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A hybrid organic–inorganic molecular daisy chain†

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A hybrid organic–inorganic molecular daisy chain has been synthesised in one pot reaction. The molecule contains two {Cr₆Zn₂} rings linked through an organic molecule that acts as both template and ligand. Magnetic and spectroscopic data reveal the magnetic complexity of the daisy chain, which can be casted to two magnetic isomers through comparison of experimental and simulated data for Cr(III) chains.

Hybrid organic–inorganic materials that combine features of both chemistries have been developed in recent years, where the combination of the physical properties associated with inorganic systems, such as the magnetic or spectroscopic properties, with those associated with organic systems, *i.e.* dynamism and/or molecular recognition, seems in principle an attractive goal. In the field of metal–organic frameworks[1] examples of organic–inorganic materials can be found, as well as in coordination polymers and interlocked systems in supramolecular chemistry.[2]

One particular type of supramolecular hybrid materials are the organic–inorganic rotaxanes, where inorganic and organic structural units are interconnected mechanically at the molecular level.[3] In these systems the inorganic part is formed by {Cr₇M} molecular nanomagnets,[4] which are excellent subjects for studies of fundamental physics, such as quantum tunnelling of total spin,[5] and possible long term applications as qubits for quantum information processing (QIP).[6,7]
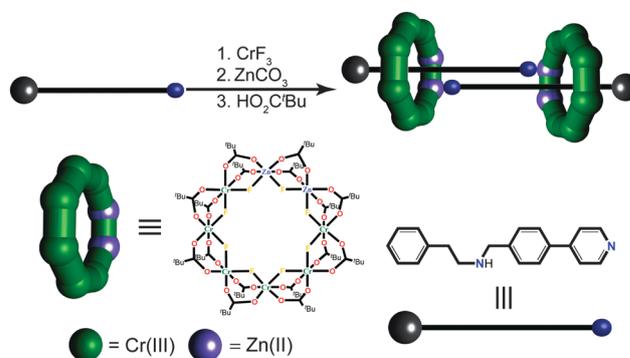
A step forward in terms of complexity and sophistication, beyond rotaxanes, are the molecular daisy chains.[8] This term was first coined by Stoddart[9] more than a decade ago, for systems formed by a linear thread and a threadable macrocycle, which are covalently bound. Introduction of a stopper unit prevents dethreading of these supramolecularly assembled chains and therefore converts the supramolecular binding into a mechanical bond, leading to mechanically interlocked system. The molecular daisy chains reported so far are mainly organic based on cyclodextrins,[10] crown ethers or curcubit[6]uril[11] as macrocyclic components, where the driving force for the interlocked system formation is the host–guest supramolecular interaction, with only a few examples of anions or metals used as templates.[12] Potential applications for daisy chains range from drug delivery systems, switches, molecular motors to machines, as well as nanovalves and molecular actuators.[13]

Here we report the first hybrid organic–inorganic molecular daisy chain (Scheme 1). The inorganic part consists of a {Cr₆Zn₂} ring, with a metal core reminiscent of {Cr₇M} wheels.[4]

The organic thread acts as both a template and a ligand. At the centre is an alkylammonium group, used to template the formation of the eight member metallic ring. A phenyl-group acts as a stopper at one end of the thread, to prevent dethreading of the template from the inorganic ring. The other end of the thread has a phenylpyridine that acts as a stopper and also as an N-donor ligand coordinating to a metal site in the second ring to form the interconnected rotaxane dimer.

The daisy chain was synthesised from the reaction between CrF₃·4H₂O, ZnCO₃, pivalic acid (HO₂CᵗBu) and the thread

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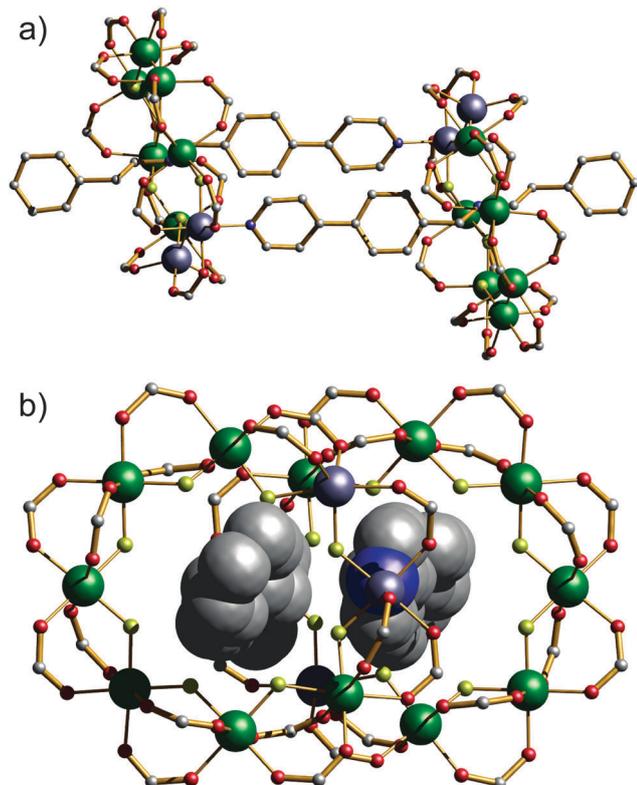

Scheme 1 Schematic description of the formation of the daisy chain (**1**), involving the organic axle (L) and the inorganic wheel ({Cr₆Zn₂}).

a)

b)

Fig. 1 Crystal structure of **1** (ball and stick) viewed (a) in the plane of the {Cr$_6$Zn$_2$} and (b) perpendicular to the plane of the {Cr$_6$Zn$_2$}. Colours: Cr, green; Zn, tale; F, yellow; O, red; C, grey; N, blue. H-atoms and ^{t}Bu groups of pivalates omitted for clarity.

(L = N-[(1,1'-biphenyl)-4-ylmethyl]-4-phenylethane-1-amine) (7 : 2 : 18 : 1 molar ratio) resulting in a dimer with molecular formula [Cr$_6$Zn$_2$(μ-F)$_8$(O$_2$C^{t}Bu)$_{15}$(L)]$_2$ (**1**) in good yield (35%). While templating of such rings about ammonium cations is now well-known[4] and the ability of the pyridine from the thread of a rotaxane to act as a ligand has been reported previously,[14] both happening simultaneously is new. The mechanism of the self-assembly process is unclear, but previous work suggests formation of {Cr$_5$} and {Cr$_6$} chains H-bonded to L in an early step, followed by ring closure by addition of the divalent metal ions.[17]

The solid-state structure of **1** was determined on a single crystal grown from a saturated toluene solution (Fig. 1).§ Each inorganic ring contains on average two Zn(II) and six Cr(III) ions, confirmed by elemental analysis; the metal ions in each ring are arranged in a regular octagon (Fig. 1b), bridged on the inner edges by eight fluorides and on the outer edges by fifteen pivalates. The peripheral pivalates are arranged so that eight lie close to the plane of the eight metal centres, described as the equatorial sites, and the other seven alternate above and below the plane of the ring, described as axial sites.

From chemical considerations the five-coordinate metal site within each ring is likely to be Zn(II). The location of the second Zn(II) site in each ring is not so easily determined. To understand the problem, we number the metal sites with the five-coordinate Zn(II) site as 1. Two alternative isomers need to be considered: where the Zn ions are at 1,2-(**A**) or 1,3-(**B**) in the structure (Fig. 2).
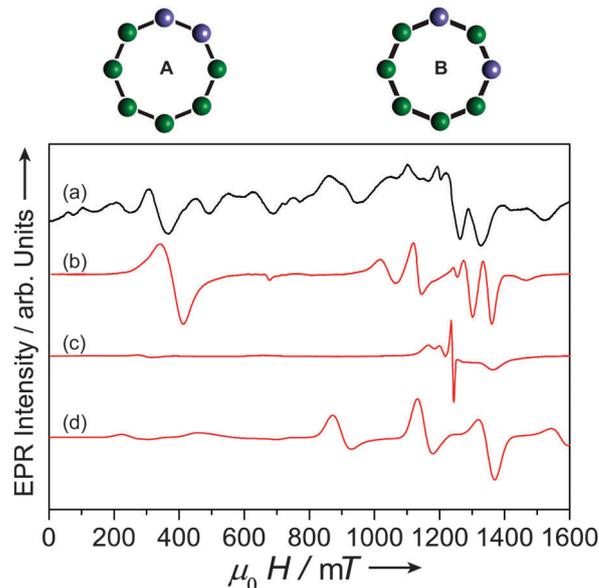
Fig. 2 (top) Representation of two possible isomers of **1**; (bottom) Q-band EPR of **1** at 5 K (a) and comparison with experimental data for: (b) {Cr$_6$} chain; (c) {Cr$_5$} chains; and (d) a calculated spectrum for a single Cr(III) ion using the parameters described in the text.

Six of the six-coordinate sites have average distances between 1.93367(9)–1.96567(8) Å, consistent with Cr(III) ions.[4] The 3-site has bond lengths averaging 2.014 ± 0.040 Å; this is closer to the average that would be expected for a six-coordinate Zn(II) site (*ca.* 2.09 Å) but a little short. Refinement of the structure as exclusively isomer **B** gives a respectable R-factor, but the anisotropic displacement parameters for the 2- or 3-metal sites are not ideal (too large for the 3-site as 100% Zn, too small for the 2-site as exclusively Cr); an ordered structure does not fit with magnetic data (see below). Based on the magnetic data (we fixed the site occupancies so that isomer **A** is present 30% and isomer **B** 70%). This leads to better anisotropic displacement parameters. Similar partial disorder of the divalent metal site in {Cr$_7$M} rings has been discussed recently.[4e]

The compound can be recrystallized successfully from non-coordinating solvents (toluene, CH$_2$Cl$_2$, Et$_2$O, THF), but attempts to characterise compound **1** in solution were unsuccessful; NMR spectroscopy does not work due to the paramagnetism of the sample, while the mass of the entire daisy-chain takes the sample outside the window we can reach by electro-spray mass spectrometry.

The magnetic behaviour is only consistent with a mixture of isomers within the rings. Isomer **A** contains a single {Cr$_6$} chain, which will have a diamagnetic ground state due to nearest neighbour anti-ferromagnetic exchange. In isomer **B** the Zn(II) there is an isolated Cr(III) ion, and a {Cr$_5$} chain; each will have an S = 3/2 spin ground state. The presence of isomers **A** and **B** can be probed through electron paramagnetic resonance (EPR) spectroscopy. Data collected at Q-band frequency at 5 K shows a rich EPR spectrum, which contains more features than could be expected from a single isomer.

It is not possible to simulate the spectrum, however it can be compared to experimental data for isolated {Cr$_5$} and {Cr$_6$}

chains.[14,15] This allows us to assign major features *ca.* 330, 1150, 1300 and 1380 mT to a $\{Cr_6\}$ containing isomer (Fig. 2b; the features arise from the $S = 1$ and 2 excited states of a $\{Cr_6\}$ chain). A $\{Cr_6\}$ chain suggests isomer **A** is present. One feature at *ca.* 1250 mT appears to come from a $\{Cr_5\}$ chain (Fig. 2c); it is due to the $S = 1/2$ first excited state of the $\{Cr_5\}$ and is sharper in the isolated chain. The other features from a $\{Cr_5\}$ chain are due to the ground $S = 3/2$ state and lie in the same region as features from the $\{Cr_6\}$ chain.

If a $\{Cr_5\}$ chain is present, this must be isomer **B**, which also contains a single isolated Cr(III) ion (Fig. 2d). A spectrum was calculated for an individual Cr(III) ion in this environment using parameters ($g = 1.98$ and an axial zero-field splitting parameter of $D = -0.34$ cm^{-1})[18] obtained from previous studies of heterometallic rings through a variety of techniques.[4b,14] This simulates most of the remaining features of the spectra (Fig. 2d). Adding together the spectra calculated for each fragment involves assumptions about relative transition probabilities in the different isomers.

The other transitions observed in the experimental data, could be due to long-range exchange interaction, or other parameters (*e.g.* single ion rhombic anisotropy). Choosing which of these further parameters to include would be arbitrary at this stage. Attempts to fit the spectra using isomer **B** but with weak exchange interactions between the isolated Cr(III) site and the $\{Cr_5\}$ chain were largely unsuccessful (Fig. S5, ESI†).

We have studied the magnetic susceptibility behaviour of polycrystalline samples of **1** in the temperature range 2–300 K under 1 kOe applied magnetic field (Fig. 3). $\chi_M T$ of **1** (where χ_M is the molar magnetic susceptibility) at room temperature is 22.4 cm^3 K mol^{-1}, which is quite close to 22.1 cm^3 K mol^{-1}, which would be expected for twelve non-interacting Cr(III) ions ($g_{Cr} = 1.98$, $S = 3/2$). Upon cooling $\chi_M T$ decreases reaching a value of 4.8 cm^3 K mol^{-1} at 2 K, as a consequence of the antiferromagnetic interactions between the Cr(III) sites within each ring (Fig. 3a).

The best measurement of the spin ground state comes from the molar magnetisation (M), which was studied at 2 and 4 K in the field range of 0–7 T (Fig. 3b). The observed behaviour is not consistent with an ordered structure, *i.e.* with isomer **A**, a $\{Cr_6\}$ chain,[14] nor with isomer **B**, containing a mixture of a $\{Cr_5\}$ chain and a single Cr(III) site (see Fig. S4, ESI†). To fit the magnetic data, both $\chi_M T(T)$ and $M(H)$ were calculated for isomers **A** and **B** using an isotropic Heisenberg Hamiltonian ($\hat{H} = \mu_B \hat{S}_i g \vec{B} - 2\sum_{ij} J_{ij} \hat{S}_i \hat{S}_j$); with $g = 1.98$ and $J = -5.8$ cm^{-1} as used previously for $\{Cr_7Zn\}$ rings.[5a] To simulate the experimental data the contributions of each isomer **A** and **B** were weighted and added, with the only free parameter being the relative contribution of each isomer; this gave a 3 : 7 weighting values for isomer **A** to **B**. The model assumes magnetic interactions between rings would be much weaker. Attempts to fit the $M(H)$ data to isomer **B**, but with a weak exchange interaction between the single chromium site and the $\{Cr_5\}$ chain produces a very poor agreement (Fig. S4, ESI†).

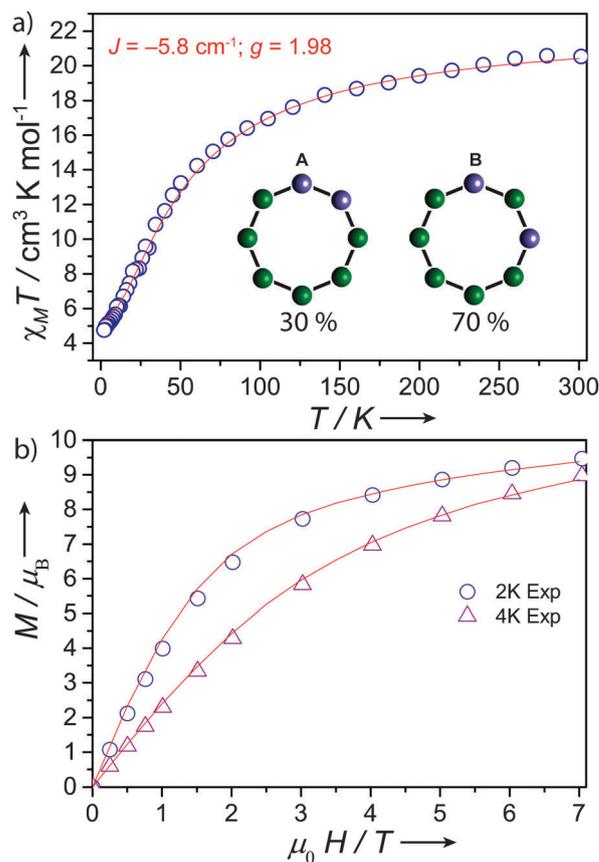In summary, a hybrid organic–inorganic daisy chain has been synthesised. The magnetic and spectroscopic properties

Fig. 3 (a) Variation of $\chi_M T$ *vs.* T for **1** at 1 kOe from 2–300 K; (b) M *vs.* H for **1** from 0–7 T at 2 and 4 K and simulation with the model described in the text (solid lines).

of the system were studied through X-ray, SQUID and EPR techniques, and the best interpretation of this data requires presence of two isomers, **A** and **B**, in approximately 3 : 7 ratio. Extending the organic axle, including more quaternary amine stations, could be the next step towards mechanically controlled magnetic systems at molecular level. This could lead to a method to switch the interaction through distance between the magnetic units of the structures by external stimuli, bringing the possibility of connecting molecular motion with magnetism.

Notes and references

§ Crystal data for **3** [C$_{95}$H$_{156}$Cr$_6$F$_8$N$_2$O$_{30}$Zn$_2$]: M_r = 2400.95, monoclinic, space group $P2_1/c$, T = 270.1(2) K, a = 23.6326(12), b = 22.5386(11), c = 37.8111(15) Å, β = 126.954(3), V = 16094.2(14) Å^3, Z = 4, ρ = 0.991 g cm^{-3}, total data = 22 942, R_1 = 0.0831 for $I \geq 2\sigma(I)$ and wR_2 = 0.2321. The data was collected on an Agilent SuperNova CCD diffractometer with MoK$_\alpha$ radiation (λ = 0.71073 Å), solved using SUPERFLIP,[16a] and refined on F^2 using SHELX-14[16b] in Olex2.[16c]

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