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Short communication

Three complexes with helical frameworks based on L-glutamine and L-asparagine: Crystal structures and circular dichroism properties

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ABSTRACT

Three novel complexes with helical two dimensional (2D) frameworks, $[Ni(Asn)_2(H_2O)]$ (1) (HAsn = L-asparagine), $[Cd(Gln)_2]_n$ (2) (HGln = L-glutamine) and $[Zn(Gln)_2]_n$ (3), have been studied based on X-ray single crystal diffraction analysis. L-asparagine induces two kinds of chirality, the chiral Ni(II) center and the supramolecular *M*-helixes, into complex 1. L-glutamine induces one kind of chirality, the helixes, into complexes 2 and 3, respectively. Combining the crystal structures of complexes 1–3, the final aggregate chirality induced by coordinated bond interactions can be detected by the liquid state circular dichroism (CD) spectra while the solid state CD spectra of complexes 1–3 additionally reflect the final aggregate chirality induced by weak interactions.

Chirality is a fundamental and interesting topic in chemistry, biology and material science [1]. With the emergence of various chiral materials and novel chirality phenomenon, the term of chirality would have more contents [2]. Usually, introducing chirality into solid-state materials at a molecular level can create, tune, or modulate their functions, inducing potential applications in enantioselective separation, asymmetric catalysis, nonlinear optics, medicine, and chiral magnets [3]. So, studies on molecular chirality and its transfer to homochirality of materials are growing topics of interest in light of their importance in controllable synthesis of chiral material [4], which are still challenges to chemists.

As we know, integrating natural L-amino acids into metal–organic frameworks (MOFs) is attractive due to the inherent chirality of the starting building blocks [5]. How does the chirality of L-amino acids transfer to their metal complexes? At present, self-assembly is a distinctive method to construct chiral materials from chiral or achiral constituents [6]. The covalent interactions (metal–ligands) [7] and the noncovalent bond interactions such as H-bonding, aromatic stacking, and electrostaticsare vital in the self-assembly process and in determining the final geometry of materials [8]. L-Amino acids can use their functional groups of carboxyl group (-COOH) and amino group ($-NH_2$) to coordinate to metal center by covalent interactions (metal–ligands) leading to the construction of a new chiral center [9]. And also the tendency of intramolecular protonation with protonated amino groups (NH_3^+) and deprotonated carboxylic acid groups (COO^-), zwitterions [10], are potentially supramolecular building blocks for constructing supramolecular chirality [11].The above two features of L-amino acids provide green channel for the transfer of chirality from L-amino acids to their materials [12].

Circular dichroism (CD) measurement is the most important method for the analysis of chirality of molecules and materials. Generally, CD measurement applying to coordination complexes of amino acids is often in liquid [13] and is rare in solid-state [14]. The combination of liquid- and solid-state CD spectra will be very helpful for the assignment of absolute configurations of molecules and for understanding the relationship between molecular chirality and material chirality [15].

In this work, a coordination complex of L-asparagines, $[Ni(Asn)_2(H_2O)]$ (1), and two kinds of coordination complexes of L-glutamines, $[Cd(Gln)_2]_n$ (2) and $[Zn(Gln)_2]n$ (3), were obtained and studied based on X-ray single crystal diffraction analysis. The liquid- and solid-state circular dichroism (CD) measurements were carried out to study the chirality of the three complexes. The decomposition of the organic component of complexes 1–3 begins at 200 °C (Fig. S7).

Complex 1 has an octahedral coordination environment for the Ni(II) center, formed by the oxygen atom O7 (water molecule), the oxygen atom O1 (carboxyl), nitrogen atom N1 (amino group) and oxygen atom O3 (acylamino group) of a tridentate coordinated L-asparagine, and the oxygen atom O4 (carboxyl) and nitrogen atom N3 (amino group) of a bidentate coordinated L-asparagine (Fig. 1). The bidentate

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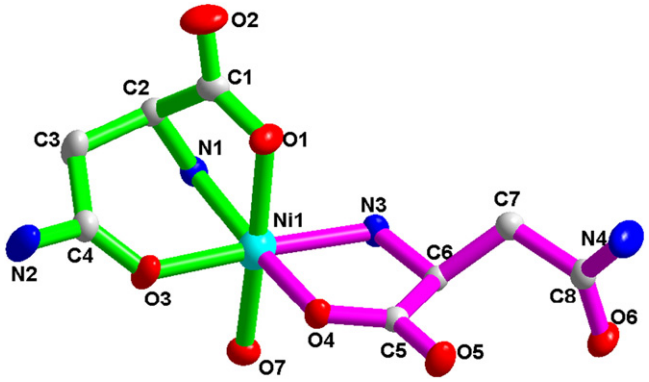

Fig. 1. The coordination environment of chiral Ni(II) center. The tridentate coordinated *L*-asparagine and a coordinated water molecule are shown in green bonds and the bidentate coordinated *L*-asparagine is shown in pink bonds.

coordinated *L*-asparagine constructs a chelating five-membered ring while the tridentate coordinated *L*-asparagine constructs both a six-membered ring and a five-membered ring with nickel ion, which induce the Ni(II) center to be a chiral one [16]. The Flack absolute structure parameters (0.011(9)) clearly prove the homochiral character of complex 1 [17]. It was found that the nickel ion center of 1 used for the present X-ray analyses consists of the Λ enantiomer [16], as shown in Fig. 1. In previous reports, the *L*-asparagines display multiply coordination model influenced by pH, the coordination characteristics of center metals and so on [18,19]. As we know, in complex 1, this is the first report that *L*-asparagine acts as both a tridentate coordinated ligand and a bidentate coordinated ligand in one complex, which introduces asymmetric coordinating model into a metal center and further indicates that *L*-asparagine is a good candidate for constructing multiply structures with chirality. The adjacent mononuclear molecules are connected by hydrogen bonds (N2–H6···O2, 2.134 Å, N2–O2, 2.890 Å, N2–H6···O2, 157.01°) (Table S5) between two tridentate coordinated *L*-asparagines to extend a one-dimension (1D) left-handed chain (*M*-helix) (Fig. 2a), and the adjacent mononuclear molecules also can construct another *M*-helix (Fig. 2b) by hydrogen bonds (N1–H2···O6, 2.205 Å, N1–O6, 2.931 Å, N1–H2···O6, 149.60°) (Table S5) between bidentate coordinated *L*-asparagines and tridentate coordinated *L*-asparagines, which is another new kind of chirality induced by *L*-asparagine in complex 1 [20]. The above two kinds of alternant *M*-helixes construct the two-dimensional (2D) helical frameworks (Fig. 2c) in complex 1. The detail connecting relationship between two kinds of *M*-helixes in the 2D helical frameworks can be simplified to a model (Fig. 2d). The paralleled 2D chiral frameworks are packed together by H-bonding interactions (O7–H8···O5, 1.929 Å, O7–O5, 2.733 Å, O7–H8···O5, 175.67°) (Fig. 2e) between bidentate coordinated *L*-asparagines and coordinated water molecules to extend the 3D supramolecular framework in complex 1 (Fig. 2f). In complex 1, the chirality of *L*-asparagines is first transferred to the Ni(II) center by the functional groups (-NH_2, -$CONH_2$ and -COO^-) of *L*-asparagines asymmetrically coordinating to Ni(II) center and then they are transferred to two kinds of supramolecular *M*-helixes by H-bonding interactions between carboxyl group and amidogen group, which further proves that chiral amino acids are good building blocks for constructing new chiral materials.

Complex 2 reveals infinite helical 2D coordination networks. Each Cd(II) center adopts a slightly distorted octahedral geometry by coordinating to two carboxyl oxygen atoms (O1, O5) and two amino nitrogen atoms (N1, N3) of two *L*-glutamines in the equatorial plane and to two carboxyl oxygen atoms (O2, O4) of another two *L*-glutamines in the axial positions (Fig. 3). *L*-glutamines in complex 2 possess two kinds of torsional conformations. Conformation I: the dihedral angle between the carboxyl group plane (O4, C6, O4) and the acylamino group plane (N4, C10, O6) is 89.961° and the distance between C10 and C6 is 4.3277 Å (Fig. S8a). Conformation II: the dihedral angle between the carboxyl group plane (O1, C1, O2) and the acylamino group plane (N2,

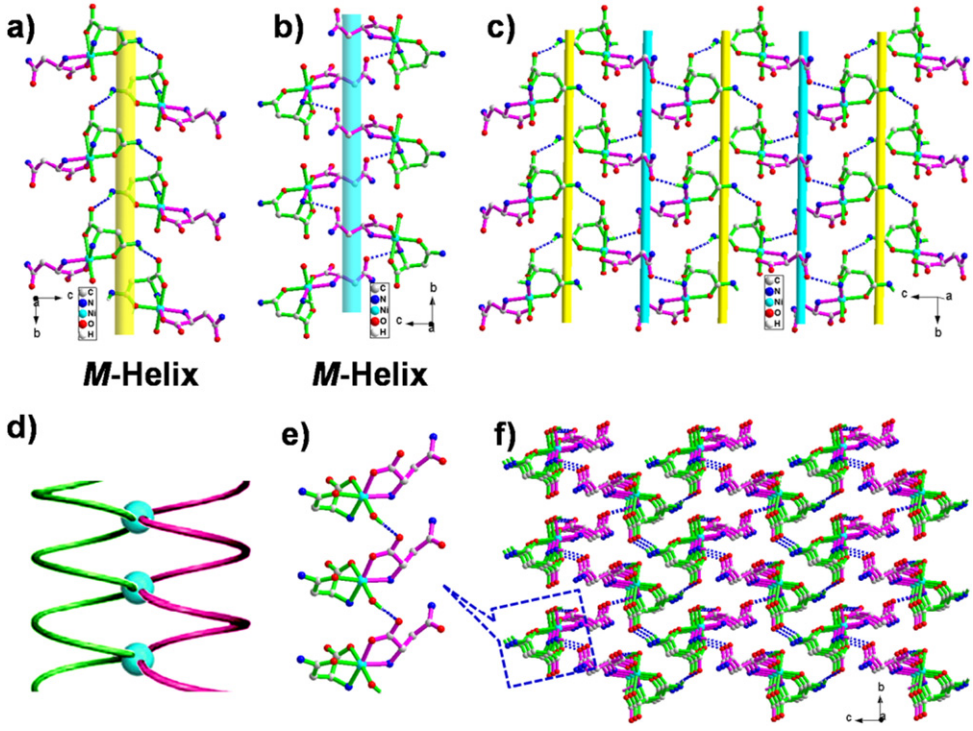

Fig. 2. a) A left-handed supramolecular helix (*M*-helix) is constructed by H-bonding interactions between the tridentate coordinated *L*-asparagines; b) a left-handed supramolecular helix (*M*-helix) is constructed by H-bonding interactions between the bidentate coordinated *L*-asparagines and tridentate coordinated *L*-asparagines; c) a 2D helical framework is constructed by above alternant two kinds of *M*-helixes; d) the model stands for the connecting relationship between two kinds of *M*-helixes in the 2D helical frameworks; e) the hydrogen bonds link 2D frameworks together to extended to (f) the three-dimensional (3D) chiral supramolecular framework in complex 1.