Synthesis and characterization of copper (I) and copper (II) complexes with 1,5-bis (benzimidazol-2-yl)-3-thiapentane

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Complexes with formula \([\text{Cu(BBES)}_2X]_{\text{2}+} \text{H}_2\text{O}\) have been synthesized where BBES is a tridentate ligand containing bis-benzimidazolyl as pendant coordinating group and X is an exogenous anionic ligand (X = \text{HCOO}^-, \text{CH}_3\text{COO}^-, \text{Cl}^-, \text{Br}^-, \text{NO}_3^-). Solution EPR spectroscopy on these complexes reveals that the ground state in these copper (II) complexes comprises \(d_{x^2-y^2}\) orbital. Cyclic voltammetric studies reveal that \(E_{1/2}\) for \(\text{Cu(II)/Cu(I)}\) couple shifts cathodically with \(\text{HCOO}^-\) as the anionic ligand, implying that binding of this anion stabilizes the \(\text{Cu(II)}\) state whereas \(E_{1/2}\) data for \(\text{NCS}^-\) indicates that this anion destabilizes \(\text{Cu(II)}\) state. Copper (I) complex has also been synthesized in the presence of hydroquinone which shows a well-resolved NMR spectrum in the range 0-10 ppm.

Coordination of \(\text{Cu(I)}\) and \(\text{Cu(II)}\) by bis-benzimidazole ligand has been the subject of extensive investigation during the last decade. Copper coordination chemistry of bis-benzimidazole complexes has been extensively studied because of their potential as low molecular weight mimics for the active sites in many metalloproteins\(^1,2\). Keeping the above background in mind we were prompted to synthesize \(\text{Cu(II)}\) and \(\text{Cu(I)}\) complexes with \(1,5\)-bis (benzimidazol-2-yl)-3-thiapentane which provides a \(\text{N}_2\text{S}\) donor environment and characterised the complexes using spectral and electrochemical techniques. Synthesis of a few copper(II) complexes with the title ligand BBES has been reported earlier\(^3\).

Materials and Methods

All chemicals used were of A.R. grade and used as received.

Elemental analyses were obtained from the micro-analytical Laboratory of CDRI, Lucknow & RSIC, Chandigarh.

I.R. spectra were taken on a Shimadzu IR-435 spectrophotometer and electronic spectra were taken on a Perkin-Elmer-554 spectrophotometer. X-band EPR spectra were taken on a Jeol JES-Fe 3 XG spectrometer with a variable temperature liquid nitrogen cryostat at USIC, University of Delhi; \(^1\)H NMR spectra were taken on a 90 MHz Perkin-Elmer R-32 spectrometer. Cyclic voltammetric measurements were done on a BAS CV 50W instrument. A mixed solvent system DMSO : \(\text{CH}_3\text{CN} (1:9)\) was employed for the CV studies with \(0.1M \text{NaClO}_4\) as the supporting electrolyte. Magnetic susceptibilities of complexes were determined at 29°C in the solid state at USIC, University of Roorkee, Roorkee.

The free ligand \(1,5\)-bis(benzimidazol-2-yl)-3-thiapentane (BBES) was synthesised as described earlier\(^4\), with minor modifications in the procedure adopted.

Preparation of \(1,5\)-bis(benzimidazol-2-yl)-3-thiapentane (BBES)

To a mixture of \(3,3\)-thiodipropionic acid (9.0 g, 0.05 mol) and \(\alpha\)-phenylenediamine (10.9 g, 0.1 mol) was added \(4M \text{aqueous HCl} (250 ml)\). The solution was refluxed for 30-36 hr and was filtered while hot. As the filtrate cooled, the blue crystals formed were dried \textit{in vacuo}. These dihydrochloride crystals were then dissolved in water and the free base was obtained by treatment with excess of aqueous ammonia (1:1). The pinkish white precipitate that separated was dissolved in ethanol containing decolorising charcoal and was refluxed for 10 min; this was then filtered. A fluffy white compound crystalized on gradual addition of water. This was then isolated and dried \textit{in vacuo} (10.5g, 70%).

The ligand was characterised by C, H, N analysis, I.R., UV and \(^1\)H NMR techniques. C.H,N analysis is given in Table I. NMR spectrum (DMSO-\(d_6\)): 7.48 (m, 4H),
Table 1 — Micro-analytical, electronic, magnetic moment and electrochemical data of copper (II) and (I) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (%)</th>
<th>Calc (%)</th>
<th>Cu</th>
<th>(\mu_{\text{eff}}) (BM)</th>
<th>(E_{\text{1/2}}) (V)</th>
<th>(\lambda_{\text{max}}) (log e) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cu(BBES)Cl] (_2) (\cdot)H(_2)O</td>
<td>68.0(67.1)</td>
<td>5.7(5.6)</td>
<td>18.2(17.4)</td>
<td>14.4(13.9)</td>
<td>1.60 +0.24</td>
<td>678(2.4)</td>
</tr>
<tr>
<td>[Cu(BBES)(CH(_3)COO(_2)) (\cdot)H(_2)O</td>
<td>51.7(50.6)</td>
<td>6.1(5.0) 11.3(10.8)</td>
<td>12.6(12.2)</td>
<td>1.90</td>
<td></td>
<td>635(2.18)</td>
</tr>
<tr>
<td>[Cu(BBES)(HCOO(_2))] (\cdot)H(_2)O</td>
<td>47.6(48.6)</td>
<td>4.9(4.5)</td>
<td>11.5(11.4)</td>
<td>11.9(12.8)</td>
<td>1.81 +0.18</td>
<td>673(2.7)</td>
</tr>
<tr>
<td>[Cu(BBES)(Br(_2))] (\cdot)H(_2)O</td>
<td>37.8(38.3)</td>
<td>3.6(3.6)</td>
<td>10.3(10.0)</td>
<td>10.2(11.2)</td>
<td>2.10 +0.30</td>
<td>675(2.67)</td>
</tr>
<tr>
<td>[Cu(BBES)(NO(_3))(_2)(\cdot)2H(_2)O</td>
<td>39.8(39.6)</td>
<td>3.7(4.0)</td>
<td>15.1(15.4)</td>
<td>12.3(11.7)</td>
<td>1.72 +0.32</td>
<td>650(2.22)</td>
</tr>
<tr>
<td>[Cu(BBES)(NCS(_2))</td>
<td>47.2(47.8)</td>
<td>3.8(3.6)</td>
<td>16.9(16.8)</td>
<td>12.4(12.6)</td>
<td>1.74 +0.41</td>
<td>697(2.28)</td>
</tr>
<tr>
<td>[Cu(BBES)(C(_2)H(_4)O(_2))(NO(_3))(\cdot)2H(_2)O</td>
<td>48.6(48.6)</td>
<td>3.7(4.3)</td>
<td>12.6(11.9)</td>
<td>11.6(10.7)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Error bar equals \(\pm 0.05\) BM

7.16 (m, 4H), 3.2 (m, 4H), 3.07 (m, 4H).

Synthesis of complexes: \([Cu(L)X_2]_n\) \(\cdot\)H\(_2\)O (where \(L = BBES\) and \(X = Cl^-, Br^-, NO\(_3^-\), NCS\(^-\), HCOO\(^-\), CH\(_3\)COO\(^-\)):

(i) \(X = Cl^-, Br^-, NO\(_3^-\)

To a stirred solution of 2 mmol of copper salt in 20 ml of methanol was added 2 mmol of ligand BBES. Stirring was continued for 5-6 hr. The resulting blue/greenish-blue solution was cooled overnight in a refrigerator and blue-green crystalline product was produced. This was collected over a frit and washed with a mixture of methanol/ether (1:2). The product was air-dried and stored over P\(_2\)O\(_5\) in vacuo.

(ii) \(X = CH_3COO^-, HCOO^-, NCS^-

In the case of acetate and formate complexes, precipitated copper hydroxide (2 mmol) was suspended in methanol and a solution of acetic or formic acid in methanol (1:1 solution) was added dropwise till the precipitate dissolved to give a clear solution, while for the thiocyanate complex a saturated solution of potassium thiocyanate in methanol was added to a solution of copper chloride (2 mmol) in methanol. The precipitated potassium chloride was filtered to get a clear pale yellow solution.

These respective solutions were then reacted with ligand BBES in the manner described in (i).

Synthesis of Cu(I) complex

To a stirred blue solution of copper nitrate (2 mmol) in 20 ml methanol was added 2 mmol of hydroquinone solution. On adding 2 mmol of BBES in MeOH, the resulting solution turned dark green and on stirring a dirty white product separated which was finally washed with 1:10 methanol-ether mixture and stored over P\(_2\)O\(_5\) in vacuo. Analytical data of copper complexes are given in Table 1.

Results and Discussion

Solution EPR spectra of these complexes were recorded in MeOH at liquid nitrogen temperature. All
Fig. 1 — X-band EPR spectra of complexes at microwave power = 10 mW, microwave frequency = 9.03 GHz; modulation amplitude = 2 x 1 G; T = 143 K, centred at 2500 G.

(a) 5000 G scan of frozen methanol solution of [Cu(BBES)Cl2]. receiver gain = 2 x 10^2; (b) 5000 G scan of frozen methanol solution of Cu (BBES) (CH3COO)2. receiver gain = 2 x 10^2, resolved at 5 x 10^2; (c) 5000 G scan of frozen methanol solution of [Cu(BBES) (HCOO)2]. receiver gain = 1 x 10^2, resolved at 6.3 x 10^2; (d) 5000 G scan of frozen methanol solution of [Cu(BBES)Br2]. receiver gain = 2.5 x 10^2, resolved at 6.3 x 10^2; (e) 5000 G scan of frozen methanol solution of [Cu(BBES) (NO3)2]. receiver gain = 2.5 x 10^2, resolved at 5 x 10^2; (f) 5000 G scan of frozen DMF solution of [Cu(BBES) (NCS)2]. receiver gain = 7.9 x 10^2.

| Complex                  | g || | g || | g || | X 10^4 | \alpha^2 |
|--------------------------|---|---|---|---|---|---|---|
| [Cu(BBES)Cl2]           | 150 | 2.34 | 2.11 | 156 | 0.53 |
| [Cu(BBES)(CH3COO)2]     | 125 | 2.32 | 2.04 | 185 | 0.52 |
| [Cu(BBES)(HCOO)2]       | 125 | 2.34 | 2.08 | 187 | 0.56 |
| [Cu(BBES)Br2]           | 133.4 | 2.33 | 2.11 | 175 | 0.51 |
| [Cu(BBES)NO3]2         | 150 | 2.33 | 2.08 | 155 | 0.53 |
Cu(II) complexes show resolution of $g$ and $g_z$ with $g > g_z > 2.0$ (Table 2, Fig. 1) with $A$ values falling in the range 125-150 gauss. This range of $A$ is quite low in comparison to that for Cu(II) complexes having a $\text{N}_2\text{O}_2$ environment. Further, high values of $g_z$, $A$ are typically in the range generally observed for five-coordinated Cu(II) complexes in square-pyramidal geometries and are indicative of coordination of sulphur besides the two nitrogen atoms from pendant benzimidazole rings. EPR spectrum of thiocyanato complex shows $g_1 = 2.03$, $g_2 = 2.11$, $g_3 = 2.20$. The ratio of $g_2 - g_1 / g_3 - g_1$ is less than one which is indicative of $d_{2s}$ as ground state. Thus $g$ value pattern indicates a distorted five-coordinate geometry for [Cu(BBES) (NCS)$_2$] complex and strengthens the view that this ligand acts as a T-shaped facially coordinating tridentate ligand, with two coordinating N atoms in...
trans positions in the equatorial plane and sulphur atom linked apically. It is found that some of the Cu(II) complexes show more than four hyperfine lines in the g region which could be due to the presence of more than one species in solution. The second species would arise if the ligand adopts a meridional configuration (where both the N and S atoms bind in the equatorial plane). Existence of two such species in solution will not give exactly overlapping g hyperfine lines leading to the observation of more than four lines in EPR spectra.

A look at A data shows that one could group the series into two categories. The chloride and nitrate with higher A values are indicative of a solution structure in which the equatorial plane is relatively more planar in comparison to complexes having HCOO⁻, CH₃COO⁻ and Br⁻ anions.

Also EPR investigation was undertaken in the solid state at X-band for Cu(I) complex and no signal indicates a diamagnetic ground state for Cu(I) complex.

¹H NMR spectrum of Cu(I) complex prepared in presence of hydroquinone was taken in d₆-pyridine. The spectrum shows expected broadening of peaks and slight shifts of aliphatic / aromatic / NH protons of the ligand. Well-defined sharp multiplet that arises in free ligand due to aromatic protons is also broadened in the Cu(I) complex. Most pronounced effect is found in the NH proton signal, which in free ligand is observed at 9.2, and shifts to δ 10.0-10.6 ppm in the spectra of Cu(I) complexes. The above ¹H NMR with broad peaks and small shifts is typical of Cu(I) bound to a free ligand.

Fig. 2 shows the cyclic voltammograms of Cu(II) complexes taken in DMSO/CH₃CN solvent. All complexes
exhibit a quasi-reversible reduction wave in the range +0.12 to +0.48 V. This quasireversible couple is assigned to a Cu(II)/Cu(I) couple. The $E_{1/2}$ data (Table I) for this couple indicates that the least positive potential is for the chloro, bromide, nitrate and thiocyanate complexes.

Since a cathodic shift in $E_{1/2}$ potential of Cu(II)/Cu(I) couple results in the stabilization of Cu(II) state in the complexes, we therefore conclude that the binding of formate anion stabilizes the Cu(II) state whereas the binding of N-bonded thiocyanate anion tends to stabilize the Cu(I) state in comparison to Cu(II) state.

Cu(II) complexes show three UV bands in the range 240-280 nm, characteristic of benzimidazole group and also show a charge transfer band in the region 300-325 nm which is ascribed to benzimidazole.

$\sigma (N) \rightarrow Cu(II)$. Their respective extinction coefficients have been reported in Table I (Fig. 3). For the acetato and formato complexes in addition to the above charge transfer band, another band is observed at 400 nm. All these copper(II) complexes show one major absorption in the range 630-700 nm (16000-14000 cm$^{-1}$) assigned to transitions $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{yz}$ and large molar extinction coefficients in range of 150-400 $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ indicating that copper site in the complexes is of low symmetry$^8$. A low energy band in some of the cases is observed near 900 nm and could be due to $d_{x^2-y^2} \rightarrow d_{xy}$ transition.

In IR spectrum of free ligand (in KBr) a strong band observed at 1435 cm$^{-1}$ along with a weaker band at 1420 cm$^{-1}$; the latter is attributed to stretching mode of $\equiv \text{C} = \equiv \text{N}$. While the latter one is an overtone or combination band$^9$. In the present case we find a shift of $\approx 10-20$ cm$^{-1}$ in the spectra of copper complexes which implies direct coordination of imine nitrogen atoms to Cu(II) center$^{10}$. Thiocyanato complex show an additional band at 2050 cm$^{-1}$ showing presence of N-bonded NCS$^-$ group$^{11,12}$ while acetato and formato complexes show additional bands at 1545, 1390 and 1340 cm$^{-1}$ respectively which suggest the presence of coordinated acetate/formate in unidentate mode of binding$^{13}$. Magnetic susceptibility data (Table I) reveal spin-only values for all the Cu(II) complexes except for the chloro complex where the value is slightly lower than 1.73 BM. Thus, an intermolecular interaction in solid state may not be ruled out in this case.

On the basis of analytical and other spectroscopic studies, the proposed structure of these complexes is as shown in structure (I).

References