Stable Anionic Complexes of Copper(II) with Cyanide, Iodide & Thiocyanate

C M DANI
Research and Control Laboratory
Rourkela Steel Plant, Rourkela 769011
and
A K DAS*
Bonaigarh College, Bonaigarh (Orissa)

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Six stable anionic complexes of copper(II) with reducing ligands like cyanide, iodide and thiocyanate and bidentate nitrogen donor ligand like 2,2'-bipyridyl and 1,10-phenanthroline have been prepared. The complexes have the composition \([\text{enH}_2][\text{CuX}_4\text{L}]\) where \text{en} = ethylenediamine; \text{X} = \text{CN}^-, \text{I}^-, \text{NCS}^-; and \text{L} = 2,2'-bipyridyl or 1,10-phenanthroline. The complexes have been characterized on the basis of analytical, magnetic moment, conductance, infrared and electronic spectral data.

The strong tendency of cyanide, iodide and thiocyanate to reduce Cu(II) to Cu(I) in aqueous solution prevents the formation of simple cyano, iodo and thiocyanato complexes of Cu(II). However, very few Cu(II) cyano\(^3\), iodo\(^4\)-\(^9\) and thiocyanato\(^4\) complexes have been stabilised in presence of some mono and bidentate nitrogen donor ligands. The present note reports for the first time the preparation and characterisation of six novel anionic complexes of Cu(II) with reducing ligands like cyanide, iodide and thiocyanate and nitrogen containing ligands like 2,2'-bipyridyl and 1,10-phenanthroline.

All the chemicals used were of AR quality.

**Preparation of \([\text{enH}_2][\text{CuCl}_4]\)**

The starting complex, \([\text{enH}_2][\text{CuCl}_4]\), where \text{en} = ethylenediamine, was prepared according to the following method. To a requisite amount of ethanolic solution of ethylenediamine, dilute hydrochloric acid was added dropwise with shaking till the solution became slightly acidic. The resulting solution was added to an ethanolic solution of CuCl\(_2\).2H\(_2\)O in 1:1 ratio. On concentrating and keeping the solution overnight, a greenish yellow crystalline compound separated out. The compound was filtered, washed with ethanol and ether repeatedly and dried *in vacuo.*

**Preparation of \([\text{enH}_2][\text{CuX}_4\text{L}]\)** where \text{en} = ethylenediamine; \text{X} = \text{CN}^-, \text{I}^- or \text{NCS}^- and \text{L} = 2,2'-bipyridyl or 1,10-phenanthroline

A solution of 2,2'-bipyridyl or 1,10-phenanthroline in ethanol was added to the ethanolic solution of complex \([\text{enH}_2][\text{CuCl}_4]\) in 1:1 stoichiometric ratio and refluxed for 30 min. Then a solution of the reducing salt KCN, KI or KCNS in ethanol-water (70:30, v/v) was added dropwise to the above solution in 4:1 molar ratio, with vigorous shaking over a period of 5 min when coloured amorphous powders separated out. The complexes were washed with water, ethanol and ether and dried *in vacuo.*

Carbon and hydrogen were analysed microanalytically; copper, cyanide, iodide and thiocyanate were estimated by standard methods. Magnetic susceptibilities of the compounds were measured by a Gouy balance using Hg[Co(NCS)]\(_4\) as the calibrant. Electrolytic conductances of the complexes were measured using their 10\(^{-3}\)M solutions in nitrobenzene at room temperature and a Systronic direct reading conductometer \(-303\). Infrared spectra in the range 4000-2000 cm\(^{-1}\) and electronic spectra in the visible range were recorded at CDRI, Lucknow using Perkin Elmer 577 and Hitachi 320 spectrophotometers respectively.

The elemental analyses correspond to the formulation of the complexes given in Table I. The molar conductance values (33-35 mhos cm\(^{-1}\) mol\(^{-1}\)) of the complexes in nitrobenzene indicate 1:1 electrolytic nature. The high melting point values further support the ionic nature of the complexes. The magnetic moment values (1.77-1.82 B.M.) of the complexes are indicative of the presence of Cu(II) ion with one unpaired electron.

Presence of ethylenediamine in the complexes was well substantiated by appearance of bands due to \(\nu(N-H)\) and \(\delta(N-H)\) modes around 3440 and 1600-1630 cm\(^{-1}\) respectively in the IR spectra of the complexes. The two main stretching modes of thiocyanate moiety, \(\nu(C==N)\) and \(\nu(C-S)\), appear around 2075 and 795 cm\(^{-1}\) respectively in the thiocyanato complexes indicating the involvement of M-NCS bonding. In cyano complexes three distinct bands are observed at \(\sim 2098, \sim 381\) and \(\sim 310\) cm\(^{-1}\) assignable to \(\nu(C==N)\), \(\nu(M-C)\) and \(\delta(M-C==N)\) modes respectively. Presence of nitrogen donor ligand in the complexes was authenticated by the occurrence of \(\nu(M-N)\) bands at 325-340 cm\(^{-1}\). The other bands due to 2,2'-bipyridyl or 1,10-phenanthroline were also modified on complexation.

The electronic spectra of the complexes in methanol display a strong charge-transfer band at 450 nm and one broad absorption band around 750 nm, characteristic of distorted octahedral Cu(II) complexes.\(^{17,18}\)

The authors are grateful to Prof. D V Ramana Rao, Head, P G Department of Chemistry, Regional Engineering College, Rourkela for encouragement and the Management of Rourkela Steel Plant for facilities.
### Table 1—Analytical and Physical Data of the Anionic Complexes of Copper(II)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>Found/(Calc.), %</th>
<th>μ\text{eff} (B.M.)</th>
<th>λ\text{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[en\textsubscript{H}][Cu(CN)\textsubscript{4}•.bipy]</td>
<td>Violet</td>
<td>&gt;250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 17.00 (16.47)</td>
<td>CN/1/SCN: 26.03 (26.96)</td>
<td>C: 49.01 (49.77)</td>
</tr>
<tr>
<td>[en\textsubscript{H}][Cu(CN)\textsubscript{4}•.phen]</td>
<td>Blue</td>
<td>&gt;250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 15.41 (15.51)</td>
<td>CN/1/SCN: 24.79 (25.39)</td>
<td>C: 52.98 (52.74)</td>
</tr>
<tr>
<td>[en\textsubscript{H}][CuI•.bipy]</td>
<td>Brown</td>
<td>&gt;250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 7.98 (8.04)</td>
<td>CN/1/SCN: 63.98 (64.30)</td>
<td>C: 18.90 (18.24)</td>
</tr>
<tr>
<td>[en\textsubscript{H}][CuI•.phen]</td>
<td>Brown</td>
<td>&gt;250</td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 7.21 (7.81)</td>
<td>CN/1/SCN: 61.98 (62.42)</td>
<td>C: 19.89 (20.65)</td>
</tr>
<tr>
<td>[en\textsubscript{H}][Cu(NCS)\textsubscript{4}•.bipy]</td>
<td>Green</td>
<td>&gt;250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 11.53 (12.36)</td>
<td>CN/1/SCN: 44.51 (45.18)</td>
<td>C: 36.98 (37.35)</td>
</tr>
<tr>
<td>[en\textsubscript{H}][Cu(NCS)\textsubscript{4}•.phen]</td>
<td>Green</td>
<td>&gt;250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cu: 11.88 (11.81)</td>
<td>CN/1/SCN: 42.60 (43.18)</td>
<td>C: 40.98 (40.16)</td>
</tr>
</tbody>
</table>

### References