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Dicopper(II) complexes of a tridentate pyrimidine derived Schiff base ligand: Syntheses, crystal structures and catalytic reactions

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ABSTRACT

Three new dinuclear Cu(II) complexes, $[Cu_2(L)_2(L_1)]PF_6$ (**1**), $[Cu_2(L)_2(L_2)]PF_6$ (**2**) and $[Cu_2(L)_2(L_3)]PF_6$ (**3**), of a potentially tridentate NNO-donor Schiff base ligand [HL = 2-(2-(4,6-dimethylpyrimidin-2-yl)hydrazono)methyl)phenol] and the ancillary ligands [HL_1 = benzoic acid, HL_2 = salicylic acid, HL_3 = 4-amino benzoic acid] have been synthesized and characterized by elemental analyses, IR, single crystal X-ray crystallography, spectroscopic, electrochemical and catalytic studies. The ligand HL is the [1+1] condensation product of salicylaldehyde with 2-hydrazino-4,6-dimethyl pyrimidine. In the complexes **1**, **2** and **3**, two Cu(II) centers are bridged by the carboxylic oxygen atoms of the respective acid moiety. All the metal centres have square-based pyramidal (SP) geometries (Γ = 0.120, 0.124, 0.109 for **1**, **2** and **3**, respectively). The dinuclear Cu(II) complexes show high catalytic activity and selectivity for the epoxidation of styrene, cyclohexene and cyclooctene using *tert*-butyl hydroperoxide (TBHP) as the oxidant.

1. Introduction

The catalysis of alkene oxidation by soluble transition metal complexes is an area of contemporary research interest in both biomimetic and synthetic chemistry [1,2]. Schiff base ligands and their metal complexes can be easily synthesized. They are efficient catalysts under homogeneous and heterogeneous conditions. The catalytic activity of these complexes depends on the nature of the ligands as well as on the metal centers [3,4]. Therefore, these compounds are extensively used as catalysts in oxidation [5,6]. Copper(II) Schiff base complexes are amongst the most versatile catalysts known for oxygenation reactions. The role played by the copper ions in the active sites of a large number of metalloproteins has stimulated various workers to design and characterize copper complexes as models for a better understanding of biological systems [7]. Metal complexes of pyrimidine derived Schiff base ligands have been extensively studied in recent years owing to their great variety of biological activities, including antimalarial, antibacterial, antitumoral, antiviral activities etc.[8,9], which have often been related to their chelating ability with trace metal ions. Nucleic acids, vitamins and coenzymes containing pyrimidine ring systems provide potential binding sites for metal ions. The higher π acidity and presence of more than one hetero atom in pyrimidine play an important role in its coordination chemistry compared to that of pyridine bases, and it serves as a better model in biological systems [10–13]. Epoxides are very useful and versatile intermediates for the synthesis of many commodity and fine chemicals. Studies on the epoxidation of the C=C bond have become an important research area in both organic synthesis and bioinorganic modelling of oxygen-transfer metalloenzymes [14,15]. Various metal complexes, including some metal enzymes, play an important role in oxygen atom transfer reactions [16]. Dinuclear copper complexes play an important role in biological metalloenzymes [17–26]. The best investigated dinuclear copper(II) enzymes are tyrosinase [22–24] and catecholase [25,26]. These complexes are also of interest because of their structural, magnetic, catalytic and electron transfer properties [27–30].

As a sequel to our long standing interest in pyrimidine derived ligands [31–34] we have prepared copper(II) complexes of the tridentate NNO donor Schiff base ligands synthesized from 2-hydrazino-4,6-dimethyl pyrimidine and salicylaldehyde in the presence of the ancillary ligands HL_1, HL_2 and HL_3.The catalytic epoxidation reactions of various alkenes have been performed using these dinuclear copper(II) complexes. In the present study, using copper perchlorate as the metal precursor, three new dinuclear copper(II)

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complexes have been synthesized, which have actually been crystallized as the corresponding hexafluorophosphate salts (**1**, **2** and **3**) using KPF_6. We have reported the synthetic details, spectral characterizations, catalytic epoxidation of alkenes, X-ray crystal structures and electrochemical properties of **1**, **2** and **3**, where carboxylic acids act as bridgers in the presence of the ligand.

2. Experimental

2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Salicylaldehyde, styrene, cyclooctene, cyclohexene and *tert*-butylhydroperoxide (TBHP) (70% aq.) were purchased from the Aldrich Chemical Company, USA and were used without further purification.

Caution! Although we have not encountered any problems, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive, especially in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical measurement

Elemental analyses (carbon, hydrogen and nitrogen) of the ligand and the metal complexes were determined with a Perkin–Elmer CHN analyzer 2400 at the Indian Association for the Cultivation of Science, Kolkata. The electronic spectra of the complexes in methanolic solutions were recorded on a Hitachi model U-3501 spectrophotometer. IR spectra (KBr pellet, 400–4000 cm^{-1}) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. ^1H NMR spectra of the ligands were recorded in $CDCl_3$ with a Bruker AM 300L (300 MHz) superconducting FTNMR. All electrochemical measurements were made in DMF on a BAS (Epsilon model) having a three-electrode setup consisting of a glassy carbon (polished with alumina before measurement) working, platinum wire auxiliary and Ag/AgCl reference electrodes. Oxygen was rigorously removed from the DMF solutions of the samples by purging with dry argon gas of high purity. The samples were identified and quantified by a Perkin Elmer Gas Chromatograph (Clarus 600) equipped with an FID detector and using a CP-Sil 8 CB capillary column.

2.3. Synthesis of the ligand (HL)

The ligand HL was synthesized following the literature method [35].

2.4. Preparation of the complexes

2.4.1. Preparation of complex *1*

To an aqueous methanolic solution (30 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.740 g, 2 mmol), a solution of the Schiff base HL (0.484 g, 2 mmol) was added, followed by a solution of benzoic acid (0.122 g, 1 mmol) in a minimum volume of methanol with constant stirring, and the stirring was continued for 1 h. This mixture was kept in a refrigerator at 10 °C for several days. No crystals appeared. To the solution KPF_6 (0.184 g, 1 mmol) in methanol was added, and the resulting mixture was kept in refrigerator. Green hexagonal crystals suitable for X-ray diffraction appeared after 10 days. The crystals were isolated by filtration and air-dried. Yield: 0.548 g, 65.5%. *Anal.* Calc. for $C_{33}H_{43}Cu_2N_8O_{10}F_6P$: C, 40.25; H, 4.37; N, 11.38; O, 16.26; Found: C, 40.11; H, 4.00; N, 8.01; O, 16.10%. IR (KBr; ν/cm^{-1}): 1540 (vs) ν_{as},COO^-, 1611 (s) $\nu_{c=Npym}$.

Table 1
Experimental data for crystallographic analysis of **1, 2** and **3.**

Compound	1	2	3
Empirical formula	C_{33} H_{43} Cu_2 N_8 O_{10} F_6 P	C_{33} H_{35} Cu_2 N_8 O_8 F_6 P	C_{34} H_{40} Cu_2 N_9 O_7 F_6 P
Formula weight	983.80	943.74	958.78
Temperature (K)	295	150	150
Wavelength (Å)	1.54184	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
Unit cell dimensions			
a (Å)	18.3159(6)	18.136(2)	18.1353(15)
b (Å)	16.5195(4)	16.445(1)	16.8441(14)
c (Å)	14.0459(4)	14.283(1)	14.1224(12)
α (°)	90	90	90
β (°)	109.279(3)	107.74(2)	109.834(2)
γ (°)	90	90	90
Volume ($Å^3$)	4011.5(2)	4057.3(7)	4058.1(6)
z	4	4	4
$Density_{cal}$ ($mg\ m^{-3}$)	1.629	1.515	1.517
Absorption coefficient (mm^{-1})	2.515	1.174	1.369
F(000)	2016	1880	1888
Crystal size (mm^3)	0.18 × 0.22 × 0.49	0.11 × 0.12 × 0.14	0.12 × 0.13 × 0.15
θ Range (°) for data collection	5.1–77.4	1.7–27.1	1.7–25.9
Index ranges	$-20 \leqslant h \leqslant 23$	$-23 \leqslant h \leqslant 22$	$-22 \leqslant h \leqslant 20$
	$-20 \leqslant k \leqslant 20$	$0 \leqslant k \leqslant 21$	$0 \leqslant k \leqslant 20$
	$-17 \leqslant l \leqslant 13$	$0 \leqslant l \leqslant 18$	$0 \leqslant l \leqslant 17$
Goodness-of-fit on F^2	1.065	1.088	1.084
Completeness to theta = 25.00° (%)	99.9	98.4	98.6
Independent reflections [R_{int}]	4194 [*R*(int) = 0.054]	4411[*R*(int) = 0.000]	3913[*R*(int) = 0.001]
Absorption correction	Multi-scan	Multi-scan	Multi-scan
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	4194,17,295	4411,0267	3913,0269
Reflections collected	8861	4411	3913
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0802 wR_2 = 0.2229	R_1 = 0.0508, wR_2 = 0.1573	R_1 = .0418 wR_2 = .1269
Largest difference peak and hole ($eÅ^{-3}$)	R_1 = −0.77 wR_2 = 1.18	R_1 = −0.74 wR_2 = 0.44	R_1 = −0.54 wR_2 = 0.50

*2.4.2. Preparation of complexes **2** and **3***

Complexes **2** and **3** were prepared by following the same procedure used in the case of **1**, except that salicylic acid and 4-aminobenzoic acid were added, respectively for **2** and **3**, instead of benzoic acid.

For complex **2**. Yield: 0.548 g, 65.5%. *Anal.* Calc. For $C_{33}H_{35}Cu_2N_8O_8F_6P$: C, 41.96; H, 3.70; N, 11.86; O, 13.56. Found: C, 41.51; H, 3.61; N, 11.76; O, 13.46%. IR (KBr; ν/cm^{-1}): 1541 (vs) ν_{as},COO^-, 1612 (s) $\nu_{c=Npym}$.

For complex **3**. Yield: 0.548 g, 65.5%. *Anal.* Calc. for $C_{34}H_{40}Cu_2N_9O_7F_6P$: C, 42.55; H, 4.17; N, 13.14; O, 11.68. Found: C, 42.50; H, 4.13; N, 12.00; O, 11.58%. IR (KBr; ν/cm^{-1}): 1542 (vs) ν_{as}, COO^-, 1613 (s) $\nu_{c=Npym}$.

3. Single crystal X-ray crystallography

The crystallographic data for two complexes are given in Table 1. Diffraction data were collected on an Oxford Xcalibur, Ruby, Gemini diffractometer at 295 K (for **1**) and a Bruker-APEX II SMART CCD diffractometer at 150 K (for **2** and **3**) using CuKα radiation ($\lambda = 1.54184$ Å) and graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Cell parameter refinement and data reduction were carried out using Bruker SMART [37] and CRYSALIS programs for **1** [38] and Bruker SAINT software for **2** and **3**. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using the SHELXS-97 and SHELXL-97 programs [39]. An empirical absorption correction for **1** and **2**, **3** was carried out using the ABSPACK program [40] and SADABS [41]. X-ray Crystallography, in part, was performed at the DST funded National Single Crystal Diffractometer facility at the Department of Chemistry, University of Calcutta.

4. Catalytic epoxidation reactions

Epoxidation of alkenes over $[Cu_2(L)_2(L_1)]PF_6$ (**1**), $[Cu_2(L)_2(L_2)]PF_6$ (**2**) and $[Cu_2(L)_2(L_3)]PF_6$ (**3**) catalysts with *tert*-BuOOH oxidant were carried out in a two neck round-bottom flask equipped with condenser septum cap and stirrer. In a typical run, 0.5 mmol of the alkene was taken in 10 mL solvent and into this mixture 2.0 mg of the catalyst were added. Then the mixture was equilibrated to the required temperature in an oil bath. After addition of the oxidant, *tert*-BuOOH (1 mL, 9 mmol), the reaction mixture was stirred continuously. Samples were withdrawn by syringe at different

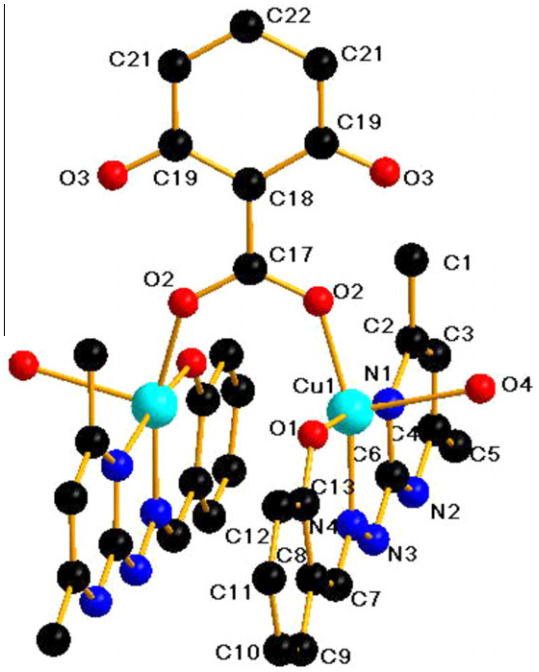

Fig. 2. Structural representation and atom numbering scheme of **2** (H-atoms are omitted for clarity).

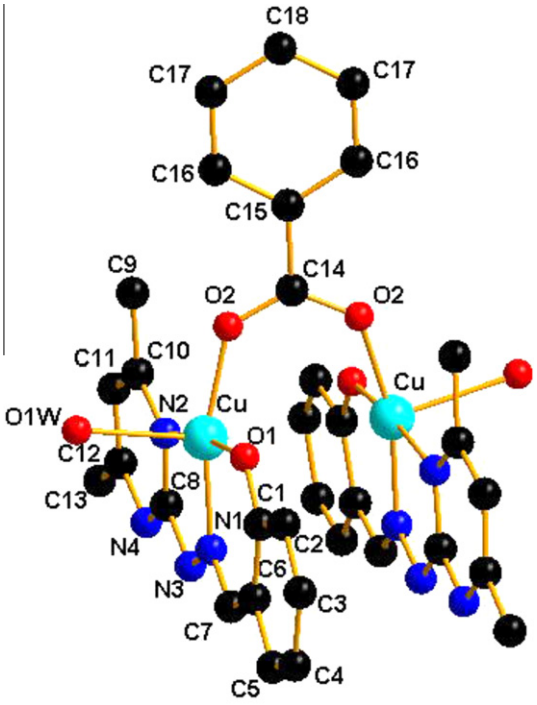

Fig. 1. Structural representation and atom numbering scheme of **1** (H-atoms are omitted for clarity).

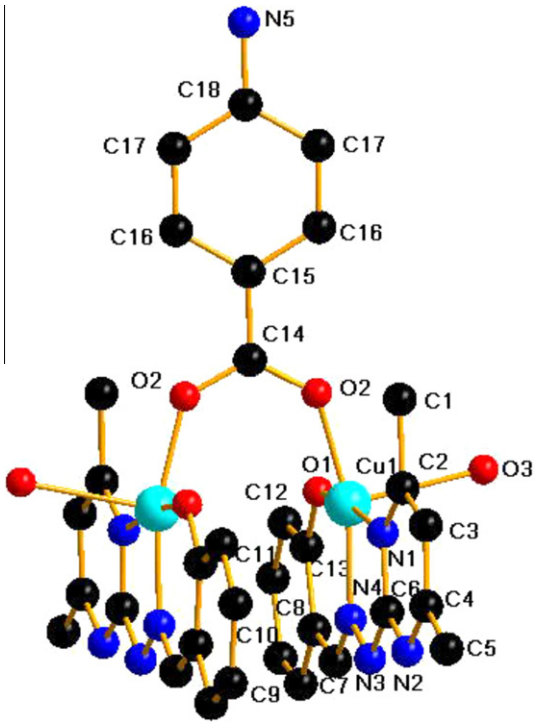

Fig. 3. Structural representation and atom numbering scheme of **3** (H-atoms are omitted for clarity).

time intervals and were identified and quantified by a Perkin Elmer Gas Chromatograph (model no. Clarus 600) equipped with an FID detector and using a CP-Sil 8 CB capillary column.

5. Result and discussion

5.1. Syntheses

The ligand HL was synthesized following the literature method [35]. The complexation behavior of HL toward Cu(II) salts was investigated. Complexes **1**, **2** and **3** were obtained by reacting the ligand HL, Cu(II) perchlorate salt and different carboxylic acids, taken in a 1:1:2 molar ratio in methanol. X-ray quality crystals of **1**, **2** and **3** were obtained upon slow evaporation of the respective reaction mixtures in the presence of KPF_6 (1 mol) at 10 °C in a refrigerator.

5.1.1. Structural description of complexes *1*, *2* and *3*

Perspective views of complexes **1**, **2** and **3**, with the atom-labelling schemes, are shown in Figs. 1–3 respectively. All the complexes crystallize in the space group C2/c. In each structure two CuL units are bridged by carboxylic oxygen atoms of the ancillary ligands HL_1, HL_2 and HL_3, respectively. The unit cells of **1**, **2** and **3** comprise of six molecules. In the complexes, each Cu(II) centre is in a five-coordinate environment with an N_2O_3 chromophore and with a distorted square pyramidal geometry. The basal plane for each Cu(II) centre is formed by the O atoms from the alkoxy group and bridging carboxyl group, and N atoms from the pyrimidine ring and azomethine group. The axial position is occupied by a coordinated oxygen O atom from a water molecule, to complete the five coordinate geometry. The average Cu-Npym distance falls in the range 1.951(2)–2.039(3) Å, Cu-Nazomethine 1.944(3)–1.951(2) Å, Cu-Ocarboxy 1.959(2)–1.940(2) Å, Cu-Ow 2.304(3)–

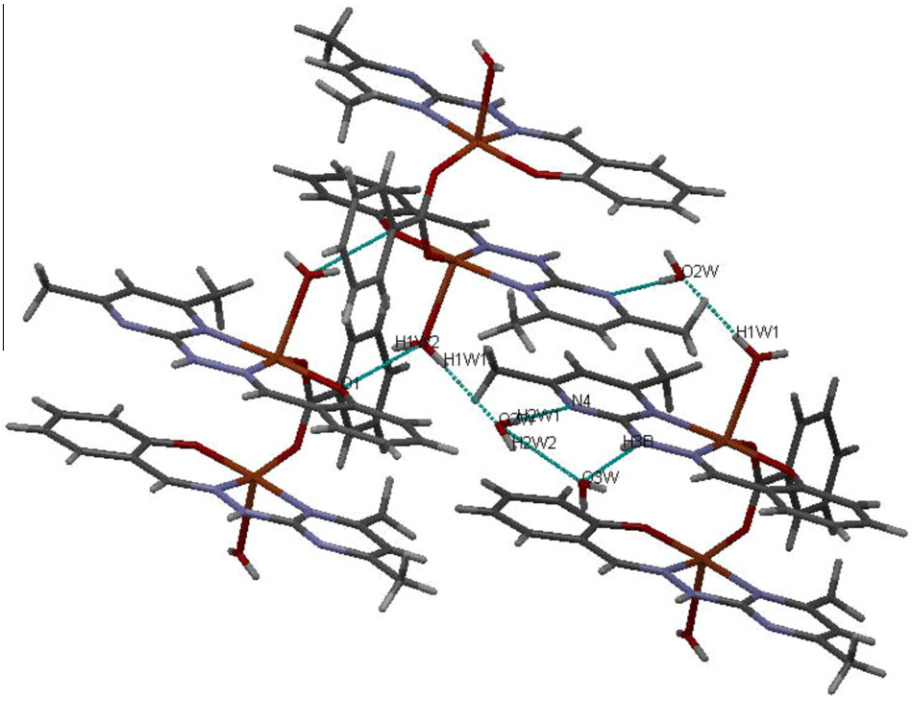

Fig. 4. Hydrogen bonding interactions in complex **1**.

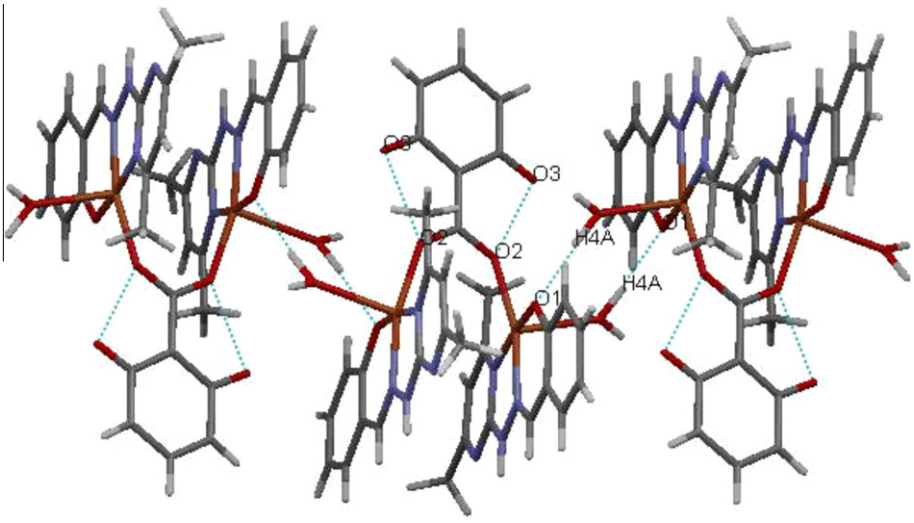

Fig. 5. Hydrogen bonding interactions in complex **2**.

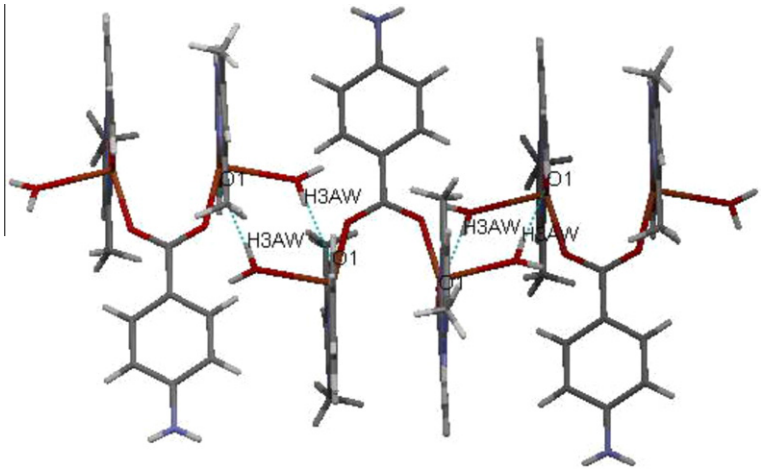

Fig. 6. Hydrogen bonding interactions in complex **3**.

2.384(3) Å and Cu-Oalkoxy 1.905(3)–1.911(2) Å. The Addison parameter (τ) values of the pentacoordinate Cu(II) centre are 0.120, 0.124, 0.109 for **1**, **2** and **3**, confirming their square-based pyramidal (SP) geometry. The two Cu(II) centres are separated by 3.553, 3.288 and 3.262 Å, and the upward deviations of the copper(II) centres from the basal plane are 0.139, 0.146, 0.120 Å for complexes **1**, **2** and **3,** respectively. The structures are stabilized by a network of intermolecular hydrogen bonding. (O1 of the salicyl hydroxy oxygen and H1W2 of a water molecule, O2W and H1W1 of water molecules, O3W and H2W2 of water molecules, O3W of a water molecule and H3B of the imine, N4 of the pyrimidine and H2W1 of a water molecule) (Fig. 4), (O1 of the salicyl hydroxy oxygen and H4A of a water molecule) (Fig. 5) and (O1 of the hydroxy oxygen and H3AW of a water molecule) (Fig. 6). Details of the hydrogen bonding are given in Table 3. In all the structures **1**, **2** and **3**, intramolecular π–π stacking serves as one of the important features that impart extra stability to the structures [the distances between the centroids of the π-stacked rings are almost same for the complexes, 3.520, 3.521 and 3.542 Å for **1**, **2** and **3,** respectively].

Table 2
Selected bond distances (Å) and angles (°) in **1, 2** and **3.**

Selected bonds	Value (Å)	Selected angles	(°)
Complex 1			
Cu-O1	1.911(2)	O1-Cu-O1 W	91.18(9)
Cu-O1W	2.327(2)	Cu-O1 W-H1W2	115.9(16)
Cu-O2	1.9526(17)	O1-Cu-O2	87.52(8)
Cu-N1	1.951(2)	O1-Cu-N1	91.11(8)
Cu-N2	2.040(2)	O1-Cu-N2	172.18(8)
		O1 W -Cu-O2	94.62(8)
		O1 W-Cu-N1	100.37(8)
		O1 W-Cu-N2	90.53(8)
		O2-Cu-N1	164.97(8)
Complex 2			
Cu1-O1	1.905(3)	O2-Cu -N2	99.95(9)
Cu1-O2	1.959(2)	N1-Cu-N2	81.08(9)
Cu1-O4	2.304(3)	O1-Cu1-O2	87.54(10)
Cu1-N1	2.039(3)	O1-Cu1-O4	93.29(12)
Cu1-N4	1.944(3)	O1-Cu1-N1	172.04(11)
		O1-Cu1-N4	91.10(11)
		O2-Cu1-O4	92.43(11)
		O2-Cu1-N1	99.91(11)
		O2-Cu1-N4	164.59(11)
		O4-Cu1-N1	89.22(11)
		O4-Cu1-N4	102.98(11)
		N1-Cu1-N4	80.97(12)
		Cu1-N4-N3	113.3(2)
			87.37(10
Complex 3			
Cu1-O1	1.906(3)	O1-Cu1-O2	87.37(10)
Cu1-O2	1.940(2)	O1-Cu1-O3	90.16(10)
Cu1-O3	2.384(3)	O1-Cu1-N1	172.03(10)
Cu1-N1	2.034(3)	O1-Cu1-N4	91.16(10)
Cu1-N4	1.948(2)	O2-Cu1 -O3	93.07(9)
		O2-Cu1-N1	100.57(11)
		O2-Cu1-N4	165.48(10)
		O3-Cu1-N1	90.16(10)
		O3-Cu1-N4	101.38(9)
		N1-Cu1-N4	80.97(11)
		Cu1-N4-N3	113.56(19)
		Cu1-O3-H3AW	118.00

5.2. Catalytic epoxidation of alkenes

The catalytic activity of the immobilized catalysts, $[Cu_2(L)_2(L_1)]PF_6$ (**1**), $[Cu_2(L)_2(L_2)]PF_6$ (**2**) and $[Cu_2(L)_2(L_3)]PF_6$ (**3**) for the epoxidation of different alkenes were studied using *tert*-BuOOH as an oxidant. The resultant conversions, selectivities and turnover frequencies (TOFs) are given in Table 4. The epoxidation of styrene shows 98% conversion with epoxide selectivity of ~59% for $[Cu_2(L)_2(L_1)]PF_6$ (**1**). For $[Cu_2(L)_2(L_2)]PF_6$ (**2**) and $[Cu_2(L)_2(L_3)]PF_6$ (**3**) the styrene conversion is 40% and 30%, respectively. Cycloalkenes, such as cyclooctene and cyclohexene, (Table 2) have also been effectively converted by $[Cu_2(L)_2(L_1)]PF_6$ (**1**) selectively to cyclooctene oxide (conversion 95%) and cyclohexene oxide (conversion 80%), respectively.

Thus a comparison of the results of the catalytic activities of **1**, **2** and **3** summarizes that **1** shows the highest styrene epoxidation activity (98%) compared to that of 40% for **2** and 30% for **3**. In case

Table 3
Details of hydrogen bond distances (Å) and angles (°) for **1, 2** and **3**.

D–H...A	*d*(D–H)	*d*(H...A)	*d*(D...A)	∠(DHA)
Complex 1				
O1W–H1W1... O2W	0.770(19)	2.11(2)	2.876(5)	176(2)
O1W–H1W2...O1	0.75(3)	2.13(3)	2.800(3)	149(3)
O2W–H2W1...N4	0.83(2)	2.06(2)	2.889(4)	173(7)
N3–H3B...O3W	0.8600	2.0500	2.882(4)	163.00
O2W–H2W2...O3W	0.82(6)	2.11(4)	2.840(9)	148(6)
Complex 2				
O4–H4A...O1	0.9600	1.8600	2.817(4)	175.00
Complex 3				
O3–H3AW...O1	0.7400	2.0500	2.788(3)	173.00

Table 4
Epoxidation reaction of alkenes catalysed by $[Cu_2(L)_2(L_1)]PF_6$ (**1**), $[Cu_2(L)_2(L_2)]PF_6$ (**2**), $[Cu_2(L)_2(L_3)]PF_6$ (**3**).[a]

Catalyst	Substrate	Reaction time (h)	Reaction temp. (°C)	Conversion[b] (wt %)	Yield of products (%)		TOF[e] (h^{-1})
					Epoxide	Others	
$[Cu_2(L)_2(L_1)]PF_6$ (**1**)	Styrene	24	80	98	60	38[c]	48
	Cyclooctene	24	80	95	95	–	44
	Cyclohexene	20	75	90	80	10[d]	67
$[Cu_2(L)_2(L_2)]PF_6$ (**2**)	Styrene	24	80	40	26	14[c]	19
	Cyclooctene	22	80	75	75	–	36
	Cyclohexene	22	75	56	47	9[d]	37
$[Cu_2(L)_2(L_3)]PF_6$ (**3**)	Styrene	24	80	30	25	5[c]	14
	Cyclooctene	22	80	50	50	–	24
	Cyclohexene	20	75	35	25	10[d]	25

[a] Reaction condition: solvent: CH_3CN, oxidant: *tert*-BuOOH, substrate 0.50 mmol.
[b] The products of the epoxidation reactions were collected at different time intervals and were identified and qualified by gas chromatograph (GC).
[c] Benzaldehyde.
[d] 2-Cyclohexen-1-Ol was formed.
[e] TOF (Turnover Frequency) = moles converted/(mol of active site time).

of cyclooctene, 95% activity is recorded for **1** while 75% and 50% is recorded for **2** and **3**, respectively. Furthermore, when cyclohexene is used, **1** shows 90% activity compared to 56% and 30% for **2** and **3**, respectively.

6. Characterization of the complex species

6.1. Infrared spectroscopy

The infrared spectra of the complexes are consistent with the X-ray crystal structure studies. The asymmetric stretching mode for the carboxylate groups are observed at 1540, 1541 and 1542 cm^{-1} for complexes **1**, **2** and **3**, respectively. The strong νC=N bands occurring at 1611, 1612 and 1613 cm^{-1} for **1**, **2**, **3**, respectively are shifted considerably towards lower frequencies compared to that of the free Schiff base ligand (1635 cm^{-1}), indicating the coordination of the imino nitrogen atom [36].

6.2. Electronic spectra

The electronic solution spectra of the complexes were recorded in MeOH solution**.** The spectra of the Cu(II) complexes **1**, **2** and **3** exhibit a strong band at 386, 387 and 390 nm, respectively, which could be attributed to the pyrimidine to Cu(II) charge transfer (LMCT) transition (d^9 electronic configuration). The low-intensity absorption bands at 602, 604 and 605 nm in the spectra of complexes **1**, **2** and **3**, respectively, are associated with a d–d transition of the copper centre.

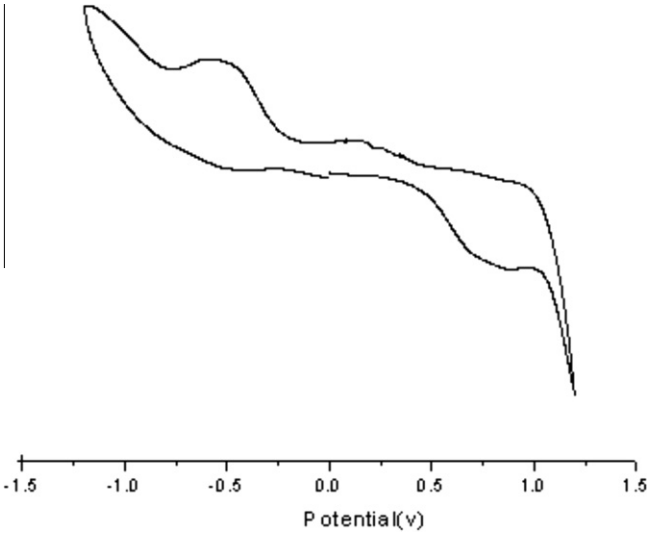

Fig. 7. Cyclic voltammogram of complex **1.**

6.3. Electrochemistry

A study of the electrochemical behavior of complex **1** was carried out in the positive range. Fig. 7 displays a representative cyclic voltammogram of **1**. Complex **1** exhibits an irreversible reduction peak ($E_{1/2}$) in DMF solution near +0.15 V versus SCE due to the Cu(II)/Cu(I) couple, and the ΔEpa value of 145 mV suggests an irreversible one electron process.

7. Concluding remarks

Three dimeric copper(II) complexes with an NNO donor ligand and carboxylic acids have been synthesized and structurally characterized by X-ray crystallography. The metal ions have a square-pyramidal N_2O_3 chromophore in these complexes. In the dimers, the carboxylate ions of the acids act as diatomic bidentate bridging units. The dinuclear Cu(II) complexes have shown excellent catalytic activities in epoxidation reactions towards various olefins. Notably, $[Cu_2(L)_2(L_1)]PF_6$ (**1**) shows an impressive conversion (98%) of styrene with tert-butylhydroperoxide (*tert*-BuOOH) as the oxidant.

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Appendix A. Supplementary data

CCDC 871301, 871302 and 871303 contain the supplementary crystallographic data for **1**, **2** and **3**. 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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