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1	Mononuclear and dinuclear salen type Copper(II) Schiff base complexes: synthesis,
2	characterization, crystal structures and catalytic epoxidation of cyclooctene
3	
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10	
11	Abstract
12	A series of salen type Schiff base ligands and their mononuclear (CuL ^{n} , $n = 1-4$) or dinuclear Cu(II)
13	complexes (Cu ₂ (L ⁵) ₂) were synthesized and characterized by ¹ HNMR, IR and UV-Vis spectroscopy as
14	well as elemental analyses. The ligands were synthesized from the condensation of meso-1,2-diphenyl-
15	1,2-ethylenediamine with various salicylaldehyde derivatives (x-salicylaldehyde for H_2L^n , x = H (n = 1),
16	5-Br (n = 2), 5-Br-3-NO ₂ (n = 3), 3-OMe, (n = 5)) and 2'-hydroxyacetophenone (n = 4). Crystal
17	structures of two complexes $(CuL^4 \text{ and } Cu_2(L^5)_2)$ were determined. Catalytic performance of the
18	complexes was studied in the epoxidation of cyclooctene using tert-butylhydroperoxide (TBHP) as
19	oxidant. Various factors including reaction temperature, solvent type, time, catalyst amount and substrate
20	to oxidant ratio were optimized. High catalytic activity and epoxides selectivity was found. Solvent free
21	epoxidation of cyclooctene was also studied and higher catalytic activity, epoxide selectivity and lower
22	reaction times were observed.
23	Keywords: Copper(II); Schiff base; Crystal structure; dinuclear; epoxidation

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26 **1. Introduction**

27 Schiff base complexes of transition metal ions have received great attention for their biological, medicinal, industrial and catalytic activities [1-10]. These complexes show great catalytic activity in 28 29 various fundamentally and industrially important reactions [11-15]. Among the most extensively studied such reactions are the oxidation of hydrocarbons to a variety of value-added oxygen containing 30 31 compounds such as alcohols, aldehydes, ketones and epoxides [16-18]. Catalytic epoxidation of alkenes 32 is an important industrial reaction since the epoxides are used as suitable precursors for the production of a wide variety of fine chemicals. Various copper salts have been used as catalysts for the epoxidation of 33 34 olefinic compounds [19]. Among them, copper (II) complexes of salen type Schiff base ligands have received considerable attention [19-23]. Hence, and in continuation of our previous studies, we herein 35 report the synthesis, characterization, crystal structures, and catalytic performance of a series of copper(II) 36 37 complexes of Schiff base ligands derived from the condensation meso-1,2-diphenyl-1,2-ethylenediamine with salicylaldehyde derivatives as well as 2'-hydroxyacetophene. The new complexes were tested as 38 39 catalysts in the epoxidation of cyclooctene with TBHP under various conditions to find the optimum operating conditions. The complexes showed high catalytic activity and epoxide selectivity. On the other 40 hand, Schiff base catalyzed epoxidation reactions are usually performed in organic solvents and solvent 41 free conditions are rarely studied. Therefore, we herein report the results of our solvent free epoxidation 42 43 studies of cyclooctene to cycloocteneoxide using Cu(II) Schiff base complexes. Higher catalytic activities, epoxide selectivity and lower reaction times were achieved. 44

45

46 2. Experimental

47 **2.1.** Materials and methods

All chemicals were purchased from commercial sources and were used as received. *Meso*-1,2-diphenyl-1,2-ethylenediamine [24], H_2L^n (n = 1-5) ligands [25-27] and CuL¹ complex [28] were synthesized as described elsewhere. Melting points were obtained on a thermoscientific 9100 apparatus. Elemental analyses were performed using a Perkin-Elmer 2400II CHNS-O elemental analyzer. IR spectra were

obtained as KBr plates using a Bruker FT-IR instrument. UV-Vis spectra were obtained on a Shimadzu UV-1650PC spectrophotometer in DMSO solutions. A Metrohm 757 VA computerace instrument was employed to obtain cyclic voltammograms. X-ray data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo/Kα radiation ($\lambda = 0.71073$ Å).

56

57 2.2. Synthesis of the complexes

The complexes were synthesized in good yields by equimolar reaction between the ligands (H_2L^{1-5}) and 58 Cu(OAc)₂,H₂O in ethanol following similar procedure as described elsewhere for the parent complex, 59 CuL¹ [26]. In a typical experiment, a solution of 0.46 g (1 mmol) of H_2L^4 in 15 mL of ethanol was placed 60 in a round bottom two-necked flask equipped with a magnetic stirrer, a dropping funnel and a reflux 61 condenser. This solution was heated to about 60 °C while being vigorously stirred and then a solution of 62 63 0.20 g Cu(OAc)₂.4H₂O (1mmol) in 15 mL of ethanol was added drop-wise from the dropping funnel. The color of the solution gradually turned green. The reaction mixture was heated for 3 h and then was left 64 undisturbed overnight. The resulting precipitate was filtered off, washed with 10 mL of ethanol and air 65 dried. Recrystallization from acetonitrile yielded single crystals of CuL^4 suitable for x-ray 66 crystallography. Scheme 1 shows the schematic representation of the synthetic procedure for the 67 preparation of the ligands and complexes and spectroscopic and analytical data for the complexes are 68 collected in table 1. 69 ç¢





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76 2.3. X-ray crystallography

Diffraction data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo/K α radiation ($\lambda = 0.71073$ Å). Data collections, cell refinements, data reductions and absorption corrections were performed using multi-scan methods with Bruker software [29]. The structures were solved by direct methods using SIR2004 [30]. The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F² using SHELXL [31]. All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collections and analyses are reported in table 2.

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85 2.4. Cyclic voltammetry

A Metrohm 757 VA computerace instrument was employed to obtain cyclic voltammograms in DMSO
solutions at room temperature (25°C) under nitrogen atmosphere using 0.1 M tetra-n-octylammonium
bromide (TOAB) as supporting electrolyte. A platinum working electrode, a platinum auxiliary electrode
and an Ag/AgCl reference electrode was used.

91 **2.5. General oxidation reactions**

92 **2.5.1.** Oxidation of cyclooctene in different solvents

These Copper(II) Schiff-base complexes were used as catalysts for the study of the oxidation of 93 94 cyclooctene using TBHP as oxidant in different solvents and various reaction conditions. The progress of the reaction was monitored by GC at 60 min intervals. The retention times for the starting materials and 95 the products were determined by comparison with authentic samples. In the absence of the complexes, 96 97 very little oxidation products were observed. Oxidation of cyclooctene gave cycloocteneoxide as the major product of the reaction. The conversion percentages (%) and the TONs were calculated by the 98 following equations, in which C_i and C_f are initial and final concentration of the substrate, respectively, 99 and [Q] is the concentration of the catalyst. 100

Eq. 1. Conversion
$$\% = [(C_i - C_f)/C_i] \times 100$$

102 Eq. 2. Turnover =
$$(Conversion \% \times C_i)/[Q]$$

103 In a typical experiment, $10 \,\mu\text{mol}$ of CuL² catalyst was dissolved in 10 mL of solvent and then 15 mmol of 104 cyclooctene and 30 mmol of TBHP were added. The reaction mixture was refluxed while being stirred 105 and the reaction progress was monitored at 60 min intervals by GC.

106

107 2.5.2. Solvent free oxidations

Typically, a mixture of 10 µmol of the catalysts, 15 mmol of cyclooctene, and 30 mmol of TBHP were
refluxed and the progress of the reaction was monitored at 30 min intervals by GC.

110

111 **3. Results and discussions**

112 **3.1.** Spectroscopic characterizations

113 In the IR spectra of the complexes (table 1), intense bands at around 1600 cm⁻¹ were due to the stretching

vibrations of the C=N groups. Compared to the free ligands, these bands were shifted to lower wave

numbers upon coordination which was indicative of the participation of these groups in coordination [25].

Furthermore, the IR spectra of the ligands showed broad bands above 3300 cm⁻¹ due to the stretching 116 vibrations of the hydroxyl groups which were not observed in the IR spectra of the complexes. This meant 117 that the ligands have acted as dianionic ligands with the deprotonation of the phenolic OHs. The UV-Vis 118 119 spectra of the complexes showed three bands. The two lower wavelength bands, which were present in the UV-Vis spectra of the ligands, were assigned to the $\pi \rightarrow \pi^*$ transitions. The first bands at around 270 120 nm which appeared without considerable shifting compared to their parent ligands were assigned to the 121 $\pi \rightarrow \pi^*$ transitions in the phenyl rings. The second lower wavelength bands which were considerably red 122 shifted compared to the free ligands were assigned to the $\pi \rightarrow \pi^*$ transitions of the C=N groups. These red 123 shifts further confirmed the coordination of the azomethine groups to the Cu(II) ions. The third weak 124 bands at above 550 nm were attributed to the d-d transitions. Analytical data were also in good agreement 125 NAS 126 with the proposed structures.

127

3.2. Description of the crystal structure of CuL⁴ 128

Single crystals of CuL⁴ suitable for X-ray crystallography were obtained by slow evaporation of 129 acetonitrile solution. The complex was crystallized in the monoclinic space group P2₁/c with 2 formula 130 units in the unit cell. The ORTEP representation of the complex with the common atom numbering 131 scheme is given in figure 1 and relevant X-ray diffraction data are listed in Table 2. Table 3 also collects 132 some of the selected bond lengths and angles. The crystal structure of CuL^4 confirmed a tetradentate N₂O₂ 133 coordination of the Schiff base ligand. The coordination environment of Cu was satisfied by the two 134 phenoxo oxygen and imine nitrogen atoms of the Schiff base ligand. The complex has adopted a distorted 135 136 square planar geometry with both the O(1)–Cu–N(2) and O(2)–Cu–N(1) bond angles smaller than 180° 137 measuring 171.23(10) and 171.48(10) degrees, respectively. The angle defined by the two NCCCO chelating rings is 31.58(2) degrees which confirmed the tetrahedral distortion around the metal center. 138 139 The Cu-N bond distances are nearly identical and are slightly longer than the Cu-O bond distances. All distances are comparable with previously reported Cu-N and Cu-O bond distances [27]. 140



143 **Figure 1.** ORTEP representation of CuL⁴. Displacement ellipsoids are drawn at the 50% probability level

and H atoms are shown as small spheres of arbitrary radii, Solvent of crystallization (CH₃CN) is omitted

- 145 for clarity.
- 146



147

Figure 2. ORTEP representation of $Cu_2(L^5)_2$. Displacement ellipsoids are drawn are the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Solvent of crystallization (2CH₂Cl₂) are omitted for clarity.

Compound	CuL ⁴	$Cu_2(L^5)_2$
Empirical formula	$2(C_{30}H_{26}CuN_2O_2), C_2H_3N$	$C_{62}H_{56}Cl_4Cu_2N_4O_8$
Formula weight	1061.19	1253.99
T (K)	298(2)	298(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinie
space group	$P2_1/c$	P-1
Unit cell dimensions (Å, °)		
<i>a</i> (Å)	10.9358(4)	11.5933(7)
<i>b</i> (Å)	14.8839(5)	11.9384(8)
<i>c</i> (Å)	16.6289(6)	13.2492
α (°)	90.00	63.547(3)
β (°)	99.126(2)	82.777(4)
γ (°)	90.00	63.638(3)
Volume (Å ³), Z	2672.38(16), 2	1465.09(17), 1
Calculated density (Mg/m ³)	1.319	1.421
Absorption coefficient (mm ⁻¹)	0.848	0.966
F(000)	1104	646
θ range for data collection (°)	2.33 to 25.00	2.06 to 27.00
Limiting indices	-13≤h≤13	$-14 \le h \le 14$
	-17≤k≤17	-15≤ k≤ 15
	-19 <u><</u> 1 <u>9</u>	-16≤1≤16
Data / restraints / parameters	4687 / 0 / 332	6384 / 0 / 363
Total reflections	85421	54325

Table 2. Crystal data, data collection and structure refinement parameters for CuL⁴

Unique reflections (R _{int})	4687 [$R_{(int)} = 0.1136$]	$6384 [R_{(int)} = 0.0261]$				
Completeness	99.8 % (θ = 25.00)	99.9 % (θ = 27.00)				
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F ²				
Goodness-of-fit on F^2	1.214	1.154				
Final R index $[I > 2\sigma(I)]$	$R_1 = 0.0515, wR_2 = 0.1522$	$R_1 = 0.0364, wR_2 = 0.1090$				
R index [all data]	$R_1 = 0.0553, wR_2 = 0.1605$	$R_1 = 0.0417, wR_2 = 0.1161$				
Largest difference peak and hole (e $Å^{-3}$)	1.534 and -0.478	0.741 and -0.599				
Table 3. Selected bond lengths and angles for CuL^4 and $Cu_2(L^5)_2$						

Table 3. Selected bond lengths and angles for CuL^4 and $Cu_2(L^5)_2$

Complex	Selected Bond length	ns (Å)	Selected Bond angl	es (°)
CuL^4	Cu(1)-O(1)	1.884(2)	O(1)-Cu(1)-O(2)	88.35(9)
	Cu(1)-O(2)	1.871(2)	O(1)-Cu(1)-N(1)	93.42(9)
	Cu(1)-N(1)	1.956(2)	O(2)-Cu(1)-N(1)	171.48(10)
	Cu(1)-N(2)	1.942(2)	O(1)-Cu(1)-N(2)	171.23(10)
	0		O(2)-Cu(1)-N(2)	93.11(9)
			N(1)-Cu(1)-N(2)	86.40(9)
$Cu_2(L^5)_2$	Cu(1)-O(1)	1.8980(14)	O(1)-Cu(1)-O(2)	90.16(6)
	Cu(1)-O(2)	1.9196(14)	O(1)-Cu(1)-N(1)	92.90(7)
	Cu(1)-N(1)	1.9391(16)	O(2)-Cu(1)-N(1)	176.20(6)
	Cu(1)-N(2)	1.9498(16)	O(1)-Cu(1)-N(2)	176.41(6)
			O(2)-Cu(1)-N(2)	92.85(6)
			N(1)-Cu(1)-N(2)	84.01(7)

Description of the crystal structure of $Cu_2(L^5)_2$ 155

An ORTEP representation of $Cu_2(L^5)_2$ complex is shown in figure 2 and the crystallographic data and 156 157 selected bond lengths and angles are collected in tables 2 and 3. In the crystal structure of this complex, 158 two symmetry related moieties are joined together through weak interactions from the oxygen atoms of 159 the phenolate groups of the Schiff base ligands to the axial position of the copper atoms at a distance of 2.736(2) Å. Although the distance is very long but is less than the sum of the van der Waals radii for 160 copper(II) and oxygen (2.92 Å) [32-33]. Therefore, a weak bond is considered to be formed between the 161 two units. Comparable distances have been regarded as bond in several other reported systems [34]. 162 Therefore, the structure of the complex could be described as square-based pyramid with the N₂O₂ group 163 forming the basal plane of the pyramid and the bridging oxygen atom of the phenolate group occupying 164 nA 165 the axial position.

166

3.3. Electrochemistry 167

Electrochemical studies of the complexes were performed by means of cyclic voltammetry in the 168 potential range of +1 to -2 volts. The CVs were obtained in DMSO solutions at room temperature (298 K) 169 under nitrogen atmosphere using 0.1 M tetra-n-octylammonium bromide (TOAB) as supporting 170 electrolyte. A platinum working electrode, a platinum auxiliary electrode and an Ag/AgCl reference 171 electrode was used to obtain cyclic voltammograms. The ligands were electro-inactive in the studied 172 range. The electrochemical data of the complexes are collected in table 4. In the cyclic voltammogram of 173 each of the complexes, a quasi-reversible wave was observed for the $Cu^{II}L^{x} + 1e \rightarrow Cu^{I}L^{x}$ process. Figure 174 3 shows the cyclic voltammogram of CuL^4 as an example. 175



177

Figure 3. cyclic voltammogram of 10^{-3} mol L⁻¹ solutions of CuL⁴ in DMSO solutions containing 0.1 mol

179 L^{-1} TOAB and scan rate 100 mV s⁻¹.

180

Table 4. Electrochemical data for 10^{-3} mol L⁻¹ solutions of the complexes in DMSO solutions containing 0.1

-	CuL ⁿ	$Ep_a(V)$	$Ep_c(V)$	ΔE (V)	$E^{0}(\mathbf{V})$	
_						
	CuL^1	-1.01	-1.12	0.11	-1.06	
	CuL^2	-0.91	-1.03	0.12	-0.97	
	CuL ³	-1.14	-1.22	0.08	-1.18	
	CuL ⁴	-1.03	-1.13	0.10	-1.08	
	$Cu_2(L^5)_2$	-1.00	-1.13	0.13	-1.06	

182 mol L^{-1} TOAB and scan rate 100 mV s⁻¹. Data are in Volts.

183

184

185 **3.4. Catalytic activity studies**

186 The catalytic oxidation of cyclooctene with these new catalysts gave three products (Scheme 2). Several 187 reaction conditions including solvent type and amount, reaction time, catalyst type, amount of the 188 catalyst, and oxidant to substrate ratio were optimized. In order to find the most efficient CuL^n catalyst for 189 the cyclooctene oxidation reaction, 10 µmol of each of the complexes were dissolved in 10 mL of freshly

distilled methanol and then 15 mmol of cyclooctene and 30 mmol of TBHP were added and the reaction mixtures were stirred and refluxed for 48 h. The progress of the reaction was monitored at 60 min intervals by GC. Two important results were obtained. First, it was observed that the conversion percentages gradually increased up to 24 h and reached their plateau, and hence, 24 h was chosen as the optimized reaction time. Second, as it could be seen from table 5 which collects the results of the optimization of catalyst type, CuL^2 was the most efficient catalyst and was chosen to study the effect of other variables.



197

198 Scheme 2. Products of the catalytic oxidation of cyclooctene with the new catalysts and TBHP oxidant199

TON	Selectivity		Conversion %	CuL ⁿ
	Other products %	Epoxide %	_	
510	49	51	34	CuL ¹
1215	44	56	82	CuL^2
345	52	48	23	CuL ³
450	52	48	31	CuL^4
375	51	49	25	$Cu_2(L^5)_2$

200 Table 5. The results of the optimization of the catalyst type

201

Figure 4 shows the results of the optimization of other parameters such as the solvent type, solventamount, catalyst load and the oxidant to substrate ratio.



Figure 4. The results of the optimization of solvent type solvent type (a); solvent amount (b); the oxidant
to substrate ratio (c) and catalyst load (d).

206

A comparison between the results of tables 4 and 5 also showed that the electrochemistry of the complexes was an important factor affecting the catalytic performance of the Cu(II) Schiff base catalysts. It was seen that more positive standard reduction potentials resulted in more efficiency of the catalyst.

210 One of the important conclusions drawn from these studies was that as the amount of the solvent was decreased, the conversion percentage was increased. This led us to study solvent-free oxidation of 211 cyclooctene using the synthesized Cu Schiff base catalysts. To the best of our knowledge, all previous 212 213 catalytic studies on the epoxidation of alkenes with tetradentate Schiff-base complexes of Copper(II) were performed in organic solvents. Our studies showed that oxidation of cyclooctene in solvent-free 214 conditions with these complexes were almost complete within three hours. Table 6 shows the results of 215 216 the oxidation of cyclooctene under solvent-free conditions. Other parameters were kept similar to the 217 conditions obtained in the optimized solvent. As it could be seen from table 6, similar trends for the catalytic performance of the copper complexes were observed and CuL^2 was still the most efficient 218 catalyst with the highest conversion. Besides the reaction time was much lower than that of acetonitrile 219 which was the optimized solvent. Higher catalytic activity and epoxide selectivity was also achieved. 220

221

Table 6. The results of the solvent-free oxidation of cyclooctene with CuLⁿ catalysts, using TBHP as
oxidant.

TON	Selectivity		Conversion percent (%)	Catalysts
	Other products %	Epoxide selectivity %	-	
930	36	64	60	CuL^1
1275	38	62	85	CuL^2
795	33	67	54	CuL ³
915	33	67	61	CuL^4
1110	36	64	74	$Cu_2(L^5)_2$

Conditions: 10 µmmol catalyst, 15 mmol cyclooctene, 30 mmol TBHP, Reflux, 3h.

225 Conclusions

Three new mononuclear, and one dinuclear salen type Schiff base complexes of copper(II), as well as a
previously reported one, were synthesized and characterized. X-ray crystal structures of two complexes, a

²²⁴

mononuclear (CuL⁴) and a dinuclear (Cu₂(L⁵)₂) one, were also determined. These complexes were tested 228 as catalyst for the oxidation of cyclooctene using TBHP as oxidant both in various solvents and solvent-229 230 free conditions. High catalytic activity and epoxide selectivity was observed. Besides, in solvent-free 231 conditions higher catalytic activity, epoxide selectivity and lower reaction times were achieved. 232 Comparison of these data with our previously published results for similar ligands but different metal ions (VO²⁺ [17, 25] and Ni²⁺ [27]) showed that these complexes were much efficient homogeneous catalyst 233 than the Ni²⁺ analogous but slightly less efficient compared to our oxidovanadium(IV) analogous. 234 235 Besides, structural correlations with the catalytic properties of these complexes were also explained.

236

237 Appendix A. Supplementary material

CCDC 941326 and 941299 contains the supplementary crystallographic data for CuL^4 and $Cu_2(L^5)_2$, 238 239 respectively. 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, 240 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. 241 242

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- 292 A series of salen type Schiff base ligands and their mononuclear or dinuclear Cu(II) complexes were
- synthesized and were tested as epoxidation catalysts. High catalytic activity and epoxide selectivity wereachieved.
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297 Highlights

- 298 A dinuclear and four mononuclear salen type complexes were synthesized. •
- Crystal structures of two complexes were characterized. 299 ٠
- Accepter The complexes were tested as catalyst for epoxidation of cyclooctene. 300 •
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