

Synthesis, characterization and catalytic oxidation of tetrahydrofuran with 16-membered pentaazabis(macrocyclic) copper(II) complexes; $\{[\text{Cu}([\text{16}]\text{aneN}_5)]_2\text{R}\}^{4+}$ (R = aromatic nitrogen–nitrogen linkers)

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Abstract New square-planar bis(macrocyclic)copper(II) complexes containing phenylene bridges between 16-membered pentaaza macrocyclic subunits have been synthesized *via* in-situ one pot template condensation reaction (IOPTCR) of aromatic nitrogen-nitrogen linker (R = 1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenyl methane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone), formaldehyde, bis(1,3-diaminopropane)copper(II) perchlorate and 1,3-dibromopropane in a 1:4:2:2 molar ratio results in the formation of new series of binuclear copper(II) complexes; 1-phenyl- (1); 1,1'-phenyl- (2); 1,1'-diphenylmethan- (3); 1,1'-diphenylether- (4); 1,1'-diphenylsulfone- (5) bis(1,3,7,11,15-pentaazacyclohexadecane)copper(II)), $\{[\text{Cu}([\text{16}]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$. The formation of the macrocyclic framework and the mode of bonding of the complexes have been confirmed by data obtained from elemental analyses, UV-visible, FT-IR, $^1\text{H-NMR}$, electronic spectral studies, conductivity and magnetic susceptibility measurements. These bis(macrocyclic) complexes catalyzed efficiently the selective oxidation of tetrahydrofuran into tetrahydrofuran-2-one and a small amount of tetrahydrofuran-2-ol and 4-hydroxybutyraldehyde using *dil.* H_2O_2 as the oxidant.

Keywords Copper (II) · Bis(macrocyclic) · 16-membered · Pentaaza · Oxidation

Introduction

The design and synthesis of complexes featuring two or more metal centers held in close proximity has received considerable attention because of the potential application of such complexes as models for the active sites of metallo-proteins [1], catalytic reagents that function through the concerted action of multiple metal centers [2], and in the study of magnetic exchange interactions between paramagnetic metal centers [3]. Recently, there has also been interest expressed in the use of polynuclear complexes as selective receptors for a variety of substrate molecules, including phosphates [4], barbiturates [5], oligonucleotides [6], poly-imidazoles [7], phosphorylated peptides [8], and histidine-bearing proteins [9].

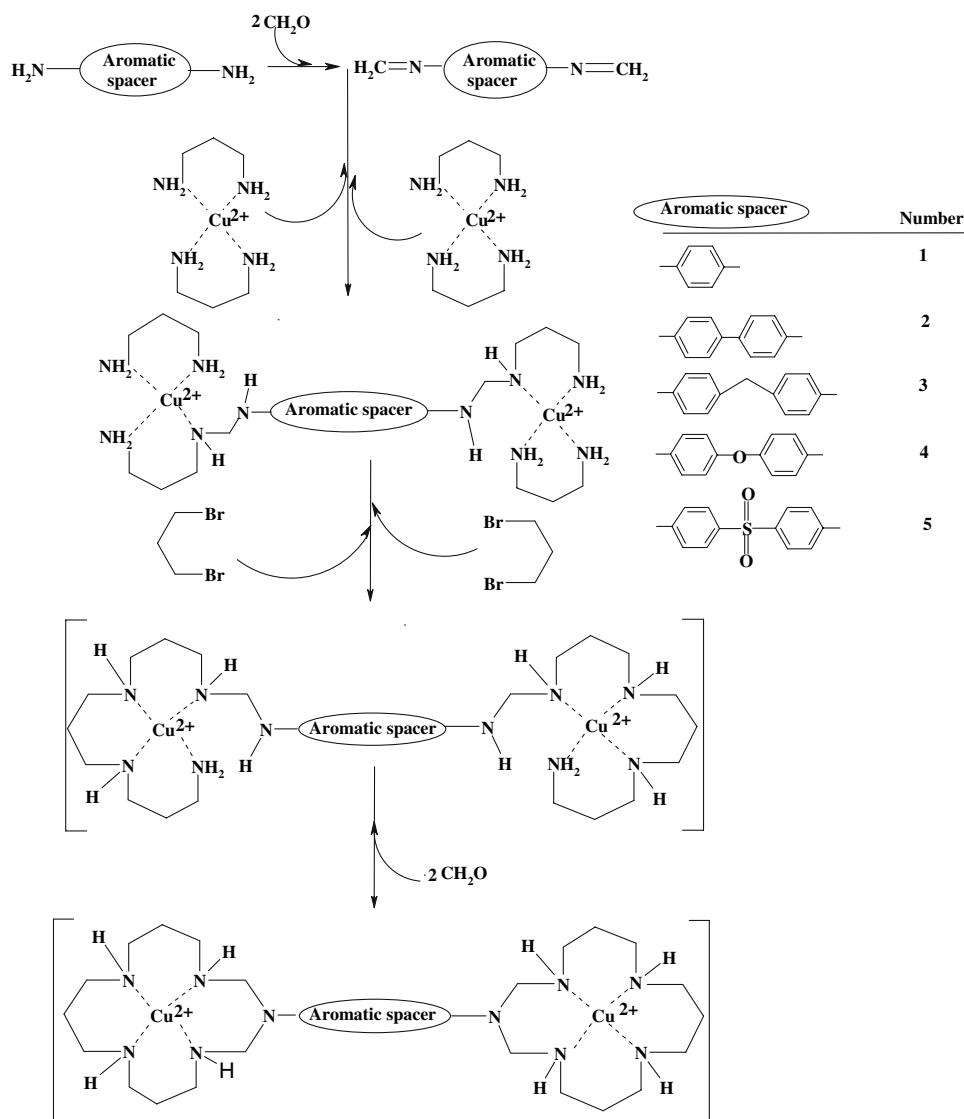
Several articles have been published that cover the various aspects of polyaza macrocyclic complexes [10]. Significant progress has been made in the synthesis of cyclam-based binucleating ligands and structural and physical studies of the corresponding homo- and heterobinuclear complexes. Aspects of bis-cyclam derivatives and some themes involving supramolecular chemistry have been reported so far [11]. Two macrocyclic ligands can be linked through a variety of bridges involving donor atoms (a) N,N-bridged bis(macrocyclics), (b) C–C bonded bi(macrocyclics) and (c) 6,6-C-spirobi(macrocyclics) linking the framework of each tetraaza macrocycle, and many of these bis(macrocyclics) based on cyclam have been studied [11]. The preparation of bis(macrocyclic) nitrogen donor ligands with binucleating properties towards transition metals has recently attracted much attention, and a variety of systems of this type have been reported [12]. Bis(macrocyclics) appear to be better electrocatalysts than are the corresponding mononuclear species [13]. The high thermodynamic and kinetic inertness of transition metal

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complexes of polyaza macrocyclic ligands are significant since they enhance a number of important industrial applications [14–17].

In this paper we report the synthesis and characterization of new bis(macrocyclic) binuclear copper(II) complexes of 1-phenyl-; 1,1'-diphenyl-; 1,1'-diphenylmethane-; 1,1'-diphenylether-; and 1,1'-diphenylsulfone-; bis(1,3,7,11,15-pentaazacyclohexadecane)copper(II) perchlorate, {[Cu([16]aneN₅)₂R}(ClO₄)₄ (**1–5**), (Scheme 1). These binuclear complexes were prepared from the in-situ one pot template condensation reaction (IOPTCR) of nitrogen–nitrogen linker (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone), formaldehyde and bis(1,3-diaminopropane)copper(II) and 1,3-dibromopropane in a 1:4:2:2 molar ratio. These binuclear complexes were then used as catalysts in tetrahydrofuran oxidation reaction by H₂O₂ Fig. 1.

Scheme 1 Formation and suggested structures of the macrocyclic complexes



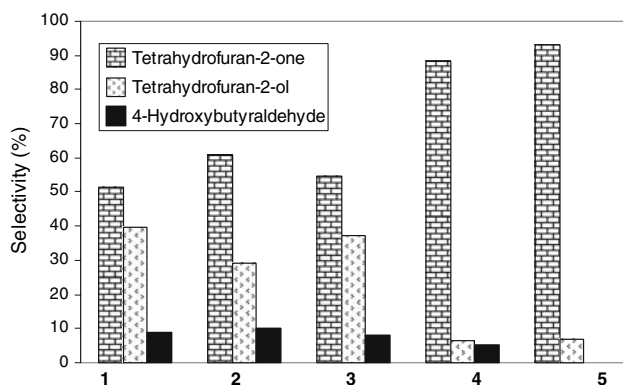


Fig. 1 Oxidation products distribution of tetrahydrofurane with hydrogen peroxide with 16-membered pentaaza bis(macrocyclic) binuclear copper(II)

50, 70 eV. $^1\text{H-NMR}$ spectra were determined for solution in CDCl_3 with tetramethylsilane as internal standard on a Bruker AC 80. The copper contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100–1319) using a flame approach. Magnetic moments were calculated from magnetic susceptibility data obtained using a Johnson Matthey MK–1 magnetic susceptibility balance and conductance measurements with a Metrohm Herisau conductometer E 518. Chlorine was determined gravimetrically.

Preparation of $\{[\text{Cu}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ (**1–5**)

A methanol solution (ca. 50 mL) of bridging diamine (2.5 mmol) “1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone” was placed in a two necked flask and a methanol solution (50 mL) of formaldehyde (10 mmol, 0.85 mL) was added. After 10 min a MeOH solution (50 mL) of bis(1,3-diaminopropane)copper(II) perchlorate (5 mmol) was added and the resulting mixture was stirred for ca. 4 h at reflux. Finally a methanol solution (60 mL) of 1,3-dibromopropane (5 mmol, 1.01 g) were added and the resulting mixture was stirred for ca. 8 h at room temperature. The brown solid product was obtained, filtered, washed with methanol and dried over fused CaCl_2 in desiccators. The crystals were recrystallized from hot methanol. Anal. Calcd for **1**: Cu, 12.01; C, 31.79; H, 5.34; N, 13.23. Found: Cu, 11.81; C, 31.57; H, 5.23; N, 13.37%; Yield: ~40%; μ_{B} , 1.71 B.M.; Λ_{M} , 450 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3230 cm^{-1} ; $\nu(\text{C-N})$, 1180 cm^{-1} ; $\delta(\text{N-H})$, 1650 cm^{-1} ; $\nu(\text{M-N})$, 400 cm^{-1} ; $\text{d} \leftrightarrow \text{d}$, 17860 cm^{-1} ($\epsilon = 80 \text{ M}^{-1} \text{cm}^{-1}$, CH_3NO_2). Anal. Calcd for **2**: Cu, 11.21; C, 36.01; H, 5.33; N, 12.35. Found: Cu, 11.06; C, 35.81; H, 5.25; N, 12.44%; Yield: ~45%; μ_{B} , 1.70 B.M.; Λ_{M} , 458 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3235 cm^{-1} ; $\nu(\text{C-N})$, 1190 cm^{-1} ; $\delta(\text{N-H})$, 1655 cm^{-1} ; $\nu(\text{M-N})$, 405 cm^{-1} ; $\text{d} \leftrightarrow \text{d}$, 18200 cm^{-1}

($\epsilon = 74 \text{ M}^{-1} \text{cm}^{-1}$, CH_3NO_2). Anal. Calcd for **3**: Cu, 11.07; C, 36.62; H, 5.44; N, 12.20. Found: Cu, 10.88; C, 36.50; H, 5.30; N, 12.32%; Yield: ~53%; μ_{B} , 1.71 B.M.; Λ_{M} , 450 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3225 cm^{-1} ; $\nu(\text{C-N})$, 1185 cm^{-1} ; $\delta(\text{N-H})$, 1645 cm^{-1} ; $\nu(\text{M-N})$, 395 cm^{-1} ; $\text{d} \leftrightarrow \text{d}$, 17950 cm^{-1} ($\epsilon = 89 \text{ M}^{-1} \text{cm}^{-1}$, CH_3NO_2). Anal. Calcd for **4**: Cu, 11.05; C, 35.51; H, 5.26; N, 12.17. Found: Cu, 10.88; C, 35.39; H, 5.13; N, 12.30%; Yield: ~55%; μ_{B} , 1.72 B.M.; Λ_{M} , 470 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3240 cm^{-1} ; $\nu(\text{C-N})$, 1200 cm^{-1} ; $\delta(\text{N-H})$, 1660 cm^{-1} ; $\nu(\text{M-N})$, 406 cm^{-1} ; $\text{d} \leftrightarrow \text{d}$, 18100 cm^{-1} ($\epsilon = 90 \text{ M}^{-1} \text{cm}^{-1}$, CH_3NO_2). Anal. Calcd for **5**: Cu, 10.61; C, 34.09; H, 5.05; N, 11.68. Found: Cu, 10.47; C, 33.89; H, 4.92; N, 11.75%; Yield: ~40%; μ_{B} , 1.73 B.M.; Λ_{M} , 450 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3250 cm^{-1} ; $\nu(\text{C-N})$, 1210 cm^{-1} ; $\delta(\text{N-H})$, 1670 cm^{-1} ; $\nu(\text{M-N})$, 410 cm^{-1} ; $\text{d} \leftrightarrow \text{d}$, 18,300 cm^{-1} ($\epsilon = 90 \text{ M}^{-1} \text{cm}^{-1}$, CH_3NO_2).

Preparation of $\{[\text{Ni}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ (R = Benzidine)

This bis(macrocyclic) dinuclear nickel(II) complexes was prepared by a method similar to that for $\{[\text{Cu}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ except that $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was used instead of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Anal. Calcd for $\text{C}_{28}\text{H}_{56}\text{N}_{10}\text{Cl}_4\text{O}_{16}\text{Ni}_2$: Ni, 11.15; C, 31.94; H, 5.36; N, 13.30. Found: Ni, 11.01; C, 31.80; H, 5.24; N, 13.39%; Yield: ~46%; μ_{B} , -0.08 B.M.; Λ_{M} , 455 ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$); $\nu(\text{N-H})$, 3225 cm^{-1} ; $\nu(\text{C-N})$, 1175 cm^{-1} ; $\delta(\text{N-H})$, 1670 cm^{-1} .

Oxidation of tetrahydrofuran; general procedure

In a typical procedure, a mixture of $\{[\text{Cu}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ (**1–5**) as catalyst (0.35 mmol) and THF (0.05 mol) was stirred for 30 min in a 50 mL round bottom two-necked flask equipped with a condenser and dropping funnel, under N_2 atmosphere. Then 0.05 mol of the H_2O_2 (30% in H_2O) was added *via* the dropping funnel. The mixture was then heated under reflux for 8 h. The product yields were determined by GC analysis using naphthalene as internal standard. The solvent was removed under reduced pressure and the residue purified by chromatography to give γ -butyrolactone, which was further confirmed by $^1\text{H-NMR}$ analysis [δ_{H} (CDCl_3) 2.26 (2H, q, J 6.6, CH_2), 2.46 (2H, t, J 7.0, CH_2) and 4.32 (2H, t, J 6.9 Hz, CH_2)], a small amount of the corresponding tetrahydrofuran-2-ol and 4-hydroxybutyraldehyde.

Result and discussion

Novel 16-membered pentaazabis(macrocyclic) copper(II) complexes; $\{[\text{Cu}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$; have been synthesized by in-situ one pot template condensation reaction

(IOPTCR) between aromatic nitrogen–nitrogen linkers (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenyl methane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone), formaldehyde, bis(1,3-diaminopropane) copper(II) perchlorate and 1,3-dibromopropane in a 1:4:2:2 molar ratio (Scheme 1). All of the complexes are soluble in polar solvents like DMSO, DMF, CH₃CN and H₂O. The results of elemental analyses agree well with the proposed bis(macrocyclic) copper(II) complexes. The molar conductances of the complexes in methanol show that they are electrolytes.

The prominent IR spectral bands are presented in experimental section. In all of these complexes a single sharp band in the region 3230–3250 cm⁻¹ corresponds to the coordinated $\nu(\text{N-H})$ vibration of a secondary amine moiety. The IR spectra show no bands assignable to primary amine groups, expected from either 1,3-diaminopropane or aromatic nitrogen–nitrogen linkers, or the carbonyl group stretching vibrations corresponding to formaldehyde indicating that the proposed bis(macrocyclic) bimetallic complexes have been formed. The weak-intensity band appearing at 1650–1670 cm⁻¹ is assigned to $\delta(\text{N-H})$ vibrations for secondary amine. All the complexes show a strong band in the region 1180–1210 cm⁻¹ assignable to the $\nu(\text{C-N})$ group. All of the complexes show strong bands in the regions 2855–2965 and 1420–1450 cm⁻¹ which may corresponds to $\nu(\text{C-H})$ and $\delta(\text{C-H})$ vibrations, respectively. The spectra of perchlorate complexes gave additional bands at 900–1000 cm⁻¹ consistent with the perchlorate group.

For more investigation of structure, we synthesized the diamagnetic bis(macrocyclic) dinickel(II) complex, $[(\text{Ni}([\text{16}]\text{aneN}_5))_2\text{R}](\text{ClO}_4)_4$ (R = benzidine). The magnetic moments ($-0.08 \mu_{\text{B}}$) of the nickel(II) complexes measured in the solid state correspond to the square-planar coordination geometry of the complexes. The diamagnetic

nature of the nickel(II) complex of $[(\text{Ni}([\text{16}]\text{aneN}_5))_2\text{R}](\text{ClO}_4)_4$ has allowed its characterization by NMR spectroscopy. ¹H-NMR spectra of the $[(\text{Ni}([\text{16}]\text{aneN}_5))_2\text{R}](\text{ClO}_4)_4$ complex exhibit very broad peaks in D₂O, CH₃CN-d₃, and Me₂SO-d₆ but sharp resolvable peaks in CH₃NO₂-d₃. This indicates that a considerable amount of paramagnetic octahedral species of $[(\text{Ni}([\text{16}]\text{aneN}_5))_2\text{R}](\text{Solvent})_2^{4+}$ exists in the donating solvents, where as the Ni(II) complex of “ $([\text{16}]\text{aneN}_5)_2\text{R}$ ” exist primarily as diamagnetic square-planar in CH₃NO₂-d₃. The ¹H-NMR spectra of bis(macrocyclic)dinickel(II); $\{[\text{Ni}([\text{16}]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$; complex recorded in CH₃NO₂-d₃ show a multiplet in the region 6.30–6.38 ppm ascribed to –NH (8H) protons. A multiplet appearing in the region 3.30–3.40 ppm may be assigned to methylene protons of the aminal moiety [N–CH₂–N–(8H)]. Another multiplet in the region 1.90–2.10 ppm may be assignable to methylene protons [C–CH₂–C (12H)] of the propane chain moiety. The complexes also show a multiplet in the ~7.37 ppm region, assigned to aromatic ring protons. Furthermore, a multiplet observed for all the complexes in the region 2.29–2.40 may correspond to the methylene protons [C–CH₂–N– (24H)] of the propylene diamine moiety.

The electronic spectra of bis(macrocyclic) binuclear complexes are comparable to of square-planar copper(II) complexes with similar macrocycles, indicating that the tetraaza ligands of this study do not differ significantly from the similar ligands with respect to the ligand field strength [11, 19]. The brown complexes $\{[\text{Cu}([\text{16}]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$, readily dissolve in polar solvents such as H₂O, CH₃CN, CH₃NO₂, Me₂SO₂. The $\{[\text{Cu}([\text{16}]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$, are extremely stable in the solid state and in solution.

The trend observed in Table 1 can be explained by the donor ability of ligand available in the complex catalysts.

Table 1 Substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 16-membered pentaaza bis(macrocyclic) binuclear copper(II) complexes^a

Catalyst	Conversion (%)	Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-hydroxybutyraldehyde
1	53.4	51.3	39.6	9.1
2	88.5	60.6	29.1	10.3
3	60.4	54.5	37.4	8.1
4	79.6	88.4	6.5	5.1
5	92.7	93.2	6.8	–
Cu(ClO ₄) ₂	45.7	40.8	37.6	21.6

^a Conditions: Catalyst = 0.35 mmol, THF = 0.05 mol, H₂O₂ = 0.05 mol, Time = 8 h, Reflux

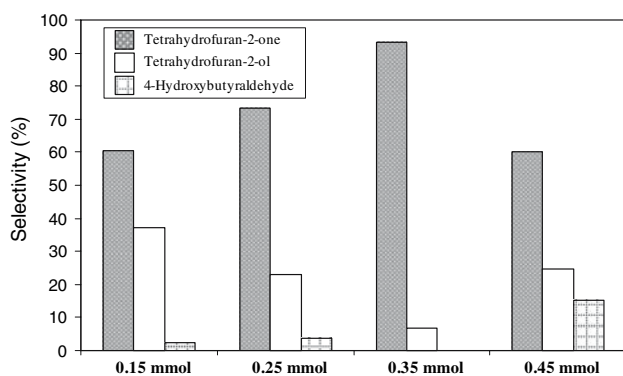


Fig. 2 Effect of catalyst concentration on substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H_2O_2 in the presence of **5** as catalyst (Conditions: THF = 0.05 mol, H_2O_2 = 0.05 mol, Time = 8 h, Reflux)

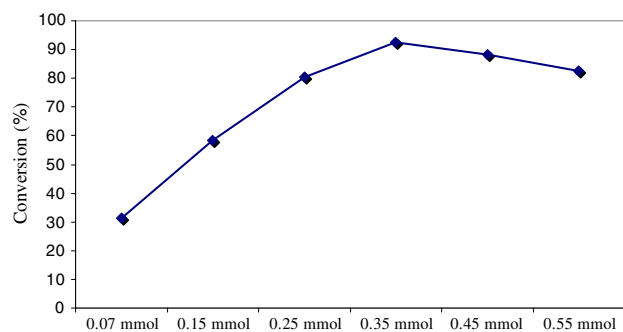


Fig. 3 Effect of catalyst concentration on substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H_2O_2 in the presence of **5** as catalyst (Conditions: THF = 0.05 mol, H_2O_2 = 0.05 mol, Time = 8 h, Reflux)

As Wang and co-workers have pointed out recently, the key point in the conversion of THF to the products is the reduction of L-M^{n+} to $\text{L-M}^{(n-1)+}$. This reduction to $\text{L-M}^{(n-1)+}$ is facilitated with the ligands available around the metal cation [20].

The effect of varying the catalyst concentration on the oxidation of tetrahydrofuran with hydrogen peroxide and **5**

as catalyst is shown in Figs. 2 and 3. With an increase in the concentration of the catalyst a decrease in the yield of tetrahydrofuran-2-ol was observed, while there was an increase in the yield of tetrahydrofuran-2-one. The yield of 4-hydroxybutyraldehyde remained almost constant. The decrease in percentage conversion at higher catalyst concentration is attributed to the formation of μ -oxo dimers, which inhibit the catalytic cycle.

Effect of time on the reaction results were studied by running the tetrahydrofuran reaction in 2, 4, 6, 8, 10, 12 and 14 h. As we can see in Table 2 increasing time from 2 to 8 h has increased the conversion percentages from 50.7 to 92.7. No conversion enhancement was observed beyond 8 h.

The effect of various solvents (Tables 3, 4, 5) on the oxidation of tetrahydrofuran with **1–5** as catalysts was also studied. In all the oxidation reactions, tetrahydrofuran-2-one was formed as the major product. When the reaction was carried out in a coordinating solvent like MeCN the conversion decreased. This might be attributed to the donor number of MeCN (14.1) and therefore, its higher ability to occupy the vacant spaces around the metal center and prevent the approach of oxidant molecules. The efficiency of the catalysts for oxidation of tetrahydrofuran in different solvents decreases in the order: THF > MeNO_2 > MeOH > MeCN (Fig. 4).

Conclusions

Square-planar copper(II) complexes of [1-phenyl-(**1**); 1,1'-phenyl-(**2**); 1,1'-diphenylmethane-(**3**); 1,1'-diphenylether-(**4**); 1,1'-diphenylsulfone-(**5**)] bis(1,3,7,11,15-pentaazacyclohexadecane)copper(II), $\{[\text{Cu}(\text{[16]aneN}_5)_2\text{R}](\text{ClO}_4)_4\}$ have been prepared by the one-pot template reactions of nitrogen–nitrogen linker (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone), formaldehyde, bis(1,3-diaminopropane)copper(II) perchlorate and 1,3-dibromopropane

Table 2 Effect of time on substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H_2O_2 in the presence of **5** as catalyst^a

Time (h)	Conversion (%)	Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-hydroxybutyraldehyde
2	50.7	41.0	59.0	–
4	71.4	53.1	46.9	–
6	86.5	74.6	25.4	–
8	92.7	93.2	6.8	–
10	89.3	91.8	5.7	2.5
12	84.5	91.1	5.1	3.8
14	80.7	89.9	4.7	5.4

^a Conditions: THF = 0.05 mol, H_2O_2 = 0.05 mol, Catalyst = 0.35 mmol, Reflux

Table 3 Substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 16-membered pentaaza bis(macrocylic) binuclear copper(II) complexes in methanol^a

Catalyst	Conversion (%)	Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-hydroxybutyraldehyde
1	37.5	46.1	42.6	11.3
2	70.4	53.8	33.7	12.5
3	43.7	49.1	40.1	10.8
4	63.8	77.2	13.2	9.6
5	75.9	78.1	14.5	7.4

^a Conditions: THF = 0.05 mol, H₂O₂ = 0.05 mol, Catalyst = 0.35 mmol, Time = 8 h, Reflux

Table 4 Substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 16-membered pentaaza bis(macrocylic) binuclear copper(II) complexes in nitromethane^a

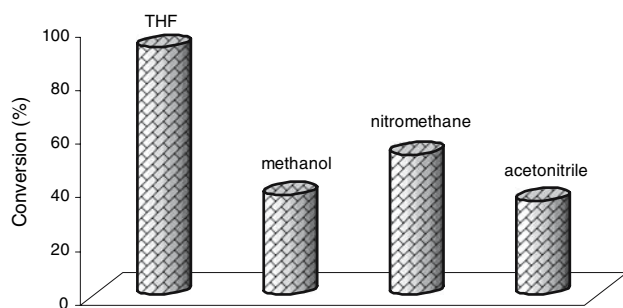
Catalyst	Conversion (%)	Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-hydroxybutyraldehyde
1	52.6	49.1	40.2	10.7
2	86.1	58.3	31.9	9.8
3	58.4	53.4	39.1	7.5
4	76.0	82.7	12.6	4.7
5	88.3	84.5	13.1	2.4

^a Conditions: THF = 0.05 mol, H₂O₂ = 0.05 mol, Catalyst = 0.35 mmol, Time = 8 h, Reflux

Table 5 Substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H₂O₂ in the presence of 16-membered pentaaza bis(macrocylic) binuclear copper(II) complexes in acetonitrile^a

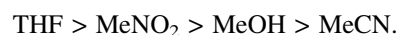
Catalyst	Conversion (%)	Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-hydroxybutyraldehyde
1	35.2	43.6	43.7	12.7
2	66.7	52.1	34.5	13.4
3	40.4	47.2	41.2	11.6
4	60.1	74.1	14.7	11.2
5	72.6	75.1	15.3	9.6

^a Conditions: THF = 0.05 mol, H₂O₂ = 0.05 mol, Catalyst = 0.35 mmol, Time = 8 h, Reflux

**Fig. 4** Oxidation of tetrahydrofuran with hydrogen peroxide in various solvent with 16-membered pentaaza bis(macrocycle) binuclear copper(II) complexes in the presence of **5**

in a 1:4:2:2 molar ratio. The spectra of **1–5** show that the four nitrogen atoms are coordinated to the copper(II) ion. These complexes are found to be effective catalysts in the selective oxidation of tetrahydrofuran. The following points may be noted:

- The major oxidation product of tetrahydrofuran in this study is tetrahydrofuran-2-one.
- Tetrahydrofuran alone, in the absence of bis(macrocycle) was not catalytically active.
- The activity of tetrahydrofuran oxidation decreases in the series: **5** > **2** > **4** > **3** > **1**.
- The reactions show appreciable solvent effects and activity of oxidation decreases:



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