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Hybrid organic-inorganic rotaxanes, including a hetero-hybrid [3]rotaxane featuring two distinct heterometallic rings and a molecular shuttle

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Abstract: [2] and [3] hybrid rotaxanes are reported based on {Ti_7M} rings (where M = a trivalent metal such as Fe^{III} or Ga^{III}}. NMR studies show that [2]rotaxanes can act as molecular shuttles, while EPR studies of [3]rotaxanes show weak interactions between the paramagnetic components of the supramolecular assemblies.

Hybrid organic-inorganic rotaxanes consist of an organic template about which a cyclic coordination compound or metal ring can be grown.[1,2] They differ from metallocrowns[3] and other metal rings[4] in that the design of the organic template, or thread, is such that bulky groups or stoppers are included to prevent the thread leaving the ring. This allows inclusion of coordinating groups at the end of the threads, building complex structures including [4], [5] and [7]-rotaxanes.[5] It is also possible to add additional paramagnetic centres such as Cu^{II} ions[6] or organic radicals.[7] While there are several mechanically interlocked molecules featuring metal ions,[8] they remain unusual. Here we report a new family of hybrid rotaxanes, based on {Ti_7M^{III}} rings.[9] The long term aim here is to create complex diamagnetic hosts into which we can dope supramolecular assemblies containing multiple paramagnetic centres, allowing implementation of universal gates for quantum information processing.[10,11]

The simplest possible route to a [3]rotaxane is to use a di-amine where there is a long chain between the amine centres and large groups at each the end to act as stoppers. Therefore, we dissolved an oxo-centered triangle of a trivalent metal (Fe^{III}, Ga^{III}, Cr^{III} or Mn^{III}) in pivalic acid in the presence of dibenzyldecane-1,10-diamine [$(PhCH_2NH_2)_2(CH_2)_{10}$ **A**] and trimethylacetic anhydride; [$Ti(O^iPr)_4$] is then added. All manipulations were carried out under nitrogen with rigorous exclusion of water. The oxo-centered triangles were: $Fe_3O(O_2C^tBu)_6(H_2O)_3](O_2C^tBu)$. $^tBuCO_2H$;[12] [$Ga_3O(O_2C^tBu)_7(CH_3CN)$] 0.5 $^tBuCO_2H$;[9] [$Cr_3O(O_2C^tBu)_7(HO_2C^tBu)_2$] generated *in situ*;[13] [$Mn_3O(O_2CMe)_7(HO_2CMe)]_n$.[14]

The result is the formation of a [3]rotaxane, {[**A**][$(Ti_7MO_8(O_2C^tBu)_{16})]_2$} (M = Fe^{III} **1**, Ga^{III} **2**, Cr^{III} **3** or Mn^{III} **4**) (Figure 1). The synthesis of **4** used [$TiO(O_2C^tBu)_2]_8$ as the starting material[15] as the reaction involving [$Ti(O^iPr)_4$] reduced Mn^{III} to Mn^{II}. The structure of the {Ti_7M^{III}} ring is an octagon of metal sites with each edge bridged by an oxide and two pivalates, and is unchanged from the simple ring formed using n-$Pr_2NH_2^+$ as the template.[9] Here two rings are present, linked by the ten-carbon chain of the organic thread.

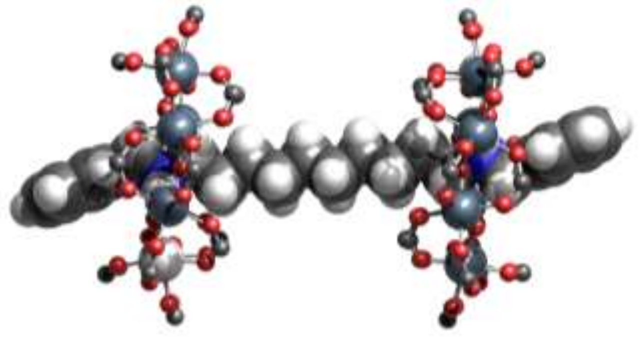

Figure 1. Representation of the structure **2** in the crystal. [A] is represented as a spacefilling model with the remainder ball and stick. T-Butyl moieties omitted for clarity. Ti = grey, Ga = light grey, O = red, N = blue, C = dark grey, H = white

We wished to examine if hybrid molecular shuttles could be prepared by this route.[1] Therefore, we used dibenzyl-1,8-diamine [$(PhCH_2NH_2)_2(CH_2)_8$ **C** in the reaction used to give **2**. The aliphatic chain is too short to allow a [3]rotaxane to form, so the [2]rotaxane, {[**C**][$Ti_7GaO_8(O_2C^tBu)_{16}$]} **5** forms (Figure 2). As **5** contains two ammonium "stations" we can then study the motion use 2-dimensional exchange spectroscopy (EXSY) experiments[16] to study the motion of the {Ti_7Ga} ring along the organic thread and find that it exchanges between the two ammonium stations. EXSY measurements at 310 K in $C_2D_2Cl_4$ gave a rate of exchange of 0.15 s^{-1} for shuttling corresponding to a free energy of activation $\Delta G^‡$ of 19.4 kcal mol^{-1}. This is comparable with the motion of {Cr_7Co} rings along an organic thread.[1] (Figure S1).

While this chemistry is beautifully simple, as a route to supramolecular assemblies it is limited by the availability and solubility of organic threads containing multiple amine groups. An alternative route is via synthesis of rotaxanes and *pseudo*-rotaxanes that contain coordinating groups.[5] Therefore we prepared a [2]rotaxane containing $PyCH_2NH_2CH_2CH_2Ph$ **B** as the thread giving {[**B**][$(Ti_7MO_8(O_2C^tBu)_{16})$]} (M = Fe^{III} **6**, Ga^{III} **7**) (Figure 3a). As **B** is terminated by a pyridine group, **6** can be used as a ligand and reaction of **6** with [$Cu_2(O_2C^tBu)_4$] gives the assembly, [$Cu_2(O_2C^tBu)_4$]{[**B**][$Ti_7Fe^{III}O_8(O_2C^tBu)_{16}$]}$_2$ **8** (Figure 3b), which is a [3]rotaxane. The {Cu_2} "lantern" structure is similar to those found as bridges in other supramolecular assemblies.[17]

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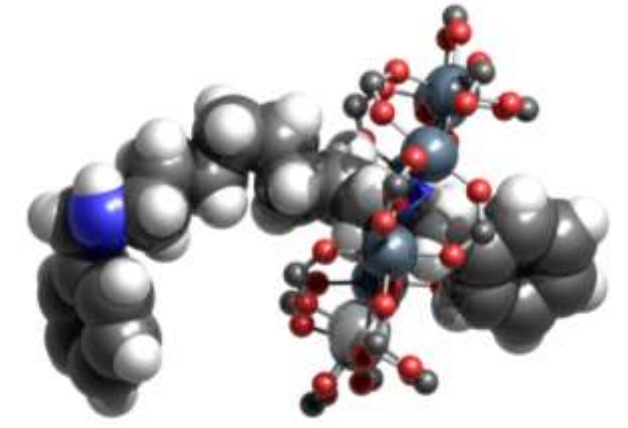

Figure 2. Representation of the structure of **4** in the crystal. [C] is represented as a spacefilling model with the remainder ball and stick. T-Butyl moieties omitted for clarity. Ti = grey, Ga = light grey, O = red, N = blue, C = dark grey, H = white

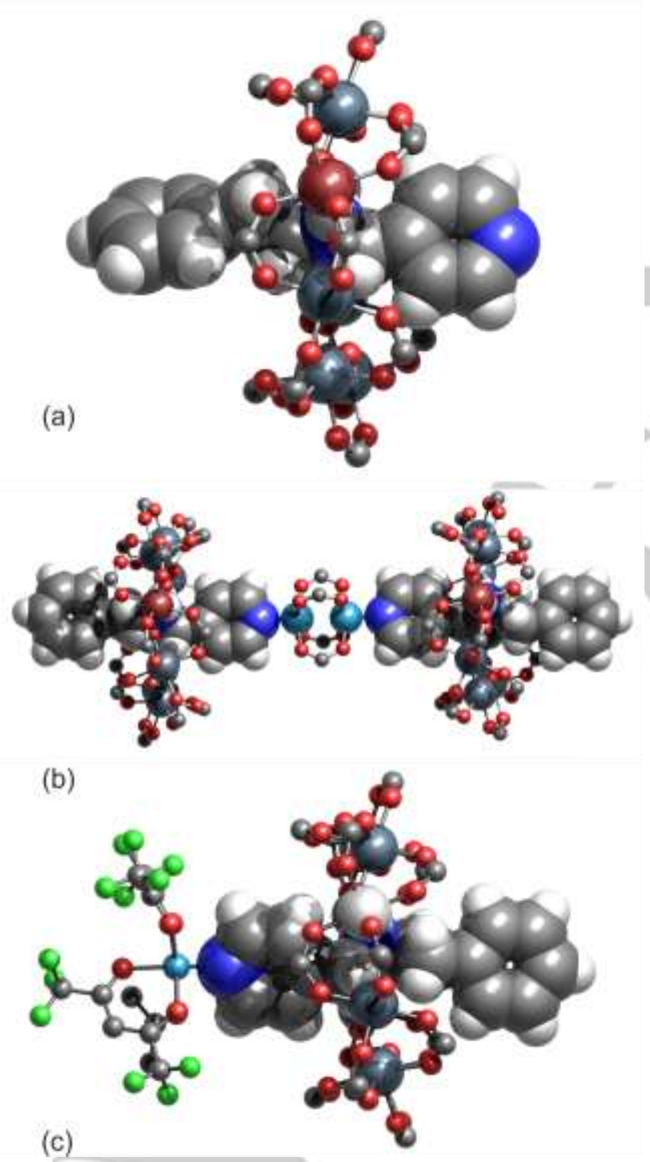

Figure 3. Representation of the structures of a. **6**, b. **8** and c. **9** in the crystal. [B] is represented as a space filling model with the remainder ball and stick. T-Butyl moieties omitted for clarity. Ti = grey, Fe = maroon, Cu = light blue, Ga = light grey, O = red, N = blue, C = dark grey, F, green, H = white

The [2]rotaxane **6** can also be used as a ligand for monometallic copper(II) complexes such as $Cu(hfac)_2$ giving $[Cu(hfac)_2]\{[\mathbf{B}][Ti_7Fe^{III}O_8(O_2C^tBu)_{16}]\}$ **9** (Hhfac = 1,1,1,6,6,6-hexafluoroacetylacetonate) (Figure 3c). To interpret the EPR spectra of **8** we also synthesised the isostructural compound $[Cu(hfac)_2]\{[\mathbf{B}][Ti_7Ga^{III}O_8(O_2C^tBu)_{16}]\}$ **10** via reaction of **7** with $Cu(hfac)_2$.

The ability to grow isostructural but different heterometallic rings around similar threads has also allowed us to make a hetero-heterometallic-hybrid [3]rotaxane. Using **A** as the thread we can first grow the very stable $\{Cr_7Ni\}$ ring[4] around one ammonium group (see SI for experimental details), and then grow a $\{Ti_7Fe\}$ ring around the second ammonium giving: $\{[\mathbf{A}][Cr_7NiF_8(O_2C^tBu)_{16}][Ti_7FeO_8(O_2C^tBu)_{16}]\}$ **11** which has the same structure as compounds **1 – 4** (Figure 1). Synthesis of [3]rotaxanes with different rings as components is unusual, and the ability to grow a supramolecule with two heterometallic components is unique. Evidence for the hetero-heterometallic rings is provided by full elemental analysis, EPR spectroscopy (see below) and the reaction chemistry to give **11**.

EPR spectroscopy on the paramagnetic rotaxanes definitively shows incorporation of the paramagnetic ions (Figure S2); the exception is **4** as Mn^{III} is EPR silent at the frequencies we have used. Spectra of the [2]rotaxane **6** are those of an isolated high spin Fe^{III} ion ($S = 5/2$) with axial ($|D|$) and rhombic (E) zero-field splitting parameters of 0.17 and 0.045 cm^{-1}, respectively. There are some minor spectral changes in the [3]rotaxane **1** that can be modelled as small changes in E. Similarly, spectra of **3** can be modelled as a single $S = 3/2$ ($D = -0.53$, $E = 0.03$ cm^{-1}) due to Cr^{III}. The larger $|D_M|$ and smaller rhombicity (E/D) for M = Fe *cf*. Cr in $\{Ti_7M\}$, and also the magnitudes of D and E, are typical for monometallic $\{MO_6\}$ complexes, e.g. $[M(diketonates)_3]$.[18,19] The D_{Cr} value in $\{Ti_7Cr\}$ is ca. significantly larger than that in the parent $\{Cr_7M\}$ family:[20] this must be a function of the $\{Cr(O^{carboxylate})_4(O)_2\}$ vs. $\{Cr(O^{carboxylate})_4(F)_2\}$ crystal fields. The implication is that oxide is acting as a better π-donor, resulting in a weaker crystal field and hence larger ZFS via mixing with excited states, and that this is more important than the greater charge.

There is no direct evidence of any interaction between the $\{Ti_7M\}$ components in spectra of the homo-[3]rotaxanes **1** and **3** (Figure S2), with only slight broadenings or minor changes in ZFS compared to isolated $\{Ti_7M\}$,[5] nor in that of the hetero-[3]rotaxane **11** (Figure S3) which comprises a superposition of features for $\{Ti_7Fe\}$ ($S = 5/2$) and $\{Cr_7Ni\}$ ($S = ½$ ground state with $g = 1.8$)[16]. The exchange interactions in the $\{Cr_7Ni\}$ ring appear to be unchanged from isolated $\{Cr_7Ni\}$ rings.[4] Test calculations show that interactions of > 0.01 cm^{-1} would introduce observable changes, hence giving a gross upper limit to any interaction (Figure S3). This is unsurprising: the nearest ring…ring distances are ca. 14 Å which would correspond to dipolar interactions of ca. 20 MHz (of the order 10^{-3} cm^{-1}) and there is no obvious through-bond exchange pathway. Previous pulsed EPR studies on [3]rotaxanes of $\{Cr_7Ni\}$ rings with tri-aryl threads (ring…ring ca. 1.6 nm) gave interactions of the order of 10 MHz.[21]

However, spectra of **9**, which has {Ti_7Fe} bound to Cu(II) via the pyridyl head-group on the thread **B**, do show evidence of exchange coupling, with a clear additional splitting compared to a simple superposition spectrum (Figure 4). Simulation gives an exchange interaction of J = -0.03 cm^{-1} ($-2J\hat{s}_{Fe}\cdot\hat{s}_{Cu}$ exchange Hamiltonian). This is similar to the J = -0.016 cm^{-1} found by EPR for the [$Cu(hfac)_2$]{[**B**][$Cr_7Ni^{II}O_8(O_2C^tBu)_{16}$] analogue[6] and, as with that system, the mechanism is unclear given the lack of covalent interaction between the components (the leading component of the dipolar interactions is of ca. -0.003 cm^{-1}).

These results show we can prepare diamagnetic [3]rotaxanes into which we will, in the future, dope paramagnetic [3]rotaxanes, seeking to perform two-qubit gates in orientated single crystals. The preparation of compound **11**, where we have included two distinct heterometallic rings without exchange of metals between the two rings suggests this approach is promising.

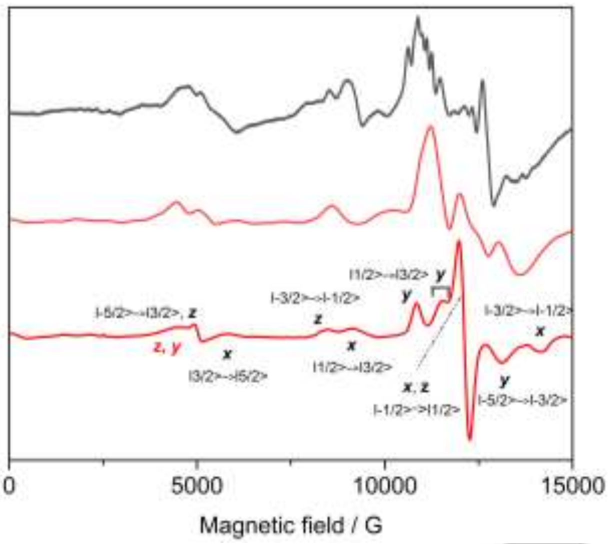

Figure 4. Q-band (34.0463 GHz) EPR spectrum of a powder sample of **9** (top; black) measured at 5 K. Calculated spectra (red) with: S_{Fe} = 5/2, g_{Fe} = 2.00, D_{Fe} = -0.19, $|E_{Fe}|$ = 0.04 cm^{-1} (E/D = 0.21), S_{Cu} = 1/2, $g_{Cu(x,y,z)}$ = 2.05,2.05,2.30, and J_{FeCu} = -0.03 cm^{-1} (middle) and nil (bottom). Calculated spectra with allowed (black) and forbidden (red) transitions used a 150 G intrinsic linewidth and strain in the zero-field splitting matrix and J of 0.01 cm^{-1}.

Acknowledgements

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Keywords: rotaxanes, heterospin, qubits, quantum gate, quantum computing, quantum information processing

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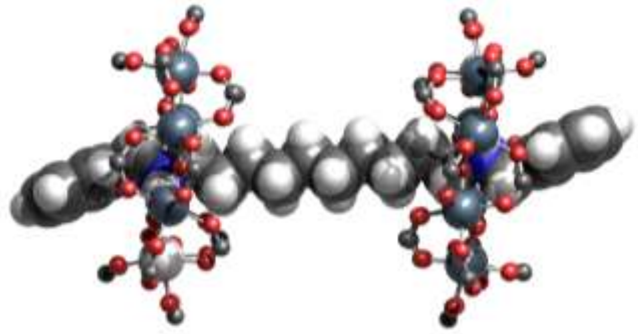

New [2] and [3]rotaxanes are reported based on {Ti_7M} rings.

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