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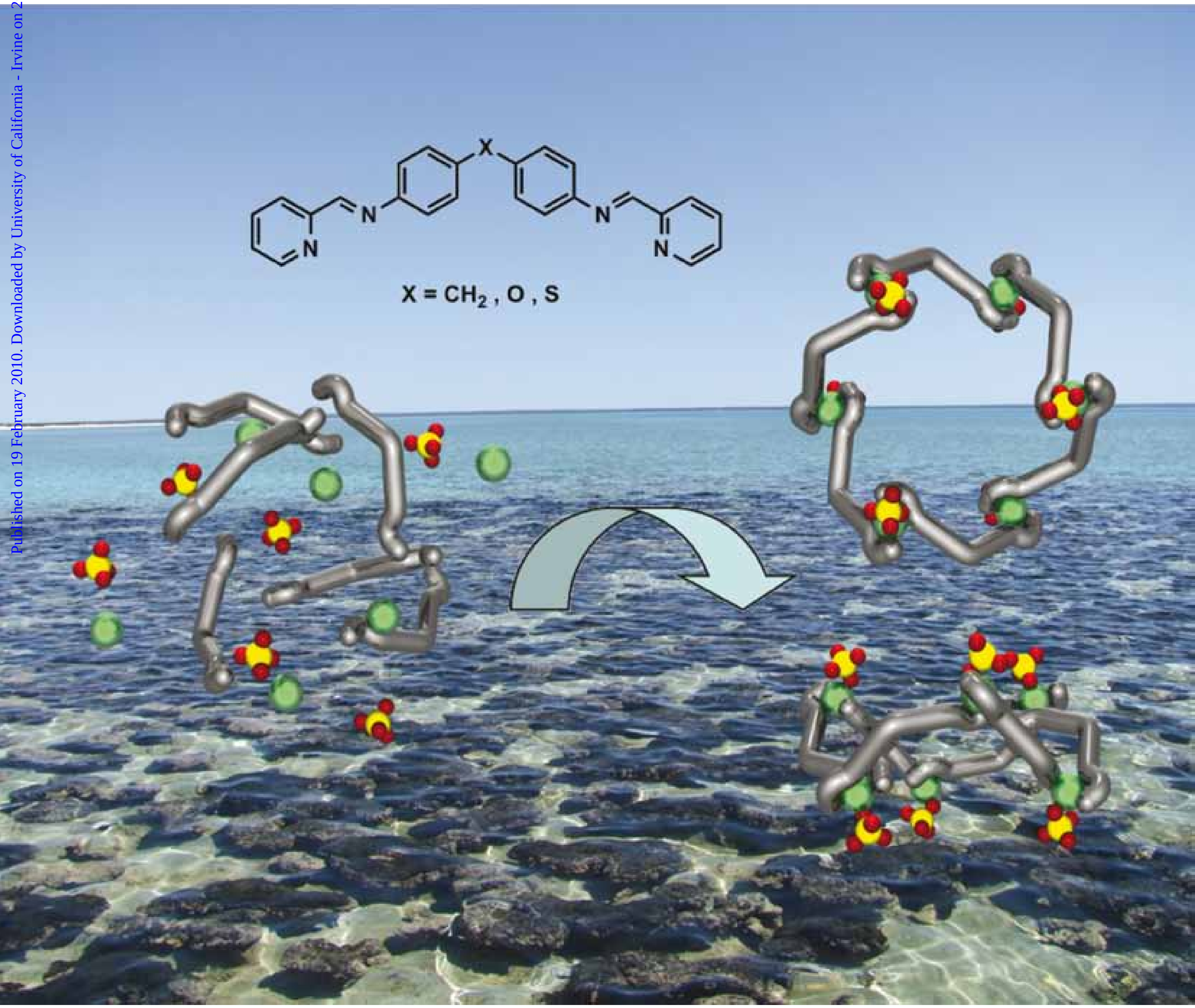

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Self-assembly of neutral hexanuclear circular copper(II) *meso*-helicates: topological control by sulfate ions†

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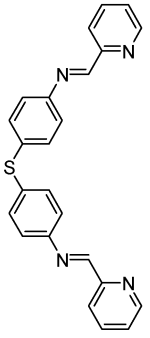
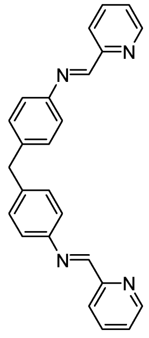
Bis-pyridylimine ligands with different linking elements are capable of forming unique hexanuclear circular Cu(II) *meso*-helicates; the self-assembly is controlled by coordination of sulfate ions to the metal centres.

Nature's most impressive structural motif, the helix, is now established as a versatile building block in the field of metallo-supramolecular chemistry.[1] The spontaneous formation of metal-based helical entities is controlled by the subtle interplay of both geometric influences and the binding preferences of the metal centre as well as by structural features of the ligand: in particular, the inherent disposition of the binding sites and spacer units present. Further factors that may influence the fine tuning of the topology are the nature of the solvent system, the chosen counter anion (if one is required) and the concentrations of the components employed.[2] Since Lehn *et al.* introduced the term helicate,[3] a large number of metal based helicate and related *meso*-helicate architectures with different topologies have been characterized, especially those with double- and triple-stranded arrangements; in comparison the number of circular helicates and *meso*-helicates are quite rare.[2] It remains a challenge to elucidate the principles controlling the self-assembly of metallo-supramolecular systems of both these types. Among the ligand types used for both linear and cyclic helical assemblies with d-block cations multidentate pyridine, imine and related mixed donor systems have been of considerable interest.[4] In a series of seminal publications Lehn *et al.* reported the formation of circular Fe(II), Ni(II) and Cu(I) helicates with 2,2′-bipyridine derivatives;[5] other examples include selected d-block cations in a varying pyridine environment.[6] It is interesting to note that in many of these cases the resulting structures are cationic species, with the counter anions often undertaking a templating role.

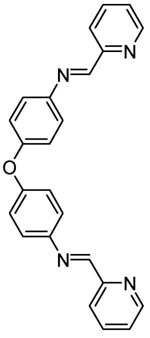
A central goal of our studies is to specify the anion influence on self-assembly processes involving structure-related azaligand systems. Herein we report the syntheses and X-ray crystal structures of three remarkable hexanuclear circular Cu(II) *meso*-helicates with the uniform composition $[CuL(SO_4)]_6{\cdot}24H_2O$, each incorporating the structurally analogous bis-pyridylimine ligands **L**^{1}–**L**^{3}.‡ The latter differ from each other in the linking element (–S–, –CH$_2$–, –O–) present between the two bidentate chelating subunits. These ligands are known for their ability to form double- and triple-helicates, metallacyclic boxes or coordination polymers that depend on the preferred coordination sphere of the metal ion employed.[7] Until now in the case of Cu(II) only the triple-helicate $[Cu_2(L^2)_3](ClO_4)_4{\cdot}3MeCN$ has been reported.[7h]



L^1



L^2



L^3

Reaction of **L**^{1}–**L**^{3} with $CuSO_4{\cdot}5H_2O$ in a MeOH/H$_2$O/MeCN mixture (v/v 2 : 1 : 2) gave brown (**1**) and green complexes (**2**, **3**) of uniform composition $[CuL(SO_4)]_6{\cdot}24H_2O$ in almost quantitative yields. In each case single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the corresponding reaction mixture. All three complexes crystallize isostructurally with one independent [CuL(SO$_4$)] fragment in the asymmetric unit yielding essentially superimposable hexanuclear circular helical arrangements (Fig. 1a) *via* the symmetry operations of space group $R\bar{3}$. The six Cu(II) ions alternately have Λ- and Δ-configurations leading to overall centrosymmetric *meso*-helicates. Two of the six Cu(II) centres are twisted out of plane allowing a chair-like conformation of the complexes (Fig. 1b). The distances of adjacent Cu(II) ions in **1**, **2** and **3** are 12.58, 12.49, and 12.46 Å, respectively, all three being significantly longer than the corresponding distance (11.38 Å) in the triple-helicate species derived from **L**^{2}.[7h] In the title complexes each Cu(II) has a severely distorted octahedral coordination environment involving interactions with two bidentate pyridylimine strands of different ligands and one bidentate sulfate ion (Fig. 1c). This binding pattern leads to a neutral hexanuclear complex with three anions located at the top and three at the bottom of the molecule. The coordinating sulfate anions clearly play a major role in formation of the hexanuclear *meso*-helicates; on changing the anion from SO_4^{2-} to ClO_4^- or NO_3^- only the cationic, non-cyclic triple-helicate

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† Electronic supplementary information (ESI) available: Synthetic procedures, thermogravimetric analysis, additional figures and tables for selected bond lengths and angles. CCDC 732800 (**1**), 732802 (**2**) and 732801 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b925469b

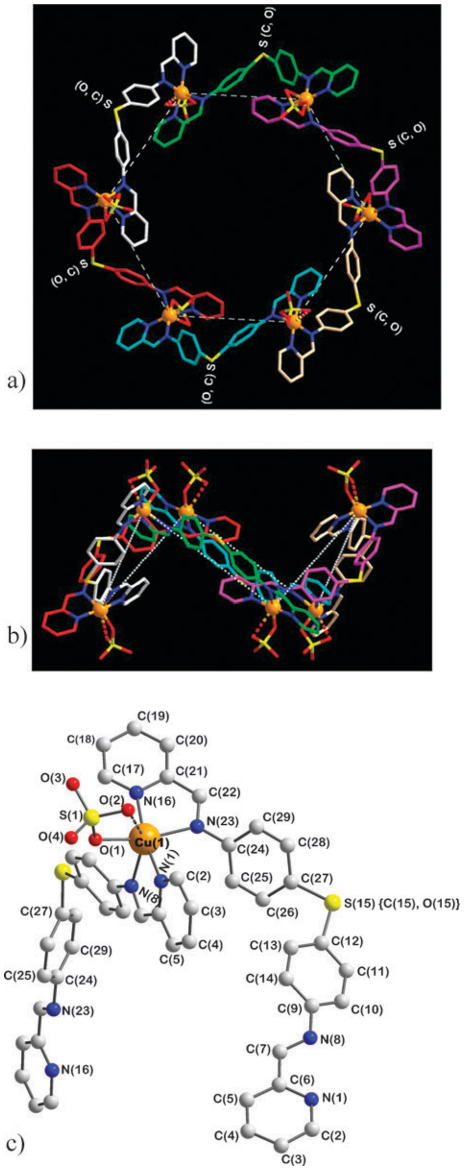

Fig. 1 Molecular structure of the circular *meso*-helicates $[CuL(SO_4)]_6$ showing the hexagonal arrangement (a), the chair-like conformation (b) and the binding mode (c) of a single Cu(II) ion. The ligands are shown in different colours in (a) and (b); Cu in orange, N in blue, O in red, S in yellow. H atoms are omitted for clarity.

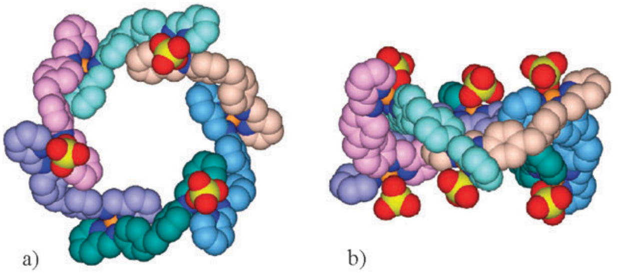

Fig. 2 Space-filling representation of the molecular structure of $[Cu\mathbf{L}^2(SO_4)]_6$: (a) top view; (b) side view. The six ligands $\mathbf{L}^2$ are shown in different colours; Cu in orange, N in blue, O in red, S in yellow. H atoms are omitted for clarity.

$[Cu_2(\mathbf{L}^2)_3]^{4+}$ was formed under the same conditions. As expected, the characteristic bond lengths of the complexes vary with the donor atom type and position, and are in agreement with data for structurally related systems: Cu–$N_{pyridyl}$ (2.02–2.03 Å), Cu–N_{imine} (2.05–2.26 Å) and Cu–$O_{sulfate}$ (1.97; 2.79 Å). Bond lengths are shorter in the equatorial ($2 \times N_{pyridyl}$, $1 \times N_{imine}$, $1 \times O_{sulfate}$) than in the axial positions ($1 \times N_{imine}$, $1 \times O_{sulfate}$) reflecting the presence of Jahn–Teller distortions. In particular, the axial Cu–$O_{sulfate}$ bonds (2.77–2.79 Å) are very weak; each of these oxygen atoms forms one weak hydrogen bond CH···$O_{sulfate}$ (2.47–2.54 Å) to a neighbouring pyridyl unit. In addition, the *meso*-helicates incorporate six weak π–π interactions (Cg2···Cg3: 3.90–3.94 Å) between pyridyl rings of one ligand and xylenyl spacers of an adjacent ligand. The space-filling model of the *meso*-helicate structure (Fig. 2) clearly illustrates the nanometre-scale dimensions of the complex assembly: $d_{cavity} \approx 2.2$ nm, width ≈ 2.5 nm and height ≈ 1.7 nm.

The crystal packing is characterized by a dense supramolecular assembly of puckered hexameric *meso*-helicates with an ABC stacking sequence reflecting the motif of a cubic close packing (Fig. 3). Each sulfate ion is surrounded by hydrogen-bonded disordered H_2O molecules which are mainly arranged in two slightly distorted cubic clusters. One of these clusters is linked *via* additional H_2O molecules to SO_4^{2-} by OH···O hydrogen bonds forming a 3D network. If O···O distances up to 3 Å are considered, each SO_4^{2-} is bound to 4 (**1**, **2**) or 5 H_2O (**3**) molecules. The second cluster is loosely hydrogen bonded to the ligands without connection to SO_4^{2-}. Altogether each complex molecule is linked with six neighbouring molecules in the assembly by 24 moderate (2.19–2.24 Å) and weak (2.41–2.60 Å) CH···O hydrogen bonds involving the sulfate oxygen atoms. Furthermore

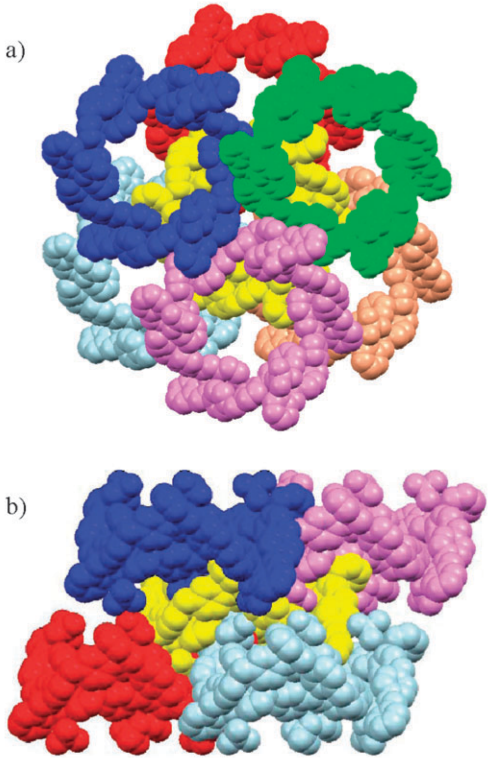

Fig. 3 Dense 3D packing of the *meso*-helicates $[Cu\mathbf{L}^2(SO_4)]_6$ driven by hydrogen bonding and π–π stacking: (a) top view; (b) side view. Each helicate is shown in a different colour. H atoms are omitted for clarity.

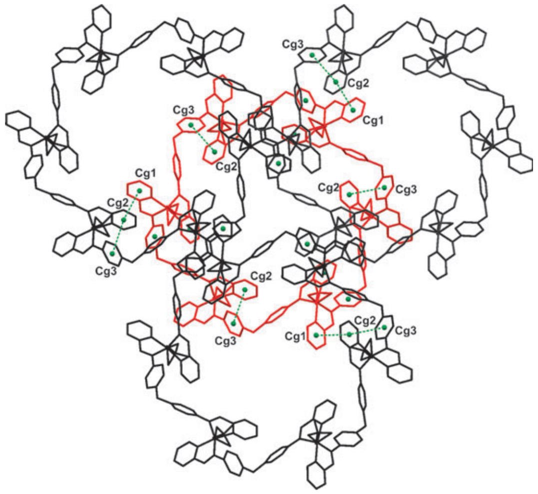

Fig. 4 Representation of a part of the self-assembly of $[CuL^2(SO_4)]_6$ showing the π–π stacking interactions. H atoms are omitted for clarity.

12 relatively strong π–π stacking interactions (Cg1···Cg2: 3.61–3.64 Å) between pyridyl rings of neighbouring molecules stabilize the arrangement (Fig. 4).

The unusual hexanuclear *meso*-helicates are, to the best of our knowledge, the first examples of nanometre-scale neutral circular helicates fully self-assembled around Cu(II) under the influence of hydrogen bonding and π–π stacking interactions. Topological control of the assembly process is clearly associated with the bidentate coordination of the sulfate anions which direct the formation of a double rather than a triple-stranded structure around the octahedrally coordinated Cu(II) centres. Surprisingly, the variation in the linker function on the ligands L^1–L^3, which significantly changes the linking angle of the pyridylimine strands, has little influence on the resulting structures. Finally, it is noted that in work currently in progress, the successful synthesis of a mixed-ligand (L^1 and L^3) Cu(II) *meso*-helicate with a structure related to the above structures has been achieved.

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Notes and references

‡ The X-ray-data were collected on a Bruker-AXS Kappa Apex II CCD diffractometer with an Oxford Cryosystems coldhead attached. Programs used: APEXII,[8] SAINT,[9] SHELX-97,[10] DIAMOND3.1[11] and SADABS.[12] The crystals of **1**, **2** and **3** showed several residual electron density peaks after refinement. Calculations[13] of the voids available for solvents in the structures indicated that each crystal may contain about four water molecules per asymmetric unit, which is in reasonable agreement with the analytical data. Thus the electron density peaks were modeled as disordered water molecules. *Crystal data* for (**1**); $C_{144}H_{156}Cu_6N_{24}O_{48}S_{12}$, M_r = 3756.89, trigonal space group $R\bar{3}$, a = 23.7647(6) Å, c = 25.3824(8) Å, V = 12414.5(6) $Å^3$, T = 173(2) K, λ = 0.71073, Z = 3, ρ_{calcd} = 1.51 g cm^{-3}, $F(000)$ = 5814, $\mu(MoK\alpha)$ = 1.00 mm^{-1}, θ_{max} = 27.50°. 45 135 reflections collected, 6315 unique (R_{int} = 0.045), 353 parameters refined; empirical absorption correction.[12] Final R indices: R_1 = 0.054, wR_2 = 0.158, the final difference Fourier: 1.09/−0.62 e $Å^{-3}$. *Crystal data* for (**2**); $C_{150}H_{168}Cu_6N_{24}O_{48}S_6$, M_r = 3648.68, trigonal space group $R\bar{3}$, a = 23.6595(2) Å, c = 25.3773(4) Å, V = 12302.3(2) $Å^3$, T = 150(2) K, λ = 0.71073, Z = 3, ρ_{calcd} = 1.43 g cm^{-3}, $F(000)$ = 5670, $\mu(MoK\alpha)$ = 0.93 mm^{-1}, θ_{max} = 31.00°. 71 838 reflections collected, 8702 unique [R_{int} = 0.070], 352 parameters refined; empirical absorption correction.[12] Final R indices: R_1 = 0.050, wR_2 = 0.138, final difference Fourier: 0.91/−0.52 e $Å^{-3}$. *Crystal data* for (**3**); $C_{144}H_{156}Cu_6N_{24}O_{54}S_6$, M_r = 3660.53, trigonal space group $R\bar{3}$, a = 23.4688(3) Å, c = 25.3619(5) Å, V = 12097.5(3) $Å^3$, T = 150(2) K, λ = 0.71073 Å, Z = 3, ρ_{calcd} = 1.49 g cm^{-3}, $F(000)$ = 5670, $\mu(MoK\alpha)$ = 0.95 mm^{-1}, θ_{max} = 32.0°. 55 153 reflections collected, 8975 unique [R_{int} = 0.052], 355 parameters refined; empirical absorption correction.[12] Final R indices: R_1 = 0.048, wR_2 = 0.143, the final difference Fourier: 0.89/–0.55 e $Å^{-3}$. CCDC 732800 (**1**), 732802 (**2**) and 732801 (**3**).

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