The Copper(II) Complexes of Two Alpha-omega Diamino Dicarboxylic Acids

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Synthesis and isolation of two unreported complexes of copper(II) and 2,5-diamino adipic and 2,6-diamino pimelic acids are described together with proposed structures and analytical data. Attempts to synthesize group VIII metal complexes using these two acids as ligands are mentioned; these were for the most part unsuccessful. The ratio of copper(II) to ligand is 1:1 with one molecule of water, and it is predicted that the structures involve two ligands acting as double bidentates and bridging two copper ions. The exceedingly low solubility of the compounds leads to the conclusion that they are non-ionic.

Experimental

Synthesis of 2,5-diamino adipic acid and 2,6-diamino pimelic acid

These prospective ligands were not immediately commercially available and were therefore synthesized according to the procedure of SHEEHAN and BOLHOFER for 2,5-diamino adipic acid. With this technique, dimethyl 2,5-diphthalimido adipate is first prepared from dimethyl-2,5-dibromo adipate and is then in turn converted to 2,5-diamino adipic acid by long refluxing with hydrobromic and glacial acetic acids. The yield in the final step was in excess of ninety per cent, and the melting point compares closely with that previously reported. The 2,6-diamino pimelic acid was prepared in a similar manner using starting materials with an additional methylene group. Infrared and ultraviolet spectra of both acids were prepared for later comparison with coordination compounds formed. Although this procedure was useful in the two cases stated above, all attempts to prepare alpha-omega diamino dicarboxylic acids containing more than seven carbon atoms were unsuccessful.

Synthesis of the Copper(II) complexes

The procedure used in preparing the copper(II) complexes of the two ligands was based on that of HAWKINS and PERRIN, who have reported a copper(II) complex of 2,7-diamino suberic acid. In the case of the 2,5-diamino adipic acid complex, 1.4 millimoles of the ligand and 0.9 millimoles of copper(II) sulfate pentahydrate were dissolved in ten milliliters of 1 N hydrochloric acid in a fifty milliliter beaker and heated to 95 °C. The colorless solution was then titrated with dilute ammonia to the neutralization point, and a blue crystalline precipitate formed rapidly. The crystals charred at 220 °C; yield was 81% of theoretical. The 2,6-diamino pimelic acid complex was prepared in a similar manner with similar results. These blue crystals also charred at 220 °C; the yield was 77 per cent.

Attempts were also made to prepare coordination compounds from the two acids and nickel (II), palladium (II), and platinum (II). Except in the case of platinum (II), results were negative, and the platinum (II) compound could not be isolated and hence characterized.

Analytical and Spectral Data

Elemental analyses for carbon and hydrogen are given in Table I for the two complexes:

Theoretical percentages are based on a stoichiometry of one metal cation to one ligand to one molecule of water. This, also, is in keeping with the report of HAWKINS and PERRIN. Infrared spectra were obtained by means of potassium bromide tablets because of the extreme insolubility of the complexes. These spectra, when compared with those obtained from the acids, showed strong suppression or elimination of absorption peaks in the area between 3.0 and 3.8 microns and at 4.7 microns. These areas correspond to stretch-

<table>
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<th>Cation</th>
<th>Ligand</th>
<th>Theoretical C [%]</th>
<th>H [%]</th>
<th>Analytical C [%]</th>
<th>H [%]</th>
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</thead>
<tbody>
<tr>
<td>copper (II)</td>
<td>2,5-diamino adipic</td>
<td>28.18</td>
<td>4.75</td>
<td>27.94</td>
<td>5.00</td>
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<td></td>
<td>acid</td>
<td>31.30</td>
<td>5.23</td>
<td>30.73</td>
<td>5.33</td>
</tr>
<tr>
<td>copper (II)</td>
<td>2,6-diamino pimelic</td>
<td>28.18</td>
<td>4.75</td>
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</tr>
</tbody>
</table>

Table I. Carbon-Hydrogen Analyses of Complexes.

1 J. SHEEHAN and W. BOLHOFER, J. Amer. chem. Soc. 72, 1786 (1950).
ing frequencies for O—H and N—H in the former case, and in N—H stretch in —NH₃⁺ in the latter. The absorption at 4.7 microns in the acids disappeared completely in the spectra of the complexes. From these data we conclude that both the amino nitrogen and the oxygen served as sites of attachment, and further that both amino groups and both carboxyl groups were involved in bonding typical of the alpha amino acids such as glycine. Attempts were made to obtain suitable ultraviolet spectra to aid in structural analysis, but no solvent was found which was capable of dissolving the complexes; these included water, 1 N hydrochloric acid, ethanol, diethyl ether, cyclohexane, benzene, and carbon tetrachloride. Thus, the potassium bromide tablets prepared for infrared use were unused in specially designed cell holders. Even though great care was taken in the preparation of the tablets, results useful in ligand field calculations could not be obtained.

**Physical Properties**

The extreme insolubility of the two complexes prevented any determination of molecular weight. This, however, together with the relatively low decomposition temperature, leads to the conclusion that both complexes are non-ionic, although the blue colors are characteristic of non-penetration complexes.

**Conclusions**

**Structure of the Complexes**

The one to one ratio of metal cation to ligand allows the possibilities of a molecule containing a single copper ion and a single ligand functioning as a tri- or tetradeicate, a species consisting of two copper ions bridged by two ligand molecules in which both ends of each ligand function as bidentates, or as a polymeric entity. Because it is sterically impossible for either molecule to occupy more than two square planar positions on a single cation, the first possibility must be ruled out. Using Hirschfelder models, it is possible to construct a reasonable molecule in which each of two ligands function as bridge units with the formation of a cyclic compound involving four five-membered rings involving copper(II) ions:

\[
\begin{align*}
\text{O} & \text{C—C—(CH₂)n—C—C=O} \\
\text{Cu} & \text{NH₂ H₂N} \\
\text{O} & \text{C—C—(CH₂)n—C—C=O}
\end{align*}
\]

This structure is similar to one proposed for the copper(II) complex with 2,7-diamino suberic acid by Hawkins and Perrin. Various polymeric forms are also possible, but in the absence of molecular weight data, these cannot be checked. However, the structure proposed above seems a reasonable one. The two compounds would then be named Di-μ-(2,5-diaminoadipato)-dicopper(II) hydrate and Di-μ-(2,6-diaminopimelato)-dicopper(II) hydrate. A structure such as that presented above could exist in a number of forms, such as cis-cis, trans,trans, etc.