Water-assisted self-assembly of harmonic single and triple helices in a polymeric coordination complex

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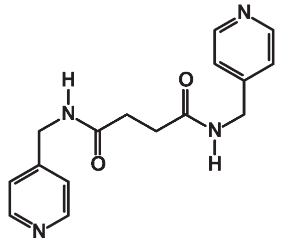
A novel two-dimensional coordination polymer containing infinite, coherently pitched single and triple helical motifs is formed by the self-assembly of Cd^{2+}, succinate, water and a bipyridyl ligand.

The natural occurrence of molecular helices has inspired interest in analogous synthetic systems. The chirality inherent in spiral structures can be associated with enantioselectivity, interesting optoelectronic properties as well as models of biological systems. Supramolecular chemists are primarily interested in the architectures of helices in order to better understand the processes governing their self-organisation.[1] Surprisingly, very few hydrogen bonded helices have been characterised sufficiently well to provide useful structural information.[2] While examples of infinite organic,[3] inorganic[4] and metal–organic[5] single (common) and triple (rare) helices are known to exist, Qin *et al.* only recently reported, for the first time, a structure containing both single and triple helical arrangements of a single ligand.[6]



Scheme 1 *N*,*N*′-Bispyridin-4-ylmethylsuccinamide (L).

In this contribution we describe a polymeric metal–organic complex featuring the coexistence of two quite dissimilar helices formed by infinite propagation of different ligands. The structure of ($[Cd(succinate)L]\cdot H_2O)_\infty$ contains both single and triple helical motifs and the two types of ligand adjust their conformations such that the pitch of each strand of L is exactly equal to three times that of the succinate ligand. The metal centres serve as nodes that bind the single and triple helices together to form a two-dimensional coordination polymer.

Pursuant to our studies of supramolecular systems that contain molecular cavities in addition to biologically relevant functional groups (*e.g.* amide groups and aromatic rings), the neutral, water-soluble, *exo*-bidentate ligand L was synthesised from the reaction of 4-aminomethylpyridine with succinyl dichloride.[7] Crystals of ($[Cd(succinate)L]\cdot H_2O)_\infty$ suitable for single crystal X-ray diffraction analysis† were grown from a solution of $Cd(NO_3)_2$, succinic acid and excess L in a 2 : 1 mixture of DMF and H_2O. The asymmetric unit is shown in Fig. 1: each Cd^{2+} ion is coordinated to two succinate anions, one water molecule and two ligands, L.

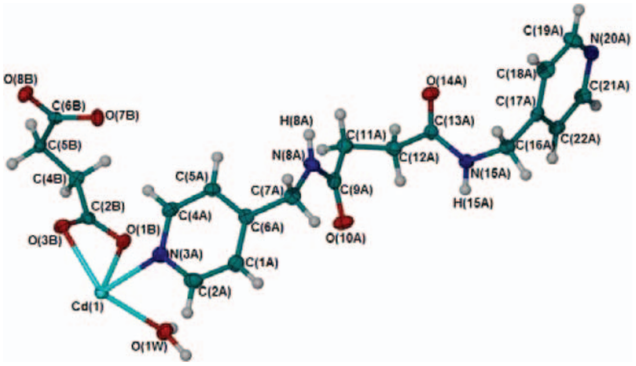


Fig. 1 Thermal ellipsoid (50% probability) plot of the asymmetric unit of ($[Cd(succinate)L]\cdot H_2O)_\infty$ with atomic labelling scheme indicated.

The most striking feature of the extended structure is the presence of both single and triple infinite helices (Figs. 2a and 2b). The triple helix consists of three intertwined chains of L bounded by two rows of metal centres running along [010]. Each strand of the triple helix has a repeat unit consisting of Cd–L–Cd–L to give a pitch of 31.0 Å. The single helix is formed by twisted succinate ligands and has a repeat unit comprised of Cd–succinate–Cd–succinate with a pitch of 10.33 Å. The two CH_2 groups of the succinate ligand are in the *gauche* conformation. A CSD search reveals that the *gauche* and *anti* arrangements are equally common and the torsion angle C(2B)–C(4B)–C(5B)–C(6B) of 67.5° is thus quite normal.[8] It is therefore surprising that no helical structures involving succinate ligands appear to have been encountered until now. At each extremity of the succinate ligand, both oxygen atoms are coordinated to a common metal centre and each metal centre is thus heptavalent.

Hydrogen bonded contacts (Fig. 2c) between the coordinated water molecule and the amide oxygen atoms of L (average O···O distance = 2.697 Å) constrain the conformation of L and are apparently essential to the formation of the triple helix. Indeed, hydrogen bond formation between water molecules and amide functional groups is an important factor influencing the conformation of biological macromolecules. An additional conformational constraint of L occurs as a result of hydrogen bonding between the amide NH moieties and the coordinated succinate oxygen atoms O(1B) and O(8B) (average N···O distance = 2.985 Å,

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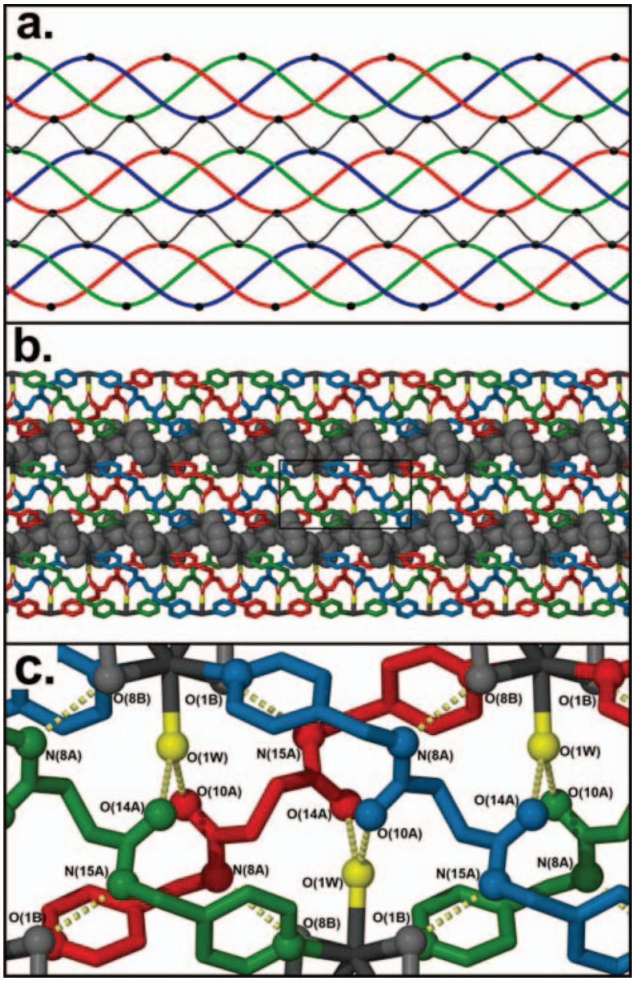

Fig. 2 (a) Schematic diagram showing the single (grey) and triple helices (red, blue and green strands). The Cd^{2+} ions are shown as black circles. (b) A corresponding perspective view of the polymeric complex in capped-stick representation with the exception that the succinate ligand is shown in space filling representation. Hydrogen atoms are omitted for clarity. The inset rectangle is shown magnified in (c) with hydrogen bonds represented as fragmented yellow cylinders.

average M–O distance = 2.476 Å). The two remaining succinate oxygen atoms O(3B) and O(7B) do not participate in hydrogen bonding and their average M–O distance is 2.333 Å.

The single helix is formed between metal centres of two adjacent triple helices and thus serves to bind the latter together to form a two-dimensional coordination polymeric framework. Within each two-dimensional sheet, the single helix as well as the three strands of the triple helix spiral in the same direction. However, the crystal structure is centric, and adjacent layers are enantiomers of one another. Fig. 3 shows how two adjacent layers are stacked relative to one another with only van der Waals interactions occurring between the two sheets. The surface of each sheet is necessarily chiral and the existence of alternating stacks of *M* and *P* conformations implies that each surface is topologically selective towards its enantiomer.

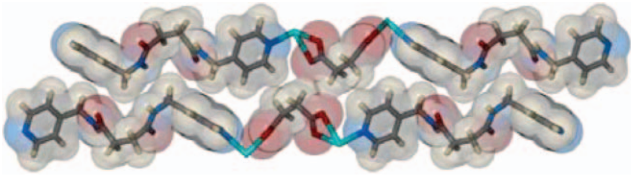

Fig. 3 Perspective view showing stacking of two adjacent, enantiomeric layers of two-dimensional coordination polymeric sheets. The complexes are shown as capped-stick models with semitransparent van der Waals surfaces superimposed.

We believe that the helicity inherent in the structure is due to the combination of two relatively flexible *exo*-multidentate ligands. Both ligands have a strong affinity for the Cd^{2+} metal centres and must therefore adjust their conformations in order to reach a compromise whereby each is coordinatively satisfied by a given Cd···Cd spacing. Indeed, there are several indications of some conformational stress in L. Firstly, although the ligand as shown in Scheme 1 could potentially adopt either C_2 or C_i symmetry, its molecular structure in the crystal is asymmetrical. Secondly, the two CH_2 groups C(11A) and C(12A) are in the *gauche* conformation as might be expected in the most flexible region of a helical conformation, but the torsion angle C(9A)–C(11A)–C(12A)–C(13A) of −71.7° suggests a modest amount of strain. Furthermore, the bond angle N(3A)–Cd(1)–N(20A) of 165.3° deviates considerably from the ideal angle of 180° and enhances the overall twist of the –L–M–L–M– chain in order to accommodate the spatial requirements for triple helicity.

A surprisingly large number of triple helices involving flexible bipyridyl ligands are already known to exist.[9] In the structure of $([Cd(succinate)L]\cdot H_2O)_\infty$ it is interesting to note that, in forming a triple helix, L has also enforced helicity onto the normally non-helical succinate. Although L is much longer than succinate, the two ligands cooperate with one another to share regularly spaced metal centres. This cooperation is achieved by the adjustment of conformational flexibility such that the metal–ligand–metal distances for the different ligands occur as harmonics of one another. As an additional consequence, helicity of one ligand is transferred to the other. To the best of our knowledge, the design of mixed helical motifs is a new concept in crystal engineering

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Notes and references

† Crystal data for $C_{20}H_{24}CdN_4O_7$, M = 544.83, colorless plate, 0.20 × 0.15 × 0.10 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 12.332(12), b = 10.334(10), c = 16.890(17) Å, β = 102.652(16)°, V = 2100(4) $Å^3$, Z = 4, D_c = 1.723 g cm^{-3}, F_{000} = 1104, MoKα radiation, λ = 0.71073 Å, T = 150(2)K, $2\theta_{max}$ = 56.5°, 12333 reflections collected, 4817 unique (R_{int} = 0.0562). Final GooF = 1.022, $R1$ = 0.0495, $wR2$ = 0.1268, R indices based on 3717 reflections with $I > 2\sigma(I)$ (refinement on F^2), 297 parameters, 3 restraints. Lp and absorption corrections applied, μ = 1.091 mm^{-1}. The structure was solved and refined using the SHELX-97 suite of programs[10] and the X-Seed[11] interface. The figures were prepared using X-Seed[11] and POV-Ray.[12] CCDC 260452. See http://www.rsc.org/suppdata/cc/b5/b500235b/ for crystallographic data in .cif or other electronic format.

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