

## The Chiral Symmetry Breaking occurred in asymmetric metal complexes

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### 1. Presentation

The Chiral Symmetry Breaking is of current interest due to its contribution to investigations of the origin of the homochirality in the biosphere. In the context of a study on a distant origin of homochirality, we have focused on the generation of the chirality of the basal plane of square pyramidal tetradentate five coordinated metal complex, and its chiral alternations according to the trans interchanges of the fifth apical ligand to the opposite side ligand. The generated chirality of basal plane is named Planar-R and Planar-S in this stage as shown in Scheme 1. We report here the Chiral Symmetry Breaking of the planar chirality started by the polarized very weak irradiation.

### 2. Synthesis

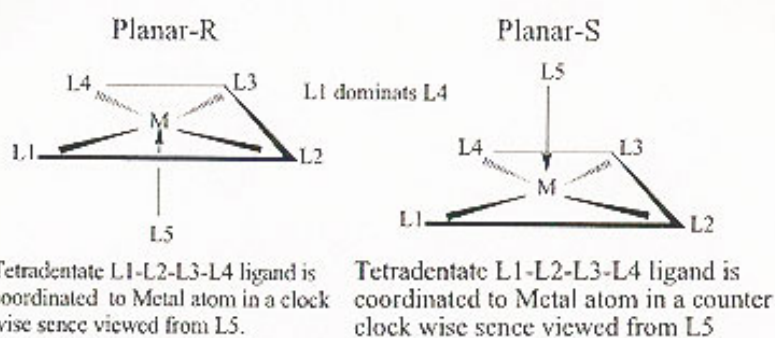
The tetradentate ligand was produced by the reaction of Histamine (L-Histidine) and 2, 6-pyridinedicarbonyl dichloride under the basic conditions as shown in scheme 2. Aqua[(6-carboxyl-2-pyridilamide)-histaminato]copper 1 and Aqua[(6-carboxyl-2-pyridilamide)-L-histidinato]copper 2 and their corresponding copper complexes were synthesized by the coupling reaction between the tetradentate ligand and copper sulfate under the acidic conditions. These complexes are square pyramidal tetradentate five coordinated copper (II) complexes, and each of them has asymmetric basal plane with respect to the fifth ligand of a water molecule occupying the apical position as shown in Scheme 3.

### 3. Results

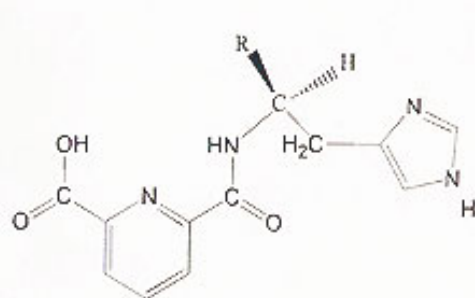
Though the tetradentate ligand derived from Histamine has no asymmetric atom, 1 gave significant large specific rotation value after a mutarotation as shown in Table 1. It was due to the copper complex formation and resulted in the rich distribution of either side of the planar-R or planar-S molecules in an aqueous solution. Besides, the mutarotation is repeatable in every time for detecting specific rotation values. These phenomena mean that the fifth apical water molecule is interchangeable to the opposite side ligand in the coordination sphere under symmetric conditions, and the start of the polarized irradiation makes the chance of Chiral Symmetry Breaking of planar chirality and resulted in giving the significant large specific rotation value after a mutarotation. It is very curious phenomenon even in the organic compounds to have the same minus specific rotation value -350 degree, -750 degree for 2 and 3. These phenomena are very natural for them, because the planar chirality of basal plane is independent to the equatorial asymmetric carbon. On the other hand, it is easily known that these specific rotation values were resulted from the Chiral Symmetry Breaking and following mutarotations of 2 and 3 in aqueous solutions as seen in case of 1. 5 gave very large specific rotation value (+2000degree) and no mutarotation. It was due to the steric hindrance (barrier) of OEt group on S-carbon, which prevented the fifth ligand from approaching to the central copper atom from the planar-S side. Consequently, the fifth ligand of 5 has the only one coordination mode from the planar-R side to approach to the copper atom, and results in no mutarotation. It was induced that 6 gave no specific rotation value as shown in Table 1. The fifth apical ligand molecule of 6 could not interchange to the opposite side ligand owing to the steric hindrance of OEt groups on both R- and S-carbons.

### 4. Conclusions

1. The fifth apical water molecule is interchangeable to the opposite side ligand molecule in aqueous solution.
2. The continuous one way irradiation of Polarimeter not like the alternate irradiations of CD apparatus is the origin of the generation of the planar chirality.
3. The Chiral Symmetry Breaking was started by the chance of the polarized very weak irradiation in a range of Polarimeter power.
4. The distribution between the planar-R and the planar-S molecules shifts toward the either side of them under the continuous polarized irradiation.

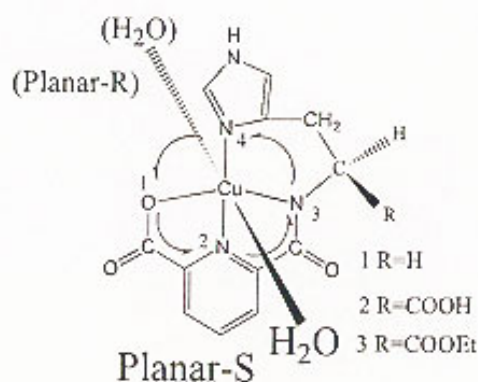


Scheme 1



The tetradentate ligand

Scheme 2



Scheme 3

Table 1 The specific rotation values

	pH 7	pH 2
Hist : 1	-1240 (after mutarotation)	0
L-COOH : 2	-350 (after mutarotation)	-41
D-COOH : 3	-750 (after mutarotation)	+41
DL-COOH : 4	-560 (after mutarotation)	0
L-COOEt : 5	+2000* (no mutarotation)	----
DL-COOEt : 6	0* (no mutarotation)	----
color of solution	blue	color less

HORIBA, SEPA-200  $[\alpha]_D^{20}$  c 0.220 H<sub>2</sub>O+MeOH solution, \* EtOH (trace H<sub>2</sub>O) solution