Mössbauer, EPR, magnetic properties and thermally induced stereochemical studies on some double complex salts of cyclic ligand containing cationic copper(II) complexes and hexacyanoferrate(III) anion in the solid state

Parimal Kundu\textsuperscript{a}, Subrata Kumar De\textsuperscript{b}, Chirantan Roy Choudhury\textsuperscript{b}, Dilip Banerjee\textsuperscript{c}, Sanjoy Kumar\textsuperscript{c},
Ranga Lal Bhattacharya \& Samiran Mitra\textsuperscript{a,b}

\textsuperscript{a}Department of Chemistry, Ramanada College, Bishnupur, Bankura, India
\textsuperscript{b}Department of Chemistry, Jadavpur University, Kolkata 700 032, India,
E-mail: smitra_2002@yahoo.com; Fax No.: 91-33-2414-6266
\textsuperscript{c}Department of Physics, Calcutta University, Kolkata 700 032, India

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Novel cyanide-bridged double complex salts of cationic copper(II) salts with cyclic ligand, viz., morpholine (Morph), N-methyl morpholine (Me-Morph) and homopiperazine (Hpz) and hexacyanoferrate(II) ion have been synthesized and characterized. Mössbauer spectra of the complexes have been recorded at 80 K and 300 K to investigate the metal-metal charge transfer and the impact of cyclic ligand present in the cationic part of the double complex salt on the Mössbauer spectra of hexacyanoferrate(III) ion. Metal-metal charge transfer transition has been supported by electronic spectra and magnetic susceptibility values. Variable temperature EPR spectra have been recorded to study the distortion of crystal systems. Activation energy and inception temperature for the thermochemical reactions show that the order of stability of the double complex salts follows the trend, Hpz>Me-Morph>Morph.

Studies on double complex salts and cyanide-bridged complexes containing cationic M(II/III) complexes and hexacyanoferrate(III/II) ion are of particular interest for the electron transfer phenomena in the solid state. Unfortunately, no well-characterized complex has been reported except for those containing cationic Ru\textsuperscript{III} and Mn\textsuperscript{II} complexes as counterpart or counterion. Further studies are needed for advanced elucidation of electron transfer reactions of metal complexes in the solid state. Uehara \textit{et al.}\textsuperscript{3} have studied thermal and electronic properties of double complex salts and cyanide bridged complexes containing cationic copper(II) complexes having acyclic diamine ligand and hexacyanoferrate(II) ion. They have reported that the charge transfer from Fe\textsuperscript{II} to Cu\textsuperscript{II} and stability of the [Cu(L\textsubscript{2})\textsuperscript{2+} moieties decreases due to the influence of [Fe(CN)\textsubscript{6}]\textsuperscript{3-} ion. The aim of the present work is to synthesize some double complex salts and cyanide-bridged complexes containing cationic Cu\textsuperscript{II} complexes having cyclic ligand and hexacyanoferrate(III) ion in order to study the charge transfer phenomena and the influence of [Fe(CN)\textsubscript{6}]\textsuperscript{3-} on the stability of Cu\textsuperscript{II} complexes containing cyclic ligand.

The structure and Mössbauer spectral studies on Prussian blue type complexes have been reported\textsuperscript{4}. But Mössbauer study on the double complex salt having copper(II) cation containing cyclic ligand and hexacyanoferrate(III) ion has not been reported. So another purpose of the present work is to study the Mössbauer spectra and interpret the difference in spectral parameters from that of Cu\textsubscript{2}[Fe(CN)\textsubscript{6}]\textsubscript{3} due to the presence of cyclic ligand in cationic copper(II) unit. Attempts have also been made to draw some conclusion about the crystal system due to insertion of cyclic ligand in the cationic part of the complexes.
from the temperature dependence EPR spectra. Variable temperature magnetic moment has been recorded to show the absence of metal-metal interaction.

Though thermally induced stereochemical changes of cyclic ligand complexes in the solid state have been reported, it has not been reported for the double complex salts. The present paper also reports the stereochemical changes during thermal investigation. Kinetics and thermodynamic parameters for the dehydration and decomposition reactions in solid state have also been calculated. The order of stability of the complexes with respect to methyl group substitution and ring expansion in the cyclic ligand has been discussed.

Materials and Methods

Metal salts were of AR grade and used as received. Morpholine (S.D. Fine Chemicals, Kolkata), N-methylmorpholine (Spectrochem, Mumbai) and homopiperazine (Fluka, Switzerland) were used as received.

C, H, and N were estimated on a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analyses (TGA and DTA) were carried out on a Shimadzu DT-50 thermal analyzer under a dynamic nitrogen atmosphere with a heating rate of 10°C min⁻¹ and α-alumina as a standard. Infrared spectra were recorded using Perkin-Elmer 595 spectrometer in KBr as a medium. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG&G PAR 155 vibrating sample magnetometer at room temperature. Variable temperature magnetic measurements were carried out with a Faraday type magnetometer (Manics DSM8) equipped with an Oxford helium continuous-flow cryostat working in the range 4.2-300K and a Drusch EAF 16UE electromagnet. Electronic spectra were recorded in solid state using Hitachi U-3400 (UV-vis.) electronic spectrophotometer. EPR spectra were recorded at 4K, 77K and 298K with a Bruker-190 spectrometer equipped with a continuous flow cryostat. Iron-57 Mössbauer spectra were obtained using CMTE constant-acceleration drive (model-250) with approximately 5 mci ⁵⁷Co in Pd as source. The transmission spectra were obtained using ECIL krypton-methane filled proportional counter and associated components to limit detection to only 14.37 KeV γ ray. The transmitted radiation was registered in a 4K PCA card in multiscaler (MCS) mode. The spectra were recorded at 300K and 80K.

Results and Discussion

Analytical data, colour and magnetic moment values of the double complex salts 1, 2 and 3 are given in Table 1. All the double complex salts have lattice water molecules, which are confirmed by IR spectral bands observed at around 3400 cm⁻¹ [v(OH)] and 1650 cm⁻¹ [δ(HOH)]. On heating, these compounds lose the water molecules. Mass loss in TGA curves confirm the presence of three molecules of water in 1, four molecules of water in 2 and seven molecules of water in 3 (Fig. 1). In these compounds the cyclic ligands function as a chelate and exist in the boat form as shown by the appearance of more IR

Table I—Analytical data (calculated values in parentheses) for the double complex salts

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Colour</th>
<th>Analysis (%)</th>
<th>μ_eff (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>[CuL₂²⁺][L₂²CuCNFe(CN)₅]₂·3H₂O</td>
<td>Maroon</td>
<td>36.2</td>
<td>21.3</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td>(36.3)</td>
<td>(21.2)</td>
</tr>
<tr>
<td>[CuL₂²⁺][L₂²CuCNFe(CN)₅]₂·4H₂O</td>
<td>Maroon</td>
<td>38.6</td>
<td>19.5</td>
</tr>
<tr>
<td>(2)</td>
<td></td>
<td>(39.0)</td>
<td>(19.5)</td>
</tr>
<tr>
<td>[CuL₂²⁺][L₂²CuCNFe(CN)₅]₂·7H₂O</td>
<td>Purple</td>
<td>37.2</td>
<td>25.0</td>
</tr>
<tr>
<td>(3)</td>
<td></td>
<td>(37.6)</td>
<td>(25.1)</td>
</tr>
</tbody>
</table>
bands between 700-1400 cm\(^{-1}\) than for the free ligand which exists in the chair form. The bands at 2090 for 1, 2095 for 2 and 2085 cm\(^{-1}\) for 3 are assigned to the bridging cyanide stretching while the other bands at 2040 for 1, 2065 for 2 and 2060 cm\(^{-1}\) for 3 are assigned to the terminal cyanide stretching mode\(^9,10\).

In the present complexes, IR spectral bands for v(CN) appeared at lower frequency region than for v(CN) of \(K_3[Fe(CN)_6]\), which indicates that the charge on \(Fe^{III}\) reduces to some extent in compound 1, 2 and 3, i.e., charge transfer phenomena is occurring in the compounds. This fact is supported by electronic and Mössbauer spectra and magnetic moment values.

Electronic spectra of all the double complex salts were recorded in the solid state. An extra band (shoulder) is observed at 1040 nm, 1045 nm and 1063 nm for (1), (2) and (3) respectively which was not observed in the spectra of the individual complex species of the double complex salts indicating the occurrence of charge transfer from metal to metal\(^3\).

Mössbauer spectra of the compounds were recorded and the isomer shift (\(\delta\)) and quadrupole splitting (\(\Delta\)) values (Table 2) were determined by computer curve fit program\(^11\). For the double complex salts (1), (2) and (3), the values of \(\delta\) (mm sec\(^{-1}\)) are close to zero and quadrupole splittings (\(\Delta\)) are zero. So instead of obtaining the characteristic quadrupole splitting and isomer shift for hexacyanoferrate(III), the spectra indicates hexacyanoferrate(II) with no detectable hexacyanoferrate(III) at room temperature. The line width at half height (\(\Gamma/2\)) of all the three samples were appreciably large. Mössbauer spectra of the compounds at 80 K contained one quadrupole doublet and one singlet (Table 3). The small quadrupole splitting of the doublet indicates the presence of hexacyanoferrate(III) and the singlet corresponds to hexacyanoferrate(II). So in this compound, a certain percentage of hexacyanoferrate(III) is present which is not observed at room temperature. From this we conclude that charge transfer is taking place in this compound. The lowering of \(\Gamma/2\) value with the lowering of temperature for hexacyanoferrate(II) indicates the lowering of distortion of the system with the lowering of temperature\(^12\). With lowering of temperature, absorption percentage increases which indicates the presence of polymeric lattice. The Mössbauer spectral parameters of the double complex salts (1), (2) and (3) are different from that of \([Cu_3[Fe(CN)]_6]\). \(Cu_3[Fe(CN)]_6\) has some definite quadrupole splitting.

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**Table 2—Mössbauer parameters\(^a\) for double complex salts**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Isomer shift(^b, c) (mm sec(^{-1}))</th>
<th>Quadrupole splitting (mm sec(^{-1}))</th>
<th>(\Gamma/2)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>+0.01680</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>2</td>
<td>+0.01500</td>
<td>0</td>
<td>0.35</td>
</tr>
<tr>
<td>3</td>
<td>+0.0003</td>
<td>0</td>
<td>0.45</td>
</tr>
<tr>
<td>(Cu_3[Fe(CN)]_6)</td>
<td>-0.1800</td>
<td>0.400</td>
<td>-</td>
</tr>
<tr>
<td>(K_3[Fe(CN)]_6)</td>
<td>+0.0400</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>(K_3[Fe(CN)]_6)</td>
<td>-0.1240</td>
<td>0.280</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Unless otherwise stated experimental temp. is 300K.

\(^b\) Relative to \(\alpha\)-iron,

\(^c\) Velocity scale is calibrated by Co\(^{57}\) Pd source and \(\alpha\)-Fe and \(\alpha\)-Fe\(_2\)O\(_3\) absorbers.

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**Table 3—Mössbauer parameters for double complex salts at 80K**

<table>
<thead>
<tr>
<th>Comp.</th>
<th>For the singlet</th>
<th>For the quadrupole doublet</th>
</tr>
</thead>
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<tr>
<td></td>
<td>I.S.(^b)</td>
<td>Q.S.</td>
</tr>
<tr>
<td>1</td>
<td>0.0018</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.0016</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.0021</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^b\) Relative to \(\alpha\)-iron,

\(^c\) Velocity scale is calibrated by Co\(^{57}\) Pd source and \(\alpha\)-Fe and \(\alpha\)-Fe\(_2\)O\(_3\) absorbers.

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The line width at half height (\(\Gamma/2\)) of all the three samples were appreciably large. Mössbauer spectra of the compounds at 80 K contained one quadrupole doublet and one singlet (Table 3). The small quadrupole splitting of the doublet indicates the presence of hexacyanoferrate(III) and the singlet corresponds to hexacyanoferrate(II). So in this compound, a certain percentage of hexacyanoferrate(III) is present which is not observed at room temperature. From this we conclude that charge transfer is taking place in this compound. The lowering of \(\Gamma/2\) value with the lowering of temperature for hexacyanoferrate(II) indicates the lowering of distortion of the system with the lowering of temperature\(^12\). With lowering of temperature, absorption percentage increases which indicates the presence of polymeric lattice. The Mössbauer spectral parameters of the double complex salts (1), (2) and (3) are different from that of \([Cu_3[Fe(CN)]_6]\). \(Cu_3[Fe(CN)]_6\) has some definite quadrupole splitting.
and isomer shift values (Table 3). So this difference arises due to the cyclic ligand attached with Cu(II) ion. The magnetic moment values of the compound (1), (2) and (3) at room temperature are much lower than the expected values. Variable temperature magnetic moment values of the compound (1), (2) and (3) are almost constant indicating that no antiferromagnetic coupling is present in these compounds. From the above discussions we conclude that the charge transfer is taking place in all the compounds and the direction is L → CuII → FeIII. This is further supported by the higher thermal stability of the cationic Cu(II) cyclic ligand complexes in the double complex salts as compared to that of the [CuL2]X2 complexes6-8. The variable temperature EPR spectrum of 1 in solid state shows that with the lowering of temperature, the difference in EPR spectral bands at the Cu2+ center gradually decreases (Fig. 2). It has been reported that Prussian blue analogues have face-centered cubic symmetry13. We, therefore tentatively conclude from EPR spectra that some distortion appears in the crystal system due to the insertion of ligand in the Cu(II) ion, which gradually decreases with lowering of temperature. This is also observed in the Mössbauer spectra.

On heating, all the compounds undergo decomposition followed by dehydration and show mass loss in TGA curves and endothermic peaks in DTA curves (Fig. 1). For the decomposition process, mass loss in the TGA curve corresponds to three molecules of cyclic ligand for the compounds (2) and (3) and two molecules of cyclic ligand for the compound (1). Keeping the rate of heating at about 1°C at the maximum decomposition temperature the intermediate product in each case was isolated and characterized. From IR spectra, it has been observed that the cyclic ligand in the intermediate complexes exists in the chair form (the number of IR active bands between 700-1400 cm⁻¹ is less than if it had existed in the boat form)6-8. Activation energy Ea and order of reaction for the dehydration and decomposition processes have been evaluated from the TGA curves. Data show that thermal decomposition occurs at the copper center only without disturbing the hexacyanoferrate(III) ion as IR spectra showed v(CN) band after decomposition. From Table 3 we observed that decomposition of the double complex salts starts at a temperature higher than that of Cu(II) complexes of the same ligand. This is due to the presence of hexacyanoferrate(III) ion, which is explained earlier in the paper.

Among the compounds (1) and (2), compound (2) is more stable (with respect to Ea and inception temperature) than (1). This is due to more influence of inductive effect than the steric factor14. If we compare the stability of the three compounds, the trend is Hpz>Morph>Morph. The extra stability of homopiperazine is due to the increase of cyclic ring by introducing one CH₂ group between the amine functions, which reduces the strain in the chelate ring15.

Acknowledgement
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References