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Proton-controlled inter-conversion between an *achiral* discrete molecular square and a *chiral* interpenetrated double-chain architecture

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Proton-controlled reversible inter-conversion between an *achiral* Cu^{II} molecular square, and a 1D spontaneously resolved *chiral* interpenetrated double-chain with Cu_4 cavities, based on bis(3-propionyloxy)-1,5-diazacyclooctane (H_2L), has been successfully achieved.

One of the ultimate goals of supramolecular chemistry is to control the structure of target products with desired functions. In most earlier studies this has been reliant mainly on spontaneous self-assembly.[1] Concurrent with this has been the development of polymeric architectures, such as molecular squares,[2] especially frameworks with chiral cavities.[3] As a further development of this fascinating area, metal complexes capable of reversible inter-convertion by inputting external information (*e.g.* protons) would be most interesting and challenging,[4] and might afford new functional materials with switching ability.

The carboxylate group has been proved to be a versatile ligand displaying a variety of coordination modes.[5] In addition, the work by us and others[6,7] has shown that diazamesocyclic ligands, such as 1,5-diazacyclooctane (DACO) modified by appropriate donor pendants, could be good building blocks for constructing polynuclear systems with unique structures and functions. Thus, we anticipated that the incorporation of the carboxylate group on DACO could lead to fascinating structures upon complexation with metal centers, and a unique tetrameric Ni^{II} cluster with planar triangular topology has been reported recently.[8] Here we report the successful realization of the reversible inter-conversion, *in a controlled manner*, between an *achiral* molecular square $[Cu(\mu\text{-H}\mathbf{L})(H_2O)_{0.5}]_4(ClO_4)_4$ **1** and a *chiral* double-chain motif $\{[Cu_3(\mu\text{-}\mathbf{L})_2Cl](ClO_4)_2(H_3O)_2Cl_\infty$ **2** ($H_2\mathbf{L}$ = bis(3-propionyloxy)-1,5-DACO).

The versatility of $H_2\mathbf{L}$[8] and the selection of experimental conditions (pH value) give rise to two different species that can be inter-converted.† Complex **1** (dark-blue) was synthesized by reacting $Cu(ClO_4)_2$ with $H_2\mathbf{L}$ in MeOH/H_2O. When the pH value of this solution is raised by the addition of KOH, a color change from dark to light blue is observed. The pH dependence of the electronic spectra obtained upon dropwise addition of aqueous solution of KOH to the MeOH solution of the crystals of **1** up to pH = 5.7 was studied. The original UV–vis spectrum of **1** (λ_{max} 653 nm) changes to that of a new species **2** (λ_{max} 620 nm). Conversely, when an aqueous HCl solution is added to the resulting solution of **2**, the intensity of the *d–d* band absorption at 620 nm for **2** decreases and that of the *d–d* band around 653 nm for **1** increases. This indicates that varying the proton content can control the inter-conversion between **1** and **2** in the solution.

The crystal structures of **1** and **2**‡ afford illuminating pictures of the molecular square and 1D double-chain motif. **1** consists of a *syn–anti* carboxylate-bridged cyclic tetranuclear cation $[Cu(\mu\text{-HL})(H_2O)_{0.5}]_4^{4+}$ with S_4 symmetry (Fig. 1) and ClO_4^-. Each Cu^{II} center exhibits distorted square-pyramidal (CuN_2O_3) coordination geometry with both nitrogen atoms of the same $H\mathbf{L}^-$ ligand and two oxygen atoms of different $H\mathbf{L}^-$ occupying the basal positions, and an aqua moiety at the apical site. It is interesting that the ligand $H_2\mathbf{L}$ is mono-deprotonated in **1**: the deprotonated carboxylate groups and Cu^{II} ions form a 16-membered ring $(\text{–Cu–O–C–O–})_4$with the four Cu^{II} ions located at the corners of a flattened square. The adjacent Cu···Cu distance in this square is 4.693 Å and the diagonal separation is 6.584 Å. There is no close intermolecular contact in the unit cell, consisting of a packing of well-isolated tetrameric cations (the shortest intermolecular Cu···Cu length is 8.765 Å) and ClO_4^-.

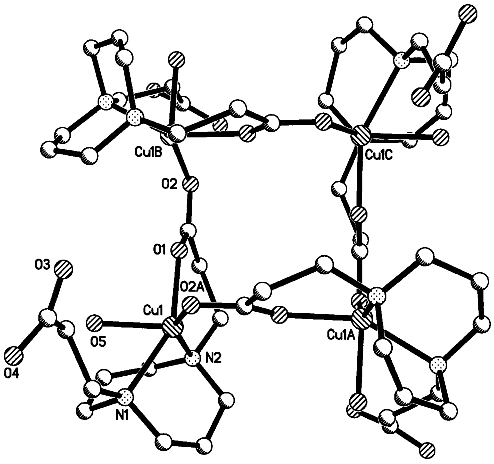

Fig. 1 Structure of the tetranuclear $[Cu(\mu\text{-HL})(H_2O)_{0.5}]_4^{4+}$ cation in **1**.

Complex **2** is a conglomerate composed of *spontaneously resolved chiral* crystals (space group $P2_12_12_1$ with Flack parameter of 0.02(3), indicating that each individal crystal of **2** consists of a single enantiomer in the solid state, however, the question of whether the single enantiomer undergoes racemization in solution still remains unsolved because the individual *chiral* crystals are too small to allow any meaningful circular dichroism measurement).[9] The structure is composed of interlinked adjacent tetranuclear Cu_4 subunits that share the common Cu2 center, forming a 1D chain with a cavity, in which the carboxylato ligands act in the *syn–anti* mode. Another alternative description, perhaps more revealing, is to consider two almost perpendicular 1D chains linked through the common Cu2 ions to form a unique interpenetrated double-chain topology (Fig. 2). Chain *A* is made up of Cu1–Cu2–Cu1–Cu2··· and chain *B* of Cu3–Cu2–Cu3–Cu2···. There are thus three

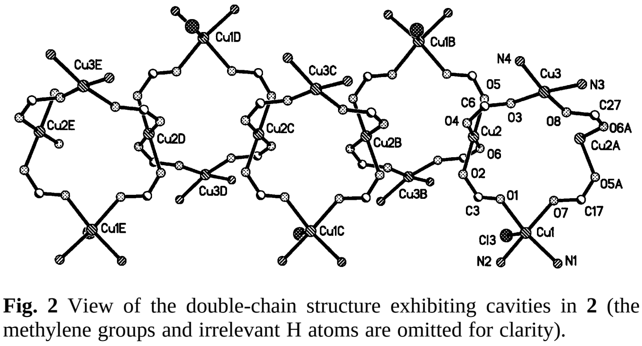

Fig. 2 View of the double-chain structure exhibiting cavities in **2** (the methylene groups and irrelevant H atoms are omitted for clarity).

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kinds of non-equivalent Cu^{II} atoms: the environment of Cu1 is square pyramidal with Cl3 occupying the axial position, Cu2 is square planar (with two additional ClO_4^- oxygen atoms in a pseudo-octahedral geometry) and Cu3 is distorted square planar with an additional apical Cu3–O12 weak interaction (2.687 Å). In chain *A*, the adjacent Cu1$\cdots$Cu2 distances are 5.111 and 5.136 Å, and in chain *B* the adjacent Cu2$\cdots$Cu3 separations are 5.036 and 5.010 Å, consecutively. This unique chiral 1D topology may be applicable in enantioselective recognition or inclusion.[3]

The temperature dependences of $\chi_M T$ for **1** and **2** are characteristic of intramolecular ferromagnetic interactions (Fig. 3). For **1**, the additional decrease in $\chi_M T$ at low temperature indicates a small intermolecular anti-ferromagnetic interaction and/or the presence of *ZFS* in $S = 2$ ground state. These data were further confirmed by the reduced molar magnetization curves at 2 K from 0 to 5 T. For **1**, the curve indicates a balance between the intermolecular antiferromagnetic interactions active at low field and intramolecular ferromagnetic interactions at high field. For **2**, the curve indicates the presence of active ferromagnetic coupling that is independent of the magnetic field. To fit the magnetic data of **1** we used the equation[10] for an isolated Cu$_4$ square system in which weak intermolecular interactions (J') superimpose on a dominant intramolecular isotropic interaction (J) in a tetranuclear unit.[11] The best-fit parameters are $J = 11.54$ cm^{-1} (due to the carboxylato bridge), $J' = -1.64$ cm^{-1} (inter-molecular interactions), $g = 2.3$, $R = 5.9 \times 10^{-6}$. For **2**, there are two non-equivalent interpenetrated 1D systems, we used two different models: (a) taking into account the small structural variations of two chains, the equation for ferromagnetic $S = \frac{1}{2}$ system[11] with only an average J value, could be appropriate. The best-fit parameters are $J = 15.06$ cm^{-1} (due to the carboxylato bridge), $g = 2.11$, $R = 2 \times 10^{-4}$; (b) assuming two different J values and using the CLUMAG program,[12] the best-fit parameters are $J_1 = J_2 = 15.09$ cm^{-1}, $g = 2.11$, $R = 1.5 \times 10^{-4}$. The two J values are equal and exactly correspond to that found for the uniform chain as described above. The ferromagnetic coupling value is comparable to that obtained for **1**.

In **1**, four Cu^{II} ions are equivalent, in an intermediate between square pyramidal (SP) and trigonal bipyramidal (TBP) geometry. In a crude approximation, O1, O2, N1, N2 can be considered as pseudo-planar (two atoms up and two down) and O5 as axial. Thus, as distorted SP geometry, the magnetic orbital with the unpaired electron, $d_{x^2-y^2}$, is oriented to the ligands of the basal plane, and O1 and O2 participate in the magnetic pathway. On the other hand, assuming possible TBP geometry, the d_{z^2} electron density would be oriented towards O1 and N1, thus diminishing the magnetic pathway. The two magnetic pathways in **2** are Cu1–O1–O2–Cu2–O5–O7A–Cu1B and Cu3–O3–O4–Cu2–O6–O8A–Cu3B, being similar to that for **1** but the TBP contribution is almost nil. It must be pointed out that all carboxylato bridges coordinate to Cu^{II} in *syn–anti* mode in **1** and **2**, and the *J* values reported here are in agreement with those of other similar Cu^{II} complexes.[13]

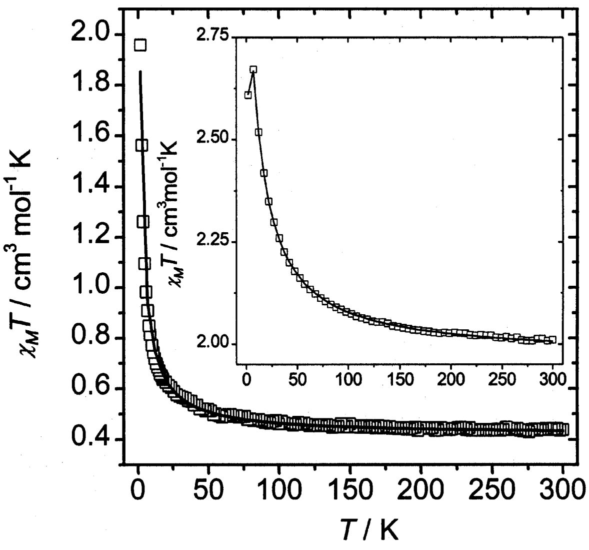

Fig. 3 $\chi_M T$ *vs.* *T* for **1** (insert) and **2**. Solid lines show the best fit.

In conclusion, this work represents a successful example of pH-controlled reversible inter-conversion between an *achiral* molecular square and a spontaneously resolved *chiral* double-chain. This is new proof of the versatility of the bridging possibilities of carboxylato ligands and opens up new perspectives for experimentalists. The procedures described here may be generally applicable for other ligands with proton sensitive groups. The global ferromagnetic coupling observed in both complexes indicate that they may be precursors of new molecular-based magnetic materials. Complex **1** can also be regarded as the secondary building unit for **2**,[14] information gained here may be useful in tailoring other *chiral* molecular congeries from *achiral* building units.

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Notes and references

† **1**: Cu(ClO$_4$)$_2$·6H$_2$O (1 mmol) and H$_2$**L**·2HCl (1 mmol) were reacted in MeOH/H$_2$O (15 mL). The pH value of this solution was adjusted to ~2 with dilute KOH aqueous solution. The reaction mixture was filtered and left in vacuum at room temperature. Dark-blue crystals were obtained by very slow evaporation of the solvent in *ca.* 20% yield. IR (KBr pellet, cm^{-1}): 3432b, 1613vs, 1459m, 1429m, 1406m, 1338w, 1098vs, 624s.

2: The same synthetic procedure as for **1** was used except that the pH was adjusted to ~6, giving light-blue crystals in 35% yield. IR (KBr pellet, cm^{-1}): 3490b, 1569vs, 1463s, 1410m, 1340w, 1108vs, 626s.

‡ *Crystal data* for **1**: C$_{48}$H$_{88}$Cl$_4$Cu$_4$N$_8$O$_{34}$, $M_r = 1717.24$, tetragonal, space group $I4_1/a$, $a = b = 13.4001(10)$, $c = 34.747(4)$ Å, $V = 6239.2(10)$ Å^3, $F(000) = 3552$, $Z = 4$, $\mu = 1.622$ mm^{-1}, $D_c = 1.828$ g cm^{-3}, 6541 reflection measured, 2265 unique (R_{int} 0.0796) with $I > 2\sigma(I)$. Final *R*, *wR* and *S* values are 0.1390, 0.3252 and 1.195 (the crystal quality was poor, and intensity data collected from several samples gave similar results). For **2**: C$_{24}$H$_{44}$Cl$_4$Cu$_3$N$_4$O$_{18}$, $M_r = 1009.05$, orthorhombic, space group $P2_12_12_1$, $a = 10.1565(9)$, $b = 13.7346(13)$, $c = 27.005(3)$ Å, $V = 3767.1(6)$ Å^3, $F(000) = 2060$, $Z = 4$, $\mu = 2.041$ mm^{-1}, $D_c = 1.779$ g cm^{-3}, 15492 reflection measured, 6553 unique (R_{int} 0.0472) with $I > 2\sigma(I)$. Final *R*, *wR* and *S* values are 0.0597, 0.1518 and 1.030. CCDC reference numbers 178167/8. See http://www.rsc.org/suppdata/cc/b2/b207294g/ for crystallographic data in CIF or other electronic format.

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