Preparation and Analysis of Copper(II) Acetate Amide Complexes

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EXPERIMENTAL

Copper(II) acetate monohydrate was obtained from Aldrich Chemical Co. and used without further purification. Formamide (FA), N-methylformamide (NMF), and N,N-dimethylformamide (DMF) were also supplied by Aldrich Chemical Co. Amides were stored over 3A molecular sieves and purified by the method described in reference 9. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected. Elemental analysis was carried out using a Carlo-Erba 1106 Elemental Analyser.

Preparation of copper(II) acetate FA dimer complex. A solution of copper acetate monohydrate dimer (2.0 g, 20 mmol) in FA (20.0 mL) was stirred vigorously for 6 h at room temperature under a nitrogen atmosphere. The precipitates were collected by filtration and washed with ether (20 mL). Cu₂(CH₃COO)₄ · 2FA was obtained in 88.7% yield (2.10 g) as a greenish blue powder. mp: 214–215°C. Anal. Calcd. for Cu₁₀H₁₄N₂O₁₉Cu₂: C, 26.55; H, 3.98; N, 6.19. Found: C, 26.35; H, 3.77; N, 6.11.

Preparation of copper(II) acetate NMF dimer complex. The complex was prepared by the same method as for the FA dimer. Cu₂(CH₃COO)₄ · 2NMF was obtained in 79.4% yield (1.91 g) as a greenish blue powder (a little darker than the FA dimer). mp: 249–250°C. Anal. Calcd. for Cu₁₀H₁₄N₂O₁₉Cu₂: C, 29.93; H, 4.57; N, 5.82. Found: C, 29.64;
H, 4.38; N, 5.98.

Instrumentals. Solid state diffuse reflectance visible spectra were recorded in the range 200-800 nm using an integrating sphere diffuse reflectance attachment on the P-E 550 spectrophotometer (barium sulphate reference) fitted with a Pye-unican SP 890 diffuse reflectance accessory. Magnetic measurements were carried out by the Gouy method on an apparatus obtained from JMC Equipment Division. Infrared spectra were recorded on a Perkin-Elmer 598 spectrophotometer.

RESULTS AND DISCUSSION

Solid Diffuse Reflectance Spectra. The solid diffuse reflectance spectra consist of three characteristic peaks which correspond to those of copper(II) acetate: the bands at 700, 375 and 300 nm. Table 1 shows the data obtained from the diffuse reflectance spectra. Yamada et al.\textsuperscript{10} stated that the band at 700 nm is due to the normal metal-ligand interaction, and the band at 300 nm is due to the coordinated acetate groups. Tsuchida and Yamada\textsuperscript{11} has assumed that the copper-to-copper linkage in the copper(II) dimer appears at 375 nm. These assignments have been confirmed further in their later work\textsuperscript{10} for the copper(II) propionate monohydrate. Bukowska-Strazyewska et al.\textsuperscript{12} reported that the band at 380 nm in tetrakis(μ-crotonate) bis(quinoline)dicopper(II) is due to the d-d transition, \((d_{xz}, d_{yz}) \rightarrow (d_{xy}^2, \Gamma)\). Therefore, the bands at 370 nm and 371 nm shown in Table 1 should be based on the copper-to-copper bond. This is different from that of a typical copper(II) compound which shows only two peaks: one in the visible region and the other in the UV region.\textsuperscript{2}

Infrared Spectra. The frequencies of the acetate groups are almost identical to the corresponding groups in the copper acetate hydrate. The notable shifted frequencies are: \(v_{\text{CN}} (3375, 3235 \text{ cm}^{-1})\); \(v_{\text{CH}} (2924 \text{ cm}^{-1})\); \(\rho_{\text{NH}_2} (1053 \text{ cm}^{-1})\); \(v_{\text{COO}} (355 \text{ cm}^{-1})\) for \(\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{FA}\) and \(v_{\text{CN}} (3353 \text{ cm}^{-1})\); \(v_{\text{CH}} (2911 \text{ cm}^{-1})\); \(\rho_{\text{NH}} (670 \text{ cm}^{-1})\); \(\rho_{\text{CN}} (366 \text{ cm}^{-1})\) for \(\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot \text{2NMF}\). The above assignments have been made on the basis of the published ones.\textsuperscript{24-15} If we assume that the Cu (II) interacts with the oxygen of the amide, the C-N distance of amide will shorten and consequently the amide frequencies will increase. On the other hand, if the Cu(II) interacts with the nitrogen of the amide, the free rotation of the pyramidal would exist about the C-N single bond,\textsuperscript{15} and then the C-N distance will be lengthened and the frequency will shift towards lower frequencies. The IR data show that the N-H and C-H stretching modes with the C-N twist mode are shifted to higher frequencies while the N-H and NH\textsubscript{2} rocking modes are shifted towards lower frequencies.

Magnetic Moment. Copper(II) acetate monohydrate with its subnormal magnetic moment is a dimeric molecule containing two copper ions. The effective magnetic moment, \(\mu_{\text{eff}}\), can be calculated by use of the formula: \textsuperscript{2}

\[
\mu_{\text{eff}} = 2.829(\chi_s T)^{1/2} \quad (1)
\]

where, \(\chi_s\) is the magnetic susceptibility per copper (II) ion corrected for the diamagnetic nonmetal part of the molecule. The values of diamagnetic susceptibility for corrections were obtained from Emsley et al.\textsuperscript{16} Unfortunately, the magnetic susceptibility of NMF could not be found in the literature. Therefore, the magnetic susceptibility of N-methylformamide was measured at room temperature and the value \((22.553 \times 10^{-6} \text{ cgs, emu})\) was obtained.

The values of \(\mu_{\text{eff}}\) obtained from the above

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Table 1. The data obtained from the reflectance spectra

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>(\nu) (cm(^{-1}))</th>
<th>E (kJ Mol(^{-1}))</th>
<th>(v_{\text{CN}})</th>
<th>(v_{\text{CH}})</th>
<th>(\rho_{\text{NH}_2})</th>
<th>(\rho_{\text{NH}})</th>
<th>(\rho_{\text{CN}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O})</td>
<td>694</td>
<td>369</td>
<td>292</td>
<td>694</td>
<td>370</td>
<td>292</td>
<td>690</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{OAc})_4 \cdot 2\text{FA})</td>
<td>14409</td>
<td>27100</td>
<td>34247</td>
<td>14409</td>
<td>27027</td>
<td>34247</td>
<td>14451</td>
</tr>
<tr>
<td>(\text{Cu}_2(\text{OAc})_4 \cdot 2\text{NMF})</td>
<td>171.5</td>
<td>322.5</td>
<td>480.5</td>
<td>171.5</td>
<td>321.6</td>
<td>407.5</td>
<td>172.0</td>
</tr>
</tbody>
</table>

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formula (Eq. 1) are given in Table 2. As shown in Table 2, they are not significantly different from the corresponding values, \( \mu_{\text{eff}} \) of Cu(II) 1.8-2.1 B.M\(^2\), in the copper(II) acetate dimer. However, the values of the two products are lower than that of the copper acetate dihydrate. The magnetic interaction is affected by the nature of the attached ligand. The bulky ligands of the amides can supply less electron density to the central copper ions. Therefore, the values shown in Table 2 are fairly reasonable on this assumption. The value for Cu\(_2\)(CH\(_3\)COO)\(_4\) \cdot 2H\(_2\)O is in excellent agreement with that of Jotham and Kettle.\(^\text{17}\)

The results suggest that the copper(II) acetate amides have been obtained and their structures seem to be dimeric. The solid diffuse reflectance spectra give strong evidence for the dimeric structures. In the copper(II) acetate amides, three bands based on copper-to-copper bond have been observed whereas typical Cu(II) compounds show only two peaks. The results of vibrational studies also give the evidence that the copper(II) acetate amide complexes are oxygen-bonded. In other words, both amides are coordinated via their oxygen atom to the copper(II) ion. The magnetic susceptibility of N-methylformamide at room temperature is 22.553 \times 10^{-6} \text{ cgs, emu}.

However, we were unable to synthesize the copper acetate DMF dimer by using the same method as for FA and NMF complexes.

### Table 2. Magnetic properties of copper(II) compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \chi \times 10^{-6} )</th>
<th>( \chi \times 10^{-6} )</th>
<th>( \mu_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)(OAC)(_4) 2H(_2)O</td>
<td>4.066</td>
<td>1790.3</td>
<td>2.065, 2.04*</td>
</tr>
<tr>
<td>Cu(_2)(OAC)(_4) 2FA</td>
<td>2.790</td>
<td>1448.5</td>
<td>1.858</td>
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<tr>
<td>Cu(_2)(OAC)(_4) 2NMF</td>
<td>2.942</td>
<td>1602.3</td>
<td>1.954</td>
</tr>
</tbody>
</table>

*Data from Ref. 7

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## REFERENCES

9. Solodovnikov, V. V.; Selemeleva, Z. I.; Streltsova, C. I.; Kusin, V. V.; Smirnov, A. A. *Okrytiya Izobret.* 1985, 27, 89.