

# 16-Membered pentaaza bis(macrocyclic) nickel(II) complexes containing aromatic nitrogen–nitrogen linkers, $\{[\text{Ni}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ : Synthesis, characterization and catalytic oxidation of cyclohexene with molecular oxygen

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## Abstract

New square-planar bis(macrocyclic)dinickel(II) complexes containing phenylene bridges between 16-membered pentaaza macrocyclic subunits have been synthesized *via* in situ one pot template condensation reaction of aromatic nitrogen–nitrogen linker (R = 1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfon), formaldehyde, bis(1,3-diaminopropane) nickel(II) perchlorate and 1,3-dibromopropane in a 1:4:2:2 molar ratio results in the formation of new series of binuclear nickel(II) complexes; 1-phenyl- (1); 1,1'-phenyl- (2); 1,1'-diphenylmethane- (3); 1,1'-diphenylether- (4); 1,1'-diphenylsulfon- (5) bis(1,3,7,11,15-pentaazacyclohexadecane) nickel(II),  $\{[\text{Ni}([\text{16}] \text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$ . The formation of the macrocyclic framework and the mode of bonding of the complexes have been confirmed by data obtained from elemental analyses, FAB, UV–vis, FT-IR,  $^1\text{H}$  NMR, electronic spectral studies, conductivity and magnetic susceptibility measurements. These complexes have been found to be effective catalysts for the selective oxidation of cyclohexene to 2-cyclohexene-1-one and 2-cyclohexene-2-ol with molecular oxygen as the oxidant.

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**Keywords:** Nickel(II); Bis(macrocyclic); 16-membered pentaaza; Oxidation

## 1. 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. More recently, aspects of bis-cyclam derivatives and some themes involving supramolecular chemistry have been reported [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 com-

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

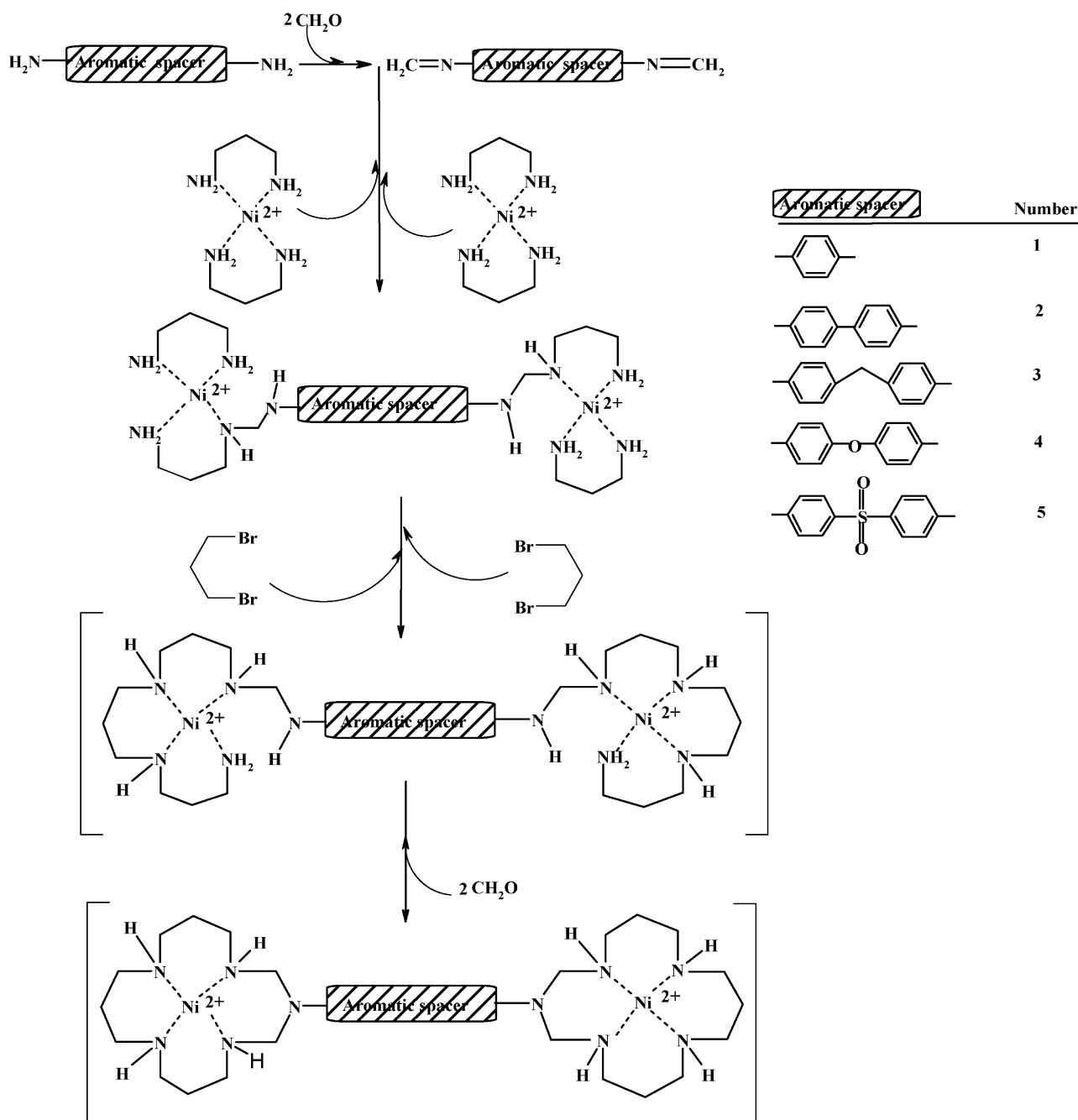
In this paper, we report the synthesis and characterization of new bis(macrocyclic) binuclear nickel(II) complexes of 1-phenyl-; 1,1'-diphenyl-; 1,1'-diphenylmethane-; 1,1'-diphenyl-ether- and 1,1'-diphenylsulfone-; bis(1,3,7,11,15-pentaaza-cyclohexadecane)nickel(II) perchlorate,  $\{[\text{Ni}([\text{16}]\text{aneN}_5)]_2\text{R}\}(\text{ClO}_4)_4$  (**1–5**) (Scheme 1). These binuclear complexes were prepared from the one pot template condensation reaction of nitrogen–nitrogen linker (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfone), formaldehyde and bis(1,3-

diaminopropane)nickel(II) and 1,3-dibromopropane in a 1:4:2:2 molar ratio. These complexes have been found to be effective catalysts for the selective oxidation of cyclohexene to 2-cyclohexene-1-one and 2-cyclohexene-2-ol with molecular oxygen as the oxidant.

## 2. Experimental

### 2.1. Materials and physical measurements

Safety note: perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled



Scheme 1. Formation and suggested structures of the macrocyclic complexes.

Table 1  
<sup>1</sup>H NMR data for the complexes in CD<sub>3</sub>NO<sub>2</sub> solvent

Complex	C–NH–C (8H)	N–CH <sub>2</sub> –N (8H)	C–CH <sub>2</sub> –C (12H)	C–CH <sub>2</sub> –N (24H)	Aromatic ring protons
<b>1</b>	6.30–6.38	3.30–3.40	1.90–2.10	2.29–2.40	7.37–7.45
<b>2</b>	6.26–6.31	3.35–3.38	1.94–2.16	2.33–2.44	7.33–7.40
<b>3</b>	6.28–6.34	3.37–3.41	1.96–2.17	2.35–2.46	7.35–7.42
<b>4</b>	6.32–6.40	3.39–3.43	1.98–2.19	2.30–2.38	7.39–7.48
<b>5</b>	6.38–6.49	3.40–3.46	2.01–2.20	2.36–2.40	7.42–7.49

with caution. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. For the spectroscopic measurements, H<sub>2</sub>O was distilled and organic solvents were purified according to the literature method [18]. 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 nickel contents of the samples were measured by Atomic Absorption Spectrophotometer (AAS-Perkin-Elmer 4100-1319) using a flame approach. The products were analyzed 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. 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. <sup>1</sup>H NMR (400 MHz) spectra were measured in CD<sub>3</sub>NO<sub>2</sub> solutions and referenced to the solvent signals. FAB mass spectra were recorded on a Kratos MS50TC spectrometer. The complex bis(1,3-diaminopropane)nickel(II) perchlorate; [Ni(pn)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>; was prepared according to the published procedures [19].

## 2.2. Preparation of {[Ni([16]aneN<sub>5</sub>)]<sub>2</sub>R}(ClO<sub>4</sub>)<sub>4</sub> (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 MeOH solution (50 cm<sup>3</sup>) of [Ni(pn)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (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, 0.52 g) were added and the resulting mixture was stirred for ca. 8 h at room temperature. The yellow solid product was obtained, filtered, washed with methanol and dried over fused CaCl<sub>2</sub> in desiccators. The crystals were recrystallized from hot methanol. Anal. Calcd for C<sub>28</sub>H<sub>56</sub>N<sub>10</sub>Cl<sub>4</sub>O<sub>16</sub>Ni<sub>2</sub> (**1**): 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<sub>B</sub>, –0.018 B.M.; Λ<sub>M</sub>, 455 (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); ν(N–H), 3225 cm<sup>-1</sup>; ν(C–N), 1175 cm<sup>-1</sup>; δ(N–H), 1670 cm<sup>-1</sup>, d ↔ d, 441 nm (ε = 71 M<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>NO<sub>2</sub>); FAB mass (m/z): 953 ([M–ClO<sub>4</sub>]<sup>+</sup>), 852 ([M–2ClO<sub>4</sub>–H]<sup>+</sup>). Anal. Calcd for

C<sub>34</sub>H<sub>60</sub>N<sub>10</sub>Cl<sub>4</sub>O<sub>16</sub>Ni<sub>2</sub> (**2**): Ni, 10.40; C, 36.17; H, 5.35; N, 12.40. Found: Ni, 10.28; C, 36.01; H, 5.26; N, 12.54%; yield: ~55%; μ<sub>B</sub>, –0.029 B.M.; Λ<sub>M</sub>, 450 (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); ν(N–H), 3230 cm<sup>-1</sup>; ν(C–N), 1180 cm<sup>-1</sup>; δ(N–H), 1675 cm<sup>-1</sup>, d ↔ d, 442 nm (ε = 68 M<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>NO<sub>2</sub>); FAB mass (m/z): 1030 ([M–ClO<sub>4</sub>]<sup>+</sup>), 929 ([M–2ClO<sub>4</sub>–H]<sup>+</sup>). Anal. Calcd for C<sub>35</sub>H<sub>62</sub>N<sub>10</sub>Cl<sub>4</sub>O<sub>16</sub>Ni<sub>2</sub> (**3**): Ni, 10.27; C, 36.78; H, 5.47; N, 12.25. Found: Ni, 10.14; C, 36.60; H, 5.36; N, 12.38%; yield: ~49%; μ<sub>B</sub>, –0.021 B.M.; Λ<sub>M</sub>, 465 (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); ν(N–H), 3220 cm<sup>-1</sup>; ν(C–N), 1175 cm<sup>-1</sup>; δ(N–H), 1670 cm<sup>-1</sup>, d ↔ d, 444 nm (ε = 74 M<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>NO<sub>2</sub>); FAB mass (m/z): 1044 ([M–ClO<sub>4</sub>]<sup>+</sup>), 943 ([M–2ClO<sub>4</sub>–H]<sup>+</sup>). Anal. Calcd for C<sub>34</sub>H<sub>60</sub>N<sub>10</sub>Cl<sub>4</sub>O<sub>17</sub>Ni<sub>2</sub> (**4**): Ni, 10.25; C, 35.66; H, 5.28; N, 12.22. Found: Ni, 10.11; C, 35.50; H, 5.19; N, 12.34%; yield: ~42%; μ<sub>B</sub>, –0.017 B.M.; Λ<sub>M</sub>, 460 (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); ν(N–H), 3235 cm<sup>-1</sup>; ν(C–N), 1190 cm<sup>-1</sup>; δ(N–H), 1660 cm<sup>-1</sup>, d ↔ d, 446 cm<sup>-1</sup> (ε = 72 M<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>NO<sub>2</sub>); FAB mass (m/z): 1046 ([M–ClO<sub>4</sub>]<sup>+</sup>), 945 ([M–2ClO<sub>4</sub>–H]<sup>+</sup>). Anal. Calcd for C<sub>34</sub>H<sub>60</sub>N<sub>10</sub>Cl<sub>4</sub>O<sub>18</sub>Ni<sub>2</sub>S (**5**): Ni, 9.84; C, 34.23; H, 5.07; N, 11.73. Found: Ni, 9.75; C, 34.10; H, 4.88; N, 11.85%; yield: ~48%; μ<sub>B</sub>, –0.035 B.M.; Λ<sub>M</sub>, 455 (Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); ν(N–H), 3260 cm<sup>-1</sup>; ν(C–N), 1195 cm<sup>-1</sup>; δ(N–H), 1670 cm<sup>-1</sup>, d ↔ d, 440 nm (ε = 68 M<sup>-1</sup> cm<sup>-1</sup>, CH<sub>3</sub>NO<sub>2</sub>); FAB mass (m/z): 1094 ([M–ClO<sub>4</sub>]<sup>+</sup>), 993 ([M–2ClO<sub>4</sub>–H]<sup>+</sup>).

## 2.3. Oxidation of cyclohexene with molecular oxygen; general procedure

Generally, 10 ml of cyclohexene and 1.0 mg of homogeneous catalyst (**1–5**) were added to a glass reactor with a gas inlet tube connected to a gas burette and an oxygen storage bottle. The mixture was heated to 70 °C in water bath and stirred with a magnetic stirring bar. The oxidation reactions were performed under atmospheric pressure of molecular oxygen in the absence of solvent, giving 2-cyclohexene-1-ol and 2-cyclohexene-1-one as the major products. The reaction products were monitored using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC) and by GC–MS coupling. Yields were determined by using cyclohexanone an internal standard.

## 3. Result and discussion

Novel 16-membered pentaazabis(macrocylic) copper(II) complexes; {[Ni([16]aneN<sub>5</sub>)]<sub>2</sub>R}(ClO<sub>4</sub>)<sub>4</sub>; have been synthesized by template condensation reaction between aro-

matic nitrogen–nitrogen linkers (1,4-phenylenediamine; benzidine; 4,4'-diaminodiphenylmethane; 4,4'-diaminodiphenylether; 4,4'-diaminodiphenylsulfon), 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, CH<sub>3</sub>CN and H<sub>2</sub>O. The results of elemental analyses agree well with the proposed bis(macrocyclic)nickel(II) complexes. The molar conductance's of the complexes in methanol show that they are electrolytes.

The prominent IR spectral bands are presented in Section 2. In all of these complexes a single sharp band in the region 3225–3260 cm<sup>-1</sup> 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  $\sim 1670$  cm<sup>-1</sup> is assigned to  $\delta(\text{N-H})$  vibrations for secondary amine. All the complexes show a strong band in the region  $\sim 1180$  cm<sup>-1</sup> assignable to the  $\nu(\text{C-N})$  group. All of the complexes show strong bands in the regions 2855–2965 and 1420–1450 cm<sup>-1</sup> which may correspond to  $\nu(\text{C-H})$  and  $\delta(\text{C-H})$  vibrations, respectively. The spectra of perchlorate complexes gave additional bands at 900–1000 cm<sup>-1</sup> consistent with the perchlorate group.

The magnetic moments of the nickel(II) complexes measured in the solid state correspond to the square-planar coordination geometry of the complexes (see Section 2). 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 spectrometry. <sup>1</sup>H NMR spectra of the  $[(\text{Ni}([\text{16}] \text{aneN}_5)_2\text{R})(\text{ClO}_4)_4]$  complex exhibit very broad peaks in D<sub>2</sub>O, CH<sub>3</sub>CN-d<sub>3</sub> and Me<sub>2</sub>SO-d<sub>6</sub> but sharp resolvable peaks in CH<sub>3</sub>NO<sub>2</sub>-d<sub>3</sub>. 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, whereas the Ni(II) complex of “ $([\text{16}] \text{aneN}_5)_2\text{R}$ ” exist primarily as diamagnetic square-planar in CH<sub>3</sub>NO<sub>2</sub>-d<sub>3</sub>. The <sup>1</sup>H NMR spectra of bis(macrocyclic)dinickel(II);  $\{[\text{Ni}([\text{16}] \text{aneN}_5)_2\text{R}]\}(\text{ClO}_4)_4$ ; complex recorded in CH<sub>3</sub>NO<sub>2</sub>-d<sub>3</sub> 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 amination moiety [N–CH<sub>2</sub>–N–(8H)]. Another multiplet in the region 1.90–2.10 ppm may be assignable to methylene protons [C–CH<sub>2</sub>–C (12H)] of the propane chain moiety. The complexes also show a multiplet in the  $\sim 7.37$  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–CH<sub>2</sub>–N–(24H)] of the propylene diamine moiety (Table 1).

The electronic spectra of bis(macrocyclic) binuclear complexes are comparable to of square-planar nickel(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 [11,20]. The yellow complexes  $\{[\text{Ni}([\text{16}] \text{aneN}_5)_2\text{R}]\}(\text{ClO}_4)_4$ , readily dissolve in

polar solvents such as H<sub>2</sub>O, CH<sub>3</sub>CN, CH<sub>3</sub>NO<sub>2</sub>, Me<sub>2</sub>SO<sub>2</sub>. The  $\{[\text{Ni}([\text{16}] \text{aneN}_5)_2\text{R}]\}(\text{ClO}_4)_4$ , are extremely stable in the solid state and in solution and are relatively stable against ligand dissociation even in highly acidic solutions.

The oxidation of organic compounds is an important and widely used reaction in laboratory scale organic synthesis as well as in large scale chemical industry. There are hundreds of different reagents and methods available for the oxidation of organic chemicals. Even though these methods exist and are very applicable for a laboratory scale, most of them share common disadvantages from an industrial point of view. Many industrial oxidation reactions are currently performed with a stoichiometric amount of oxidants such as peroxides or high oxidation state metal oxides. These oxidants are expensive and the processes where these oxidants are used generate organic and heavy metal waste. When reactions are scaled to tons instead of grams, the use of stoichiometric oxidants is not an attractive option. For these kind of reactions an alternative and environmentally benign oxidant is welcome. An ideal oxidant for any large scale oxidation reaction should be easily accessible, cheap and non-toxic. As it happens, the best oxidant to fit this description is dioxygen. It is easily available since it is present in air and the only by-product produced from its decomposition is water.

The reaction medium was homogeneous liquid-phase. Stirring was continued under one atmosphere of O<sub>2</sub> while oxygen was continuously replenished; periodic product sampling was conducted. Under these conditions, cyclohexene oxidized to a mixture of 2-cyclohexene-1-ol and 2-cyclohexene-1-one. The reaction was monitored by quantitative GC determination of the oxygenated products. The products were distinguished by GC–MS coupling and also products were identified by comparison with authentic samples. The product distributions and results of the cyclohexene oxidation are shown in Fig. 1 and Tables 2–4.

In the end of the reaction time, copper(II) complexes precipitate by the evaporation of cyclohexene under vacuum. There is no any evidence that show copper complexes changed or degraded. The copper complexes have same UV–vis spectra before and after the catalytic reaction. Therefore in a range

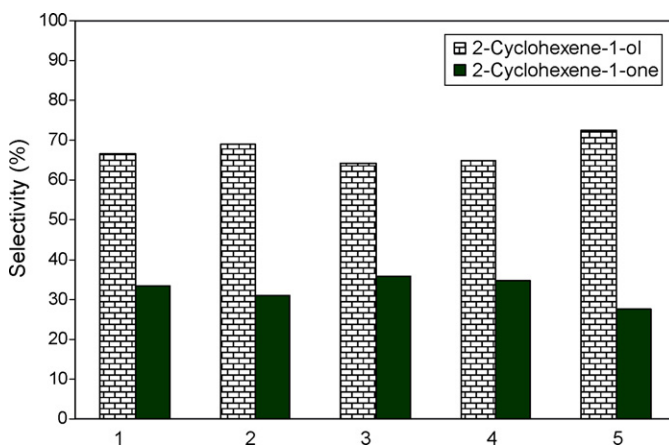


Fig. 1. Oxidation products distribution of cyclohexene with oxygen with 16-membered pentaaza bis(macrocyclic) binuclear nickel(II) complexes.

Table 2

Oxidation of cyclohexene with molecular oxygen catalyzed by neat bis(macrocyclic) dinickel(II) complexes

Catalyst	Conversion (%)	Selectivity (%)	
		2-cyclohexene-1-ol	2-cyclohexene-1-one
<b>1</b>	41.7	66.7	33.3
<b>2</b>	43.6	68.9	31.1
<b>3</b>	45.1	64.1	35.9
<b>4</b>	31.4	65.0	35.0
<b>5</b>	53.9	72.5	27.5

Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; catalyst 1 mg; substrate, cyclohexene 10 ml at 70 °C.

Table 3

Effect of the amount of catalyst (**5**) used on the reactivity

Amount of catalyst (mg)	Conversion (%)	Selectivity (%)	
		2-cyclohexene-1-ol	2-cyclohexene-1-one
0.25	30.2	86.9	13.1
0.5	42.9	79.5	20.5
1.0	53.9	72.5	27.5
2.0	50.1	68.4	31.6
3.0	43.9	60.7	39.3
4.0	24.5	56.4	43.6

Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; substrate, cyclohexene 10 ml; at 70 °C.

of 12 h these compounds play as a robust catalyst without any degradation. The results show acceptable catalytic activity and selectivity comparing to those reported in our previous works for cyclohexene oxidation [20].

The ([16]aneN<sub>5</sub>)<sub>2</sub>R catalysts are very stable to oxidative degradation under the reaction conditions. In the absence of a catalyst little or no oxidation occurs. However, after recovering, washing with acetone and drying of the catalyst, oxidation of cyclohexene under identical condition occurred with similar yields and selectivity. Complex **5** is the most active, achieving approximately 53.9 conversion in a 8 h period.

To investigate the effect of temperature on the reactivity and product selectivity of catalyst, the oxidations were carried out at temperatures between 50 and 80 °C. The results have been

Table 4

Effect of temperature on the oxidation of cyclohexene with molecular oxygen catalyzed by **5**

Temperature (°C)	Conversion (%)	Selectivity (%)	
		2-cyclohexene-1-ol	2-cyclohexene-1-one
50	6.9	52.6	47.4
60	17.5	60.9	39.1
70	53.9	72.5	27.5
80	46.5	67.9	32.1

Reaction condition: 1 atm of O<sub>2</sub>; time 8 h; substrate, cyclohexene 10 ml.

shown in Table 4. At temperatures ranging from 50 to 80 °C, the reactivity and product selectivity of the complex varies with the temperature. At 70 °C the conversion is 53.9% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-2-one is 72.5 and 27.5%, respectively, while at 50 °C the conversion is 6.9% and the selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one is 52.6 and 47.4%, respectively. The typical trend shows that reactivity and the selectivity to 2-cyclohexene-1-ol are increased with the temperature in the 50–70 °C range.

To investigate the effect of catalyst used on the reaction, the oxidation was carried out at 70 °C by varying the amount of catalyst (**5**); while holding the amount of cyclohexene constant. The results have been shown in Table 3. The catalytic conversion was found to be related to the amount of catalyst used is 1 mg in 10 ml cyclohexene. Although the amount of catalyst used obviously influenced the reactivity of the catalyst, it showed a relatively effect on the product distribution (Fig. 2).

The results clearly suggest that {[Ni([16]aneN<sub>5</sub>)<sub>2</sub>R} (ClO<sub>4</sub>)<sub>4</sub> efficiently catalyses conversion of cyclohexene to 2-cyclohexene-1-ol and 2-cyclohexene-1-one. The more activity of {[16]aneN<sub>5</sub>}<sub>2</sub>R system has clearly arisen from the existence of electron donating ligand which facilitates the electron transfer rate, a process that has previously observed in other oxidation reactions [20,21]. All conversion efficiency with high selectivity obtained in this study is significantly higher than that obtained using transition metal complexes [20,21].

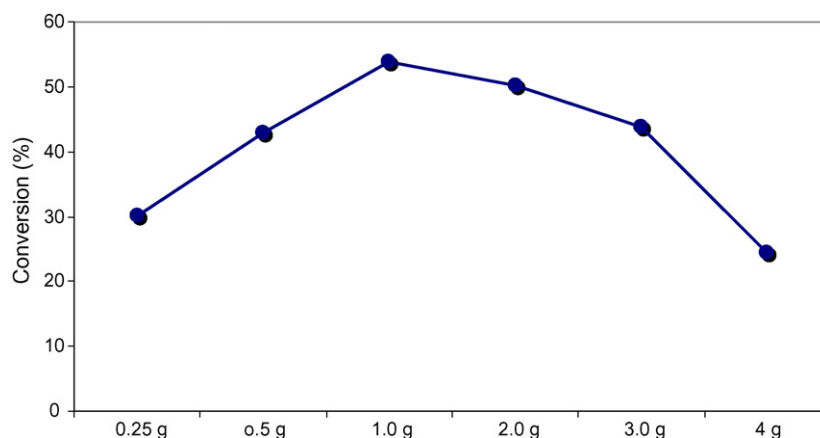


Fig. 2. Effect of catalyst concentration on substrate conversions in the oxidation of cyclohexene with O<sub>2</sub> in the presence of **5** as catalyst (reaction condition: 1 atm of O<sub>2</sub>; time 8 h; cyclohexene 10 ml, temperature 70 °C).

#### 4. Conclusions

Square-planar bis(macrocyclic) dinuclear nickel(II) complexes of “[1-phenyl- (1); 1,1'-phenyl- (2); 1,1'-diphenylmethan- (3); 1,1'-diphenylether- (4); 1,1'-diphenylsulfon- (5)] bis((1,3,6,10,13-pentaazacyclohexadecane)nickel(II)), {[Ni([16]aneN<sub>5</sub>)<sub>2</sub>R}(ClO<sub>4</sub>)<sub>4</sub>” were prepared from the ISOPTR of the appropriate aromatic nitrogen–nitrogen linker, CH<sub>2</sub>O, bis(1,3-diaminopropane)nickel(II) and 1,3-dibromopropane in a 1:4:2:2 molar ratio. These dinuclear complexes were then used as catalysts in cyclohexene oxidation reaction by O<sub>2</sub>. Cyclohexene was catalytically oxidized in the presence of molecular oxygen and {[Ni([16]aneN<sub>5</sub>)<sub>2</sub>R}(ClO<sub>4</sub>)<sub>4</sub> in the absence of solvent at 70 °C, affording 2-cyclohexene-1-ol and 2-cyclohexene-1-one.

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