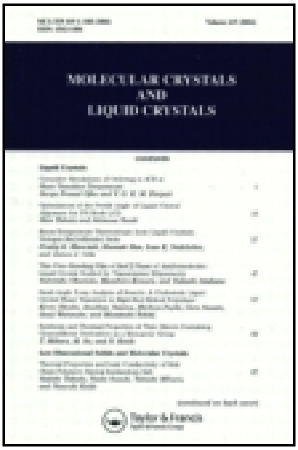

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Chiral 1D and 2D Assembly Structures of Self-Complementary Copper(II) Complexes with Imidazole-Containing Ligands

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Chiral 1D and 2D Assembly Structures of Self-Complementary Copper(II) Complexes with Imidazole-Containing Ligands

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1-D system: Copper(II) complex with pentadentate strand-type ligand involving two imidazole groups exhibits a self-complementary double-faced H-bonding recognition and enantioselective self-assembly behavior. The mono-deprotonated complex includes one imidazole and one imidazolate moiety, and due to the spiral arrangement of the acyclic ligand, induces *C*(clockwise) and *A*(anticlockwise) enantiomers. The complex functions as chiral building component and aggregates into ...*CCCC*... and ...*AAAA*... homochiral 1D zigzag-chains, owing to hydrogen-bonding between the imidazole and imidazolate groups of adjacent homochiral units.

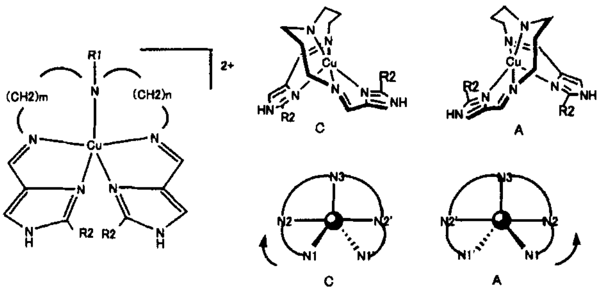
2-D system: Copper(II) complex with a hexadentate tripod-type ligand involving three imidazole groups induces a chirality of *C*(clockwise) and *A*(anticlockwise) enantiomers due to the screw coordination arrangement of the tripod-type ligand around the metal ion. Further, the hemi-deprotonated species functions as a chiral self-complementary double-faced H-bonding recognition unit and form a two-dimensional extended honeycomb structure due to the intermolecular imidazole-imidazolate hydrogen bondings. The generated honeycomb structure is a chiral layer constructed by homochiral aggregation.

INTRODUCTION

Self-assembly and self-organization are the keys to the areas of supramolecular chemistry and crystal engineering.[1] The directed manipulation of intermolecular interactions (coordination bond, hydrogen bond, π-π interaction,..) gives supramolecular assemblies through the design of instructed monomeric and polymeric species. Chirality has been an important subject not only in chemistry but also in living organisms, pharmacy, and the chemical industry. Chirality is expressed on both the molecular and supramolecular levels, and supramolecular chirality results not only from the properties of the components, but also from the way in which they associate. When a chiral molecule crystallizes to form a crystalline racemate, it would be either a (1) racemic compound, (2) racemic mixture (conglomerate), or (3) racemic solid solution.[2] The separation of two enantiomers forming a conglomerate does not require any optically active auxiliary agent since resolution spontaneously occurs during the course of crystallization. Spontaneous resolution, which is characteristic of a conglomerate, was discovered for the first time in ammonium sodium tartrate by L. Pasteur in 1848.[3] Since this historic discovery by Pasteur a large number of chiral molecules have been synthesized and investigated, but only a limited number of molecules have been known to be conglomerate. In order to design the molecule inducing spontaneous resolution, it is primarily necessary to use substantially strong interaction such as coordination-bond[4] and hydrogen-bond[5] and to look for the factors producing homochiral enantioselectivity. If an enantioselective homochiral interaction was extended from adjacent two molecules to 1D(one-dimensional), 2D, and 3D system, a self-resolution will be achieved in crystal. Along this line, chiral metal complex with self-complementary multiple-faced H-bonding recognition unit is a good candidate to produce conglomerate. We will report chiral 1D and 2D extended assembly structures derived from intermolecular homochiral interaction of self-complementary metal complex.[6]

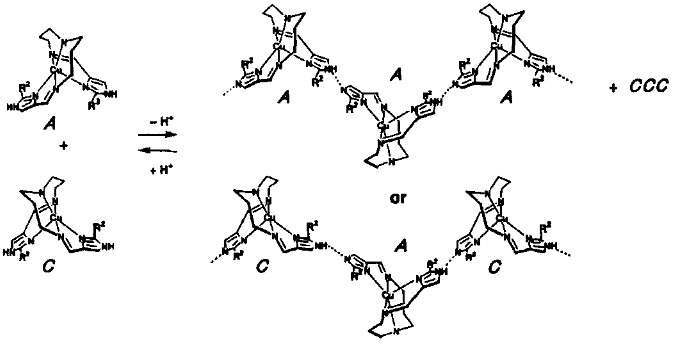
RESULTS AND DISCUSSION

1-D system: Copper(II) complexes with pentadentate ligand involving two imidazole groups exhibit a self-complementary double-faced H-bonding recognition and enantioselective self-assembly behavior. The schematic structures of the copper(II) complexes with the general chemical formula of $[Cu(H_2L^n)](ClO_4)_2$ are shown in Scheme 1. The pentadentate Schiff-base ligands H_2L^n (n = 1 – 5) were prepared through 2:1 condensation reactions between 4-formylimidazole or 2-methyl(or 2-phenyl)-4-formylimidazole and either of the linear triamines, *N*,*N*'-bis(3-aminopropyl)amine, *N*-(3-aminopropyl)-1,4-butanediamine, and *N*,*N*'-bis(3-aminopropyl)methylamine in methanol. Each ligand reaction mixture was subsequently used for the synthesis of the corresponding copper(II) complex without isolation of the ligand. The C, H, and N microanalyses of the copper(II) complexes agree well with $[Cu(H_2L^n)](ClO_4)_2\cdot xH_2O$ chemical formula. The mono-deprotonated complexes with the general chemical formula of $[Cu(HL^n)]ClO_4$ were obtained as well-grown green crystals when 2 equiv of triethylamine were added to the 1:1 mixed-solution of the ligand and copper(II) perchlorate hexahydrate in methanol.



SCHEME 1 Molecular structures of copper(II) complexes with the pentadentate ligands, where **N** (m, n, R_1, R_2) = **1** (3, 3, H, H); **2** (3, 3, H, Me); **3** (3, 4, H, Me); **4** (3, 4, H, Ph); **5** (3, 3, Me, Ph). Structures of *C*(clockwise) and *A*(anticlockwise) enantiomers.

The mono-deprotonated complexes include one imidazole and one imidazolate moiety per molecule, and due to the spiral arrangement of the acyclic ligand, *C*(clockwise) and *A*(anticlockwise) enantiomers are present in equal proportions. The complex functions as chiral building component and aggregates possibly into heterochiral (...*CACA*...) or homochiral(...*CCCC*... and ...*AAAA*...) 1D zigzag-chains, owing to hydrogen-bonding between the imidazole and imidazolate groups of adjacent homochiral units (Scheme 2).



SCHEME 2 Two possible 1D structures formed by hydrogen bonds between adjacent two enantiomers. Homochiral (upper) and heterochiral (lower) 1D zigzag-chains.

The crystal structures of the mono-deprotonated complexes were determined by the single-crystal X-ray analyses. Each copper(II) ion assumes penta-coordination with the N_5 donor set including one imidazole, one imidazolate, two imine, and the central amino nitrogen atoms of the pentadentate ligand. The Cu–N bond distance for the protonated imidazole moiety, Cu–N(1), is substantially longer than that for the deprotonated imidazolate moiety, Cu–N(7). One important structural feature is that the copper(II) complex is either Δ or Λ enantiomorph due to the spiral arrangement of the acyclic pentadentate ligand around the N(3)–Cu–N(5) axis. The imidazolate nitrogen atom N(6) of each copper(II) complex is hydrogen-bonded to the imidazole nitrogen atom N(2)* of an adjacent unit, yielding a one-dimensional zigzag-chain with intermolecular hydrogen-bonds.

The crystal lattice of **1**', **2**', and **3**' yielded either ...*CCCC*... or ..*AAAA*... isotactic 1D zigzag-chains, while the crystal lattices of **4**' and **5**' yielded ...*CACA*... syndiotactic 1D zigzag-chains. In the former compounds, two adjacent methyl or H groups at the 2-position connected by hydrogen bond arrayed in the same direction, thus allowing homochiral aggregation of the complex molecules in a 1D chain. On the other hand, in **4**' and **5**', two adjacent bulky phenyl groups require opposite orientations, thus allowing heterochiral aggregation. Enantioselective aggregation with homochirality or hetero- chirality can thus be controlled with suitable substituents. The only difference in the ligand framework of **3**' and **4**' is the 2-substituent of the imidazole moieties: a methyl group for **3**' and a phenyl group for **4**'. The phenyl groups of adjacent complex cations in **4**' need to be oriented in opposite directions, in order to avoid steric hindrance while allowing for the formation of a 1D hydrogen bonded chain-structure, as evidenced by the space filling representation. Then homochiral aggregation of the complex is not possible: only complex with opposite *C* and *A* chirality is able to interact with each other through hydrogen bonds to yield an extended syndiotactic chain-structure.

The 2-methyl groups of adjacent complexes in **3**' are oriented in the same direction. There is no steric hindrance when small substituents such as methyl groups are oriented in the same direction: the hydrogen-bonded imidazole and imidazolate moieties in **3**' are then roughly in-plane and the Cu–N and N–H bonds are roughly in-line, which is the most suitable to form the N-H· · · N hydrogen bonds. Considering the N(2)· · · N(6)* distances and N(2) –H· · · N(6)* angles, one can conclude that the alternate aggregation of *C* and *A* enantiomorphs is energetically less favorable in this type of 1D zigzag-chain structure. It is revealed how an enantioselective aggregation with homochirality can be achieved within a 1D zigzag-chain. However, the chains with homochiral ...*CCCC*... and ..AAA... array alternately to give achiral crystal.

FIGURE 1 1D zigzag-chain structure formed by hydrogen bonds of **3'**. Within a zigzag-chain, the molecules with the same enantiomorph are linked by the hydrogen bonds.

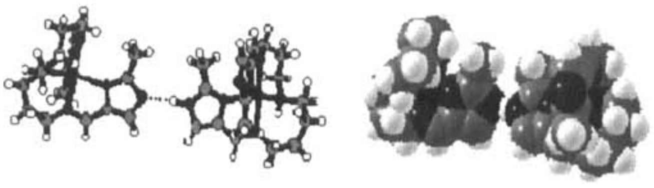
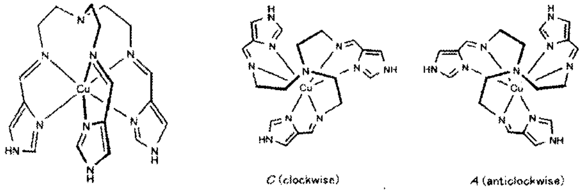


FIGURE 2 CHARON drawing and space filling representation of the two adjacent molecules linked by the hydrogen bond for **3'**.

2-D system: In order to improve the dimensionality, we have selected the complex with a hexadentate tripod-type ligand involving three imidazole groups with the chemical formula $[Cu(H_3L)](ClO_4)_2$ **6** (H_3L = *N,N',N"*-tris[2-(imidazol-4-yl-methylideneamino)-ethyl]amine). As shown in Scheme 3, the complex assumes either *C*(clockwise) or *A* (anticlockwise) enantiomorph due to the screw arrangement of the tripod ligand around metal ion.

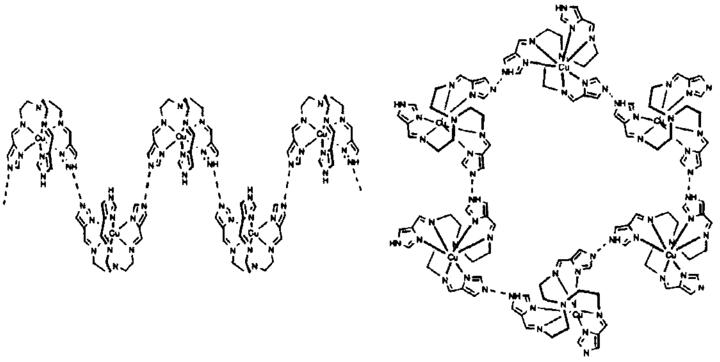


C (clockwise)

A (anticlockwise)

SCHEME 3 Molecular structure of **6**, and *C*(clockwise) and *A*(anticlockwise) enantiomorphs

Further, the hemi-deprotonated species with the formula of $[Cu(H_{1.5}L)]^{+0.5}$ can function as a chiral self-complementary double-faced H-bonding recognition unit and form a two-dimensional extended honey-comb structure due to the intermolecular imidazole-imidazolate hydrogen bondings when the hemi-deprotonated species was generated under proper pH conditions(Scheme 4).



SCHEME 4 Schematic structures of 2D honeycomb structure constructed by hydrogen bonds of **6'**. Side and top views.

The tripod-type hexadentate ligand was prepared by mixing 4-formylimidazole and tris(2-aminoethyl)amine with the 3:1 molar ratio in methanol and the resulting solution was used without the isolation of the ligand for the synthesis of the copper(II) complex **6**. The protonated copper(II) complex **6** was prepared by mixing the ligand solution and copper(II) nitrate trihydrate in methanol with the 1 : 1 molar ratio. **6** was obtained as green plates. Treatment of **6** with 2 equivalent amounts of triethylamine gave the deprotonated complex **6'** as green crystals in 78% yield. The elemental analysis agreed with $[Cu(H_{1.5}L)](NO_3)_{0.5}0.5H_2O$, indicating that 1.5 proton per Cu dissociated. The IR spectrum of **6'** showed the characteristic bands assignable to the C=N stretching vibration of the Schiff-base ligand at 1640-1615 cm^{-1}, the N–O vibration of the nitrate ion at 1385 cm^{-1}, and the broad absorption bands with fine structures in the region 2700-2300 cm^{-1} which suggest the presence of the stretching vibration of N–H groups associated with H-bonding interaction. The crystal structure of **6'** was determined by the single-crystal X-ray analysis. **6'** crystallizes in a noncentrosymmetric trigonal space group *P*321. Copper(II) ion is coordinated octahedrally by the N_6 donor atoms of the tripod ligand, and the Cu–N(2) and Cu–N(3) distances are 2.142(7) and 2.101(8) Å, respectively. There are two possible configurations for the metal complex with the tripod-ligand, clockwise (*C*) and anticlockwise (*A*) configurations. Each copper(II) complex is linked by the hydrogen-bond between the imidazole group of a molecule and the imidazolate group of the adjacent molecule with N···N distance of 2.72(2) Å. The *C* isomer aggregates only with the *C* isomer and the *A* isomer aggregates only with the *A* isomer to produce a chiral 2D honeycomb structure. Further, the layers with the same chirality are stacked along the *c*-axis to form a chiral crystal consisting of homochiral molecule. The X-ray analysis demonstrated that the separation of the two enantiomers spontaneously occurred during the course of the crystallization. Flack parameter defined as $|F| = (1\text{-}x)|F(+)| + x|F(-)|$ was refined to be nearly zero.[7]

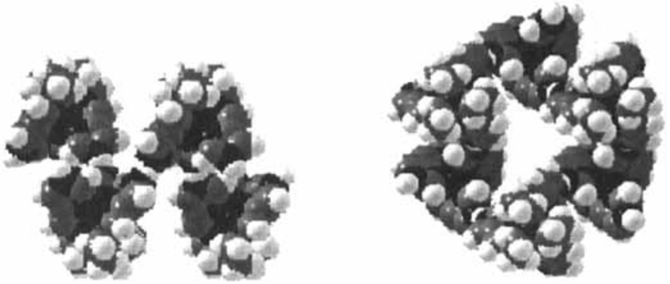


FIGURE 3 Chiral 2D honeycomb structure made by hydrogen bonds: a side-view and one unit of honeycomb structure.

A crystal piece of **6'** was selected and ground into a powder. The CD spectrum of the spectrum of the powdered sample was measured in the range of 400-1000 nm by the Nujol mull method. The spectrum showed a negative and positive peak at 800 and 650 nm, respectively, and the spectrum of another crystal showed an enantiomeric CD pattern. The CD spectra are shown in Fig. 4. The results give further evidence for spontaneous resolution of the complex.

The noteworthy character of the complex is that the unit molecule functions as a chiral building component and the molecules with homochirality aggregate due to the hydrogen bonds to give the chiral honeycomb layer. There are two possible honeycomb structures, i.e., homochiral and heterochiral 2D layer structures. Of the two structures, homochiral structure is much preferable in this system.

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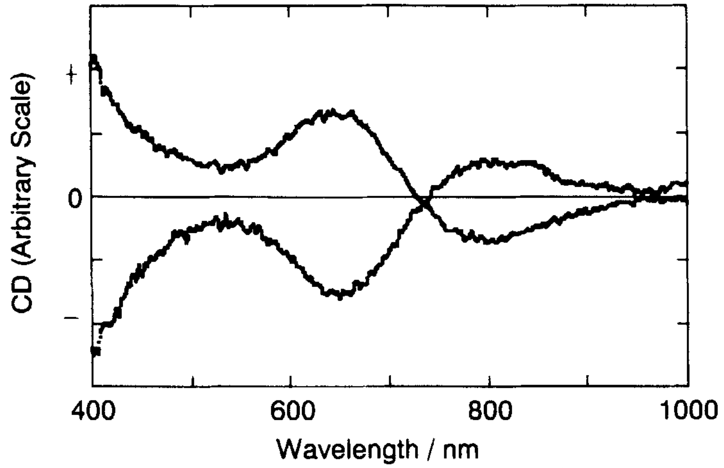

FIGURE 4 CD spectra of the powdered sample of **6'**.recorded as Nujol mulls.

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