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Copper(II) Schiff base complexes derived from 2,2'-dimethyl-propandiamine: Synthesis, characterization and catalytic performance in the oxidation of styrene and cyclooctene

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1. Introduction

Transition metal catalyzed transfer of oxygen atoms to organic substrates is of interest in the study of bioinorganic mechanisms. In particular, the catalysis of alkene oxidation by soluble transition metal complexes is of 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 substituents as well as the metal center [3–6]. Therefore, these compounds have been extensively used as catalysts in various reactions, such as oxidation [7-9], ring opening reactions of epoxides [10,11], aldol condensation [12-14] and epoxidation [3,15-24]. The major advances in this field have been achieved with chiral Mn(III) Schiff base complexes [25–32]. The activity of Cr(III) [33], Mn(II) [34,35], oxovanadyl(IV) [36,37], Co(II) [38,39], Ni(II) [40], Cu(II) [41–51], Zn(II) [22], Ru(III) [29,30,52] and Ru(II) [53,54] Schiff base complexes in oxidation reactions have also been explored. Oxidants, such as iodosylbenzene [28], molecular oxygen [55], H₂O₂ [56], Bu₄NIO₄ [57], dimethyldioxirane [58] and m-chloroperbenzoic acid [59], with these complexes were also considered.

ABSTRACT

Two new mononuclear copper(II) complexes ($[CuL^1]$ ·CHCl₃(1) and $[CuL^2]$ (2)) have been prepared by the reaction of two ONNO type Schiff base ligands, ([bis(2-hydroxy-propiophenone)2,2'-dimethylpropan-diamine] (H_2L^1) and [bis(5-bromosalicylaldehyde)2,2'-dimethyl-propandiamine] (H_2L^2)) with Cu(OAc)₂·H₂O in 1:1 molar ratios. The complexes have been characterized by elemental analyses, IR and UV-Vis spectroscopy. The structures have been confirmed by X-ray single crystal analysis at 100 K. The Cu(II) atom in 1 is coordinated equatorially by a N_2O_2 donor set of the tetradentate, dinegative Schiff-base $(L^1)^{2-}$ in a distorted square planar arrangement. While in $[CuL^2]$ (2), the Cu(II) ion possesses an additional weak intermolecular contact with one bromine atom of the ligand, thus the coordination sphere of 2 can be described as strongly distorted square pyramidal. The catalytic performance of the prepared copper complexes for the oxidation of styrene and cyclooctene with tert-butyl hydroperoxide has been evaluated.

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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 efforts to design and characterize copper complexes as models for a better understanding of biological systems [41]. 2-Hydroxy Schiff base ligands have recently received particular attention owing to their different crystallographic, structural and magnetic characteristics [60-64]. More and more studies are still being carried out on the synthesis of modified and supported reagents for catalysis and material chemistry [65].

As part of our interest in hydrocarbon oxidation catalyzed by copper(II) complexes, we are reporting here the synthesis, characterization and X-ray single crystal determination of mononuclear Cu(II) complexes of two Schiff base ligands derived from 2,2'-dimethylpropandiamine, with a view to use them as active catalysts for oxidation/epoxidation of styrene and cyclooctene using tert-butyl hydroperoxide (TBHP) as an oxidant.

2. Experimental

2.1. General considerations

Solvents (ethanol, chloroform, methanol, dichloromethane, 1,2-dichloroethane and acetonitrile) were dried and distilled by standard methods before use [66]. 2,2-Dimethylpropylenediamine (Merck, 98%), 2'-hydroxypropiophenone (Across, 97%), 5-bromosalicylaldehyde (Across, 97%) were used as received. Infrared spectra



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were recorded as KBr pellets using a Unicam Mattson 1000 FT-IR. Elemental analysis (C, H, and N) were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analyse systeme, GmbH, Germany). A digital melting point measuring device (Electrothermal 9100) was used. A double beam spectrophotometer (Shimadzu, UV-240) was used for the UV–Vis absorption determination. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column (phenyl methyl siloxane 30 m \times 320 mm \times 0.25 mm) and a flame ionization detector.

2.2. Crystal structure analyses of 1 and 2 (Table 1)

The selected crystals of $[CuL^1]CHCl_3$ (1) and $[CuL^2]$ (2) were covered with perfluorinated oil and mounted on the top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and the unit cell dimensions were determined from 8000 (1) and 4000 (2) reflections (Stoe IPDS 2T, graphite-monochromated MoK α radiation ($\lambda = 71.037$ pm); see Table 1). The intensities were corrected for Lorentz and polarizations effects. In addition, absorption corrections were applied for 2 (numerical). The structures were solved by direct methods for both compounds using SIR-92 and were refined against F^2 by full-matrix least-squares using the program SHELXL-97.

The hydrogen atoms were calculated in ideal positions and were refined with a common displacement parameter. Programs used were SHELXL-97 [67], SIR-92 [68], SHELXTL-Plus [69] and PLATON [70].

2.3. Syntheses

2.3.1. Synthesis of the Schiff base ligands $(H_2L^1 \text{ and } H_2L^2)$

The Schiff bases were prepared by standard methods [71,72]. Briefly, a solution of 2,2'-dimethylpropandiamine (0.102 g, 1 mmol) was mixed with 2-hydroxypropiophenone (0.300 g, 2 mmol) and 5-bromosalicylaldehyde (0.402 g, 2 mmol) for the ligands H_2L^1 and

Table	1
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Crystal	data	and	structure	refinement fo	or 1	and 2 .
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	1	2
Empirical formula	$C_{24}H_{29}Cl_3CuN_2O_2$	$C_{19}H_{18}Br_2CuN_2O_2$
Formula mass	547.38	529.71
Crystal size (mm)	$0.25 \times 0.16 \times 0.11$	$0.12 \times 0.10 \times 0.05$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ
<i>a</i> (pm)	1155.2(1)	915.0(1)
<i>b</i> (pm)	881.1(1)	965.1(1)
<i>c</i> (pm)	2467.1(1)	1153.4(1)
α (°)	90	75.12(1)
β(°)	102.09(1)	78.65(1)
γ (°)	90	73.50(1)
$V (\mathrm{pm}^3 \times 10^6)$	2455.4(4)	935.4(2)
Ζ	4	2
D_{calc} (g cm ⁻³)	1.481	1.881
Absorption correction	none	numerical
μ (cm ⁻¹) (MoK α)	0.75	54.55
T (K)	100	100
$2\theta_{\max}$ (°)	56.74	56.76
Index ranges		
h	$-15 \rightarrow 15$	$-12 \rightarrow 12$
k	$-11 \rightarrow 11$	$-12 \rightarrow 12$
1	$-30 \rightarrow 32$	$-15 \rightarrow 15$
Reflections collected	15894	8519
Unique reflections	6048	4522
R _{int}	0.0393	0.0483
Reflections with $F_{o} > 4\sigma(F_{o})$	4801	4066
Parameters	294	238
R_1	0.0301	0.0384
wR ₂ (all data)	0.0732 ^a	0.0997 ^b
Maximum residual electron density (e pm^{-3}) × 10 ⁻⁶	0.473	1.724

^a $w = 1/[\sigma^2(F_0^2) + (0.044P)^2]; P = [max(F_0^2, 0) + 2F_c^2]/3.$

^b $w = 1/[\sigma^2(F_o^2) + (0.0747P)^2].$

 H_2L^2 , respectively, in ethanol (30 mL). The bright yellow solutions were stirred and heated to reflux for 1 h. The desired yellow precipitates were obtained, and these were filtered off, washed with diethyl ether (2 \times 5 mL) and finally dried in air.

2.3.2. Synthesis of complex 1

[CuL¹]·CHCl₃ (**1**): A solution of H₂L¹ (0.366 g, 1 mmol) in ethanol (20 mL) was added to a suspension of Cu(OAc)₂·H₂O (0.199 g, 1 mmol). The reaction mixture was refluxed for 1 h. The colored solution that formed was concentrated to yield a colored powder. The dark green precipitate that was obtained was filtered off and washed with diethyl ether (2 × 5 mL). The crude product was dissolved in 1:1 chloroform and hexane (5 mL) and kept at room temperature to give crystals of the complex after a few days. Yield: 0.407 g, 95%. M.p.: 253 °C. Anal. Calc. for C₂₄H₂₉Cl₃CuN₂O₂ (547.38): C, 52.66; H, 5.34; N, 5.12; Cu, 11.61. Found: C, 52.29; H, 5.73; N, 5.66; Cu, 11.28%. IR (KBr) [ν , cm⁻¹]: ν (C=N) 1581 s, ν (C=C) 1534 s, ν (C=O) 1220 m. UV–Vis (CHCl₃) [λ_{max} , nm (ε , m⁻¹ cm⁻¹)]: 262 (23040), 373 (9010), 388 (6890), 600 (310).

2.3.3. Synthesis of complex **2**

[CuL²] (2): A solution of H_2L^2 (0.468 g, 1 mmol) in ethanol (20 mL) was added to a suspension of Cu(OAc)₂·H₂O (0.199 g, 1 mmol). The reaction mixture was refluxed for 1 h. The colored solution that formed was concentrated to yield a colored powder. The dark green precipitate that was obtained was filtered off and washed with diethyl ether (2 × 5 mL). The crude product was dissolved in 1:1 dichloromethane and diethyl ether (5 mL) and kept at room temperature to give crystals of the complex after a few days. Yield: 0.471 g, 89%. M.p.: 241 °C. Anal. Calc. for C₁₉H₁₈Br₂CuN₂O₂ (529.71): C, 43.08; H, 3.42; N, 5.30; Cu, 12.00. Found: C, 43.71; H, 3.52; N, 5.01; Cu, 11.53%. IR (KBr) [ν , cm⁻¹]: ν (C=N) 1617 s, ν (C=C) 1519 s, ν (C=O) 1170 m. UV–Vis (CHCl₃) [λ_{max} , nm (ϵ , M⁻¹ cm⁻¹)]: 266 (23480), 374 (7230), 393 (7840), 613 (290).

2.3.4. General oxidation procedure

Catalytic experiments were carried out in a 50 mL glass reaction flask fitted with a water condenser. In a typical procedure, 0.032 mmol of the copper(II) complexes were dissolved in 10 ml of the appropriate solvent. Then 10 mmol alkene was added to the reaction mixture and 30 mmol TBHP was added. The reaction mixture was refluxed for 6 h. The reaction products were monitored after periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

3. Results and discussion

3.1. Characterization of the Schiff base ligands and copper(II) complexes

The complexation behavior of the two Schiff base ligands toward Cu(II) acetate has been investigated (Scheme 1). The new mononuclear complexes **1** and **2** are remarkably stable to air, water and heat. The complexes are neutral, with the metal charge being entirely neutralized by the doubly deprotonated Schiff base ligands. The complexes were characterized by UV–Vis and IR spectroscopy and elemental analysis. The results are in agreement with the formulae drawn in Scheme 1.

The infrared spectra of complexes **1** and **2** and a comparison of them with the spectra of the ligands provides evidence for the coordination mode of the ligands in the complexes. The Schiff base ligands exhibit broad medium intensity bands in the 2969–3430 cm⁻¹ region, which are assigned to intramolecular hydrogen bonding vibrations (O–H…N). Disappearance of these bands in the



Scheme 1. General structure of the Cu(II) complexes.

Table 2UV-Vis data for the ligands and the complexes.

-	-	
Compound	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm M}^{-1}~{\rm cm}^{-1})$	Assignment
H_2L^1	250(18780) 330(7740)	$\pi ightarrow \pi^*$ $n ightarrow \pi^*$
CuL ¹ (1)	262(23040) 373(9010) 388(6890) 600(310)	$\begin{array}{l} \pi \rightarrow \pi^{*} \\ n \rightarrow \pi^{*} \\ \text{MLCT} \\ d \rightarrow d \end{array}$
H_2L^2	260(2050) 335(9380) 430(280)	$egin{array}{ccc} \pi ightarrow \pi^* \ \pi ightarrow \pi^* \ n ightarrow \pi^* \end{array}$
CuL ² (2)	266(23480) 374(7230) 393(7840) 613(290)	$\begin{array}{l} \pi \rightarrow \pi^{*} \\ n \rightarrow \pi^{*} \\ \text{MLCT} \\ d \rightarrow d \end{array}$



spectra of the complexes indicates coordination of the phenolic oxygen after deprotonation. A sharp band due to the v(C=N) (azomethine) group of the free ligands is observed at 1614 (in H₂L¹) and 1627 cm⁻¹ (in H₂L²). Another broad band around 1570 and 1575 cm⁻¹ is related to the aromatic C=C vibration for H₂L¹ and H₂L², respectively. For the synthesized complexes the C=N band was shifted to lower frequency and appeared at 1581 (in 1) and 1617 cm⁻¹ (in 2), indicating the coordination of the azomethine nitrogen to the metal ion. The bonds are broad, probably due to their overlapping with the aromatic ring-carbon stretching [73]. The phenolic (C–O) stretching frequency was observed in the regions around 1230 and 1185 cm⁻¹ for H₂L¹ and H₂L², which shifted to the lower frequency regions around 1220 and 1170 cm⁻¹ in

Fig. 1. Molecular structure of [CuL¹] in 1 (thermal ellipsoids are at the 40% probability level).

complexes **1** and **2**, respectively, indicating coordination through the phenolic oxygen [74,75].

The electronic absorption spectral data for the Schiff base ligands and the Cu(II) complexes are given in Table 2. In the visible region, the broad absorption band at about 600–613 nm, which is assigned to a d–d transition, is consistent with the distorted square-planar geometry of the Cu(II) complexes [76]. At the higher energy region, charge transfer bands were located for both complexes. The broad, slightly intense bands between 350–380 nm and a shoulder around 390 nm could be assigned to O(phenolate) \leftrightarrow Cu^{II} (LMCT or MLCT) [77–80]. More intense bands appeared



Fig. 2. Coordination sphere of Cu1 in 1.



Fig. 3. Molecular packing in the crystal structure of 1.

Table 3

Selected bond lengths (pm) and bond angles ($^{\circ}$) for [CuL¹]·HCCl₃ (**1**).

Cu(1)-O(1)	1.890(1)	N(1)-Cu(1)-N(2)	92.85(6)
Cu(1)-N(1)	1.961(1)	O(1)-Cu(1)-N(1)	91.90(6)
O(1)-C(2)	1.312(2)	C(2)-O(1)-Cu(1)	125.2(1)
N(1)-C(7)	1.296(2)	C(7)-N(1)-Cu(1)	128.2(1)
N(1)-C(10)	1.473(2)	C(2)-C(1)-C(7)	122.7(2)
C(1)-C(2)	1.427(2)	N(1)-C(7)-C(1)	120.9(2)
C(1) - C(7)	1.469(2)	C(7)-N(1)-C(10)	122.5(1)
C(7) - C(8)	1.519(2)	O(2)-Cu(1)-N(2)	92.16(6)
Cu(1)-O(2)	1.884(1)	O(2)-Cu(1)-O(1)	88.22(5)
Cu(1) - N(2)	1.962(1)	C(17)-O(2)-Cu(1)	127.3(1)
O(2)-C(17)	1.308(2)	C(15)-N(2)-Cu(1)	128.6(1)
N(2)-C(15)	1.300(2)	C(17)-C(16)-C(15)	123.0(2)
N(2)-C(12)	1.476(2)	N(2)-C(15)-C(16)	120.9(2)
C(16)-C(17)	1.431(2)	C(15)-N(2)-C(12)	122.0(1)
C(15)-C(16)	1.471(2)	O(1)-Cu(1)-N(2)	164.21(6)
C(15)-C(22)	1.516(2)	O(2)-Cu(1)-N(1)	160.89(6)

in the range 250–340 nm. Based on their extinction coefficients, these are assigned to $\pi \to \pi^*$ and $n \to \pi^*$ ligand transitions.

3.2. Crystal structures of the Cu(II) complexes 1 and 2

3.2.1. Complex 1

Brown needles of $[CuL^1]$ HCCl₃ (**1**), suitable for X-ray diffraction studies, were obtained from a CHCl₃/C₆H₆ solution (1:1). The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. An ORTEP view of **1** is shown in Fig. 1. $(L^1)^{2-}$ acts as a tetradentate ligand. The most interesting phenomenon observed is the fact that both of the phenol groups of the ligand



Fig. 4. Molecular structure of $[{\rm CuL}^2]$ (2) (thermal ellipsoids are at the 40% probability level).



Fig. 5. Coordination sphere of Cu1 in 2.



Fig. 6. Molecular packing in the crystal structure of 2.

are coordinated as phenolate groups, which neutralizes the 2+ charge of Cu^{II}. The coordination sphere of Cu1 in **1** may be described as strongly distorted square planar (Fig. 2). The molecules are stapled in columns along [010], as shown in Fig. 3. Selected bond lengths and bond angles for the complex are summarized in Table 3.

3.2.2. Complex 2

Reddish brown needles of $[CuL^2]$ (**2**), suitable for suitable for Xray diffraction studies, were obtained from a CH₂Cl₂/Et₂O solution (1:1). The compound crystallizes in the triclinic space group

Table 4 Selected bond lengths (pm) and bond angles ($^{\circ}$) for [CuL²] (**2**).

	··· (F···) ···· ···		
Cu(1)-O(1)	1.919(2)	N(1)-Cu(1)-N(2)	90.23(9)
Cu(1)-N(1)	1.952(2)	O(1)-Cu(1)-N(1)	93.36(8)
O(1)-C(2)	1.297(3)	C(2)-O(1)-Cu(1)	126.2(2)
N(1)-C(7)	1.282(3)	C(7)-N(1)-Cu(1)	126.1(2)
N(1)-C(8)	1.471(3)	C(2)-C(1)-C(7)	123.0(2)
C(1)-C(7)	1.442(3)	N(1)-C(7)-C(1)	124.9(2)
C(1)-C(2)	1.429(3)	C(7)-N(1)-C(8)	119.3(2)
Cu(1)-O(2)	1.901(2)	O(2)-Cu(1)-N(2)	93.53(8)
Cu(1) - N(2)	1.957(2)	O(2)-Cu(1)-O(1)	92.59(8)
O(2)-C(13)	1.302(3)	C(13)-O(2)-Cu(1)	127.8(2)
N(2)-C(11)	1.283(3)	C(11)-N(2)-Cu(1)	125.8(2)
N(2)-C(10)	1.471(3)	C(13)-C(12)-C(11)	123.3(2)
C(11)-C(12)	1.443(3)	N(2)-C(11)-C(12)	125.2(2)
C(12)-C(13)	1.420(4)	C(11)-N(2)-C(10)	118.5(2)
		O(1)-Cu(1)-N(2)	151.69(9)
		O(2)-Cu(1)-N(1)	159.98(9)

Table 5

Oxidation of styrene catalyzed by CuL^1 and CuL^2 using different oxygen donors in $\text{CHCl}_{3,\overset{a}{.}}$

Entry	Oxidant	Conversion (%) ^b		TOF $(h^{-1})^{c}$
		CuL ¹	CuL ²	
1	NaIO ₄			
2	H_2O_2	5	4	12.5
3	Urea hydrogen peroxide	4	4	12.5
4	tert-Butyl hydroperoxide	100	100	134.3

^a The molar ratios for Cat.:Styrene:Ox are 0.032:10:30. The reactions were performed in chloroform under air at reflux.

 $^{\rm b}\,$ The GC yields (%) are measured relative to the starting styrene after 6 h.

^c Turnover frequency (TOF) = [mol of epoxide/(mol of catalyst)] per hour.

 $P\bar{1}$ with two molecules in the unit cell. An ORTEP drawing of **2** is shown in Fig. 4. The quadridentate ligand, H_2L^2 , is doubly deprotonated (at the phenolate oxygen atoms) and bind Cu^{II} through two oxygen phenolate atoms and two iminic nitrogen atoms. In addition, a weak contact Cu1–Br1a of 346.6(1) pm can be observed. This influences the coordination sphere of Cu1 (Fig. 5). A strongly distorted square pyramidal arrangement of the ligands around Cu1 is the result. The molecules in **2** are packed in layers parallel to (100) (Fig. 6). Selected bond lengths and bond angles for **2** are collected in Table 4.

The bond distances and angles are in agreement with the values for tetracoordinate divalent copper complexes. The Cu–O(1) (189.0(1) pm in **1** and 191.9(2) pm in **2**), Cu–O(2) (188.4(1) pm in **1** and 190.1(2) pm in **2**), Cu–N(1) (196.1(1) pm in **1** and 195.2(2) pm in **2**) and Cu–N(2) (196.2(1) pm in **1** and 195.7(2) pm in **2**) distances are comparable with the corresponding Cu–O (190 pm) and Cu–N (imine) (194 pm) distances in [Cu(L¹H₂)] (ClO₄)_{1.25}Cl_{0.75}·1.25H₂O [81], Cu–O (188 pm) and Cu–N (193 pm) distances in [Cu(L₂)]ClO₄ [82], Cu–O (190 pm) and Cu–N (195 pm) distances in [CuL³] [83]. The bond lengths and angles within the coordinated ligand are closed to the expected values.

3.3. Catalytic activity studies

The oxidation of cyclooctene and styrene using *tert*-butyl hydroperoxide (TBHP) did not proceed in the absence of catalyst under mild or reflux conditions. Therefore the oxidation of styrene and cyclooctene was carried out with the complexes as catalysts, and in a series of controlled experiments we evaluated the influence of several solvents and various oxygen donors.

3.3.1. Oxidation of styrene

The selective oxidation of styrene to benzaldehyde was carried out with CuL^1 and CuL^2 as catalysts using different oxidants, and the results are presented in Table 5. With H_2O_2 , urea hydrogen peroxide (UHP) and NalO₄ no significant product formation was observed, but using *tert*-butyl hydroperoxide 100% conversion was obtained. Production of benzaldehyde in the oxidation of styrene may be due to the further oxidation of the epoxide formed with the *tert*-butyl hydroperoxide [84].

The styrene conversion was found to be strongly dependent on the solvent nature. Accordingly, different solvents were tested in the oxidation of styrene in the presence of a catalytic amount of CuL^1 and CuL^2 (Figs. 7 and 8) and maximum conversion was obtained in the chloroform.

3.3.2. Oxidation of cyclooctene

Oxidation of cyclooctene with TBHP gave cyclooctene oxide as the sole product. The results for the oxidation of cyclooctene catalyzed by CuL^1 and CuL^2 in various solvents are presented in Figs. 9 and 10. Four different solvents (chloroform, dichloromethane, acetonitrile and 1,2-dichloromethane) were used, and the maximum conversion was obtained in acetonitrile. A comparison



Fig. 7. Effect of solvent on the oxidation of styrene with TBHP in the presence of [CuL¹].



Fig. 8. Effect of solvent on the oxidation of styrene with TBHP in the presence of [CuL²].



Fig. 9. Effect of solvent on the oxidation of cyclooctene with TBHP in the presence of [CuL¹].



Fig. 10. Effect of solvent on the oxidation of cyclooctene with TBHP in the presence of [CuL²].



Scheme 2. Proposed catalytic cycle.

of the catalyst efficiency with other Schiff base complexes shows an enhancement in the oxidation of styrene [41,44,45].

In a proposed mechanism, from the reaction of two copper Schiff base ligands and tert-butyl hydroperoxide a side-on peroxide-bridge binuclear Cu^{II}₂ intermediate (Scheme 2, I) will be formed. This side-on peroxo complex is in equilibrium with the bis-µ-oxo Cu(III) complex (Scheme 2, II) [85] that seems to be the active oxidant species.

4. Conclusion

In conclusion, we have synthesized and characterized two new mononuclear copper(II) complexes $[CuL^1]$ CHCl₃ (1) and $[CuL^2]$ (2) containing two ONNO type Schiff bases, [bis(2-hydroxy-propiophenone)2,2'-dimethylpropan-diamine] (H₂L¹) and [bis(5-bromosalicylaldehyde)2,2'-dimethyl-propandiamine] (H₂L²). Compound **1** crystallizes in the monoclinic space group $P2_1/n$ and compound **2** in the triclinic space group $P\overline{1}$. The coordination sphere of Cu1 in 1 is described as strongly distorted square planar. In 2, a weak Cu1-Br1a contact of 346.6(1) pm influences the coordination sphere of Cu1, and a strongly distorted square pyramidal arrangement of the ligands around Cu1 is the result. The oxidation of stvrene and cyclooctene was carried out with the complexes as catalysts. We evaluated the influence of several solvents and various oxygen donors. In the oxidation of styrene and cyclooctene in the presence of a catalytic amount of CuL¹ and CuL², the maximum conversion was obtained respectively with chloroform and acetonitrile as the solvent, and *tert*-butyl hydroperoxide as the oxidant.

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Appendix A. Supplementary data

CCDC 833742 and 833743 contain the supplementary crystallographic data for complexes 1 and 2. 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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