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A triple helix of double helicates: three hierarchical levels of self-assembly in a single structure[†]

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The bis-bidentate bridging ligand L reacts with Ag(1) ions to form a conventional dinuclear $[Ag_2L_2]^{2+}$ double helicate; individual double helicate units assemble *via* Ag···Ag interactions into infinite chains, three of which wrap around a central spine of anions to give a triple helical braid, which is therefore an infinite triple helix composed of molecular double helicate subunits.

Multi-stranded helices as structural motifs in supramolecular chemistry^{1,2} retain the fascination that they have had since the early examples of double³ and triple⁴ helical coordination complexes were reported. There are several reasons for this, including (i) the obvious parallel with the structure of DNA; (ii) the use of helical complexes as a test-bed for improving our understanding of self-organisation and molecular recognition in relatively simple artificial systems; and (iii) the provision of a way of introducing chirality into molecules and molecular assemblies for applications ranging from catalysis to opto-electronics.

The helical structural motif appears in synthetic inorganic systems in two quite different circumstances and on different length scales. The first type of occurrence is in the well-known set of molecular complexes which arise from wrapping two or three flexible, multitopic ligands around a central spine of metal ions, each of which coordinates to one binding site from each ligand, as in Lehn's original examples³ and countless others.¹ The second is less common and occurs in the realm of crystalline coordination polymers, when two or more infinite one-dimensional strands each adopt a helical twist and braid around one another.² In the first case the main driving force is provided by the matching of the coordination preferences of the metal ions which the number and arrangement of binding sites in the ligand: as these factors are relatively strong, directional, and susceptible to some synthetic control, design and synthesis of molecular helicates is now well known.¹ The second manifestation of helicates is rarer and much less susceptible to synthetic control, relying as it does on two things: (i) the adoption of a helically twisted conformation

by one coordination polymer chain, which can be controlled to some extent by judicious ligand design, *and* (ii) weak interactions between two or more chains which result in their association in the crystals, which is beyond our power to control reliably.²

As these two manifestations of helicates have such different origins they are independent of one another. Molecular helicate complexes generally crystallise in an unremarkable way as clearly distinct molecules in the crystal, as they do not have the capacity to form coordination polymers unless there are specific strong interactions between molecular units such as Ag...Ag contacts.⁵ The separate chains that make up multistranded helical coordination polymers are based on a combination of metal ion and bridging ligand that is designed to form a one-dimensional chain, and therefore they bear no particular chemical relationship to helical complexes which are discrete molecular species.

We report here a remarkable example of a crystalline assembly which combines both forms of helical motif on quite different length scales: it comprises triple helical infinite chains in which each of the three infinite strands in the triple helix is formed from end-to-end association of double helical molecular complexes joined by Ag...Ag contacts. It is, in effect, a triple helix of double helicates. It is based on the bridging ligand L in which two bidentate chelating pyrazolyl-pyridine units are connected to a central benzophenone spacer via flexible methylene hinges. With two bidentate sites separated by a flexible spacer this ligand is ideally disposed for formation of dinuclear double helicates with ions such as Ag(I) that commonly form four-coordinate complexes, and the ability of this ligand to form such a helicate will be facilitated by the non-planar diaryl ketone spacer which is a component of other ligands known to form helical structures.⁶



The ligand L was prepared in the usual way⁷ by reaction of 3-(2-pyridyl)pyrazole with 4,4'-bis(bromomethyl)benzo-phenone in basic conditions, and gave satisfactory analytical data. \ddagger A crystal structure was also obtained and is shown in ESI. \ddagger It is unremarkable with a *transoid* arrangement of the two near-planar rings in each pyrazolyl-pyridine fragment, and an

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Fig. 1 ORTEP view of the double helical $[Ag_2L_2]^{2+}$ unit of $[Ag_2L_2](CIO_4)_2$ ·MeNO₂, showing thermal ellipsoids at the 30% probability level; one ligand is shown with paler colours for clarity.

angle of 55.4° between the two aromatic rings of the benzophenone unit which imparts a twist to the ligand.

Reaction of L with AgClO₄ or AgBF₄ in a 1:1 ratio in MeOH/CH₂Cl₂ for 24 h afforded a white precipitate of $[Ag_2L_2]X_2$ (X = BF₄, ClO₄) in each case according to ES mass spectrometry.¶ X-ray quality crystals were grown by diffusion of ethyl acetate vapour into solutions of the complexes in MeNO₂.∥ The two crystal structures are essentially identical; the perchlorate salt $[Ag_2L_2](ClO_4)_2$ ·MeNO₂ has a better refinement so the discussion is focussed on that.

The core of the structure is a conventional dinuclear double helicate (Fig. 1) in which two bridging ligands wrap around two Ag(1) ions, each of which is four coordinate from two pyrazolyl-pyridine chelating units. Ag...N distances lie in the range 2.23–2.38 Å and the angle between the two AgNN planes is 57.9°. The Ag...Ag separation is 11.48 Å, due to the length of the benzophenone spacer, which is oriented such that the ketonic O atoms are directed externally. There are weak inter-ligand interactions such as a CH... π contact between H(62) of one ligand and the aromatic ring C(51)–C(56) of the other [separation between H(62) and plane of aromatic ring towards which it is directed, 3.25 Å]. This double helical unit lies on a twofold axis such that both metal ions are crystallographically equivalent, as are both ligands.

More interesting than the structure of the double helicate is the fact that short Ag···Ag contacts connect these units end-to-end to form a 1-D chain which is itself helical (Fig. 2). This *inter*molecular Ag···Ag separation is 2.99 Å, well within the range of an attractive argentophilic interaction,⁸ and in addition results in aromatic π -stacking between the pyrazolylpyridine groups of each Ag(1) centre (*i.e.* between adjacent double helical subunits, Fig. 2a). The chain is oriented along the *c* axis and forms a shallow helical spiral with a pitch length of 77.25 Å which corresponds to three unit cell lengths in that direction; this involves six double helical complex units to make one complete turn.

Three of these (homochiral) helical chains are entwined around each other to complete the supramolecular organisation in the crystal (Fig. 3). This results in a quasi-cylindrical assembly with a channel down the centre which is occupied by perchlorate ions. The O atoms of these are disordered



Fig. 2 Assembly of double helical $[Ag_2L_2]^{2+}$ units into infinite onedimensional helical chains *via* Ag···Ag contacts: (a) a view showing the interaction between two adjacent helical units; (b) a view showing six helical units which form one complete turn of the helical chain. In both diagrams, alternate ligands are coloured separately for clarity.

over 8 sites (site occupancy 50% each); the Cl···Cl separation between adjacent perchlorate ions is 6.44 Å, which is one quarter of the unit cell length in that direction. Although the O atoms are disordered it is clear that they must lie sufficiently close to inwardly-directed H atoms from the ligands L to participate in CH···O hydrogen-bonding (non-bonded C···O separations ≈ 3.3 Å), particularly involving the methylene groups C(26) and C(36) whose H atoms are inwardly directed. In addition contacts characteristic of CH··· π and π - π interactions between ligand fragments in different strands can be identified. Interestingly the sense of twist of the supramolecular triple helicate (each strand proceeds clockwise as it moves into the page, Fig. 3b) is opposite to the sense of twist in the molecular helical subunits (Fig. 1 and 2). The chiral space group means that all triple-helical strands have the same



Fig. 3 The triple helical array arising from wrapping of three separate infinite strands of double helical subunits (*cf.* Fig. 2) around each other, with each main strand coloured separately for clarity. (a) A space-filling view emphasising of the threefold helical array; (b) an end-on view of the same fragment showing the central cavity down the centre of the helix; (c) a stick diagram from the same perspective as (b), but showing the anions.

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chirality in the crystal which has therefore spontaneously resolved on formation.

The structure of $[Ag_2L_2](BF_4)_2 \cdot MeNO_2 \cdot (H_2O)_{0.33}$ is presented in ESI:†|| it differs from that of the perchlorate salt only in being in a lower symmetry space group such that each $[Ag_2L_2]^{2+}$ unit has no internal symmetry with the two Ag(I) ions (and the two ligands) being crystallographically independent. The $Ag \cdot \cdot Ag$ contacts between $[Ag_2L_2]^{2+}$ units, and the organisation of three of the resulting strands into a triple helical arrangement around a core of counter-ions, are essentially identical to what is observed in $[Ag_2L_2](CIO_4)_2 \cdot MeNO_2$ and again a chiral space group is adopted.

Individually the three different types of interaction resulting in formation of this structure are well known in other contexts. Bridging ligands that wrap around metal ions to assemble into double helicates are commonplace.¹ Argentophilic interactions that connect Ag(1) complexes into chains are also well known,^{2b} with significant recent examples being assembly of Ag(1)-containing double helicates into one dimensional oligomers or polymers (as here).⁵ And finally the presence of weak interactions between coordination polymer chains, leading to formation of multi-stranded helical assemblies in crystals, is known with many recent examples.² What is remarkable about the structures reported here however is the presence of all three levels of supramolecular organisation occurring in the same compound in a clear hierarchical sequence in which there is a nice parallel with the different levels of organisation in a protein. If the structure of the ligand L is analogous to the primary covalent sequence of a protein, then (i) formation of local order (assembly of the double helicate molecule) is akin to secondary protein structure; (ii) Ag. Ag contacts bringing together the locallyordered components into a complete chain corresponds to the tertiary structure (cf. formation of a complete protein subunit); and (iii) the wrapping of three such chains around each other promoted by weak ligand/ligand and ligand/anion interactions, to give an infinite triple helix of molecular double helicates, corresponds to the quaternary structure of proteins in which subunits associate via weak interactions between them. This combination of different types of self assembly at both the molecular and crystal growth levels illustrates the power of self-assembly to achieve order on different scales if only the 'rules' behind self-assembly can be fully understood.

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Notes and references

‡ Synthesis of L. A mixture of 4,4'-bis(bromomethyl)benzophenone (ref. 9) (1.00 g, 2.7 mmol) and 3-(2-pyridyl)pyrazole (ref. 10) (0.78 g, 5.4 mmol; 2 equivalents) in THF (60 cm³) containing aqueous NaOH (2.16 g in 10 cm³ H₂O) was heated to reflux for 20 h. After cooling the solution was filtered, dried with MgSO₄ and reduced to dryness to yield a white powder which was washed with diethyl ether and dried (0.93 g, 1.9 mmol, 70%). ¹H NMR (400 MHz, CDCl₃): 88.65 (2H, ddd, J = 5.2, 1.2, 0.8; pyridyl H⁶), 7.95 (2H, dt, J = 7.9, 1.0; pyridyl H³), 7.77 (4H, d, J = 8.3; benzophenone H), 7.73 (2H, td, J 7.9, 1.8; pyridyl H⁴), 7.49 (2H, d, J 2.3; pyrazolyl H⁵), 6.96 (2H, d, J 2.3 Hz; pyrazolyl H⁴), 5.49 (4H, s; CH₂). ESMS: m/z 497 (M+H)⁺. Anal. Calcd for C₃₁H₂₄N₆O: C 75.0; H, 4.9; N, 16.9%. Found: C, 75.1; H, 4.7; N, 16.7%.

§ Crystal data for L: $C_{31}H_{24}N_6O$, $M = 496.56 \text{ g mol}^{-1}$, orthorhombic, space group *P*bcn, a = 8.5827(3), b = 13.3565(5), c = 21.0613(8) Å, U = 2414.36(15) Å³, Z = 4, T = 100(2)K, λ (Mo-K α) = 0.71073 Å, $\mu = 0.086 \text{ mm}^{-1}$. 19035 reflections were collected ($2\theta_{\text{max}} = 55.2^{\circ}$) which after merging afforded 2792 independent reflections with $R_{\text{int}} = 0.0715$. Final $R1 [I > 2\sigma(I)] = 0.049$; w R_2 (all data) = 0.173 (ref. 11).

¶ Synthesis of complexes. A solution of Ag(ClO₄) (0.018 g, 0.079 mmol) in MeOH (7 cm³) was added to a solution of L (0.040 g, 0.079 mmol) in CH₂Cl₂ (7 cm³). The mixture was stirred at room temperature for 24 h, and the resultant precipitate was filtered off, washed with both MeOH and CH₂Cl₂, and dried *in vacuo* to give { $[Ag_2L_2](ClO_4)^2$ }₂ as a white powder in 67% yield. ESMS: *m*/*z* 1307.9, $[Ag_2L_2](ClO_4)^+$; 604.5, $[Ag_2L_2]^{2^+}$. The tetrafluoroborate salt was prepared similarly using AgBF₄. ESMS: *m*/*z* 1295.7, $[Ag_2L_2](BF_4)^+$; 604.5, $[Ag_2L_2]^{2^+}$. X-ray quality crystals in each case were grown by slow diffusion of ethyl acetate into a solution of the complex in nitromethane: the crystals were hygroscopic when removed from the mother liquor and gave variable elemental analytical data.

|| Crystal data for $[Ag_2L_2](ClO_4)_2$ ·MeNO₂: $C_{63}H_{51}Ag_2Cl_2N_{13}O_{12}$, $M = 1468.8 \text{ g mol}^{-1}$, hexagonal, space group $P6_322$, a = b = 21.5080(7), c = 25.7514(13) Å, U = 10316.5(7) Å³, Z = 6, T = 100(2)K, λ (Mo-K α) = 0.71073 Å, $\mu = 0.714 \text{ mm}^{-1}$. 118981 reflections were collected ($2\theta_{\text{max}} = 46.5^{\circ}$) which after merging afforded 4963 independent reflections with $R_{\text{int}} = 0.0786$. Final $R1 [I > 2\sigma(I)] = 0.095$; wR_2 (all data) = 0.260; absolute structure parameter = 0.07(10) (ref. 11).

Crystal data for $[Ag_2L_2](BF_4)_2$ ·MeNO₂·(H₂O)_{0.33}: C₆₃H_{51.67}Ag₂B₂F₈-N₁₃O_{4.33}, M = 1449.5 g mol⁻¹, hexagonal, space group $P6_3$, a = b = 21.2675(6), c = 25.9142(10) Å, U = 10150.8(6) Å³, Z = 6, T = 100(2)K, λ (Mo-K α) = 0.71073 Å, $\mu = 0.656$ mm⁻¹. 154617 reflections were collected ($2\theta_{max} = 55.3^{\circ}$) which after merging afforded 15618 independent reflections with $R_{int} = 0.0629$. Final R1 [$I > 2\sigma(I)$] = 0.120; w R_2 (all data) = 0.367; absolute structure parameter = 0.20(5) (ref. 11).

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