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Physico-chemical studies of symmetric and asymmetric binary and ternary copper(I)/(II) complexes of N-(3,5-dimethylphenyl)-3-(3,5-dimethylphenylimino)butanamide

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ABSTRACT

Symmetric and unsymmetric copper(I)/(II) binary and ternary complexes have been synthesized and characterized by elemental analyses, infrared (IR) and electronic spectra, conductivity, differential thermal analysis (DTA), magnetic susceptibility, X-ray diffraction and electron spin resonance (ESR) spectra. The spectral analysis showed that the ligand behaves as neutral or monobasic bidentate ligand bonded with the copper ion via azomethine nitrogen and ketonic or enolic oxygen. The ESR spectra of solid complexes at room temperature show axial type symmetry with $g_{\parallel} > g_{\perp} > g_{e(2.0023)}$ except complex (3) and have a $d_{x^2-y^2}$ ground state. The catalytic properties of the complexes (2), (3), (6), (7) and (8) were investigated by decomposition of hydrogen peroxide. Based on magnetic and spectral studies, a distorted octahedral or tetrahedral geometry is proposed for the complexes.

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KEYWORDS

Spectroscopic studies;
Schiff base;
Thermal analysis;
Binary complexes;
Ternary complexes.

INTRODUCTION

Metal complexes with bi, tri-and tetradentate Schiff bases have received considerable attention during recent years, primarily due to remarkable antitumor, antibacterial, antifungal, antituberculosis agents and antiviral properties^[1-6]. Mononuclear copper(II) complexes of N-(2-pyrid-inyl)acetylacetamide ligand (Figure 1) have been prepared and spectroscopically characterized^[7]. Copper(II) complexes with tridentate Schiff base dianions of N-salicylidene aminoalkanoate type exhibit superoxodismutase-like activity^[8]. Mono-and binuclear copper(II) saccharinate complexes containing 2-pyridinepropanol had been prepared and character-

ized^[9]. For this reason we justify our interest in complexes with tridentate types. Other points of interest are the structures, spectroscopical, properties of these compounds in the solid state. In this paper, we report the syntheses, structures, spectroscopic and magnetic properties of copper(I)/(II) complexes of symmetric and unsymmetric ligands.

EXPERIMENTAL

Materials and methods

All the reagents employed for the preparation of the ligands and their complexes were of the best grade

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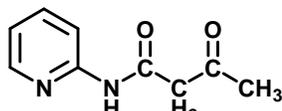


Figure 1

available and used without further purification. Solvents employed were dried and distilled before use by standard methods.

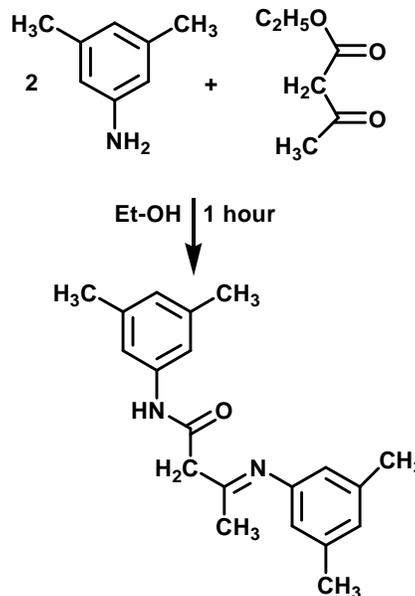
The ligand and their copper complexes were analyzed for C, H, N, Cl and copper contents at the Microanalytical Laboratory, Faculty of Science, Cairo University, Egypt. Analytical and physical data of the ligand and its copper complexes are reported in (TABLE 1). IR spectra of the ligand and its copper complexes were measured using KBr discs with a Jasco FT/IR 300E Fourier transform infrared spectrophotometer covering the range 400-4000 cm^{-1} and in the 500-100 cm^{-1} region using polyethylene-sandwiched Nujol mulls on a Perkin Elmer FT-IR 1650 spectrophotometer. Electronic spectra in the 200-900nm regions were recorded on a Perkin-Elmer 550 spectrophotometer. Magnetic susceptibilities were measured at 25°C by the Gouy method using mercuric tetrathiocyanatocobaltate(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant^[10]. The magnetic moments were calculated from the equation:

$$\mu_{\text{eff}} = 2.84\sqrt{\chi_{\text{M}}^{\text{corr}}T}$$

Molar conductances were measured on a Tacussel type CD₆NG conductivity bridge using 10⁻³M DMF solutions. DTA analysis was carried out in air using a Shimadzu DT-30 thermal analyser. ¹H NMR spectrum was obtained on Bruker Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The ESR spectra of solid complexes at room temperature were recorded using a Varian E-109 spectrophotometer. DPPH was used as a standard material. X-ray powder diffraction patterns were carried out using a Shimadzu XD-3 diffractometer. The TLC of all complexes confirmed their purity.

Synthesis of ligand

A hot (70°C) solution of 3,5-dimethylaniline (10g, 0.08 mol) in ethanol (20mL) was mixed with a hot (70°C) solution of ethylacetoacetate (5.4g, 0.04 mol) in ethanol (15 mL). The mixture was refluxed for 1h. and then left to cool at room temperature. The yellow



N-(3,5-dimethylphenyl)-3-(3,5-dimethylphenylimino)butanamide

Scheme 1: Preparation of the ligand

precipitate formed, was filtered off, washed several times with ethanol and recrystallized from absolute ethanol (yield 70%), Scheme 1. ¹H NMR (400 MHz, d⁶-DMSO): δ = 8.72 (s, 1H, NH)^[11], 6.65-7.48 (aromatic, 6H), 3.50 (s, 2H, CH₂), 2.36 (s, 6H, 2 CH₃), 2.33 (s, 6H, 2 CH₃) and 2.26 (s, 3H, CH₃)^[12].

Synthesis of copper complexes

All the copper complexes were prepared by refluxing ligand with copper salts using (1L:2M), and (3L:1M) molar ratios in ethanol solution. In the case of complexes (8), (9) and (10), the molar ratios used were the following (1 ligand: 1 Cu(OAc)₂·H₂O: 2 acetylacetonone) (8), (1 ligand: 1 Cu(OAc)₂·H₂O: 1,3-(hydroxyimino) pentane-2,4-dione (DMO)) (9), and (2 ligand: 1 Cu(OAc)₂·H₂O: 2 pipredine) (10). The reaction mixtures were refluxed for 1-3 h range accompanied by stirring for 30 min. The products, which precipitated, were filtered off, washed with hot ethanol (40°C) and dried in a vacuum desiccator over P₄O₁₀. The analytical data are given in TABLE 1.

Catalytic activity

The catalytic activities of the complexes (2), (3), (6), (7) and (8) towards decomposition of hydrogen peroxide (as model reaction) were determined from the rates of oxygen evolution at room temperature^[13]. A

TABLE 1 : Analytical and physical data of the ligand and its copper complexes

No.	Compound	Mole.wt. calcd.	color	Yield	M.P.°C	Ω^{-1} mol ⁻¹ cm ²	μ_{eff} (B.M.)	Found (Calc.)				
								C	H	N	Cu	Cl
1	HL (C ₂₀ H ₂₄ N ₂ O)	308.4	Yellow	73	247	-	-	79.9(77.9)	7.9(7.8)	9.0(9.1)	--	--
2	L ₂ (HL)Cu	986.8	Y. brown	75	213	7.3	2.1	72.9(73.0)	7.3(7.2)	8.3(8.5)	6.2(6.4)	--
3	[L ₂ Cu]. ½ H ₂ O	687.4	Brown	60	208	11.6	2.2	69.7(69.9)	7.0(6.9)	8.3(8.2)	9.2(9.3)	--
4	HLCuClH ₂ O	425.4	P. green	67	207	14.1	Dia.	56.5(56.5)	6.3(6.2)	6.7(6.6)	14.8(14.9)	8.1(8.3)
5	[(HL) ₂ ClCu].2H ₂ O	751.9	P. green	75	205	16.8	Dia.	63.8(63.9)	7.1(7.0)	7.6(7.5)	8.4(8.5)	4.4(4.7)
6	[(HL) ₂ CuCl ₂].½ H ₂ O	760.3	Green	68	212	20.2	1.90	63.0(63.2)	6.7(6.5)	7.6(7.4)	8.3(8.4)	9.1(9.3)
7	[L ₂ Cu(H ₂ O) ₂].H ₂ O	732.4	P. green	73	205	13.1	1.88	65.4 (65.6)	7.3(7.2)	7.9(7.7)	8.6(8.7)	--
8	(HL)(acac) ₂ Cu	574.2	D. green	70	220	10.8	1.85	62.7(62.8)	7.6(7.4)	5.0(4.9)	10.9(11.1)	--
9	(HL)(DMO)Cu(H ₂ O) ₂	508.1	D. brown	71	238	14.1	1.82	56.4(56.7)	6.9(6.7)	8.5(8.3)	12.2(12.5)	--
10	[(HL) ₂ (pip) ₂ Cu]H ₂ O	866.6	Y. brown	66	215	10.0	1.92	69.0(69.3)	7.3(7.0)	9.9(9.7)	7.1(7.3)	--
11	[(L)Cu(OAc)(H ₂ O) ₃].2H ₂ O	521.1	Green	67	260	10.4	1.86	48.1(48.4)	7.3(7.0)	5.6(5.4)	11.9(12.2)	--

* Ω^{-1} cm²mol⁻¹, in 10⁻³ M DMF p = pale, d = dark, y = yellowish

TABLE 2 : Important IR bands of the ligand and its copper complexes (cm⁻¹)

Comp. No.	v(NH)	v(H ₂ O)	v(C=O)	v(C=N)	v(C=C)	v(C=CH)	v(C-O)	v(Cu-N)	v(Cu-O)	v(Cu-Cl)
1	3265s	-	1645v.s	1615s	1600m	-	-	-	-	-
2	3292s	-	1635s	1605m	1598m	1555m	1350m	605m	520m	-
3	3290s	3560br	-	1611m	1600m	1555m	1320m	660w	570m	-
4	3295s	3420br	1632s	1608m	1600m	-	-	660w	581w	298m
5	3278s	3580br	1633s	1604m	150m	-	-	600m	515w	400w
6	3284s	3600br	1629s	1605m	1590m	-	-	630w	560m	360m
7	3290s	3610br, 3440br	-	1610m	1590w	1555m	1380m	660w	565m	-
8	3288s	-	1660s, 1630s	1610m	1600m	1545m	1290m	650m	560m, 540w, 515m	-
9	3280s	3450br	1670s	1608m, 1575m	1597m	1550m	1305m	690m, 675m	510m, 530m	--
10	3292s	3458	1630s	1606m	1595m	-	-	665m	570w	-
11	3289s	3620br, 3450br	---	1609m	1576m	1535m	1340m	620w	517m	--

0.5mL of H₂O₂ (30%) was mixed with 20mL distilled water in a thermo stated glass vessel and 50mg of complex was introduced. The reaction was followed by measuring the volume of oxygen gas released.

RESULTS AND DISCUSSION

The analytical and physical data (TABLE 1), spectral data (TABLE 2 and 3) are compatible with the suggested structures (Figure 2). The complexes are colored, stable in air and insoluble in H₂O, ethanol and non-polar solvents such as benzene. However, they are soluble in polar solvents such as DMF and DMSO. All the complexes are non-electrolytes (TABLE 1).

Infrared spectra (IR)

The bonding modes of the ligand and its copper

complexes have been deduced from the IR spectroscopy. Important spectral bands are presented in TABLE 2. The infrared spectrum of the ligand HL showed a strong band located at 1645cm⁻¹ which may be assigned to carbonyl group v(C=O)^[14,15], whereas the medium band appeared at 3265cm⁻¹ may be assigned to the v(NH) group^[16]. The spectrum of the ligand also showed relatively strong bands at 1615 and 1600cm⁻¹ may be assigned to the v(C=N) of the azomethine group^[17] and aromatic v(C=C)^[15] respectively.

The mode of coordination of the ligand can be obtained by comparing the infrared spectra of the complexes with that of the free ligand. The ligand behaved either as neutral bidentate ligand coordinating through C=O and C=N. In case of complexes (4), (5), (6), (8) and (10), the mode of coordination was suggested by the following evidences: (i) the shift of v(C=N) to lower

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TABLE 3 : Electronic spectra of the ligand and its copper complexes

Comp. No.	λ_{\max} (nm) in nujol mull	λ_{\max} (nm) in DMF
1		367 ($\epsilon = 2.9 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$) 310 ($\epsilon = 0.1 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$)
2	620, 500, 410, 350, 320	600, 490, 400, 360, 315
3	580, 420, 355, 310	575, 410, 345, 320
4	560, 420, 380, 325	540, 410, 390, 310
5	610, 490, 425, 370, 320	595, 470, 400, 345, 300
6	610, 580, 430, 390, 325	590, 450, 400, 355, 305
7	630, 520, 410, 375, 330	610, 460, 420, 380, 310
8	660, 595, 410, 365, 310	645, 575, 400, 370, 315
9	630, 595, 425, 370, 315	610, 565, 465, 395, 290
10	625, 560, 490, 380, 300	600, 535, 420, 390, 280
11	645, 495, 415, 350, 325	628, 480, 405, 365, 320

frequency ($5\text{--}10\text{cm}^{-1}$) together with its weak appearance, which indicates the coordination of the azomethine nitrogen^[18,19], (ii) the band due to the ketone group is weakened and shifted to lower wave number by $13\text{--}16\text{cm}^{-1}$, (iii) the simultaneous appearance of new bands in the $600\text{--}665$ and $515\text{--}581\text{cm}^{-1}$ regions due to the $\nu(\text{Cu--N})$ and $\nu(\text{Cu--O})$ vibrations^[20], respectively.

Monobasic bidentate ligand coordinating through enolic C-O and C=N. In case of complexes (3), (7), (9) and (11), the mode of coordination was suggested by the following evidences:

- The shift of $\nu(\text{C=N})$ to lower frequency ($6\text{--}15\text{cm}^{-1}$) together with its weak appearance, which indicates the coordination of the azomethine nitrogen^[18,19].
- The disappearance of the band due to the ketone and the appearance of new bands in the ranges $1535\text{--}1555$ and $1305\text{--}1380\text{cm}^{-1}$ ranges which may be assigned to the $\nu(\text{CH=C})$ and $\nu(\text{C--O})$ respectively^[15,21], which indicates the coordination of the ligand in enolic form.
- The simultaneous appearance of new bands in the $620\text{--}690$ and $510\text{--}570\text{cm}^{-1}$ regions due to the $\nu(\text{Cu--N})$ and $\nu(\text{Cu--O})$ vibrations, 20 respectively. In case of complex (2), the complex possesses the ligand in both forms neutral and monobasic bidentate ligand.

The mode of coordination was suggested by the following evidences:

- The shift of $\nu(\text{C=N})$ to lower frequency (10cm^{-1}) together with its weak appearance, which indicates

the coordination of the azomethine nitrogen^[18,19].

- The band due to the ketone group is weakened and shifted to lower wave number by 10cm^{-1} , (iii) the appearance of new bands at 1555 and 1350cm^{-1} ranges which may be assigned to the $\nu(\text{CH=C})$ and $\nu(\text{C--O})$ respectively^[15,21], (iv) the simultaneous appearance of new bands at 605 and 520cm^{-1} due to the $\nu(\text{M--N})$ and $\nu(\text{Cu--O})$ vibrations, respectively^[20].

In chloro complexes (4), (5) and (6), the appearance of a new band in the $298\text{--}400\text{cm}^{-1}$ range may be due to the presence of $\nu(\text{M--Cl})$. The appearance of two characteristic bands at 1575cm^{-1} and 1370cm^{-1} in case of complex (11) was attributed to $\nu_{\text{asym.}}(\text{COO}^-)$ and $\nu_{\text{sym.}}(\text{COO}^-)$, respectively, indicating the participation of the carboxylate oxygen in the complexes formation^[14,22,23]. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the $\nu_{\text{asym.}}(\text{COO}^-)$ and $\nu_{\text{sym.}}(\text{COO}^-)$. The separation value between $\nu_{\text{asym.}}(\text{COO}^-)$ and $\nu_{\text{sym.}}(\text{COO}^-)$ in this complex was more than 200cm^{-1} (205cm^{-1}) suggesting the coordination of carboxylate group in a monodentate fashion^[24]. The IR spectrum of complex (9) showed band at 1670cm^{-1} may be due to $\nu(\text{C=O})$ group of the diacetylmonoxime. Another peaks are observed at 1575 and 1170cm^{-1} may be assigned to $\nu(\text{C=N})$ and $\nu(\text{N=O})$ of the oximato group. In case of complex (8), the ligand pentane-2,4-dione coordinated through enolic C-O and ketonic C=O which was supported by:

- The appearance of two bands at 1545 and 1290 assignable to $\nu(\text{C=O})$ and $\nu(\text{C--O})$, respectively.
- The band due to the ketone group of HL is weakened and shifted to lower wave number by $13\text{--}16\text{cm}^{-1}$.
- The simultaneous appearance of new bands at 540 and 515cm^{-1} due to the $\nu(\text{Cu--O})$ vibrations^[20].

The IR spectra of complex (10), showed ring breathing of the piperidine at 810cm^{-1} but no bands corresponding to the NH was found indicating its coordination in monobasic monodentate fashion. Some complexes included water molecules. The broad bands in the $3600\text{--}3400\text{cm}^{-1}$ region are due to coordinated water or water of crystallization. The bands for water of crystallization are different from those of coordinated water, the latter has a band in the $600\text{--}400\text{cm}^{-1}$ region,

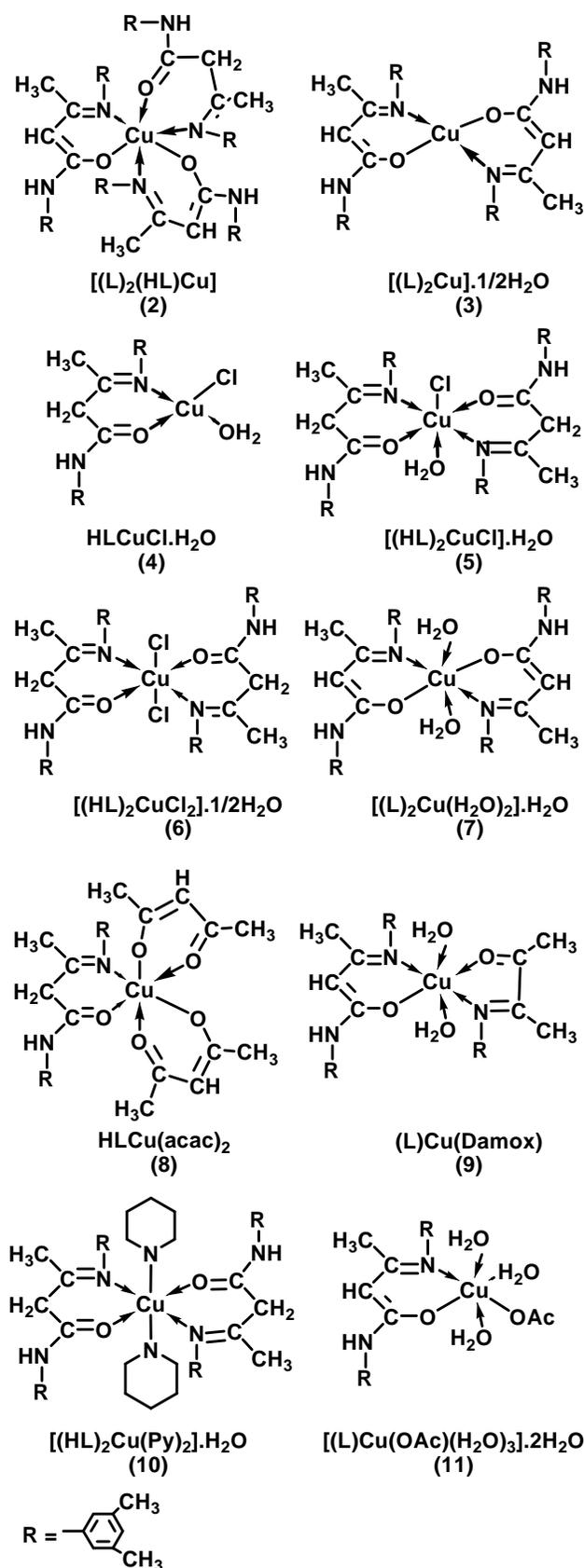


Figure 2 : Structure representation of the copper(II)/(I) complexes

but the absence of these bands in the spectrum of complexes (3), (5), (6) and (10) indicates the hydrated water rather than coordinated ones. The presence of water molecules within the coordination sphere in the hydrated complexes (4), (7), (9) and (11) is supported by the presence of bands at 3480cm^{-1} , 1610cm^{-1} , 950cm^{-1} and 630cm^{-1} due to OH stretching, HOH deformation, H_2O rocking and H_2O wagging, respectively^[25,26].

Molar conductivity

The molar-conductance of the copper complexes (TABLE 1) are in the $10.0\text{-}20.2\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ range, indicating their non-electrolytic nature. The considerably high conductance values for some complexes may be ascribed to the partial solvolysis by DMF^[27].

Electronic spectra

The electronic spectral data of the ligand and its copper complexes in Nujol mull and dimethylformamide (DMF) are given in TABLE 3. In DMF, the ligand gives bands at 310nm ($\epsilon = 0.1 \times 10^4\ \text{mol}^{-1}\text{cm}^2$) and 367nm ($\epsilon = 2.9 \times 10^4\ \text{mol}^{-1}\text{cm}^2$) ascribed to the benzene $\pi\text{-}\pi^*$ and imino $n\text{-}\pi^*$ transitions respectively^[15]. Compared to the free ligand, the imino $n\text{-}\pi^*$ transitions of the complexes was shifted to some extent, probably due to imino-nitrogen coordination to the metal ion. In Nujol mull, the complexes (2) and (5-11) showed three bands in the $410\text{-}490$, $490\text{-}595$ and $610\text{-}660\text{nm}$ ranges, however, in DMF, the peaks appear in the $400\text{-}465$, $480\text{-}575$ and $590\text{-}645\text{nm}$ ranges. These bands corresponds to the ${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions of a copper ion in a tetragonally elongated octahedron^[28]. Complexes (3) and (4) in Nujol mull show bands at 580 , 420 and 560 , 420nm , however in DMF, the bands appear at 575 , 410 and 540 , 410nm . These bands are typically found for a tetrahedral configuration^[29].

Magnetic moments

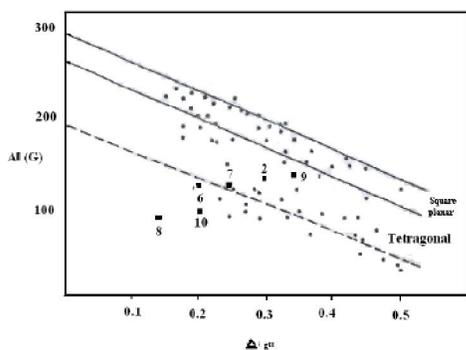
The magnetic moments for the complexes are presented in TABLE 1. Complexes (2), (3) and (6-11) show values in the $1.86\text{-}2.2$ B.M. range, suggesting the presence of one unpaired electron per copper ion in an octahedral or tetrahedral arrangement^[30]. Complexes (4) and (5) are diamagnetic due to d^{10} configuration.

Electron spins resonance (ESR)

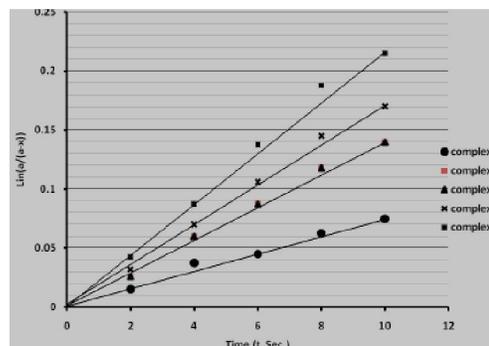
The ESR spectra of solid complexes (2) and (6-

TABLE 4: ESR parameters of the copper(II) complexes

Comp. No.	g_{\parallel}	g_{\perp}	g_{iso}	$A_{\parallel}(G)$	$A_{\perp}(G)$	$A_{iso}(G)$	G^b	$g_{\parallel}/A_{\parallel}$ (cm)	$\Delta E_{xy}(cm^{-1})$	$\Delta E_{xz}(cm^{-1})$	K_{\perp}	K_{\parallel}	K	$\alpha^2(Cu)$	β^2	β_1^2
2	2.30	2.06	2.14	140	40	73.3	5.00	153	16129	24390	0.92	0.85	0.60	0.77	1.10	0.94
3	-	-	2.10	-	-	-	-	-	-	-	-	-	-	-	-	-
6	2.20	2.08	2.12	130	50	76.7	2.50	169	16393	23256	1.04	0.70	0.94	0.64	1.70	0.76
7	2.25	2.07	2.13	120	38	65.3	3.60	178.6	15873	24390	1.00	0.77	0.92	0.67	1.50	0.88
8	2.14	2.05	2.08	90	28	48.7	2.80	240	15129	24390	0.84	0.58	0.76	0.45	1.57	0.75
9	2.35	2.05	2.15	150	25	66.7	7.00	165	15873	23529	0.68	0.83	0.85	0.85	0.80	0.98
10	2.19	2.06	2.10	100	30	53.3	3.20	219	16000	20408	0.84	0.67	0.78	0.53	1.35	0.85

Figure 3 : Plot of A_{\parallel} versus Δg_{\parallel} for a range of copper(II) complexes (2), (6-10)

10) at room temperature are characteristic of a monomer, d^9 , configuration and having an axial type of $d_{x^2-y^2}$ ground state, which is the most common for copper(II) complexes.^[31-33] Complex (3) shows an isotropic spectrum with $g_{iso} = 2.1$, characteristic of a tetrahedral geometry around the Cu(II) ion^[29]. The other complexes show $g_{\parallel} > g_{\perp} > 2.0023$, indicating a tetragonal distortion around the Cu(II) ion^[33-35], corresponding to elongation along the four fold symmetry axis z . This result is further confirmed by the Symons plot (Figure 3)^[36], which indicates that complexes falling close to the line can be considered to be distorted tetragonal species rather than octahedral or square planar. The ESR parameters are presented in TABLE 4. The g -values are related by the expression.^[37] $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$. If $G > 4.0$, then, local tetragonal axes are aligned parallel or only slightly misaligned, if $G < 4.0$, significant spin exchange coupling is present. Complexes (6-8) and (10) showed $G < 4.0$ (TABLE 4), indicating the presence of spin exchange interactions between the Cu(II) ions, however, complexes (2) and (9) show values > 4.0 , indicating the presence of tetragonal axes in this complex. Also, the $g_{\parallel}/A_{\parallel}$ values, considered as diagnostic of stereochemistry^[38], in the range reported for square planar complexes are 105 to 135 cm^{-1} and for tetragonal dis-

Figure 4 : Catalytic activity of complexes (2), (3), (6), (7) and (8) on the decomposition of H_2O_2

torted complexes 150 to 250 cm^{-1} . The $g_{\parallel}/A_{\parallel}$ values lie just within the range expected for tetragonal distorted complexes (TABLE 4). The g -values of copper(II) complexes with a $^2B_{1g}$ ground state ($g_{\parallel} > g_{\perp}$) may be expressed by^[39-41].

$$g_{\parallel} = 2.002 - \left(\frac{8K_{\parallel}^2 \lambda^{\circ}}{\Delta E_{XY}} \right) \quad (1)$$

$$g_{\perp} = 2.002 - \left(\frac{8K_{\perp}^2 \lambda^{\circ}}{\Delta E_{XZ}} \right) \quad (2)$$

Where K_{\parallel} and K_{\perp} are the parallel and perpendicular components respectively of the orbital reduction factor (K), λ° is the spin-orbit coupling constant for the free copper, ΔE_{xy} and ΔE_{xz} are the electron transition energies. From the above relations, the orbital reduction of covalency^[40,41] can be calculated. For an ionic environment, $K = 1$ and for a covalent environment $K < 1$, the lower the value of K , the greater is the covalent character.

$$K_{\perp}^2 = \frac{(g_{\perp} - 2.002)\Delta E_{XZ}}{2\lambda^{\circ}} \quad (3)$$

$$K_{\parallel}^2 = \frac{(g_{\parallel} - 2.002)\Delta E_{XY}}{8\lambda^{\circ}} \quad (4)$$

$$K^2 = \frac{(K_{\parallel}^2 + 2K_{\perp}^2)}{3} \quad (5)$$

The K values for Cu(II) complexes (2), (6-11) are indicative of their covalent nature TABLE 4^[42,43]. Kivelson and Neiman noted that, for an ionic environment $g_{\parallel} > 2.3$ and for a covalent environment $g_{\parallel} < 2.3$ ^[44]. Theoretical work by Smith^[41] seems to confirm this view. The g-values reported here (TABLE 4) show considerable covalent bonding character^[15,43], except complex (9), the g_{\parallel} -value indicates covalent-ionic bond character. The values of K_{\parallel} and K_{\perp} for the complexes suggest marked amount of π -contribution to the axial bonding is much smaller.

Also, the in-plane σ -covalency parameter, $\alpha^2(\text{Cu})$ was calculated by

$$\alpha^2(\text{Cu}) = (A_{\parallel}/0.036) + (g_{\parallel} - 2.002) + 3/7(g_{\perp} - 2.002) + 0.04 \quad (6)$$

The calculated values (TABLE 4) suggest covalent bonding^[43]. The in-plane and out-of plane π -bonding coefficients (β_1^2 and β^2) are dependent upon the values of ΔE_{xy} and ΔE_{xz} in the following equations^[43,46].

$$\alpha^2\beta^2 = \frac{(g_{\perp} - 2.002)\Delta E_{xz}}{2\lambda^{\circ}} \quad (7)$$

$$\alpha^2\beta_1^2 = \frac{(g_{\parallel} - 2.002)\Delta E_{xy}}{8\lambda^{\circ}} \quad (8)$$

In this work, the Cu(II) complexes show β_1^2 values in the (0.75-0.94) range (TABLE 4) indicating a moderate degree of covalency in the in-plane π -bonding, while $\beta^2 > 1.0$ (TABLE 4) indicates the ionic character of the out-of-plane π -bonding^[43,47,48]. However, complex (11) shows broad signal in the low field region, indicating spin exchange interactions take place between copper(II) ions through acetate group.

X-ray diffraction

X-ray diffraction patterns of the ligand and its copper complexes show that, the ligand has strong lines, indicating a high degree of crystallinity. Comparing with its complexes; it was shown that, the tetrahedral complexes (3) and (4) are of more degree of crystalline than those of the distorted octahedral complexes. This can be inferred from the peak intensities^[49]. The order of the degree of crystallinity is:

$$(1) > (4) > (3) > (6) > (7) > (5) > (2) > (8) > (9) > (10) > (11)$$

TABLE 5 : DTA peaks and their assignments for the copper complexes

Comp. No.	DTA peaks (°C)		Assignment
	Endo.	Exo.	
2	75	-	Dehydration process
	213	-	M.P. of the complex
	-	350-500	Decomposition of the complex
5	85	-	Dehydration process
	150	-	Thermal dissociation of coordinated H ₂ O
	205	-	M.P. of the complex
	-	370-610	Decomposition of the complex
6	70	-	Dehydration process
	212	-	M.P. of the complex
	-	300	Thermal dissociation of chloride atoms
	-	410-590	Decomposition of the complex
7	140	-	Thermal dissociation of coordinated H ₂ O
	205	-	M.P. of the complex
	-	350-550	Decomposition of the complex
11	80	-	Dehydration process
	165	-	Thermal dissociation of coordinated H ₂ O
	265	-	M.P. of the complex
	-	310	Thermal dissociation of acetate group
	-	380-620	Decomposition of the complex

Differential thermal analysis (DTA)

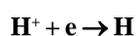
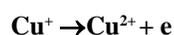
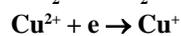
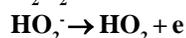
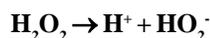
The DTA curves in the 20-800°C range show that, all the complexes are thermally stable up to 70°C when dehydration begins. This fact is characterized by the appearance of endothermic peaks within the 70-85°C range, corresponding to be hydration water^[50,51]. Another peak was observed in (5), (7) and (11) complexes at 150, 140°C and 165°C respectively, corresponding to the loss of coordinated water. The existence of an exothermic peak in the DTA curve at the same temperature suggests that they are all in the same chemical environment^[52]. The product is stable up to 350°C, when the organic constituents of the complexes start decomposing, finally leaving the metal oxide (500-620°C). The DTA data for the complexes are shown in TABLE 5.

Catalytic activity

The decomposition of H₂O₂ was used as a model for oxidation-reduction to measure the catalytic activity of the complexes obtained. The decomposition reaction was found to follow first-order kinetics. The re-

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sults of H_2O_2 decomposition over the complexes (2), (3), (6), (7) and (8) are presented in figure 5. The data are plotted as $\ln a/(a-x)$ versus time, where "a" is the initial concentration of H_2O_2 and "x" the concentration after time "t"; the rate constant of H_2O_2 values for the complexes (2), (3), (6), (7) and (8) are 0.014, 0.005, 0.01, 0.019 and 0.026 respectively. As seen in figure 5, the rate of catalytic activity of octahedral complexes (2), (6), (7) and (8) are larger than a square planar complex (3). The order of activity are (8), $\text{O}_5\text{N} > (7)$, $\text{O}_4\text{N}_2 > (2)$, $\text{O}_3\text{N}_3 > (6)$, $\text{O}_2\text{N}_2\text{Cl}_2 > (3)$, O_2N_2 . Previous researchers reported that, the $\text{Cu}^{2+}/\text{Cu}^+$ system forms catalytic active sites which responsible for the decomposition of H_2O_2 [53,54]. The Cu^{2+} was identified as the species, which control the catalytic activity of the complexes. The decomposition of H_2O_2 in the presence of complex (8) may be represented as follows:



On the basis of elemental analysis, magnetic susceptibility, conductivity, IR and UV-VIS spectra and ESR measurements, the following tentative structures are suggested as shown in figure 2.

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