

Scientific paper

Tetranuclear Copper(II) Complexes Derived from 5-Bromo-2-((2-(2-hydroxyethylamino)ethylimino)methyl)phenol: Synthesis, Characterization, Crystal Structures and Catalytic Oxidation of Olefins

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Abstract

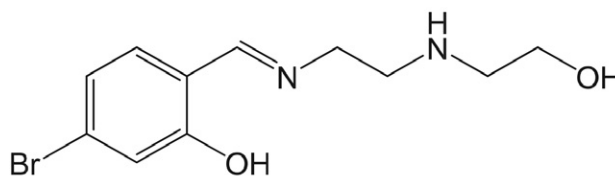
An acetate bridged tetranuclear copper(II) complex, $[\text{Cu}_4\text{L}_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_6(\text{CH}_3\text{OH})_2]$ (**1**), and a chloride, phenolate and azide co-bridged tetranuclear copper(II) complex, $[\text{Cu}_4\text{L}_2\text{Cl}_2(\mu\text{-Cl})_2(\mu_{1,1}\text{-N}_3)_2]2\text{CH}_3\text{OH}$ (**2**), where L is the deprotonated form of the Schiff base 5-bromo-2-((2-(2-hydroxyethylamino)ethylimino)methyl)phenol (HL), have been synthesized and characterized by elemental analysis, IR and UV spectra, and single crystal X-ray diffraction. Single crystal X-ray analysis revealed that the Cu atoms in both complexes are in square pyramidal geometry. In complex **1**, two $[\text{CuL}]$ units and $[\text{Cu}_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_4]$ core are linked through two acetate ligands. In complex **2**, $[\text{Cu}_2\text{LCl}(\mu\text{-Cl})]$ units are linked together by two end-on azido ligands. The Schiff base ligand coordinates to the Cu atoms through four N and O donor atoms. The molecules of both complexes are linked through hydrogen bonds to generate three dimensional networks. The catalytic property of the complexes for epoxidation reactions of some alkenes was studied using *tert*-butylhydroperoxide as the terminal oxidant under mild conditions in acetonitrile.

Keywords: Schiff base; copper complex; crystal structure; tetranuclear complex; catalytic property.

1. Introduction

Transition metal complexes with Schiff bases as ligands have received much attention for their structures, biological, pharmaceutical, magnetic and catalytic properties.¹ The complexes have been widely studied on the catalytic processes in many fundamentally and industrially important reactions.² Among the catalytic reactions, the epoxidation of olefins is of remarkable interest, because the products are necessary precursors for the production of fine chemicals. Copper complexes with Schiff base ligands are of particular interest due to their versatile structures and catalytic properties.³ Some copper complexes have been used as catalysts for the epoxidation reactions. Among them, those with Schiff base ligands have received particular attention.⁴ A number of reports used hydrogen peroxide as oxidant in the catalytic reactions. However, due to the explosive nature of hydrogen peroxide, industrial processes prefer to use *tert*-butylhydroperoxide (TBHP) as the oxidant.⁵ Although the catalytic properties of Schiff base copper(II) complexes toward oxidation re-

actions both in homogeneous and heterogeneous conditions are well documented, catalytic oxidation of alkenes involving tetranuclear Schiff base copper(II) complexes has rarely reported. Notably, TBHP has seldom been used as an oxidant in the catalytic oxidation reactions by copper(II) complexes as homogeneous catalysts.⁶ In this work, two new tetranuclear copper(II) complexes, namely $[\text{Cu}_4\text{L}_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_6(\text{CH}_3\text{OH})_2]$ (**1**) and $[\text{Cu}_4\text{L}_2\text{Cl}_2(\mu\text{-Cl})_2(\mu_{1,1}\text{-N}_3)_2]2\text{CH}_3\text{OH}$ (**2**), where L is the deprotonated Schiff base 5-bromo-2-((2-(2-hydroxyethylamino)ethylimino)methyl)phenol (HL; Scheme 1), have been synthesized, characterized and studied on their catalytic epoxidation efficacy towards some alkenes.



Scheme 1. The Schiff base HL.

2. Experimental

2. 1. Materials and Methods

All solvents used were of AR grade and used as received. 4-Bromosalicylaldehyde, 2-(2-aminoethylamino) ethanol, copper acetate monohydrate, copper chloride dihydrate and sodium azide were purchased from Aladin Chemical Co. Ltd. and were used as received. Styrene, cyclooctene, cyclohexene and TBHP were purchased from Aldrich and were used as received. Infrared spectra (4000–400 cm^{-1}) were recorded as KBr discs with a FTS-40 Bio-Rad 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. Crystallographic data of the complexes were collected on a Bruker SMART 1000 CCD area diffractometer with graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 298(2) K.

Caution! Transition metal azido complexes are potentially explosive especially in the presence of organic ligands. Although we have not encountered any problem during our study, yet a small quantity of materials should be prepared and it should be handled with care.

2. 2. X-Ray Crystallography

Absorption corrections were applied by using the SADABS program.⁷ Structures of the complexes were solved by direct methods and successive Fourier difference syntheses, and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares procedure against F^2 using SHELXTL and SHELXL-97

packages.⁸ All non-hydrogen atoms were refined anisotropically. The amino and hydroxyl H atoms of the Schiff base ligands in both complexes were located from difference Fourier maps and refined isotropically. The N–H and O–H distances were restrained to 0.90(1) and 0.85(1) \AA , respectively. The crystallographic data and experimental details for the structural analysis are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

2. 3. Synthesis of $[\text{Cu}_4\text{L}_2(\mu_2\text{-}\eta^1\text{-}\eta^1\text{-CH}_3\text{COO})_6(\text{CH}_3\text{OH})_2]$ (1)

4-Bromosalicylaldehyde (1.0 mmol, 0.20 g) and 2-(2-aminoethylamino)ethanol (1.0 mmol, 0.10 g) were mixed and stirred in methanol (30 mL) for 30 min at 25 $^\circ\text{C}$. Then, copper acetate monohydrate (2.0 mmol, 0.40 g) was added. The final mixture was further stirred for 30 min. The deep blue solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding deep blue solid product of the complex. Yield: 0.41 g (69%). Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from methanol. Anal. calcd for $\text{C}_{34}\text{H}_{46}\text{Br}_2\text{Cu}_4\text{N}_4\text{O}_{16}$ (%): C 34.59, H 3.93, N 4.75. Found (%): C 34.37, H 4.02, N 4.83. IR data (KBr, cm^{-1}): 3285, 3067, 2929, 2873, 1632, 1565, 1512, 1431, 1418, 1349, 1299, 1248, 1207, 1193, 1138, 1097, 1056, 1020, 995, 930, 911, 875, 803, 682, 623, 468, 443. UV-Vis data in acetonitrile [λ_{max} (nm), ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$): 227, 6.89×10^3 ; 249, 6.91×10^3 ; 270, 4.57×10^3 ; 365, 1.51×10^3 ; 640, 83.

2. 4. Synthesis of $[\text{Cu}_4\text{L}_2\text{Cl}_2(\mu\text{-Cl})_2(\mu_{1,1}\text{-N}_3)_2]2\text{CH}_3\text{OH}$ (2)

4-Bromosalicylaldehyde (1.0 mmol, 0.20 g) and 2-(2-aminoethylamino)ethanol (1.0 mmol, 0.10 g) were

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

	1	2
Empirical formula	$\text{C}_{34}\text{H}_{46}\text{Br}_2\text{Cu}_4\text{N}_4\text{O}_{16}$	$\text{C}_{24}\text{H}_{36}\text{Br}_2\text{Cl}_4\text{Cu}_4\text{N}_{10}\text{O}_6$
Formula weight	1180.73	1116.41
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
$a, \text{\AA}$	8.1594(11)	21.6461(16)
$b, \text{\AA}$	10.4407(13)	9.7999(15)
$c, \text{\AA}$	12.9744(12)	18.9698(17)
$\alpha, ^\circ$	88.6530(10)	90
$\beta, ^\circ$	84.1000(10)	116.908(2)
$\gamma, ^\circ$	77.3890(10)	90
$V, \text{\AA}^3$	1072.9(2)	3588.4(7)
Z	1	4
$F(000)$	592	2208
Data/restraints/parameters	3960/2/280	3341/2/234
Goodness-of-fit on F^2	1.070	1.032
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0299, wR_2 = 0.0808$	$R_1 = 0.0281, wR_2 = 0.0645$
R indices (all data)	$R_1 = 0.0360, wR_2 = 0.0838$	$R_1 = 0.0376, wR_2 = 0.0679$

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

1			
Cu(1)–O(1)	1.894(2)	Cu(1)–N(1)	1.950(2)
Cu(1)–O(3)	1.9801(19)	Cu(1)–N(2)	2.028(2)
Cu(1)–O(2)	2.348(2)	Cu(2)–O(5)	1.962(2)
Cu(2)–O(7)	1.964(2)	Cu(2)–O(6A)	1.970(2)
Cu(2)–O(8A)	1.977(2)	Cu(2)–O(4)	2.143(2)
O(1)–Cu(1)–N(1)	92.95(10)	O(1)–Cu(1)–O(3)	87.61(9)
N(1)–Cu(1)–O(3)	164.84(10)	O(1)–Cu(1)–N(2)	176.83(10)
N(1)–Cu(1)–N(2)	84.18(10)	O(3)–Cu(1)–N(2)	95.51(9)
O(1)–Cu(1)–O(2)	101.13(10)	N(1)–Cu(1)–O(2)	105.97(10)
O(3)–Cu(1)–O(2)	88.75(9)	N(2)–Cu(1)–O(2)	78.46(9)
O(5)–Cu(2)–O(7)	89.25(10)	O(5)–Cu(2)–O(6A)	168.40(9)
O(7)–Cu(2)–O(6A)	90.03(9)	O(5)–Cu(2)–O(8A)	90.00(10)
O(7)–Cu(2)–O(8A)	168.33(9)	O(5)–Cu(2)–O(4)	94.32(9)
O(7)–Cu(2)–O(4)	101.00(9)	O(6)–Cu(2)–O(4A)	97.18(9)
O8–Cu(2)–O(4A)	90.67(9)		
2			
Cu(1)–N(1)	1.882(3)	Cu(1)–O(1)	1.891(2)
Cu(1)–N(2)	1.936(3)	Cu(1)–Cl(1)	2.2248(8)
Cu(1)–O(2)	2.280(2)	Cu(2)–O(1)	1.9344(18)
Cu(2)–N(3)	1.947(3)	Cu(2)–N(3B)	1.955(3)
Cu(2)–Cl(2)	2.1834(9)	Cu(2)–Cl(1)	2.4889(9)
N(1)–Cu(1)–O(1)	92.33(10)	N(1)–Cu(1)–N(2)	85.05(12)
O(1)–Cu(1)–N(2)	172.71(10)	N(1)–Cu(1)–Cl(1)	156.24(8)
O(1)–Cu(1)–Cl(1)	88.77(6)	N(2)–Cu(1)–Cl(1)	96.37(8)
N(1)–Cu(1)–O(2)	110.16(10)	O(1)–Cu(1)–O(2)	95.45(9)
N(2)–Cu(1)–O(2)	79.14(11)	Cl(1)–Cu(1)–O(2)	93.35(6)
O(1)–Cu(2)–N(3)	169.70(11)	O(1)–Cu(2)–N(3B)	94.55(10)
N(3)–Cu(2)–N(3B)	76.96(15)	O(1)–Cu(2)–Cl(2)	95.16(7)
N(3)–Cu(2)–Cl(2)	95.13(9)	N(3)–Cu(2)–Cl(2B)	147.00(10)
O(1)–Cu(2)–Cl(1)	80.48(6)	N(3)–Cu(2)–Cl(1)	96.78(10)
N(3)–Cu(2)–Cl(1B)	109.98(9)	Cl(2)–Cu(2)–Cl(1)	102.71(3)

Symmetry codes: A: 1 – x, 1 – y, 2 – z; B: 1/2 – x, 3/2 – y, 1 – z.

mixed and stirred in methanol (30 mL) for 30 min at 25 °C. Then, copper chloride dihydrate (2.00 mmol, 0.34 g) and sodium azide (2.00 mmol, 0.13 g) were added. The final mixture was further stirred for 30 min. The deep blue solution was evaporated to remove three quarters of the solvents under reduced pressure, yielding deep blue solid product of the complex. Yield: 0.43 g (77%). Well-shaped single crystals suitable for X-ray diffraction were obtained by re-crystallization of the solid from methanol. Anal. calcd for C₃₄H₄₆Br₂Cu₄N₄O₁₆ (%): C 25.82, H 3.25, N 12.55. Found (%): C 43.75, H 4.31, N 15.56. IR data (KBr, cm⁻¹): 3415, 3243, 2962, 2083, 1658, 1585, 1538, 1470, 1445, 1420, 1383, 1293, 1265, 1207, 1138, 1086, 1065, 1021, 989, 930, 910, 846, 805, 725, 686, 626, 608, 591, 556, 463. UV-Vis data in acetonitrile [λ_{\max} (nm), ϵ (L mol⁻¹ cm⁻¹): 226, 1.45 × 10⁴; 245, 1.14 × 10⁴; 275, 7.27 × 10³; 367, 2.60 × 10³; 640, 74.

2. 5. Catalytic Reactions

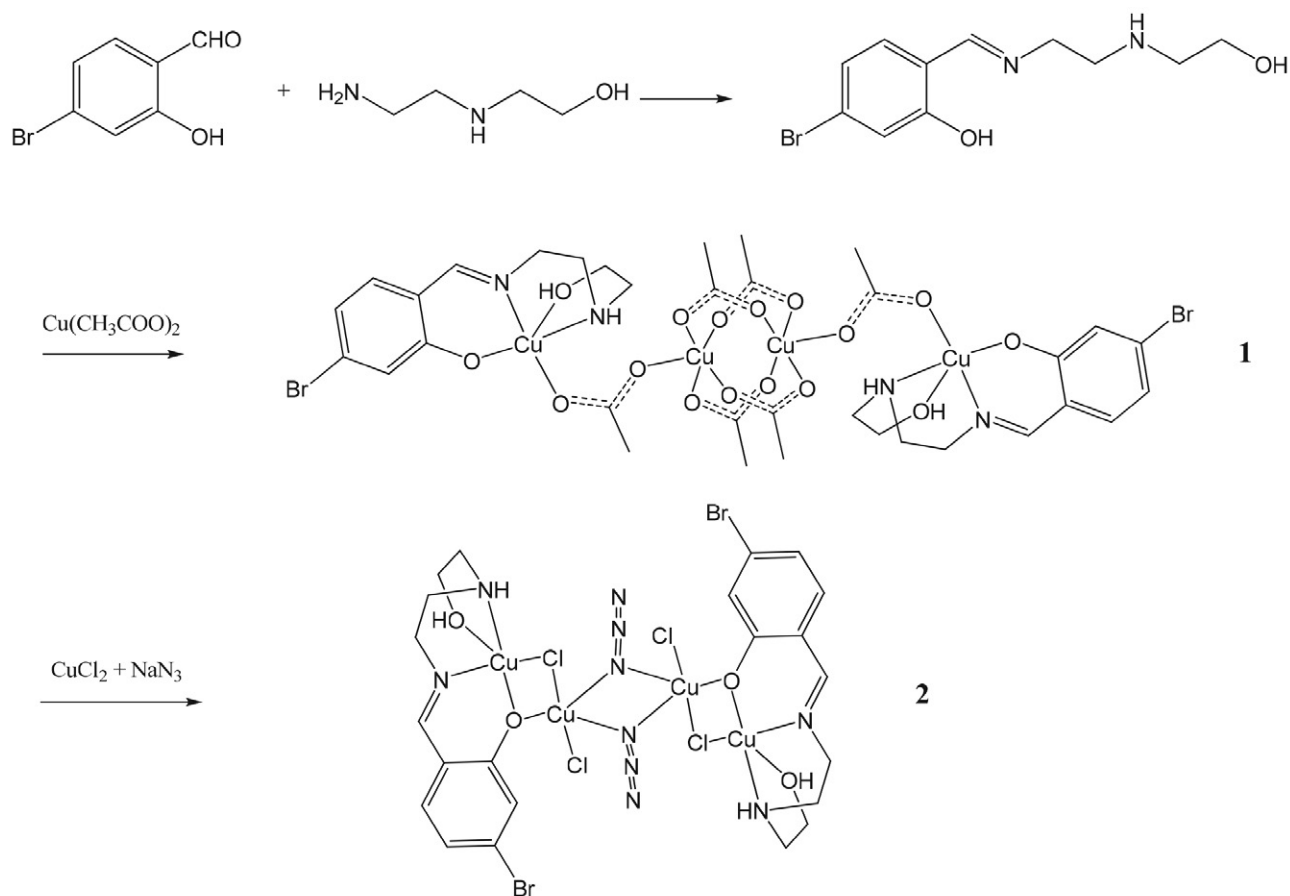
The catalytic reactions were performed according to the procedure described as follows. Substrate (10 mmol),

solvent (8 mL) and the complex as catalyst (0.005 mmol) were mixed in a flask. The mixture was equilibrated to 65 °C. Then, TBHP (20 mmol) was added to the mixture. The final mixture was further stirred for 24 h. The products of the oxidation reactions at different time intervals were collected and identified by gas chromatograph.

3. Results and Discussion

3. 1. Chemistry

The synthetic procedure of the complexes is shown in Scheme 2. The Schiff base 5-bromo-2-((2-(2-hydroxyethylamino)ethylimino)methyl)phenol was formed by reaction of 4-bromosalicylaldehyde and 2-(2-aminoethylamino)ethanol in methanol, which was not isolated and used directly to prepare the complexes. Complex 1 was synthesized by reaction of the Schiff base with copper acetate monohydrate, and complex 2 was synthesized by reaction of the Schiff base with copper chloride dihydrate and sodium azide. The reaction progresses are accompanied by



Scheme 2. The preparation of the complexes.

an immediate color change of the solution from yellow to deep blue. The elemental analyses are in good agreement with the general formulae determined by single crystal X-ray determination. The molar conductivities ($\Lambda_M = 27 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for **1** and $35 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for **2**) measured in methanol are consistent with the values expected for non-electrolyte.⁹

3. 2. Structure Descripton of Complex 1

The ORTEP plot of complex **1** is shown in Fig. 1. The molecule of the complex possesses crystallographic inversion center symmetry. The two [CuL] units and the central $[\text{Cu}_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CH}_3\text{COO})_4]$ core are linked through two $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-acetate}$ ligands. In the central $[\text{Cu}_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CH}_3\text{COO})_4]$ core (tetraacetatodicopper(II)), the two Cu atoms has a distance of 2.627(1) Å. The central Cu atom is coordinated by five acetate oxygen atoms, forming a wonderful square pyramidal geometry. The *cis* and *trans* angles in the basal plane are in the ranges of 88.36(9)–90.03(9)° and 168.33(9)–168.40(9)°, respectively. The bond angles among the apical and basal donor atoms are in the range of 90.67(9)–101.00(9)°. The Cu–O bond lengths are comparable to those observed in acetate bridged copper complexes.¹⁰ The Cu atom in [CuL] unit is coordinated in a square

pyramidal geometry, with the phenolate oxygen (O(1)), imino nitrogen (N(1)) and amino nitrogen (N(2)) of the Schiff base ligand, and the acetate oxygen (O(3)) defining the basal plane, and with the hydroxyl oxygen (O(2)) of the Schiff base ligand occupying the apical position. The Cu(1) atom deviates from the basal plane by 0.122(2) Å. The square pyramidal coordination is distorted from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the basal plane are in the ranges of 84.18(10)–105.97(10)° and 164.84(10)–176.83(10)°, respectively. The bond angles among the apical and basal donor atoms are in the range of 78.46(9)–105.97(10)°. The distortion is mainly caused by the strain created by the five-membered chelate

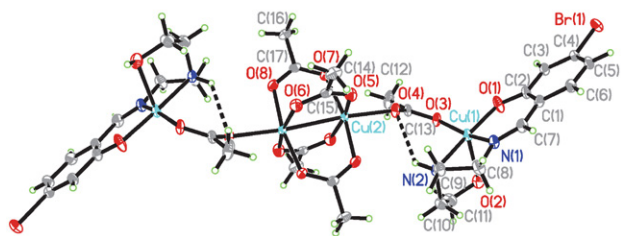


Fig. 1. ORTEP diagram of complex **1** with 30% thermal ellipsoid. Unlabeled atoms are related to the symmetry operation $1 - x, 1 - y, 2 - z$. Hydrogen bonds are shown as dashed lines.

rings Cu(1)-N(1)-C(8)-C(9)-N(2) and Cu(1)-N(2)-C(10)-C(11)-O(2). The Cu(1)-O and Cu(1)-N bond lengths are comparable to those observed in Schiff base copper complexes.¹¹ The intramolecular hydrogen bond between N(2) and O(4) locks the conformation of the Schiff base ligand.

In the crystal structure of the complex, the molecules are linked through O-H...O and C-H...Br hydrogen bonds (Table 3), to form three-dimensional network (Fig. 2).

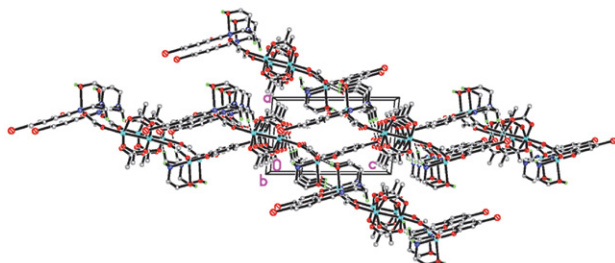


Fig. 2. Molecular packing structure of complex 1 linked by hydrogen bonds.

3. 3. Structure Descripton of Complex 2

The ORTEP plot of complex 2 is shown in Fig. 3. The molecule of the complex possesses crystallographic inversion center symmetry. The two $[\text{Cu}_2\text{LCl}(\mu\text{-Cl})]$ units are linked together by two end-on azido ligands. The Cu atom in the $[\text{Cu}_2\text{LCl}(\mu\text{-Cl})]$ unit is coordinated in a square pyramidal geometry, with the phenolate oxygen (O(1)), imino nitrogen (N(1)) and amino nitrogen (N(2)) of the Schiff base ligand, and the bridging chloride atom (Cl(1)) defining the basal plane, and with the hydroxyl oxygen (O(2)) of the Schiff base ligand occupying the apical position. The Cu(1) atom deviates from the basal plane by 0.159(2) Å. The square pyramidal coordination is distort-

ed from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the basal plane are in the ranges of 85.05(12)–96.37(8)° and 156.24(8)–172.71(10)°, respectively. The bond angles among the apical and basal donor atoms are in the range of 79.14(11)–110.16(10)°. The distortion is mainly caused by the strain created by the five-membered chelate rings Cu(1)-N(1)-C(8)-C(9)-N(2) and Cu(1)-N(2)-C(10)-C(11)-O(2), and the four-membered chelate ring Cu(1)-O(1)-Cu(2)-Cl(1). The Cu(1)-O and Cu(1)-N bond lengths are comparable to those observed in Schiff base copper complexes.¹⁰ In the central azido bridged $[\text{Cu}_2(\mu_{1,1}\text{-N}_3)_2]$ core, the two Cu atoms has a distance of 3.054(1) Å. The central Cu atom is coordinated in a square pyramidal geometry, with the phenolate oxygen (O(1)) of the Schiff base ligand, the terminal chloride ligand (Cl(2)), and two azido nitrogen (N(3) and N(3A)) defining the basal plane, and with the bridging chloride ligand (Cl(1)) occupying the apical position. The Cu(2) atom deviates from the basal plane by 0.255(2) Å. The square pyramidal coordination is distorted from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the basal plane are in the ranges of 76.96(15)–95.16(7)° and 147.00(10)–169.70(11)°, respectively. The bond angles among the apical and basal donor atoms are

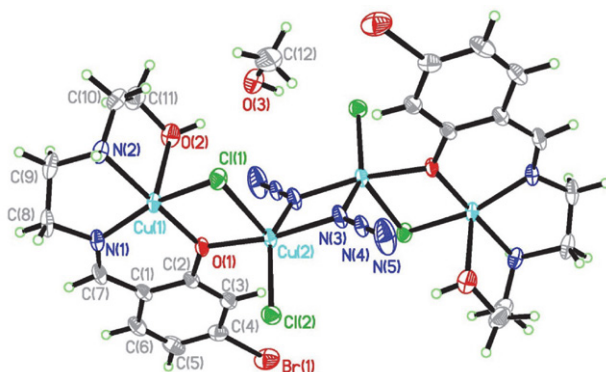


Fig. 3. ORTEP diagram of complex 2 with 30% thermal ellipsoid. Unlabeled atoms are related to the symmetry operation $1/2 - x, 3/2 - y, 1 - z$.

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

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	Angle (D-H...A)
1				
O(2)–H(2)···O(3) ^{#1}	0.84	1.90	2.7318	168
C(9)–H9B···Br(1) ^{#2}	0.97	2.93	3.6688	134
2				
N(2)–H(2)···Cl2 ^{#3}	0.89	2.51	3.2061	135
O(2)–H(2)A···O(3) ^{#4}	0.84	1.82	2.6347	164
O(3)–H(3)···Cl2 ^{#5}	0.82	2.28	3.0680	162
C(5)–H(5)···Cl2 ^{#6}	0.93	2.76	3.4815	136
C(8)–H8A···Cl1 ^{#3}	0.97	2.68	3.4459	137
C(8)–H8B···O(2) ^{#7}	0.97	2.50	3.4587	171
C(9)–H(9A)···N(6) ^{#5}	0.97	2.52	3.2450	132

Symmetry codes: #1: $1 - x, -y, 1 - z$; #2: $-x, 1 - y, 1 - z$; #3: $1/2 - x, 1/2 - y, 1 - z$; #4: $1/2 - x, 1/2 + y, 1/2 - z$; #5: $2 - x, 1 - y, 1 - z$; #6: $1 - x, 1 - y, 1 - z$; #7: $1/2 - x, -1/2 + y, 1/2 - z$.

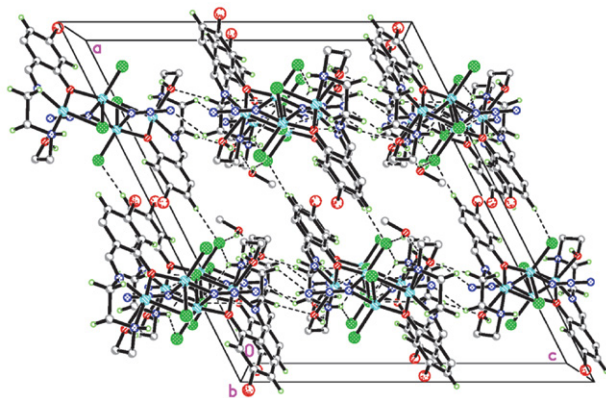


Fig. 4. Molecular packing structure of complex 2 linked by hydrogen bonds.

in the range of 80.48(6)–109.98(9)°. The Cu–Cl and Cu–N bond lengths are comparable to those observed in chlorido and azido coordinated copper complexes.¹²

There are two independent methanol molecules of crystallization. In the crystal structure of the complex, the methanol molecules and the coordination moieties are linked through O–H...O, N–H...Cl, O–H...Cl, C–H...Cl, C–H...O and C–H...N hydrogen bonds (Table 3), to form three-dimensional network (Fig. 4).

3. 4. Infrared and Electronic Spectra

The infrared spectra of the complexes were recorded in the region of 4000–400 cm⁻¹ using KBr pellets. The sharp absorptions at 3285 cm⁻¹ for **1** and 3243 cm⁻¹ for **2** are attributed to the N–H bonds of the Schiff base ligands. Peaks at 3400–3500 cm⁻¹ are attributable to O–H stretching vibrations of solvent or hydroxyl group of the Schiff base ligand. Several weak peaks observed in the range 3100–2870 cm⁻¹ likely to be due to C–H stretches. Complex **1** displays peak at 1632 cm⁻¹, and complex **2** displays peak at 1658 cm⁻¹, which are assigned to the C=N stretches of the Schiff base ligands.¹³ The different frequencies are in accordance with the bond lengths of C=N, *viz.* 1.279(4) Å for **1**, and 1.230(4) Å for **2**. The Ar–O stretching bands are observed at 1248 cm⁻¹ for **1** and 1265 cm⁻¹ for **2**. The asymmetric and symmetric stretching vibrations of the acetate groups in **1** appear at 1565 and 1418 cm⁻¹, respectively. The difference between $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ ($\Delta\nu = 147 \text{ cm}^{-1}$), which is smaller than 164 cm⁻¹ observed in ionic acetate, reflects the bidentate bridging coordination mode.¹⁴ The occurrence of medium and sharp intensity peaks at 2083 cm⁻¹, suggests the presence of N=N stretching frequency of the end-on azide group.¹⁵ In addition, new bands observed in the region of 440–600 cm⁻¹ for the complexes due to $\nu(\text{Cu–O})$, $\nu(\text{Cu–N})$ and $\nu(\text{Cu–Cl})$.¹⁶

In the UV-Vis spectra of the complexes, the bands at 245–250 nm and 270–275 nm are attributed to the $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions of the aromatic rings and the C=N groups.¹⁷ The bands at about 365 nm can be attributed to the ligand to Cu(II) charge transfer transition (LMCT).^{15b}

The visible spectra of complexes display weak single broad *d-d* bands centered at about 640 nm, which are consistent with the five-coordinate geometry of the Cu(II) complex.^{15b}

3. 5. Catalytic Property

Some aromatic and aliphatic alkenes reacted with TBHP to produce the corresponding oxides and epoxides in good yields and selectivity in acetonitrile when catalyzed by the two complexes (Figs. 5 and 6). The results are summarized in Table 4. The oxidation of styrene with TBHP gave styrene epoxide in 43% yield for **1** and 45% yield for **2** (selectivity 48–49%) under the homogeneous conditions. Besides, benzaldehyde with yields of 44–48% was produced. The oxidation of cyclohexene and cyclooctene with TBHP catalyzed by the complexes gave good conversion of 95–98% and 82–85%, respectively. The epoxide yields are about 32–38% for both complexes, while the other oxides like cyclohex-2-en-1-ol, cyclohex-2-en-1-one and cyclooctane-1,2-diol were produced in high yields (49–61%).

The solvent effects on the oxidation reactions of cyclohexene catalyzed by the complexes have been studied (Table 5). It is clear that acetonitrile is a preferred solvent for this reaction.

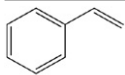


The proposed mechanism for the catalytic reaction is depicted in Scheme 3. Both copper complexes contain unsaturated penta-coordinated Cu spheres, which can be used as Lewis acidic catalysts under homogeneous conditions. The peroxy group of TBHP coordinates to the Cu atoms of both complexes to form the pre-catalysts containing LCu–OOH units. The oxo-functionality transferred to the olefins to produce the oxidized products.

Table 5. The catalytic results^a

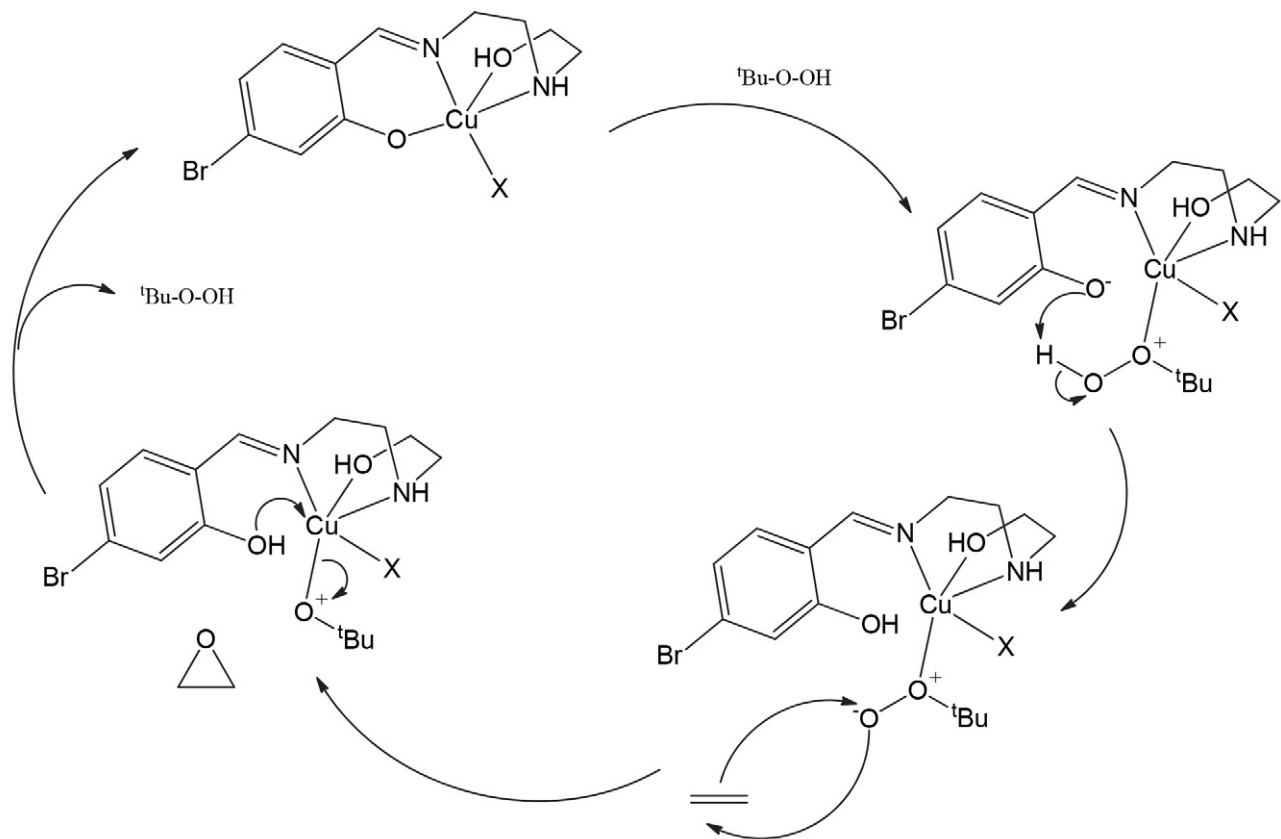
Complex	MeCN	MeOH	CH ₂ Cl ₂	CHCl ₃
1	95	63	85	82
2	98	57	81	78

^a The reaction time is 24 h, and the temperature is 70 °C.

Table 4. The catalytic results^a

Substrate	Complex	Conversion (wt%)%	Yield of products	
			Epoxide	Others
	1	87	43	44
	2	93	45	48
	1	95	38	57
	2	98	37	61
	1	82	32	50
	2	85	36	49

^a The reaction time is 24h, and the temperature is 70 °C.



Scheme 3. The proposed mechanism of the catalytic reactions by the complexes as catalysts.

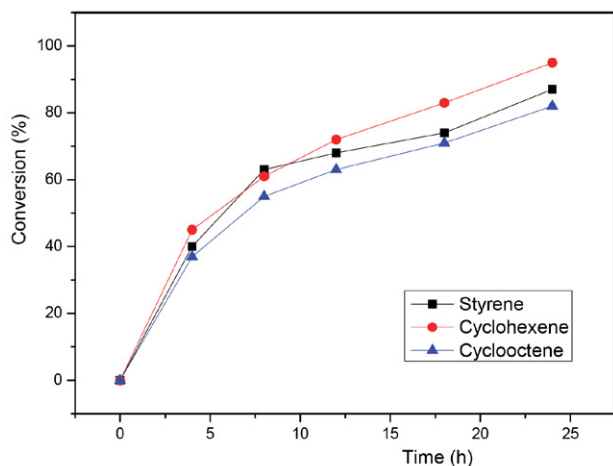


Fig. 5. The conversion plot for the oxidation reactions with complex 1 as the catalyst.

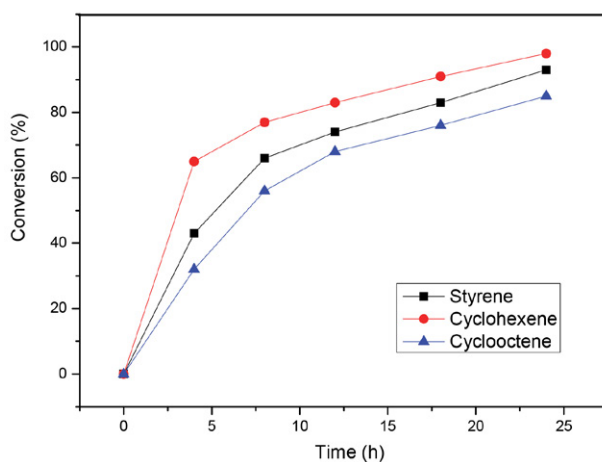


Fig. 6. The conversion plot for the oxidation reactions with complex 2 as the catalyst.

4. Conclusion

Two new tetranuclear copper(II) complexes derived from the Schiff base 5-bromo-2-((2-(2-hydroxyethylamino)ethylimino)methyl)phenol were prepared and characterized. All Cu atoms in the complexes are in square pyramidal coordination. The μ_2 - η^1 : η^1 -acetate, chloride and

end-on azide bridging ligands play important role in the formation of these polynuclear complexes. Both complexes have good catalytic property for the industrially important epoxidation reactions of styrene, cyclohexene and cyclooctene under homogeneous condition in acetonitrile with TBHP as the oxidant.

Supplementary Material

CCDC 2059783 (1) and 2059784 (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.

6. References

- (a) S. H. Sumrra, W. Zafar, S.A. Malik, K. Mahmood, S. S. Shafqat, S. Arif, *Acta Chim. Slov.* **2022**, *69*, 200–216; DOI:10.17344/acsi.2022.7842
(b) M. Abdi, A.F. Shojaei, M. Ghadermazi, Z. Moradi-Shoeili, *Acta Chim. Slov.* **2020**, *67*, 476–486; DOI:10.17344/acsi.2019.5466
(c) S. Dasgupta, S. Paul, D. Samanta, S. Hansda, E. Zangrando, D. Das, *Inorg. Chim. Acta* **2020**, *501*, 119336; DOI:10.1016/j.ica.2019.119336
(d) C. Spinu, A. Kriza, *Acta Chim. Slov.* **2000**, *47*, 179–185; DOI:10.1023/A:1014014631732
(e) S. Rayati, E. Khodaei, P. Nafarieh, M. Jafarian, B. Elmi, A. Woitczak, *RSC Advances* **2020**, *10*, 17026–17036; DOI:10.1039/D0RA02728F
(f) P. K. Mudi, N. Bandopadhyay, M. Joshi, M. Shit, S. Paul, A. R. Choudhury, B. Biswas, *Inorg. Chim. Acta* **2020**, *505*, 119468. DOI:10.1016/j.ica.2020.119468
- (a) V. Thamilarasan, P. Revathi, A. Praveena, J. Kim, V. Chandramohan, N. Sengottuvelan, *Inorg. Chim. Acta* **2020**, *508*, 119626; DOI:10.1016/j.ica.2020.119626
(b) S. Parveen, H. H. Nguyen, T. Premkumar, H. Puschmann, S. Govindarajan, *New J. Chem.* **2020**, *44*, 12729–12740; DOI:10.1039/D0NJ01016B
(c) A. Mandal, A. Sarkar, A. Adhikary, D. Samanta, *Dalton Trans.* **2020**, *49*, 15461–15472; DOI:10.1039/D0DT02784G
(d) B. Rezazadeh, A. R. Pourali, A. Banaei, H. Behniafar, *J. Coord. Chem.* **2019**, *72*, 3401–3416; DOI:10.1080/00958972.2019.1691724
(e) N. C. Jana, M. Patra, P. Brandao, A. Panja, *Inorg. Chim. Acta* **2019**, *490*, 163–172; DOI:10.1016/j.ica.2019.03.017
(f) N. C. Jana, M. Patra, P. Brandao, A. Panja, *Polyhedron* **2019**, *164*, 23–34. DOI:10.1016/j.poly.2019.02.024
- (a) S. Esmaielzadeh, E. Zarenezhad, *Acta Chim. Slov.* **2018**, *65*, 416–428; DOI:10.17344/acsi.2018.4159
(b) Y. Soberanes, K. A. Lopez-Gastelum, J. Moreno-Urbalejo, A. J. Salazar-Medina, M. D. Estrada-Montoya, R. Sugich-Miranda, J. Hernandez-Paredes, A. F. Gonzalez-Cordova, B. Vallejo-Cordoba, R. R. Sotelo-Mundo, E. F. Velazquez-Contreras, F. Rocha-Alonzo, *Inorg. Chem. Commun.* **2018**, *94*, 139–141; DOI:10.1016/j.inoche.2018.06.010
(c) B. K. Kundu, V. Chhabra, N. Malviya, R. Ganguly, G. S. Mishra, S. Mukhopadhyay, *Microporous Mesoporous Mater.* **2018**, *271*, 100–117; DOI:10.1016/j.micromeso.2018.05.046
(d) R. Vafazadeh, M. Alinaghi, A.C. Willis, A. Benvidi, *Acta Chim. Slov.* **2014**, *61*, 121–125;
(e) I. Demir, M. Bayrakci, K. Mutlu, A. I. Pekacar, *Acta Chim. Slov.* **2008**, *55*, 120–124;
(f) A. A. Alemi, B. Shaabani, *Acta Chim. Slov.* **2000**, *47*, 363–369. DOI:10.1353/dss.2008.0061
- (a) M. Karman, G. Romanowski, *Inorg. Chim. Acta* **2020**, *511*, 119832; DOI:10.1016/j.ica.2020.119832
(b) S. S. Hosseinyzade, F. M. Zonoz, B. Bahramian, *Catal. Lett.* **2018**, *148*, 1324–1335; DOI:10.1007/s10562-018-2354-z
(c) S. R. Pour, A. Abdolmaleki, M. Dinari, *J. Mater. Sci.* **2019**, *54*, 2885–2896; DOI:10.1007/s10853-018-3035-4
(d) K. Moghe, A. K. Sutar, I. K. Kang, K. C. Gupta, *RSC Advances* **2019**, *9*, 30823–30834. DOI:10.1039/C9RA05811G
- L. F. Veiros, A. Prazeres, P. J. Costa, C. C. Romao, F. E. Kuhn, M. J. Calhorda, *J. Chem. Soc. Dalton Trans.* **2006**, *11*, 1383–1389. DOI:10.1039/b515484g
- C. Adhikary, R. Bera, B. Dutta, S. Jana, G. Bocelli, A. Cantoni, S. Chaudhuri, S. Koner, *Polyhedron* **2008**, *27*, 1556–1562. DOI:10.1016/j.poly.2008.01.030
- Bruker, SMART (Version 5.625) and SAINT (Version 6.01). Bruker AXS Inc., Madison, Wisconsin, USA, **2007**.
- (a) G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8; DOI:10.1107/S2053273314026370
(b) G.M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3–8.
- W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81–122. DOI:10.1016/S0010-8545(00)80009-0
- (a) B. Sarkar, M. G. B. Drew, M. Estrader, C. Diaz, A. Ghosh, *Polyhedron* **2008**, *27*, 2625–2633; DOI:10.1016/j.poly.2008.05.004
(b) R. N. Patel, D.K. Patel, V. P. Sondhiya, K. K. Shukla, Y. Singh, A. Kumar, *Inorg. Chim. Acta* **2013**, *405*, 209–217. DOI:10.1016/j.ica.2013.05.024
- (a) S. Khan, S. Sproules, L. S. Natrajan, K. Harms, S. Chattopadhyay, *New J. Chem.* **2018**, *42*, 1634–1641; DOI:10.1039/C7NJ03990E
(b) I. Buta, L. Cseh, C. Cretu, D. Aparaschivei, C. Maxim, P. Lonneck, E. Hey-Hawkins, N. Stanica, E. Ohler, E. Rentschler, M. Andruh, O. Costisor, *Inorg. Chim. Acta* **2018**, *475*, 133–141. DOI:10.1016/j.ica.2017.10.024
- (a) A. Pradhan, S. Haldar, K. B. Mallik, M. Ghosh, M. Bera, N. Sepay, D. Schollmeyer, S.K. Ghatak, S. Roy, S. Saha, *Inorg. Chim. Acta* **2019**, *484*, 197–205; DOI:10.1016/j.ica.2018.09.026
(b) H. Chowdhury, R. Bera, C. Rizzoli, C. Adhikary, *J. Coord. Chem.* **2020**, *73*, 3062–3078. DOI:10.1080/00958972.2020.1836360
- X. M. Chen, Y. X. Tong, T. C. W. Mak, *Inorg. Chem.* **1994**, *33*, 4586–4588. DOI:10.1021/ic00098a029
- (a) U. Kumar, J. Thomas, N. Thirupathi, *Inorg. Chem.* **2010**, *49*, 62–72; DOI:10.1021/ic901100z
(b) H. Grove, M. Julve, F. Lloret, P. E. Kruger, K. W. Tornroos, J. Sletten, *Inorg. Chim. Acta* **2001**, *325*, 115–124. DOI:10.1016/S0020-1693(01)00642-9
- (a) S. Shit, P. Talukder, J. Chakraborty, G. Pilet, M. S. El Fallah, J. Ribas, S. Mitra, *Polyhedron* **2007**, *26*, 1357–1363;

DOI:10.1016/j.poly.2006.11.013

(b) A. Ray, D. Sadhukhan, G.M. Rosair, C.J. Gomez-Garcia, S. Mitra, *Polyhedron* **2009**, *28*, 3542–3550.

DOI:10.1016/j.poly.2009.07.017

16. A. Jayamani, M. Sethupathi, S.O. Ojwach, *Inorg. Chem. Commun.* **2017**, *84*, 144–149. DOI:10.1016/j.inoche.2017.08.01317. H. Chowdhury, R. Bera, C. Rizzoli, C. Adhikary, *Transition Met. Chem.* **2020**, *45*, 605–612.

DOI:10.1007/s11243-020-00415-7

Povzetek

Sintetizirali smo štirijedrni kompleks bakra(II) z mostovnimi acetatnimi ligandi, $[\text{Cu}_4\text{L}_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CH}_3\text{COO})_6(\text{CH}_3\text{OH})_2]$ (**1**), in štirijedrni kompleks bakra(II) s kloridnimi, fenolatnimi in azidnimi mostovnimi ligandi, $[\text{Cu}_4\text{L}_2\text{Cl}_2(\mu\text{-Cl})_2(\mu_{1,1}\text{-N}_3)_2]2\text{CH}_3\text{OH}$ (**2**), pri čemer je L deprotonirana oblika Schiffove baze 5-bromo-2-((2-(2-hidroksietilamino)etilimino)metil)fenol (HL). Produkta smo karakterizirali z elementno analizo, IR in UV spektroskopijo ter rentgensko monokristalno difrakcijo. Strukturna analiza na monokristalu je v obeh spojinah pokazala kvadratno planarno geometrijo okoli bakrovih atomov. V kompleksu **1** dva acetatna liganda povezujeta dve enoti $[\text{CuL}]$ z jedrom $[\text{Cu}_2(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-CH}_3\text{COO})_4]$. V kompleksu **2** so enote $[\text{Cu}_2\text{LCl}(\mu\text{-Cl})]$ povezane z azido ligandi. Schiffova baza kot ligand je koordinirana na bakrov atom preko štirih N in O donorskih atomov. Vodikove vezi povezujejo molekule obeh kompleksov v tridimenzionalno mrežo. Katalitske lastnosti kompleksov smo preučevali v reakcijah epoksidacije alkenov s tert-butilhidroperoksidom kot terminalnim oksidantom pod blagimi pogoji v acetonitrilu.



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