Copper(II) complexes with bis thiazole based ligands: Spectral, cyclic voltammetric and EPR studies

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A series of complexes with stoichiometry corresponding to [CuLX₂] has been synthesised, where L is a potentially tridentate ligand carrying pendant benzothiazolyl groups and X = ClO₄, Cl, NO₃, CH₃COO and HCOO. EPR spectra of the complexes examined as a frozen DMF solution reveal a distorted tetragonal geometry. The visible band energy for these copper(II) complexes is found to fall in the range observed for N₂O₂ type donor environment, while the plot of the reduction potential versus d-d band energy indicates that increasing covalency leads to a decrease in dₓ²-y² orbital energy and a concomitant anodic shift.

Coordination of histidine-imidazole and methionine thioether is well known to give rise to a distorted geometry around Cu(II) in a number of copper containing enzymes, leading to a large change in their electronic structure. In this note we describe some copper(II) complexes of a potentially tridentate ligand containing two benzothiazole moieties, and one ether oxygen donor group. The five coordinate copper(II) complexes with distorted geometry may have relevance to the type (II) copper site in enzymes such as tyrosinase.

Experimental

Solvents and reagents were of A R grade and used without further purification.

Preparation of ligand

N,N'-bis(benzothiazolyl)ether was prepared as reported earlier; the preparation method consisted of the following steps:

Diglycolic acid 4 g (0.029 mol) and p-aminothiophenol (7.75 g, 0.058 mol) were mixed and added to 25 ml of polyphosphoric acid, the temperature of the mixture was raised to 140°C and maintained at this value with efficient stirring for 4 hr. The reaction mixture was allowed to cool to room temperature and poured into vigorously stirred water (200 ml). A yellowish precipitate formed, was filtered and dried. This was recrystallized from ethanol. Pale yellow crystals, were isolated.

The ligand was characterized by elemental analysis (Table 1) and ¹H N.M.R. spectroscopy. ¹H N.M.R. (CDCl₃): 7.3 (4 H, m), 6.9 (4 H, m), 4.4 (4 H, s).

Synthesis of complexes

[Cu(DGBT)X₂].nH₂O, X = Cl, NO₃, OAC, HCOO, ClO₄⁻

The ligand (DGBT), (312 mg 1 mmol) and hydrated copper chloride/nitrate (CuX₂.nH₂O), (1 mmol) were separately dissolved in methanol (30 ml), and mixed. The reaction mixture was stirred for 1 hr on a warm water bath, which resulted in the precipitation of the desired compounds. This precipitate was collected, washed with methanol and dried over P₂O₅ in vacuo. In the case of the perchlorate, acetate and formate, precipitated copper hydroxide was suspended in methanol and dissolved by addition of dilute (1:5) perchloric acid, acetic acid and formic acid respectively. This solution of the copper salt was then reacted with the ligand in a manner similar to that reported above and desired products were isolated. Except the perchlorate complexes which analysed for a 1:2 metal-ligand system, all other complexes were of 1:1 type (Cu: ligand).

Caution: Although no accident occurred with the present copper (II) perchlorate complexes during the experimental work, it should be remembered that perchlorates are potentially explosive.

Elemental analyses were obtained from microanalytical laboratory of RSIC, University of Punjab, Chandigarh, India. Copper was estimated by atomic absorption spectroscopy using a Shimadzu AA-64-13 instrument. Electronic spectra were measured using a KONTRON UVIKON 930 uv-vis spectrophotometer. ¹H NMR spectra were taken on a Bruker 300 MHz FT-NMR spectrometer at RSIC, Chandigarh. X-band EPR spectra were obtained on VARIAN E-112 ESR spectrometer with a variable temperature liquid nitrogen cryostat at IIT Madras, India. IR spectra were recorded in the solid state as KBr pellets except for the perchlorate complex in which case IR was
taken in nujol on a Perkin-Elmer spectrum 2000 FT-
IR spectrometer.

Cyclic-voltammetric measurements were carried
out using a BAS, CV-50W electrochemical analysing
system. High purity, HPLC grade DMSO & CH3CN
solvent was employed for the CV studies with 0.1 M
NaClO4 as supporting electrolyte. A three electrode
configuration was used, comprising platinum disk
working electrode, platinum wire counter electrode
and Ag/AgNO3 references electrode. Electrode
performance was monitored by observing the ferrocenium/ferrocnene (Fc+/Fc) couple in the above
solvent system. Experiments were carried out at room
temperature (20°C) under dry nitrogen.

Results and discussion

Electronic spectra and electrochemistry

Figure 1 shows the electronic spectra of copper(II)
complexes, their band positions and extinction
coefficients are shown in Table 1. The bands obtained
in UV region are due to n-π* transitions. These bands
show blue shifts in their respective complexes and
support the binding of benzothiophenyl ring through
imine nitrogen to the metal center. All the copper
complexes show a major absorption band in the
visible region, which, in general, is split indicating
lowered site symmetry for copper(II) in the respective
complexes. This is further confirmed by their large
extinction coefficients which are in the range of
(75.4-144.5 L m-1 cm-1).

Figure 2a-e shows cyclic voltammograms of all the
complexes. These were recorded in 2:8
DMSO:MeCN solvent system. All the complexes
exhibit a quasireversible CuII-CuI reduction wave, with
peak to peak width much larger than that observed for
the one-electron couple Fc+/Fc ion in the same
solvent system. Larger peak widths for the one-
electron CuII → CuI couple in their respective
complexes is not an uncommon observation11. We
were prompted to study the scan rate dependence of
the redox peak for the compound shown in Fig. 2(a).
Plot of \( \frac{2}{i_{pc}} \) vs \( v^{1/2} \) (scan rate) is nearly linear which is
known to be observed for quasi-reversible/reversible
behaviour12. Further, a plot of \( \frac{2}{i_{pc}} \) vs \( v^{1/2} \) shows a
near straight line suggesting that adsorption on
electrode surface if any is negligible13. All the present
Fig. 2—C.V. Spectra of (a) Cu(DGBT)(Cl)$_2$; (b) Cu(DGBT)(OAC)$_2$·2H$_2$O; (c) Cu(DGBT)(NO$_3$)$_2$; (d) Cu(DGBT)(HCOO$^-$)+2·3H$_2$O; (e) Cu(DGBT)$_2$(Cl)$_2$ and all in 2:8 DMSO:CH$_3$OH solvent. Scan rate—100 mVs$^{-1}$. 
Table 2—Cyclic voltametric data of copper(II) complexes at 298 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pc}$(V)</th>
<th>$E_{pa}$(V)</th>
<th>$E_{mp}$(V)</th>
<th>$i_{pa}/i_{pc}$</th>
<th>$\Delta E_p$</th>
<th>DPV(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(DGBT)$_2$(ClO$_4$)$_2$] [1]</td>
<td>-0.050</td>
<td>0.128</td>
<td>0.039</td>
<td>1.04</td>
<td>0.178</td>
<td>0.05</td>
</tr>
<tr>
<td>[Cu(DGBT)Cl] [2]</td>
<td>-0.051</td>
<td>0.12</td>
<td>0.034</td>
<td>1.06</td>
<td>0.171</td>
<td>0.04</td>
</tr>
<tr>
<td>[Cu(DGBT)(NO$_3$)$_2$] [3]</td>
<td>-0.119</td>
<td>0.178</td>
<td>0.029</td>
<td>1.02</td>
<td>0.207</td>
<td>0.05</td>
</tr>
<tr>
<td>[Cu(DGBT)(OAC)$_2$]2H$_2$O [4]</td>
<td>-0.098</td>
<td>0.110</td>
<td>0.006</td>
<td>1.05</td>
<td>0.208</td>
<td>0.001</td>
</tr>
<tr>
<td>[Cu(DGBT)(CIO$_4$)$_2$]3H$_2$O [5]</td>
<td>-0.099</td>
<td>0.083</td>
<td>-0.008</td>
<td>0.95</td>
<td>0.182</td>
<td>-0.005</td>
</tr>
</tbody>
</table>
complexes show a peak current ratio \( i_{p2}/i_{p1} \) near to unity [Shown in Table (2)]. However, the \( \Delta E_p \) values are greater than the nernstian value (\( \Delta E_p \approx 59 \text{ mV} \)) for a one-electron redox system. This indicates a considerable reorganisation of the coordination sphere during electron transfer as has been observed for a number of other copper (II) complexes. The following order of increasing \( E_{1/2} \) values is found: 

\[
\text{HCOO} < \text{CH}_2\text{COO} < \text{NO}_3 < \text{Cl} < \text{ClO}_4^- 
\]

The large \( E_{1/2} \) values together with a visible band energy \((d-d)\) indicates the retention of exogenous anion with the central metal ion in solution. The above stabilization/destabilization of the Cu(II) centre may further be understood by comparing the covalency, \(d-d\) band energy and \(E_{1/2}\) value. Smaller the value of \(\alpha^2\), larger will be the covalency and lower will be the repulsion between the \(d_{x^2-y^2}\)-Cu\(^{II}\) equatorial bond. Consequently, a decrease in \(d_{x^2-y^2}\) orbital energy will cause an anodic shift in Cu\(^{II}\)-Cu\(^{II}\) reduction potential. This is evident from the graph plotted between \(E_{1/2}\) and \(d-d\) visible band energy which yields a straight line.

### EPR spectroscopy

Figure 3 shows a representative X-band EPR spectrum of the above complexes examined at 77 K as a frozen DMF solution. Since \(g_2 > g_1 > 2.003\) has been found in all the complexes, spectra are fairly typical of tetragonally distorted copper(II) environment. The spin Hamiltonian parameters \( (g_1, g_2, A_1) \) in all the complexes are very similar to those found in N-coordinated benzimidazole copper (II) complexes and are given in Table 3. Therefore, the benzothiazole ligand binds to copper(II) through the imine nitrogen atom in the equatorial plane, rather than the sulphur. This is because, a significant change in \(g_1\) and \(A_1\) would have been observed if S-atom were to replace nitrogen atom in the equatorial plane in the present series of complexes.

The above complexes have a large \(g_1\) and a small \(A_1\). The large \(g_1/A_1\) ratio has been interpreted in terms of tetrahedral distortion of the basal plane and is also supported by the low energy \(d-d\) bands exhibited by the above complexes in the range of 709-892 nm region in DMF. The low value of \(A_1\) in case of chloride and nitrate complexes in comparison to acetate and formate complexes together with the fact that the \(d-d\) bands are shifted to longer wavelength in both chloride and nitrate complexes is indicative of stronger axial interaction than that in the corresponding acetate and formate complexes. It is, therefore, concluded that at least one anionic ligand attaches in the axial position. This would then place the tridentate ligand in a meridional arrangement rather than facial. No nitrogen superhyperfine splitting has been observed in any of these complexes. This may be due to loss of tetragonality, because of steric constraints of the ligand. EPR spectra of perchlorate complex [Fig. 3(d)] shows the presence of four prominent and three weak \(g_1\) lines. This could be explained on the basis of the presence of at least two copper(II) species in solution having similar \(g_1\) and \(g_2\) values. This situation may arise, if 1:2 perchlorate complex dissociates in solution to form a small percentage of 1:1 species. It is for this reason that the stick diagram in Fig. 3(d) indicates which \(g_1\) components have been utilised for the calculation of \(A_1\) values.

### Infrared spectroscopy

IR spectra were taken in KBr pellets. In free ligand,
a strong band is found at ca 1460 cm\(^{-1}\) with another weaker band at ca 1490 cm\(^{-1}\). By analogy with assigned bands for imidazole, the 1460 cm\(^{-1}\) band is attributed to \(\nu_s (C=N-C=C)\), while the other band is assigned to an overtone or combination band\(^{15}\). These bands are shifted by ca 10-20 cm\(^{-1}\) in the complexes. This result implies a direct coordination of the imine nitrogen atoms with the metal site. Bands at 1470 and 1320-1340 cm\(^{-1}\) are assigned to \(\nu_{asym} (NO_2) \nu_{sym} (NO_2)\) and \(\nu_{asym} (NO)\) respectively suggesting a unidentate mode of binding of nitrate group\(^{17}\). In the copper(II) perchlorate complex appearance of strong bands at 1080 and 910 cm\(^{-1}\) suggests the presence of ionic perchlorate\(^{18}\).

The above spectral studies allow us to propose a meridional structure for the five-coordinate complexes, containing one DGBT ligand and two anions (I), while a distorted octahedral geometry for the six coordinate, perchlorate complex with two DGBT ligands in a facial arrangement (II) as shown below:

![Diagram of complexes](image)

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**References**