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The Spontaneous Resolution of a Copper(II) α-Amino Acid Complex: $[Cu(II)(H_3N{\cdot}C_5H_{10}{\cdot}CH{\cdot}NH_2{\cdot}COO)_2][HgI_3]_2$

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Spontaneous resolution [1] remains a subject of fascination to the chemist interested in optical activity. In cases where 'entrainment' [2] is possible it may provide a convenient and economic method of separating enantiomorphs. Although the copper complex of L-asparagine has been used [3] to resolve other α-amino acids we know of no copper(II) α-amino acid complexes which spontaneously resolves. In this communication we wish to report that the cationic copper(II) complex with lysine, precipitated by mercury(II) triiodide first described by Taurins [4], spontaneously resolves.

The quantitative precipitation of $[Cu(II)(H_3N{\cdot}C_2H_5{\cdot}CH{\cdot}NH_2{\cdot}COO)_2)$ by $[HgI_3]$ as previously described [4] was shown to occur. Micro analysis (C, H, N and Cu) confirmed the above formulation; infra-red, electronic and electron spin resonance spectra were consistent with 'glycine like' co-ordination at copper(II), as suggested by Taurins [4].

Under the conditions previously described we have carefully investigated the phases precipitating with both L and DL-lysine. X-ray powder diffraction** (Fig. 1) shows the phases precipitating (under all conditions investigated by us at temperatures between 20 and 80 °C) with both L and DL-lysine to be strictly isomorphorus. Infra-red, electronic, and electron spin resonance spectra of all samples were also identical. There are two possible explanations for this, racemization (only the DL complex isolated) or spontaneous resolution (a mixture of the bis L and bis D-complexes isolated). Compared to other systems [5] racemization would have proceeded extremely rapidly; polarimetry of the complex prepared from L-lysine (in 2 *M* HCl) revealed the lysine to have remained optically active. Spontaneous resolution is hence the only possible explanation for these observations.

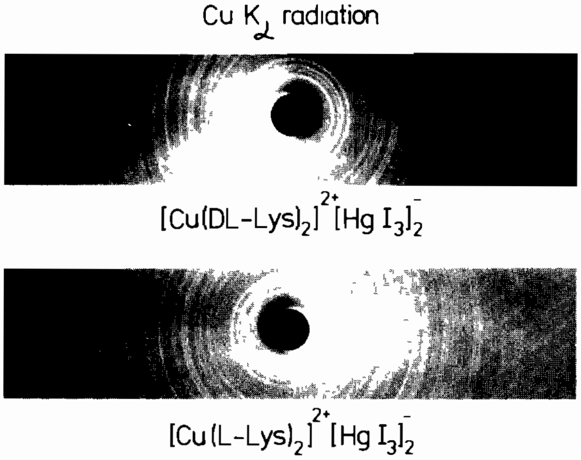

Fig. 1. X-ray powder diffraction.

From hot dilute solutions of DL or L-lysine and copper(II) good single crystals of $[Cu(H_3N{\cdot}C_2H_5{\cdot}CH{\cdot}NH_2{\cdot}COO)_2][HgI_3]_2$ could be precipitated with the $[HgI_3]^-$ reagent. Microscopic examination revealed no significant differences between the crystals precipitating from solutions of DL and L-lysine. We could detect no features on these needle shaped crystals to enable hand separation of the enantiomorphs. Attempts to entrain [2] the system and thus separate one hand of lysine have to date been unsuccessful; we suspect this is due to difficulty in controlling the rate of crystallization.

Work is in hand to discover the molecular nature of the stereoselectivity observed by X-ray crystallography, determine if the counter ion $[HgI_3]^-$ is crucial for the separation and to ultimately develop a novel method of resolving lysine.

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**A typical list of d spacing for a complex precipitating from a DL and an L solution have been deposited as a supplementary publication.

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