

Structure and properties of a new double-stranded tetranuclear $[\text{Cu}^{\text{II}}_2]_2$ helicate†

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A novel double-stranded tetranuclear helicate composed of a pair of $[\text{Cu}^{\text{II}}_2]$ dimers has been prepared and characterized by exploiting the flexibility, chelating ability and bridging potential of a hexadentate bis-oximate ligand.

The group of multimetallic helicates is a consolidated family within the area of supramolecular coordination chemistry.^{1,2} Identification of the stereochemical preferences of metal ions in combination with the appropriate binding possibilities of ligands has led to a large variety of such complexes, most of which are di- or trinuclear and where, with few exceptions,^{3,4} the principle of maximization of site occupancy is fulfilled. Cluster helicates constitute an emerging and sophisticated subgroup of compounds within the family of metallohelicates.^{5–7} Since very few examples exist which have been identified as such, a precise definition is not currently available. Finding one is indeed a challenging enterprise given the increased complexity of these compounds. A possible way of doing this is by accommodating the existing definition² for conventional helicates (*i.e.* a discrete helical supramolecular complex constituted by one or more covalent organic strands wrapped about and coordinated to a series of ions defining the helical axis; see Scheme 1, left) and adding to it the condition that the ions must group into aggregates that repeat themselves along the helical axis. The examples claimed so far to be in this category indeed display clusters of interacting ions defining a helical axis, but these clusters are not truly differentiated into equivalent units disposed along this axis. We report here the first tetranuclear helicate composed of two well defined (dinuclear) groups of interacting metals defining the helical axis and wrapped by two symmetric ligand strands (Scheme 1, right).

We have been using for some time large polydentate ligands as a way to assemble Cu^{II} ions into aggregates with relevance in areas such as bioinorganic chemistry^{8,9} or molecular magnetism.^{9,10} The



Scheme 1 Chart for a double-stranded dinuclear helicate and a double-stranded cluster helicate.

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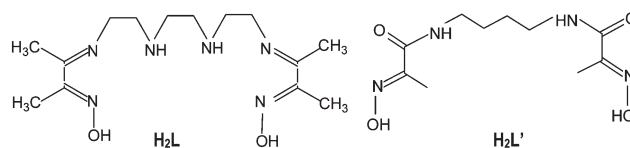
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focus here is on a hexadentate amine/imine ligand, H_2L ,[‡] incorporating two oxime functionalities (Scheme 2). Oximes have shown promise as bridging ligands for the preparation of polynuclear complexes.^{11,12} Ligand H_2L is known to bind cobalt and nickel centers octahedrally with two pendant uncoordinated oxime oxygen donors.^{13,14} On the other hand, the related bis-oxime ligand $\text{H}_2\text{L}'$ (Scheme 2) has been shown to react with Cu^{II} ions to give a double-stranded non-helical dinuclear complex of the type $[\text{Cu}_2(\mu_2\text{-L}')_2(\text{H}_2\text{O})_2]^{2+}$.¹⁵ It was hoped that the greater flexibility of H_2L would allow the oxime oxygen atoms to become involved in the coordination.

The reaction of H_2L with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the presence of NEt_3 led to the assembly of the tetranuclear complex $[\text{Cu}_4(\mu_4\text{-L})_2](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O} (1 \cdot 2\text{H}_2\text{O})$ according to the very simple chemical equation below (eqn (1)). $2\text{H}_2\text{L} + 4\text{Cu}(\text{ClO}_4)_2 + 4\text{NEt}_3 \rightarrow [\text{Cu}_4(\mu_4\text{-L})_2](\text{ClO}_4)_4 + 4(\text{NH}_4\text{Et}_3)(\text{ClO}_4)$.

The cation of **1** (Figs. 1 and 2, see also Figs. S1 and S2†) consists of two pairs of bis-oxime bridged (in a head-to-tail manner) Cu^{II} ions wrapped around and linked together in a helical fashion by two deprotonated ligands L^{2-} , thus forming a double stranded



Scheme 2 Oxime ligands H_2L and $\text{H}_2\text{L}'$.

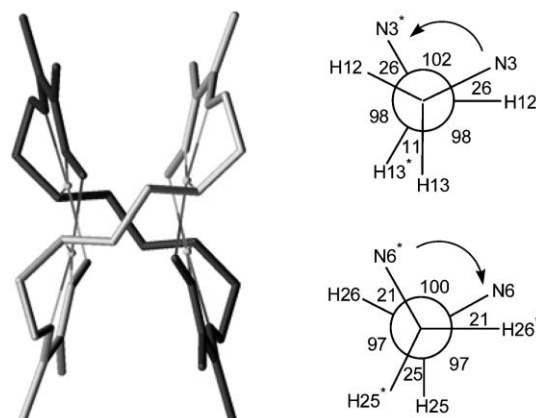


Fig. 1 Left: stick representation of the molecular structure of $[\text{Cu}_4(\mu_4\text{-L})_2]^{4+}$ (the cation of **1**) emphasizing the double-stranded helical arrangement of two ligands (in light grey and dark grey). Right: stereochemistry (*gauche* conformer) of the central ethylene spacers of the ligands in **1** as indicated by Newman projections.

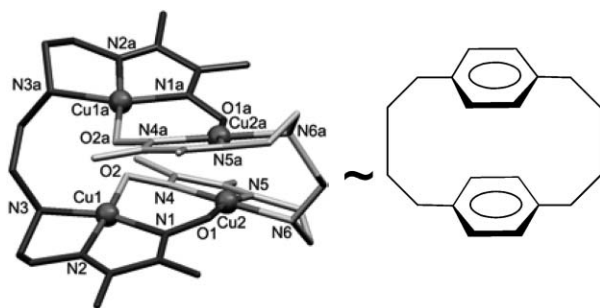
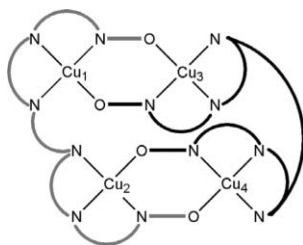


Fig. 2 Left: labelled stick representation of the molecular structure of $[\text{Cu}_4(\mu_4\text{-L})]^{4+}$ (the cation of **1**) with ligand strands highlighted (in light grey and dark grey). Cu atoms are shown as balls. Hydrogen atoms are not shown. Selected distances (Å) and angles (deg); N1–Cu1–O2, 106.3(1), N4–Cu2–O1, 106.9(1), Cu1–O2–N4, 116.7(2), Cu2–O1–N1, 117.8(2), Cu2–N4–O2, 127.7(2), Cu1–N1–O1, 127.4(2), N1–Cu1–N2, 79.0(1), N2–Cu1–N3, 84.0(2), N3–Cu1–O2, 90.7(1), O1–Cu2–N6, 88.2(1), N5–Cu2–N4, 80.2(1), N5–Cu2–N6, 84.3(2), Cu1···Cu2, 3.606(7), Cu2···Cu2a, 3.268(6), Cu–O_{ave}, 1.914(3), Cu–N_{ave}, 1.993(4). [Symmetry code a: $-x, y, \frac{1}{2} - z$.] Right: scheme of a conventional *p*-cyclophane, showing its analogy with the new metallacyclophane **1**.

helicate of two $[\text{Cu}^{\text{II}}_2]$ pairs. In a recent report a strategy for making cluster helicates was proposed that consisted of introducing a pendant soft donor to a polydentate ligand thereby forming neutral dinuclear helicates with M^{II} atoms, while producing uncharged tetranuclear cluster helicates with soft M^{I} ions. The preparation of **1** shows that electroneutrality does not need to be the driving force behind the formation of such types of species. The assembly of this new example of cluster helicate comes about thanks to the presence of functional groups providing the link between metals within the repeating cluster, $[\text{Cu}_2(\mu\text{-NO})_2]$, in combination with enough flexibility in order to ensure the formation of the helicate (Scheme 3). This flexibility arises in part from the presence of the central ethylene diamine moiety of the ligand, which contributes to helicity by exhibiting a much larger (101.94°) N–C–C–N torsion angle (Fig. 2, right) than observed for this type of ligand in mononuclear compounds (37.74°).¹⁶ Each ligand is thus acting in a $\mu_4\text{-L}^{2-}$ fashion, both halves being symmetrically related and each chelating a Cu^{II} ion through three N-donors and binding another one *via* the O-atom from the corresponding oxime group.

The cation of **1** can also be viewed as the first example of a metallacyclic *para*-cyclophane coordination complex (Fig. 2, left). The hexagonal $\text{Cu}_2\text{N}_2\text{O}_2$ metallacycles composing this cyclophane are disposed face-to-face in a non-eclipsed fashion, separated by 2.921 Å on average and displaying a 1,4-O,O-boat conformation (see caption of Fig. 2 for parameters within the ring). It is



Scheme 3 The $[\text{Cu}^{\text{II}}_2]_2$ helicate.

interesting to note that the Cu···Cu distance within the boat is significantly longer (3.606(7) Å) than one of the inter-dimer Cu···Cu distances (3.268(6) Å). The shortest inter-ring Cu···O distances are in the range 2.438–2.500 Å and these define weaker interactions which are undoubtedly determining the mutual orientation of both rings (Fig. 2, left). The coordination geometry around the metal ions is essentially square planar (square pyramidal if the longer inter-ring Cu···O interactions are taken into consideration). The main parameters around the metals are summarized in the caption of Fig. 2. The C–N and N–O distances of the oximate ($-(\text{CH}_3)\text{C}=\text{N}-\text{O}$) moieties are in the range of 1.288(5) to 1.294(5) and 1.346(4) to 1.347(4) Å, respectively. These distances are consistent with the deprotonated form of the oxime functionalities.^{17–19} The C=N_{imine} distances (1.263(6)–1.270(6) Å) are significantly shorter than the C=N_{oximate} distances. The average Cu–O bond distance (1.914(3) Å) is significantly shorter than that of Cu–N (1.992(4) Å) distance as expected from the electronegativity considerations. The average Cu–N_{imine} (1.943(4) Å) and Cu–N_{amine} (2.031(4) Å) distances are distinctly different. Cu–N_{amine} distances are in the usual range for a bivalent metal ion and are not longer due to their participation in bridging. In the crystal lattice, the tetranuclear helicates are stacked along the *c*-axis with the perchlorate ions in between, as shown in Fig. 3. The dotted lines indicate potential H-bonding interactions.

Variable-temperature magnetic susceptibility measurements of compound **1** were performed in the 2–300 K temperature range under the influence of a constant magnetic field of 1 T. The molar paramagnetic susceptibility, χ_{m} , was obtained after correction for the diamagnetic contribution from the sample ($-725 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) by use of Pascal's constants and subtraction of a temperature independent paramagnetism (TIP) parameter ($240 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$). The results are represented in Fig. 4 as a χ_{m} vs. *T* plot. In this plot, the value of χ_{m} remains very low over most of the temperature range (approximately $2.7 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$) and increases dramatically in the vicinity of 20 K. This reflects the fact that the magnetic behavior of the title complex is determined by very strong antiferromagnetic interactions within the molecule. Molecular paramagnets displaying strong antiferromagnetic exchange show a maximum of the χ_{m} vs. *T* plot. The inset of Fig. 4 shows that this maximum for compound **1** is probably located just above 300 K. The coupling within this compound can be described by the simplest possible Heisenberg Spin Hamiltonian

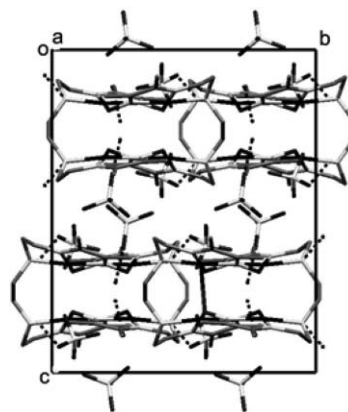


Fig. 3 Packing diagram of **1** projected along the *a*-axis. Dotted lines indicate H-bonding interactions.

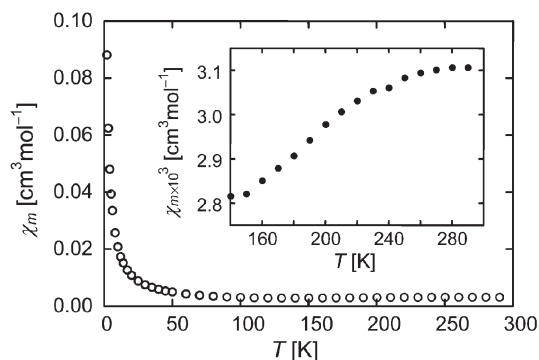


Fig. 4 Plot of χ_m vs. T for compound **1**. The inset shows an expansion of the data above 140 K, to emphasize the maximum of χ_m near room temperature.

multiplied by 2 in order to account for the two dimers: $H = 2 \times [-2JS_1S_2]$. This is because the coupling between the dimers is expected to be negligible in front of the strong intradimer antiferromagnetism. Indeed, the Cu(II) ions of different pairs are only connected by the ethylenediamine-type bridges or very long axial Cu \cdots O interactions and initial attempts to include this interaction in a model to fit the data were indifferent to its J value. The above Hamiltonian was solved by use of the Kambe vector coupling approach²⁰ and the Bleaney–Bowers equation was fit to the experimental data. This calculation was made for the data in the temperature range 140–300 K, where the contribution of the paramagnetic impurity to the susceptibility of the system was considered negligible (see Fig. S3 for $\chi_m T$ vs. T). The fit provided a $2J$ value of -286.0 cm^{-1} , where a g value of 2.09 had been used as obtained from X-band solid state EPR measurements. As expected, the magnetic interactions between Cu(II) ions within each pair is strongly antiferromagnetic. The coupling takes place by super-exchange *via* the σ -framework of the oximate moieties, which bridge the metals in a basal–basal manner. Since the magnetic orbital in axially elongated Cu(II) is primarily of $d_{x^2-y^2}$ character, only spanning equatorial positions, the (through ligand) overlap between magnetic orbitals is very high and the resulting coupling thus very strong. The magnitude of the coupling, however, was found to be weaker than most previous examples of such bridged Cu^{II} pairs, usually displaying J values stronger than -500 cm^{-1} .^{21,22} This is caused, presumably, by the deviation from planarity of the Cu–(NO)–Cu moieties, as gauged by the Cu–N–O–Cu torsion angle, which diminishes the overlap between magnetic orbitals. In the present case, the distortion is significant with torsion angles of 36.08 and 72.81°, respectively.

In conclusion, we have described the preparation and structure of a novel double-stranded tetranuclear [Cu^{II}₂]₂ helicate. Magnetic studies show that the metal ions composing the tetranuclear assembly within the helicate are strongly interacting (antiferromagnetically). This is a promising contribution to this emerging sub-field within coordination supramolecular chemistry, which aims at combining the advantages of structural control and diversity attained within supramolecular edifices with the properties arising from the interaction of metals within polynuclear assemblies.

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Notes and references

‡ 3,14-Dimethyl-4,13-diaza-7,10-diazahexadeca-3,13-diene-2,15-dione dioxime.

§ Crystallographic data for **1**·2H₂O: C₂₈H₅₆N₁₂O₂₂Cl₄Cu₄, $M_r = 1308.81$, monoclinic, space group $C2/c$ (No. 15), $a = 22.032(4) \text{ \AA}$, $b = 13.538(2) \text{ \AA}$, $c = 16.990(3) \text{ \AA}$, $\beta = 100.96(1)^\circ$, $V = 4975.2(15) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.747 \text{ g cm}^{-3}$ and $Z = 4$. With the use of 5828 unique reflections ($I \geq 2\sigma(I)$) collected at 298 K with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) out to $\theta = 27.5^\circ$ on a single-crystal X-ray diffractometer, the structure was solved on a PC 486 using the DIRDIF92-PATY programme system and refined by full-matrix least squares methods. The refinement converged to final $R1 = 0.0390$, $wR2 = 0.0430$ ($I > 2\sigma(I)$); and $\text{GOF} = 1.034$ with the largest difference peak and hole as 0.64 and -0.44 e \AA^{-3} respectively. CCDC reference number 264417. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514126e

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