2-Cu1-Cl1	164.01 (6)
N2 <sup>i</sup> -Cu1-N1	106.59(6)	01-Cu1-Cl1	99.25 (5)
02-Cu1-N1	154.67(6)	N1-Cu1-Cl1	99.59 (6)
N1 <sup>i</sup> -Cu1-N1	86.27(9)	N2-Cu1-Cl1 <sup>ii</sup>	103.61 (6)
02-Cu1-02 <sup>i</sup>	90.90(9)	01-Cu1-Cl1 <sup>ii</sup>	95.48 (5)
N2-Cu1-N1	78.32(6)	N1-Cu1-Cl1 <sup>ii</sup>	91.71 (5)
		Cl1-Cu1-Cl1 <sup>ii</sup>	92.38 (2)
		Cu1-Cl1-Cu1 <sup>ii</sup>	87.62 (2)

Symmetry code: i = -x + 2, -y + 1, z; ii = -x + 1, -y, -z + 1.

(1.345(2) Å) and C(7)-O(2) (1.277(2) Å) distances bear testimony to the delocalization over the deprotonated hydrazone backbone, which leads to the planarity of the ligand. The Cu(II) center may be considered to be in an axially compressed (along N(2)-Cu(1)-N(2A)) Jahn-Teller distorted octahedral geometry. There is intramolecular hydrogen bonding between the salicyloyl –OH moiety and the N(3) atom (O(1)-H(14)···N(3)) of a given ligand.

A comparison of the structural parameters of the complex **1** with those of **2**, **4** and  $[Cu(L_1)(L_1H)]ClO_4$  EtOH, as well as with that of  $[Cu(L_5)_2]$ , reported earlier, is given in Table 3. It is interesting to note that while in the structure of **1** both the ligands are equivalent and related by a  $C_2$  axis passing through the copper center, similar to that found in  $[Cu(L_5)_2]$ , in the structures of **2** and **4** the two

Table 3	
Comparisons of the structural parameters of <b>1</b> with those of related compounds.	

	1	<b>2</b> [29,34]	<b>4</b> [9,17]	Cu(L <sub>5</sub> ) <sub>2</sub> [31]	[Cu(L <sub>1</sub> )(HL <sub>1</sub> )] ClO <sub>4</sub> [35]
Cu–N <sub>Py</sub> (Å)	2.1054(16)	2.130(3); 2.286(3) average = 2.208(3)	2.180(6); 2.234(7) average = 2.207(7)	2.156(3)	2.277(4); 2.081(3) average = 2.179(4)
Cu-N <sub>imine</sub> (Å)	1.9889(15)	1.940(3); 1.972(3) average = 1.956(3)	1.949(6); 1.956(6) average = 1.952(6)	1.966(3)	2.043(4); 1.930(4) average = 1.986(4)
Cu–O (Å)	2.1017(16)	2.099(2); 2.294(3) average = 2.196(3)	2.124(5); 2.173(5) average = 2.148(5)	2.158(3)	2.334(4); 2.062(3) average = 2.198(3)
$N_{Py}$ -Cu-O (°)	154.67(6)	155.01(10); 150.11(9) average = 152.56(10)	153.36(12); 148.58(11)	152.95(10)	
$N_{imine}$ -Cu- $N_{imine}$ (°)	173.48(10)	172.20(11)	176.6(2)	172.1(2)	



Fig. 2. ORTEP diagram for 5 (Atoms with label 'a' refers to symmetry code ii).

ligands were inequivalent and the Cu(II) were in an axially elongated octahedral geometry, with the longest Cu–N(py) and Cu–O distances being 2.286(3) and 2.294(3) Å, respectively for **2**, while for **4** the corresponding values are 2.234(7) and 2.173(5) Å, respectively. However, the average Cu–N(imine) distance at 1.956(3) Å for **2** and 1.952(6) Å for **4** are slightly shorter than that observed for complex **1** (1.9889(15) Å).

The molecular structure and atom numbering scheme for the complex **5** is shown in Fig. 2. It turned out to be a binuclear Cu(II) complex, with two chloride ions bridging the Cu(II) centers in an axial–equatorial manner. Each Cu(II) is in a square pyramidal environment ( $\tau = 0.08$ ) [37], coordinated by pyridine nitrogen (N(1)), imine nitrogen (N(2)) and enolate oxygen (O(1) of a deprotonated tridentate mono-anionic hydrazone ligand, along with a chloride ion (Cl(1)), forming the equatorial plane, whereas another chloride (Cl(1a)) related by symmetry element 1 - x, -y, 1 - z (symmetry element ii), is coordinated axially. The two halves of the binuclear

unit are related by a center of inversion passing through the middle of  $[Cu_2(\mu-Cl)_2]$  rectangle. Expectedly the equatorial Cu–Cl distance at 2.2505(6) Å is much shorter than the corresponding axial Cu–Cl bond length at 2.6686(6) Å. The metal ligand distances involving the tridentate hydrazone ligand follow the same trend as observed for the mononuclear complex **1**. However, each of the individual bond distance in the binuclear complex is much shorter than the corresponding bond distance in the mononuclear complex, probably due to lower coordination number of Cu(II) in the former. There are weak Cu···N(3)<sup>iii</sup> complementary interactions (symmetry element iii = 2 - x, -y, 1 - z, Cu···N(3)<sup>iii</sup> distance being 3.626(2) Å), which leads to an infinite one dimensional chain along the [100] base vector. Like the mononuclear complex **1**, in **5** also there are intramolecular hydrogen bonding between the salicyloyl –OH moiety and the N(3) atom (O(2)–H(2a)···N(3)).

A comparison of the structural parameters of **5** with those of similar binuclear Cu(II) complexes are given in Table 4. Among

Table 4	
Comparisons of structural	parameters of 5 with those of related compounds.

	5	<b>6</b> [25]	$Cu_2(\mu-Cl)_2(L_2)_2$ [30]	$[Cu(\mu_{1,3}-NCS)(L_1)_2]_n$ [38]	$Cu_2(\mu_{1,1}\text{-}OAc)_2(L_2)_2$ [30]	$Cu_2(\mu_{1,1}-N_3)_2(L_2)_2$ [34]
$\begin{array}{c} Cu-N_{Py}\left(\mathring{A}\right)\\ Cu-N_{imine}\left(\mathring{A}\right)\\ Cu-O\left(\mathring{A}\right)\\ Cu-X_{eq}\left(\mathring{A}\right)\\ Cu-X_{ax}\left(\mathring{A}\right)\\ Cu-X-Cu\\ X_{xy}-Cu+X_{yy}\\ Cu-X-Cu\\ X_{xy}-Cu+X_{yy}\\ \end{array}$	1.9722(17) 1.9352(19) 2.0102(19) 2.2505(6) (X = Cl) 2.6686(6) (X = Cl) 87.62(2) 92.38(2)	2.013(2) 1.928(2) 1.964(2) 2.2603(7) (X = Cl) 2.6434(7) (X = Cl) 86.80(2) (X = Cl) 93.20(2) (X = Cl)	2.028(2) 1.9299(19) 1.9853(17) 2.2440(9) (X = Cl) 2.6682(10) (X = Cl) 86.89(3) (X = Cl) 93.11(3)	2.038(3) 1.925(4) 1.990(3) 1.930(5) (Cu-N <sub>eq</sub> , X = NCS) 2.709(2) (Cu-S <sub>ax</sub> , X = NCS)	2.033(6) 1.924(6) 1.989(5) 1.935(5) 2.286(6) (X = OAc) 101.4(2) (X = $\mu_{1,1}$ -OAc) 78.6(2) (X = $\mu_{2,1}$ -OAc)	2.007(6); 2.022(6) 1.929(6); 1.935(6) 1.978(4); 1.965(4) 2.460(5); 1.970(6) 2.460(5); 2.386(5) 92.2(2), 94.8(2) 85.6(2) 87.4(2)



Fig. 3. Electronic spectra of the mononuclear complexes. The d-d bands are shown in the inset. Color codes are same for both the graphs.



Fig. 4. Electronic spectra of the binuclear complexes. The d-d bands are shown in the inset. The color codes are same in both the graphs.

the complexes whose structural data are given Table 4, all have center of inversion at the middle of  $[Cu_2(\mu-X)_2]$  rectangle, except  $Cu_2(\mu_{1,1}-N_3)_2(L_2)_2$ , where the bridge is asymmetric [35]. It is seen

from Table 4 that in **5** the Cu–N<sub>py</sub> distance is shortest while the Cu–O and Cu–N<sub>imine</sub> distances are slightly longer compared to the other structures. The equatorial Cu-X distance is expectedly

Table 5	
Electrochemical data for the Cu (II) complex	es.

Compounds	$E^{1/2}_{OX}/V$	$E^{1/2}_{red}/V (\Delta E/mV)$
-	$(\Delta E/mV)$	
1	0.93 <sup>a,b</sup>	-0.98 <sup>a,b</sup>
		$-0.75^{c,d}$ , $-1.58^{c,d}$ , $-1.8^{c,d}$
2	1.20 <sup>a,b</sup>	$-0.64(385)^{d}$ , $-1.37^{a,d}$ , $-1.84(120)^{d}$ $-0.85^{b,c}$ ,
		-1.20 <sup>b,c</sup> , -1.70 <sup>b,c</sup>
3	1.16 <sup>a,b</sup>	$-0.85^{a,b}$ , $-1.29^{a,b}$
		$-0.30(350)^{d}$ , $-0.90^{a,d}$ , $-1.56^{a,d}$
		$-0.20^{a,c}$ , $-0.75^{a,c}$ , $-1.55^{a,c}$ , $-1.80^{a,c}$
4	1.25 <sup>a,b</sup>	$-0.54(179)^{d}$ , $-0.80^{a,d}$ , $-1.75(100)^{d}$
		$-0.50^{c,d}$ , $-0.75^{c,d}$ , $-1.7^{c,d}$ , $-1.95^{c,d}$
5	1.06 <sup>b,c</sup>	$-0.57(250)^{b}$
		$-0.30^{b,c}$ , $-0.55^{b,c}$
6	1.04 <sup>a,b</sup>	$-0.22(270)^{\text{b}}$ , $-0.88(E_{\text{p.c}})^{\text{b}}$ , $-0.78(E_{\text{p.a}})^{\text{b}}$ , $-0.48$
		$(E_{\rm p.a})^{\rm b}$
		$-0.30^{a,c}$ , $-0.80^{a,c}$
7	1.08 <sup>a,b</sup>	$-0.22 (220)^{b}, -0.56^{a,b}, -0.86^{a,b}$
		$-0.30^{b,c}$ , $-0.77^{b,c}$
8	1.03 <sup>a,b</sup>	$-0.12 (150)^{\rm b}, -0.55(100)^{\rm b}$
		$-0.10^{a,c}$ , $-0.30^{a,c}$ , $-0.50^{a,c}$ , $-0.80^{a,c}$

<sup>a</sup> Irreversible response.

<sup>b</sup> Pt-electrode.

<sup>c</sup> Response obtained from DPV.

<sup>d</sup> Glassy carbon working electrode.



Fig. 5. Cyclic voltammogram of  ${\bf 2}$  at scan rate of 100 mV/s at a glassy carbon electrode.

larger for X = Cl, compared to X = NCS, OAc or N<sub>3</sub>, whereas the axial Cu–X distance follow the order Cu–SCN > Cu–Cl > Cu–N (azide) > - Cu–OAc.

# 3.3. Infrared spectra

In the infrared spectra the disappearance of characteristic v(N-H) band of free hydrazone ligand at 3190–3280 cm<sup>-1</sup> region, along with bathochromic shift of the amide-I band from 1630–1660 cm<sup>-1</sup> in the ligands to 1590–1610 cm<sup>-1</sup> in the complexes suggest coordination via enol form, by deprotonation of the N-H proton, during the complexation process. The amide-II vibration at 1550–1570 cm<sup>-1</sup> of the free ligands shifts to 1480–1500 cm<sup>-1</sup> in the complexes. The azomethine ( $v_{C=N}$ ) band is often buried under the amide-II band in the ligands and amide-I band in the complexes. The phenolic OH group of the free ligands (L<sub>1</sub>H and L<sub>5</sub>H) appears as a broad band around 3470 cm<sup>-1</sup> region, which in the corresponding complexes is observed at around 3440 cm<sup>-1</sup>.



Fig. 6. Cyclic voltammogram of  ${\bf 4}$  at scan rate of 100 mV/s at a glassy carbon electrode.



**Fig. 7.** Cyclic voltammogram of **8** at scan rate of 100 mV/s at a Pt-electrode. The inset shows the second reductive couple only.

## 3.4. Electronic spectra

The mononuclear complexes **2** and **4** and the binuclear complexes **6** and **7** show one weak, broad band at 680–750 nm (Figs. 3 and 4). The binuclear complex **5** shows number of weak shoulders/ broad bands at 600–950 nm region, while the complex **8** shows two overlapping broad and weak transitions at 677 and 732 nm. These bands are typical of d–d band of Jahn–Teller distorted Cu(II) complexes in distorted octahedral or square pyramidal geometry. One or two strong bands at 380–440 nm for the mononuclear complexes and 370–400 nm for the binuclear complexes are assigned to ligand to metal charge transfer transitions. Bands at higher energy are due to intraligand transitions. Our spectral data is consistent with those reported by earlier workers [17,29,30,32].

# 3.5. Electrochemical studies

The electrochemical data for the eight complexes are summarized in Table 5. The free ligands in their deprotonated form were found to show an irreversible oxidation at 0.8 V and a quasi-reversible reductive response at -0.8 V (Supplementary Figs. S1 and S2). The mononuclear complexes show a ligand based irreversible oxidation at 0.9-1.2 V, for the binuclear complexes a similar irreversible oxidative response at 1.03-1.08 V region were observed. On the negative side of Ag/AgCl electrode, the mononuclear complexes show a quasi-reversible/irreversible response at -0.5 to -0.9 V, which sometimes (e.g. for 3 and 4) resolves into two overlapping peaks (Figs. 5 and 6 and Supplementary Figs. S3-S5). We tentatively assign the response at -0.5 to -0.9 V to overlapping Cu<sup>2+</sup>/ Cu<sup>+</sup> and a ligand based reduction processes [30,36,39,40]. Two more reductive waves at -1.3 to -1.5 V and -1.8 to -2.0 V (Figs. 5 and 6 and Supplementary Figs. S3-S5) are assigned to ligand based reductions [15]. For the binuclear complexes, there are often two irreversible/quasi-reversible reductions at -0.2 to -0.4 V and -0.5 to -0.8 V (Fig. 7 and Supplementary Figs. S7-S11). The first reduction is assigned to Cu<sup>2+</sup>/Cu<sup>+</sup> couple [30,41], while the reductive response at more negative potential is due to combined ligand centered and a second metal centered reductions.

# 4. Conclusions

The tridentate aroyl hydrazone ligands reported here, obtained by condensation of pyridine-2-carbaldehyde and 2-acetyl pyridine with four aroyl hydrazides, were found to form mononuclear octahedral or dichloro bridged binuclear Cu(II) complexes with square pyramidal geometry. It is found that aroyl hydrazones of pyridine-2-aldehyde and 2-acetyl pyridine have very similar reducing power and it is probably the kinetic factor that is responsible for only the later being able to reduce perchlorate to chloride at ambient conditions. Presence of excess ligand in the reaction medium always leads to bis-(hydrazone)Cu(II) complex, in spite of the fact that the mononuclear octahedral complexes are thermodynamically much less stable than the binuclear complexes. Thus the formation of binuclear complexes with 2-acetylpyridine aroyl hydrazone ligands on reaction with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in 2:1 M ratio is due to ligand deficiency in the reaction medium, caused by partial oxidative degradation of the ligands by perchlorate.

# Acknowledgments

Satayajit Mondal thanks CSIR for a NET JRF. S.K.C. acknowledges AICTE for funding the purchase of CH1120A potentiostat. Infrastructural facility created in our department through DST-FIST, UGC-SAP and MHRD special grants are also thankfully acknowledged. Steven R. Herron gratefully acknowledges the use of the X-ray facility at Brigham Young University for determining the Xray crystal structure of **5**.

## Appendix A. Supplementary material

CCDC 870577 and 870578 contain the supplementary crystallographic data for compounds **5** and **1**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.12.018.

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