Magnetism in metal-organic capsules

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5 Nickel and cobalt seamed metal-organic capsules have been isolated and studied using structural, magnetic and computational approaches. Antiferromagnetic exchange in the Ni capsule results from coordination environments enforced by the capsule framework.

The synthesis and characterisation of polymetallic cages of paramagnetic transition metal ions is an area of intense current research since such molecules may exhibit fascinating physical properties,1
10 potentially acting as, for example, single-molecule magnets (SMMs),2 molecular coolants3 and spin phonon traps.4 Indeed the initial (serendipitous) discovery of all these phenomena has subsequently inspired much beautiful chemistry and physics that promises exciting potential application.5 Introducing new preparative routes towards the synthesis of transition metal cages is thus of interest for the discovery of completely new structural types and as a means of building up families of related
15 compounds so that structure-property relations can be developed.6 Organic ligands thus play a crucial role in successful cage construction, but their nature and variety is surprisingly restricted.7 A family of ligands almost completely ignored in this respect, with a few notable exceptions are calixarenes.8

C-Alkylpyrogallol[4]arenes (general formula PgCn) are cyclic molecules that are typically bowl-shaped and that have been shown to assemble through non-covalent interactions into a) nano-
20 tubular arrays,9 b) dimeric capsules,10 and c) hexameric nano-capsules.11 The dimeric and hexameric capsules possess typical internal volumes of ~150 and ~1250 Å3 respectively, and this feature provides them with great potential for study as new host-guest systems. Nanometer scale metal-organic polyhedra are often assembled from many molecular components,12 and we have recently shown that various PgCns can be assembled with different metals into either open or closed shell hexameric
25 metal-organic nano-capsules from Cu, Ga, Ga+Cu or Ga+Zn.13 In addition to this, closed shell dimeric octa-metallated capsules have also been synthesized by reaction of PgCns with a pre-formed zinc(II) nitrate pyridine complex in either pyridine or methanol.14 Given that we had formed a Zn8 wheel as part of a molecular metal-organic capsule, we reasoned that the incorporation of paramagnetic metal centres (e.g. Co or Ni in place of Zn) in the capsule seam may be possible, though
30 a search of the CCDC database reveals that there are no known isostructural Co8, Ni8 and Zn8 cages. This would therefore afford species with potential interest in molecular nanomagnetism, whilst also representing a paradigm shift in the chemistry of molecular capsules and their uses. We also reasoned that the inner phase of the capsule arrangement may have an important effect on the overall magnetic properties of these species by the incorporation of different guest molecules. Herein we report an
35 expedient route to a new family of octa-metallated dimeric capsules comprising Ni8 and Co8 wheels, and their initial magnetic properties. These new metal-organic capsules are synthesised from PgC2 by similar methods, and scrutiny of their structures shows important differences to the Zn analogues. Ligation of endo capsule solvent molecules to metal centres around the metal wheels results in different coordination number patterns for the two transition metals.
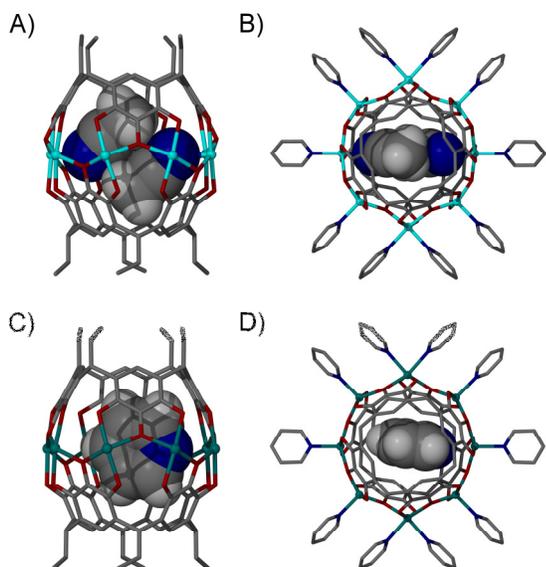
Fig. 1 A). Side view of 2 showing encapsulated MeCN molecules (in one of two disordered positions) in space filling representation. B) Orthogonal view of 2 showing alternating coordination number for Ni centres around the capsule periphery. C) Side view of 3 showing encapsulated Py molecule (in one of four disordered positions) in space filling representation. D) Orthogonal view of 3 showing the irregular coordination number pattern for Co centres around the capsule periphery. Hydrogen atoms (except for guest species), Py ligands (A and C), and lower rim ethyl groups (B and D) are omitted for clarity.

The Ni8 dimeric capsule, 2 (Figure 1A and B), was readily synthesized by mixing acetonitrile (MeCN) solutions of Ni(NO3)2·(Py)4 and PgC2. Following addition, a dark green/brown precipitate rapidly forms, and this can be filtered and dried to afford a fine powdered form of 2. Recrystallisation of this precipitate from pyridine with slow evaporation resulted in the formation of large yellow single crystals that were studied using synchrotron radiation. The crystals are in an orthorhombic cell, and structure solution was performed in the space group Fddd. The asymmetric unit comprises one quarter of the octa-metallated capsule skeleton, 2.5 exo-capsule Py ligands, two endo-capsule MeCN guest molecules (that are disordered over two positions, Figure S1), and 1.75 pyridines of crystallisation (that occupy space between neighbouring capsules). Although the guest MeCN molecules are disordered over two positions, they are well resolved and show coordination to two Ni centres at opposite points within the capsule framework (Figure 1B). This host-guest arrangement is reminiscent of the encapsulation of two MeCN molecules within ionic dimeric PgCn capsules,15 and results in an alternating 6-5-6-5-6-5-6-5 coordination pattern around the capsule periphery. The 6-coordinate Ni centres are pseudo-octahedral, while the 5 coordinate centres have a coordination environment between the extremes of square pyramidal and trigonal bipyramidal geometries. A search of the Cambridge Structural Database for this particular 5-coordinate environment for Ni (with two catechol and one pyridine ligand) returns no results.16 This suggests that this particular coordination environment in the current system is unique. In addition the search shows that Ni8 wheels are rarely observed17 and this synthetic route offers easy access to such species.

The Co8 dimeric capsule, 3 (Figure 1C and D), was synthesized by mixing MeCN solutions of Co(NO3)2·(Py)4 and PgC2 to afford a dark precipitate. Recrystallisation from pyridine with slow evaporation afforded large yellow single crystals that were studied using synchrotron radiation. The crystals are in an orthorhombic cell and structure solution was also performed in the space group Fddd. The asymmetric unit is near-identical to that of 2, but shows a difference in the guest species within the capsule. A pyridine molecule occupies the capsule interior (Figure 1C) and is disordered over four closely related positions (Figure S2). The disordered endo-capsule Py molecule shows a weak

interaction with a Co centre (N⋯Co distance of 2.819 Å) at one of two positions that are opposite one another within the capsule. The result of this is an irregular 6-5-6-5-6-5-5-5 coordination pattern around the capsule periphery (Figure 1D), differing slightly to that observed in 2 (Figure 1B).

DFT and CASSCF calculations were performed on 2 to determine the lowest energy spin state –
5 singlet versus triplet – in model complexes.[18,19] For a low spin (closed shell) d8 Ni centre, the typical coordination environment observed is square planar. Our calculations show that in optimising a closed shell square pyramidal Ni centre with two catechol ligands and one axial pyridine, the latter effectively dissociates to afford the expected square planar geometry. Calculations further show that the distorted square pyramidal Ni geometry (akin to that in 2, and that lies between square pyramidal and trigonal
10 bipyramidal) has a triplet state (i.e. high spin) that is ~ 1.6 eV lower in energy than a singlet state (i.e. low spin). Alternative model complexes also display this behaviour, giving the lowest energy configuration $(dxy)2(dyz)2(dxz)2(dx2-y2)1(dz2)1$.[18] For the two unique pseudo-octahedral Ni centres in 2, similar calculations show that these possess triplet states that are lower in energy by ~ 2.0 eV than respective singlet states. Although this is expected for regular octahedral d8 configuration, the
15 distortion in the 6-coordinate centres here does not favour the low spin state. This is borne out in the magnetic measurements. The variable temperature magnetic behavior of 2 and 3, measured using an applied field of 0.1T, is plotted as the $\chi_m T$ product versus T (where χ_m is the molar magnetic susceptibility) in Figure 2. The room temperature $\chi_m T$ value of ~7.3 cm3 K mol-1 for 2 is below that expected for eight non-interacting s = 1 Ni2+ ions (8 cm3 K mol-1 for g = 2). As the temperature is
20 decreased the value of $\chi_m T$ decreases very gradually reaching a value of ~5 cm3 K mol-1 at 75 K, below which it decreases more rapidly reaching a value of ~1 cm3 K mol-1 at 5 K. This behavior is indicative of weak anti-ferromagnetic exchange between the metal centres and a diamagnetic ground state. The data was satisfactorily simulated with the simple 1J-model of equation (1) that assumes all eight metals ions are equivalent, affording the parameters J = -11.0 cm-1, g = 2.10. Anti-
25 ferromagnetically coupled rings are of great interest in molecular magnetism,[20] and those of s = 1 metal ions may have relevance to the Haldane gap problem.[21] A paper detailing the physics of this system will be reported elsewhere.

$$H = -2J(S1·S2+S2·S3+S3·S4+S4·S5+S5·S6+S6·S7+S7·S8+S8·S1) \qquad (1)$$

The explanation of magnetic behavior of cobalt(II) complexes is complicated by the orbitally
30 degenerate ground state of the ion and so precise derivation of the magnitude of the exchange interactions between cobalt centres is difficult. Therefore only a qualitative report of the magnetic susceptibility data for 3 follows. The room temperature $\chi_m T$ value of ~17.0 cm3 K mol-1 is consistent with the presence of eight s = 3/2 ions with a g-value of 2.15 (17.3 cm3 K mol-1). As the temperature is decreased the value of $\chi_m T$ decreases constantly reaching a minimum value of ~3 cm3 K mol-1 at 5
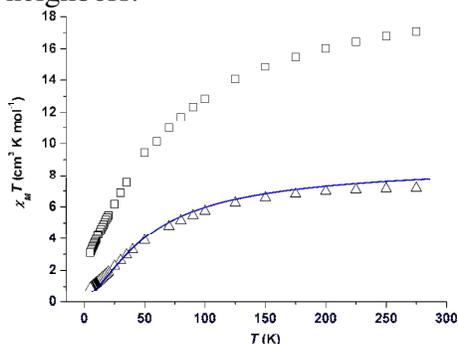35 K (Figure 2). Again this is consistent with weak anti-ferromagnetic exchange between nearest neighbors.

Fig. 2 Plot of $\chi_m T$ versus T for 2 (Δ) and 3 (□) in the 300 - 5 K temperature range, measured in an applied field of 0.1 T. The solid line is a fit of the experimental data with the Hamiltonian of Equation
40 1.

In conclusion, we have demonstrated the formation of paramagnetic metal containing molecular capsules. Octameric nickel wheels are scarce in the literature, and these can now be formed with relative ease. The solvents / guest molecules employed in capsule synthesis are key in determining coordination environments around the capsule periphery, with metal centres in ligand-enforced coordination environments. The ability to substitute peripheral ligands and guest molecules with zinc analogues suggests that we may be able to fine tune the magnetic properties of these new magnetic metal-organic capsules. The formation of larger paramagnetic metal containing hexameric capsules is also underway.

Notes and references

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‡ General experimental details: C-Ethylpyrogallol[4]arene was synthesized according to literature procedure.[22] Nickel (II) nitrate hexahydrate and cobalt(II) nitrate hexahydrate were purchased from Aldrich and used as supplied. Synthesis of [Ni8(C-ethyl-pyrogallol[4]arene)2(pyridine)10 ⊂(MeCN)2] (2): A solution of [NiII(NO3)2(pyridine)4] (1.50 g, 3.01 mmol) in MeCN (10 mL) was added to a solution of PgC2 (0.50 g, 0.752 mmol) in MeCN (10 mL) in an open container. Precipitation of a dark green solid was observed and the mixture was briefly sonicated to ensure reaction completion. The precipitate was filtered and dried under vacuum. Yield: 0.46 g. Synthesis of [Co8(C-ethylpyrogallol[4]arene)2(pyridine)10 ⊂(pyridine)] (3): A solution of [CoII(NO3)2(pyridine)4] (1.5 g, 3.01 mmol) in MeCN (10 mL) was added to a solution of PgC2 (0.50 g, 0.752 mmol) in MeCN (10 mL) in an open container. Precipitation of a dark solid was observed and the mixture was briefly sonicated to ensure reaction completion. The precipitate was filtered and dried under vacuum. Yield: 0.79 g.

Crystals of 2 and 3 were prepared by dissolving respective precipitates in a minimal volume of hot pyridine followed by cooling and slow evaporation. General crystallographic details: Single crystal X-ray diffraction data were collected at 100(2) K on a Bruker Apex II CCD diffractometer operating with synchrotron radiation at a wavelength of 0.77490 Å. Crystal Data for 2: $C_{644}H_{620}N_{76}Ni_{32}O_{96}$, M = 12838.88, CCDC 742757, Yellow Block, 0.20 □ 0.10 □ 0.10 mm3, orthorhombic, space group Fddd (No. 70), a = 19.7468(9), b = 27.6774(13), c = 53.647(3) Å, V = 29320(2) Å3, Z = 2, 2□max = 58.0º, 39692 reflections collected, 7504 unique (Rint = 0.0766). Final GooF = 1.018, R1 = 0.0576, wR2 = 0.1646, R indices based on 5462 reflections with I >2sigma(I) (refinement on F2). A number of restraints were applied due to disorder in exo-capsule and ligated pyridine molecules. Crystal Data for 3: $C_{652}H_{620}Co_{32}N_{68}O_{96}$, M = 12829.92, CCDC 742756, Yellow Block, 0.13 □ 0.12 □ 0.05 mm3, orthorhombic, space group Fddd (No. 70), a = 18.6001(8), b = 28.4944(11), c = 54.266(2) Å, V = 28761(2) Å3, Z = 2, 2□max = 42.9º, 26582 reflections collected, 3163 unique (Rint = 0.0644). Final

GooF = 1.047, R1 = 0.0531, wR2 = 0.1354, R indices based on 2163 reflections with I >2sigma(I) (refinement on F2). The crystals were weakly diffracting and a number of restraints were applied due to disorder in endo-, exo-capsule and ligated pyridine molecules.

General magnetic susceptibility information: Variable-temperature, solid-state direct current (dc) magnetic susceptibility data were collected on powdered microcrystalline samples on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. The sample was restrained in eicosane to prevent torquing.

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