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ORIGINAL ARTICLE

Synthesis, characterization and catechol oxidase biomimetic catalytic activity of cobalt(II) and copper(II) complexes containing N_2O_2 donor sets of imine ligands



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Abstract New tetradentate imine ligands are derived from Schiff base condensation in a 1:2 molar ratio of the 1,2,4,5-tetra-amino benzene with 2-hydroxy benzaldehyde (L^1), 2,4-dihydroxy benzaldehyde (L^2) and 2-hydroxy naphthaldehyde (L^3). These ligands react with $CoCl_2$ and $CuCl_2$ in refluxing ethanol to yield a series of cobalt(II) and copper(II) complexes of the type $[M_2^{II}L^n]nH_2O$. The structure of the obtained ligands and their metal(II) complexes were characterized by various physicochemical techniques, *viz.* elemental analysis, molar conductance, magnetic susceptibility measurements, thermal analysis (TGA & DTG), IR, electronic absorption and ESR spectral studies. Four-coordinate tetrahedral and square-planar structures were proposed for cobalt(II) and copper(II) complex species respectively. The ability of the synthesized complexes to catalyze the aerobic oxidation of 3,5-di-*tert*-butylcatechol (3,5-DTBC) to the light absorbing 3,5-di-*tert*-butylquinone (3,5-DTBQ) has been investigated. The results obtained show that all complexes catalyze this oxidation reaction and slight variations in the rate were observed. The probable mechanistic implications of the catalytic oxidation reactions are discussed.

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1. Introduction

A number of enzymes found in Nature are able to catalyze the activation of dioxygen from the atmosphere, and use it to af-

fect a wide variety of remarkable reactions (Bugg, 2003, 1997; Kaim and Schwederski, 1995). Enzymes that are able to activate dioxygen include the oxidases, which use oxygen as an oxidant, and reduce dioxygen to hydrogen peroxide or water. One such enzyme is catechol oxidase (copper enzyme), which catalyzes the aerobic oxidation of *o*-diphenols (catechols) to the highly reactive *o*-quinones (Bugg, 2003, 1997; Kaim and Schwederski, 1995). Catechol oxidase, an enzyme ubiquitous in plants, insects and crustaceans (Hughes, 1999), is a type III copper protein containing a binuclear active site specializing in the two-electrons oxidation of a broad range of *o*-diphenols (catechols) to the highly reactive *o*-quinones

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(Solomon et al., 1992, 1996; Gerdemann et al., 2002) that auto polymerizes producing the pigment, melanin, which in turn, guards the damaged tissues against pathogens and insects among many of its protective functions (Deverall, 1961) Catechol melanin, the black pigment of plants (black banana and black sugar) is a polymeric product formed by the oxidative polymerization of catechol. Melanin exists in the hair, brain and eyes of Mammals and it is produced in pigment cells (ca. 1500 cell/mm² in human) of the skin (Reedijk, 1993). Melanin plays a role in the prevention of organism damage *in vivo* by the absorption of ultraviolet light. Melanin is the major paramagnetic organic compound *in vivo* and acts as a scavenger of toxic radicals formed *in vivo*. The role of melanin in the brain is to assist in electron-transfer processes. Melanin in the eyes is excited by ultraviolet light to form tyrosyl radicals, which apparently play a role in visual perception (Reedijk, 1993). The formation of melanin does not always proceed rapidly with tyrosinase. This slow formation accounts for the phenomenon of sunburn of skin, which occurs when irradiation is faster than melanin formation. Some attempts have been reported on the development of catalysts which either promote the formation of melanin or retard the multistage processes of the oxidation reaction (Reedijk, 1993). The catechol oxidase enzyme thus plays an important role in disease resistance in Mammals, bacteria, fungi and higher plants.

The study of chemical models that mimic oxidases has been developed with the objective of providing bases for understanding enzymatic activity and to develop simple catalytic systems that under mild conditions, exhibit appreciable catalytic activity (Jorge and Bernt, 1997; Olivia et al., 2002; Lakshmi et al., 1996; Moya and Coichev, 2006; Girenko et al., 2002; Ramadan and El-Mehasseb, 1998; Ramadan et al., 2006, 2011; Hassanein et al., 2005; Simandi et al., 1995, 2003; Jung and Pierpont, 1994; Qiu et al., 2005; Kovala-Demertzi et al., 1998; Dilworth et al., 1977). Synthetic model studies on the reactivity of cobalt complexes toward the oxidation of ascorbic acid and phenolic substrates, implicate both structural and electronic factors as being responsible for the catalytic activity (Jorge and Bernt, 1997; Olivia et al., 2002; Lakshmi et al., 1996; Ramadan et al., 2006; Yang and Vigeo, 1991).

Therefore, the structural and electronic properties of the synthesized cobalt(II) and copper(II) imine complexes are of interest. Synthesis, characterization and catecholase biomimetic catalytic activity of the reported cobalt(II) and copper(II) imine complexes as functional catecholase models are the subjects of the present article.

2. Experimental

2.1. Materials

Cobalt(II) and copper(II) salts, 1,2,4,5-tetra-amino benzene, 2-hydroxy benzaldehyde, 2,4-dihydroxy benzaldehyde and 2-hydroxy naphthaldehyde were procured from Aldrich. All chemicals used are of high purity analytical grade.

2.2. Synthesis of imine ligands

The reported imine ligands were prepared by the following procedure. To a solution of 1,2,4,5-tetra-amino benzene (0.1 mol) was added a solution of the corresponding carbonyl compound (0.2 mol) in absolute EtOH (50 ml). The reaction

mixture was stirred and boiled under reflux for 2 h. On cooling, the solid product that precipitated was removed by filtration and washed with cold EtOH. The crude product was recrystallized from hot EtOH to give dark red fine powders, which were filtered off washed with cold EtOH and finally dried in vacuum over CaO. The purity of these ligands was checked by elemental analysis, constancy of the melting point, and spectral measurements.

2.3. Synthesis of the metal chelates

A hot solution of cobalt(II) or copper(II) chloride (0.02 mol) in absolute EtOH (50 ml) was added to a boiling solution of the imine ligand (0.01 mol) in absolute EtOH (50 ml) and the reaction mixture was refluxed for 4 h. The reaction mixture was then allowed to stand at room temperature overnight, whereby a microcrystalline product was formed. All complexes thus obtained were filtered off, washed several times with EtOH, then Et₂O, and finally dried in evacuated desiccators over anhydrous CaO.

2.4. Physical measurements

The IR spectra were recorded using KBr disks in the 4000–200 cm⁻¹ range on a Unicam SP200 spectrophotometer. The electronic absorption spectra were obtained in methanolic solution with a Shimadzu UV-240 spectrophotometer. Magnetic moments were measured by Gouy's method at room temperature. ESR measurements of the polycrystalline samples at room temperature were made on a Varian E9 X-band spectrometer using a quartz Dewar vessel. All spectra were calibrated with DPPH ($g = 2.0027$). The specific conductance of the complexes was measured using freshly prepared 10⁻³ M solutions in electrochemically pure MeOH or DMF at room temperature, using an YSI Model 32 Conductivity meter. The thermogravimetric measurements were performed using a Shimadzu TG 50-Thermogravimetric analyzer in the 25–800 °C range and under an N₂ atmosphere. Elemental analyses (C, H, and N) were carried out at the Micro analytical Unit of Cairo University.

2.5. Catechol oxidase biomimetic catalytic activity

A mixture of 1.0 ml of 3,5-di-*tert*-butylcatechol (3,5-DTBC) solution (30 mM) in methanol and 1.0 ml of metal complex solution (~3 mM) in DMF was placed in a 1 cm path length optical cell containing 1.0 ml of DMF in a spectrophotometer. The final concentration of reaction mixture is catechol (20 mM) and complex (1 mM). The formation of 3,5-di-*tert*-butyl-catequinone (3,5-DTBQ) was followed by observing the increase of characteristic quinone absorption band at 400 nm. For each set of observation, a curve of concentration of 3,5-DTBQ formed (calculated by using corresponding ϵ value) *versus* time was plotted and initial rates were calculated by drawing a tangent to curve at $t = 0$ and finding its slope. After this initial fast phase, the average rate of reaction was also calculated. The above described experiment was repeated under two sets: (i) in the reaction mixture the concentration of catalyst was varied (0.5, 1.0, 1, 2.0 mM) and concentration of DTBC was kept constant at 20 mM. (ii) Concentration of DTBC was varied (10, 20, 30, 40 mM) and concentration of

catalyst was kept fixed at 1.0 mM. For each set of data initial rates were calculated and graphs of rate *versus* concentration of catalyst and rate *versus* concentration of catechol were plotted.

3. Results and discussion

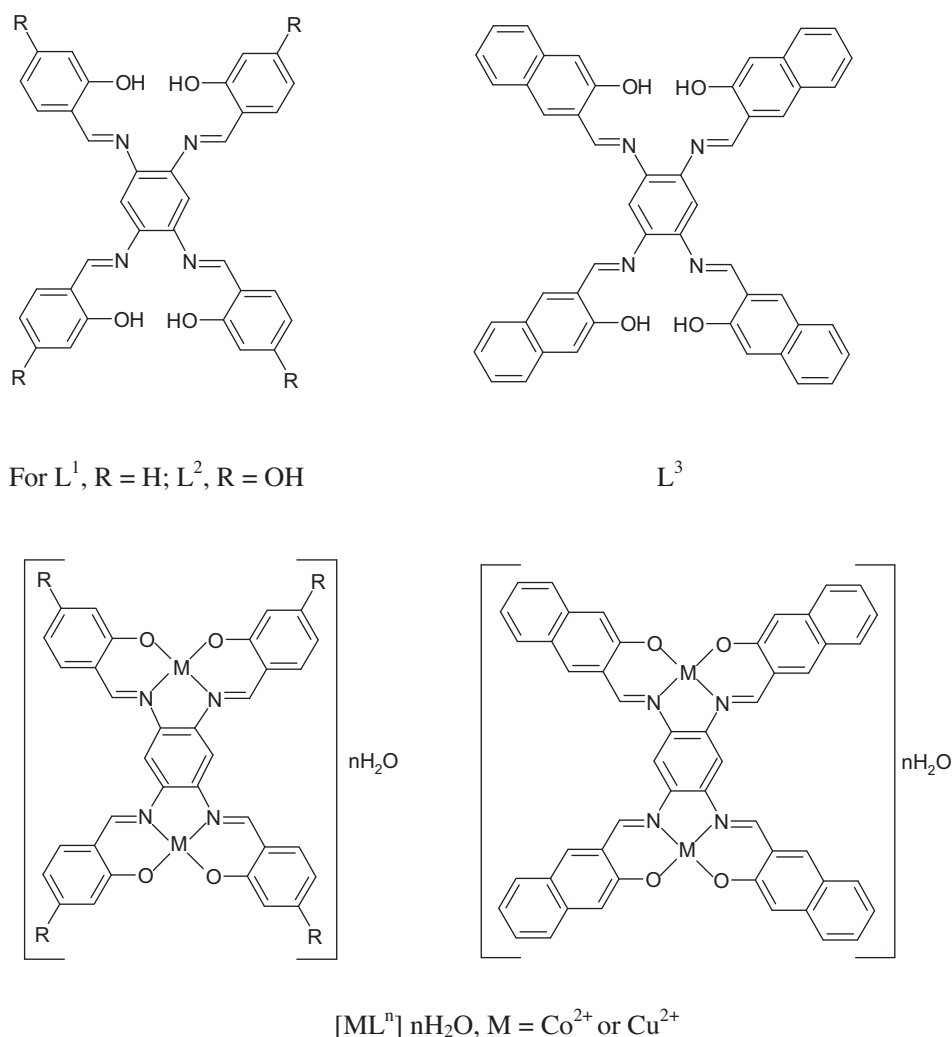
3.1. General

The imine ligands used in this study are derived from Schiff base condensation in a 1:1 molar ratio of the 1,2,4,5-tetra-amino benzene with 2-hydroxy benzaldehyde, (L^1), 2,4-dihydroxy benzaldehyde (L^2) and 2-hydroxy naphthaldehyde, (L^3), as shown in Scheme 1. Interaction of cobalt(II) or copper(II) salts with the title ligands in 1:2 (L:M) molar ratio in ethanolic solution produces a series of metal chelates (1–6) in an appreciable yield. The pure products were characterized by the elemental analysis and spectroscopic techniques chemical analysis and some physical properties of the pure isolated cobalt(II) and copper(II) complexes are listed in Table 1. The analytical results demonstrate that all the complexes have (2:1) metal–ligand stoichiometry. The microcrystalline chelates are various

shades of brown and they are stable as solid or in solution under the atmospheric conditions. These pure complexes are freely soluble in DMF, DMSO and completely insoluble in water and the common organic solvents. The molar conductivities obtained in DMF solution demonstrate that these complexes are non-electrolytes with Λ_M values lying in the 23.64–41.66 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range. This fact confirms the analytical results and the accordance of the suggested chemical formulae of these metal chelates.

3.2. Mode of bonding

Important vibration bands of the free ligands and their cobalt(II) and copper(II) complexes along with their assignments, which are useful for determining the mode of coordination of the ligands, are given in Table 2. The free imine ligands exhibit medium bands in the region 3412–3541 cm^{-1} assigned to the OH, stretching (Dilworth et al., 1977). This band disappears on complexation, indicating the replacement of the phenolic hydrogen by the metal ion. Several significant changes, with respect to the spectra of the ligands, are observed in the spectra of the corresponding metal complexes. A new band



Scheme 1 Structure of L^1 , L^2 , L^3 and their complexes of cobalt(II) and copper(II) ions.

Table 1 Molecular formulae, elemental analyses and physical properties of cobalt(II) and copper(II) complexes.

Complex	Color	Found (calcd.)				
		C	H	N	M	
1	[Co ₂ L ¹] 3H ₂ O	Deep red	53.98 (53.34)	3.89 (3.55)	8.03 (8.30)	16.97 (17.45)
2	[Co ₂ L ²] 4H ₂ O	Red	47.57 (47.56)	3.63 (3.43)	7.18 (7.40)	15.20 (15.56)
3	[Co ₂ L ³] 5H ₂ O	Dark red	60.66 (60.94)	3.88 (3.97)	6.17 (6.18)	13.43 (13.00)
4	[Cu ₂ L ¹] 5H ₂ O	Brown	49.66 (49.99)	3.85 (3.88)	7.49 (7.78)	17.17 (17.64)
5	[Cu ₂ L ²] 3H ₂ O	Faint Brown	48.86 (48.62)	3.59 (3.20)	7.17 (7.49)	16.36 (16.98)
6	[Cu ₂ L ³] 2H ₂ O	Yellowish brown	63.90 (64.10)	3.55 (3.48)	6.29 (6.50)	14.40 (14.75)

Table 2 The characteristic IR spectral bands of the imine ligands Lⁿ and their cobalt(II) and copper(II) complexes.

Compound	$\nu(\text{O-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
L ¹	2846 ^b	1612	1200
[CoL ¹]		1595	1228	513	440
[CuL ¹]		1585	1218	511	456
L ²	2335	1600	1210
[CoL ²]		1595	1220	517	455
[CuL ²]		1590	1242	519	467
L ³	2362	1600	1217
[CoL ³]		1595	1230	507	446
[CuL ³]		1590	1237	513	449

appearing in the 1247–1289 cm⁻¹ region in the spectra of complexes was assigned to the $\nu(\text{C-O})$ of the phenolate mode (Ramadan and Issa, 2005; Vergopoulos et al., 1993). The bonding of phenolate oxygen to the metal ion is further supported by the appearance of new absorption band at 510–550 cm⁻¹, which is not observed in the spectra of the free ligands. This band is characteristic of $\nu(\text{M-O})$ stretching Nakamoto, 1986.

In all complexes, the azomethine band of the Schiff-base linkage undergoes a remarkable shift toward lower wave numbers (5–27 cm⁻¹) compared with its position in the spectra of the free ligands, as a consequence of coordination of the nitrogen atom to the metal ion (Maroney and Rose, 1984). Coordination of the azomethine group to the metal ion is expected to reduce the electron density on the Schiff-base linkage (C=N), causing a reduction in its vibrational frequency. However, the corresponding absorption band appears to be slightly shifted to lower frequency in complexes [CoL³] and [CuL³] in agreement with other reported results (Ramadan and Issa, 2005). Coordination of the nitrogen atoms to M²⁺ ion is further supported by the appearance of a new absorption band at 440–467 cm⁻¹ range which are assigned to the $\nu(\text{N-M})$ Nakamoto, 1986.

The spectra of all complexes reveal an absorption band in the region 1200–1220 cm⁻¹ characteristic to the α -diimine moiety of the metal chelates (Rai and Prasad, 1994). This finding has been observed in several α -diimine containing tetraaza-macrocyclic Schiff-base complexes (Maroney and Rose, 1984).

For all complexes, broad bands present in the range 3450–3550 cm⁻¹, assignable to $\nu(\text{OH})$, clearly confirm the presence of surface and crystalline water (Nakamoto, 1986; Ferraro, 1971). Since vibrational modes such as wagging, twisting and rocking activated by coordination to the metal have not been found in the expected ranges, it appears that coordinated water

is not present. These results are consistent with the thermogravimetric studies, using TG and DTG techniques. In fact this water is lost in the 42–100 °C range.

3.3. Electronic absorption spectra

The electronic absorption spectra of the reported ligands and their cobalt(II) and copper(II) complexes were measured at room temperature in DMF solution and the corresponding data are given in Table 3. The spectra of the free ligands give rise to high energy absorption below 300 nm, due to $\pi \rightarrow \pi^*$ transition of the naphthyl and phenyl moieties. The strong absorption band at ≈ 310 nm of the uncoordinated ligands is assignable to the $n \rightarrow \pi^*$ transition originating from the azomethine linkage of the Schiff base moiety (West et al., 1988, 1991). The absorption spectral data in Table 3 show that there is a significant change in the energy of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ band on complexation. The band maximum in the spectra of chelates is shifted to lower frequencies relative to those in the free ligands. This bathochromic shift may result from the extended conjugation in the ligand forced by the chelated metal ion (Ismael, 1997; Gang and Yuan, 1994).

In the low energy region the spectra of cobalt(II) complexes, **1–3**, exhibit two low-intensity bands, the $^4\text{A}_2 \rightarrow ^2\text{T}_1$ (F) (ν_2) and $^4\text{A}_2 \rightarrow ^2\text{T}_1$ (P) (ν_3) transitions respectively, supporting the tetrahedral geometry (Gaber et al., 2008; Lever, 1970) second of which is present as a shoulder in the 18,999–19,230 cm⁻¹ range.

The spectra of the four-coordinate complexes **4**, **5** and **6** display three electronic absorptions in the 14,525–15,051, 16,524–17,490 and 18,035–19,450 cm⁻¹ ranges which can unambiguously be assigned to the three spin allowed transitions: $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$, $^2\text{B}_{1g} \rightarrow ^2\text{A}_{1g}$ and $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$, respectively (Lever, 1970; Singh et al., 2007; Li et al., 2008). These spectral features support the square-planar geometry around copper(II) center (Khan et al., 2009; Ramadan et al., 2005).

3.4. ESR-spectra and magnetic moment measurements

The effective magnetic moments (BM) measured at room temperature indicate that the reported cobalt(II) and copper(II) complexes are magnetically dilute (Dutla and Syamal, 2007). The magnetic moments of the three complexes namely [CoL¹], [CoL²] and [CoL³] are 4.1, 3.98 and 4.3 BM respectively. These values lie in the range expected for the four-coordinated tetrahedral cobalt(II) complexes of a high spin type, *i.e.*, these magnetic moments are in agreement with the spin only value for three unpaired electrons (Dutla and Syamal,

Table 3 Electronic absorption spectra (cm^{-1}) of cobalt(II) and copper(II) imine complexes 1–6.

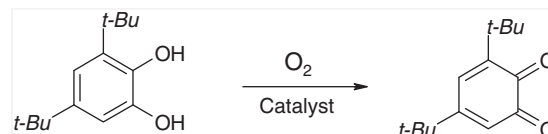
Complex	λ_{max} (cm^{-1})			
	${}^4A_2 \rightarrow {}^2T_1(\text{F})$	${}^4A_2 \rightarrow {}^2T_1(\text{P})$	$n \rightarrow \pi^*$	$\pi \rightarrow \pi^*$
[CoL ¹]	16,384	19,186	35,097	40,816
[CoL ²]	16,772	19,230	37,735	40,596
[CoL ³]	15,897	18,999	37,027	38,461
	${}^2B_{1g} \rightarrow {}^2B_{2g}$	${}^2B_{1g} \rightarrow {}^2A_{2g}$	${}^2B_1 \rightarrow {}^2E_{1g}$	
[CuL ¹]	14,525	17,490	18,035	27,777
[CuL ²]	15,051	17,062	19,450	28,169
[CuL ³]	14,839	16,524	18,976	27,624

Table 4 Magnetic moments and ESR spectral data of copper(II) imine complexes.

Complex	g_{\parallel}	g_{\perp}	g_{av}	G	μ_{eff} (BM)
[CuL ¹]	2.222	2.055	2.107	4.036	2.24
[CuL ²]	2.235	2.055	2.115	4.273	1.93
[CuL ³]	2.255	2.061	2.126	4.180	1.88

2007). The data Table 4 reveal that the observed magnetic moments fall in the range 1.88–2.10 BM. These values are close to the spin only ($S = 1/2$) behavior of 1.73 BM for d^9 configuration and reflect the absence of any metal-metal interaction with the neighboring molecules. This finding is further confirmed from the clear resolution of the ESR spectra.

The X-band ESR spectra of the polycrystalline samples of the reported copper(II) complexes 4, 5 and 6 were recorded at room temperature. The g_{\parallel} and g_{\perp} values were computed from the spectrum using DPPH ($g = 2.0027$) as “ g ” marker. Based on the g -values Table 4, the copper(II) ion in these complexes is in an axial distorted ligand field. Since the g_{\parallel} and g_{\perp} values are close to 2 and $g_{\parallel} > g_{\perp}$ suggesting a tetragonal distortion around the copper(II) ion corresponding to the elongation along the four fold symmetry Z -axis (West et al., 1995). However, all complex species show parameters which are characteristic of the axial symmetry with the elongation of axial bonds and the orbital $d_{x^2-y^2}$ is the ground state. Elongated square planar or distorted square-pyramidal stereochemistries would be consistent with these data, but trigonal-pyramidal involving compression of the axial bonds should be excluded (Fernandes et al., 2007). The spectra of most complexes show one signal and the absence of the hyperfine splitting may be attributed to a strong dipolar interaction between the copper(II) ions in the unit cell. The analysis of the spectra gives the trend: $g_{\parallel} > g_{\perp} > g_e$ (2.0023), which supports that the orbital $d_{x^2-y^2}$ is the ground state (West et al., 1995). It is well known that for an ionic environment g_{\parallel} is normally 2.3 or larger, but for covalent environment g_{\parallel} is less than 2.3. The observed g_{\parallel} value for the investigated complexes is less than 2.3; consequently the coordination environment is covalent. The trend g_{\parallel} (2.222–2.255) $>$ g_{\perp} (2.055–2.068) observed for all complexes was found to be in accordance with the criterion of Kivelson and Neiman implying the presence of the unpaired electron that is localized in $d_{x^2-y^2}$ orbital for copper(II) ion characteristic of the axial symmetry (Kivelson and Neiman, 1961). Tetragonal elongated structure is confirmed for the reported copper(II) complexes.

**Scheme 2** Catalytic aerobic oxidation of 3,5-di-tert-butylcatechol (3,5-DTBC) to 3,5-di-tert-butylquinone (3,5-DTBQ).

The value of the exchange interaction (G) between the copper(II) centers in a polycrystalline solid has been calculated using the relation $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ (Raman et al., 2005). According to Hathaway *et al.* if the $G > 4$, the exchange interaction is negligible, while $G < 4$ indicates considerable exchange interaction in the solid complexes (Hathaway and Billing, 1970). The data in Table 4 reflect the absence of any exchange interaction between copper(II) centers in the solid complexes in accordance with the results of magnetic moment measurements.

Great effort to grow crystals of these metal imine complexes suitable for X-ray structure determination so far has been unsuccessful. However, based on the composition of these complexes, their IR and electronic spectra, conductivity measurements, magnetic studies (vide infra), these complexes are proposed to have a tetrahedral geometry for cobalt(II) ion and a square-planar environment in the case of copper(II) species, as shown in Scheme 2. The plausible structure of these complexes is further illustrated by the following thermal studies.

3.5. Thermal studies

3.5.1. Thermogravimetric analysis (TGA–DTG)

The content of a particular component in a complex changes with its composition and structure. Thus, the content of such components can be determined based on the mass losses of these components in the thermogravimetric plots of the complexes. Therefore, in order to throw more insight into the structure of the reported complexes, thermal studies on the solid complexes using the thermogravimetric (TG) and differential thermogravimetric (DTG) techniques were performed. The TG and DTG thermograms of complexes 1–6 were recorded under a dynamic N_2 atmosphere and some of the important characteristics, *e.g.* the decomposition stages temperature ranges, maximum decomposition peaks DTG_{max} , percentage losses in mass, and the assignment of decomposition moieties

Table 5 Thermogravimetric analysis data of cobalt(II) and copper(II) imine complexes.

Complex	Temperature range °C	DTG T °C	% Weight loss found (calcd.)	Species formed
[Co ₂ L ¹] 3H ₂ O	42–100	42.30	07.37 (07.47)	[CoL ¹]
	100–600	568.19	68.60 (69.87)	Co ₂ O ₃
[Co ₂ L ²] 4H ₂ O	45–95	49.44	09.51 (09.51)	[CoL ²]
	95–750	571.62	69.98 (70.45)	Co ₂ O ₃
[Co ₂ L ³] 5H ₂ O	50–100	60.94	09.21 (09.93)	[CoL ³]
	100–750	687.69	72.84 (73.18)	Co ₂ O ₃
[Cu ₂ L ¹] 5H ₂ O	50–100	68.56	10.97 (12.49)	[CuL ¹]
	100–650	525	64.86 (65.48)	CuO
[Cu ₂ L ²] 3H ₂ O	60–100	45	05.57 (07.42)	[CuL ²]
	100–600	460	72.84 (73.05)	CuO
[Cu ₂ L ³] 2H ₂ O	60–100	45	04.57 (04.81)	[CuL ³]
	100–650	450	78.84 (79.58)	CuO

are listed in Table 5. The TG curve was redrawn as mg mass loss versus temperature and typical TG and DTG curves for complexes [CoL³] 5H₂O and [CuL³] 2H₂O are represented in Fig. 1.

The thermogravimetric curves of complexes 1–6 are similar and show two stages of decomposition within the temperature range of ambient temperature to 750 °C. The thermal decomposition occurs in two stages within the temperature range 45–750 °C. The first stage shows the dehydration process which starts at 45 °C and comes to an end at 100 °C. The weight losses are corresponding to the volatilization of 2–5 surface and lattice water molecules and the activation energy values are in the 26.87 and 55.22 kJ mol⁻¹ range. The second thermal degradation stage comprises several successive and unresolved steps within the temperature range 100–750 °C, with the maximum decomposition peaks DTG_{max} lying at 723 and 960°K range. The corresponding mass losses are due to the complete decomposition and removal of the organic ligand. The mass losses in this stage are in good agreement with calculated mass losses and the final product is quantitatively proved to be anhydrous metallic oxide Co₂O₃ for cobalt(II) complexes and CuO for copper(II) chelates. The observed overall weight loss amounts Table 5, are in good agreement with the calculated values based on the suggested formulae of these complexes and consistent with the thermal material decomposition and elimination of the complex molecule contents. The activation energies of the thermal dehydration and pyrolytic processes of these complexes are 26.87–55.22 and 111.15–205.53 kJ mol⁻¹ respectively.

3.5.2. Kinetic aspects

The kinetic activation parameters of the thermal decomposition of the investigated cobalt(II) and copper(II) imine complexes, namely the activation energy E^* in kJ mol⁻¹ is evaluated graphically by using the Coats–Redfern method (Coats and Redfern, 1964):

$$\log[g(x)/T^2] = \log(AR/E\beta)[1 - 2RT/E] - E/2.303RT$$

where α is the fraction of the sample decomposition, T the temperature, A the pre-exponential factor, $g(x)$ the kinetic mechanism function, R the gas constant, β the heating rate and E the activation energy.

In the present investigation $\log[g(x)/T^2]$ plotted against $10^3/T$ gives straight lines whose slope and intercept are used to evaluate the kinetic parameters ΔH^* and ΔG^* by the least

squares method. The goodness of fit is checked by calculating the correlation coefficient.

The entropy of activation (ΔS^*) was computed by employing the following relation: $\Delta S^* = R \ln(Ah/K_B T_s)$.

Where k is the Boltzmann's constant, T_s the DTG peak temperature, h the Plank's constant and R the gas constant. All the calculations were done with the help of a computer program.

The thermodynamic parameters of the TGA studies permit coordinated and uncoordinated water molecules, to distinguish. The TG curves of the reported complexes demonstrated that, two thermal processes can be observed: (a) dehydration and (b) pyrolytic decomposition.

3.5.2.1. Dehydration processes. The first stage that takes place in thermal decomposition of the complexes 1–6 is assigned to the dehydration processes of the outer coordination sphere water molecules, *i.e.*, the surface and lattice water molecules. The data in Table 6 reveal that, the activation energy (E^*) and the dehydration enthalpy (ΔH^*) values depend on the number of water molecules present in complex molecule. The first weight loss calculations obtained from the TGA curves of the complexes 1–6 are assigned as dehydration of the physically adsorbed water molecules. The difference in the thermal data (E^* , ΔH^*) is attributed to the difference in water content that exists per complex molecule.

3.5.2.2. Pyrolytic decomposition. Once dehydrated, the investigated cobalt(II) and copper(II) complexes are subjected to decomposition of nearly the same manner and all ended with the formation of metal oxide. The larger E^* and ΔH^* values for the dehydrated complex species namely [CoL³] and [CuL¹] compared to the other complexes may be due to strong thermal agitation accompanying the successive thermal elimination of organic ligand. This points to the existence of these complexes in an associated structure and supports the proposed dimeric forms.

For all dehydrated complexes the thermodynamic parameter values of the pyrolytic decomposition stages were found to be higher than that of the dehydration stage which indicates that the rate of the pyrolytic stage is lower than that of the dehydration stage. This may be attributed to the structural rigidity of the coordinated imine ligand as compared with H₂O which requires lower energy for its rearrangement before undergoing any compositional changes associated with its

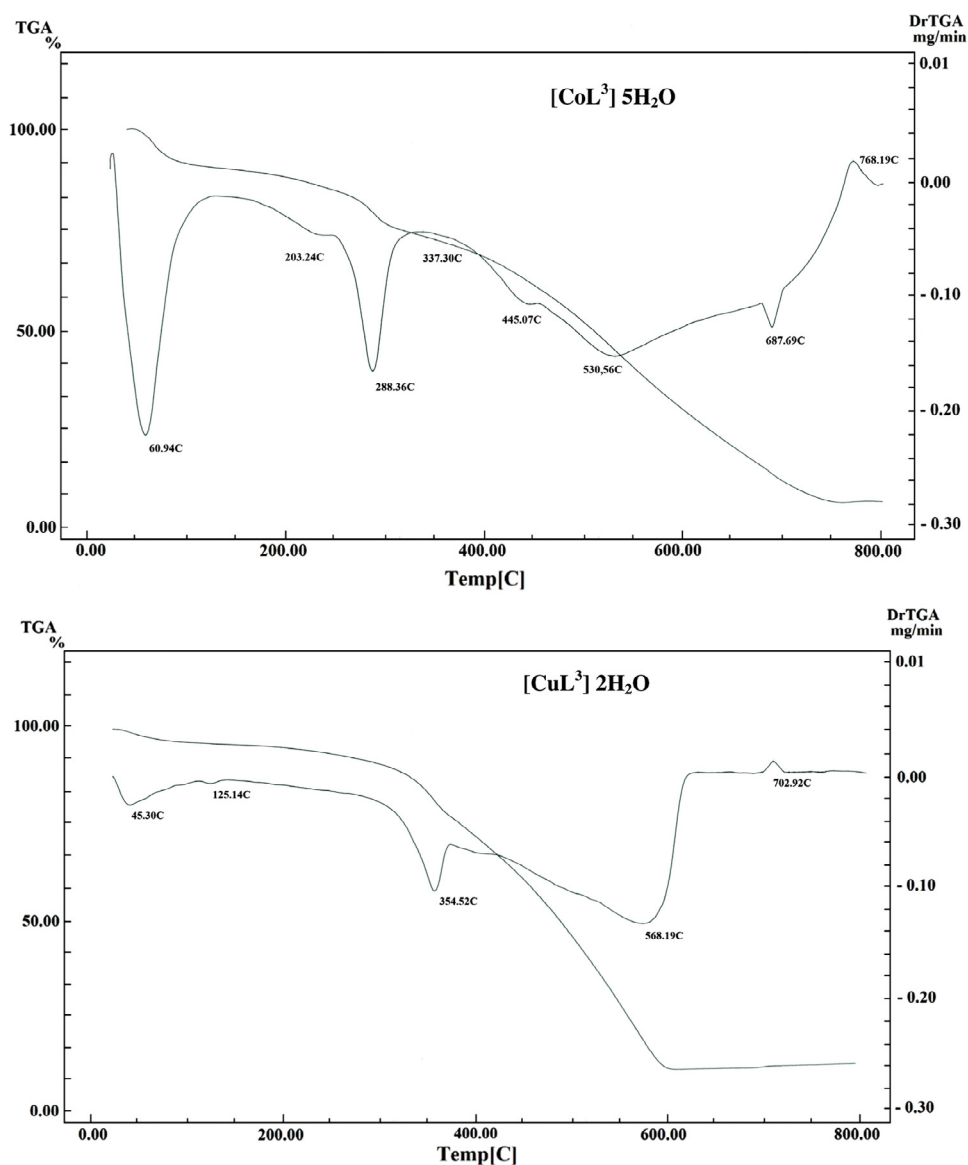


Figure 1 Thermogravimetric (TGA/DTG) curves of $[\text{CoL}^3] 5\text{H}_2\text{O}$ and $[\text{CuL}^3] 2\text{H}_2\text{O}$ complexes.

Table 6 Kinetic parameters of cobalt(II) and copper(II) imine complexes.

Complex	Stage	T (K)	A (s^{-1})	E^*	ΔH^*	ΔS^*	ΔG^*
$[\text{Co}_2\text{L}^1] 3\text{H}_2\text{O}$	1	315	0.4529	026.87	023.95	-0.2546	124.21
	2	841	11.740	111.15	108.23	-0.2326	274.13
$[\text{Co}_2\text{L}^2] 4\text{H}_2\text{O}$	1	332	8.790	38.900	34.04	-0.2300	113.63
	2	844	11.401	186.96	181.54	-0.2349	294.94
$[\text{Co}_2\text{L}^3] 5\text{H}_2\text{O}$	1	333	3.840	55.22	52.30	-0.2353	106.77
	2	960	10.510	205.53	202.61	-0.2337	393.35
$[\text{Cu}_2\text{L}^1] 5\text{H}_2\text{O}$	1	341	1.4200	54.830	51.920	-0.2451	118.82
	2	798	10.610	204.35	201.44	-0.2335	389.70
$[\text{Cu}_2\text{L}^2] 3\text{H}_2\text{O}$	1	319	10.110	37.82	34.90	-0.2263	118.02
	2	733	1.917	156.51	153.59	-0.2472	248.74
$[\text{Cu}_2\text{L}^3] 2\text{H}_2\text{O}$	1	313	10.110	28.82	25.90	-0.2263	108.02
	2	723	1.917	126.51	123.59	-0.2472	228.74

E^* , ΔH^* and ΔG^* are in kJ mol^{-1} , ΔS^* in J K mol^{-1} .

Table 7 Kinetic parameters (k_{cat} , K_m and V_{max}) in methanolic solution at 298 K of the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ.

Complex	k_{cat} (h^{-1})	$K_m \times 10^2$ (M)	$V_{\text{max}} \times 10^4$ (MS^{-1})
1	270.00	9.76	4.50
2	222.00	8.57	3.70
3	150.00	5.47	2.50
4	390.00	10.92	6.50
5	352.20	10.03	5.87
6	187.20	6.14	3.12

Complexes details are as listed in Table 1.

elimination. The negative values of ΔS^* for all complexes (Table 6), indicate that during thermal decomposition stages the resulting transition states (the activated complexes) are more orderly, *i.e.* in a less random molecular configuration, than the reacting complexes. The data in Tables 6 and 7 reveal also that the values of the free energy ΔG^* increase for the subsequent decomposition stages due to increase in the values of $T\Delta S$ from one step to another which override the value of ΔG^* . This increase reflects that the rate of the subsequent removal of the organic ligand moiety is lower than that of the surface and lattice water molecules. The positive values of ΔH^* means that the thermal decomposition processes are endothermic.

3.6. Catechol oxidase biomimetic catalytic activity studies

The catechol oxidase biomimetic catalytic activity of the reported cobalt(II) and copper(II) imine complexes, as functional models has been determined by the catalytic oxidation of catechols (Selmezi et al., 2003; Neves et al., 2002; Seneque et al., 2002; Belle et al., 2007) (Scheme 2). Among the different catechols used in catechol oxidase model studies, 3,5-di-*tert*-butylcatechol (3,5-DTBC) is the most widely used substrate for catecholase activity of *tyrosinase* (Monzani et al., 1998, 1999; Bolus and Vigeo, 1982; Zippel et al., 1996). Its low redox potential for the, quinone-catechol couple, makes it easy to be oxidized to the corresponding quinone 3,5-DTBQ, and its bulky substituents, make further oxidation reactions such as ring opening remote. The product 3,5-di-*tert*-butyl-*o*-quinone (3,5-DTBQ), is considerably stable and exhibits a strong absorption at $\lambda_{\text{max}} = 400 \text{ nm}$ ($\epsilon = 1900 \text{ M}^{-1} \text{ cm}^{-1}$ in MeOH) (Gentshev et al., 2000). Therefore, activities and reaction rates can be determined using electronic spectroscopy by following the appearance of the characteristic absorption of the 3,5-di-*tert*-butyl-*o*-quinone (3,5-DTBQ). The reactivity studies were performed in DMF solution because of the solubility of the complexes as well as the substrate. When the oxidation reaction was allowed to continue for 48 h at room temperature, only *o*-quinone was detected. The exceptionally high stability found for *o*-quinone at room temperature suggests that a single reaction pathway is being followed and that the *o*-quinone produced does not undergo further oxidative cleavage.

3.6.1. Initial rate studies

Prior to a detailed kinetic study, it is necessary to get an estimation of the ability of the complexes to oxidize catechol. The

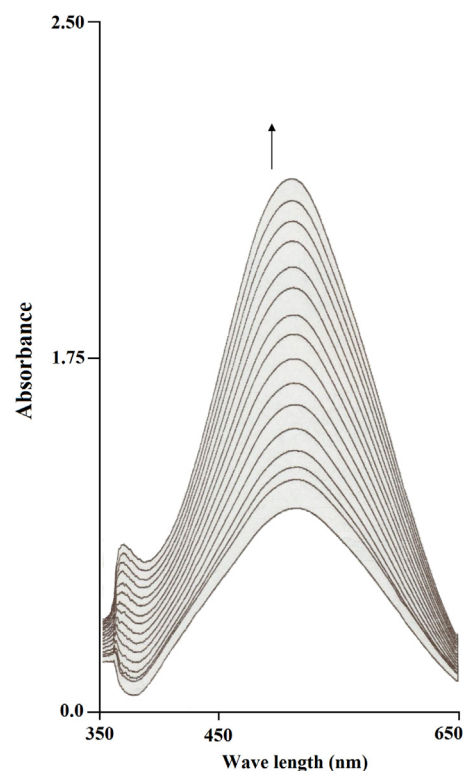


Figure 2 Monitoring the increase in the characteristic *o*-quinone absorption band at 390 nm as a function of time.

kinetic data were determined by the method of initial rates by monitoring the growth of the λ at 400 nm band of the product 3,5-DTBQ, formed due to aerobic oxidation of 3,5-DTBC in the presence of metal(II) complexes. For this purpose $1 \times 10^{-4} \text{ M}$ solutions of 1–4 in DMF were treated with 100 equivalent of 3,5-DTBC in the presence of air. The absorbance was continually monitored at $\lambda = 400 \text{ nm}$ over the first 20 min and the case for complex $[\text{CuL}^1]$ is presented in Fig. 2. Initial rates for 1–6 were determined from the slope of the tangent to the absorbance *versus* time curve at $t = 0$. Fig. 2 shows the time course of the reaction of $[\text{CuL}^1]$ with 5-DTBC. The first apparent result is that the reactivity of the complexes does not differ significantly from each other. Under identical conditions, without the presence of a possible catalyst no significant quinone formation was observed. Important is the comparison of the reactivity of $[\text{Cu}_2\text{L}^3]$ and $[\text{Co}_2\text{L}^3]$ with the other reported complexes that displayed lower reactivity. The low catechol oxidase activity of $[\text{Cu}_2\text{L}^3]$ and $[\text{Co}_2\text{L}^3]$ may be attributed to the steric effect of the naphthalene moiety in L^3 . For all complexes, the reactivity order is: $[\text{Cu}_2\text{L}^1] \geq [\text{Cu}_2\text{L}^2] > [\text{Co}_2\text{L}^1] \geq [\text{Co}_2\text{L}^2] > [\text{Cu}_2\text{L}^3] \geq [\text{Co}_2\text{L}^3]$. The observed difference in the catalytic activity of these catechol oxidase functional models could be ascribed to the values of the redox potential of the couple M^{2+}/M^+ during the catalytic cycle where the metal ion behaves as a redox center.

To determine the dependence of the rates on the substrate concentration, solutions of the complexes 1–6 were treated with increasing amounts of 3,5-DTBC. A first order dependence was observed at low concentrations of the substrate, whereas saturation kinetics was found for all complexes 1–6

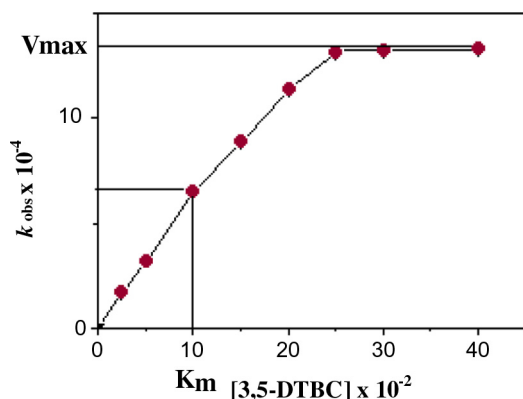
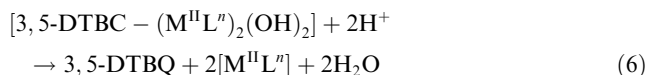
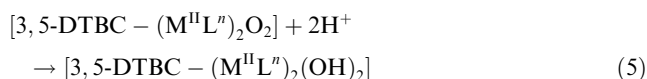
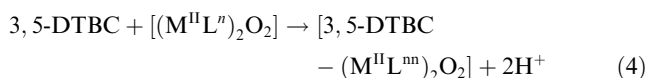


Figure 3 The dependence of the reaction rate on the 3,5-DTBC concentration for the aerial oxidation reaction catalyzed by complex 4 (1×10^{-4} M) at 296 K.

at higher concentrations and a representative plot is given in Fig. 3. A treatment on the basis of the Michaels–Menten model, originally developed for enzyme kinetics, was applied. In our case we can also propose a pre-equilibrium of free complex and substrate on one hand, and a complex-substrate adduct on the other hand. The irreversible conversion into complex and quinone can be imagined as the rate-determining step. Although a much more complicated mechanism may be involved, the results show this simple model to be sufficient for a kinetic description.

The dependence of the reaction rate on the catalyst concentration is illustrated in Fig. 4, and from it one can see that at constant concentration of DTBC, O_2 and a variation amount of the catalyst, the initial rate is linearly dependent on the square of the catalyst concentration. As the curves in Fig. 4 pass through the origin *i.e.* without intercept, it can be stated that there is no measurable rate of oxidation in the absence of the catalyst. It has been reported earlier that for a single mononuclear complex, the rate of DTBC oxidation depends linearly on the copper(II) complex concentration in accordance with our results in this study.

Based on the above kinetic and catalytic investigations a probable catalytic reaction sequence can be represented as follows:



For the synthesized cobalt(II) and copper(II) complexes 1–6, it is believed that the nonprotonated catechololate anion DTBC^{2-}

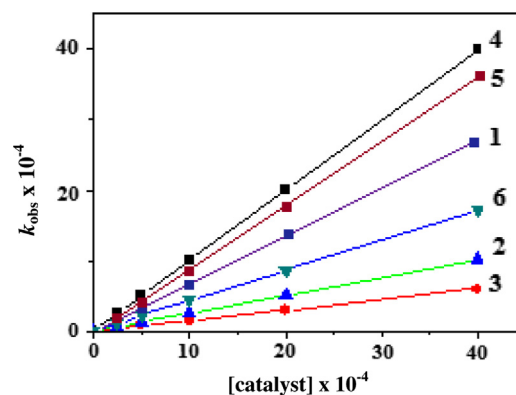


Figure 4 A comparison of the dependence of k_{obs} on catalyst concentration for the aerial oxidation of 3,5-DTBC in DMF at 296 K.

first binds to two molecules of the catalyst in a reversible pre-equilibrium step (Eq. (1)). The produced [catechololate–(ML)₂] intermediate oxidizes the coordinated catechololate anion (3,5-DTBC²⁻) in a fast reaction step to the corresponding light absorbing *o*-quinone (3,5-DTBQ) and forming the metal(I) species (M^IL) (Eq. (2)). Two molecules of this metal(I) complex then react in an irreversible reaction with dioxygen in a slow step to form the metal dioxygen complex [(M^{II}L)₂O₂] (Eq. (3)). [(M^{II}L)₂O₂] reacts then with DTBC₂ in fast reaction steps (Eq. (4)–(6)) to give the products DTBQ and two molecules of H₂O and the catalyst is regenerated in its original active form in closing up the catalytic cycle.

4. Conclusion

The present study describes the syntheses and characterization of a series of cobalt(II) and copper(II) complexes with the tetradentate imine ligands. The characterization of the synthesized compounds was achieved by several physicochemical methods namely, elemental analysis, thermal studies, magnetic, electrochemical and spectroscopic techniques. The reported complexes contain a four-coordinated metal(II) ion in an oxygen and nitrogen rich environment in the tetrahedral stereochemistry for cobalt(II) ion and square-planar geometry in the case of copper(II) complexes. The catecholase biomimetic catalytic activity of the synthesized complexes has been investigated. The results obtained show that all the complexes catalyze the aerobic oxidation of catechol to the corresponding light absorbing *o*-quinone.

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