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*Scientific paper*

# Synthesis, Crystal Structures, Characterization and Catalytic Property of Copper(II) Complexes Derived from Hydrazone Ligands

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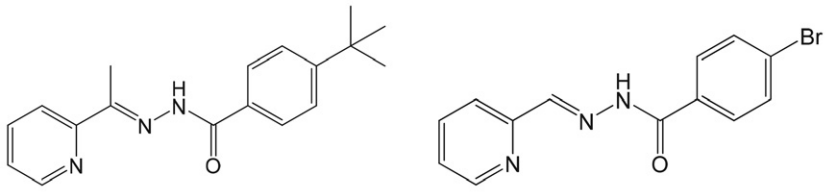
## Abstract

A new bromido-coordinated mononuclear copper(II) complex $[Cu(HL^1)Br_2]$ (**1**), and a new mononuclear copper(II) complex $[CuL^2(HL^2)]ClO_4 \cdot 0.5H_2O$ (**2**), with the hydrazone ligands 4-*tert*-butyl-*N*'-(1-(pyridin-2-yl)ethylidene)benzohydrazide ($HL^1$) and 4-bromo-*N*'-(pyridin-2-ylmethylene)benzohydrazide ($HL^2$), have been synthesized and structurally characterized by physico-chemical methods and single crystal X-ray determination. X-ray analysis indicates that the Cu atom in complex **1** is in distorted square pyramidal coordination, and that in complex **2** is in octahedral coordination. The catalytic property for epoxidation of styrene by the complexes was evaluated.

**Keywords:** Copper complex; hydrazone ligand; crystal structure; catalytic property

## 1. Introduction

Hydrazone compounds, containing the typical -CH=N-NH-C(O)- groups, represent one of the most attractive series of ligands in coordination chemistry. The hydrazone ligands are capable of binding various transition and rare earth metal atoms to form complexes with versatile structures and properties.[1] To date, most hydrazone complexes have been reported to have interesting catalytic properties, such as asymmetric epoxidation, oxidation of sulfides, and various type of polymerization.[2] Among the complexes, those with Cu centers are of particular interest for their catalytic properties.[3] To date, a large number of metal complexes with the hydrazones derived from salicylaldehyde and its analogues are reported. This type of hydrazone ligands usually act as dianionic form during coordination.[4] However, the complexes with the hydrazones derived from 2-acetylpyridine and 2-pyridinecarboxaldehyde, which act as mono-anionic form in the complexes are rare.[5] Shaabani and coworkers have reported copper(II) complexes with the ligand pyridine-2-carboxaldehyde 4-hydroxy benzol hydrazone, and their interesting antibacterial activities.[6] In pursuit of new copper(II) complexes with mono-anionic hydrazone ligands, we report herein the syntheses, X-ray crystal structures, and catalytic properties of a new bromido-coordinated mononuclear copper(II) complex $[Cu(HL^1)Br_2]$ (**1**), and a new mononuclear copper(II) complex $[CuL^2(HL^2)]ClO_4 \cdot 0.5H_2O$ (**2**), with the hydrazone ligands 4-*tert*-butyl-*N*'-(1-(pyridin-2-yl)ethylidene)benzohydrazide ($HL^1$) and 4-bromo-*N*'- (pyridin-2-ylmethylene)benzohydrazide ($HL^2$) (Scheme 1).




**Scheme 1.** The preparation of the hydrazone ligands $HL^1$ and $HL^2$.

# 2. Experimental

## 2. 1. Materials

Copper bromide, copper perchlorate, 2-acetylpyridine, 2-pyridinecarboxaldehyde, 4-*tert*-butylbenzohydrazide, and 4-bromobenzohydrazide were purchased from Aldrich. All other reagents with AR grade were used as received without further purification.

*Caution:* Copper perchlorate is potentially explosive. Only small quantities should be used and handled with great care.

## 2. 2. Physical Measurements

Infrared spectra (4000–400 $cm^{-1}$) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. The electronic spectra were recorded on a Lambda 35 spectrometer. Microanalyses (C,H,N) of the complex were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298K using a DDS-11 conductivity meter. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph.

## 2. 3. X-ray Crystallography

Crystallographic data of the complexes were collected on a Bruker SMART CCD area diffractometer with graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 298(2) K. Absorption corrections were applied by using the multi-scan program.[7] The structures of the complexes were solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against $F^2$ (SHELXL-97).[8] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located at calculated positions, and refined isotropically with $U_{iso}$(H) values constrained to 1.2 $U_{iso}$(C) and 1.5 $U_{iso}$(O and methyl C). The perchlorate anion of complex **2** is disordered over two sites, with occupancies of 0.565(3) and 0.435(3), respectively. The Cl-O and O···O distances are restrained to 1.40(1) and 2.30(2) Å, respectively. The atoms of the disordered perchlorate anion are refined as isotropic behavior. The resolution and bond precision of complex **2** are low, which is due to the poor quality of the crystal. There is a large solvent accessible void in the structure of complex **2**, which might indicate the presence of solvent molecules. The crystallographic data and experimental details for the structural analysis are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

## 2. 4. Synthesis of $[Cu(HL^1)Br_2]$ (1)

2-Acetylpyridine (1.0 mmol, 0.12 g) and 4-*tert*-butylbenzohydrazide (1.0 mmol, 0.19 g) were mixed and stirred in methanol (20 mL) for 30 min. Then, copper bromide (1.0 mmol, 0.22 g) was added to the mixture, and the final mixture was further stirred at room temperature for 30 min. The deep blue reaction solution was

**Table 1.** Crystallographic data for the single crystal of the complexes

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{72}H_{84}Br_8Cu_4N_{12}O_4$ | $C_{52}H_{40}Br_4Cl_2Cu_2N_{12}O_{13}$ |
| Formula weight | 2074.95 | 1558.58 |
| Temperature (K) | 298(2) | 298(2) |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ |
| $a$ (Å) | 8.0883(11) | 10.0284(10) |
| $b$ (Å) | 13.2359(13) | 12.0977(11) |
| $c$ (Å) | 18.8467(12) | 13.9005(15) |
| $\alpha$ (°) | 90 | 83.955(2) |
| $\beta$ (°) | 101.400(2) | 77.755(2) |
| $\gamma$ (°) | 90 | 89.579(2) |
| $V$ (Å$^3$) | 1977.8(4) | 1638.7(3) |
| $Z$ | 1 | 1 |
| $F$(000) | 1028 | 772 |
| Collected data | 11413 | 9964 |
| Unique data | 3651 | 4390 |
| Observed data [$I > 2\sigma(I)$] | 2553 | 1551 |
| Restraints | 0 | 80 |
| Parameters | 230 | 431 |
| Goodness-of-fit on $F^2$ | 1.022 | 0.903 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0456, 0.1013 | 0.0859, 0.1502 |
| $R_1$, $wR_2$ (all data) | 0.0773, 0.1142 | 0.1806, 0.2141 |

**Table 2.** Selected bond distances (Å) and bond angles (°) for the complexes

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| **1** | | | |
| Cu(1)–N(1) | 2.010(4) | Cu(1)–N(2) | 1.978(4) |
| Cu(1)–O(1) | 2.037(3) | Cu(1)–Br(1) | 2.5519(9) |
| Cu(1)–Br(2) | 2.3801(9) | | |
| N(2)–Cu(1)–N(1) | 78.95(17) | N(2)–Cu(1)–O(1) | 78.10(15) |
| N(1)–Cu(1)–O(1) | 156.59(17) | N(2)–Cu(1)–Br(2) | 145.42(13) |
| N(1)–Cu(1)–Br(2) | 99.22(13) | O(1)–Cu(1)–Br(2) | 97.01(11) |
| N(2)–Cu(1)–Br(1) | 107.43(13) | N(1)–Cu(1)–Br(1) | 97.18(13) |
| O(1)–Cu(1)–Br(1) | 94.04(12) | Br(2)–Cu(1)–Br(1) | 107.05(3) |
| **2** | | | |
| Cu(1)–N(1) | 2.292(10) | Cu(1)–N(2) | 2.005(10) |
| Cu(1)–N(4) | 2.094(12) | Cu(1)–N(5) | 1.849(13) |
| Cu(1)–O(1) | 2.379(8) | Cu(1)–O(2) | 2.048(9) |
| N(5)–Cu(1)–N(2) | 177.6(5) | N(5)–Cu(1)–O(2) | 78.4(5) |
| N(2)–Cu(1)–O(2) | 99.3(4) | N(5)–Cu(1)–N(4) | 79.2(5) |
| N(2)–Cu(1)–N(4) | 103.1(5) | O(2)–Cu(1)–N(4) | 157.3(4) |
| N(5)–Cu(1)–N(1) | 105.4(5) | N(2)–Cu(1)–N(1) | 74.2(4) |
| O(2)–Cu(1)–N(1) | 100.2(3) | N(4)–Cu(1)–N(1) | 89.5(4) |
| N(5)–Cu(1)–O(1) | 108.7(4) | N(2)–Cu(1)–O(1) | 71.7(4) |
| O(2)–Cu(1)–O(1) | 86.1(3) | N(4)–Cu(1)–O(1) | 97.4(4) |
| N(1)–Cu(1)–O(1) | 145.9(3) | | |

evaporated to remove three quarters of the solvents under reduced pressure, yielding blue solid of the complex. Yield: 45%. Well-shaped single crystals suitable for X-ray diffraction were obtained by recrystallization of the solid from methanol. Elemental analysis found: C, 41.15; H, 4.23; N, 7.92%. $C_{72}H_{84}Br_8Cu_4N_{12}O_4$ calcd: C, 41.68; H, 4.08; N, 8.10%. IR data (KBr, $cm^{-1}$): 3453 (w, OH), 3183 (w, NH), 1635 (s, C=O), 1603 (s, CH=N), 1502, 1461, 1346, 1165, 1073, 963, 860, 637, 540, 515, 446. UV-Vis data ($\lambda_{max}$, nm): 276, 320, 375, 515, 681.

## 2. 5. Synthesis of $[CuL^2(HL^2)]ClO_4 \cdot 0.5H_2O$ (2)

2-Pyridinecarboxaldehyde (1.0 mmol, 0.11 g) and 4-bromobenzohydrazide (1.0 mmol, 0.21 g) were mixed and stirred in methanol (20 mL) for 30 min. Then, copper perchlorate hexahydrate (1.0 mmol, 0.37 g) was added to the mixture, and the final mixture was further stirred at room temperature for 30 min. The deep blue reaction solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding blue solid of the complex. Yield: 37%. Well-shaped single crystals suitable for X-ray diffraction were obtained by recrystallization of the solid from methanol. Elemental analysis found: C, 40.23; H, 2.68; N, 10.71%. $C_{52}H_{40}Br_4Cl_2Cu_2N_{12}O_{13}$ calcd: C, 40.07; H, 2.59; N, 10.78%. IR data (KBr, $cm^{-1}$): 3482 (w, OH), 3197 (w, NH), 1638 (s, C=O), 1592 (s, CH=N), 1565, 1487, 1445, 1367, 1306, 1293, 1222, 1150, 1107, 1066, 1010, 919, 845, 777, 751, 671, 623, 580, 523, 476. UV-Vis data ($\lambda_{max}$, nm): 293, 378, 656.

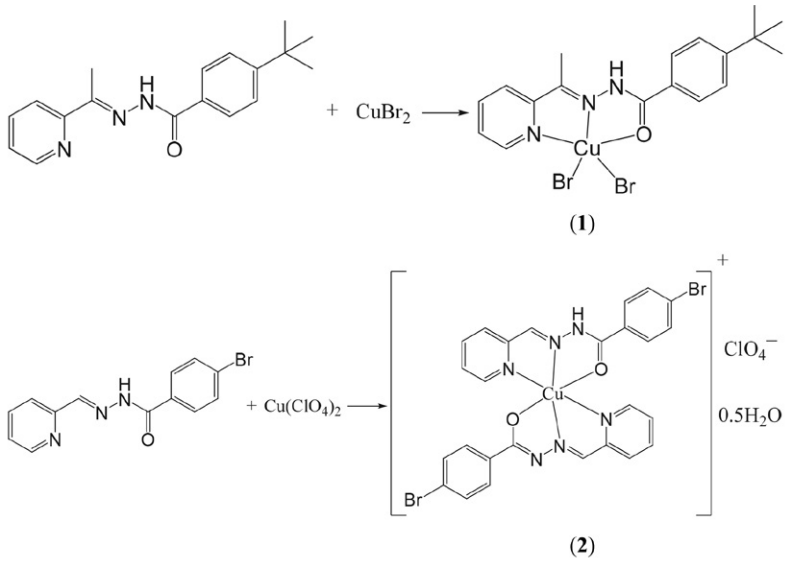
## 2. 6. Styrene Epoxidation

The epoxidation reaction was carried out at room temperature in acetonitrile under $N_2$ atmosphere with constant stirring. The composition of the reaction mixture was 2.00 mmol of styrene, 2.00 mmol of chlorobenzene (internal standard), 0.10 mmol of the complex (catalyst) and 2.00 mmol iodosylbenzene or sodium hypochlorite (oxidant) in 5.00 mL freshly distilled acetonitrile. When the oxidant was sodium hypochlorite, the solution was buffered to pH 11.2 with $NaH_2PO_4$ and NaOH. The composition of reaction medium was determined by GC with styrene and styrene epoxide quantified by the internal standard method (chlorobenzene). All other products detected by GC were mentioned as others. For each complex the reaction time for maximum epoxide yield was determined by withdrawing periodically 0.1 mL aliquots from the reaction mixture and this time was used to monitor the efficiency of the catalyst on performing at least two independent experiments. Blank experiments with each oxidant and using the same experimental conditions except catalyst were also performed.

# 3. Results and Discussion

## 3. 1. Chemistry

The hydrazones were readily prepared by condensation reaction of 2-acetylpyridine with 4-*tert*-butylbenzohydrazide, and 2-pyridinecarboxaldehyde with 4-bromobenzohydrazide, respectively, in methanol. The com-




**Scheme 2.** The preparation of the complexes.

plexes **1** and **2** were prepared by the reaction of the hydrazones with copper bromide (for **1**) and copper perchlorate hexahydrate (for **2**) in methanol (Scheme 2). The reaction progresses are accompanied by an immediate color change of the solution from colorless to deep blue. The molar conductivities ($\Lambda_M$ = 28 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **1** and 153 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ for **2**) are consistent with the values expected for non-electrolyte and 1:1 electrolyte.[9]

## 3. 2. Crystal Structure Description of Complex 1

Single-crystal X-ray analysis reveals that compound **1** is a bromido-coordinated mononuclear copper(II) complex. The ORTEP plot of the complex is shown in Fig. 1. The copper atom is in a distorted square pyramidal geometry, which is coordinated by the $N_2O$ donor atoms of the hydrazone ligand and one Br atom in the basal plane, and one Br atom at the apical position. The distortion of the square pyramidal coordination of the structure can be observed from the bond angles (Table 2) related to the Cu atom. The *cis*- and *trans*- angles related to the Cu atom at the basal plane are in the range of 78.10(15)–99.22(13)° and 145.42(13)–156.59(17)°, respectively. The bond angles among the apical and basal donor atoms are in the range of 94.04(12)–107.43(13)°. The bond lengths of Cu–O and Cu–N (Table 2) are close to those in other Cu complexes with Schiff base ligands.[9] The question arises as to whether the coordination polyhedron around the five-coordinated metal ion can be described as a distorted square pyramid or a distorted trigonal bipyramid. Further information can be obtained by determining the structural index $\tau$ which represents the relative amount of trigonality (square pyramid, $\tau$ = 0; trigonal bipyramid, $\tau$ = 1); $\tau = (\beta - \alpha)/60°$, $\alpha$ and $\beta$ being the two largest angles

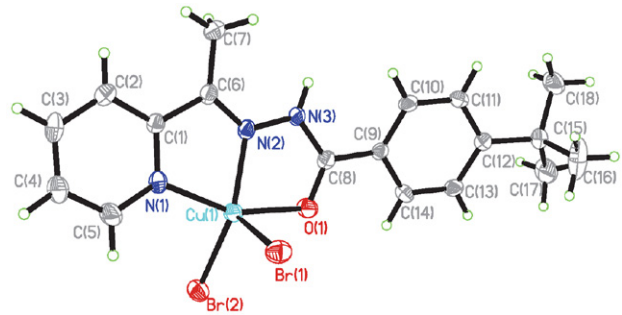



**Fig. 1.** ORTEP diagram of complex **1** with 30% thermal ellipsoid.

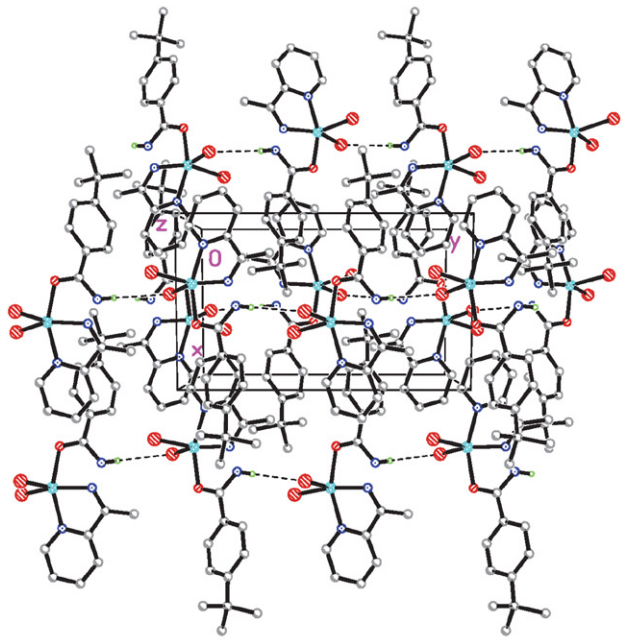



**Fig. 2.** Molecular packing structure of complex **1** linked by hydrogen bonds.

around the central atom.[10] The value of $\tau$ is 0.366. Thus, the coordination geometry of the copper atom is approximately described as a severely distorted square pyramid. The hydrazone ligand coordinates to the Cu atom through neutral state. The molecules are linked through N-H···Br hydrogen bonds (Table 3), to generate chains along the *y* axis (Fig. 2).

## 3. 3. Crystal Structure Description of Complex 2

Single-crystal X-ray analysis reveals that compound **2** is a mononuclear copper(II) complex. The ORTEP plot of the complex is shown in Fig. 3. The compound contains a [$CuL^2(HL^2)$] cation, a perchlorate anion and half water molecule of crystallization. The ORTEP plot of the complex is shown in Fig. 1b. The copper atom is in a distorted octahedral geometry, which is coordinated by the $N_2O$ donor atoms of one neutral hydrazone ligand and one mono-anionic hydrazone ligand. The distortion of the octahedral coordination of the structure can be observed from the bond angles (Table 2) related to the Cu atom. The *cis*- and *trans*- angles related to the Cu atom are in the range of 74.2(4)–108.7(4)° and 145.9(3)–177.6(5)°, respectively. The bond lengths of Cu–O and Cu–N (Table 2) are close to those in other Cu complexes with Schiff base ligands.[9] The perchlorate anions are linked to the complex cations through N-H···O hydrogen bonds (Table 3; Fig. 4).

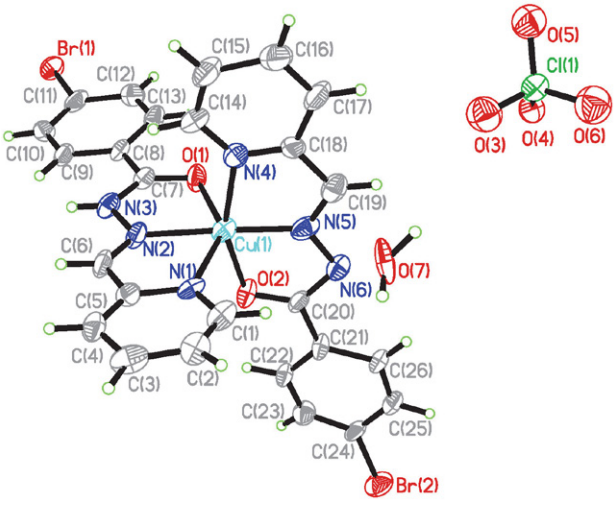



**Fig. 3.** ORTEP diagram of complex **2** with 30% thermal ellipsoid.

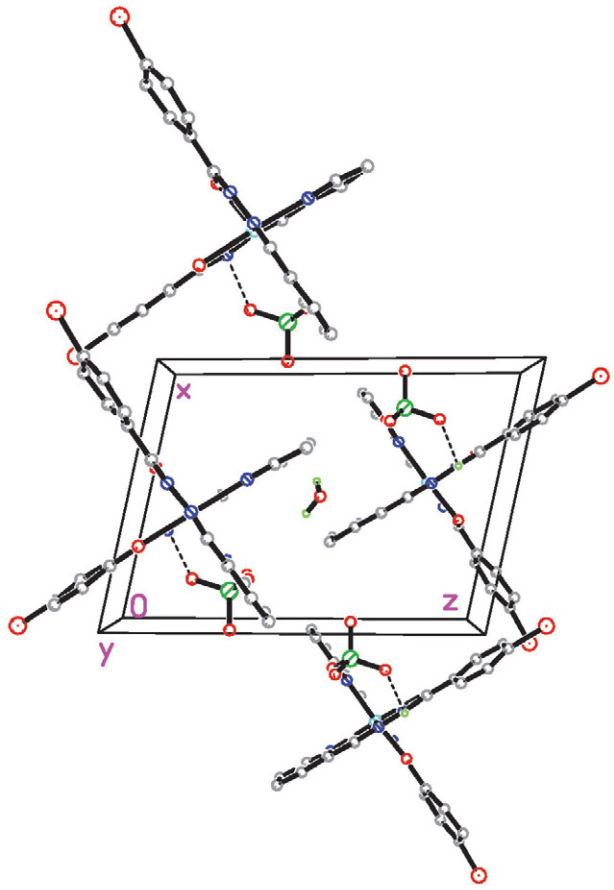



**Fig. 4.** Molecular packing structure of complex **2** linked by hydrogen bonds.

## 3. 4. IR and UV-vis Spectra of the Complexes

The weak and broad absorptions in the region 3350–3500 $cm^{-1}$ are attributed to the O-H bonds of the water molecules. The weak absorptions at 3180–3200 $cm^{-1}$ are assigned to the stretching vibration of the N–H groups. The intense bands at 1635 $cm^{-1}$ for **1** and 1638 $cm^{-1}$ for **2** are assigned to the vibration of the C=O groups. The typical bands for the azomethine groups, ν(C=N), are observed at 1595–1603 $cm^{-1}$ for both complexes.[11] The in-

**Table 3.** Hydrogen bond distances (Å) and bond angles (deg) for the complexes

| *D*–H···*A* | *d*(*D*–H) | *d*(H···*A*) | *d*(*D*···*A*) | Angle (*D*–H···*A*) |
|---|---|---|---|---|
| **1** | | | | |
| N3–H3···Br2$^{\#1}$ | 0.86 | 3.05 | 3.910(4) | 178(5) |
| **2** | | | | |
| N3–H3A···O4$^{\#2}$ | 0.86 | 2.45 | 3.036(19) | 126(5) |

Symmetry codes: #1: 1 – *x*, –*y*, 1 – *z*; #2: *x*, –1 + *y*, *z*.

tense bands in the range of 1060–1110 $cm^{-1}$ for the spectrum of complex **2** are due to the vibration of the perchlorate anion.[12] The weak bands in the range of 400–650 $cm^{-1}$ are assigned to the vibrations of the Cu–O and Cu–N bonds.

In the UV-Vis spectra of the complexes, the bands at 375 nm for **1** and 378 nm for **2** are attributed to the azomethine chromophore π-π* transition. The bands at higher energy (276 and 320 nm for **1** and 293 nm for **2**) are associated with the benzene π-π* transition.[13] The weak and less well-defined bands at 681 nm for **1** and 656 nm for **2** are assigned to the *d*–*d* transitions.

### 3. 5. Catalytic Properties of the Complexes

The percentage of conversion of styrene, selectivity for styrene oxide, yield of styrene oxide and reaction time to obtain maximum yield using both the oxidants are given in Table 4. The data reveals that the complexes as catalysts convert styrene most efficiently in the presence of both oxidants. Nevertheless, the catalysts are selective towards the formation of styrene epoxides despite of the formation of by-products which have been identified by GC-MS as benzaldehyde, phenylacetaldehyde, styrene epoxides derivative, alcohols *etc.* From the data it is also clear that the complexes exhibit excellent efficiency for styrene epoxide yield. When the reactions are carried out with PhIO and NaOCl, styrene conversions of complexes **1** and **2** were about 87% and 75%, and 79% and 73%, respectively. It is evident that between PhIO and NaOCl, the former acts as a better oxidant with respect to both styrene conversion and styrene epoxide selectivity. The epoxide yields for the complexes **1** and **2** using PhIO and NaOCl as oxidants are 79% and 72%, and 70% and 65%, respectively.

## 4. Conclusion

Two new mononuclear copper(II) complexes derived from hydrazone ligands were prepared and characterized. Single crystal X-ray analysis indicates that the Cu atom in complex **1** is in distorted square pyramidal coordination, and that in complex **2** is in octahedral coordination. The complexes have effective catalytic property for the epoxidation of styrene, with conversions over 70% and selectivities over 90%.

### Supplementary Material

CCDC 1858019 for **1** and 1858021 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.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.

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**Table 4.** Catalytic epoxidation results of complexes **1** and **2***

| | **1** | **1** | **2** | **2** |
|---|---|---|---|---|
| Oxidant | PhIO | NaOCl | PhIO | NaOCl |
| Conversion (%) | 87 | 79 | 75 | 73 |
| Epoxide yield (%) | 79 | 72 | 70 | 65 |
| Selectivity (%) | 91 | 92 | 93 | 90 |

* The time is 2 h for PhIO, and 3 h for NaOCl.

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## Povzetek

Sintetizirali smo nov z bromidom koordiniran enojedrni bakrov(II) kompleks $[Cu(HL^1)Br_2]$ (**1**) in nov enojedrni bakrov(II) kompleks $[CuL^2(HL^2)]ClO_4 \cdot 0.5H_2O$ (**2**) s hidrazonskim ligandom 4-*t*-butil-*N*'-(1-(piridin-2-il)etiliden)benzohidrazidom ($HL^1$) in 4-bromo-*N*'-(piridin-2-ilmetilen)benzohidrazidom ($HL^2$). Kompleksa smo okarakterizirali s fiziko-kemijskimi metodami in monokristalno rentgensko difrakcijo. Strukturna analiza je razkrila, da ima Cu atom v kompleksu **1** popačeno kvadratno piramidalno geometrijo, v kompleksu **2** pa oktaedrično geometrijo. Določili smo tudi katalitične aktivnosti za epoksidacijo stirena.