

Formation of a Dimer of Trinuclear Helicates which Encapsulates an Array of Six Hydrogen-Bonded Anions

Robert A. Faulkner, Lindsay P. Harding, Joshua Higginson, Craig R. Rice,* and Christopher Slater

Abstract: The amine-containing ligand *L*, composed of two bidentate pyridyl-thiazole moieties linked by a 1,3-diaminophenylene unit, reacts with copper(II) ions to form a dinuclear double helicate $[\text{Cu}_2\text{L}_2]^{4+}$. Reaction of $[\text{Cu}_2\text{L}_2]^{4+}$ with dihydrogen phosphate (0.5 equivalents) gives the unsaturated dinuclear double helicate $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$. $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$ further reacts with another 0.5 equivalents of dihydrogen phosphate to give a trinuclear circular helicate which then self-assembles into a hexameric cluster $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}]^{26+}$.

Self-assembly is a process in which large and complex molecular species are spontaneously formed from small subunits which contain sufficient molecular information to assemble into complex architectures.^[1] One area of metallo-supramolecular self-assembly that has received much attention is the design of polynuclear helicates.^[2] These linear structures form by self-assembly and consist of two or more multidentate ligand strands which are helically wrapped around metal cations. Not only can polynuclear double-, triple-, and quadruple-stranded helicates now be made in a predictable fashion, they can also be programmed to express certain structural features of higher-order complexity.^[2] Self-assembly of multidentate ligand strands can also result in the formation of cyclic helicate systems^[3] which are similar to the linear helicates, that is, they retain the “over-and-under” ligand motif requisite of helical chirality. The cyclic oligomers, of general formula $[\text{M}_n(\text{L})_n]$ ($n > 2$), can feature higher-order complexity giving head-to-tail and heteroleptic systems.^[4]

Another area of self-assembly is the formation of hydrogen-bond-directed assemblies, which require molecules containing hydrogen-bond donor and acceptor groups resulting in the self-assembly of discrete molecular species.^[5] For example, the capsules prepared by Rebek et al. are self-assembled species formed by dimerization of two imide-functionalized resorcinarenes by complimentary amide-carbonyl donor–acceptor interactions.^[6] However, generally self-assembly relies on the use of one mechanism to express the chemical information (e.g. either a metallo-supramolecular or hydrogen-bond-directed mechanism). Herein, we

demonstrate how a ligand (*L*), upon reaction with copper(II) ions and OPO_3H_2^- ions, gives a trinuclear circular helicate $[\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3]^{3+}$. The helicate then interacts with another trinuclear assembly through hydrogen-bonding interactions between the P–OH units to give the dimeric assembly $[\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3]_2^{6+}$. The overall self-assembly process is driven by two orthogonal interactions, that is, metallo-supramolecular assembly to give the trinuclear species and subsequent hydrogen-bonding interactions which result in the formation of the dimer. Formations of synthetic supramolecular systems which contain hierarchical levels of self-assembly are rare, with a notable example described by Ward et al. where a Ag^+ -containing dinuclear double helicate forms infinite chains through $\text{Ag}\cdots\text{Ag}$ interactions.^[7] Three of these chains wrap around a central spine of anions (by hydrogen-bonding and $\text{CH}\cdots\pi$ interactions) giving a triple helix of double helicates.^[7] Furthermore, metallo-supramolecular assemblies which form cages that encapsulate oxoanions have also been studied^[8] as well as metal–organic frameworks that contain protonated water clusters.^[9]

The ligand *L* (Figure 1), which contains two bidentate pyridyl-thiazole domains bridged by a 1,3-diaminophenylene unit, was prepared by reaction of phenyl-1,3-diurea and 2-(α -bromoacetyl)pyridine heating in ethanol at reflux. Reaction

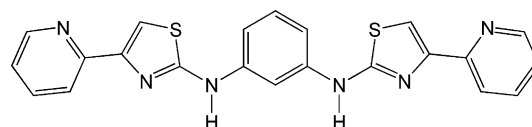


Figure 1. The structure of bis-bidentate ligand *L*.

of the ligand with $\text{Cu}(\text{BF}_4)_2$ in MeNO_2 gives a dark-blue solution from which dark-blue crystals are formed upon diffusion of diisopropyl ether into the solution. Analysis by single-crystal X-ray diffraction showed that in the solid state a dinuclear double helicate ($[\text{Cu}_2\text{L}_2]^{4+}$) is formed (Figure 2).

In the crystal, each of the copper ions adopts a distorted tetrahedral coordination geometry arising from coordination by two pyridyl-thiazole units, one from each ligand (Cu–N bond lengths 1.991 (4)–1.973 (4) Å). The ligands wrap around one another giving a twist indicative of a linear helicate. Self-assembly in such a manner creates a cavity which encapsulates a tetrafluoroborate anion which forms hydrogen bonds between the fluoride atoms and to two of the amines (average (av.) bond length: $\text{N}\cdots\text{F}$ 2.847 Å) and two phenyl hydrogen atoms (av. $\text{C}\cdots\text{F}$ 3.520 Å). As a result of the constraints of the

[*] R. A. Faulkner, Dr. L. P. Harding, J. Higginson, Prof. C. R. Rice, C. Slater
Department of Chemical and Biological Sciences
University of Huddersfield
Huddersfield HD1 3DH (UK)
E-mail: c.r.rice@hud.ac.uk



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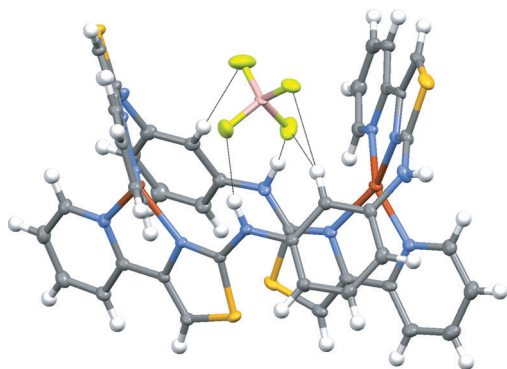


Figure 2. Molecular structure of $[\text{Cu}_2\text{L}_2](\text{BF}_4)_3^{3+}$. Thermal ellipsoids are set at 50% probability and the remaining anions have been omitted for clarity. Atom colors: C = gray; H = white; N = blue; S = yellow; Cu = red; F = green; B = pink.

geometry required to form the helicate, the two remaining amine units do not interact with the anion but point outwards from the complex forming hydrogen bonds with other tetrafluoroborate anions. An essentially isostructural assembly was obtained using $\text{Cu}(\text{ClO}_4)_2$ that is, a dinuclear double helicate that encapsulates a perchlorate anion. ESI-MS analysis gave an ion at m/z 1281 corresponding to the fragment $\{(\text{Cu}_2\text{L}_2)(\text{ClO}_4)_3\}^+$.

Reaction of $[\text{Cu}_2\text{L}_2](\text{ClO}_4)_4$ with $\text{Bu}_4\text{N}(\text{OPO}_3\text{H}_2)$ (0.5 equivalents) in nitromethane and a small amount of methanol (approximately 5% v/v) results in the color of the solution changing from dark blue to light brown. Slow diffusion of ethyl acetate into the solution gave olive-colored crystals which were analyzed by single-crystal diffraction. Examination of the solid-state data shows that a dinuclear double-helicate assembly is still present, for example, $[\text{Cu}_2\text{L}_2]^{4+}$ (Figure 3). In this structure, the ligand partitions into two bidentate pyridyl-thiazole domains, each of which coordinates a different metal ion (Cu–N bond lengths: 1.996(3)–2.357(3) Å). However, unlike the previous structure, the coordination geometry of the metal ions is completed by coordination of a dihydrogen phosphate anion which bridges the two metal ions (av. Cu–OP 1.979 Å).^[10] The coordination sphere is supplemented by weak interactions with oxygen atoms from the perchlorate anions (av. Cu–OCl 2.763 Å) resulting in a pseudo-octahedral geometry. The dihydrogen phosphate ion also forms hydrogen bonds to two of the amines on the ligand unit (average N···O distance 2.745 Å) and, in an analogous fashion to $[\text{Cu}_2\text{L}_2]^{4+}$, the two remaining amines point away from the complex. As further ligands are present completing the coordination geometry of the metal ion, this species is termed an unsaturated helicate.

It is assumed that as there are three perchlorate anions present in the crystal structure, the dihydrogen phosphate is still only mono-anionic.^[10] Analysis of the ESI-MS gave an ion at m/z 1279 which corresponds to $\{[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)(\text{ClO}_4)_2]^{3+}$ and although the masses for OPO_3H_2^- and ClO_4^- are similar, they are sufficiently different to differentiate between the fragments $\{[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)(\text{ClO}_4)_2]^{3+}$ and $\{[\text{Cu}_2\text{L}_2(\text{ClO}_4)_3]^{3+}$.

Reaction of either $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$ with 0.5 equivalents of the dihydrogen phosphate anion (or reaction of one

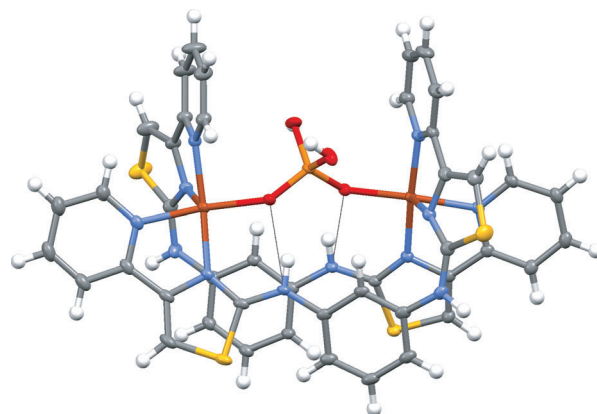


Figure 3. Molecular structure of $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$, showing one dihydrogen phosphate anion which bridges the two Cu centers. Thermal ellipsoids are set at 50% probability and the remaining anions have been omitted for clarity. Atom colors: C = gray; H = white; N = blue; S = yellow; Cu = dark orange; P = light orange; O = red.

equivalent of the same anion with $[\text{Cu}_2\text{L}_2]^{4+}$ in nitromethane and a small amount of methanol (approximately 5% v/v) upon slow diffusion of diisopropyl ether produced light-brown crystals. Single-crystal X-ray diffraction showed that in the solid state an unsaturated trinuclear triple helicate had formed (Figure 4a).

In the solid state, each of the copper ions is pentacoordinate which arises from coordination of two bis-bidentate N-donor units from different ligands (Cu–N bond lengths 1.947(5)–4.9(5) Å) and a monodentate dihydrogen phosphate anion (Cu–OP 1.988(5)–2.008(4) Å).^[11] It is again assumed that the dihydrogen phosphate is mono-anionic as three tetrafluoroborate anions are present within the crystal structure (e.g. $[\text{CuL}(\text{OPO}_3\text{H}_2)]_3(\text{BF}_4)_3$).^[11] The 1,3-diaminophenylene spacers bridge each of the bidentate domains in an “over-and-under” conformation giving rise to the helical cyclic oligomer. From each ligand, both of the amine units form a hydrogen bond to the dihydrogen phosphate anion through different types of interactions. It is not unusual for an anion to induce the change in formation of a linear helicate to its cyclic analogue through either templation^[3b,c] or metal ion coordination.^[3m] However, what is novel is the inclusion of three anions within the central core of the cyclic helicate (rather than a single anion which is usual for cyclic-helicate templation).

It is clear from the dihydrogen-phosphate-bridged double helicate $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$ that there is sufficient conformational flexibility to allow the additional dihydrogen phosphate ions in this structure to occupy the coordination sites previously occupied by the perchlorate anions. The coordination of the two dihydrogen phosphate anions to both metal ion centers does not necessitate the formation of the trinuclear oligomer.

This arrangement is presumably a consequence of hydrogen bonding between the amine $\text{NH}\cdots\text{O}$ and phenyl $\text{CH}\cdots\text{O}$, hydrogen bonding between the ligand strands and the anions (N···O distances 2.890–3.053 Å; C···O distances 3.335–3.471 Å), as well as the H-bonding interactions within the

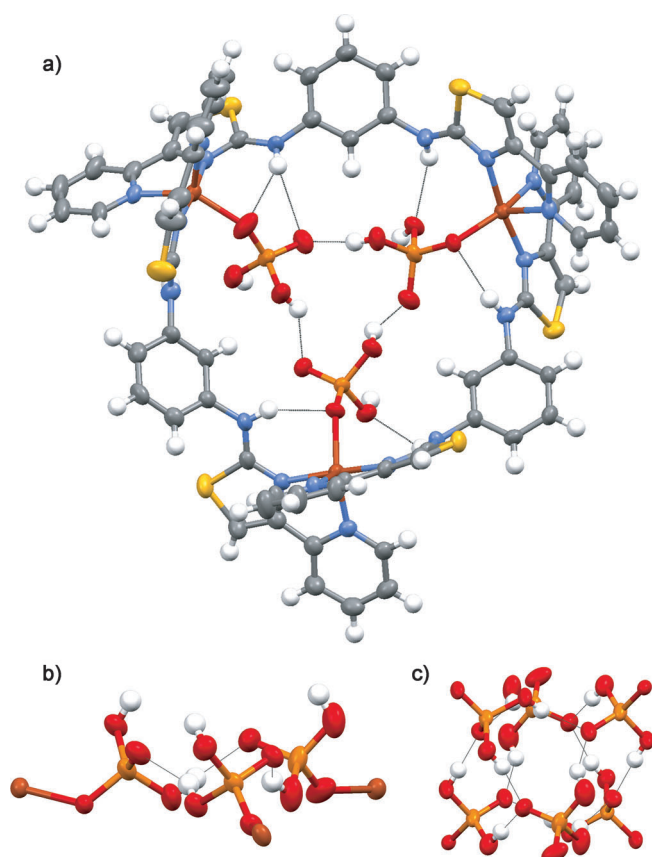


Figure 4. Crystal structure of $[\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3]^{3+}$. a) Top view of the trinuclear circular triple helicate showing the intramolecular hydrogen bonding to three dihydrogen phosphate anions. b) View showing the H-bonding interactions within the cyclic trimer of the three dihydrogen phosphate anions. c) View of the six dihydrogen phosphate anions involved in both intra- and intermolecular hydrogen-bonding interactions. Thermal ellipsoids are set at 50% probability and the remaining anions have been omitted for clarity.

cyclic trimer of dihydrogen phosphate anions ($\text{P}=\text{O}\cdots\text{O}-\text{P}$ distances 2.603–2.680 Å).^[12]

Furthermore, the remaining three $\text{P}-\text{OH}$ bonds not involved in the intramolecular hydrogen bonding all point outwards from the core in the same direction (Figure 4b). The three hydrogen atoms interact with another three oxygen acceptor atoms from the $\text{P}=\text{O}$ bonds encapsulated within another trinuclear oligomer, giving a cyclic array of six ($\cdots\text{HO}-\text{P}=\text{O}\cdots$) donor/acceptor units (Figure 4c). The intermolecular $\text{P}-\text{O}\cdots\text{O}=\text{P}$ distances are in the range 2.546–2.605 Å and are, on average, shorter than the intramolecular distances of the same type. This results in dimerization of the trinuclear circular helicates giving $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}]_2^{6+}$ (Figure 5a–c). Thus a combination of Cu^{2+} and ligand interactions in the cyclic helicate and anion–ligand and anion–anion hydrogen bonds results in this unusual assembly which encapsulates six dihydrogen phosphate anions in a cylinder-like array. ESI-MS showed a signal m/z 1966 which corresponds to $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}(\text{ClO}_4)_2]^+$, a signal at m/z 4036 which corresponds to the dimer $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}_2(\text{ClO}_4)_5]^+$, and a signal at m/z 1279 which corresponds to $[\{\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)(\text{ClO}_4)_2\}]^+$.

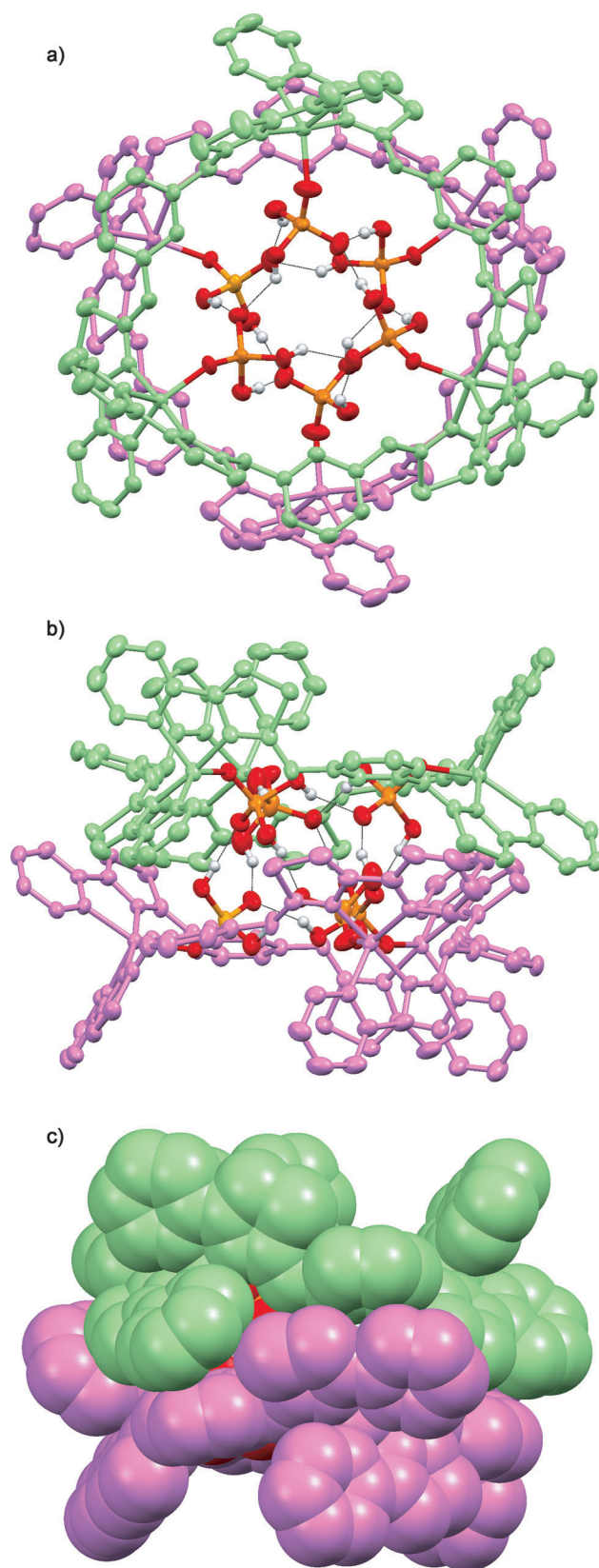


Figure 5. Crystal structure of $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}]_2^{6+}$. a) Top view of the trinuclear circular helicate dimer showing the intramolecular hydrogen bonding. b) Side view of the dimer. c) Space-filling view of the dimer. Thermal ellipsoids are set at 50% probability and the remaining anions have been omitted for clarity. Colors: P = orange; O = red; H = white; one helicate is colored green, the other is colored purple.

It is clear that ligand L upon reaction with Cu^{2+} forms a dinuclear double helicate both in solution and the solid state and, upon reaction with dihydrogen phosphate (0.5 equivalents), an unsaturated dinuclear double helicate is formed. Furthermore, reaction with a further half equivalent of dihydrogen phosphate results in the formation of a trinuclear circular helicate which dimerizes by hydrogen bonding and is formed both in solution and the solid state. However, it is important to note that whilst crystallization of $[\text{Cu}_2\text{L}_2]^{4+}$ results in a homogeneous mass of dark-blue crystals, crystallization of $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$ produces both blue and olive green crystals (from X-ray analysis, the blue crystals correspond to $[\text{Cu}_2\text{L}_2]^{4+}$). Crystallization of $[\{\text{Cu}_3\text{L}_3(\text{OPO}_3\text{H}_2)_3\}]_2^{6+}$ produces olive and light-brown crystals (with the olive crystals composed of the $[\text{Cu}_2\text{L}_2(\text{OPO}_3\text{H}_2)]^{3+}$ complex). This mixture of species indicates that the unsaturated double helicate and the trinuclear circular helicate are in equilibrium and the formation is dependent on dihydrogen phosphate concentration. Regardless, the formation of the hydrogen-bonded dimer of the trinuclear circular helicate does occur both in solution and the solid state.^[13]

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