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# Copper(II) complexes of symmetrical and unsymmetrical tetradentate Schiff base ligands incorporating 1-benzoylacetone: Synthesis, crystal structures and electrochemical behavior

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## Abstract

Three new copper(II) complexes $[CuL^1]_2(ClO_4)_2$ (**1**), $[CuL^2]ClO_4$ (**2**) and $[CuL^3]$ (**3**) with three Schiff base ligands [$HL^1$ = 1-phenyl-3-{3-[(pyridin-2-ylmethylene)-amino]-propylimino}-butan-1-one, $HL^2$ = 1-phenyl-3-[3-(1-pyridin-2-yl-ethylideneamino)-propylimino]-butan-1-one and $H_2L^3$ = 3-[3-(1-methyl-3-oxo-3-phenyl-propylideneamino)-propylimino]-1-phenyl-butan-1-one] have been synthesized and structurally characterized by X-ray crystallography. The mono-negative tetradentate asymmetric Schiff base ligands $(L^1)^-$ and $(L^2)^-$ are chelated in complexes **1** and **2** to form square planar copper(II) complexes. In complex **1**, the two units are associated weakly through ketonic oxygen of benzoylacetone fragment to form the dimeric entity. The square planar geometry of complex **3** is unusually distorted towards tetrahedral one. All three complexes exhibit reversible cyclic voltammetric responses in acetonitrile solution corresponding to the $Cu^{II}/Cu^{I}$ redox process. The $E_{1/2}$ (−0.47 V versus SCE) of **3** shows significant anodic shift due to the tetrahedral distortion around Cu(II) compare to that of **1** and **2** (−0.82 and −0.87 V versus SCE, respectively).

*Keywords:* Copper(II); Unsymmetrical Schiff base; 1-Benzoylacetone; Crystal structure; Electrochemical behavior

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## 1. Introduction

The interest in the design, synthesis and characterization of the transition metal complexes of unsymmetrical Schiff base ligands has come from the realization that coordinated ligands around central metal ions in natural systems are unsymmetrical [1]. Recently, this class of compounds has also attracted much attention in the field of optoelectronic technologies for their large nonlinear responses [2]. Compare to their symmetrical counterpart, syntheses of such ligands are rather difficult because simple condensation methodology with three components is no longer applied. However, since the first reports on the synthesis of 7-amino-4-methyl-5-azahept-3-en-2-one (AMAH) [3] and 8-amino-4-methyl-5-azaoct-3-en-2-one (AMAO) [4], the monocondensation products of 2,4-pentanedione with 1,2-ethanediamine and or 1,3-propanediamine, respectively, these 'half units' have been used extensively as precursors for the preparation of unsymmetrical quadridentate Schiff base ligands [2,5]. In most of the ligands reported so far, the acetylacetoneiminato side is usually kept unchanged and the other side of the diamine is condensed with various aromatic carbonyl compounds to study the variation and fine tuning of stability, reactivity and electronic properties of such complexes [5,6]. The apparent reason for keeping the acetylacetoneiminato fixed, seems to be the facile synthesis of the 'half unit' by high dilution method [3,4]. Recently, we successfully synthesized the analogous tridentate Schiff base by monocondensation of 1-benzoylacetone

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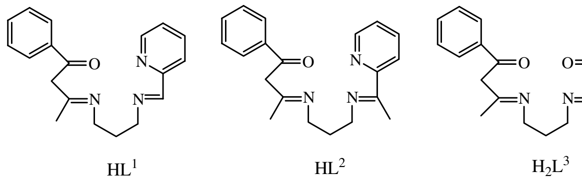

Scheme 1.

with 1,2-ethanediamine or 1,2-propanediamine under the similar conditions and used those ligands to synthesize trinuclear Cu(II) complexes with a $\mu_3$-OH core [7]. On the contrary, the corresponding 'half unit' of 1,3-propanediamine did not result the similar trinuclear complex, instead underwent hydrolysis during complex formation indicating its lower stability [7]. This encourages us to synthesize tetradentate Schiff base using the precursor 7-amino-3-methyl-1-phenyl-4-azahept-1,3-dien-1-ol (HAMPA, the monocondensation product of 1,3-diaminopropane and 1-benzoylacetone) and to explore if the double condensed ligands are stable enough to result in the formation of complexes with copper(II).

In this paper, we report synthesis, spectral characterization, crystal structures and electrochemical behavior of three Cu(II) complexes. Two of them are derived from the unsymmetrical tetradentate Schiff bases HL$^1$ and HL$^2$ formed by the condensation of free amine group of HAMPA with pyridine-2-carboxaldehyde and 2-acetylpyridine, respectively, and the other one from symmetrical Schiff base H$_2$L$^3$ containing 1-benzoylacetone at the both ends of 1,3-diaminopropane (Scheme 1). The significant structural differences of these complexes from their acetylacetone analogs are also discussed here.

## 2. Experimental

All chemicals were of reagent grade and used without further purification.

### 2.1. Synthesis of the precursor tridentate ligand, HAMPA

The precursor mono-condensed Schiff base, HAMPA was synthesized by high dilution technique [7,8]. 1-Benzoylacetone (10 mmol, 1.6 g) in chloroform (50 cm$^3$) was added drop wise to a solution of 1,3-propanediamine (10 mmol, 0.76 cm$^3$) in chloroform (50 cm$^3$). After completion of the addition, the solution was stirred for an additional 3 h and then chloroform was evaporated under reduced pressure, yielding HAMPA as a viscous liquid.

### 2.2. Synthesis of the ligands, 1-phenyl-3-{3-[(pyridin-2-ylmethylene)-amino]-propylimino}-butan-1-one (HL$^1$) and 1-phenyl-3-[3-(1-pyridin-2-yl-ethylideneamino)-propylimino]-butan-1-one ( HL$^2$)

To synthesize HL$^1$, a methanolic solution (15 cm$^3$) of pyridine-2-carboxaldehyde (10 mmol, 0.95 cm$^3$) was added to a methanolic solution (25 cm$^3$) of HAMPA (10 mmol). The mixture was warmed at 50 °C for 1 h and cooled to room temperature. HL$^2$ was prepared in the same way as HL$^1$ using 2-acetyl pyridine (10 mmol, 1.12 cm$^3$) instead of pyridine-2-carboxaldehyde. The tetradentate ligands HL$^1$ and HL$^2$ were not isolated and the methanol solutions were used for the synthesis of the complexes.

### 2.3. Synthesis of complex [CuL$^1$ClO$_4$]$_2$ (**1**), [CuL$^2$ClO$_4$] (**2**)

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (10 mmol, 3.7 g) in methanol (20 cm$^3$) was added to the resulting methanol solution of each tetradentate ligands HL$^1$ and HL$^2$ with continuous stirring. Brown colored solid of complex **1** separated immediately. The dark brown single crystal of **1**, suitable for X- ray diffraction was obtained on dissolving it in acetonitrile. In case of complex **2**, separation of brown mass took place on keeping the mixture overnight in a refrigerator. The reddish-brown single crystal for suitable for X- ray diffraction was obtained on dissolving the mass in a mixture of acetonitrile and methanol (1:2).

Complex **1**: Yield: 1.9 g (57%). *Anal.* Calc. for $C_{38}H_{40}Cl_2Cu_2N_6O_{10}$: C, 48.62; H, 4.29; N, 8.95; Cu, 13.54. Found: C, 48.74; H, 4.12; N, 8.87; Cu, 13.46%. $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) (acetonitrile), 631 (144); IR: $\nu$(C=N), 1525, 1572 cm$^{-1}$, $\nu$($ClO_4^-$), 1086 cm$^{-1}$.

Complex **2**: Yield: 2.0 g (55%). *Anal.* Calc. for $C_{20}H_{22}ClCuN_3O_5$: C, 49.69; H, 4.59; N, 8.69; Cu, 13.15. Found: C, 49.86; H, 4.61; N, 8.53; Cu, 13.19%. $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) (methanol), 607 (152); IR: $\nu$(C=N), 1522 and 1557 cm$^{-1}$, $\nu$($ClO_4^-$), 1091 cm$^{-1}$.

### 2.4. Synthesis of complex [CuL$^3$] (**3**)

The symmetrical Schiff base in complex **3** was formed by the condensation of 1-benzoylacetone at both end of 1,3-propanediamine. To synthesize H$_2$L$^3$, a methanolic solution (15 cm$^3$) of 1-benzoylacetone (10 mmol, 1.6 g) was added to a methanolic solution (20 cm$^3$) of HAMPA (10 mmol). The mixture was warmed at 50 °C for 1 h and cooled to room temperature. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (10 mmol, 3.7 g) in methanol (20 cm$^3$) was added to the resulting solution of the tetradentate ligand with continuous stirring. The resulting solution was left overnight when greenish blue crystalline compound suitable for X-ray analysis were separated out.

Complex **3**: Yield: 1.7 g (45%). *Anal.* Calc. for $C_{12}H_{15}CuN_3O_3$: C, 65.15; H, 5.71; N, 6.61; Cu, 14.99. Found: C, 65.32; H, 5.66; N, 6.57; Cu, 14.87%. $\lambda_{max}$/nm ($\varepsilon_{max}$/dm$^3$ mol$^{-1}$ cm$^{-1}$) (methanol), 568(159); IR: $\nu$(C=N), 1520 cm$^{-1}$.

### 2.5. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer and the copper contents in all the complexes were estimated spectrophotometrically. The IR spectra in KBr (4500–500 $cm^{-1}$) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. The electronic spectra in methanol (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. Cyclic voltammetry was carried out using Sycopel model AEW2 1820F/S instrument. The measurements were performed at 300 K in acetonitrile solutions containing 0.2 M TEAP and $10^{-3}$ M Cu(II) complex deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were a platinum wire, a platinum coil, and an SCE.

### 2.6. Crystallographic studies

The data for complex **1** were collected at room temperature with Mo Kα radiation on Bruker AXS Smart single crystal diffractometer with CCD (area detector).The absorption correction was performed with the method inserted in SHELXTL-NT V5.1 [9]. The structure was solved by direct methods with the software SHELXTL-NT V5.1 inserted in the Bruker AXS software [9].

The data for complexes **2** and **3** were collected at room temperature with Cu Kα radiation on Siemens AED single crystal diffractometer with a local program [10]. The preliminary cell parameters were obtained from least squares of the ($\theta$, $\chi$, $\phi$) angular values of 3897 and 1948 reflections ($\theta$ range = 4–70° and 5.5–70°) respectively for complexes **2** and **3**, accurately well centered on the diffractometer. The intensity of one standard reflection, recorded for every 100 reflections, showed no significant changes. The recorded data were corrected for polarization and Lorentz effects. The absorption correction was performed with the method of Walker and Stuart [11] with a program written by Gluzinski [12].

The crystal structures of the three complexes were solved by direct methods using SHELXS-97 [13] program and refined by using SHELXL-97 [13]. The nonhydrogen atoms were refined anisotropically while the hydrogen atoms were located from difference Fourier map. The positional and thermal parameters were kept fixed during refinement. Neutral atom scattering factors were taken from Cromer and Weber [14] and anomalous dispersion effects were included in $F_{calc}$ [15]. In complex **2** there are disordered carbon atoms in the diamine fragments. The site occupation factors of the disordered pairs of atoms (C3A and C3B; C4A and C4B) were constrained to be unity and were tied to FVAR. The crystallographic illustrations were prepared using ORTEP-3 [16]. Significant crystallographic data are summarized in Table 1.

## 3. Results and discussion

### 3.1. IR and electronic spectra

All these compounds contain no significant peak in the region of 3100–3250 $cm^{-1}$, which clearly indicates that there is no free $–NH_2$ group i.e. all are the quadridentate ligands that form the complexes. The bands corresponding to azomethylene group (C=N) are distinct in all three complexes and appear within 1572–1520 $cm^{-1}$. The sharp, strong, single peak at 1086 and 1091 $cm^{-1}$ for complexes **1** and **2** clearly indicates the presence of anionic perchlorate group. As expected, complex **3** does not show any such peak.

The electronic spectral data in acetonitrile solution suggest basically square planar geometry for **1** and **2**. In general square-planar complexes are known to exhibit one or two bands [17]. Complexes **1** and **2** show a broad band at 631 and 607 nm, respectively, as was also observed for

Table 1
Crystal data and structure refinement of complexes **1**–**3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{38}H_{40}Cl_2Cu_2N_6O_{10}$ | $C_{20}H_{22}ClCuN_3O_5$ | $C_{46}H_{48}Cu_2N_4O_4$ |
| $M$ | 938.76 | 483.41 | 847.96 |
| Crystal System | triclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $P21/c$ | $Cc$ |
| $a$ (Å) | 7.627(3) | 7.525(2) | 12.188(2) |
| $b$ (Å) | 11.847(3) | 12.372(3) | 20.503(2) |
| $c$ (Å) | 12.263(3) | 21.807(2) | 9.154(2) |
| $\alpha$ (°) | 67.11(2) | 90 | 90.00 |
| $\beta$ (°) | 75.75(2) | 96.070(2) | 116.97(3) |
| $\gamma$ (°) | 85.14(2) | 90 | 90.00 |
| $V$ ($Å^3$) | 989.3(5) | 2018.8(7) | 2038.7(6) |
| Z | 1 | 4 | 4 |
| $D_{calc}$ ($g\ cm^{-3}$) | 1.576 | 1.590 | 1.381 |
| $\mu$ ($mm^{-1}$) | 1.276 [Mo Kα] | 3.083 [Cu Kα] | 1.669 [Cu Kα] |
| $R_{int}$ | 0.026 | 0.019 | 0.218 |
| Number of unique data | 4561 | 3806 | 1948 |
| Number of data with $I > 2\sigma(I)$ | 3412 | 3231 | 1842 |
| $R_1$, $wR_2$ | 0.0562, 0.1872 | 0.0463, 0.1475 | 0.0512, 0.1750 |
| Goodness-of-fit on $F^2$ | 0.930 | 1.000 | 1.155 |

the complexes of similar asymmetric ligands [5,18,19]. The appearance of similar d-d transition in both **1** and **2** confirms the semi-coordinated character of the ketonic oxygen of the ligand in **1**, which does not significantly affect the square planar geometry around the Cu(II) ions of the complex. At the higher energy region, the ligand to metal charge transfer bands were located for both the complexes (319 and 281 nm for complex **1** and 345 and 284 nm for complex **2**). Complex **3** also shows a broad band centering at 568 nm for the d-d transition and 341 and 301 nm for ligand to metal charge transfer transitions.

### *3.2. Description of structures of complexes **1**, **2** and **3***

#### *3.2.1. Complexes **1** and **2***

The structures of the complexes **1** and **2** are shown in Figs. 1 and 2, respectively, with common atom numbering scheme. For both compounds, the structures consist of $[CuL]^+$ cation together with perchlorate anion. In complex **1**, two symmetry related $(1-x, -y, 1-z)$ cations are joined together through very weak interaction from the oxygen atom of the benzoylacetone moiety to the axial position of copper atom at a distance of 2.767(3) (Fig. 3). Although the distance is very long but is less than the sum of the van der Waals radii for copper(II) and oxygen (2.92 Å) [20]. Therefore, a weak bond is considered to be formed between the two. Comparable distances have been regarded as bond in several other reported systems [21]. In **2**, the complex cations are discrete; the closest copper–oxygen distance between the two neighboring units is 3.029 Å. In both complexes, the deprotonated ligands $L^1$ and $L^2$ are quadridentate forming two adjacent six-membered and one five-membered chelate rings (6-6-5). The copper(II) ions have square-planar co-ordination with a slight tetrahedral distortion in both the complexes. Deviations of donor atoms O(1), N(1), N(2) and N(3) from the mean plane passing through them are −0.057(2), 0.054(4), −0.059(3) and 0.062(3) Å, respectively, for **1** and −0.047(2), 0.043(3), −0.047(3) and 0.051(2) Å, respectively, for **2**. The central Cu(II) atom deviates negligibly (0.0037(3) Å) in complex **1** and slightly more (0.0274(4) Å) in complex **2** from the same plane. The tetrahedral distortion is apparent since one pair of diagonal donor atoms clearly lies below the plane while the other pair is above the plane with the metal ion in the mean plane. The dihedral angles between the two planes [N(1)–Cu–O(1) and N(2)–Cu–N(3)] is 6.09° for complex **1** and 4.82° for complex **2**

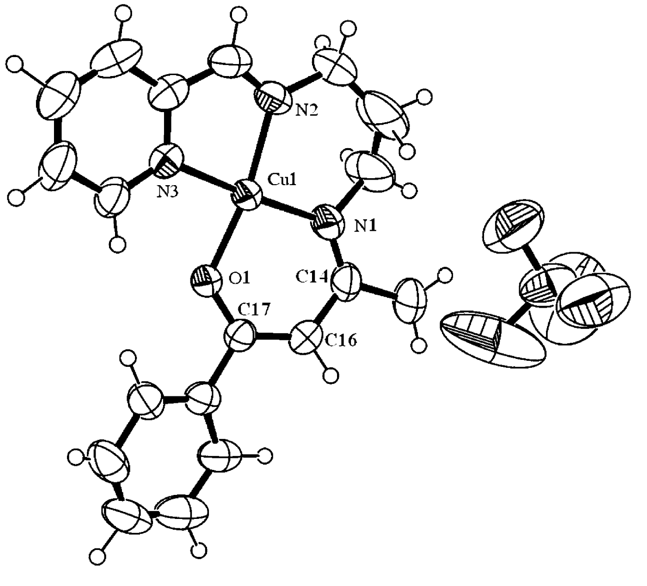

Fig. 1. ORTEP plot of **1** with atom-numbering scheme; ellipsoids at 50% probability.

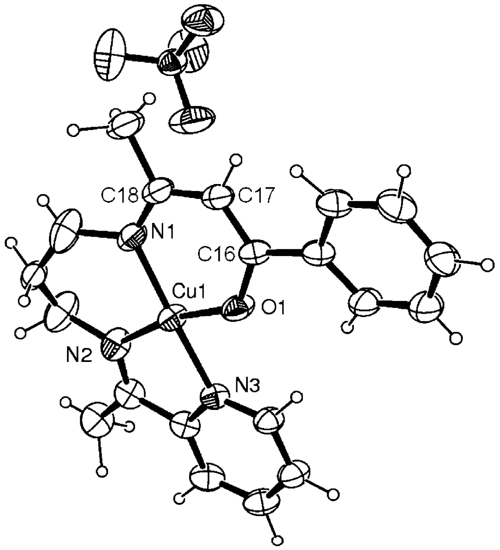

Fig. 2. ORTEP plot of **2** with atom-numbering scheme; ellipsoids at 50% probability.

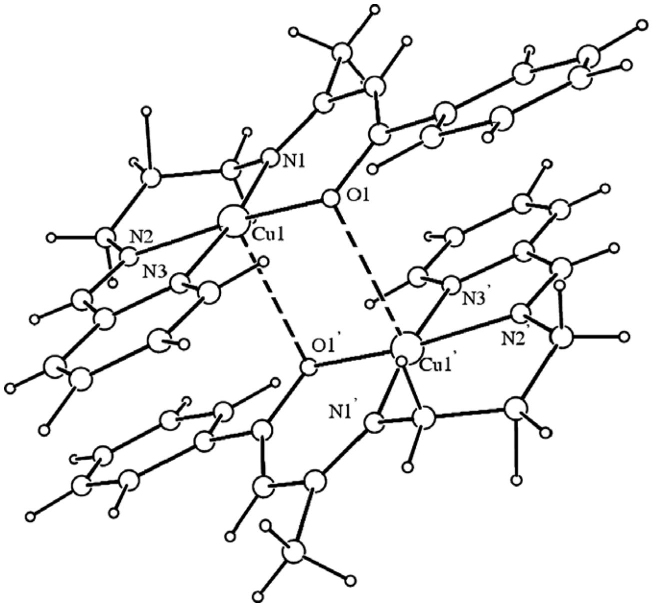

Fig. 3. A view (PLUTO) of the dimer of **1**. Perchlorate ions are not shown for clarity. Symmetry transformation: $' = (1-x, -y, 1-z)$. Dashed bonds represent the weak axial bond.

compares with 0° for a perfectly square-planar arrangement and 90° for a perfect tetrahedral arrangement. The two diagonal N–Cu–O and N–Cu–N angles of complex **1** [169.3(1) and 172.8(1)°] and **2** [168.0(1) and 174.7(1)°] are less than 180° as a result of this tetrahedral distortion. The metal ion is not perfectly centered, and the four bond distances between donor atoms to metal ion are significantly different as shown in Table 2. In both the complexes, the mean Cu–N distances (1.999 and 1.988 Å for **1** and **2**, respectively) are slightly longer than that of Cu-O (1.916 and 1.906 Å for **1** and **2**, respectively). This elongated Cu–N bond than the Cu–O is also observed for similar Schiff bases [5,19]. It is worth mentioning that, the Cu–O(1) bonds in complexes **1** and **2** are slightly greater than the similar known copper systems having acetylacetone residue [5].

The six-membered chelate ring incorporating the benzoylacetone moiety is delocalized by the influence of coordination to the metal. In complex **1**, this ring containing Cu(1), N(1), C(14), C(16), C(17) and O(1); the C(16)–C(17) distance of 1.379 Å is much shorter than the normal sp$^2$–sp$^2$ C–C single bond (1.51 Å), the C(14)–N(1) distance of 1.288 Å is a little longer than normal imine C=N double bond (1.28 Å) and the C(17)–O(1) bond length of 1.299 Å is shorter than normal sp$^2$ C–O single bond (1.34 Å). All these changes in bond length indicate delocalization of the chelating ring containing the benzoylacetone fragment. The same trend in bond lengths is also found in the ring of the benzoylacetone fragment in complex **2** with the C(16)–C(17), C(18)–N(1) and C(16)–O(1) distances of 1.370, 1.301 and 1.302 Å, respectively. It is clear that the replacement of acetylacetone residue by a benzoylacetone, slightly increases the C–O (ketonic) and C(16)–C(17) bond distances (1.280 and 1.342 Å, respectively, in the acetylacetone derived complex [5]). However, other bond distances (C–C and C=N) do not show significant changes.

The chelating ring tends to remain planar as a result of this delocalization to form a stable conjugation structure with no atoms deviating from the least square plane by 0.021 and 0.026 Å for complexes **1** and **2**, respectively. It is interesting to note that the mean plane of this ring is not coplanar with the benzene plane, the angles between the two planes are 17.27° and 17.91° for complexes **1** and **2**, respectively. The other six-membered ring incorporating the diamine fragment is not planar as all the carbon atoms are sp$^3$ hybridized. Two of the carbon atoms (C3 and C4) in **2** are disordered (occupancy of C3b is 0.59(7) and that for C4b is 0.60(1)). Therefore, we perform the conformational analysis with C3b and C4b. The conformation of the chelate ring is intermediate between chair and half-chair conformation for both complexes **1** ($Q = 0.258$ Å, $\theta = 47.7°$ and $\phi = 147.1°$) and **2** ($Q = 0.273$ Å, $\theta = 36.7°$ and $\phi = 17°$) [22]. The bond distances and bond angles of this part of Schiff base are comparable with those of related Cu(II) complexes with other nonsymmetrical Schiff base ligands [5].

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**

| | 1 | 2 |
|---|---|---|
| Cu(1)–O(1) | 1.916(2) | 1.906(2) |
| Cu(1)–N(1) | 1.948(4) | 1.945(2) |
| Cu(1)–N(2) | 2.017(3) | 2.007(3) |
| Cu(1)–N(3) | 2.032(4) | 2.012(2) |
| Cu(1)–O(1)′ | 2.767(3) | |
| O(1)–Cu(1)–N(1) | 94.50(13) | 94.21(9) |
| O(1)–Cu(1)–N(2) | 169.29(14) | 167.95(10) |
| O(1)–Cu(1)–N(3) | 89.49(12) | 88.38(8) |
| O(1)–Cu(1)–O(1)′ | 85.34(9) | |
| N(1)–Cu(1)–N(2) | 96.21(15) | 97.85(11) |
| N(1)–Cu(1)–N(3) | 172.83(14) | 174.65(10) |
| N(1)–Cu(1)–O(1)′ | 100.59(13) | |
| N(2)–Cu(1)–N(3) | 79.88(14) | 79.63(10) |
| N(2)–Cu(1)–O(1)′ | 92.53(11) | |
| N(3)–Cu(1)–O(1)′ | 85.65(11) | |

Symmetry transformations: ′ = 1 − $x$, −$y$,1 − $z$.

The dimerization of **1** through the ketonic oxygen bridge seems to be a noteworthy phenomenon for this type of complexes as the acetylacetone analogue of complex **1** is a discrete monomer [5]. The similar bridging property of phenoxo group is well documented in the literature [23] but the ketonic oxygen of acetylacetone or its derivatives is considered as nonbridging in asymmetrical or symmetrical tetradentate ligands. Till date, the bridging property of such ketonic oxygen is illustrated only in conjunction with other stronger bridging group e.g. hydroxo, oximato, etc. [7,8a,8d,24]. Therefore, to our knowledge, complex **1** is the first example of dimerization in Cu(II) complexes containing tetradentate Schiff base ligand via solely ketonic oxygen bridges.

In both complexes the intermolecular packing is controlled by π-stacking interaction between the aromatic rings. In **1**, there is a strong π–π interaction between the phenyl ring and the pyridyl ring of a neighboring ($2 - x$, $-y$, $1 - z$) dimer with a slip angle of 28.87°, dihedral angle of 5.93° and centroids separation of 3.863(3) Å to form a one-dimensional chain along the a axis as illustrated in Fig. 4. In **2** also there is similar π–π interaction between the phenyl ring and the pyridyl ring of a neighboring ($2 - x$, $-y$, $1 - z$) units ( slip angle = 31.71°, dihedral angle = 4.65° and centroid separation = 4.145(2) Å) resulting the stack of molecule along the *a*-axis (Fig S1).

### 3.2.2. *Complex* 3

The structure of complex **3** with atomic numbering scheme is shown in Fig. 5. The structure consists of discrete four coordinate copper(II) complex having quadridentate symmetrical Schiff base ligand. Selected bond distances and bond angles given in Table 3. The chelated deprotonated ligand, (L$^3$)$^{2-}$ forms three adjacent six-membered rings (6-6-6); the two terminal rings are consist of benzoylacetone fragments and the one at the middle by the starting diamine. The central Cu(II) atom has a distorted square planer coordination with a significant tetrahedral distortion. The coordinating atoms N1, N2, O1 and O2 deviates

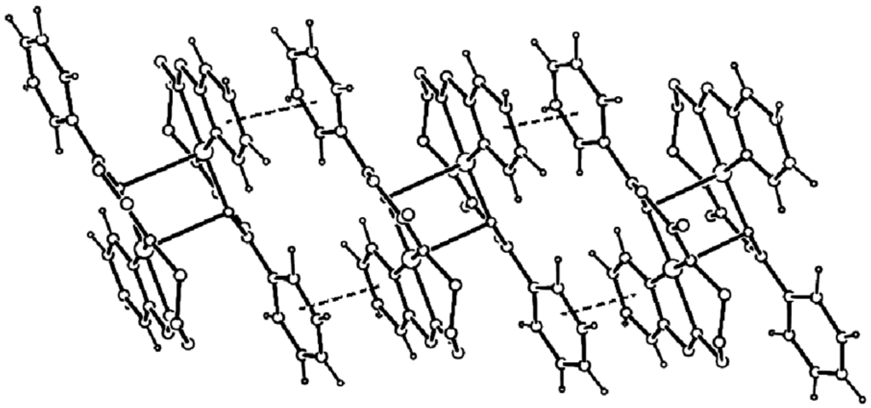

Fig. 4. One-dimensional π–π interactions shown in the dotted lines in complex **1**. Hydrogen atoms of the diamine fragments are not shown for clarity.

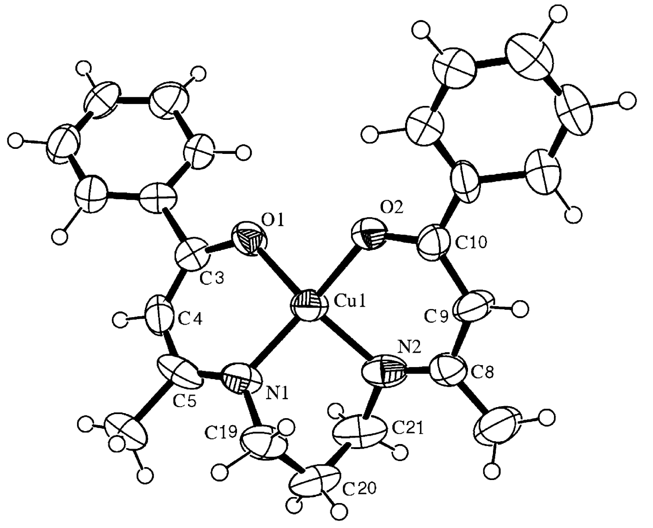

Fig. 5. ORTEP plot of **3** with atom-numbering scheme; ellipsoids at 50% probability.

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **3**

| | |
|---|---|
| Cu(1)–O(1) | 1.898(9) |
| Cu(1)–O(2) | 1.924(9) |
| Cu(1)–N(1) | 1.928(11) |
| Cu(1)–N(2) | 1.955(12) |
| O(1)–Cu(1)–O(2) | 90.7(4) |
| O(1)–Cu(1)–N(1) | 95.4(4) |
| O(1)–Cu(1)–N(2) | 151.5(4) |
| O(2)–Cu(1)–N(1) | 156.3(4) |
| O(2)–Cu(1)–N(2) | 93.5(5) |
| N(1)–Cu(1)–N(2) | 92.0(5) |

from the least-square mean plane through them by – 0.442(3), 0.427(3), −0.427(3), 0.442(3) Å. The Cu atom is located 0.039 Å from the same plane. The dihedral angles between the two planes [N(1)–Cu–O(1) and N(2)–Cu–O(2)] is 35.98°, which is much greater than that in the similar tetracoordinated copper(II) complexes like bis-(benzoylacetone)-ethylenediiminato-*N*,*N*′copper(II) complex (3.73°) [25], $[Cu(acactn)H_2O]_2$ (7.77°) and $[Cu_2(acactn)2KClO_4]_2$ (10.85° and 4.6°) where $H_2$acactn is bis(acetylacetone)-trimethylenediimine [6a] and also than the two asymmetric complexes **1** (6.09°) and **2** (4.82°) reported here. The only known tetradentate copper(II) complex having much distorted system is Cu(sal$_2$tmput) [26] ($H_2$sal$_2$tmput is 2,5-bis(salicylaldimino)-2,5-dimethylhexane (48.5°)) where the diamine (2,5-dimethylhexane-2,5-diamine) fragment produces a more flexible seven membered chelate ring.

These six-membered chelate rings derived from benzoylacetone are not identical with respect to bond distances and bond angles though both the chelating rings are delocalized by the influence of the metal, which is comparable to complexes **1** and **2**. In complex **3**, the first ring containing Cu(1), O(1), C(3), C(4), C(5) and N(1), the C(3)–C(4) distance of 1.379 Å, the C(5)–N(1) distance of 1.294 Å and the C (17)-O(1) bond length of 1.283 Å. Whereas in the second, the chelate ring containing Cu(1), O(2), C(10), C(9), C(8) and N(2), the C(9)–C(10), C(8)–N(2) and C(10)–O(2) distances are 1.427, 1.294 and 1.291 Å, respectively. The angles between the mean plane of these rings with the benzene plane are 24.57° and 24.77° indicating greater nonplanarity compare to that in complexes **1** and **2**. The conformation of six-membered chelate ring incorporating the diamine is an intermediate between boat and twist-boat confirmation [22] ($Q = 0.858$ Å, $\theta = 88.7°$ and $\phi = 265.4°$). Unlike **1** and **2** there is no significant π–π interaction between the molecules in complex **3**. A comparison of the structure of **3** with its acetylacetone analogue [6a] reveal that although the bond angles and distances do not show any significant change, the geometry around the copper atom shows unusually high tetrahedral distortion in **3**.

### 3.3. Electrochemical study

The cyclic voltammograms of the complexes are recorded in acetonitrile solvent and the diagrams are shown in Fig. 6. As is evident from Fig. 6, all three complexes show reversible reductive responses. The reduction potentials for **1** and **2** are observed at −0.86 and −0.90 V

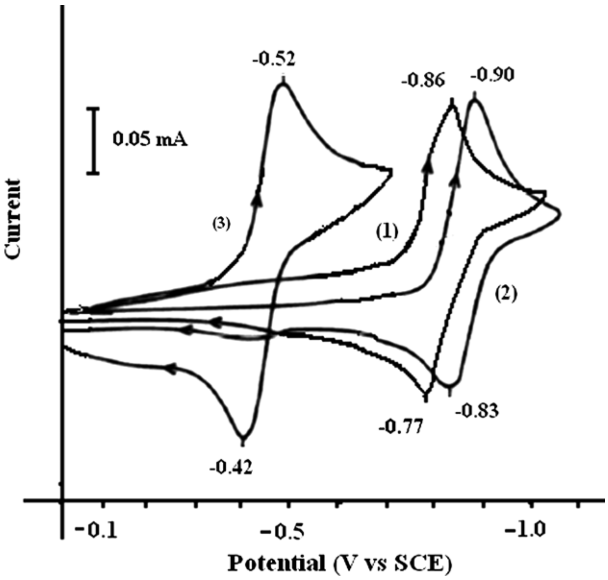

Fig. 6. The cyclic voltammogram of **1**, **2** and **3** in acetonitrile solution (scan rate 100 mV/s).

($E_{pc}$). The corresponding $E_{pa}$ values are observed at −0.77 and −0.83 V. The $E_{1/2}$ values of **1** and **2** are −0.82 and −0.87 V (versus SCE), respectively. Under identical experimental conditions the potential values for **3** are −0.52 V ($E_{pc}$), −0.42 V ($E_{pa}$) and −0.47 V ($E_{1/2}$) (versus SCE). It is well known that in four-coordinate systems, Cu(II) and Cu(I) have very distinct preference for square-based and tetrahedral geometry, respectively [27]. This preference is well reflected in the redox behavior of these systems. More is the distortion in the coordination geometry around the metal towards tetrahedral arrangement, higher is the anodic shift of the $Cu^{II}/Cu^{I}$ redox potentials [27]. Thus the anodic shift of the potential of **3** compared to **1** and **2** and also to other similar systems corroborates the severe tetrahedral distortion of the copper atom from square planar geometry as observed in the X-ray structural analysis. A similar shift of the potential value and distortion were also observed earlier [26,28].

## 4. Conclusion

The inability of complex formation of 7-amino-3-methyl-1-phenyl-4-azahept-1,3-dien-1-ol (HAMPA) with Cu(II) but facile synthesis of Cu(II) complexes with three tetradentate ligands, $HL^1$, $HL^2$, and $HL^3$ derived from HAMPA reveals that the singly condensed Schiff bases are more prone to hydrolysis. The successful syntheses of complexes **1** and **2** are significant as they prove that 1-benzoylacetone can also be used like acetylacetone for the synthesis of complexes with unsymmetrical ligands. The crystal structure determination of the complexes shows for the first time that dimerization can occur in this type of systems only through ketonic oxygen bridges. The remarkably different molecular structures of the complexes from their acetylacetone analogues opens up a scope for their potential use in understanding the intricate differences that occur in NLO responses or in natural systems with slight variations in the ligand fragments.

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## Appendix A. Supplementary material

CCDC 655614, 655615 and 655616 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.10.021.

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