

Infinite chiral single-helical structures formed by the self-assembly of Cu(II)-*N*-(2-pyridylmethyl)-aspartate complexes†‡

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Two crystal structures of [Cu(L-pasp)(H₂O)]·4H₂O and [Cu(D-pasp)(H₂O)]·4H₂O [pasp = *N*-(2-pyridylmethyl)-aspartate] were determined using X-ray crystallography and the Cu(II)-pasp complexes were demonstrated to self-assemble through the formation of a Cu–O bond between Cu(II) and the side-chain carboxylate, forming left-handed and right-handed helical coordination polymers, respectively.

In recent years, the study of helical coordination polymers formed by the assembly of metal complexes has been a topic of great interest in supramolecular and materials chemistry due to the formation of fascinating structures and potential applications in nonlinear optics and host–guest interactions.¹ Most coordination helices are formed by the self-assembly of achiral or racemic ligands with metal ions and therefore yield racemates of P (right-handed) and M (left-handed) helices.² In a few cases, the use of enantiopure ligands leads to the formation of chiral helices.³ In nature, α -helices in proteins are typically single-stranded helices and appear in a right-handed conformation as a result of the selective incorporation of L-amino acids.^{4,5} Conversely, α -helices composed of D-amino acids show a left-handed conformation.⁶ The chirality in the α carbon of amino acids plays a critical role in controlling the orientation (P or M) of α -helices. In order to control the orientation of coordination helices,

understanding of how the chirality of each building unit affects the orientation of helices is a key issue.

Inspired by naturally occurring α -helices in proteins, we report on the design of two aspartate-based ligands (L-pasp and D-pasp) and the assembly of their Cu(II) complexes into infinite single helices in the crystalline phase. The ligands are *N*-(2-pyridylmethyl)-aspartic acids with differing α -carbon chiralities. The chirality of the ligand pasp determines the direction of the side-chain carboxylate. In Fig. 1, the direction of the side chain of L-pasp is out of the page, whereas in the case of D-pasp it is into the page. Pasp is a [3 + 1]-type tetradentate ligand in which one pyridine nitrogen, one amine nitrogen and one main-chain carboxylate oxygen function as a tridentate ligand for metal ion binding whilst the side-chain carboxylate is a monodentate ligand which binds to an adjacent metal complex. The self-assembly of Cu(II)-pasp complexes is facilitated by the bond (Cu–O) formation between Cu(II) and the side-chain carboxylate. The side-chain carboxylate also functions as a conformational turn for coordination helices. The chirality of the ligand pasp directly influences the orientation of the helical coordination polymers by controlling the direction of the side-chain carboxylate. According to the crystal structures obtained using X-ray diffraction, the complexes [Cu(L-pasp)(H₂O)] and [Cu(D-pasp)(H₂O)] form left-handed and right-handed helices, respectively. This differs from the α -helices in proteins, which are composed of L-amino acids and form right-handed helices.

The ligands L-pasp and D-pasp were synthesized by mixing 2-pyridinecarboxyaldehyde with L-aspartate or D-aspartate to form a Schiff base, followed by reduction using NaBH₄.⁷ The ligands were then characterized using ¹H and ¹³C NMR spectroscopy. The crystals of Cu(II)-pasp complexes were obtained by mixing Cu(acetate)₂ with L-pasp or D-pasp in an aqueous solution of pH 4 followed by incubation at room temperature for several days. Single crystal X-ray diffraction studies revealed that both complexes crystallized in orthorhombic cells (space groups *P*2₁2₁2₁ and *P*2₁2₁2 for L- and D-pasp, respectively). The difference between two crystals is the symmetry in the *c* axis; one is 2₁ and the other is C₂. Both complexes have the same chemical formula (CuC₁₀H₂₀N₂O₉). In addition to the Cu(II) ion and the pasp ligand, five water molecules are also attached to the complex. According to the crystal structures of both

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis of *N*-(2-pyridylmethyl)-aspartic acid, [Cu(L-pasp)(H₂O)]·4H₂O and [Cu(D-pasp)(H₂O)]·4H₂O, X-ray crystallographic data, and CIF files. CCDC reference numbers 700823 and 700824. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b817157m

‡ Crystal data for [Cu(L-pasp)(H₂O)]·4H₂O: C₁₀H₂₀CuN₂O₉, *M* = 375.82, 0.30 × 0.22 × 0.20 mm³, orthorhombic, space group *P*2₁2₁2₁ (no. 19), *a* = 8.5157(3), *b* = 10.8984(3), *c* = 17.6615(6) Å, *V* = 1639.12(9) Å³, *Z* = 4, *D*_c = 1.523 Mg m^{−3}, λ = 0.71073 Å, *T* = 293(2) K, Flack parameter, −0.02 (3); absorption coefficient = 1.376, reflections collected = 8932, independent reflections = 4071 [*R*(int) = 0.0370]; refinement method, full-matrix least-squares on *F*²; goodness-of-fits on *F*² = 1.103; Final *R* indices [*I* > 2 σ (*I*)], *R*1 = 0.0522, *wR*2 = 0.1227; *R* indices (all data), *R*1 = 0.0728, *wR*2 = 0.1657. Crystal data for [Cu(D-pasp)(H₂O)]·4H₂O: C₁₀H₂₀CuN₂O₉, *M* = 375.82, 0.30 × 0.12 × 0.09 mm³, orthorhombic, space group *P*2₁2₁2 (no. 18), *a* = 11.2411(3), *b* = 16.5043(5), *c* = 8.4442(3) Å, *V* = 1566.62(8) Å³, *Z* = 4, *D*_c = 1.593 Mg m^{−3}, λ = 0.71073 Å, *T* = 296(2) K, Flack parameter, 0.00(3); absorption coefficient = 1.440, reflections collected = 8270, independent reflections = 3743, [*R*(int) = 0.0413], Refinement method, full-matrix least-squares on *F*²; goodness-of-fits on *F*² = 1.078; final *R* indices [*I* > 2 σ (*I*)], *R*1 = 0.0361, *wR*2 = 0.0968; *R* indices (all data), *R*1 = 0.0549, *wR*2 = 0.1494.

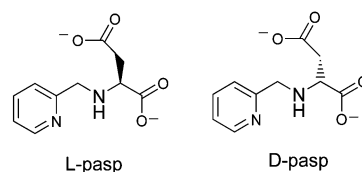


Fig. 1 Molecular structures of L-pasp and D-pasp.

complexes, one water molecule is bound to the Cu(II) ion and the other four water molecules surround each Cu(II) complex, resulting in $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$. The chemical formulae of both complexes are also supported by elemental analysis. The IR spectra of both complexes exhibit strong signals at 1630 and 1400 cm^{-1} for the ligand pasp. A broad peak at 3446 cm^{-1} is consistent with the presence of water molecules in both complexes.

Geometrically, Cu(II)-pasp complexes form square pyramids in which Cu(II) is bound with two nitrogens, two carboxylate oxygens and one H_2O oxygen as shown in Fig. 2. In the N_2O_2 plane of the

complex $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$, the bond lengths of Cu– N_{py} and Cu– N_{amine} are 2.001(4) and 1.977(4) Å whilst the bond lengths of Cu– $\text{O}_{\text{main chain}}$ and Cu– $\text{O}_{\text{side chain}}$ are 1.994(4) and 1.930(3) Å, respectively. The Cu– $\text{O}(\text{H}_2\text{O})$ bond is perpendicular to the N_2O_2 plane with a longer bond length of 2.280(3) Å and the H_2O group is found on the same side as the proton in the α -carbon (C7) within the N_2O_2 plane. The H_2O group is also located in the opposite direction of the side-chain carboxylate. In Fig. 2, two Cu(II)-pasp complexes are connected through the bond (Cu–O) between Cu1 and O3A. The O4A oxygen atom in the side chain is located on the opposite side of the OW1

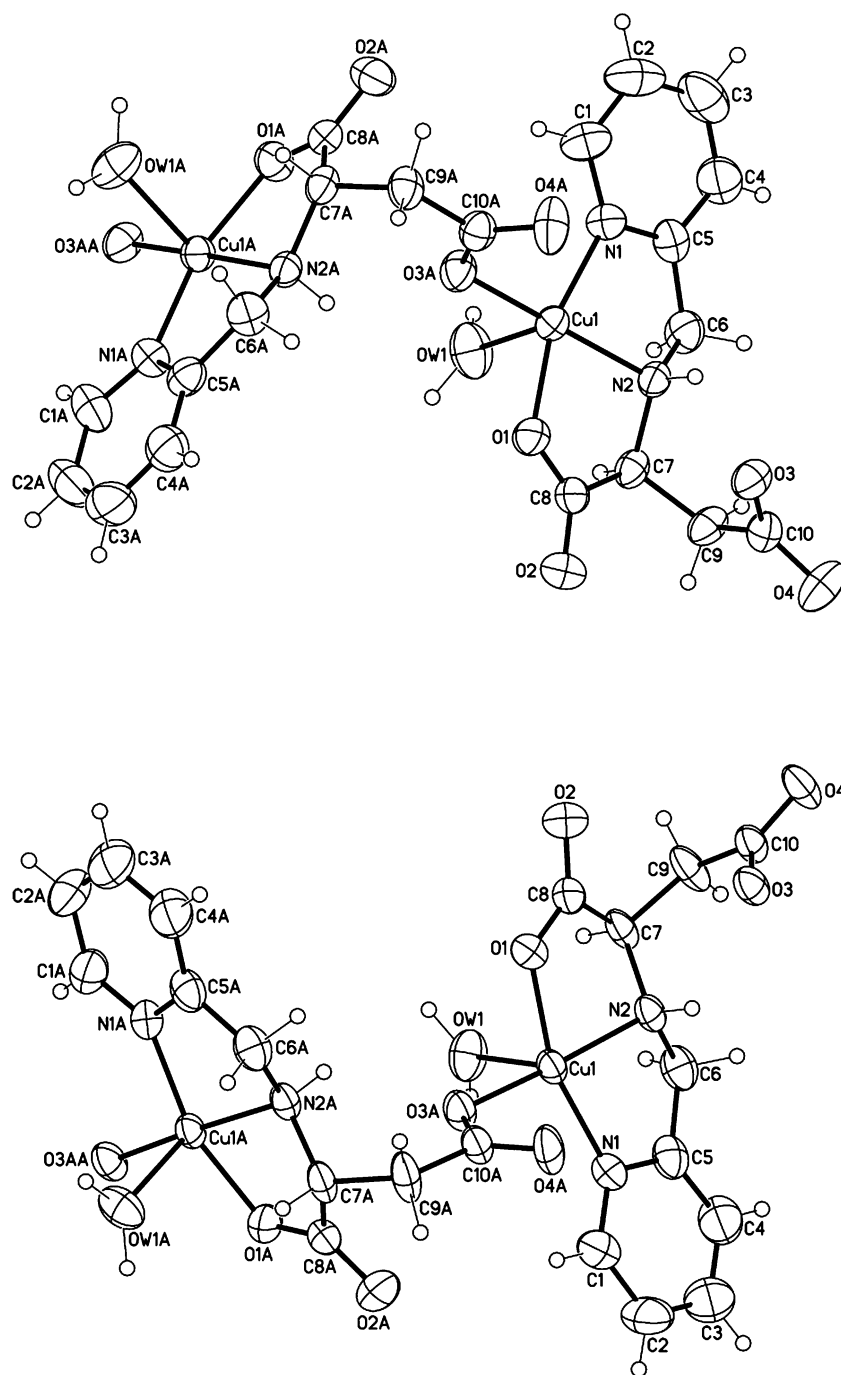


Fig. 2 The structures of the two complexes $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]_2$ (top) and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]_2$ (bottom). The symmetry operations used to generate the atoms with the label A: L-pasp, $-x + 1, y + 1/2, -z + 1/2$; D-pasp, $x - 1/2, -y + 3/2, -z + 1$.

water {where the torsion angle $\angle \text{OW1-Cu1-O3A-O4A}$ is equal to $168.9(1)^\circ$ (L-pasp) or $167.0(2)^\circ$ (D-pasp)}. There is a hydrogen bond (O—HN) formed between O3A and the proton on N2A with bond length, $2.211(1)$ Å (L-pasp) or $2.291(2)$ Å (D-pasp). This hydrogen bond plays an important role in restricting the orientation of the carboxylate group. In addition, the two adjacent Cu(II) complexes are almost perpendicular to each other. The angles between the two pyridine rings in the adjacent Cu(II) complexes are $86.2(2)^\circ$ (L-pasp) and $85.4(3)^\circ$ (D-pasp), respectively. In comparing to these structural data, both forms of Cu(II)-pasp complexes appear to be almost identical. However the chirality of the ligand pasp is not the same, which results in two Cu(II) complexes with differing stereochemistry. As depicted in Fig. 2, the two complexes, $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]_2$ and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]_2$, are not superimposed but show mirror images of each other.

The chirality of the ligand pasp determines the orientation of the helices. In Fig. 3, the two complexes, $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]$ and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]$, form left-handed and right-handed helices, respectively (also see Fig. S5 in the ESI†). A 2_1 axis is located between two Cu(II) lines plotted by connecting Cu(II) ions on the same side of the structure. Cu(II) complexes that are on the same side are parallel to each other. The repeat number of the coordination helix is 2 and the Cu—Cu pitches are $10.898(4)$ Å for $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]$ and $11.241(3)$ Å for $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]$. The distances between the two adjacent Cu(II) ions are $5.743(3)$ Å for $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]$ and $5.911(3)$ Å for

$[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]$. In contrast to right-handed α -helices in proteins, the L-pasp ligand forms left-handed coordination helices. This difference stems from the way in which the chirality of the α -carbon influences the orientation of the helices. α -Helices are formed through intramolecular hydrogen bonding between amide protons and carbonyl oxygens.⁵ The steric hindrance between side-chain atoms and the main-chain carbonyl moiety plays a key role in determining the orientation of α -helices in proteins by energetically favoring the right-handed conformation. Here the orientation of Cu(II)-pasp coordination helices is directly determined by the direction of the side chain, which is determined by the chirality of the ligand pasp.

In addition to coordination helices formed by Cu(II)-pasp complexes in the crystal, there are water chains perpendicular to the coordination helices. Fig. 4 shows the hydrogen bonds between the water molecules in both crystals. The water molecules are located between the Cu(II)-pasp coordination helices and the distance between two water molecules is in the range of $2.629(1)\sim 2.876(2)$ Å. In the crystal structure of $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$, the water chain is along the a axis with 2_1 symmetry. In the crystal structure of $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$, the water chain is also perpendicular to the coordination polymers, but the overall symmetry is C_2 along the c axis which accounts for the $P2_12_12$ space group of $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$.

In conclusion, we have developed a reasonable synthetic approach toward chiral single-stranded helices using *N*-(2-pyridylmethyl)-aspartate as a ligand for complexation with Cu(II). Pasp is a $[3+1]$ -type tetradentate ligand and the Cu(II) ions function as a hub for coordination polymer formation. The orientation of helical coordination polymers is controlled by the chirality of the pasp ligand. L-pasp and D-pasp form left-handed and right-handed helical

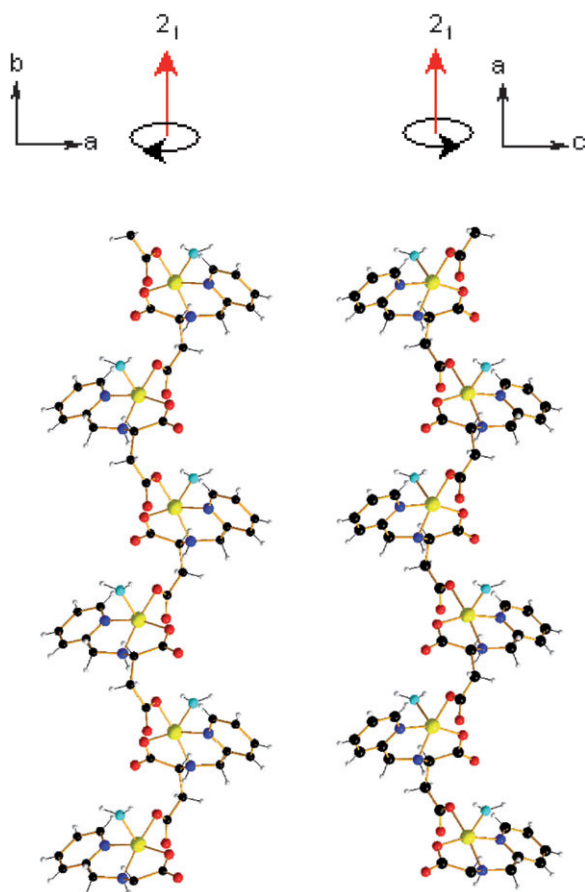


Fig. 3 Helical structures of the two complexes $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]$ (left) and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]$ (right). C (black), N (dark blue), O (red), Cu (yellow), water (light blue).

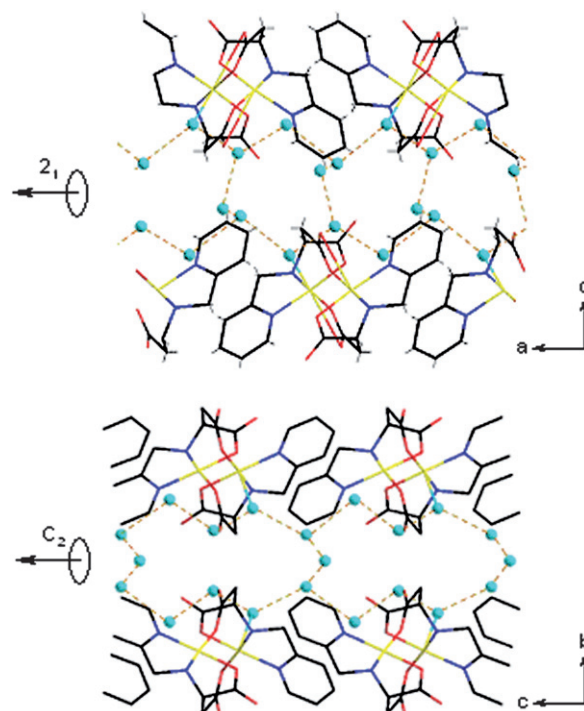


Fig. 4 Water chains in the crystalline structures of $[\text{Cu}(\text{L-pasp})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (top) and $[\text{Cu}(\text{D-pasp})(\text{H}_2\text{O})]\cdot 4\text{H}_2\text{O}$ (bottom). C (black), N (dark blue), O (red), Cu (yellow), water (light blue).

coordination polymers with Cu(II) ions, respectively. The pasp ligand was shown to be an excellent example of the way in which the chirality of a ligand can control the orientation of coordination polymers. This approach can be applied for the design of chiral coordination helices in the future.

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