

Molecular Parity Violation of Copper Complexes

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Abstract: Aqua[(6-carboxyl-2-pyridilamide)histaminato]copper(II) **1** was synthesized for study of MPV (molecular parity violation). Crystal structure of **1** was defined by X-ray crystallographic analysis to give racemic structure consisting of **planar-R (pR)** and **planar-S (pS)** enantiomers. Each enantiomer was square pyramidal five coordinated copper complex with the fifth apical ligand of H₂O molecule. Specific rotation of the time development analysis of **1** gave mutarotation phenomenon from **pR** enantiomer priority side ($[\alpha]_D: +2,450^\circ$) to **pS** enantiomer priority state ($[\alpha]_D: -1,240^\circ$) in MeOH. Chiral irradiation energy of the detector from outside gave dynamic equilibrium between enantiomers, resulted to give **pS** enantiomer priority state with dissipative process. MPV of **1** was followed that the parity inversion of chiral restraint dz^2 orbital brought about inversion of chiral coordination sphere along z-axis for alternative replacement of the fifth apical ligand to solvent molecule on copper atom. SMPV (spontaneous molecular parity violation) of **1** was observed vice versa on transfiguration of specific rotation from the last **pS** enantiomer priority state ($[\alpha]_D: -1,240^\circ$) to **pR** enantiomer priority side ($[\alpha]_D: +2,450^\circ$) without chiral irradiation of optical detector, until reset analysis of the same sample. Therefore, the **pR** enantiomer priority state had existed in the lowest free energy of the ground state as visually unobservable SMPV state of **1** in the solvent.

Key words: MPV, SMPV, copper complex.

1. Introduction

There have been many discussions concerned with MPV (molecular parity violation) since Hund's Paradox [1] and "Question of Parity Conservation in Weak Interactions" by Lee, and Yang [2]. It was followed as a conception that hydrogen atom would have optical activity by the chiral WNC (weak neutral current) between an electron and a proton. Harris [3] presented the theory that Hund's Paradox was combined with quantum vibration to amplify MPVED (molecular parity violating energy difference) resulting in molecular chiral vibrational state appeared for some long time. In the context of parity violation of dz^2 orbital of copper atom in chiral restraint sphere, we have studied about MPV of copper complexes, because copper atom gives the square pyramidal five coordinated conformation with the fifth apical ligand replaced by solvent molecule alternatively [4]. The basal planar coordination of

asymmetric tetradentate ligand (1~4) to copper atom on x-y plane divides dz^2 orbital to give **pR** and **pS** axial vector electrons as shown in Fig. 1 (center). The dz^2 orbital of copper atom has even parity in the ground state, besides the dz^2 orbital has either even or odd parity under restraint sphere by apical ligand coordination in accordance with theorem of Schrödinger equation. Oxygen atom of solvent molecules such as H₂O, MeOH coordinates to copper atom using chiral divided dz^2 orbital to give chiral square pyramidal five coordinated tetradentate copper complex, as shown in Fig. 1. Therefore, chiral behavior of the fifth apical ligand (L5 in Fig. 1) of copper complex gives very important information in solvent. The continuous alternative replacement of the fifth apical ligand by solvent molecules on copper atom brought about visually observable MPV phenomena with dissipative process in time development optical rotational analysis. Visually unobservable SMPV phenomenon of copper complex was revealed existing against the optical rotational energy behind the optical analysis as shown in Fig. 1.

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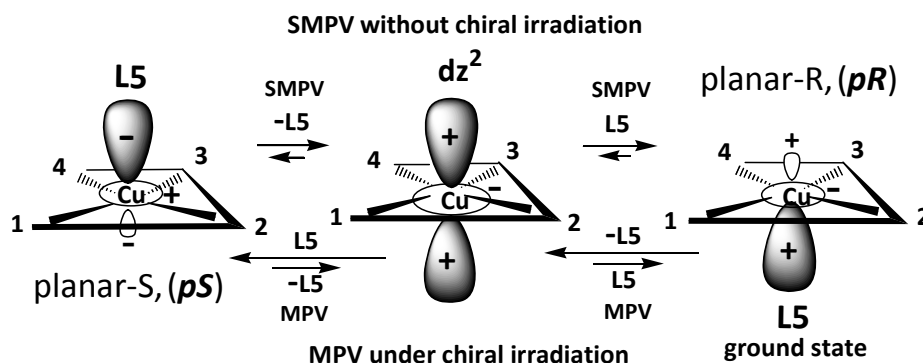
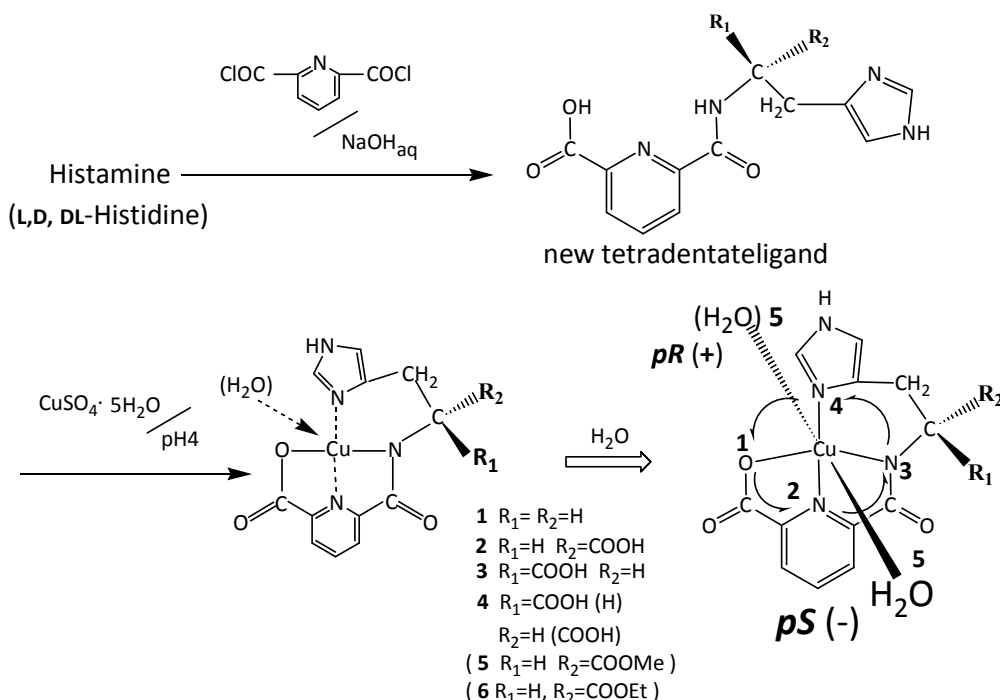


Fig. 1 MPV under chiral irradiation and visually unobservable SMPV. The planar tetradentate asymmetric ligand divides dz^2 orbital of copper atom to chiral pR and pS vector electron. The fifth ligand of L5 coordinates to copper atom with lability. It follows next replacement of solvent molecule using chiral vector electron to give pR enantiomer spontaneously as ground state, vice versa to give pS enantiomer priority under chiral irradiation in solvent.



Scheme 1 Synthetic methods of new tetradentate ligands and copper complexes [5].

2. Experimental Setup

The specific rotations were measured by HORIBA SEPA-200 (Na-lamp; 22.1 W).

3. Results and Discussions

Aqua[(6-carboxyl-2-pyridilamide)-histaminato]copper(II) **1** was synthesized from histamine as the starting material, as shown in scheme 1.

Crystal structure of **1** was defined by X-ray crystallographic analysis. **1** was consisting of racemic copper complex structure of pR and enantiomers as shown in left of Fig. 2 [6]. The asymmetric tetradentate ligand of basal plane of **1** gives pR or pS chirality depending on the coordination modes of the fifth apical ligand to central copper atom by the sequence rule of Cahn-Ingold-Prelog rule [7]. The clockwise sense of atom order of basal tetradentate

ligand seeing from the apical ligand gives *pR* chirality to copper complex. The counterclockwise sense of atom order of basal ligand gives *pS* chirality to copper complex as shown in Scheme 1 and Fig. 2. The fifth apical ligand H₂O was replaced by surrounding solvent molecules such as H₂O, MeOH, as shown in Scheme 1 and Figs. 1 and 2.

The methoxy substituted racemate of **1** had the same crystal structure [8] of **1**. Racemic copper complex **1** gave mutarotation phenomenon in optical rotational time development analysis in methanol as shown in Fig. 3. Assignment of specific rotational sign (+) was given to *pR* enantiomer by the steric resolution later. Plots of specific rotation from +2,000° to +2,450° at just start of detection owe to delay of mechanical response of the detector. The dotted line slope of specific rotation indicated *pR* enantiomer priority at the start of +2,450°, and decreased gradually to cross 0°, and resulted in showing -1,240° constantly as *pS* enantiomer priority state finally in time development analysis, as shown in Fig. 3.

It was revealed that there was time-dependent dynamic proportional equilibrium between *pR* and *pS* enantiomer with dissipative process under irradiation energy of the detector from outside of this system. It was followed that there was MPVED (molecular parity violating energy difference) exactly between *pR* and *pS* enantiomers of **1**. It indicated that the racemic state is not the lowest free energy state in the solution

system such as the fifth apical ligand replaced alternatively by solvent molecules under irradiation energy of detector.

For the analytical sample of **1** indicating $[\alpha]_D$: -1,240° under an equilibrium of *pS* enantiomer priority, the reset analysis, followed at a few minutes after, gave the same mutarotation phenomenon as shown in Fig. 4, and it was very repeatable in further more reset analysis. So that, the specific rotation of **1** returned from -1,240° to over 2,500° without any chiral irradiation.

Thus, SMPV phenomena were observed in spontaneous transfiguration of specific rotation from the latest equilibrium ($[\alpha]_D$: -1,240°) to starting point ($[\alpha]_D$: +2,000°) without chiral irradiation. It revealed that the SMPV had already existed to be *pR* enantiomer priority as the ground state in solution, unless the optical detection. It means that the internal energy deference between *pR* and *pS* enantiomers exists stringently in the ground state as SMPVED in solution system. Therefore, MPVED under the optical rotational irradiation of the detector was calculated to be 6.26×10^{-23} J/molecule/s, taking into account that the optical rotational energy was shared with all of both enantiomers through from the 5 mm caliber of the detection sell and 20 cm far from the Na-lump. It is notable that the MPVED is almost the same value of Boltzmann's constant 1.38×10^{-23} J/K. Therefore, SMPVED between *pR* and *pS* enantiomers was

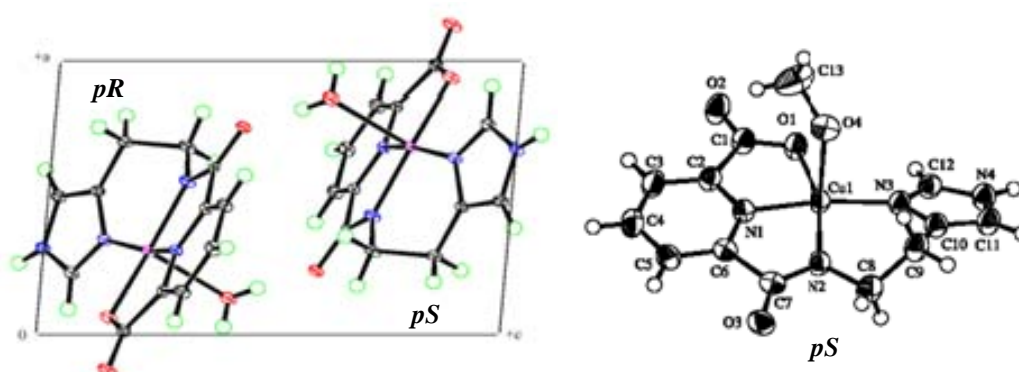


Fig. 2 Racemic crystal structure of **1** (space group Pi , left), and ORTEP drawing of methoxy substituted *pS* enantiomer at 50% probability (right) [8]. The single crystal was grown from MeOH to give **1** with the fifth apical ligand replaced by methoxy groups.

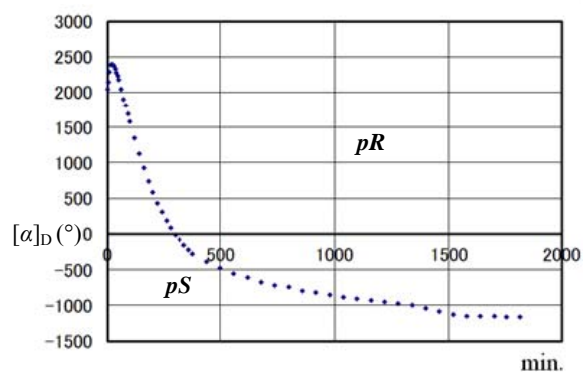


Fig. 3 MPV phenomenon with dissipative process. Specific rotations of time development analysis of **1** in MeOH (c 0.220, 20 °C).

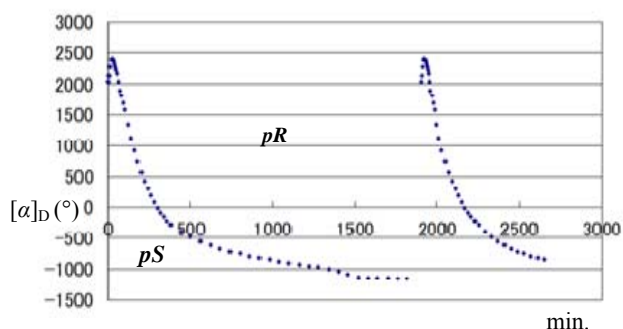


Fig. 4 The reset specific rotational analysis of **1** for the same sample. SMPV (spontaneous molecular parity violation) phenomenon was shown until the reset analysis.

expected to be smaller than the value of the MPVED. So that, the role of detector was not only detector but also the source of energy to give MPV for enantiomers opposite side of SMPV state. Therefore, SMPV phenomena of **1** existed as visually unobservable ground state behind observable MPV phenomena. Therefore, SMPV phenomenon suggests that the transition of specific rotation of the racemate should exist in (+) intensity area. If the enantiomers dissolve into solvent freely from crystal state before the optical detection, it would be in (+) intensity area.

Copper complexes **2**, **3**, **4**, **5**, **6** related to **1** were synthesized according to the synthetic method of **1**. **2**, **3**, **4** synthesized from L-, D-, DL-histidine, respectively. **5** was derived from esterification of L-histidine by methanol and treated in the same procedure. **6** was given by esterification of **4** using ethanol. **2**, **3**, **4** showed

mutarotation phenomena as almost the same shapes as in case of **1** under time development optical analysis as shown in Fig. 5. These optical rotational intensities gave some large values comparing with intensities of Fig. 3. As the energy of the optical rotational detector was shared with all complex molecules in each solution, the rotational intensities were in inverse proportion to the concentrations of these solutions.

So that, it was reasonable that **1** gave $-3,000^\circ$ (c , 0.10 g/dL) in Fig. 5, and gave $-1,240^\circ$ (c , 0.22 g/dL) in Fig. 2. Besides, the optical rotational analysis of a little density solution of **4** (c , 0.30 g/dL) gave $+4,000^\circ$ over and not stable. The irradiation energy from detector would not be enough even to all enantiomers for giving dissipative equilibrium in this solution. The reset optical specific analysis of copper complexes **2**, **3**, **4** gave the same and repeatable SMPV phenomena, respectively as in case of **1**. **5**, **6** gave continuous specific rotational intensity of $+2,000^\circ$ and $+1,000^\circ$ respectively. Each steric hindrance of methoxy and ethoxy substituent of **5** and **6** prevented the solvent molecule from taking the same *pS* side of carboxyl group on copper atom, and resulted in giving *pR* enantiomer priority constantly in each solvent. Assignment of the specific rotational value (+) was given to *pR* enantiomer as the pursuing assignment as shown in Figs. 5 and 8 later.

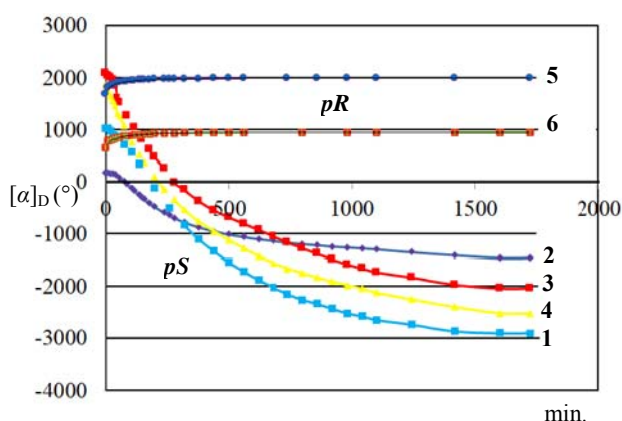


Fig. 5 Specific rotational intensities of copper complexes **1**, **2**, **3**, **4** in time development analysis. (**1**, **2**, **3**, **4**: c 0.10~0.12 g/dL, MeOH aq. **5**: c 0.20 g/dL, MeOH **6**: c 0.20 g/dL, EtOH, 20°C).

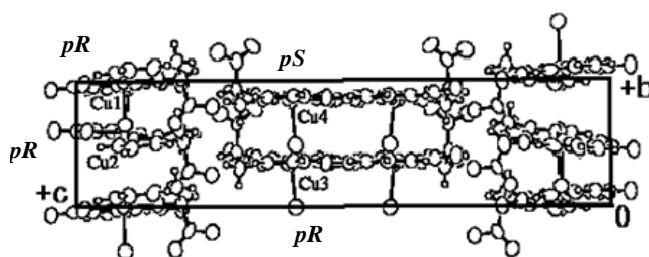


Fig. 6 Single crystal structure of **2**. It gave co-crystal in 3 to 1 ratio of *pR* to *pS* enantiomers (space group P21) [8].

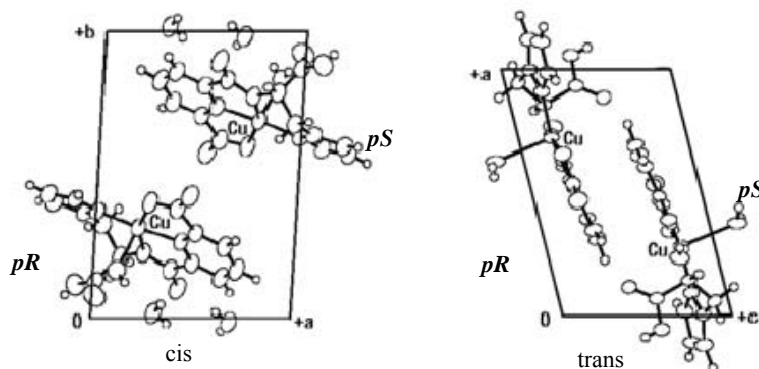


Fig. 7 Crystals of **4** were racemic *cis* and racemic *trans* crystal mixture, with respect to the fifth apical ligand on copper atom to axial carboxyl group on basal plane. *Cis* and *trans* racemic crystals were produced in a ratio of 5 to 95 from the same HPLC (high performance liquid chromatography) fraction.

Aqua[(6-carboxyl-2-pyridilamide)-L-histidinato]copper(II) **2** was synthesized from L-Histidine by the same method of **1**. X-ray crystal crystallographic analysis revealed that the copper atom had the fifth apical ligand to give co-crystal in 3 to 1 ratio of *pR* to *pS* enantiomers with space group P21, as shown in Fig. 6. The detail data had been reported in *Acta Cryst C* [5]. As the SMPV phenomenon was visually unobservable state, it was notable that one of SMPV states was isolated in the same lattice of single crystal state of **2**. It was owing to diastereomeric effect between alternative coordination of apical H₂O ligand using chiral divided d_{z^2} orbital of copper atom and the configurational S-carbon of L-Histidine moiety. If the crystal structure was given for the steric hindrance, *pS* enantiomer should have not been produced in the same single crystal, because bulky carboxyl group and the fifth apical ligand of water molecule were in the same side of *pS* enantiomer.

Aqua[(6-carboxyl-2-pyridilamide)-DL-histidinato]copper(II) **4** gave two kinds of characteristic crystal

mixture treated by recrystallization of HPLC fraction on an ODS (OctaDecylSilyl) column (H₂O:MeOH, 0.5:1.5). Each crystal was separated under a microscope operation individually, and detected by X-ray crystal structural analysis respectively. They were *cis* and *trans* racemate with respect to the fifth apical ligand on copper atom to carboxyl group of tetradentate ligand as shown in Fig. 7. *Cis* and *trans* conformational isomers were given in 5 to 95 ratio under a microscope outlook. The *trans* conformational racemate was given as a priority in crystal state, owing to the steric barrier between the fifth apical ligand and bulky carboxyl group being smaller than that of *cis* conformational racemate. The individual crystal isolation of *cis* and *trans* racemates from the same solution showed that the internal energy difference between them was larger than the energy of building co-crystal of *pR* and *pS* enantiomers like as in case of **2**. These experimental evidences revealed that the lowest free

Table 1 Specific rotations of copper complexes 1, 2, 3, 4 and their solution colors under neutral and acidic conditions at room temperature. The maximum rotational values of tetradentate ligands of 6-carboxyl-2-pyridylamide histamine and of L-, D-, DL-histidine derivatives were shown.

Copper complexes	pH 7 (deg*., after mutarotation)	pH 2 (deg.)
1	-1,240	0
2	-350	-41
3	-750	+41
4	-560	0
Color of solution	Blue	Colorless

HORIBA SEPA-200, c 0.220 g/dL, MeOH, *20 °C.

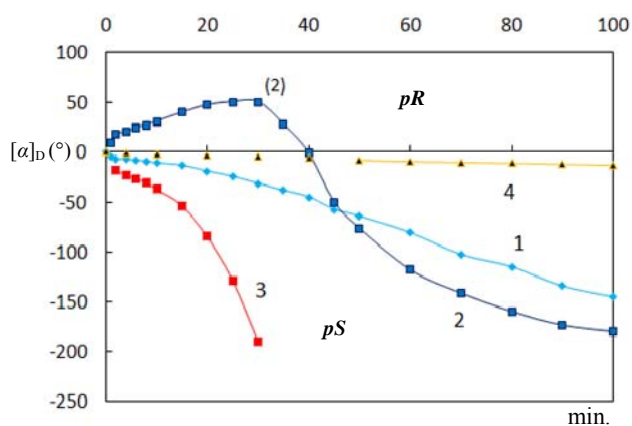


Fig. 8 The optical rotational transition in MeOH. Quantum feedback control phenomena of chiral information thermo dynamics with dissipative process under irradiation energy of optical rotational detector.

energy of this system is in SMPV state in solution as the ground state, and a little higher energy state is in a racemic solid states of 1 and 4. The next higher middle energy state is in a solid state of 2. The highest free energy state was in solution system of all copper complexes with dissipative process under optical rotational irradiation energy of detector.

Copper complex was used to collapse and to release its ligand in solution under strong acid conditions. All of copper complexes of 1, 2, 3, 4 left their tetradentate ligands in acidic solutions of pH 2. Therefore, each ligand of copper complexes gave the maximum specific rotation respectively, as shown in Table 1. The maximum specific rotation of -41° was given by the designed tetradentate ligand of

6-carboxyl-2-pyridylamide-L-histidine of 2. On the other hand, the value of $+41^\circ$ was given by the ligand of 6-carboxyl-2-pyridylamide-D-histidine of 3.

Both ligands of 6-carboxyl-2-pyridylamide-L-histamine and 6-carboxyl-2-pyridylamide-DL-histidine of 1 and 4 gave specific rotation 0° , respectively because, tetradentate ligand of 1 synthesized from histamine has no chiral atom. Tetradentate ligand of 4 synthesized from DL-histidine is racemate, as shown in Table 1 and Scheme 1.

Each racemate of 1 and 4 gave the optical rotational transition from 0° to -150° as *pS* enantiomer priority for the very start of crystal dissolving into MeOH solvent as shown in Fig. 8. On the other hand, 2 maintained showing optical rotational sign (+) being *pR* enantiomer priority for the first 40 min for its structure maintaining against the optical rotational irradiation energy. It was expected for 2 from the crystal structure of *pR* enantiomer priority by 3 to 1 ratio, as shown in Fig. 6.

It revealed that, when each enantiomer of crystal dissolved into the solvent one after another, the chiral irradiation energy of detector affected each enantiomer against moving SMPV state (*pR* enantiomer priority state), and resulted in giving *pS* enantiomer priority. All of optical mutarotational phenomena of free dissolving processes of each crystal of 1, 2, 3, 4 into MeOH solvent enabled us to undertake quantum feedback control of chiral information thermo dynamics [9] under optical rotational irradiation, as shown in Fig. 8. The optical irradiation energy has a role of the Maxwell's demon [9]. The dotted line slopes of copper complexes depended on each solubility of crystals to methanol.

4. Conclusions

The theorem of square-well potential resolution of Schrödinger equation had shown that the orbital possessing even parity in the ground state has either even and/or odd parity in the restraint sphere. So, the equation of the ground state of chiral divided d_z^2

orbital of copper atom has even parity in the ground state, and has even and/or odd parity in restraint coordination sphere as expected from the equation. However, Schrödinger equation had not given yet any more resolutions whether the dz^2 orbital of copper atom would have either even or odd parity in chiral coordination sphere, and it has symmetry or not symmetry for the nod of z-axis. Furthermore, the equation has limitation to give some resolutions for time dependent chiral phenomena.

The experimental findings revealed that MPV of the copper complexes gave *pS* enantiomer priority with dissipative process against SMPV in solution system by optical analysis. It was based on quantum feedback control of chiral information thermo dynamics under chiral irradiation energy, which was a role of Maxwell's demon [9]. The SMPV was brought about the insertion of chiral dz^2 vector electron as ground state between *pR* and *pS* enantiomer for alternative replacement of the fifth ligand, as shown as presentation of the outline in Fig. 1. So, *pR* enantiomer should be priority being in even parity as ground state based on Schrödinger equation. The alternative replacement of the fifth ligand was followed by parity inversion jointly inversion of coordination sphere along z-axis, as shown in Fig. 1. The SMPVED should depend on spontaneous quantum feedback control of chiral information thermo dynamics without the demon. Therefore, SMPV was visually unobservable ground state to give *pR* enantiomer priority. Time-dependent phenomena

would be owing to scattering time of solvent molecules as rate-determining step. The experimental evidences of SMPV and MPV phenomena have been shown in front of us.

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References

- [1] Hund, F. 1927. "Hund's Paradox." *Z. Phys.* 43: 805.
- [2] Yang, C. N., and Lee, T.-D. 1956. "Question of Parity Conservation in Weak Interactions." *Phys. Rev.* 104: 254.
- [3] Harris, R. A. 1978. "Quantum Beats in Optical Activity and Weak Interactions." *Phys. Lett. B* 78: 313.
- [4] Jameson, R. F., and Neillie, W. F. S. 1965. "Stability Constants of Metal-Ion Complexes [with] Supplement." *J. Inorg. Nuclear Chem.* 27: 2623.
- [5] Kato, T., Sugimoto, K., and Yamasaki, M. 2001. "Aqua[*N*-(6-Carboxylato- κ O-pyridine-2-carbonyl- κ N)-L-Histidinato- κ^2 N, N']Copper (II)." *Acta Cryst.* 57: 1256.
- [6] Kato, T., and Yamasaki, M. 2007. "Crystal and Molecular Structure of Racemic Aqua[(6-carboxyl-2-pyridilamide)-Histaminato]Copper(II) Complex." *ANAL. SCI. X-Ray Structural Analysis* 23: X37.
- [7] Cahn, R. S., Ingold, C. K., and Prelog, V. 1966. "Specification of Molecular Chirality." *Angew. Chem. Intern. Ed. Engl.* 5: 3856.
- [8] Kato, T. 1998. "A Probability of Absolute Asymmetric Synthesis of Metal Complex Compounds." *Viva Origino* 26: 197.
- [9] Toyabe, S., Sagawa, T., Ueda, M., Muneyuki, E., and Sano, M. 2010. "Experimental Demonstration of Information-to-Energy Conversion and Validation of the Generalized Jarzynski Equality." *Nature Physics* 6: 988.