

# Binuclear copper(II) complexes of new bis(macrocyclic) 16-membered pentaaza subunits are linked together by bridging nitrogen of amine: Synthesis, characterization and catalytic activity

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## Abstract

New bis(macrocyclic) dicopper(II) complexes containing phenylene bridges between 16-membered pentaaza macrocyclic subunits have been synthesized via one-pot template condensation of nitrogen–nitrogen linker (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfon), formaldehyde, 1,3-diaminopropane, copper(II) and 2,4-pentanedione in a 1:4:4:2:2 molar ratio results in the formation of new series of binuclear copper(II) complexes; “dichloro[1-phenyl- (1); 1,1'-phenyl- (2); 1,1'-diphenylmethane- (3); 1,1'-diphenylether- (4); 1,1'-diphenylsulfon- (5)] bis(8,10-dimethyl-1,3,7,11,15-pentaazacyclohexadeca-7,11-diene)copper(II),  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{RCl}_4]\}^+$ .  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{R}]\}(\text{ClO}_4)_4$  (6–10) was prepared by a method similar to that for  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{RCl}_4]\}$  (1–5) except that copper(II) perchlorate was used instead of copper(II) chloride. Elemental analyses, IR, UV–vis spectroscopy, conductometric and magnetic measurements have been used to characterize the new bis(macrocyclic) binuclear copper(II) complexes. The spectra of  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{R}]\}^{+4}$  shows that the four nitrogen atoms are coordinated to the copper(II) ion. 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 diluted  $\text{H}_2\text{O}_2$  as the oxidant. The influence of solvent, time and concentration of catalyst has been studied. 1,1'-Diphenylsulfonbis(8,10-dimethyl-1,3,7,11,15-pentaazacyclohexadeca-7,11-diene)copper(II) perchlorate (10) shows significantly higher catalytic activity than other bis(macrocyclic) binuclear copper(II) complexes.

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**Keywords:** One-pot template; Bis(macrocyclic); Copper(II); Oxidation

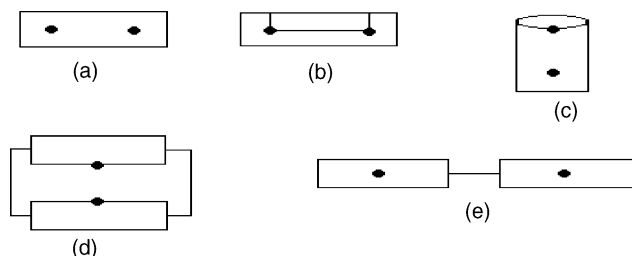
## 1. Introduction

Binuclear copper(II) complexes containing two metal centers in close proximity are the interesting topic subject of recent extensive investigation since this structural unit is involved in a variety of important biochemical processes, such as oxygen activation by oxidase and monooxygenase enzymes [1–9]. The active sites of hemocyanin and tyrosinase possess this type of molecular arrangement and are thought to be relatively similar based on spectroscopic ev-

idence [10], in sharp contrast with their different biological functions. On one hand, there is a theoretical interest for such compounds, since one can expect that two metal centers (especially if paramagnetic) kept at a fixed distance not too far from each other will interact. This is often reflected in their magnetic properties or in their electrochemistry.

Macrocyclic have often been selected for this purpose because, being more rigid than open chain ligands, they allow one to fix the position, and therefore, the distance between the two metal ions in an easier way. Schematically, the different strategies are shown in Scheme 1. The first type of such ligands consists of a ring large enough to

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Scheme 1. Possible topologies for macrocyclic binuclear complexes.

accommodate two metal ions in it (Scheme 1a) [11]. Variations of the structures have produced systems in which the metal–metal distance can be controlled, and thus different exogenous ligands can be bound. The idea of large rings has also been developed into macrobicyclic systems with axial (Scheme 1b), lateral (Scheme 1c) and cylindrical (Scheme 1d) topologies [12,13]. A different approach is found in the case of bis(macrocyces) (Scheme 1e) in which two rings are connected either by a carbon–carbon [14] or a nitrogen–nitrogen [15] linker. Depending on its length, the metal–metal interaction can be controlled and thus tuned. Most of the bis(macrocyces) are homotopic, i.e. have two identical rings with the same donor sets. However, heteroditopic bis(macrocyces) have also been prepared [16], although their synthesis is more demanding than that of homoditopic systems.

Several articles have been reported in recent years on the coordination chemistry of bis(macrocylic) molecules in which two potentially coordinating tetraaza subunits are linked together by bridging the amine nitrogen or carbon atom of the ligand backbone [14–16]. In order to gain further insight into the above properties of macrocyclic complexes, the synthesis and characterization of two new series of binuclear bis(macrocylic) complexes were recorded here (Scheme 2). These binuclear complexes were then used as catalysts in tetrahydrofuran oxidation reaction by  $\text{H}_2\text{O}_2$ .

## 2. Experimental

### 2.1. Materials

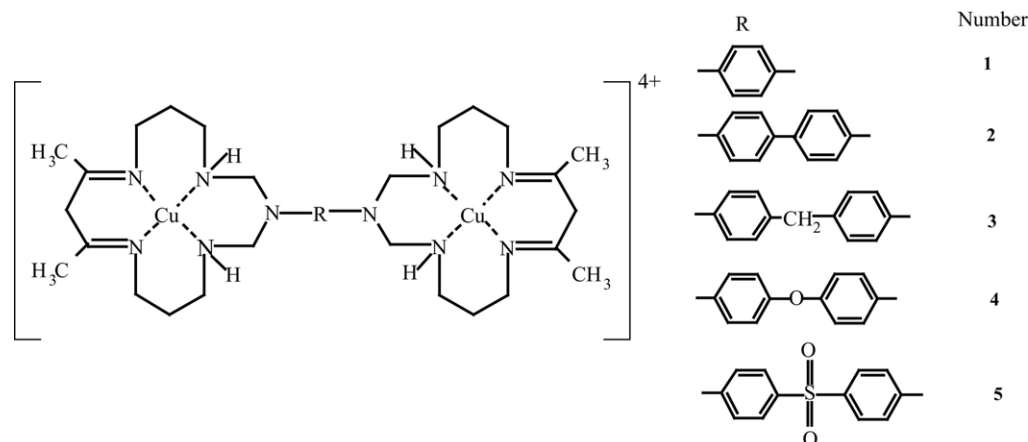
All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. For the spectroscopic measurements,  $\text{H}_2\text{O}$  was distilled and organic solvents were purified according to the literature method [17].

### 2.2. Safety note

Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

### 2.3. Physical measurements

FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectra of the complexes were taken on a Shimadzu UV–vis scanning spectrometer (Model 2101 PC). The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. The products were analysed by GC–MS, using a Philips Pu 4400 Chromatograph (1.5 m, 3% OV-17 Column), Varian 3400 Chromatograph (25 m, DB-5 Column) coupled with a QP Finnegan MAT INCOF 50, 70 eV. H NMR spectra were determined for solution in  $\text{CDCl}_3$  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.



Scheme 2.

#### 2.4. Preparation of $\{[Cu(Me_2[16]aneN_5)]_2RCl_4\}$ (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'-diaminodiphenylsulfon” was placed in a two necked flask and a methanol solution (50 ml) of formaldehyde (0.01 mol, 0.85 ml) was added. After 10 min, a methanol solution (50 ml) of 1,3-diaminopropane (0.01 mol, 0.83 ml) was added simultaneously. Finally, a methanol solution (60 ml) of the  $CuCl_2 \cdot 2H_2O$  (5 mmol, 0.85 g) and 2,4-pentanedione (5 mmol, 0.52 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  $[Cu_2(1)Cl_4]$ : C, 45.26; H, 6.59; N, 16.49; Cu, 14.97. Found: C, 45.14; H, 6.47; N, 16.55; Cu, 14.87%. Anal. calcd. for  $[Cu_2(2)Cl_4]$ : C, 49.32; H, 6.48; N, 15.13; Cu, 13.74. Found: C, 49.25; H, 6.39; N, 15.22; Cu, 13.65%. Anal. calcd. for  $[Cu_2(3)Cl_4]$ : C, 49.87; H, 6.60; N, 14.90; Cu, 13.53. Found: C, 49.77; H, 6.51; N, 15.02; Cu, 13.44%. Anal. calcd. for  $[Cu_2(4)Cl_4]$ : C, 48.50; H, 6.37; N, 14.87; Cu, 13.50. Found: C, 48.39; H, 6.29; N, 14.96; Cu, 13.41%. Anal. calcd. for  $[Cu_2(5)Cl_4]$ : C, 46.13; H, 6.06; N, 14.15; Cu, 12.85. Found: C, 46.01; H, 5.92; N, 14.26; Cu, 12.74%.

#### 2.5. Preparation of $\{[Cu(Me_2[16]aneN_5)]_2R\}(ClO_4)_4$ (6–10)

These bis(macrocyclic) dinuclear copper(II) complexes were prepared by a method similar to that for  $\{[Cu(Me_2[16]aneN_5)]_2RCl_4\}$  (1–5) except that  $Cu(ClO_4)_2 \cdot 6H_2O$  was used instead of  $CuCl_2 \cdot 2H_2O$ . Anal. calcd. for **6**: C, 34.78; H, 5.07; N, 12.67; Cu, 11.50. Found: C, 34.65; H, 4.97; N, 12.76; Cu, 11.41%. Anal. calcd. for **7**: C, 38.64; H, 5.08; N, 11.85; Cu, 10.76. Found: C, 38.52; H, 4.98; N, 11.97; Cu, 10.68%. Anal. calcd. for **8**: C, 39.19; H, 5.19; N, 11.71; Cu, 10.63. Found: C, 39.05; H, 5.07; N, 11.82; Cu, 10.50%. Anal. calcd. for **9**: C, 38.12; H, 5.01; N, 11.70; Cu, 10.62. Found: C, 38.00; H, 4.89; N, 11.85; Cu, 10.50%. Anal. calcd. for **10**: C, 36.65; H, 4.82; N, 11.24; Cu, 10.21. Found: C, 36.53; H, 4.70; N, 11.36; Cu, 10.10%.

#### 2.6. Preparation of $\{[Ni(Me_2[16]aneN_5)]_2R\}(ClO_4)_4$

This bis(macrocyclic) dinuclear nickel(II) complexes were prepared by a method similar to that for  $\{[Cu(Me_2[16]aneN_5)]_2R\}(ClO_4)_4$  except that  $Ni(ClO_4)_2 \cdot 6H_2O$  was used instead of  $Cu(ClO_4)_2 \cdot 6H_2O$ . Anal. calcd. for  $C_{38}H_{48}O_{17}N_{10}Cl_4Ni_2$ : C, 38.31; H, 4.94; N, 11.85; Ni, 9.78. Found: C, 38.44; H, 5.05; N, 11.79; Ni, 9.89%.

#### 2.7. Oxidation of tetrahydrofuran; general procedure

In a typical procedure, a mixture of  $\{[Cu(Me_2[16]aneN_5)]_2R\}(ClO_4)_4$  (6–10) as catalyst (0.35 mmol) and THF

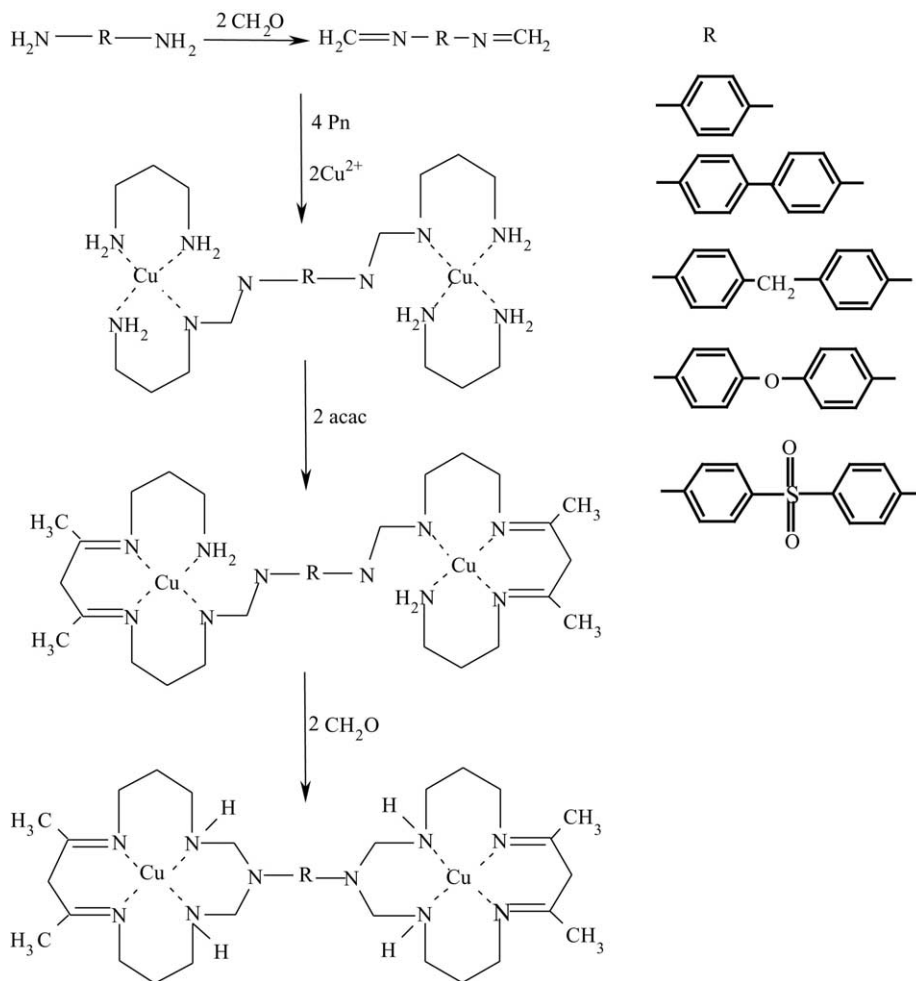
(0.05 mol) was stirred for 30 min in a 50 ml round bottom two-necked flask equipped with a condenser and dropping funnel, under  $N_2$  atmosphere. Then, 0.05 mol of the  $H_2O_2$  (30% in  $H_2O$ ) was added via the dropping funnel. The mixture was then heated under reflux for 8 h. The product yields 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  $\gamma$ -butyrolactone, which was further confirmed by  $^1H$  NMR analysis [ $\delta_H$  ( $CDCl_3$ ) 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.

### 3. Result and discussion

#### 3.1. Synthesis and characterization

Sixteen-membered pentaaza bis(macrocyclic) copper(II) complexes were prepared by reacting 1 equivalent of diamine as bridging unites (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulfon), 4 equivalent of formaldehyde, 4 equivalent of 1,3-diaminopropane with 2 equivalent of 2,4-pentanedione in the presence of the copper(II) ion (Schemes 2 and 3). It was observed that the 16-membered pentaaza bis(macrocyclic) product obtain from the reaction was largely effected by the molar ratio of the reactant.  $\{[Cu(Me_2[16]aneN_5)]_2R\}(ClO_4)_4$  was prepared by a method similar to that for  $\{[Cu(Me_2[16]aneN_5)]_2RCl_4\}$  except that copper(II) perchlorate was used instead of copper(II) chloride. The synthesis was remarkably facile and proceeds smoothly. The complexes are stable in the atmosphere and are polycrystalline. Elemental analysis agrees with the bis(macrocyclic) complex formula as shown in Scheme 2. The molar conductance's of all the  $\{[Cu(Me_2[16]aneN_5)]_2RCl_4\}$  complexes in DMSO show that they are non-electrolytes.

The important IR spectral bands of all the complexes (in Table 1) exhibit an intense band in the 3240–3300  $cm^{-1}$  region, which may be assigned [18] to  $\nu_{(N-H)}$  of the coordinated secondary amino group. All the complexes show bands in the 1597–1621  $cm^{-1}$  region, attributed to coordinated  $\nu_{(C=N)}$  [19]. Together with these results, the most important feature is that the spectra of the bis(macrocyclic) complexes have no bands assignable to carbonyl group stretching modes. A band in the 1172–1185  $cm^{-1}$  region is assigned to the  $\nu_{(C-N)}$  vibration in all complexes, and absorption bands in the 2800–2850  $cm^{-1}$  and 1445–1455  $cm^{-1}$  region, corresponding to  $\nu_{(C-H)}$  and  $\delta_{(C-H)}$ , respectively. Bands in the 445–466  $cm^{-1}$  and 312–321  $cm^{-1}$  regions may be assigned to  $\nu_{(M-N)}$  and  $\nu_{(M-Cl)}$ , respectively. The spectra of perchlorate complexes gave additional bands at 900–1000  $cm^{-1}$  consistent with the perchlorate group [20].



Scheme 3.

The magnetic moment of the bis(macrocycle) binuclear copper(II) complexes is a little higher than the calculated value in accordance with typical, well-known octahedral complexes of  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)]_2\text{RCl}_4\}$  [21]. The magnetic moments of the  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$

measured in the solid state correspond to the square-planar coordination geometry of the complexes. The paramagnetic nature of the copper(II) complexes have not allowed to characterization by NMR spectroscopy. For more investigation, diamagnetic nickel(II)  $\{[\text{Ni}(\text{Me}_2[16]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$

Table 1  
IR, UV–vis, magnetic and conductance data of bis(macrocycle) dinuclear copper(II) complexes

Complex	Electronic spectra $\lambda_{\text{max}}$ (nm) ( $\epsilon$ , $\text{mol}^{-1} \text{cm}^{-1}$ )	IR (KBr, $\text{cm}^{-1}$ )					$\Lambda$ ( $\text{cm}^2 \Omega^{-1} \text{mol}^{-1}$ )	$\mu_{\text{eff}}$ (B.M.)
		$\nu_{\text{N-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-N}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$		
<b>6</b>	20800 <sup>a</sup> , 20200 <sup>b</sup>	3245	1597	1172	445	–	440 <sup>a</sup>	1.76
<b>1</b>	(14800, 21600) <sup>c</sup>	3260	1604	1175	457	312	11 <sup>c</sup>	1.75
<b>7</b>	20960 <sup>a</sup> , 20280 <sup>b</sup>	3265	1608	1177	450	–	445 <sup>a</sup>	1.75
<b>2</b>	(14860, 21750) <sup>c</sup>	3272	1610	1179	461	314	20 <sup>c</sup>	1.74
<b>8</b>	20850 <sup>a</sup> , 20240 <sup>b</sup>	3260	1606	1175	448	–	447 <sup>a</sup>	1.73
<b>3</b>	(14810, 21580) <sup>c</sup>	3266	1614	1180	460	314	18 <sup>c</sup>	1.76
<b>9</b>	20980 <sup>a</sup> , 20300 <sup>b</sup>	3280	1610	1179	453	–	447 <sup>a</sup>	1.68
<b>4</b>	(14830, 21810) <sup>c</sup>	3285	1616	1184	464	318	15 <sup>c</sup>	1.75
<b>10</b>	21050 <sup>a</sup> , 20380 <sup>b</sup>	3290	1615	1181	457	–	451 <sup>a</sup>	1.66
<b>5</b>	(14870, 21860) <sup>c</sup>	3297	1621	1185	466	321	12 <sup>c</sup>	1.74

<sup>a</sup> In nitromethane solutions unless otherwise specified.

<sup>b</sup> In water solutions.

<sup>c</sup> In DMSO solutions.

(R = 1,1'-diphenylsulfon-)" complex was synthesized and studied by  $^1\text{H}$  NMR.  $^1\text{H}$  NMR spectra of the complex exhibit very broad peaks in  $\text{D}_2\text{O}$ ,  $\text{CH}_3\text{CN}-d_3$  and  $\text{Me}_2\text{SO}-d_6$  but sharp resolvable peaks in  $\text{CH}_3\text{NO}_2-d_3$ . This indicates that a considerable amount of paramagnetic octahedral species of  $\{[\text{Ni}(\text{Me}_2[16]\text{aneN}_5)]_2\text{R}(\text{solvent})_2\}^{+4}$  exists in the donating solvents, whereas the Ni(II) complexes of **10** exist primarily as diamagnetic square-planar in  $\text{CH}_3\text{NO}_2-d_3$ . The  $^1\text{H}$  NMR spectra of the bis-macrocyclic nickel(II) complex shows two multiplet signal in the 6.16–6.20 and 3.15–3.28 ppm regions which correspond to the secondary amino protons and methylene protons of the aldehyde moiety (C–NH–C, 4H; N–CH<sub>2</sub>–N, 8H), respectively. Three more multiplet signals were observed for the complex in the 2.20–2.25, 2.34–2.39 and 2.50–2.53 ppm regions may be due to the three non-equivalent methylene protons (N–CH<sub>2</sub>–C, 8H; C–CH<sub>2</sub>–C, 8H and C–CH<sub>2</sub>–N=, 8H) of the amine moiety. The complex shows a multiplet signal in the 7.31–7.42 ppm region, which is assigned to aromatic ring protons. Furthermore, two sharp signal in the 2.10 and 2.75 ppm regions may be attributed to the imines methyl and methylene protons of acetyl acetone (CH<sub>3</sub>–C=N, 12H and N=C–CH<sub>2</sub>–C=N, 4H), respectively.

The electronic spectra (Table 1) of bis(macrocyclic) binuclear complexes are comparable to those of square-planar copper(II) complexes with tetraaza macrocycles, indicating that the pentaaza ligands of this study do not differ significantly from the tetraaza ligands with respect to the ligand field strength [22–31]. The brown complexes  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$  readily dissolve in polar solvents such as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{Me}_2\text{SO}_2$ . The  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$  are extremely stable in the solid state and in solution and are relatively stable against ligand dissociation even in highly acidic solutions. The molar conductance values of ( $440 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ ) measured in water corresponds to 1:4 electrolytes.

### 3.2. Catalytic activities

One of the major current challenges in synthetic organic chemistry is the selective oxidation of organic compounds using  $\text{O}_2$ , TBHP,  $\text{H}_2\text{O}_2$  and PhIO as oxygen donors in the presence of transition metal catalysts [32]. The selective oxidative functionalization at the  $\alpha$  C–H bond of ethers is one of the most useful reactions in organic synthesis, because it

provides for the efficient preparation of esters (or lactones in the case of cyclic ethers) [33]. Such conversions are usually accomplished by the use of either stoichiometric amounts of  $\text{CrO}_3$ ,  $\text{Pb}(\text{OAc})_4$  and  $\text{RuO}_3$  as oxidants [34,35], or the catalytic amounts of  $\text{RuO}_4$  in the presence of  $\text{OCl}^-$  or  $\text{IO}_4^-$  [36]. Most recently, several new oxidation systems have been described using transition metal complexes for the transformation of ethers to ester [37], THF was also oxidized to the corresponding hydroxyaldehyde with cobalt(II) porphyrin by employing a combination of dioxygen and 2-methylpropanal [38]. Furthermore, Sudalaj and co-workers have reported that the titanium silicates (TS-1, TS-2) catalyzed efficiently the selective oxidation of THF with  $\text{H}_2\text{O}_2$  as the oxidant to  $\gamma$ -butyrolactone [39]. In our recent publications, we reported the role of some transition metals and their complexes included within zeolite Y as catalysts [40–43]. In both cases, it was observed that these catalysts were able to transfer oxygen from TBHP and  $\text{H}_2\text{O}_2$  to the substrate and hydroxylate to the hydrocarbons. Recently, we found that air-stable iron(III) and manganese(II) bipyridine complexes included in zeolite Y or bentonite and copper(II) complexes with 14-membered hexaaza macrocycle “[Cu(R<sub>2</sub>[14]aneN<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub> (R = Me, Et, Pr, Bu and benzyl)” within the cavities of zeolite Y can easily catalyse the oxidation of THF under  $\text{H}_2\text{O}_2$ , when TBHP as oxidant to give tetrahydrofuran-2-ol and tetrahydrofuran-2-one with minor amounts of 2,3-dihydrotetrahydrofuran [40–43].

In this study, we synthesized several copper(II) complexes with ligands of 16-membered pentaaza bis(macrocyclic) which catalyzed the oxidation of THF with  $\text{H}_2\text{O}_2$ . 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  $\gamma$ -butyrolactone, which was further confirmed by  $^1\text{H}$  NMR analysis [ $\delta_{\text{H}}(\text{CDCl}_3)$  2.26 (2H, q,  $J$  6.6, CH<sub>2</sub>), 2.46 (2H, t,  $J$  7.0, CH<sub>2</sub>) and 4.32 (2H, t,  $J$  6.9 Hz, CH<sub>2</sub>)], a small amount of tetrahydrofuran-2-ol and 4-hydroxybutyraldehyde. All catalysts were also examined under the same reaction conditions and their conversions and selectivity are summarized in Tables 2–4.

The effect of varying the catalyst concentration on the oxidation of tetrahydrofuran with hydrogen peroxide and **10** as catalyst is shown in Table 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

Table 2

Substrate conversions and product selectivity in the oxidation of tetrahydrofuran with  $\text{H}_2\text{O}_2$  in the presence of 16-membered pentaaza bis(macrocyclic) binuclear copper(II) complexes<sup>a</sup>

Catalyst	Conversion (%)	Yield (%)		
		Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-Hydroxybutyraldehyde
<b>6</b>	60.6	54.6	38.1	7.3
<b>7</b>	96.6	63.6	27.8	8.6
<b>8</b>	68.5	58.9	35.0	6.1
<b>9</b>	86.4	94.3	3.6	2.1
<b>10</b>	100	100	–	–

<sup>a</sup> Conditions: catalyst = 0.35 mmol, THF = 0.05 mol,  $\text{H}_2\text{O}_2$  = 0.05 mol, time = 8 h, reflux.

Table 3

Effect of catalyst concentration on substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H<sub>2</sub>O<sub>2</sub> in the presence of **10** as catalyst<sup>a</sup>

Catalyst (mmol)	Conversion (%)	Yield (%)		
		Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-Hydroxybutyraldehyde
0.15	70.7	69.1	29.2	1.7
0.25	92.6	77.8	19.9	2.3
0.35	100	100	–	–
0.45	91.7	67.0	20.6	12.4
0.55	80.4	58.2	24.2	17.6

<sup>a</sup> Conditions: THF = 0.05 mol, H<sub>2</sub>O<sub>2</sub> = 0.05 mol, time = 8 h, reflux.

Table 4

Effect of time on substrate conversions and product selectivity in the oxidation of tetrahydrofuran with H<sub>2</sub>O<sub>2</sub> in the presence of **10** as catalyst<sup>a</sup>

Time (h)	Conversion (%)	Yield (%)		
		Tetrahydrofuran-2-one	Tetrahydrofuran-2-ol	4-Hydroxybutyraldehyde
2	65.4	47.6	52.4	–
4	76.8	60.6	39.4	–
6	88.2	75.2	24.8	–
8	100	100	–	–
10	90.6	86.4	9.0	4.6
12	81.2	78.5	14.6	6.9
14	76.8	64.6	27.3	8.1

<sup>a</sup> Conditions: catalyst = 0.35 mmol, THF = 0.05 mol, H<sub>2</sub>O<sub>2</sub> = 0.05 mol, reflux.

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  $\mu$ -oxo dimers, which inhibit the catalytic cycle.

The effect of various solvents (Table 2 and Figs. 1–4) on the oxidation of tetrahydrofuran with **6–10** 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<sub>2</sub> > MeOH > MeCN.

In continuation of our investigation, we found that among a few intermediates that are listed as before the relative reactivity of compounds **6–10** was decreased. The above com-

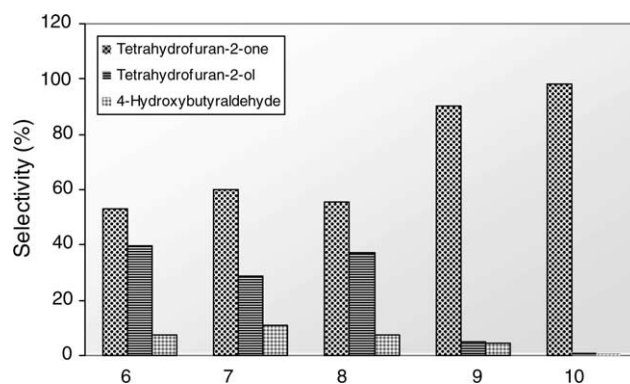


Fig. 2. Oxidation products distribution of tetrahydrofurane with hydrogen peroxide in nitromethane with 16-membered pentaaza bis(macrocycle) binuclear copper(II) complexes.

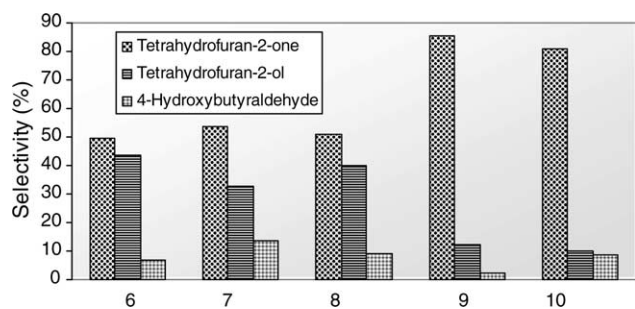


Fig. 1. Oxidation products distribution of tetrahydrofurane with hydrogen peroxide in methanol with 16-membered pentaaza bis(macrocycle) binuclear copper(II) complexes.

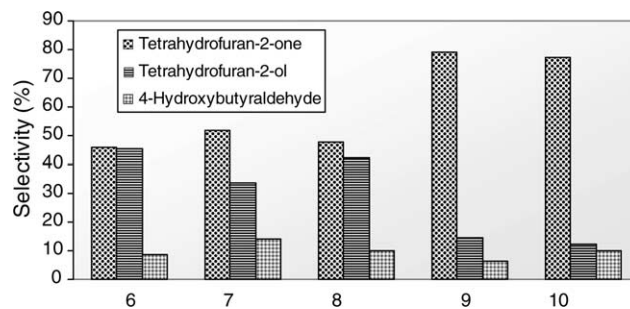


Fig. 3. Oxidation products distribution of tetrahydrofurane with hydrogen peroxide in acetonitrile with 16-membered pentaaza bis(macrocycle) binuclear copper(II) complexes.

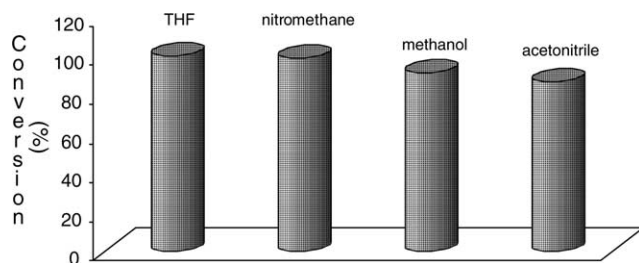


Fig. 4. Oxidation of tetrahydrofuran with hydrogen peroxide in various solvent with 16-membered pentaaza bis(macrocycle) binuclear copper(II) complexes in the presence of 10.

pounds were used as catalyst in the radical reactions. In fact, the compound (**10**) is the most suitable one. Because of the existence of d-orbitals in sulfur. Therefore, delocalization of  $\Pi$ -bonds is caused more stability and more velocity. Compound (**7**) is more suitable than compound (**9**), it is clear that, in compound (**9**) the existence of oxygen atom is an inhabitation for delocalization of  $\Pi$ -bonds.

#### 4. Conclusions

Square-planar copper(II) complexes of [1-phenyl- (**1**); 1,1'-phenyl- (**2**); 1,1'-diphenylmethan- (**3**); 1,1'-diphenylether- (**4**); 1,1'-diphenylsulfon- (**5**)] bis(8,10-dimethyl-1,3,7,11,15-pentaazacyclohexadeca-7,11-diene)copper(II),  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{RCl}_4]\}$  have been prepared by the one-pot template reactions of nitrogen–nitrogen linker (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethan; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfon), formaldehyde, 1,3-diaminopropane, copper(II) and 2,4-pentanedione in a 1:4:4:2:2 molar ratio.  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{R}](\text{ClO}_4)_4$  (**6–10**) was prepared by a method similar to that for  $\{[\text{Cu}(\text{Me}_2[16]\text{aneN}_5)_2\text{RCl}_4]\}$  (**1–5**) except that copper(II) perchlorate was used instead of copper(II) chloride. The spectra of **1–10** 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: **10** > **7** > **9** > **8** > **6**.
- The reactions show appreciable solvent effects and activity of oxidation decreases: THF > MeNO<sub>2</sub> > MeOH > MeCN.

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