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Homogeneous and heterogenized copper(II) complexes as catechol oxidation catalysts

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Abstract

Two macroacyclic ligands represented as L_1 and L_2 with $3N_2O$ and 5N donor atoms, respectively, have been synthesized by Schiff base condensation. They were subsequently grafted on a silica surface via covalent bonds. The organic ligands L_1 and L_2 as well as the heterogenized ligands $L_1{\cdot}SiO_2$ and $L_2{\cdot}SiO_2$ reacted with copper(II) leading to the formation of dinuclear copper(II) complexes. Catalytic oxidation of 3,5-di-*t*-butylcatechol (DTBC) by dioxygen was studied using as catalysts the homogeneous $Cu_2(L_1)$ and $Cu_2(L_2)$ and the heterogenized $Cu_2(L_1){\cdot}SiO_2$ and $Cu_2(L_2){\cdot}SiO_2$ complexes. These complexes were found to be very effective catalysts for DTBC oxidation producing mainly 3,5-di-*t*-butylquinone (DTBQ). During the catalytic process the formation of an *o*-semiquinone radical has also been confirmed. The immobilized on modified silica surface copper(II) complexes gave significantly higher DTBC conversion than the homogeneous copper(II) complexes.

Keywords: Dinuclear copper(II) complexes; Schiff base; Catalytic catechol oxidation; Heterogenized catalysts

1. Introduction

The binding and activation of small molecules like dioxygen under mild operating conditions by enzymic systems and biomimetic complexes is a very active research field connecting the chemical synthesis and catalysis with the technological world [1–4]. In oxidative catalysis, transition metal complexes with polydentate ligands as Schiff bases are often used featuring structural or functional properties of non-heme enzymes [5–7].

On the other hand the heterogenization of homogeneous catalysts, presents a rapidly expanding research area providing advantages such as easy handling and product separation, and catalyst recovery. A wide variety of heterogenized catalysts are the metal complexes anchored on silica support [8–10]. Many of them have been developed by chemically modified silica gels with organic functionalities [11]. Nevertheless, few reports are available on the inorganic matrix immobilized Schiff bases and their applications in catalysis [12–15].

As far as catechol oxidation by copper complexes is concerned, several mononuclear and dinuclear copper complexes have been studied investigating their reactivity towards dioxygen [16–23]. These copper

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compounds have served as models for the active sites of copper proteins and the observed biomimetic activity has been correlated to their structural features [16–23].

Herein we report on the synthesis and immobilization of two macroacyclic Schiff base ligands derived from phenylacetone on a silica surface. Their anchoring is achieved via covalent bonding on the inorganic support. The catalytic activities of the silica supported Cu(II) complexes were evaluated for the oxidation of 3,5-di-*t*-butylcatechol by air dioxygen.

2. Experimental

Infrared spectra were recorded on a Spectrum GX Perkin-Elmer FT-IR System, UV-Vis spectra were recorded using a UV/VIS/NIR JASCO Spectrophotometer and electron paramagnetic resonance (EPR) spectra were recorded at liquid helium temperatures with a Bruker ER 200D X-band spectrometer equipped with an Oxford Instruments cryostat or a Varian E-line Spectrometer. Thermogravimetric analyses were carried out using Shimadzu DTG-60 analyser. High performance liquid chromatography (HPLC) analysis was performed using a Dionex liquid chromatograph equipped with a C18 column, the eluent being a mixture of methanol and water (30/70 vol.%) at a flow rate of 0.6 ml min^{-1}, detection at 280 and 418 nm. Solution NMR spectra were obtained in a Bruker AMX-400 MHz spectrometer with external TMS as reference.

2.1. Synthesis of the macroacyclic ligand 3-{2-[2-(3-oxo-1,3-diphenyl-propylideneamino)-ethylamino]-ethylimino}-1,3-diphenyl-propan-1-one (L_1) and its Cu(II) complex ($Cu_2(L_1)$)

In a solution of iso-PrOH (20 ml) containing 1,3-diphenyl-propan-1,3-dione (4 mmol), 2 mmol of diethylenetriamine were added slowly. The resulting mixture was stirred at 40–50 °C for 24 h. After reducing the volume of the reaction solvents by evaporation and cooling, the ligand was precipitated. The final product was recrystallized from ethanol. Anal. calcd. for $C_{34}H_{33}N_3O_2{\cdot}H_2O$: C, 76.45; N, 7.87; H, 6.56. Found: C, 76.08; N, 8.01; H, 6.61. IR (KBr, cm^{-1}, selected peaks) 3400: ν(OH); 3350: ν(NH); 3141, 3050, 3029, 2843: $\nu(CH_2)$; 1600: ν(C=N); 1535 (br), 1467 (br): ν(C=C) + δ(NH), ν(C=C) + $\delta(CH_2)$; 1398: ν(C–O); 1263: ν(OH); 1058: ν(C–N); 755: $\rho(CH_2)$. ^{1}H NMR ($CDCl_3$, δ) 7.9 (m), 7.5 (m): phe-**H**; 6.7 (s): C=O–CH_2–CN; 4.6 (s): N**H**; 2.8 (t): CN–C**H**$_2$–CH_2; 2.68 (t): CN–CH_2–C**H**$_2$. ^{13}C NMR ($CDCl_3$, δ) 188: **C**O; 162: **C**N; 138, 136, 128, 126: phe-**C**; 93: C=O–**C**H_2–CN; 55: CN–**C**H_2–CH_2; 42: CN–CH_2–C**H**$_2$.

To a stirred solution of methanol (10 ml) containing the ligand L_1 (100 mg, 0.19 mmol), a solution of $CuCl_2$ (51.09 mg, 0.38 mmol) in absolute EtOH was added. The resulting mixture was stirred for 2 h at room temperature and finally a solid product was separated. The complex, $Cu_2(L_1)$, was washed with EtOH and dried under reduced pressure. Anal. calcd. for $Cu_2Cl_2C_{34}H_{31}N_3O_2{\cdot}H_2O$: C, 55.97; N, 5.76; H, 4.53; Cu, 17.42. Found: C, 55.45; N, 5.65; H, 4.43; Cu, 17.15. IR (KBr, cm^{-1}, selected peaks): 3270: ν(NH); 1575: ν(C=N); 1498: δ(NH), 1388: ν(C–O). Absorption spectrum [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: in MeOH, 850, 618.

2.2. Immobilization of (L_1) on a silica support and the preparation of the Cu(II) material, $Cu_2(L_1){\cdot}SiO_2$

To a stirred solution of 60 ml toluene containing 1.0 mmol of L_1, 1.0 mmol of (3-glycidyloxypropyl)-trimethoxysilane was added. The resulting mixture was allowed to react at 80 °C for 24 h. To this solution 3.0 g of SiO_2 and 5 ml of EtOH were added, and the slurred solution maintained at 80 °C for 24 h. The functionalized silica, $L_1{\cdot}SiO_2$, was isolated by filtration and washed with MeOH and EtOH. It was further purified with EtOH using the soxhlet extraction method and dried under reduced pressure at 80 °C for 12 h. The loading achieved is ca. 0.25 mmol g^{-1} determined by thermogravimetric analysis. DRIFTS-IR (cm^{-1}, selected peaks): 1657: ν(C=N); 1483: ν(C–O).

To a suspension of $L_1{\cdot}SiO_2$ (0.5 g) in H_2O, $CuCl_2$ (10.75 mg, 0.04 mmol) was added. The mixture was stirred for 48 h at room temperature and the resulting green material, $Cu_2(L_1){\cdot}SiO_2$, was filtered, washed with H_2O, CH_3COCH_3, and Et_2O and dried at 80 °C for 12 h. The amount of Cu^{II} was determined by back-titration of the remaining amount of Cu^{II} into the solution. DRIFTS-IR (cm^{-1}, selected peaks): 1629: ν(C=N); 1460: ν(C–O).

2.3. Synthesis of the macroacyclic ligand N-(1,3-diphenyl-3-propylimino-propylidene)-N′-[2-(1,3-diphenyl-3-propylimino-propylideneamino)-ethyl]-ethane-1,2-diamine (L_2) and its Cu(II) complex ($Cu_2(L_2)$)

In a toluene solution (10 ml) containing 4 mmol of L_1 and one drop of conc. HCl, 2 mmol of propylamine were added. The resulting mixture was stirred at 80 °C for 2 days. During this period the reaction was followed by tlc (silica gel, 4:1:1 *n*-BuOH/AcOH/H_2O). The crystalline product (L_2) separated on cooling and standing. Anal. calcd. for $C_{40}H_{47}N_5 \cdot H_2O$: C, 77.94; N, 11.37; H, 7.96. Found: C, 77.50; N, 11.14; H, 7.66. IR (KBr, cm^{-1}, selected peaks) 3432 (vbr): ν(OH); 3141, 3050, 3029, 2843: $\nu(CH_2)$; 1598: ν(C=N); 1540 (br), 1477 (br): ν(C=C) + δ(NH), ν(C=C) + $\delta(CH_2)$; 1058: ν(C–N); 756: $\rho(CH_2)$. ^{1}H NMR (CD Cl_3, δ) 7.9 (m), 7.5 (m): phe-**H**; 7.5 (s): CN–C**H**$_2$–CN; 3.4 (t): CN–C**H**$_2$–CH_2–CH_3; 2.8 (t): CN–C**H**$_2$–CH_2–NH; 2.7 (t): CN–CH_2–C**H**$_2$–NH; 1.9 (m): CN–CH_2–C**H**$_2$–CH_3; 1.2 (t): CN–CH_2–CH_2–C**H**$_3$.

To a stirred solution of methanol (10 ml) containing the ligand L_2 (100 mg, 0.17 mmol), a solution of $CuCl_2$ (45.71 mg, 0.34 mmol) in absolute EtOH was added. The resulting mixture was stirred for 2 h at room temperature where upon a solid product was separated. The complex, $Cu_2(L_2)$, was washed with EtOH and dried under reduced pressure. Anal. calcd. for $Cu_2Cl_4C_{40}H_{47}N_5 \cdot H_2O$: C, 54.30; N, 7.92; H, 5.54; Cu, 14.67. Found: C, 54.23; N, 8.15; H, 5.62; Cu, 15.10. IR (KBr, cm^{-1}, selected peaks): 1575: ν(C=N). Absorption spectrum [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: in MeOH, 800, 670.

2.4. Immobilization of (L_2) on a silica support and the preparation of Cu(II) material, $Cu_2(L_2) \cdot SiO_2$

To a stirred solution of 10 ml toluene containing 0.2 mmol of L_1, 0.38 mmol of 3-aminopropyltriethoxysilane (APTES) were added. The resulting mixture was allowed to react at 80 °C for 3 days. To this solution 1.5 g of SiO_2 and 5 ml of EtOH were added, and the slurred solution maintained at 80 °C for additional 2 h. The functionalized silica was isolated by filtration and washed with MeOH and EtOH and dried under reduced pressure at 80 °C for 12 h. The loading achieved is ca. 0.1 mmol g^{-1} determined by thermogravimetric analysis.

To detect the presence of free amino groups on the surface of silica, the Kaiser test was used [24]. It was positive indicating that small amounts of APTES have been anchored as well, on SiO_2. Reaction of immobilized APTES with $(CH_3CO)_2O$ and DIEA in 10 ml DMF for 3 h deactivates the amino-terminal group. Finally, detection of free amino groups by the Kaiser test was negative. The functionalised silica, $L_2 \cdot SiO_2$, was then purified with EtOH using the soxhlet extraction method and dried under reduced pressure at 80 °C for 12 h. DRIFTS-IR (cm^{-1}, selected peaks): 1653: ν(C=N).

To a suspension of $L_2 \cdot SiO_2$ (0.5 g) in H_2O, $CuCl_2$ (0.25 g, 0.19 mmol) was added. The mixture was stirred for 48 h at room temperature and the resulting green material, $Cu_2(L_2) \cdot SiO_2$, was filtered, washed with H_2O, CH_3COCH_3, and Et_2O and dried at 80 °C for 12 h. The amount of Cu^{II} was determined by back-titration of the remaining amount of Cu^{II} into the solution. DRIFTS-IR (cm^{-1}, selected peaks): 1638: ν(C=N).

2.5. Catalytic reactions

2.5.1. General catalytic procedure

In a typical experiment, catalyst complex (0.3 ml of a 10^{-3}M methanol solution or the corresponding amount of the supported catalyst), and 30 μl (or 300 μl) of triethylamine (10^{-1}N methanol solution) were mixed with a 2.0 ml solution (10^{-1}M methanol solution) of 3,5-di-*t*-butylcatechol. Aliquots were withdrawn during the reaction course, diluted ten times to methanol and analysed by HPLC. Blank experiments showed that without catalyst the transformation of DTBC to DTBQ does not take place. The heterogenised catalysts recovered from the catalytic reactions exhibited (a) identical IR spectra with the ‘unused’ catalysts and (b) almost the same loading determined by thermogravimetric analysis. These data show that there is no leaching of the supported catalysts during the catalytic reactions.

2.5.2. Identification and characterization of oxidation products by NMR spectroscopy

The general catalytic procedure was followed using $Cu_2(L_2) \cdot SiO_2$ as a catalyst. The reaction mixture was stirred for 48 h. After filtration of the supported

catalyst and several washings with methanol, the reaction mixture was dried under vacuum. Then 7 ml of 1M HCl, saturated with NaCl, was added to the dry residue and the organic products were extracted by diethyl ether (3 × 60 ml). After concentration of the ether extracts, the solid residue was dissolved in 1 ml deuterated DMSO ([D_6]DMSO). A 0.25 ml of this solution was diluted to 0.5 ml with [D_6]DMSO and analysed by NMR. ^{1}H NMR ([D_6]DMSO, δ) 1.20 (s): *t*Bu of DTBC; 1.32 (s): *t*Bu of BTBQ; 6.13 (s): =CH of DTBQ; 6.64(s): CH of DTBC; 6.70(s): CH of DTBC; 6.96(s): =CH of DTBQ; 7.73(br): =CH of *o*-semiquinone radical; 9.15(br): =CH of *o*-semiquinone radical.

3. Results and discussion

3.1. Synthesis and characterization of Schiff bases and their copper(II) complexes

The Schiff base L_1 (Scheme 1) was prepared by condensation of diethylenetriamine and 1,3-diphenyl-propan-1,3-dione as a non-template procedure using a molar ratio of diethylenetriamine: β-diketone equal to 1:2. The only isolated product, which was recrystallized from ethanol, exhibited a strong band at 1600 cm^{-1} attributed to the imine-stretching band, ν(C=N). The absence of bands between the 1750 and 1600 cm^{-1} was taken as evidence that, in the solid state, the ligand L_1 adopts the enolic form. This is supported by the detection of ν(C–O) and ν(OH) stretchings at 1398 and 1263 cm^{-1}, respectively. In non-polar solvents, the ^{13}C NMR data clearly suggest that the keto-form of L_1 predominates, showing the resonance of C=O carbon at 188 ppm. The IR spectrum of $Cu_2(L_1)$ contains the ν(NH), ν(C=N), δ(NH) and ν(C–O) vibrations shifted at 3270, 1575, 1498 and 1388 cm^{-1} from 3350, 1600, 1535 and 1398 cm^{-1}, respectively. The IR data indicate metal coordination to both imine- and amine-nitrogen as well as to the enolic oxygen atom. The EPR spectrum of $Cu_2(L_1)$ in frozen solution, Fig. 1, is dominated by a broad derivative centered at $g \sim 2$ plus a weaker feature at $g \sim 4$. Linewidth limitations do not allow the resolution of hyperfine couplings. The feature at $g \sim 4$ is a semiforbidden $|\Delta m_s| = 2$ transition [25] and is indicative of pairs of interacting Cu^{II} paramagnetic centers. Similar spectra as that of $Cu_2(L_1)$ have been previously reported for other dinuclear Cu^{II} complexes [26,27]. Accordingly the present EPR data show that $Cu_2(L_1)$ consists of dinuclear Cu^{II} centres.

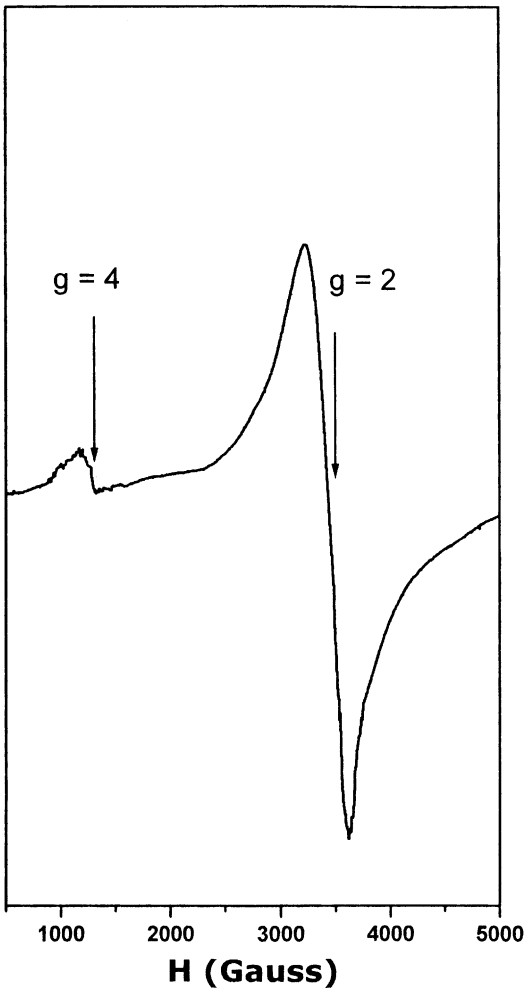
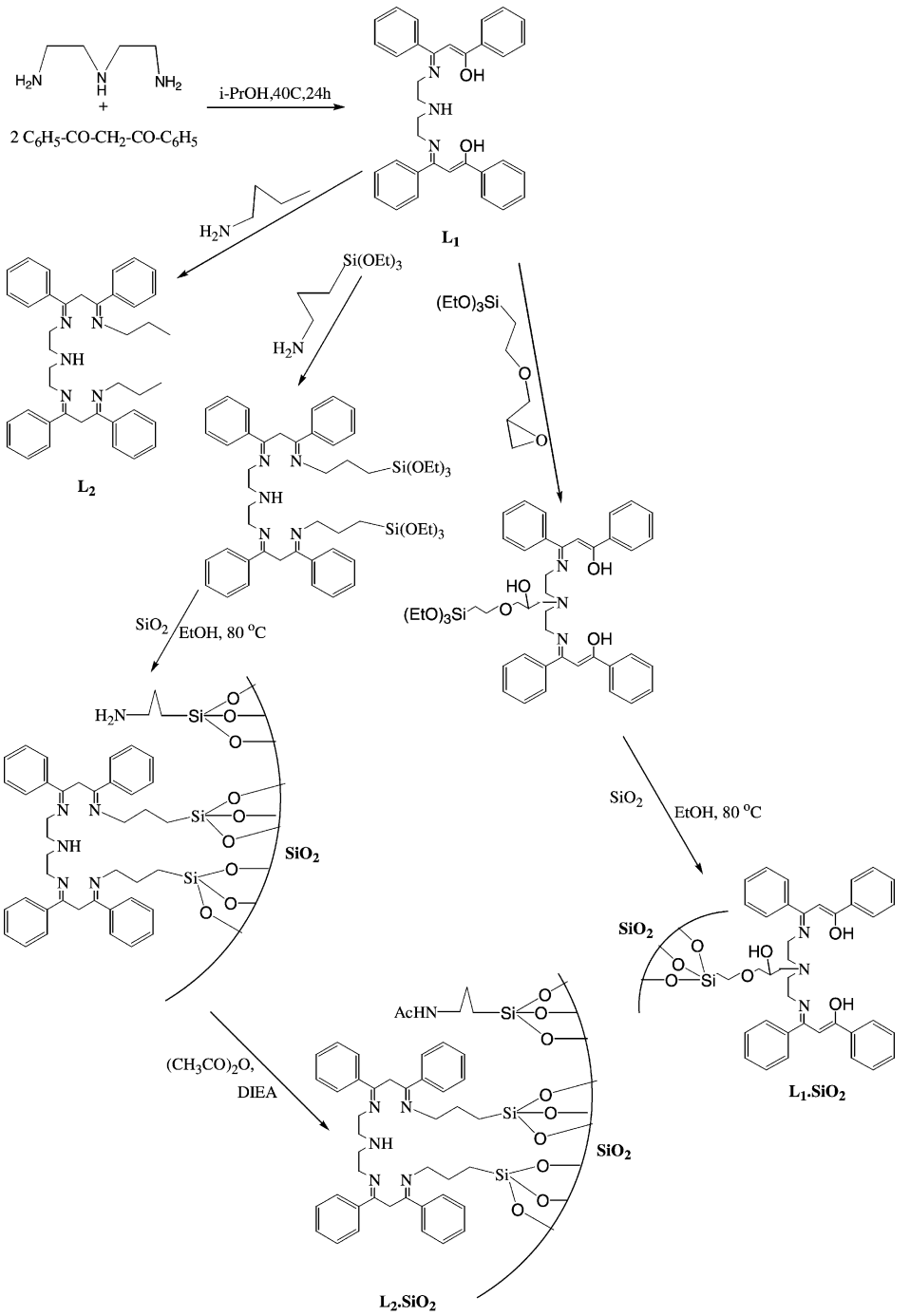


Fig. 1. Powder EPR spectrum of $Cu_2(L_1)$ in MeOH. Experimental conditions: temperature, 8.1 K; microwave frequency, 9.41 GHz; modulation amplitude, 10 G; microwave power, 32 mW; modulation frequency, 100 kHz.

The ligand L_1 was subsequently reacted with (3-glycidyloxypropyl)-trimethoxysilane in dry toluene, producing a 3-propoxy-2-hydroxypropyl-silane substituent on the secondary amine group. The new precursor was immobilized on SiO_2 by reacting at 80 °C for 24 h leading to the $L_1{\cdot}SiO_2$ hybrid material (Scheme 1). After the silica surface modification,



Scheme 1. Synthetic procedure of the supported macromolecules on a silica matrix.

Soxhlet extractions ensure that only covalently anchored ligands remain on the support corresponding to a ligand concentration of 0.25 mmol g^{-1} of silica. The infrared spectrum of the immobilized ligand shows bands at 1657 and 1483 cm^{-1} attributed to the C=N and C–O stretching vibrations [14]. The observed positive shift of these bands relative to those of the non-immobilized ligand could indicate ligand–silica matrix interactions changing the donor ability of the ligand. Encapsulation of Schiff base ligands in the supercages of zeolites or into the pores of MCM, results in a negative shift of the C=N vibration [28,29]. This vibration is also negatively shifted in the case of an anchored Schiff base on a polystyrene polymer, while at the same time the frequency of the C–O stretching is shifted to the opposite direction [30]. Therefore the present synthesis describes a successful anchoring of a glycidyl–Schiff base–silane on silica surface, in an one step procedure, instead of surface glycidylation and subsequent ligand immobilization as in previous reports [31,32].

The copper(II) containing $L_1{\cdot}SiO_2$ material presents the C=N and C–O stretching vibrations at 1629 and 1460 cm^{-1}, respectively. The powder EPR spectrum of $Cu_2(L_1){\cdot}SiO_2$ has the same qualitative features as those seen in the Fig. 1. Therefore similar to the case of $Cu_2(L_1)$ we conclude that in the SiO_2 matrix dinuclear copper complexes are formed.

The pilot condensation reaction of L_1 with propylamine results in the formation of L_2 which exhibits the C=N vibration at 1598 cm^{-1} missing any band attributable to a possible C–O bond. The ^1H NMR data clearly demonstrate the presence of additional propyl groups. The IR spectrum of $Cu_2(L_2)$ contains the ν(C=N) band shifted at 1575 cm^{-1} suggesting metal coordination to the azomethine group. The EPR spectrum of $Cu_2(L_2)$ in frozen solution, is characteristic of dinuclear Cu^{II} centers, i.e. has the characteristic semiforbidden feature at $g \sim 4$.

The reaction of L_1 with 3-aminopropyl-triethoxysilane (APTES) constitutes the formation of a new silane derivative and, finally, a different approach to immobilize covalently the L_1 on a silica matrix. This reaction occurs in dry toluene at 80 °C using a molar ratio of L_1: APTES equal to 1:1.9. Both diffuse-reflectance-FTIR data and thermogravimetric analysis clearly indicate that grafting of the organic macromolecule takes place. However, applying the Kaiser's test to this functionalised silica, which originally is used to detect the free, non-protected amino groups during the solid phase peptide synthesis [24], the presence of free amino group has been detected. This indicates that small amounts of APTES have been anchored as well, on SiO_2. To prevent any metal chemisorption by these NH_2 groups, we have deactivated them by acetylation reaction (Scheme 1). After the accomplishment of this step, the Kaiser's test was negative. The resulting $L_2{\cdot}SiO_2$ material and the copper(II) containing $L_2{\cdot}SiO_2$ material present the C=N vibration at 1653 and 1638 cm^{-1}, respectively. The powder EPR of $Cu_2(L_2){\cdot}SiO_2$ has the same qualitative features as those seen in Fig. 1. Therefore as in the case of $Cu_2(L_2)$ we conclude that in the SiO_2 matrix dinuclear copper complexes are formed.

3.2. Catalytic properties of homogeneous and heterogenized copper(II) complexes

The ability of heterogenized systems, $Cu_2(L_1){\cdot}SiO_2$ and $Cu_2(L_2){\cdot}SiO_2$, to catalyze the oxidation of 3,5-di-*t*-butylcatechol (DTBC) was evaluated and the results were compared with those found for the $Cu_2(L_1)$ and $Cu_2(L_2)$ complexes, when used as homogeneous catalysts. The oxidations were carried out in a methanol solution containing either 10 or 100 equiv. of triethylamine with a ratio of [catalyst]:[base]:[DTBC] equal to 0.3:3:200 or 0.3:30:200 always using air dioxygen as oxidant.

DTBQ formation and DTBC conversion catalyzed by the present dicopper systems are listed in Table 1. Based on these data we observe that the catalytic reaction depends upon the amount of base: by adding 100 equiv. of triethylamine instead of 10 equiv., the DTBC conversion is increased favoring clearly the DTBQ formation. Previous studies have indicated that the catalytic oxidation of substituted catechols by copper(II) complexes occurs through the formation of a dicopper–catechol complex [33] which is a precursor to the electron transfer [34]. Assuming such a complex formation, dissociation of the bridging groups of the dicopper centres must occur prior to the complexation of the substrate [35]. In this context, the added base seems to favor the formation of the initial dicopper–catechol complex by proton abstraction of DTBC. The suggested intermediate complex is represented in Scheme 2.

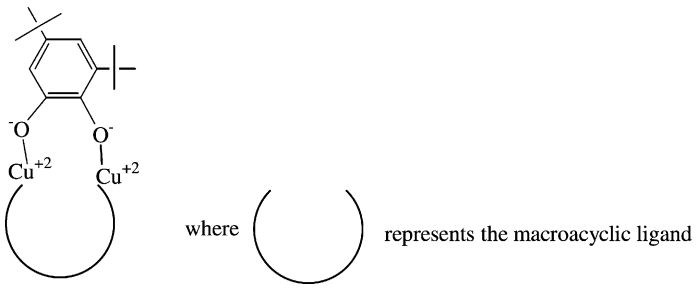
Table 1
Catalytic oxidation of 3,5-di-*t*-butylcatechol by dioxygen (catalyst:DTBC equal to 0.3:200)

Catalyst	Substrate/base	DTBQ formation (%)		DTBC conversion (%)	
		24 h	48 h	24 h	48 h
$Cu_2(L_1)$	DTBC + 10 equiv. Et_3N	7.0	8.0	35.0	36.0
	DTBC + 100 equiv. Et_3N	51.0	61.0	53.0	62.0
$Cu_2(L_1)\cdot SiO_2$	DTBC + 10 equiv. Et_3N	6.4	11.5	57.0	69.0
	DTBC + 100 equiv. Et_3N	44.7	74.0	54.6	82.0
$Cu_2(L_2)$	DTBC + 10 equiv. Et_3N	12.3	15.8	31.8	35.5
	DTBC + 100 equiv. Et_3N	44.0	49.0	59.0	69.0
$Cu_2(L_2)\cdot SiO_2$	DTBC + 10 equiv. Et_3N	14.2	22.0	50.0	54.0
	DTBC + 100 equiv. Et_3N	43.0	51.0	57.0	85.4

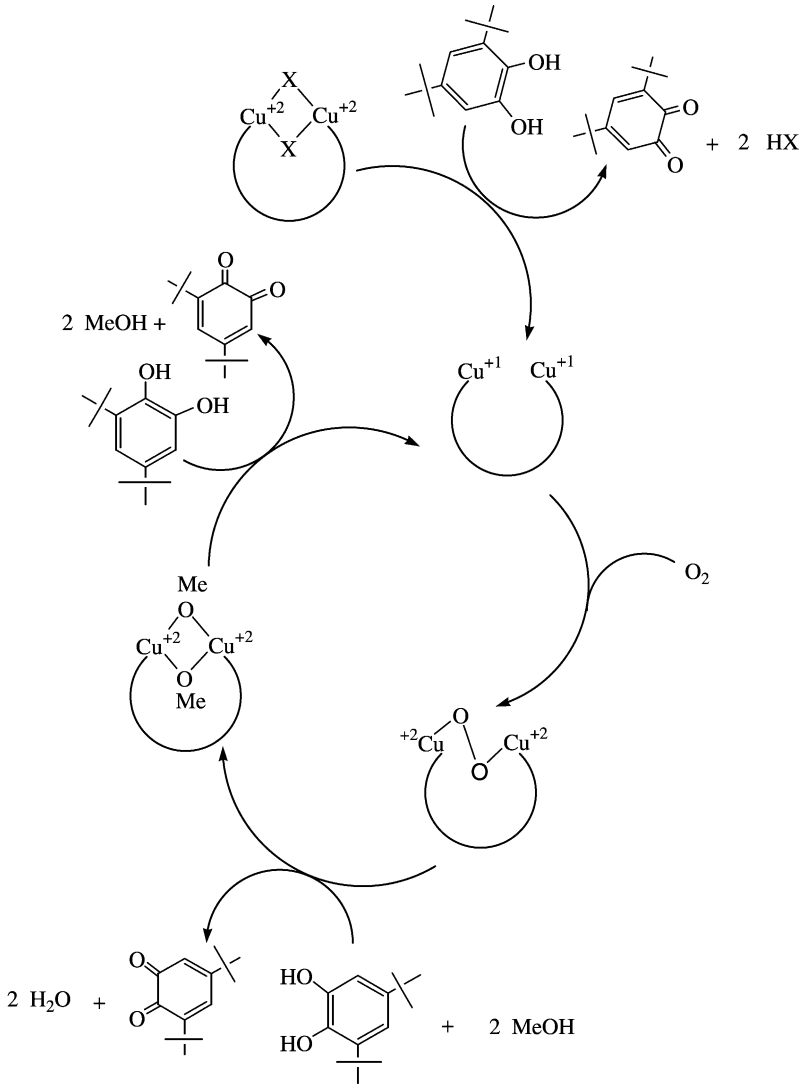
It is expected that semiquinone or quinone complexes may also be formed following to the oxidation of catechol [34]. These complexes are unstable and dissociate readily to give the respective products when DTBC, which bears electron-releasing substituents, is used as substrate [34].

The catalytic data presented in Table 1, show that the percentage of DTBC conversion does not fit in with that of DTBQ formation indicating that DTBQ is not the only oxidation product. Catechol oxidations assisted by copper ions usually result in either the production of *o*-quinones or ring-cleaved oxidation products [36] like muconic acid and its derivative γ-lactone of the muconic acid ester [37]. However, it was found that the highly substituted catechols, like DTBC, produce only quinones. This is due to the high redox potential of DTBQ [34]. In our case constituents of catalytic mixtures were identified by ^{1}H NMR to be (a) DTBC which is the remaining amount of the substrate, (b) DTBQ which is the principal oxidation product and (c) a set of signals located downfield with paramagnetic broadening.

The catalytic reaction using the $Cu_2(L_1)$ and $Cu_2(L_2)\cdot SiO_2$ as catalysts was followed by EPR. These experiments show the formation of a stable radical at room temperature (see Fig. 2). The width ($\Delta H = 9$ Gauss) and the g value ($g = 2.0044$) of this radical are characteristic of an *o*-semiquinone radical [38]. The presence of an *o*-semiquinone radical into the catalytic mixture is consistent with our NMR findings where the observed paramagnetically broadened ^{1}H NMR signals can be attributed to the protons of this radical. In general, the DTBQ formation as well as the *o*-semiquinone radical formation catalyzed by the present dicopper systems show similarities to the oxidation activity of the dicopper center of tyrosinase [39]. The tyrosinase-dependent oxidation of L-dopa and related derivatives does not appear to involve semiquinone radicals as intermediates; nevertheless some free radical species were detected by several



Scheme 2. The intermediate dicopper–catechol complex.



Scheme 3. Catalytic cycle for the oxidation of DTBC by the dinuclear copper(II) complexes in the presence of dioxygen.

authors and identified as the *o*-semiquinone anion derivatives of the corresponding catechols [40,41].

In summary, the present catalytic results show that the main catalytic product of the DTBC oxidation is the corresponding quinone. Based on this and in accordance with previous works [34,35,37,42,43], a plausible catalytic cycle for DTBC oxidation can be suggested as depicted in Scheme 3. This mechanism involves the formation of a dinuclear copper(I) complex, the possible production of a μ-peroxo species by oxygenation, and subsequent formation of a dinuclear copper(II) complex possibly with methoxy groups bridging the metal centers. During this redox procedure BTDC oxidation occurs yielding DTBQ.

In addition is should be pointed out that the catalytic activity of the homogeneous dicopper systems $Cu_2(L_1)$ and $Cu_2(L_2)$ towards the DTBC oxidation by atmospheric dioxygen is remarkable [17]. The coordination environment of $Cu_2(L_1)$ and $Cu_2(L_2)$ is different, i.e. $3N_2O$ atom donors in $Cu_2(L_1)$ and 5N atom donors in $Cu_2(L_2)$; despite that their catalytic behavior is analogous. Therefore the enhanced reactivity of

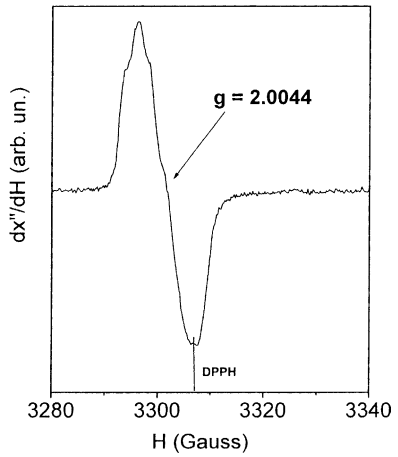


Fig. 2. EPR spectrum of the reaction mixture of DTBC oxidation catalyzed by $Cu_2(L_2)\cdot SiO_2$. The spectrum was recorded 60 min after the start of the catalytic reaction. Experimental conditions: temperature, 80 K; microwave frequency, 9.26 GHz; modulation amplitude, 1 G; microwave power, 0.63 mW; modulation frequency, 100 kHz.

$Cu_2(L_1)$ and $Cu_2(L_2)$ should not be attributed to the specific metal coordination environment, but rather to the original ligand frame which imposes the metal proximity of the dicopper systems.

The catalytic activity of the heterogenized system $Cu_2(L_1)\cdot SiO_2$, when compared with those of the homogeneous catalyst, $Cu_2(L_1)$, is further improved, in any base concentration. Namely, $Cu_2(L_1)\cdot SiO_2$ converts 69 and 82% of DTBC in lower and higher base concentration while the homogeneous catalyst converts 36 and 62%, respectively. When focused on DTBQ formation, we observe that 74% of DTBQ is formed, catalyzed by $Cu_2(L_1)\cdot SiO_2$, while 61% of DTBQ formation was catalyzed by $Cu_2(L_1)$. The DTBQ formation on the heterogenized catalyst $Cu_2(L_2)\cdot SiO_2$ (51%), with higher base concentration, is fairly similar to that on homogeneous catalyst $Cu_2(L_2)$ (49%). The immobilized catalyst converts 85.4% of DTBC while the homogeneous one converts 69% (Table 1). Finally, the catalytic activity of the supported copper catalyst $Cu_2(L_2)\cdot SiO_2$, at lower base concentration, is enhanced for DTBQ formation and DTBC conversion, compared with those of the corresponding homogeneous copper catalyst $Cu_2(L_2)$.

Homogeneous and heterogenised systems, at low base concentration, present important catalytic activity for DTBC conversion, although they exhibit lower selectivity for DTBQ. This difference is less remarkable at higher base concentration, when the $Cu_2(L_1)\cdot SiO_2$ and $Cu_2(L_1)$ are used as catalysts. In this case both the $Cu_2(L_1)\cdot SiO_2$ and $Cu_2(L_1)$ present higher selectivity for DTBQ. Factors as the nature of the ligand and the support could affect the observed selectivity. However, with the data at hand, we cannot safely draw any general correlation between the selectivity and the ligand type or the support. In addition, possible interactions between the silica support and the catechol substrate could be responsible for the observed enhanced reactivity of the heterogenized systems, i.e. favoring for example the formation of the intermediate dicopper–catechol complexes.

4. Conclusions

In the present paper the synthesis of two macroacyclic Schiff bases by a non-template procedure as well as the synthesis of their silane derivatives has been demonstrated. The grafting of these precursors on silica surface has also been described by two facile synthetic approaches. The immobilization of the organic molecules occurs via formation of covalent bonds between the ligands and the inorganic matrix. Both organic ligands and heterogenized ligands formed dicopper(II) complexes.

The catalytic properties of the copper(II) complexes have been evaluated for catechol oxidation in the presence of dioxygen, under mild and environmental friendly operating conditions. Both homogeneous and heterogenized systems were found to be effective catalysts for oxidative conversion of DTBC to DTBQ. However, during the catalytic process the presence of *o*-semiquinone radical has also been detected. By comparison, the catalytic effectiveness of the heterogenized catalysts, generally, was found to be higher than those of the homogeneous catalysts.

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