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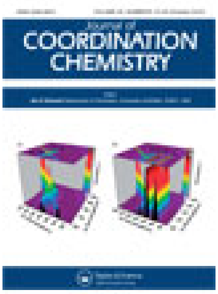

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Catalytic activity of some new copper(II) azo-complexes

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Copper(II) complexes $[Cu(L)_2] \cdot nH_2O$, where L is 3-(*p*-X-)-4-hydroxy-l,2-naphthoquinone (for L1, X = H; L2, X = CH_3; L3, X = Cl; L4, X = Br; and L5, X = NO_2), have been synthesized and characterized by analytical, electrochemical, spectroscopic (IR, UV-Vis, ESR, and ^{1}H NMR), and magnetic methods. From the data obtained, square-planar geometry has been assigned for all the complexes. $[CuL1] \cdot H_2O$ exhibits catalytic activity for oxidation of benzyl alcohol, piperonyl alcohol, and cinnamyl alcohol into their respective aldehydes in the presence of H_2O_2 as co-oxidant and in CH_3CN and H_2O as solvents at room temperature.

Keywords: Copper(II) complexes; Catalytic oxidation; Aromatic alcohols

1. Introduction

Copper(II) complexes have interesting spectroscopic and catalytic properties [1]. The development of highly active catalysts for selective oxidation of aromatic alcohols to their corresponding carbonyl compounds is important [2, 3]. Although various catalytic methods based on transition metal complexes and H_2O_2 as co-oxidant have been developed, synthesis of cheap and benign catalysts remains a major challenge [4–9]. We reported the catalytic oxidation of some aromatic alcohols by ruthenium complexes [10–12].

In this study, we report synthesis and characterization of a new series of copper(II) complexes, $[Cu(L)_2] \cdot nH_2O$ and investigate the catalytic oxidation of benzyl alcohol, piperonyl alcohol, and cinnamyl alcohol to their respective aldehydes by $[CuL1] \cdot H_2O$ with H_2O_2 as co-oxidant in CH_3CN and H_2O at room temperature.

2. Experimental

2.1. *Chemicals and general methods*

Syntheses were performed in air at room temperature. Chemicals were supplied by Sigma-Aldrich Chemicals Company (USA). All other chemicals and solvents were used without additional purification. Microanalyses were performed using a Perkin-Elmer

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CHN 2400 microanalysis unit at Cairo University (Cairo, Egypt). IR spectra were recorded as KBr discs from 4000–400 cm^{-1} on a JASCO 410 spectrophotometer. Electronic absorption spectra were obtained in DMF on a Perkin-Elmer Lambda 2 spectrophotometer. Magnetic moments were measured by Gouy's method at room temperature. ^1H NMR spectra were recorded on a Varian Unit Plus 300 MHz spectrometer in DMSO-d_6 and chemical shifts are reported in parts per million (ppm) relative to the internal standard Me_4Si. ESR measurements of the polycrystalline samples were taken on a Bruker ECS 106 EPR spectrometer using a quartz Dewar at room temperature. All spectra were calibrated with DPPH ($g = 2.0027$). Copper content was determined by using atomic absorption technique after destruction of the complexes with concentrated HNO_3. The electrochemical behavior of the complexes was studied using an electrochemical analyzer CHI 610 A (HCH Instrument). The electrochemical cell that was used in this work contains three electrodes: platinum wire as a working electrode, $Ag^+/AgCl$ as a reference electrode, and a platinum wire as a counter electrode.

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2.2. *Synthesis*

2.2.1. Preparation of the ligand. Aniline or p-substituted aniline (10 mmol) was dissolved in 10 mL of hydrochloric acid (5 mol L^{-1}). The produced aniline salt was diazotized below $-5°C$ with a solution of sodium nitrite (0.85 g, 10 mmol) in 30 mL distilled water. The produced diazonium salt was coupled with 10 mL ethanol solution of 2-hydroxy-l,4-naphthoquinone (1.74 g, 10 mmol). The produced crude dye was collected by filtration, recrystallized from ethanol, and then dried *in vacuo* over P_4O_{10}.

2.2.2. Preparation of copper(II) complexes. $CuCl_2 \cdot 2H_2O$ or $CuSO_4 \cdot 5H_2O$ (1 mmol) was dissolved in 10 mL of hot methanol, then 10 mL of hot methanol solution of the ligand (2.5 mmol) was added. The reaction mixture was refluxed on a water bath with stirring. The complexes were completely formed and precipitated after 3 h. In each case, the complex was filtered off while hot, washed several times with hot methanol, and then dried *in vacuo* over P_4O_{10} (Yield 60–70%).

2.2.3. General procedure for catalytic oxidation of alcohols. $[Cu(L1)_2] \cdot H_2O$ (0.0064 g, 0.01 mmol) was dissolved in CH_3CN (2 mL) and H_2O (10 mL), then alcohol (2 mmol) was added with stirring for 30 min. Hydrogen peroxide (2.3 mL, 30%, 10 mmol) was then added dropwise and the reaction mixture was stirred for 2 h, then reduced *in vacuo*. The residues were collected in diethylether (3 × 10 mL), filtered through a bed of silica gel, and dried over anhydrous $MgSO_4$. The produced aldehydes were quantified as their 2,4-dinitrophenylhydrazone derivatives. Similarly, large-scale oxidation for 20 mmol of benzyl alcohol was carried out using 10-fold excess of the complex, hydrogen peroxide (30%), and solvents and the reaction was stirred for 5 h.

Table 1. Elemental analysis, melting point, and color data for copper(II) complexes.

Complex	Color	Melting point (°C)	Analytical data – Found (Calcd) %C	%H	%N	%Cu
HL1	Orange	234	73 (71.52)	3.5 (3.31)	10.1 (9.27)	–
$[Cu\ (L1)_2]\cdot H_2O$	Brown	279	64 (63.02)	3.33 (3.20)	8.55 (8.16)	9.60 (9.26)
HL2	Orange	208	69.5 (68.35)	3.10 (2.79)	9.21 (8.86)	–
$[Cu\ (L2)_2]\cdot 2H_2O$	Brown	230	63 (62.33)	3.72 (3.55)	8.03 (7.65)	8.67 (8.68)
HL3	Red	236	65.5 (64.19)	2.94 (2.67)	8.53 (8.32)	–
$[Cu\ (L3)_2]$	Brown	257	60.2 (58.65)	2.66 (2.44)	8.11 (7.60)	8.60 (8.62)
HL4	Red-orange	225	59.1 (58.23)	2.65 (2.42)	8.13 (7.54)	–
$[Cu\ (L4)_2]\cdot H_2O$	Brown	259	52 (51.34)	2.45 (2.13)	6.85 (6.65)	7.50 (7.54)
HL5	Yellow	269	63.5 (62.27)	2.66 (2.59)	12.33 (12.10)	–
$[Cu\ (L5)_2]$	brown	294	57.2 (56.95)	2.45 (2.37)	11.56 (11.07)	8.50 (8.37)

3. Results and discussion

3.1. *Synthesis*

The copper(II) complexes $[Cu(L)_2]\cdot nH_2O$ were prepared by refluxing a methanol solution of $CuCl_2\cdot 2H_2O$ or $CuSO_4\cdot 5H_2O$ with a methanol solution of the ligand in 1 : 2 molar ratio. The complexes were isolated as brown stable solids, soluble in DMF, CH_3CN, and DMSO. The analytical data (table 1) are in a good agreement with the proposed molecular formulae in scheme 2.

3.2. *^1H NMR spectra of ligand*

The ^1H NMR spectra of the prepared ligands were recorded in DMSO-d_6 using TMS as reference. They are all similar and showed three mean signals. The first was 7.38–7.47 ppm with integration area corresponding to four protons; this signal is assigned to the phenylazo protons. Two medium signals were observed at 8.02 ppm and 7.81 ppm. The first signal is assigned to H5 and H8, while the second is assigned to H6 and H7 in the naphthoquinone ring.

3.3. *IR Spectra*

The most important bands occurring in the IR spectra of the free ligands and their copper(II) complexes have been compared to ascertain the bonding sites in the chelating ligand (table 2). IR spectra of the ligands display bands at 3428–3448 cm^{-1}, assignable to intramolecular hydrogen-bonding between the C-4 hydroxyl and σ-nitrogen of the azo linkage (scheme 1). IR spectra of the ligands show two medium bands at 1280–1290 cm^{-1} and 1500–1515 cm^{-1}. These bands are attributable to ν(N=N) and phenolic ν(C–O) and shifted to lower frequencies in IR spectra of the corresponding copper(II) complexes. The mode of bonding to copper(II) is further supported by appearance of two new absorption bands at 420–440 cm^{-1} and 500–530 cm^{-1} ranges, which are not observed in spectra of the free ligands. These bands are assignable to

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Table 2. Spectroscopic (IR and UV-Vis) and magnetic data for copper(II) complexes.

	IR data (cm^{-1})							
Compound	ν(N=N)	ν(C–O)	ν(OH)	ν(Cu–N)	ν(Cu–O)	μ_{eff} (BM)	UV-Vis data (cm^{-1})	
HL1	1503m	1290m	3428b	–	–	–	25,641	47,169
$[Cu(L1)_2] \cdot H_2O$	1490m	1278m	–	420w	500w	1.82	26,315	22,222
HL2	1507m	1288m	3430b	–	–	–	25,316	46,411
$[Cu(L2)_2] \cdot 2H_2O$	1488m	1270m	–	440w	520w	1.99	27,777	22,727
HL3	1510m	1289m	3435b	–	–	–	25,974	45,045
$[Cu(L3)_2]$	1489m	1275m	–	440w	530w	2.1	28,169	22,988
HL4	1500m	1285m	3442b	–	–	–	25,706	43478
$[Cu(L4)_2] \cdot H_2O$	1492m	1275m	–	435w	515w	1.68	28,985	22,727
HL5	1515m	1280m	3448b	–	–	–	25,316	44,444
$[Cu(L5)_2]$	1495m	1273m	–	430w	513w	1.92	26,315	22,573

ν(Cu–N) and ν(Cu–O), respectively [13]. IR spectra of the copper(II) complexes display two bands at 1673–1693 cm^{-1} and 1623–1670 cm^{-1}, characteristic of uncoordinated 1,2-quinone carbonyls of the ligand [14]. IR spectra of the heated complexes (up to 130°C) did not show any ν(OH) for water or MeOH. These assignments indicate that coordination of these ligands to copper(II) takes place *via* the azo-nitrogen and phenolic oxygen of the C-4 hydroxyl group of the ligand (scheme 2).

3.4. *Electronic absorption spectra*

Electronic absorption spectra of the ligands and their copper complexes were measured at room temperature in DMF, and the spectral data are given in table 2. Electronic absorption spectra of the ligands display two electronic absorptions at 25,169–25,974 and 43,478–47,169 cm^{-1}, which are assigned to $n \rightarrow \pi^*$ and intraligand $\pi \rightarrow \pi^*$ transitions, respectively [15]. The electronic spectra of the copper(II) complexes display two electronic absorptions at 22,222–26,315 and 22,988–28,985 cm^{-1}, assigned to the two spin allowed transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{xy} \rightarrow d_{xz}$) and ${}^2B_{1g} \rightarrow {}^2E_g$ ($d_{yz} \rightarrow d_{xz}$), respectively [16]. These spectral features support the square-planar geometry around copper(II) [17]. Additional bands are present in the high-energy region, assignable to ($O \rightarrow Cu$) and ($N{=}N \rightarrow Cu$) charge-transfer transitions [18]. These spectral features are in agreement with other square-planar copper(II) complexes [19].

3.5. *Magnetic measurements and ESR spectra*

The copper(II) complexes show normal room temperature magnetic moments $\mu_{eff} = 1.68$–2.1 BM, close to the spin-only value of 1.73 BM [19]. X-band ESR spectra of the polycrystalline samples of synthesized copper(II) complexes were measured at room temperature. The spectra are quite similar and exhibit the following features:

(a) All complexes show spectral parameters characteristic of axial symmetry ($g_{||} > g_{\perp}$).
(b) The unpaired electron is located in the $d_{x^2-y^2}$ orbital of copper(II) ions and the trend $g_{||} > g_{\perp}$ for these complexes indicates the orbital $d_{x^2-y^2}$ is in the ground state [16].

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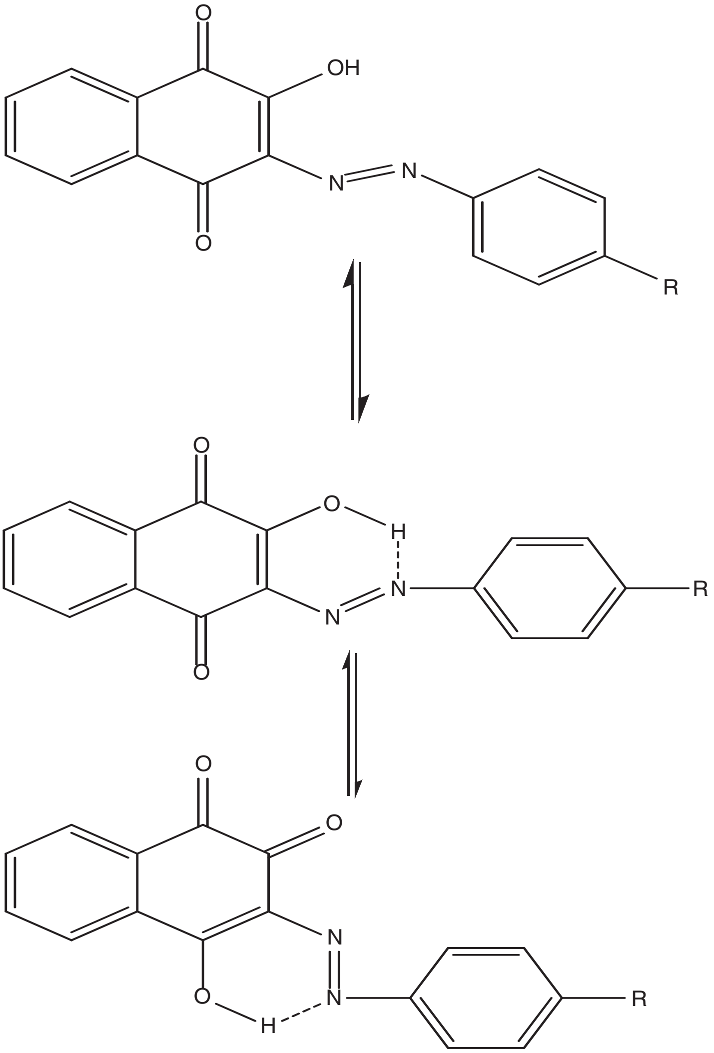

Scheme 1. General formulae of the ligands and their intramolecular hydrogen-bonding ($R = H$, CH_3, Cl, Br, and NO_2).

(c) Values of the *G*-parameter are greater than four, indicating negligible exchange interaction between Cu(II) centers in the solid state. ESR spectral features of the copper(II) complexes are similar and resemble those reported for axial-type copper(II) complexes that have square-planar stereochemistry [20–23]. Representative spectra are shown in "Supplementary material" section.

3.6. *Electrochemical properties*

Electrochemical behavior of the copper(II) complexes was studied in DMF containing $0.1\,\mathrm{mol\,L^{-1}}$ (TBAC) as supporting electrolyte. Cyclic voltammograms are similar and

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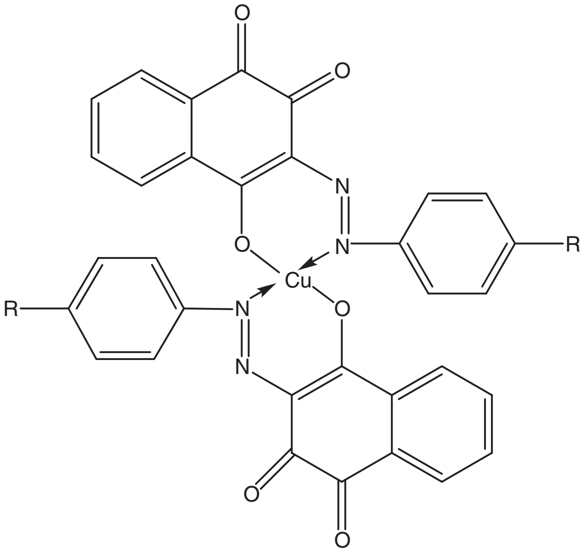

Scheme 2. The proposed structures of the $[Cu(L)_2] \cdot nH_2O$ complexes (L = L1, L2, L3, L4 and L5).

show one-electron irreversible reduction wave ($\Delta E = 0.111$–0.123 V) on the negative side and one-electron irreversible oxidation wave ($\Delta E = 0.076$–0.150 V) on the positive side against $Ag^+/AgCl$ electrode. The reduction wave is assigned to Cu(II)/Cu(I) reduction and the oxidation wave is assigned to Cu(II)/Cu(III) oxidation. The marked shift of ΔE for these two waves from 0.059 V (oxidation potential for one electron) is probably due to geometrical rearrangement around the copper center while undergoing reduction and oxidation. A representative cyclic voltammogram is shown in "Supplementary material" section.

3.7. *Catalytic oxidation of alcohols*

Many transition metals Cu [24], Cr [25], Ni [26], Fe [27], V [28], Pd [29], Ru [30], W [31], and [32] Mn have been used as catalysts for oxidation of alcohols to their respective carbonyl compounds with different co-oxidants. Vijayaraj *et al.* [24] reported the kinetics of oxidation of pyrocatechol to *o*-quinone by a series of copper(II) Schiff-base complexes, [CuL] and found the rate of oxidation of catecholase to *o*-quinone increases as the chain length of the Schiff base increased. Saha *et al.* [25] reported the kinetics and mechanism of oxidation of ethanol to acetaldehyde by a Cr(VI)-phen complex with the anionic surfactant (sodium dodecyl sulfate) and suggested the complex Cr(VI)-phen as the active catalyst.

The kinetics and mechanism of oxidation of the polyhydric alcohols, D-mannitol, and fucoidan by $[Ni(III)(Me_6\text{-}[14]aneN4)H_2O]^{3+}$ have been investigated, showing that coordination of these alcohols to the Ni(III) complex enhances the antioxidant response [26].

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However, catalytic methods based on transition metals need stringent reaction conditions and high cost of the ligand, or have disadvantages such as long reaction time and high temperature. Therefore, development of practical, inexpensive, simple, and green chemical processes for oxidations is still needed. We are interested in the use of hydrogen peroxide, since it is cheap and sufficiently environment-friendly to be used on a commercial scale.

Herein, we investigate the catalytic oxidation of three alcohols by $[Cu(L1)_2] \cdot H_2O/H_2O_2$ at room temperature. As a typical reaction procedure, oxidation experiments have been performed as follows: 10 mmol of 30% H_2O_2 was added dropwise to solution of the complex (0.01 mmol) and alcohol (2 mmol) in a mixture of CH_3CN and H_2O and the reaction mixture was stirred for 2 h. The color of the reaction mixture changes from brown to green, probably due to coordination of alcohol to copper(II).

Comparing our catalyst system with other systems in the literature [24–32], it was found that the catalyst systems, Fe(III)-Schiff-base/H_6IO_5 [27] and Pd(II)-bisquinoline/O_2 [29] oxidized benzyl alcohol to benzaldehyde in 80% at 70°C and in 60% yield at 125°C, respectively; in the latter procedure the reaction time was 27 h. After refluxing for 4 h in CH_3CN, benzyl alcohol was oxidized to benzaldehyde in 100% and 20 turnovers by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O/H_2O_2$ (bmim = 1-*n*-butyl-3-methylimidazolium) [31]. The yields of benzaldehyde in these systems are nearly comparable with the yield obtained by our catalyst system, $[Cu(L1)_2] \cdot H_2O/H_2O_2$.

Oxidation of benzyl alcohol and piperonyl alcohol gave benzaldehyde and piperonaldehyde in 90% and 80% yield with turnovers 180 and 160, respectively. Oxidation of cinnamyl alcohol gave cinnamaldehyde in 75% yield and 150 turnover. In this reaction, benzoic acid was not detected, indicating the catalyst system does not cleave the double bond in cinnamyl alcohol. Similarly, large-scale oxidation of 20 mmol of benzyl alcohol gave benzaldehyde in 90% yield and 180 turnovers.

The catalytic oxidation of benzyl alcohol as a model substrate has been performed in the absence of $[Cu(L1)_2] \cdot H_2O$ and in the presence of some other co-oxidants like $NaIO_4$, $K_2S_2O_8$, $NaBrO_3$, and NaOCl instead of H_2O_2 and gave very low yields of benzaldehyde (less than 5%). This is probably due to formation of solid precipitates $NaIO_3$, K_2SO_4, NaBr, and NaCl, which remain at the end of the reaction and make work-up difficult. We conclude that the use of H_2O_2 is preferred as co-oxidant for oxidation of these substrates in the presence of $[Cu(L1)_2] \cdot H_2O$ since it works at room temperature and gives high yields and turnovers in short reaction times.

4. Conclusion

Five copper(II) azo-complexes have been synthesized and characterized by physicochemical techniques. Electronic spectra of $[Cu(L)_2] \cdot H_2O$ indicate square-planar geometry. Cyclic voltammograms exhibit one-electron irreversible reduction wave and one-electron irreversible oxidation wave due to Cu(II)/Cu(I) reduction and Cu(II)/Cu(III) oxidation, respectively. The catalyst system, $[Cu(L1)_2] \cdot H_2O/H_2O_2$ was used for catalytic oxidation of benzyl alcohol, piperonyl alcohol, and cinnamyl alcohol to their respective aldehydes. Although some transition complexes have been found in recent literature [24–32], our catalyst system oxidizes these substrates in short reaction times with good yields and turnovers at room temperature.

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