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# A 3D network of helicates fully assembled by π-stacking interactions

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**The neutral dinuclear dihelicate $[Cu_2(L)_2]\cdot 2CH_3CN$ (1) forms a unique 3D network in the solid state due to π-stacking interactions, which are responsible for intermolecular antiferromagnetic coupling between Cu(II) ions.**

Multidimensional supramolecular architectures assembled from organic molecules and metal ions are currently of much interest in chemistry and materials science.[1] Supramolecular brick walls,[2] cylinders,[3] ladders[4] and multi-helical arrays[5] represent just four examples of this new generation of solids. One possible approach to generate these complicated assemblies was recently reported by M. J. Hannon *et al.*, and consisted of aggregating small supramolecular units into larger arrays using a *second supramolecular event*.[6] The use of supramolecular units as building blocks is an attractive synthetic method since the structural integrity of the discrete pieces can be maintained throughout the reaction, allowing their particular physical properties to be imparted to the final network assembled.[7]

In recent years we have reported a wide number of electrochemically obtained supramolecular helicates based on a terminal-tosyl design approach.[8] We have reasoned that the introduction of a large number of aniline aromatic rings in the ligand strand, that are potentially electron poor ring systems when coordinating to a metal ion, should favour the aggregation of neighbouring helicates through π-stacking interactions.[9] To this end we have designed the ligand $H_2L$ (Fig. 1), which consists of two 2-tosylaminobenzylidenimine binding groups joined by a long and flexible aromatic spacer that is, in addition, an effective moiety to support the self-assembly of metallohelicates.[10,11]

Ligand $H_2L$ was synthesized in 83% yield by Schiff-base condensation of 2-tosylaminobenzaldehyde[8] and 4,4′-methylenedianiline.† Electrochemical oxidation[8] of a Cu plate in a conducting acetonitrile solution of $H_2L$ yielded a red solution from which a red solid precipitated on concentration.

The FAB mass spectrum and elemental analysis are consistent with the formation of neutral dimeric species of formula $[Cu_2(L)_2]\cdot 2CH_3CN$ **1**, due to the bisdeprotonation of the ligand $H_2L$ in the electrochemical cell.‡

Recrystallization of the compound from acetronitrile by slow evaporation afforded dark red crystals from which we determined the molecular structure by X-ray crystallography (Fig. 2).§ The structure reveals the formation of the double stranded dihelicate $[Cu_2(L)_2]$ solvated with two molecules of $CH_3CN$. A racemic mixture of both enantiomers is observed in the unit cell.

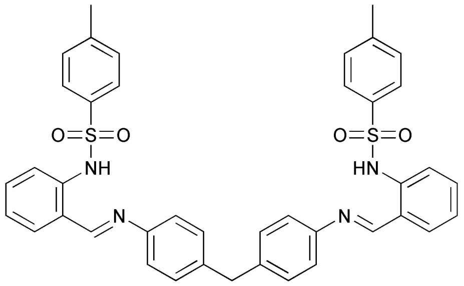

**Fig. 1** Structure of ligand $H_2L$.

Each copper(II) centre occupies a four coordinate distorted tetrahedral environment, being bound by two aminobenzylidenimine units, one from each ligand. Two oxygen atoms from the tosyl groups are weakly interacting with each metal centre (distances Cu–O of 2.62 Å). These distances could be taken as secondary intramolecular interactions, as these occur in other tosyl-derived helicates previously reported.[8] The phenyl rings of the diarylmethane spacer are face-to-face π-stacked with those on the adjacent ligand strand (distance centroid–centroid: 3.88 Å). To achieve this, the two ligand units are pulled symmetrically along the helical axis (distance Cu–Cu = 12.02 Å).

Each dihelicate uses two aromatic rings in the connection with another helical unit, one from the spacer and the other from the benzylidene binding moiety, in a double way interaction. Overall, each helicate is connected with four other molecules, through eight identical offset π–π interactions, forming an unusually compact, ordered and stable molecular solid (Fig. 3). The distance between the centroids of stacked aromatic rings is 4.64 Å. It must be remarked that the assembly of dihelicates is due to a unique supramolecular event: to the best of our knowledge, this is the first example of a 3D network of dihelicates fully assembled by π-stacking interactions. It must be noted that, recently, other 2D and 3D networks based on helicates have been reported.[11] In all these cases the aggregation of the supramolecular units is achieved *via* the complementary work of at least two different kinds of non-covalent interactions.

The distance between the two closest copper(II) centres of stacked helicates is smaller (7.08 Å) than the intramolecular Cu–Cu distance (12.02 Å). Moreover, one can envisage orthogonal sets of Cu(II) "chains", which are potentially connected through π-stacking interactions. In Fig. 3, the red arrows indicate the development of one of these chains, by means of the interaction between the aromatic rings coloured in blue (which of course are at the same time responsible for network assembly).

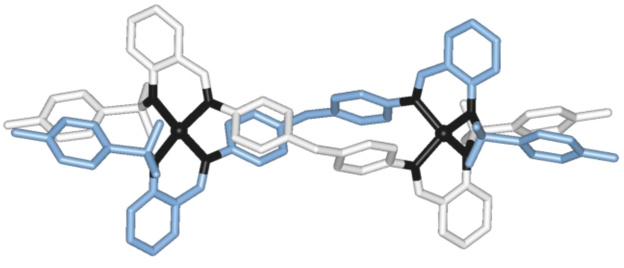

**Fig. 2** Sticks representation of the X-ray crystal structure of the neutral dinuclear double helicate $[Cu_2(L)_2]\cdot 2CH_3CN$ **1**. Solvent molecules have been omitted for clarity.

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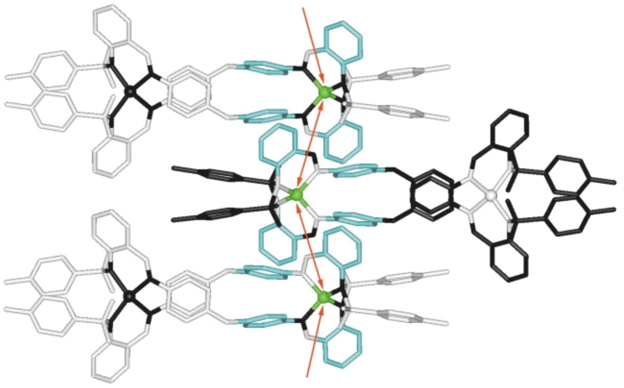

**Fig. 3** Part of the unit cell of **1**, exhibiting π-stacking interactions (in blue) between adjacent dihelicates. This is a 2D representation of the crystal cell, one must consider analogous π–π interactions in the right side of the black dihelicate that grow normal to the plane of the paper. Solvent molecules have been omitted for clarity.

The importance of these interactions is well-evidenced by the analysis of the magnetic properties of the system. Indeed, given the large distance between the Cu(II) ions, the existence of non-negligible antiferromagnetic interaction between them – evidenced by the decrease of $\chi T$ on decreasing temperature (Fig. 4) – is quite surprising at first glance. The only suitable path for the transmission of this interaction is found in the π–π interactions involving adjacent molecular units,[12] resulting in an interpenetrated network of antiferromagnetic chains.

A fit of good quality was obtained by approximating the system with an antiferromagnetic ring[13] of 10 Cu(II) ions and including saturation effects; this yielded as best fit parameters $J = 0.025 \pm 0.01\ \mathrm{cm}^{-1}$, $g = 2.141$ with an agreement factor $R = (N - n_{\mathrm{par}})^{-1}(\Sigma(\chi T_{\mathrm{calc}} - \chi T_{\mathrm{obs}})^2/\Sigma(\chi T_{\mathrm{obs}})^2)^{1/2} = 2.3 \times 10^{-4}$. It should be stressed that the inclusion of saturation effects proved of fundamental importance to obtain a correct estimate of the exchange parameters. Indeed, use of the approximate expression for antiferromagnetic regular chains,[14] which neglects the effect of the magnetic field, yielded an unrealistically large value of $J = 0.6\ \mathrm{cm}^{-1}$ with an agreement factor $R = 8 \times 10^{-3}$. The obtained $g$ value is in good agreement with that obtained from the X-Band EPR spectrum of **1** which has been simulated with $g_x = 2.066$, $g_y = 2.098$, $g_z = 2.278$ ($g_{\mathrm{ave}} = 2.147$), values that are in the expected range for the observed coordination environment of Cu(II).[15] The observation of a rhombic spectrum further supports our hypothesis of the exchange occurring through π-stacking and thus through Cu(II) ions related by an inversion centre which leads to the collinearity of magnetic axes. On the other hand, an angle of 20° between the $z$ axes of the interacting centres would occur if the exchange coupling involved the Cu(II) centres of each molecular unit and the observed exchange coupling would have been large enough to lead to a partial averaging of the anisotropy of molecular $g$ values.[16]

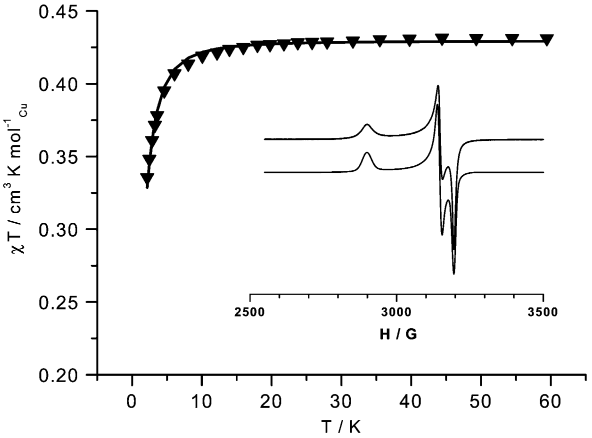

**Fig. 4** $\chi T$ *vs.* $T$ plot of **1** with best fit curve obtained by modelling the system to an antiferromagnetic ring of 10 Cu(II) ions. Best fit parameters are reported in the text. The inset show the low temperature EPR spectrum (upper) and the corresponding simulation.

In conclusion, we have shown how the careful design of a organic ligand allows us to exploit π–π interactions to ensure, at the same time: (i) the formation of a helicate; (ii) the assembly of discrete helical units into a infinite 3D array in the solid state; (iii) the presence of antiferromagnetic interactions between metal centres of the network. We believe that this approach could open some perspectives for programming magnetic coupling through intermolecular pathways.

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## Notes and references

† Selected data for $H_2L$: MS (FAB): *m*/*z* 713.1 {$H_2L$}. Elemental analysis found: C, 69.1; H, 5.2; N, 7.9; S, 8.9. $C_{41}H_{36}N_4O_4S_2$ requires C, 69.1; H, 5.1; N, 7.8; S, 9.0%.

‡ Selected data for $[Cu_2(L)_2]\cdot 2CH_3CN$ **1**: MS (FAB): *m*/*z* 774.2 {CuL}, 1549.5 {$Cu_2L_2$}. Elemental analysis found: C, 63.4; H, 4.6; N, 8.6; S, 7.7. $C_{86}Cu_2H_{74}N_{10}O_8S_4$ requires C, 63.3; H, 4.5; N, 8.6; S, 7.9%.

§ Crystal data for $[Cu_2(L)_2]\cdot 2CH_3CN$ **1**: $C_{86}H_{74}Cu_2N_{10}O_8S_4$, $M = 1630.87$, orthorhombic, space group *Fddd* (no. 70), $a = 17.156(2)$, $b = 21.443(3)$, $c = 41.221(2)$ Å, $U = 15164(3)$ Å$^3$, $D_c = 1.423$ g cm$^{-3}$, $Z = 8$, $\mu$(Cu–K$\alpha$) = 2.256 mm$^{-1}$, 3910 unique reflections of which 2360 assumed as observed ($I > 2\sigma(I)$). Final $R$ indexes ($I > 2\sigma(I)$) $R_1 = 0.0503$, $wR_2 = 0.1367$; $R$ index (all data) $R_1 = 0.1109$. CCDC 207433. See http://www.rsc.org/suppdata/cc/b3/b303549b/ for crystallographic data in .cif or other electronic format.

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