

ON THE FORMATION AND THE STRUCTURE OF [(S)-(+)-ASPARTATO] COPPER(II)

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The formation of the [(S)-(+)-aspartato] copper(II) is described. The product was studied by IR and UV spectra, optical rotation, and electrophoresis. The structure of this complex is proposed.

α -Amino acids form with Cu^{2+} ions complexes of the $\text{Cu}(\text{AB})_2$ type (where AB means an anion of amino acid). The qualitative inequality of the donor atoms (N,O) causes such complexes exist as *cis* or *trans* isomers. The absorption spectra of aqueous solutions of these complexes show a broad maximum at about 620 nm, characteristic of *trans* arrangement¹. The kinetic lability of the Cu^{2+} ions in aqueous solution causes the complexes separate in solid phase in a thermodynamically advantageous form, *i.e.* *trans* configuration². However, a series of *cis* isomers exists, prepared also in solid phase²⁻⁶. Their existence is enabled by the fact that during the separation from solution stabilisation of the thermodynamically less advantageous *cis* configuration takes place. The basis of this stabilisation is polymerisation which takes place by apical coordination. Two amino-acid rings are in *cis* orientation and form a square pyramid in the inner coordination sphere around the Cu^{2+} ion, in the apex of which the oxygen atom of the carbonyl group of the neighbouring amino acid⁶ is coordinated. From the point of view of structure the complexes of aliphatic, or also aromatic, amino acids were mainly investigated²⁻⁷. Little information is available on the complexes of multidentate amino acids. For example the structure of copper(II) monoglutamate was studied by Das Sarma⁸, while Kirschner⁹ prepared copper(II) bis(aspartate) both with a planar and an octahedral arrangement of ligands. By this he proved the tridentate character of aspartic acid.

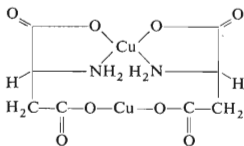
In this paper we describe another type of the aspartic acid complex the formation of which is caused by the tridentate character of this ligand. Recently¹⁰ we observed that the addition of Cu^{2+} ions to an aqueous solution of N-salicylidene(S)-(+)-aspartic acid causes its hydrolysis, leading to the isolation of copper(II) aspartate. This fact is probably a consequence of the stereospecific coordination of the tridentate (S)-(+)-aspartic acid in the ternary intermediate which is a complex with mixed ligands. During its hydrolysis all factors which decrease the stability of the complexes with mixed ligands exert their role. This is in agreement with the mechanism of the formation of complexes of Schiff's bases^{11,12} according to which the role of metal ions consists in the stabilisation of an easily hydrolysable mixed complex:



where Cu(Sal)(Asp) is the ternary intermediate formed on condensation of aspartic acid and salicylaldehyde in the presence of Cu^{2+} ions, and CuSalAsp is the corresponding complex of Schiff's base.

As was mentioned above the result of the attempt at the synthesis of copper(II) N-salicylideneaquo(S)-(+)-aspartate was the isolation of light blue needle-like crystals the elemental composition of which corresponded to copper(II) monoaspartate, *i.e.* to a structure with a coordinated β -carboxyl. The substance was insoluble in water. It dissolves only in solvents with strong donor properties, which makes it impossible to determine its molecular weight. The electrophoresis of the isolated compound dissolved in ammonia disclosed two substances containing copper, moving towards cathode on one hand and towards anode on the other. The first was identified by means of a standard as $[\text{Cu}(\text{NH}_3)_4]^{2+}$, while the second shows by its mobility that it contains a dissociated carboxyl group. This fact leads to the formulation of the isolated copper(II) aspartate as $\text{Cu}[\text{Cu}(\text{Asp})_2]$. Similar behaviour is also displayed by copper(II) aspartate during electrophoresis in a pyridine buffer.

The infrared spectrum shows maxima at 1620 and 1405 cm^{-1} due both to anti-symmetric and symmetric stretching vibrations of the carboxyl group¹³. As these are the sole maxima in this region, they prove thus the participation of both carboxyls in the bond to copper(II). Maxima at 3240 and 3150 cm^{-1} (a dehydrated sample) correspond to the NH_2 group vibration⁵, while the maximum at 2920 cm^{-1} is due to the C—H (ref.¹⁴) vibration. The maximum at 3400 cm^{-1} found in the hydrate must be due to the OH group vibration¹³. The electronic absorption spectrum contains only one broad band with λ_{max} 630 nm (in 5% ammonia) in the $d-d$ transition region, which corresponds to the spectra of copper(II) complexes of amino acids with CuN_2O_2 chromophore, and proves thus that both copper atoms exist under identical conditions. The isolated copper(II) aspartate is optically active in consequence of the vicinal effect ($[M]_{578} = +364^\circ$; $[M]_{546} = +495^\circ$; $[M]_{436} = +480^\circ$, measured in 50% pyridine), which proves that during the hydrolysis of the ternary intermediate racemisation of (S)-(+)-aspartic acid did not take place. On the basis of the mentioned facts the following structure may be proposed for the copper(II) aspartate isolated:



Hence, the complex has a *cis* configuration which is the result of the polymerisation ($2 \text{CuAsp} \rightarrow \text{Cu}_2\text{Asp}_2$) of another type than that given in the literature⁶. The complex

of an identical stoichiometric composition was prepared by Lifschitz and Schontenden¹⁵, but its structure was not investigated.

The fact that the complex easily loses all water when heated *in vacuo* at 100°C and 2 Torr also supports the proposed structure; the dehydration leads to an amorphous product (in contrast to the structure proposed by Das Sarma for the dimer of copper(II) glutamate⁸). On standing in air the dehydrated substance absorbs two molecules of water, while in an atmosphere of ammonia it takes 4 molecules of ammonia. The ammoniacate thus formed behaves in the above described manner during electrophoresis.

We also tried to prepare the described substances in a different manner. On reaction of basic copper(II) carbonate with (S)-(+)-aspartic acid a substance separates from concentrated aqueous solution which has an analogous elemental composition and physical properties.

EXPERIMENTAL

Chemicals and Apparatus Used

All the chemicals used were from Lachema. Optical rotation of (S)-(+)-aspartic acid: $[\alpha]_D +23^\circ$ (5M-HCl). The electronic absorption spectra were measured on an Optica-Milano apparatus, the infrared spectra, using KBr technique, on a Perkin-Elmer spectrophotometer. For the measurement of optical rotation a polarimeter Opton was used. Electrophoresis was carried out with a Tatrachema (Kuklov, Czechoslovakia) apparatus on Whatman No 4 paper. As electrolyte buffers $\text{NH}_4\text{Cl}-\text{NH}_3$ of pH 10 and sodium acetate in aqueous pyridine of the same pH value were employed. Potential difference 15 V/cm.

Preparation of Complexes

I. Copper(II) aspartate was isolated from a solution prepared by mixing 1.22 g (0.01 mol) of salicylaldehyde, 1.33 g (0.01 mol) of (S)-(+)-aspartic acid, and 1.99 g (0.01 mol) of copper(II) acetate dihydrate. An exact procedure is described in the literature¹⁰. For $\text{C}_4\text{H}_5\text{NO}_4\text{Cu}\cdot 3\text{H}_2\text{O}$ (248.7) calculated: 19.31% C, 4.46% H, 5.63% N; found: 19.06% C, 4.57% H, 5.38% N.

II. To a hot solution containing 1.33 g (0.01 mol) of (S)-(+)-aspartic acid a slight excess of $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ was added gradually and the mixture was heated until the evolution of CO_2 ceased. While the solution was still hot the unreacted carbonate was filtered off and the filtrate was allowed to crystallise. Needles of copper(II) aspartate crystallised out which were filtered off, washed with hot water and dried in air. For $\text{C}_4\text{H}_5\text{NO}_4\text{Cu}\cdot 4\text{H}_2\text{O}$ (266.6) calculated: 18.02% C, 4.91% H, 5.25% N; found: 18.10% C, 4.67% H, 5.18% N.

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