The coordination preferences of metal centres modulate superexchange coupling interactions in a metallo-supramolecular helical assembly[†]

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A method to modulate the strength of the superexchange coupling interaction in dinuclear helical assemblies based on the coordination preferences of the metal centres is described.

Double- and triple-stranded helicates have been extensively investigated in the past two decades as model compounds in metallo-supramolecular chemistry.¹ Although the majority of the studies on helical complexes are focused on understanding the fundamental principles of recognition and self-assembly processes, there is great interest in searching for new functionalities and properties in this class of compounds.^{2–4} In this context, helicates has been used as components in magnetic molecular devices and materials with promising properties.⁵

The recognised synthetic approaches to helicates involve the use of metal-ion induced self-assembly of ligand threads containing repeating donor units of certain denticity, so that the binding abilities of the ligand domains need to match the coordinative requirements of the metal ions. As a result, the careful selection of the metal centres based on their coordination preferences is one of the most important instruments available to control the microarchitecture and shape of helical complexes. This tool has been used, for example, as an engine of molecular-level machines based on helicates³ or in the development of novel synthetic routes to cluster helicates,⁶ but to our knowledge it has never been employed to tune the magnetic properties of a metallo-supramolecular helical assembly.

Currently we are embarked upon an extensive research program that includes the use of helicates in the construction of supramolecular networks,⁷ molecular-level devices,⁴ high-nuclearity metal clusters⁶ or novel magnetic materials.^{5a} In this context, we describe here a method to modulate the strength of

the superexchange coupling interaction in a double-stranded dinuclear helical assembly based on the coordination preferences of the metal centres.

The N_3O_2 pentadentate ligand H_2L (Chart 1), which consists of two 4-methoxybenzyl hydrazinecarboxylate arms joined by a pyridine spacer, was synthesized by Schiff base condensation between 2,6-diacetylpyridine and 2-methoxyphenylcarbazate. Electrochemical oxidation⁶ of a Cu plate in a conducting solution of H₂L in acetonitrile afforded a brown solution, from which a brown solid precipitated upon concentration. The ESI mass spectrum and elemental analysis data for this solid are consistent with the formation of the neutral dimeric species [Cu^{II}₂(L)₂], which arises from the double deprotonation of H₂L in the electrochemical cell. The solid was also characterized by IR spectroscopy. Recrystallization of this complex by slow evaporation afforded brown crystals, from which the molecular structure of the compound was determined by X-ray crystallography.[‡] The structure reveals the formation of a [5 + 5] double-stranded dihelicate $[Cu_2^{II}(L)_2] \cdot 2H_2O$ (1) (Fig. 1 and S1)[†] as a racemic mixture of the two enantiomers.

As observed in the X-ray structure, each ligand strand in **1** uses the carbonyl oxygen and the imine nitrogen atom from one of the bidentate binding domains, together with the pyridine nitrogen of the spacer, to bind one copper centre. A rotation around the adjacent C–C bond in the second domain leads to chelation of the remaining imine nitrogen and carbonyl oxygen atoms to the second copper ion, thus generating the double helical structure. The copper(II) ions exhibit distorted pentacoordinated [N₃O₂] kernels and distorted planar pyramidal geometries ($\tau_1 = \tau_2 = 0.26$). A fourth nitrogen in an axial position is found at a longer distance (2.65 Å). The intramolecular distance between the copper centres is 3.24 Å.

A careful analysis of the bond distances and angles reveals the existence of a certain degree of asymmetry in the helicate, which in turn results in the formation of distinct major and minor grooves (Fig. S2).† Such asymmetry rarely occurs in metallohelicates and is usually related to the inner asymmetry of the wrapping ligands or to the establishment of intramolecular π -stacking contacts.⁸ However, we believe that the asymmetry in **1** must be attributed to the different conformations adopted



Chart 1 Ligand H₂L.

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[†] Electronic supplementary information (ESI) available: Synthesis and experimental data for H_2L and complexes $[Cu_2(L)_2]$, $[Ni_2(L)_2]$. CIF files, ORTEP diagrams, selected bond distances and angles for 1 and 2. Ancillary figures relative to the magnetic studies. CCDC 767303 and 767304. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00338g



Fig. 1 Ball and stick representation of $[Cu^{II}_{2}(L)_{2}] \cdot 2H_{2}O(1)$. Solvated water molecules and hydrogen atoms are not depicted for clarity.

by the terminal methoxybenzyl groups of the two organic strands, which are disposed differently around the metal ions in order to avoid destabilizing steric hindrance.

The Plot of $\chi T vs. T$ for **1** is shown in Fig. 2 and this clearly shows sign of a weak intramolecular antiferromagnetic coupling, with a constant χT value of 0.82 emu K mol⁻¹ (in agreement with two uncoupled S = 1/2 and g > 2.00) between 200 and 40 K with a decrease at lower temperature. The maximum in χ vs. T at 3 K, as well as the inflection point in the field-dependent magnetization plot (Fig. S4 and S5)† at around 4 T, suggest a singlet–triplet separation of 3–4 cm⁻¹. This was confirmed by a fit using the Bleaney–Bowers equation, with best fit values of $g = 2.07 \pm 0.03$, $J = 3.5 \pm 0.1$ cm⁻¹ (H = JS_1S_2 , R² = 0.997). The weakness of this interaction is not surprising, in view of the large distance between the Cu^{II} centres and the expected ineffectiveness of possible superexchange pathways through the non-bonding nitrogen, which would involve pairs of $dx^2 - y^2$ and dz^2 orbitals on the two centres.

Having established the ability of the pentadentate ligand H_2L to form double-stranded [5 + 5] dinuclear helicates with Cu^{II} ions and having also studied the magnetic properties, we decided to explore the possibility of increasing the strength of the intramolecular magnetic interaction between adjacent metal centres in other complexes of this helicand. We reasoned that this could be achieved by replacing the Cu^{II} ions by other metal ions like Ni^{II}, which has a higher preference for an octahedral geometry.^{9–10} It is expected that the only way for H_2L to satisfy the coordination preferences of the Ni^{II} ions would be to include the pyridine donor atom as a bridge between the metal centres, thus leading to an increased



Fig. 2 Plot of $\chi T vs. T$ for **1** (squares, left axis) and **2** (triangles, right axis) along with corresponding best fit curves (parameters reported in the text).



Fig. 3 Ball and stick representation of the helical complex $[Ni^{II}_{2}(L)_{2}]$ (2). Hydrogen atoms are not shown for clarity.

efficiency in the superexchange pathway. This rather unusual arrangement has been reported previously.¹⁰

The Ni^{II} complex of H_2L was obtained electrochemically. Recrystallization of the mother liquors yielded brown crystals of [Ni^{II}₂(L)₂] (2), which were analyzed by X-ray diffraction‡ as well as by ESI mass spectrometry, elemental analysis and IR spectroscopy. The structure reveals the formation of a [6 + 6] double-stranded dinuclear helicate (Fig. 3 and S3).† A racemic mixture of both enantiomers is observed in the crystal cell.

The coordination mode of the ligand in 2 differs from that in 1 in terms of the role played by the pyridine atoms on coordination. Thus, each ligand uses one imine nitrogen atom and one carbonyl oxygen atom to bind one metal centre in 2. A rotation around the C-C bond adjacent to the pyridine ring allows the pyridine nitrogen atom to act as a bridge between the two nickel centres. The values found for the N_{Pv}-Ni bond distances (2.264-2.360 Å) in 2 are in agreement with those reported in the literature.9-10 A further twist around the adjacent C-C bond leads to chelation of the remaining imine nitrogen and carbonyl oxygen atoms to the second nickel centre. This coordination mode gives rise to a distorted octahedral environment [N₄O₂] around each nickel atom. The structural parameters referred to both nickel kernels also indicate an asymmetrical arrangement of the helicands. The metal-metal intramolecular distance is 3.00(2) Å, which is markedly shorter than that found in 1. Such diminution in the intermetallic distance is the result of the establishment of the pyridine bridges, a situation that produces some distortion of the central rhombus Ni1-N_{Py}-Ni2-N_{Py}.

The reduced distance between the metal centres and the existence of a new electronic pathway between them through the pyridine bridges could lead to an enhancement of the intramolecular metal–metal superexchange coupling in the helicate (Fig. 4). As shown by the $\chi T vs. T$ plot (Fig. 2) for 2, the exchange coupling interaction is significantly increased relative to 1. Indeed, the χT value has not reached a plateau even at 300 K, indicating that the two nickel ions are still not fully uncoupled. The relative strength of the antiferromagnetic interaction is further confirmed by the fact that χT is virtually zero below 20 K, indicating a completely populated singlet state at this temperature. Accordingly, a quantitative analysis of the magnetic data gave as best fit values $J = 65.8 \pm 0.7$ cm⁻¹,



Fig. 4 Schematic representation of the approach described herein. The ability of the central pyridine moiety of the helicand to act either as a μ_1 or μ_2 donor based on the coordination preferences of the metal centres is the factor that makes the modulation of the strength of the superexchange coupling interaction in the metallo-supramolecular helical assembly possible.

 $g = 2.30 \pm 0.02$ and the inclusion of a paramagnetic impurity $\rho = 5\%$ (R² = 0.999).

In conclusion, we have shown that the appropriate choice of metal centres with different preferential coordination geometries allows the modulation of the strength of the magnetic exchange in a double-stranded dinuclear helical assembly. To the best of our knowledge, this is the first example of a metallosupramolecular helical entity with tunable magnetic properties. We believe that this approach could open new perspectives for programming magnetic devices and materials based on helicates as we consider that it can be expanded to longer organic strands with more than two binding compartments.

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Notes and references

‡ Crystal data for [Cu₂(L)₂]·2H₂O (1): (C₅₄H₅₈Cu₂N₁₀O₁₄), Mw = 1198.18, crystal dimensions: 0.75 × 0.38 × 0.32 mm³, triclinic, $P\bar{1}$, a = 13.648(3), b = 14.042(3), c = 16.315(4) Å, $\alpha = 106.876(4)$, $\beta = 111.615(4)$, $\gamma = 97.038(4)^{\circ}$, V = 2687.5(11) Å³, Z = 2, $\mu = 0.868$ mm⁻¹, F(000) = 1244.0. Radiation λ (Mo-K α) = 0.71073 Å, T = 293(2) K, reflections collected/unique 19142/9217 ($R_{int} = 0.0875$),

 R_1 (obs data) = 0.0823, w R_2 (all data) = 0.2282, GOF = 1.099, max/min residual density 1.155/-1.362 e Å⁻³. CCDC 767303.

Crystal data for [Ni₂(L)₂] (**2**): (C₅₄H₅₄Ni₂N₁₀O₁₂), Mw = 1152.49, crystal dimensions: $0.27 \times 0.21 \times 0.14 \text{ mm}^3$, triclinic, $P\overline{1}$, a = 14.798(3), b = 14.821(3), c = 15.663(3) Å, $\alpha = 106.501(4)$, $\beta = 115.704(3)$, $\gamma = 101.319(4)^\circ$, V = 2757.4(10) Å³, Z = 2, $\mu =$ 0.75 mm^{-1} , F(000) = 1200. Radiation λ (Mo-K α) = 0.71073 Å, T = 100(2) K, reflections collected/unique 31621/11272 ($R_{\text{int}} =$ 0.0558), R_1 (obs data) = 0.0428, w R_2 (all data) = 0.1041, GOF = 1.031, max/min residual density 0.719/-0.409 e Å⁻³. CCDC 767304.

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