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Nanoscale Polymetallic Assemblies

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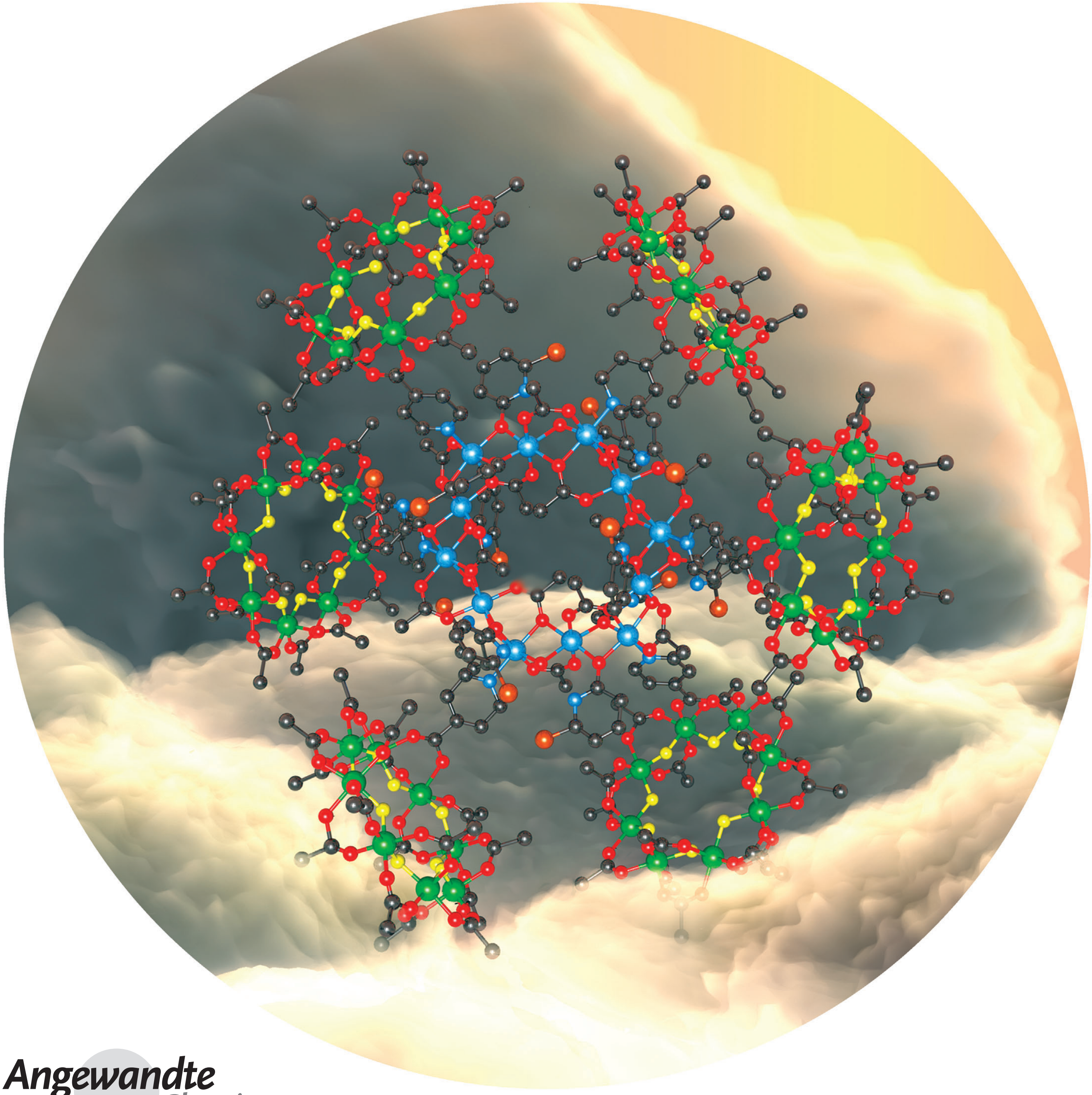
A Ring of Rings and Other Multicomponent Assemblies of Cages**

George F. S. Whitehead, Fabrizio Moro, Grigore A. Timco, Wolfgang Wernsdorfer, Simon J. Teat, and Richard E. P. Winpenny*



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If we are to make molecular devices, we will need to learn to link together multiple different molecular components and to control the communication between them. Inclusion of metal centers into such molecular components could be very useful, bringing magnetic, redox and spectroscopic behavior not found in purely organic materials. Individual components involving multiple metal centers (polymetallic cages, as there is no metal–metal bonding) have been long targeted, and are made by two distinct routes. Firstly, from coordination chemistry, using simple ligands, compounds have been made that can show unusual physics, such as retention of magnetization[1] and observation of parity effects in quantum tunneling.[2] In parallel, supramolecular chemistry has built large structures using elegant organic chemistry completed by addition of metal ions to construct molecular squares,[3] metal grids,[4,5] and spectacular structures through molecular paneling.[6] The cages made by a supramolecular approach can be used to control reactivity,[7] to direct catalytic processes,[8] or to grow monodisperse nanoparticles.[9]

The next step must be to use polymetallic complexes as the molecular components within still larger structures. This has been done in the area of metal–organic frameworks (MOFs), where metal cages are often linked through organic molecules into three-dimensional structures.[10–12] Invariably the cages used in MOFs are all identical, and they are used mainly to create large voids within the MOFs for gas absorption or separation. Similarly there have been a few examples where dimers of identical cages are linked, and such dimers have shown exchange biasing of quantum effects[13] and have been discussed in the context of quantum information processing.[14] Here we take the next step, designing a general and simple route to linking together dissimilar cages to make multicomponent assemblies. We use one cage that can act as a Lewis base and then other cages that act as Lewis acids.

Our Lewis base is a complex $[NH_2Pr_2][Cr_7NiF_8(O_2CtBu)_{15}(O_2C\text{-}C_5H_4N)]$ **1** ($HO_2CC_5H_4N$ = isonicotinic acid), which we can make in two steps in 40% overall yield from inorganic salts and the relevant carboxylic acids.[14] The metal sites are arranged in an octagon and the compound contains a pyridyl group. The pyridyl is part of an isonicotinate ligand that is bound to an edge of the octagon containing the Ni^{II} site (Supporting Information, Figure S1). Compound **1** also contains fifteen tertiary butyl groups that give the Lewis base remarkable solubility in non-polar organic solvents. This high solubility allows us to perform reactions with Lewis acids with no competition from coordinating polar solvents, which is vital for the chemistry we describe herein.

For our Lewis acids we have chosen compounds that contain labile terminal ligands, typically solvent molecules such as water or tetrahydrofuran (THF). We describe three examples that illustrate the generality of the approach; there are many more Lewis acids that can be used to construct these supramolecular assemblies. The first Lewis acid complex is a member of one of the most numerous families of cages, the oxo-centered metal carboxylate triangles[15] $[M_2M'(\mu_3\text{-}O)(O_2CR)_6L_3]^{0/+1}$, where M is a trivalent metal, M' is either a trivalent or divalent metal (which controls whether the cage is neutral or a mono-cation), HO_2CR is a carboxylic acid, and L is a terminal ligand, typically water or HO_2CR. Here we used $[Fe^{III}_2Co^{II}(\mu_3\text{-}O)(O_2CtBu)_6(HO_2CtBu)_3]$ **2**, which was reacted with three equivalents of compound **1** to give a 27-metal assembly of cages $[Fe^{III}_2Co^{II}(\mu_3\text{-}O)(O_2CtBu)_6\{[NH_2Pr_2][Cr_7NiF_8(O_2CtBu)_{15}(O_2C\text{-}C_5H_4N)]\}_3]$ **3**, with the central triangular cage surrounded by three octagonal wheels (Figure 1). The component parts of the assembly are unchanged from the starting materials. The assembly contains four different 3d metal ions, with the Fe^{III} and Co^{II} sites placed within the central triangle, while the twenty-one Cr^{III} ions and three Ni^{II} ions are found within the wheels. Each Ni^{II} site is found within the edge of the wheel that is bound to the isonicotinate ligand.

A further family of cages are the hexametallic oxo-centered edge-sharing bitetrahedra,[16] $[M'_4M_2(\mu_4\text{-}O)_2(O_2CR)_{10}L_4]$, which can be made with a series of carboxylates, terminal ligands (L), divalent metal ions (M), and trivalent

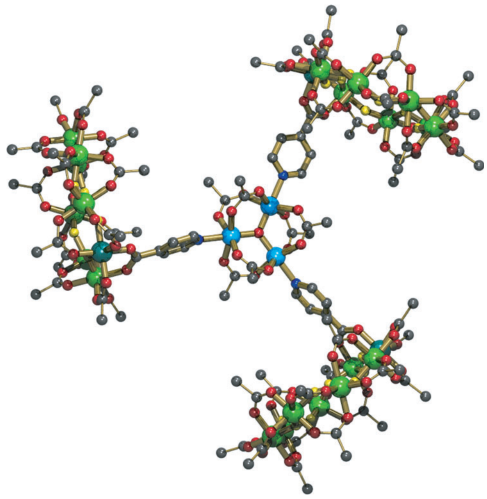

Figure 1. The structure of **3** in the crystal.[23] Colors: Cr green, Ni turquoise, Fe and Co light blue, O red, F yellow, N blue, C gray. H atoms and Me groups of pivalate groups are omitted for clarity. Note that the Ni sites in the $\{Cr_7Ni\}$ ring are disordered between the two sites bound to isonicotinate.

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[*] G. F. S. Whitehead, Dr. F. Moro, Dr. G. A. Timco,
Prof. Dr. R. E. P. Winpenny
School of Chemistry and Photon Science Institute
The University of Manchester
Oxford Road, M13 9PL, Manchester (UK)
E-mail: richard.winpenny@manchester.ac.uk
Dr. W. Wernsdorfer
Institut Néel, CNRS & UJF BP 166
38042 Grenoble Cedex 9 (France)
Dr. S. J. Teat
Advanced Light Source, Lawrence Berkeley Laboratory
1 Cyclotron Road, MS2-400, Berkeley, CA 94720 (USA)

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metal ions (M′). Here we take as an example $[Mn^{II}_4Mn^{III}_2(\mu_4\text{-}O)_2(O_2CtBu)_{10}(THF)_4]$ **4**,[17] which reacts with four equivalents of the Lewis base **1** to produce the assembly of cages $[\{Mn^{II}_4Mn^{III}_2(\mu_4\text{-}O)_2(O_2CtBu)_{10}\{[NH_2Pr_2][Cr_7NiF_8(O_2CtBu)_{15}(O_2C\text{-}C_5H_4N)]\}_4]$ **5** (Figure 2). The THF ligands are displaced by the pyridine of the Lewis base ring, producing a nanoscale assembly containing thirty-eight metal centers. This assembly allows complete control of the connectivity and positioning of the four different metal types (Cr^{III}, Ni^{II}, Mn^{III} and Mn^{II}), with the Mn^{III} sites found within the shared edge of the bi-tetrahedron, as in the precursor **4**.

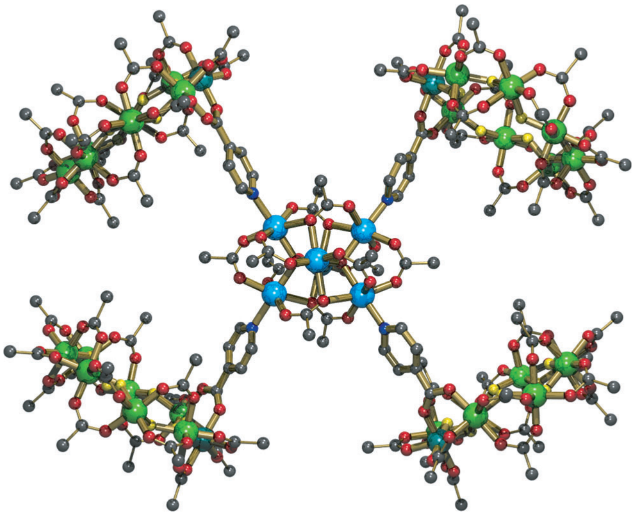

Figure 2. The structure of **5** in the crystal.[23] Colors as Figure 1 plus Mn light blue. H atoms and Me groups of pivalate groups are omitted for clarity.

The structures of the two component cages are retained in the final product in exactly the same way that the structures of organic building blocks are retained in organic supramolecules. The four labile sites on the edge-sharing metal bitetrahedra at the center of the molecule are arranged in a rectangle, and this means that the four Lewis base rings form a rectangle about this central unit. There are many other examples of both the trimetallic and hexametallic central units; all react in the same way as **2** and **4** respectively. However, crystallization is not always straightforward.

A more spectacular structure results if we use a dodecametallic ring $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **6** (Hchp = 6-chloro-2-hydroxypyridine)[18] as the Lewis acid; the nickel sites in this compound form a hexagon with a further metal at the center of each edge of the hexagon. There are terminal THF ligands coordinated to each of the nickel sites at the corners of the hexagon, which can be displaced by the Lewis base **1**. The result is a 60-metal ring of rings, $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6\{[NH_2Pr_2][Cr_7NiF_8(O_2CtBu)_{15}(O_2C\text{-}C_5H_4N)]\}_6]$ **7**, where the central nickel ring forms a core surrounded by six Lewis base cages (Figure 3). Again, the structures of the building blocks are unchanged between the reactants and the final assembly.

The chemical reactivity to make **5** and **7** is unusual. Neither **4** nor **6** dissolves in any common solvent without disruption of the polymetallic structure. However in both cases here, by adding compound **1** dissolved in acetone we can react **4** and **6** as solids; the solid dissolves and we can crystallize the large assembly stoichiometrically. This illustrates both the remarkable solubilizing ability of **1**, owing to the presence of the *tert*-butyl-groups, and also the huge advantages that can be achieved by performing coordination chemistry in the absence of competing coordinating solvents.

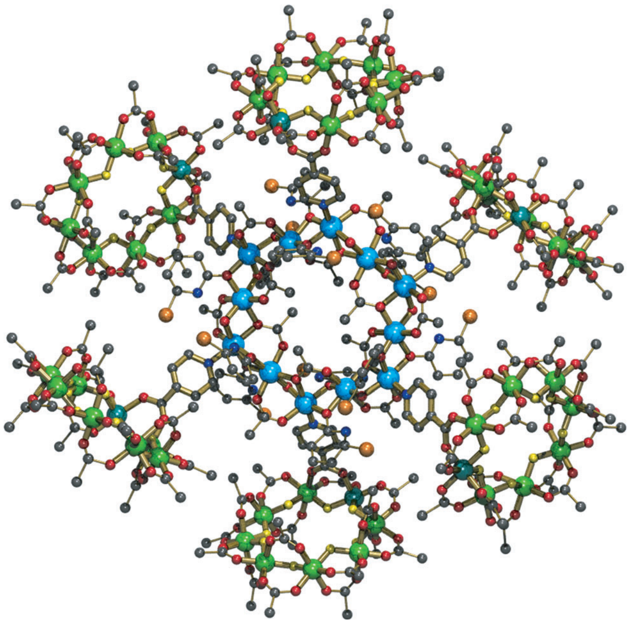

Figure 3. The structure of **7** in the crystal.[23] Colors as Figure 1 plus Ni of $\{Ni_{12}\}$ light blue, Cl orange. H atoms and Me groups of pivalate groups are omitted for clarity.

We have studied the interactions between the components within these assemblies by magnetometry. The interactions are weak, as shown by both variable temperature susceptibility and low temperature magnetisation (M) against field (H) measurements on **3**, **5** and **7**. For each assembly, the temperature dependence of susceptibility (χ_m) or the product $\chi_m T$ or the $M(H)$ behavior at 2 K are indistinguishable from the sum of the components (Supporting Information, Figure S5).

To investigate further the intercage interaction, single crystals of **7** were studied on a micro-SQUID in the temperature range 0.03 to 5 K (Figure 4). Compound **7** was chosen because the $\{Ni_{12}\}$ ring **6** is a single-molecule magnet (SMM) that shows slow relaxation of magnetization at these temperatures, leading to magnetic hysteresis (Figure 4a).[18] For compound **7**, the low-temperature magnetization measurements show no significant hysteresis (Figure 4b); the binding of $\{Cr_7Ni\}$ rings to the periphery of the $\{Ni_{12}\}$ cage has removed the SMM behavior because the weak interaction between the $S = 12$ molecule at the center of the ring-of-rings and the $\{Cr_7Ni\}$ rings provides a relaxation path. At one level this is disappointing (ideally we would have improved the SMM behavior), but it demonstrates that by bringing two complex molecules together the presence of one ring influences the behavior of the other. As a first step it is encouraging that we can observe any interaction.

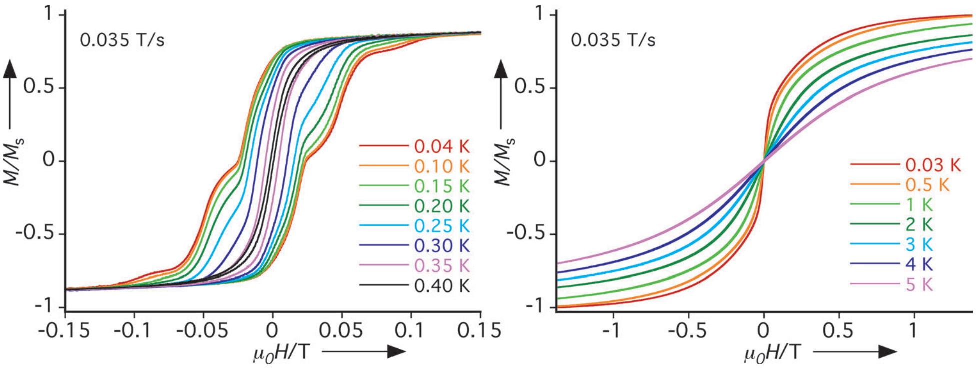

Figure 4. Magnetization (*M*) against field (*H*) measurements on a micro-SQUID at the temperatures shown. a) compound **6**; b) the ring-of-rings **7**.

The results show that large nanoscale objects can be constructed from simple ideas in coordination chemistry. Compound **7** is one of the larger polymetallic compounds that has been crystallographically characterized; for exclusively 3d metal ions, the $\{Mn_{84}\}$ ring reported by Christou and co-workers,[19] and copper(I)-chalcogenide clusters[20] reported by the Fenske group are larger. Larger polyoxometallate cages have been reported, chiefly by Müller.[21] The compounds reported here are unique in combining different metal cages into the final assembly. A related approach to making nanoscale cage compounds has recently been reported by Gao et al[22] using $\{Se_2W_{29}\}$ polyoxometallates as building blocks.

Experimental Section

See the Supporting Information for full synthetic information, crystallographic details, and magnetic data. The synthesis of **3** is given here to illustrate the approach. Compound **2** (16 mg, 0.014 mmol) was dissolved in acetone (5 mL) and added to compound **1** (0.1 g, 0.043 mmol) in hot acetone (15 mL) with stirring. The mixture was heated for 15 min, after which a precipitate formed. This was removed from the heat and left to stir overnight. The precipitate was then collected by filtration, washed with hot acetone, and extracted in diethyl ether. MeCN was added and the solution was left to crystallize by slow evaporation. Yield: (83 % based on **2**).

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[23] CCDC 932595 (**3**), CCDC 932596 (**5**), and CCDC 932597 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.