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# The Structure of the Copper(II) Complexes of Lysine $[Cu(lys)_2][HgI_3]_2$

AVI BINO and NAVA COHEN

*Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*

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The preparation and analysis of the compound $[Cu(L\text{-lysine})_2](HgI_3)_2$ were reported by Taurins in 1950 [1]. He pointed out that the same material, having the same composition and properties, was obtained when either DL-lysine or L-lysine were employed in the synthesis.

Later, the results of infra-red, electronic, electron spin resonance and X-ray spectroscopy were reported for this system [2]. Since the X-ray powder diffraction patterns and the IR spectra of the compounds prepared from DL- and L-lysine were found to be identical it was suggested that a spontaneous resolution occurs in the crystallization of the racemic compound [2]. Recently, the results of capillary gas chromatography and mass spectral analysis were reported for the two compounds [3]. The conclusion of this study [3] was that the structures of the salts formed from DL-lysine and L-lysine are so similar that conventional spectroscopic techniques cannot distinguish between the racemic and optically pure complex. In order to untangle this knotty problem which arose many years ago and to get a definite answer to the question whether spontaneous resolution or similarity of the two isomers was responsible for the experimental results [1–3], a detailed single-crystal X-ray structural analysis of this system was performed in our laboratory. The results prove that the two products are not identical. The two compounds, containing the racemic and the optically active complex of cupric lysine, precipitated by a solution of $K_2HgI_4$ are isomorphous, having almost identical unit cell dimensions but different space groups. There are two polymorphs of the L-lysine complex which differ by one water molecule of crystallization but have very similar cell parameters and belong to the same space group. The 2+ charge of the cationic cupric lysine complex in all three compounds is balanced by the dimeric $[Hg_2I_6]^{2-}$ unit rather than by two $HgI_3^-$ ions.

The following compounds were prepared and characterized: $[Cu(D\text{-lysine})(L\text{-lysine})][Hg_2I_6]$ (**1**), $[Cu(L\text{-lysine})_2][Hg_2I_6]$ (**2**) and $[Cu(L\text{-lysine})_2][Hg_2I_6]\cdot H_2O$ (**3**).

## Experimental

Single crystals of **1** were obtained by recrystallization of the crude compound from water [1]. Recrystallization of the optically active compound from water yielded crystals of **2** and **3** in an approximate 4:1 ratio respectively. Crystals of **3** lose water molecules of crystallization upon drying and decompose while crystals of **2** are very stable when exposed to the atmosphere at room temperature. Some crystallographic data are presented in Table I.

## Results and Discussion

From Table I it can be seen that all three compounds are nearly isomorphous. The relative positions of the heavy atoms in **1**–**3** are practically identical and the copper atom in all three structures is coordinated to two lysine ligands in the zwitterionic form with a square planar geometry. There is a weak axial interaction with a bridging iodine atom of the $[Hg_2I_6]^{2-}$ unit on both sides of the $CuN_2O_2$ plane with Cu···I distances of about 3.36 Å. The structure and dimensions of the $[Cu(D\text{-lysine})(L\text{-lysine})]^{2+}$

TABLE I. Crystallographic Data for 1–3

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| Formula | $C_{12}H_{28}CuHg_2I_6N_4O_4$ | $C_{12}H_{28}CuHg_2I_6N_4O_4$ | $C_{12}H_{28}CuHg_2I_6N_4O_4\cdot H_2O$ |
| Space group | $C2/c$ | $C2$ | $C2$ |
| $a$ (A) | 21.863(2) | 22.099(2) | 22.630(2) |
| $b$ (A) | 9.958(1) | 9.897(1) | 10.056(1) |
| $c$ (A) | 15.402(2) | 15.648(2) | 16.125(2) |
| $\beta$ (°) | 110.60(3) | 111.82(2) | 111.74(3) |
| $V$ ($A^3$) | 3139(1) | 3177(1) | 3409(1) |
| $Z$ | 4 | 4 | 4 |
| Data with $F_o^2 > 3\sigma(F_o^2)$ | 1460 | 1511 | 1648 |
| $R$ | 0.060 | 0.051 | 0.069 |

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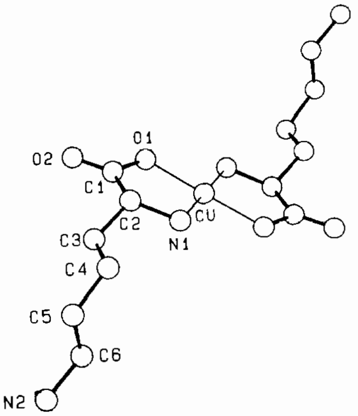

Fig. 1. The structure of [Cu(D-lysine)(L-lysine)]$^{2+}$ as found in **1**.

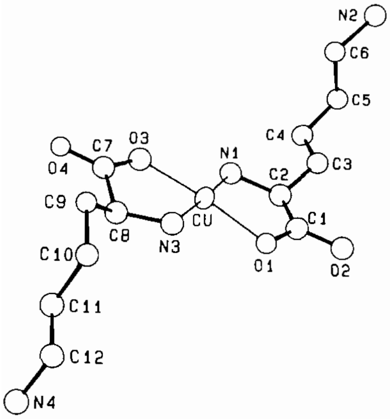

Fig. 2. The structure of [Cu(L-lysine)$_2$]$^{2+}$ as found in **2**.

unit in **1** are very similar to those found in the chloride salt of this complex [4]. In both structures the copper atom resides on a crystallographic center of symmetry. In **2** and **3** there is no crystallographic symmetry imposed upon the optically active complex.

The coordination spheres of the copper atoms in **1**–**3** are similar, with average Cu–O and Cu–N distances of 1.92(1), 1.99(2) Å; 1.96(2), 1.99(4) Å and 1.94(2), 1.99(4) Å respectively.

The structures of the copper lysine complexes in **1** and **2** are presented in Figs. 1 and 2. The structure and dimensions of the [$Hg_2I_6$]$^{2-}$ units in **1** and **3** are identical with those previously reported [5].

The results presented here explain the reason for the close resemblance of the X-ray powder diffraction patterns of the DL and the L isomers of the [$Hg_2I_6$]$^{2-}$ salts. These patterns are dominated by diffraction caused by the heavy atoms which have very similar relative positions in the isomorphous cells. The different positioning of some of the lighter elements in the compounds, such as carbon or oxygen atoms is apparently too small to be noticed.

It is noteworthy that all the other experimental techniques used for solving this problem, had failed to come up with a clear answer and that only single-crystal X-ray crystallography is a reliable tool for solving intricate problems of this nature.

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