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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Received: 19th April, 2010 ; Accepted: 29th April, 2010

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 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 $g_{||} > g_{\perp} > g_{e}(2.0023)$ 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.

INTRODUCTION
Metal complexes with bi, tri- and tetradeutate 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-pyridyl)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 characterized[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
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 400-4000cm\(^{-1}\) and in the 500-1000cm\(^{-1}\) 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:

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

Molar conductances were measured on a Tacussel type CD\(_{6}\) conductivity bridge using 10\(^{-3}\)M DMF solutions. DTA analysis was carried out in air using a Schimadzn DT-30 thermal analyser. \(^{1}\)H NMR spectrum was obtained on Brucker 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 Shimadzn 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 precipitate formed, was filtered off, washed several times with ethanol and recrystallized from absolute ethanol (yield 70%), Scheme 1. \(^{1}\)H NMR (400 MHz, d\(_6\)-DMSO): \(\delta = 8.72\) (s, 1H, NH), 6.65-7.48 (aromatic, 6H), 3.50 (s, 2H, CH\(_2\)), 2.36 (s, 6H, 2 CH\(_3\)), 2.33 (s, 6H, 2 CH\(_3\)) and 2.26 (s, 3H, CH\(_3\))\(^{[12]}\).

**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)\(_2\).H\(_2\)O: 2 acetylacetone) (8), (1 ligand: 1 Cu(OAc)\(_2\).H\(_2\)O: 1,3-(hydroxy-imino)pentane-2,4-dione (DMO)) (9), and (2 ligand: 1 Cu(OAc)\(_2\).H\(_2\)O: 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 P\(_4\)O\(_{10}\). 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
0.5mL of H$_2$O$_2$ (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 H$_2$O, 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 1645 cm$^{-1}$ which may be assigned to carbonyl group $\nu(C=O)$[14,15], whereas the medium band appeared at 3265 cm$^{-1}$ may be assigned to the $\nu(NH)$ group[16].

The mode of coordination of the ligand can be obtained by comparing the infrared spectra of the complexes...
frequency (5-10 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 13-16 cm\(^{-1}\), (iii) the simultaneous appearance of new bands in the 600-665 cm\(^{-1}\) regions due to the \(\nu(Cu-N)\) and \(\nu(Cu-O)\) vibrations, respectively\(^{[15,21]}\), (iv) the simultaneous appearance of new bands at 605 and 520 cm\(^{-1}\) due to the \(\nu(M-N)\) and \(\nu(Cu-O)\) vibrations, respectively\(^{[20]}\).

In chloro complexes (4), (5) and (6), the appearance of a new band in the 298-400 cm\(^{-1}\) range may be due to the presence of \(\nu(M-Cl)\). The appearance of two characteristic bands at 1575 cm\(^{-1}\) and 1370 cm\(^{-1}\) 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 200 cm\(^{-1}\) (205 cm\(^{-1}\)) suggesting the coordination of carboxylate group in a monodentate fashion\(^{[24]}\). The IR spectrum of complex (9) showed band at 1670 cm\(^{-1}\) may be due to \(\nu(C=O)\) group of the diacetylmonoxime. Another peaks are observed at 1575 and 1170 cm\(^{-1}\) may be assigned to \(\nu(C=O)\) and \(\nu(N=O)\) 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:

(i) The appearance of two bands at 1545 and 1290 cm\(^{-1}\) assignable to \(\nu(C=O)\) and \(\nu(C-O)\), respectively.

(ii) The band due to the ketone group of HL is weakened and shifted to lower wave number by 13-16 cm\(^{-1}\).

(iii) The simultaneous appearance of new bands at 540 and 515 cm\(^{-1}\) due to the \(\nu(Cu-O)\) vibrations\(^{[20]}\).

The IR spectra of complex (10), showed ring breathing of the piperidine at 810 cm\(^{-1}\) 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 3600-3400 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 600-400 cm\(^{-1}\) region,
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 3480 cm\(^{-1}\), 1610 cm\(^{-1}\), 950 cm\(^{-1}\) and 630 cm\(^{-1}\) due to OH stretching, OH\(_2\) deformation, H\(_2\)O rocking and H\(_2\)O wagging, respectively\[^{25,26}\].

**Molar conductivity**

The molar-conductance of the copper complexes (TABLE 1) are in the 10.0-20.2 Ω\(^{-1}\) cm\(^2\) 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 310 nm (ε = 0.1 × 10\(^4\) mol\(^{-1}\) cm\(^{-1}\)) and 367 nm (ε = 2.9 × 10\(^4\) mol\(^{-1}\) cm\(^{-1}\)) ascribed to the benzene π-π* and imino n-π* transitions respectively\[^{[15]}\]. Compared to the free ligand, the imino n-π* 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 410-490, 490-595 and 610-660 nm ranges, however, in DMF, the peaks appear in the 400-465, 480-575 and 590-645 nm ranges. These bands corresponds to the \(^{2}B\_1g \rightarrow ^{2}E\_g, ^{2}B\_1g \rightarrow ^{2}B\_2g, ^{2}B\_1g \rightarrow ^{2}A\_1g\) 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, 420 nm, however in DMF, the bands appear at 575, 410 and 540, 410 nm. 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 1.86-2.2 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-
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ICAIJ, 5(3) September 2010

An Indian Journal

Inorganic CHEMISTRY

... at room temperature are characteristic of a mono-meric, d^9, configuration and having an axial type of d^2 - y^2 ground state, which is the most common for copper(II) complexes. Complex (3) shows an isotropic spectrum with g_\| = 2.1, characteristic of a tetrahedral geometry around the Cu(II) ion. The other complexes show g_\| < g_\perp > 2.0023, indicating a tetragonal distortion around the Cu(II) ion, corresponding to elongation along the four fold symmetry axis z. This result is further confirmed by the Symons plot (Figure 3), 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. G = (g_\| - 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 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_\|/A_\| values, considered as diagnostic of stereochemistry, in the range reported for square planar complexes are 105 to 135 cm\(^{-1}\) and for tetragonal distorted complexes 150 to 250 cm\(^{-1}\). The g_\|/A_\| 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_\| > g_\perp) may be expressed by

\[
\begin{align*}
    g_\| &= 2.002 - \frac{8K_\perp^2\lambda}{\Delta E_{xy}} \\
    g_\perp &= 2.002 - \frac{8K_\|^2\lambda}{\Delta E_{xz}}
\end{align*}
\]

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

\[
\begin{align*}
    K_\| &= \frac{(g_\| - 2.002)\Delta E_{xz}}{2\lambda} \\
    K_\perp &= \frac{(g_\| - 2.002)\Delta E_{xy}}{8\lambda}
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>g_|</th>
<th>g_\perp</th>
<th>A_| (G)</th>
<th>A_\perp (G)</th>
<th>A_\perp (cm(^{-1}))</th>
<th>ΔE_{xy} (cm(^{-1}))</th>
<th>ΔE_{xz} (cm(^{-1}))</th>
<th>K_|</th>
<th>K_\perp</th>
<th>α^2(Cu)</th>
<th>β^2</th>
<th>β_1^2</th>
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<tbody>
<tr>
<td>2</td>
<td>2.30</td>
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<td>140</td>
<td>50</td>
<td>16129</td>
<td>24390</td>
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<td>0.85</td>
<td>0.60</td>
<td>0.77</td>
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<td>3</td>
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<td>2.10</td>
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<td>-</td>
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<tr>
<td>6</td>
<td>2.20</td>
<td>2.08</td>
<td>2.12</td>
<td>130</td>
<td>50</td>
<td>16939</td>
<td>23256</td>
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<td>0.70</td>
<td>0.94</td>
<td>0.64</td>
<td>1.70</td>
</tr>
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<td>7</td>
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<td>2.13</td>
<td>120</td>
<td>38</td>
<td>15873</td>
<td>24390</td>
<td>1.00</td>
<td>0.77</td>
<td>0.92</td>
<td>0.67</td>
<td>1.50</td>
</tr>
<tr>
<td>8</td>
<td>2.13</td>
<td>2.08</td>
<td>2.12</td>
<td>90</td>
<td>28</td>
<td>15129</td>
<td>24390</td>
<td>0.84</td>
<td>0.58</td>
<td>0.76</td>
<td>0.45</td>
<td>1.57</td>
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<tr>
<td>9</td>
<td>2.35</td>
<td>2.05</td>
<td>2.15</td>
<td>150</td>
<td>25</td>
<td>15873</td>
<td>23529</td>
<td>0.68</td>
<td>0.83</td>
<td>0.85</td>
<td>0.85</td>
<td>0.98</td>
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<tr>
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<td>2.19</td>
<td>2.06</td>
<td>2.10</td>
<td>100</td>
<td>30</td>
<td>16000</td>
<td>20408</td>
<td>0.84</td>
<td>0.67</td>
<td>0.78</td>
<td>0.53</td>
<td>1.35</td>
</tr>
</tbody>
</table>

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

Figure 4 : Catalytic activity of complexes (2), (3), (6), (7) and (8) on the decomposition of H\(_2\)O\(_2\)
The calculated values (TABLE 4) suggest covalent bonding character\(^{[43,46]}\). The in-plane and out-of-plane \(\pi\)-bonding coefficients (\(\beta_1^2\) and \(\beta_2^2\)) are dependent upon the values of \(\Delta E_{xy}\) and \(\Delta E_{xz}\) in the following equations\(^{[43,46]}\).

\[
\alpha^2 \beta_1^2 = \frac{(g_{||} - 2.002) \Delta E_{xy}}{2\lambda}
\]

\[
\alpha^2 \beta_2^2 = \frac{(g_{\perp} - 2.002) \Delta E_{xz}}{8\lambda}
\]

In this work, the Cu(II) complexes show \(\beta_2^2\) values in the (0.75-0.94) range (TABLE 4) indicating a moderate degree of covalency in the in-plane \(\pi\)-bonding, while \(\beta_2^2 > 1.0\) (TABLE 4) indicates the ionic character of the out-of-plane \(\pi\)-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 crystallinity 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)

**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 \(\text{H}_2\text{O}_2\) 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-
results of H$_2$O$_2$ 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$_2$O$_2$ and “x” the concentration after time "t"; the rate constant of H$_2$O$_2$ 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), O$_5$N$^>$ (7), O$_4$N$^>$O$_2$ (2), O$_3$N$_3$ (6), O$_2$N$_2$Cl$_2$ (3), O$_2$N$_2$. Previous researchers reported that, the Cu$^{2+}$/Cu$^+$ system forms catalytic active sites which responsible for the decomposition of H$_2$O$_2$. The Cu$^{2+}$ was identified as the species, which control the catalytic activity of the complexes. The decomposition of H$_2$O$_2$ in the presence of complex (8) may be represented as follows:

$$
\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}_2^- \\
\text{HO}_2^- \rightarrow \text{HO}_2 + e^- \\
\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+ \\
\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^- \\
\text{H}^+ + e^- \rightarrow \text{H} \\
\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2.
$$

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.

REFERENCES