Copper(II) Complexes of Isobutyl Methyl Ketone Semicarbazone

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Summary

Copper(II) complexes of isobutyl methyl ketone semicarbazone have been prepared and characterised by magnetic moments, i.r., electronic and e.s.r. spectral studies. The complexes were found to have CuL2X2 and CuL2X2·2H2O compositions. The electronic and e.s.r. spectra suggest a five-coordinated trigonal bipyramidal geometry, for the CuL2X2 complexes, (X = Cl-, Br-, NO3- and SO42-) and six-coordinate octahedral geometry has been suggested for CuL2X2·2H2O (X = Cl-, Br-, NO3- and SO42-).

Introduction

Campbell et al. have reported the electronic and e.s.r. spectra of copper(II) complexes, CuL2X2, where X = Cl- or Br- and the ligands are the semicarbazones of cycloheptane diacetyl ketone. Chandra et al. have found stereochemical variations in the Copper(II) complexes of cyclohexanone semicarbazone. With these facts in mind, we have synthesized copper(II) complexes of isobutyl methyl ketone semicarbazone and characterised them by standard physico-chemical techniques viz., magnetic moments, i.r., electronic and e.s.r. spectral studies. The CuL2X2 (X = Cl-, Br-, NO3-, and SO42-) complexes may be five coordinate trigonal bipyramidal, while the CuL2X2·2H2O (X = Cl-, Br-, NO3- and SO42-) possess six-coordinate octahedral geometry.

Experimental

Preparation of the ligand

Semicarbazide hydrochloride (11.15 g, 1 mol) was dissolved in sufficient quantity of the distilled H2O together with anhydrous NaOAc (13.6 g, 1 mol). The resultant solution was filtered, and to the filtrate isobutyl methyl ketone (12.5 g, 1 mol) was added, in small aliquots with constant stirring. The precipitate of isobutyl methyl semicarbazone (ligand) was filtered and dried at room temperature.

Preparation of the complex

CuL2X2. Hot solutions of the metal salts (0.05 mol) and the ligand (0.1 mol) were mixed in absolute EtOH. The mixture was boiled under reflux on a waterbath for about 1 h. On cooling, the coloured complex precipitated. It was filtered, washed with EtOH and dried in vacuo over P2O5.

CuL2X2·2H2O. A hot aqueous-solution of the metal salt (0.05 mol) was mixed with a hot H2O-EtOH solution of ligand (0.1 mol) and refluxed on a water bath for 30 min. On cooling, the complex separated out and was worked up as given above.

Physical measurements

The magnetic susceptibilities of the complexes were measured on a Gouy Balance using Hg[Co(CNS)4] (xα = 16.44 · 10⁻⁵ cgs units) as calibrant. I.r. spectra were recorded on a Perkin Elmer 621 automatic recording spectrophotometer in KBr discs. Electronic spectra of the complexes were recorded on a DMR-21 automatic recording spectrophotometer in nujol mull. E.s.r. spectra were recorded on a Varian E4-EPR spectrometer, operating at 9.4 GHz and 100 KHz field modulation with a phase-sensitive detector. The spectra were calibrated using DPPH powder. Carbon and hydrogen were determined microanalytically. The nitrogen contents were determined by Kjeldahl's method. Copper was estimated gravimetrically as CuCNS.
Table 1. Elemental analysis and colours for the complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (Calcd.) %</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>Cu</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Cu(ibsk)₂Cl₂</td>
<td>light green</td>
<td>14.1(14.2)</td>
<td>37.5(37.5)</td>
<td>6.7(6.7)</td>
<td>18.7(18.7)</td>
</tr>
<tr>
<td>Cu(ibsk)₂Br₂</td>
<td>parrot green</td>
<td>11.8(11.0)</td>
<td>31.25(31.2)</td>
<td>5.6(5.6)</td>
<td>15.6(15.7)</td>
</tr>
<tr>
<td>Cu(ibsk)₂(NO₃)₂</td>
<td>greenish grey</td>
<td>12.7(12.6)</td>
<td>35.5(33.5)</td>
<td>6.0(6.0)</td>
<td>22.3(22.2)</td>
</tr>
<tr>
<td>Cu(ibsk)₂SO₄</td>
<td>dark green</td>
<td>13.4(13.4)</td>
<td>35.5(35.5)</td>
<td>6.3(6.3)</td>
<td>17.7(17.7)</td>
</tr>
<tr>
<td>Cu(ibsk)₂Cl₂·2H₂O</td>
<td>green</td>
<td>13.1(13.1)</td>
<td>34.7(34.6)</td>
<td>7.0(7.1)</td>
<td>17.3(17.3)</td>
</tr>
<tr>
<td>Cu(ibsk)₂Br₂·2H₂O</td>
<td>light green</td>
<td>11.1(11.0)</td>
<td>29.3(29.3)</td>
<td>5.9(6.0)</td>
<td>14.6(14.4)</td>
</tr>
<tr>
<td>Cu(ibsk)₂(NO₃)₂·2H₂O</td>
<td>greenish</td>
<td>11.8(11.75)</td>
<td>31.25(31.3)</td>
<td>6.3(6.4)</td>
<td>15.6(15.8)</td>
</tr>
<tr>
<td>Cu(ibsk)₂SO₄·2H₂O</td>
<td>bright green</td>
<td>12.5(12.5)</td>
<td>33.0(33.05)</td>
<td>6.7(6.7)</td>
<td>16.5(16.4)</td>
</tr>
</tbody>
</table>

\(^a\) ibsk = isobutyl methyl ketone semicarbazone.

Results and Discussion

\textbf{CuL₂X₂ Complexes}

Elemental analyses suggest that the complexes have the general composition CuL₂X₂ (Table 1). Their magnetic moments lie in the 1.90–2.0 B.M. range, thus suggesting their monomeric nature\(^3\) (Table 2).

The i.r., electronic and e.s.r. spectral studies support a five coordinate, trigonal bipyramidal geometry for these complexes. The i.r. spectra\(^4\) of the sulphate complex suggest that the sulphate group acts as a monodentate ligand. A pentacoordinated structure is, thus, suggested for this complex. Two basic configurations\(^5\) can be adopted by complex compounds of coordination number five; the trigonal bipyramidal (TBP) and the square pyramidal (SP). In practice there appears to be very little energy \(^6\) difference between the two configurations and the large distortions from ideal geometries in the complexes of these type makes this difference still smaller.

The two configurations SP and TBP are characterised by the ground states \(d_{x^2-y^2}\) and \(d_{z^2}\) respectively\(^7\). The e.s.r. spectra of copper(II) complexes (Figure 1) provide a very good basis for distinguishing between these two ground states. For systems with \(g_3 > g_2 > g_1\), the \((g_3 - g_2)/(g_3 - g_1)\) ratio is defined as \(R\), a very useful parameter\(^8\). If the ground state is predominantly \(d_{z^2}\), the \(R\) value should be greater than unity, and when the ground state is predominantly \(d_{x^2-y^2}\), the \(R\) value should be less than unity\(^9\). The e.s.r. spectra of all these complexes give three \(g\) values (Table 2).

![Figure 1. E.s.r. spectra of: (a) Cu(ibsk)₂Cl₂·2H₂O and (b) Cu(ibsk)₂SO₄·2H₂O.](attachment://image.png)

Table 2. E.s.r. parameters of the CuL₂X₂ complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(g_1)</th>
<th>(g_2)</th>
<th>(g_3)</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(ibsk)₂Cl₂</td>
<td>2.0740</td>
<td>2.1877</td>
<td>2.2758</td>
<td>2.1792</td>
</tr>
<tr>
<td>Cu(ibsk)₂Br₂</td>
<td>2.0379</td>
<td>2.1010</td>
<td>2.2177</td>
<td>2.1188</td>
</tr>
<tr>
<td>Cu(ibsk)₂(NO₃)₂</td>
<td>2.0445</td>
<td>2.1412</td>
<td>2.2328</td>
<td>2.1395</td>
</tr>
<tr>
<td>Cu(ibsk)₂SO₄</td>
<td>2.0201</td>
<td>2.1211</td>
<td>2.2475</td>
<td>2.1296</td>
</tr>
</tbody>
</table>

The \(R\) value calculated (Table 2) for the complexes, reveal \(d_{z^2}\) as the ground state: i.e. trigonal bipyramidal geometry, for chloro and nitrato complexes; with \(d_{x^2-y^2}\) as the ground state i.e., square pyramidal geometry, for bromo and the sulphato complexes. However, the \(g_1\) values are significantly higher than the theoretical value and suggests considerable distortion from the trigonal bipyramidal geometry. The higher \(g\)-values of this order have been observed previously in several trigonal bipyramidal copper(II) complexes\(^10\). The electronic spectra of trigonal bipyramidal copper(II) complexes are known to show only one intense absorption for the A→E transition. In \(D_{3h}\) symmetry, the transition\(^11\) A→E is spin forbidden and should appear only weakly through a vibronic mechanism. The electronic spectra of the complexes under study display one broad absorption band in the 11000–11500 cm\(^{-1}\) range (Table 1). This band may be assigned to the spin-allowed transition, A→E. Similar electronic spectra have already been reported for a number of trigonal bipyramidal copper(II) complexes. On the basis of above spectral studies the following structure may be assigned to these complexes.

\[ \text{CuL}_2X_2 \cdot 2\text{H}_2\text{O} \]

The magnetic moments of the complexes lie in the 1.80–1.89 B.M. range and, together with electronic spectral bands are presented in Table 1. The complexes all show identical elec-