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Reaction of Ni(OTf)$_2$ with the bisbidentate quaterpyridine ligand L results in the self-assembly of a tetrahedral, paramagnetic cage [$\text{Ni}^{\text{II}}_4\text{L}_6$]$^{8+}$. By selectively exchanging the bound triflate from [$\text{OTf}_\text{I}\text{Ni}^{\text{II}}_4\text{L}_6$](OTf)$_7$ (1), we have been able to prepare a series of host-guest complexes that feature an encapsulated paramagnetic tetrahalometallate ion inside this paramagnetic host giving [$\text{M}^{\text{II}}\text{X}_4\text{I}\text{Ni}^{\text{II}}_4\text{L}_6$](OTf)$_6$, where $\text{M}^{\text{II}}\text{X}_4^{2-} = \text{MnCl}_4^{2-}$ (2), $\text{CoCl}_4^{2-}$ (5), $\text{CoBr}_4^{2-}$ (6), $\text{NiCl}_4^{2-}$ (7), $\text{CuBr}_4^{2-}$ (8) or [$\text{M}^{\text{III}}\text{X}_4\text{I}\text{Ni}^{\text{II}}_4\text{L}_6$](OTf)$_7$, where $\text{M}^{\text{III}}\text{X}_4^{-} = \text{FeCl}_4^{-}$ (3), $\text{FeBr}_4^{-}$ (4). Triflate-to-tetrahalometallate exchange occurs in solution and can also be accomplished through single-crystal-to-single-crystal transformations. Host-guest complexes 1-8 all crystallise as homochiral racemates in monoclinic space groups, wherein the four {$\text{NiN}_6$} vertex within a single $\text{Ni}_4\text{L}_6$ unit possess the same $\Delta$ or $\Lambda$ stereochemistry. Magnetic susceptibility and magnetisation data show that the magnetic exchange between metal ions in the host [$\text{Ni}^{\text{II}}_4$] complex, and between the host and the $\text{MX}_4^{n-}$ guest, are of comparable magnitude and antiferromagnetic in nature. Theoretically derived values for the magnetic exchange are in close agreement with experiment, revealing that large spin densities on the electronegative X-atoms of particular {$\text{MX}_4^{n-}$} guest molecules leads to stronger host-guest magnetic exchange interactions.
Exploiting Host-Guest Chemistry to Manipulate Magnetic Interactions in Metallosupramolecular $\text{M}_4\text{L}_6$ Tetrahedral Cages

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Abstract

Reaction of Ni(OTf)$_2$ with the bisbidentate quaterpyridine ligand L results in the self-assembly of a tetrahedral, paramagnetic cage [Ni$^{II}_4$L$_6$]$^{8+}$. By selectively exchanging the bound triflate from [OTf$_2$-Ni$^{II}_4$L$_6$](OTf)$_2$ (1), we have been able to prepare a series of host-guest complexes that feature an encapsulated paramagnetic tetrahalomartallate ion inside this paramagnetic host giving [M$^{III}$X$_4$-Ni$^{II}_4$L$_6$](OTf)$_6$, where M$^{III}$X$_4$ = MnCl$_6$ (2), CoCl$_6$ (5), CoBr$_6$ (6), NiCl$_6$ (7), CuBr$_6$ (8) or [M$^{III}$X$_6$-Ni$^{II}_4$L$_6$](OTf)$_6$, where M$^{III}$X$_6$ = FeCl$_6$ (3), FeBr$_6$ (4). Triflate-to-tetrahalomartallate exchange occurs in solution and can also be accomplished through single-crystal-to-single-crystal transformations. Host-guest complexes 1-8 all crystallise as homochiral racemates in monoclinic space groups, wherein the four {NiN$_6$} vertex within a single Ni$_4$L$_6$ unit possess the same $\Delta$ or $\Lambda$ stereochemistry. Magnetic susceptibility and magnetisation data show that the magnetic exchange between metal ions in the host [Ni$^{II}_4$] complex, and between the host and the MX$_6$$^{8+}$ guest, are of comparable magnitude and antiferromagnetic in nature. Theoretically derived values for the magnetic exchange are in close agreement with experiment, revealing that large spin densities on the electronegative X-atoms of particular {MX$_6$}$^{8+}$ guest molecules leads to stronger host-guest magnetic exchange interactions.

Introduction

The inherent ability of metallosupramolecular cages to encapsulate different chemical species within their cavity can be exploited for a myriad of applications, including the stabilisation of reactive species, catalysts, and drug-delivery. In all but a few cases, these cages are constructed from diamagnetic metal ions (most commonly Pd$^{II}$, Pt$^{II}$, Fe$^{III}$, Ru$^{III}$, Ga$^{III}$), and even when paramagnetic ions (e.g. Co$^{II}$) are employed, characterising magnetic properties has not been a key focus. However, the exploitation of (reversible) guest encapsulation to induce magnetic exchange interactions with the host could be used in a variety of potential applications including magnetic sensing and switching, the construction of single-molecule magnets, the encapsulation and stabilisation of highly anisotropic single ion magnets with specific geometries, dilution of magnetic molecules in the solid-state, and the organisation of electron spin based qubits within ordered structural frameworks and/or on surfaces. The latter has proven to be extremely difficult since the magnetic properties of molecules are often changed upon deposition. Introducing a magnetic guest into the cavity of a magnetic host could result in a number of potential outcomes. (1) Guest encapsulation has no effect, i.e. there is no magnetic interaction between host and guest and/or there is no geometrical change in either component. (2) There is no magnetic interaction between host and guest, but binding induces structural changes, altering the geometries of the metal ions in the cage and/or the encapsulated guest, modifying magnetic anisotropy. (3) There is a magnetic interaction between host and guest, which may or
may not also change the magnetic exchange between metals ions in the host. (4) There is a combination of points (2) and (3).

In the chemistry of porous coordination polymers, or metal-organic frameworks (MOFs), the ingress of (non-magnetic) guest molecules into the pores of 3D frameworks built from paramagnetic metal ions, such as Co\textsuperscript{1+}, has shown that even simple solvent molecules can modify the magnetic properties of the metal ions via geometry changes induced by intermolecular interactions. The resulting changes in metal anisotropies can lead to significant changes in magnetisation relaxation dynamics. In spin-crossover (SCO) MOFs the high spin - low spin transition temperature is well known to be highly guest-dependent, proffering potential application in molecular recognition. Studies of coordination cages and capsules incorporating a paramagnetic component are limited to the examination of magnetic exchange interactions between metal ions in the cage, SCO (of the cage and guest), and the interaction of organic-radicals in the cavity (with themselves or the cage) or in the host framework. The ability to understand, and ultimately control, host-guest magnetic exchange interactions and single ion magnetooanisotropies in such molecular species would represent an important step toward making coordination cages with tuneable, and potentially useful, magnetic properties. Herein, we discuss the construction of a tetrahedral cage [Ni\textsuperscript{II}L\textsubscript{6}]\textsuperscript{8+} (L = quaterpyridine) that can (reversibly) bind a range of tetrahedral, paramagnetic MX\textsubscript{4}\textsuperscript{12-} guests, inducing magnetic exchange interactions between host and guest.

**Results and Discussion**

The tetrahedral Ni\textsuperscript{II}L\textsubscript{6} cage was synthesised by combining Ni(OTf)\textsuperscript{2-} (4 equivalents) with quaterpyridine (L, 6 equivalents) in acetonitrile, followed by heating for 24 h (see Supporting Information, section 4). The ESI-MS of the isolated complex confirmed the presence of the Ni\textsuperscript{II}L\textsubscript{6} cage, with the +2 to +7 m/z cations being present. The absence of the +8 state strongly suggests that in solution a single triflate anion is bound within the cavity of the cage (Figs. S2-3). X-ray crystallography confirms that the structure of 1 is [OTf\textsubscript{2-}Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{2-} (see below). To generate the [MX\textsubscript{X}\textsubscript{Ni}\textsuperscript{II}L\textsubscript{6}]\textsuperscript{6+} host-guest complexes, the solution obtained after 24 h of heating Ni(OTf)\textsubscript{2-} and L was treated directly with one equivalent of tetraethylammonium tetrahalometallate salt, giving [M\textsuperscript{III}X\textsubscript{X}\textsubscript{Ni}L\textsubscript{6}](OTf)\textsubscript{6} where M\textsuperscript{III}X\textsubscript{X} = MnCl\textsubscript{2-} (2), CoCl\textsubscript{2-} (5), CoBr\textsubscript{2-} (6), NiCl\textsubscript{2-} (7) and CuBr\textsubscript{2-} (8); [M\textsuperscript{III}X\textsubscript{X} = FeCl\textsubscript{2-} (3) and FeBr\textsubscript{2-} (4). The displacement of the encapsulated triflate is confirmed both by X-ray crystallography (see below) and also by ESI-MS. In this case, ESI-MS (Supporting Information, section 4) shows that the highest charged species correspond to [M\textsuperscript{III}X\textsubscript{X}Ni\textsubscript{II}L\textsubscript{6}]\textsuperscript{8+} when M is a divalent metal ion, and [M\textsuperscript{III}X\textsubscript{X}Ni\textsubscript{II}L\textsubscript{6}]\textsuperscript{6+} when M is trivalent. The selectivity of the anion exchange process, wherein a single equivalent of tetrahalometallate displaces the encapsulated triflate rather than any of the external counteranions, can partly be explained by the higher charge of MX\textsubscript{2-} (e.g. where M = Mn\textsuperscript{II}, Co\textsuperscript{II}, Ni\textsuperscript{II} and Co\textsuperscript{II}). However, as singly charged FeX\textsubscript{X} (X = Cl, Br) also displaces the bound triflate, this selectivity is not purely a Coulombic effect, and is likely caused by the shape complementarity of the tetrahedral tetrahalometallate guest for the cage’s pseudo-tetrahedral cavity. Host-guest complexes 2-8 can also be reversibly forming through single-crystal-to-single-crystal transformations. For example, when orange crystals of 1 are soaked in an EtOH solution of (Et\textsubscript{3}N)\textsubscript{2}NiCl\textsubscript{2} for 2 hours, green crystals of 7 are formed. The process is reversed by soaking crystals of 7 in an EtOH solution of Bu\textsubscript{4}N\textsuperscript{+}OTf (Fig. S1).

**Crystal Structure Descriptions**

Single crystals of [OTf\textsubscript{2-}Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{2-} (1) and [MX\textsubscript{X}Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (2–8) were obtained from vapour diffusion of THF and/or Et\textsubscript{2}O into the MeCN mother liquor. Synchrotron radiation was required to obtain single crystal data for complexes 2 (MX\textsubscript{X} = MnCl\textsubscript{2-}), 7 (MX\textsubscript{X} = NiCl\textsubscript{2-}) and 8 (MX\textsubscript{X} = CuCl\textsubscript{2-}). All eight complexes crystallise in monoclinic cells, with 1–4, 7 and 8 being in the space group C2/c, and 5 and 6 in the P2\textsubscript{1}/n and P2\textsubscript{1}/c space groups, respectively (Table S1–2). The structures of compounds 1–8 are very similar, and so for the sake of brevity, a generic description is provided. Pertinent bond lengths and angles given in Table S3. The cationic cage describes a [Ni\textsuperscript{II}L\textsubscript{6}]\textsuperscript{8+} tetrahedron, which, akin to other M\textsubscript{L\textsubscript{6}} assemblies, has the Ni\textsuperscript{II} ions occupying the...
four vertices linked by bisbidentate L ligands lying on each of the six edges (Fig. 1a). The approximate dimensions of the tetrahedron in 1–8 are Ni$^{II}$–Ni$^{II}$ = 9.2–9.6 Å, with the internal cage volumes ranging from 62–81 Å$^3$. The volumes, pore diameters and average window diameters for each compound are given in Table S4.30. The Ni$^{II}$ ions are six-coordinate and in distorted NiN$_6$ octahedral geometries, with Ni-N distances between 2.03(3)–2.17(3) Å and cis/trans angles in the range 76.4(12)–102.28(13)/170.3(11)–176.6(6)$^\circ$, respectively. Each tetrahedron has T-symmetry, possessing four metallic vertices with the same stereochemistry (Δ or Λ). All compounds crystallise as racemic mixtures of the homochiral cage (i.e. an equal mixture of ΔΔΔΔ and ΛΛΛΛ stereoisomers). Consistent with the ESI-MS observations, 1 has a positionally disordered triflate anion occupying the cavity (Fig 1b). There are interactions between the O and F atoms of the anion and the inward facing ortho-pyridyl H atoms of L (O/F−H−Ar ≈ 2.52 Å). The remaining seven triflate anions surround the exterior of the tetrahedron, maintaining charge balance. These, and the solvent of crystallisation, are involved in a number of intermolecular interactions that connect neighbouring cages.

Fig. 1. (a) Framework of the empty [Ni$^{II}_{4}$L$_{6}$]$^{8+}$ tetrahedron emphasising the connectivity of the assembly. (b). Structure of the [OTf$^-$$\text{Ni}^{II}_{4}$L$_{6}$]+ host-guest tetrahedron of 1. Non-encapsulated triflate anions and solvent of crystallisation are removed for clarity, highlighting the connectivity between the bisbidentate quaterpyridine ligands L and the Ni$^{II}$ ions. Colour code: Ni = orange, N = blue, C = grey, H = white.
Complex 7, [NiCl\textsubscript{4}Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6}, is shown in Figure 2 as a representative tetrahalometallate-cage structure (for depictions of 2-6 and 8, along with pertinent bond lengths and angles, see Supporting information). With the exception of 4, which shows a 1:1 partial occupancy of FeBr\textsubscript{4}\textsuperscript{−} and OTF\textsuperscript{−}, the tetrahalometallate guests are positionally ordered with full occupancy, showing regular tetrahedral geometry. In each case the guest anion is positioned such that the MX\textsubscript{4}n− tetrahedron is inverted with respect to the cage’s [Ni\textsubscript{4}L\textsubscript{6}]	extsuperscript{8+} tetrahedron, i.e. the halide atoms point towards of the portals of the tetrahedron. The host-guest interactions are similar to 1, with the closest contacts between the tetrahalometallate halide atoms and the ortho-pyridyl positions of the cage’s ligand. For example, in 7, the distances between the host and guest are: Cl···H−Ar = 2.86 Å (Fig. 2b). As with 1, the external triflate anions and solvent of crystallisation connect neighbouring cages through a network of interactions with the host framework. In the extended structure this results in alternating layers of cages / anions and solvent molecules of crystallisation (Figs. S18–34, Table S5).
SQUID Magnetometry

The direct-current (d.c.) molar magnetic susceptibility, $\chi_m$, of polycrystalline samples of 1–8, were measured in an applied magnetic field, $B$, of 0.1 T, over the 2–300 K temperature, $T$, range. The results are plotted in Fig. 3 in the form of $\chi_m T$ product, where $\chi_m = M / B$ with $M$ the magnetisation. At room temperature the $\chi_m T$ products of 1–8 are 4.52, 8.86, 8.87, 8.82, 6.42, 6.35, 6.12 and 4.92 cm$^3$ K mol$^{-1}$, respectively. These values are close to the Curie constants expected for uncorrelated paramagnetic centres (4.54, 8.92, 8.92, 6.42, 6.42, 5.67 and 4.92) with $g = 2$ for all metal ions, except for Ni$^{II}$ where $g_{Ni} = 2.13$ (vide infra). With the exception of 7, on lowering the temperature, the $\chi_m T$ products of 1–8 are essentially constant down to the temperature range 50–20 K, whereupon a further decrease of temperature results in the gradual drop of the $\chi_m T$ products of all complexes, to reach their respective minimum values at 2 K. This behaviour is indicative of weak antiferromagnetic interactions operating in 1–8. The faster drop of the $\chi_m T$ product of 7 from ~100 K indicates that the tetrahedral Ni$^{II}$ guest displays significant magnetic anisotropy, of the same order of magnitude as the temperature.

To better define the low temperature magnetic properties of 1–8, we performed variable-temperature-variable-field (VTVB) dc magnetisation measurements on polycrystalline samples in the temperature range 2–7 K and in applied magnetic fields up to 7 T. The results of these VTVB measurements are given in the insets of Fig. 3 as the field dependent magnetisation, and as the magnetisation dependence against the reduced quantity $\mu_B B/kT$ with $\mu_B$ and $k$ the Bohr magneton and Boltzman constant, respectively, (Figs. S35–42) that expresses the ratio between Zeeman and thermal energies. Inspection of these reduced magnetisation traces reveals that the ground states of 1–8 are weakly anisotropic, as evidenced by the limited nesting of the curves. Thus, the magnetic anisotropy of the constitutive single ions is either very small, as expected for Cu$^{II}$, Fe$^{II}$ and Mn$^{II}$, or very large (Ni$^{II}$) with respect to the experimental conditions ($B$, $T$). For the quantitative interpretation of the magnetic properties of 1–8, we used spin-Hamiltonian (1):

$$\hat{H} = \hat{H}_{Host} + \hat{H}_{Guest} \quad (1)$$

$$\hat{H}_{Host} = \mu_B B g_{Ni} \sum_{i=1}^{4} \hat{S}_i + D_{Ni} \sum_{i=1}^{4} \hat{S}_{ix}^2 - \frac{S_{Ni} (S_{Ni} + 1)}{3} - 2 \sum_{i=1}^{4} \sum_{j>i} J_{ij} \hat{S}_i \cdot \hat{S}_j \quad (2)$$

$$\hat{H}_{Guest} = \mu_B B g_{Guest} \hat{S}_{Guest} + D \left[ \hat{S}_{Guest,x}^2 - \frac{S_{Guest} (S_{Guest} + 1)}{3} \right] - 2 \sum_{i=1}^{4} J_{Guest} \hat{S}_i \cdot \hat{S}_{Guest} \quad (3)$$

where $\hat{H}_{Host}$ is the spin-Hamiltonian relative to 1, $\hat{H}_{Guest}$ is the Hamiltonian relative to the guests in 2–8 and their interaction with the host 1, $i, j$ are indices that run over the constitutive centres, $g_{Ni}$ the $g$-value of Ni$^{II}$, $\hat{S}_i$ the spin operator of the $i^{th}$ paramagnetic centre, $D_{Ni}$ the single-ion axial anisotropy parameter of Ni$^{II}$, $S_{Ni} = 1$ the total spin of Ni$^{II}$, $J_{ij}$ the pairwise isotropic magnetic exchange interaction parameter between centres $i$ and $j$, with the equivalent quantities for the guests. The $\chi_m T$ product and the VTVB data for 1–8 were simultaneously fitted to spin-Hamiltonian (1), by full matrix numerical diagonalisation of its matrix representation and by use of the Simplex algorithm. For 1, fitting of the $\chi_m T$ product and the VTVB data resulted in the best-fit parameters: $g_{Ni} = 2.13$, $|D_{Ni}| = 1.575$ cm$^{-1}$ and $J_{Ni-Ni} = -0.078$ cm$^{-1}$ (Fig. 3). The relatively small uniaxial anisotropy parameter, $D_{Ni}$, of the Ni$^{II}$ centres of the host is in agreement with their approximate octahedral symmetry. These parameters were subsequently fixed for the quantitative interpretation of the magnetic properties of 2–8. For simplicity, the $g$-values of all guests were
fixed to 2, except for 7 where we set the g-value of the guest NiII ion equal to $g_{\text{Ni}} = 2.13$, as determined for 1. Thus for 2 the model contained only one free parameter, namely $J_{\text{Ni,Mn}}$. Simultaneous fitting of the $\chi_M T$ and VTVB data of 2 resulted in the best-fit parameters: $J_{\text{Ni,Mn}} = -0.041 \text{ cm}^{-1}$. Analogously, the best fit parameters for 3 were: $J_{\text{Ni,Fe}} = -0.068 \text{ cm}^{-1}$ ($D_{\text{Fe}}$ was neglected for FeIII); for 4: $J_{\text{Ni,Fe}} = -0.084 \text{ cm}^{-1}$ ($D_{\text{Fe}}$ was neglected for FeIII); for 5: $|D_{\text{Co}}| = 2.37 \text{ cm}^{-1}$ and $J_{\text{Ni,Co}} = -0.005 \text{ cm}^{-1}$; for 6: $|D_{\text{Co}}| = 6.30 \text{ cm}^{-1}$ and $J_{\text{Ni,Co}} = -0.001 \text{ cm}^{-1}$; for 7: $|D'_{\text{Ni}}| = 85.5 \text{ cm}^{-1}$ and $J'_{\text{Ni,Ni}} = -0.476 \text{ cm}^{-1}$; and for 8: $J_{\text{Ni,Cu}} = -0.062 \text{ cm}^{-1}$ ($D_{\text{Cu}}$ was neglected for CuII). The values are tabulated in Table 1 for convenience. Note that the large $D'_{\text{Ni}}$ value for the guest in 7 is of the magnitude expected for a tetrahedral NiII ion, and in agreement with the faster drop of the $\chi_M T$ product with decreasing temperature, absent for all other compounds. For these other compounds, the guest magnetic anisotropy is approximately two orders of magnitude smaller, or entirely negligible.

|        | $J$ (cm$^{-1}$) | $|D|$ (cm$^{-1}$) |
|--------|----------------|------------------|
| 1      | $J_{\text{Ni,Fe}} = -0.078$ (No MX guest - fixed for 2–8) | $|D_{\text{Fe}}| = 1.575$ (No MX guest - fixed for 2–8) |
| 2      | $J_{\text{Ni,Mn}} = -0.041$ | Neglected for MnII |
| 3      | $J_{\text{Ni,Fe}} = -0.068$ | Neglected for FeII |
| 4      | $J_{\text{Ni,Fe}} = -0.084$ | Neglected for FeII |
| 5      | $J_{\text{Ni,Co}} = -0.005$ | $|D_{\text{Co}}| = 2.37$ |
| 6      | $J_{\text{Ni,Co}} = -0.001$ | $|D_{\text{Co}}| = 6.30$ |
| 7      | $J'_{\text{Ni,Ni}} = -0.476$ | $|D'_{\text{Ni}}| = 85.5$ |
| 8      | $J_{\text{Ni,Cu}} = -0.062$ | Neglected for CuII |

**Table 1.** Exchange interactions ($J$) and axial zero-field splitting ($D$) parameters for 1–8 derived from a simultaneous fit of the susceptibility and magnetisation data employing spin-Hamiltonian (1).

**Theoretical Studies**

The magnetic properties of all eight complexes have been investigated using both DFT and *ab initio* methods. DFT calculations have been employed to estimate the isotropic exchange coupling constants ($J$) using the Hamiltonian $\hat{H} = -2J \sum_{i<j} \hat{S}_i \cdot \hat{S}_j$. On-site spin-orbit coupling / zero-field splitting (zfs) calculations require accurate estimation of excited state energies, and a single-determinant description of the wavefunction is not sufficient for systems having orbital degeneracies or those possessing low-lying excited states. For this reason, *ab initio* CASSCF/NEVPT2 calculations have been performed (see the Computational Details in the ESI for more information).

**Electronic structure of the empty Ni$_6$L$_6$ cage**

Calculations have been performed on the full X-ray structure without any geometry relaxation. The $J_{\text{Ni-Ni}}$ interaction is estimated to be $-0.062 \text{ cm}^{-1}$, very close to the experimental value of $-0.078 \text{ cm}^{-1}$ (Table 2). The magnitude of the antiferromagnetic exchange suggests that the SOMOs of neighbouring NiII ions are weakly interacting. The distance between metal ions is not particularly long (~9.5 Å), but significant twisting between the bipyridine units (Figs. 1 and 4; dihedral angle = 45–60°) hinders the spin polarisation mechanism. Spin density values on the NiII ions in 1 are found to be ~1.64, which is as expected for octahedral NiII centres possessing strong spin delocalisation (Fig. S43). The spin ground state is found to be an $S = 0$ state with two “spin-up” and two “spin-down” NiII ions. The axial zfs of the octahedral NiII ions in the cage is found to be $D = -2.25 \text{ cm}^{-1}$, in agreement with the experimental data. Such a value would be expected given the high symmetry and close-to-perfect octahedral geometry around the NiII centres. For the CASSCF/NEVPT2 calculations, the other NiII centres were substituted by diamagnetic ZnII ions.
Fig. 3. \( \chi_M T \) versus \( T \) plots for [OTf:Ni\textsuperscript{II}L\textsubscript{4}] (1) and [M\textsuperscript{II}X\textsuperscript{2−}Ni\textsuperscript{II}L\textsubscript{4}](OTf), where M\textsuperscript{II}X\textsuperscript{2−} = MnCl\textsuperscript{2−} (2), CoCl\textsuperscript{2−} (5), CoBr\textsuperscript{2−} (6), NiCl\textsuperscript{2−} (7), CuBr\textsuperscript{2−} (8) or [M\textsuperscript{III}X\textsuperscript{2−}Ni\textsuperscript{II}L\textsubscript{4}](OTf), where M\textsuperscript{III}X\textsuperscript{2−} = FeCl\textsuperscript{2−} (3), FeBr\textsuperscript{2−} (4) in the range \( T = 2–300 \) K and \( B = 0.1 \) T. The insets show the field dependence of the magnetisation measured in the \( T = 2–7 \) K and \( B = 0–7.0 \) T temperature and field ranges. The black spheres are the experimental data and the red lines the fit of the experimental data using spin-Hamiltonian (1), as explained in the text.
Electronic structure of the MX₄Ni₄L₆ cages (2–8)

For complex 2, incorporation of the MnCl₂⁻ anion inside the [Ni₄L₆]⁸⁺ cage introduces an exchange interaction between host and guest (J_{Mn-Ni}) in addition to the J_{Ni-Ni} exchange. The spin state energies of the host-guest molecules have been computed considering a pentametallic MnNi₄ unit. The J_{Ni-Ni} and the J_{Mn-Ni} exchange interactions are estimated to be −0.09 cm⁻¹ and −0.01 cm⁻¹, respectively. Here the spin ground state is S = 5/2 (Fig. 4, Fig. S44, Table S6 (BS3)).

The weaker J_{Mn-Ni} exchange originates from the dipolar Cl···H−Ar interaction which mediates the coupling. The zfs of the Mn^{II} ion is estimated to be very small, D = −0.002 cm⁻¹, in accordance with the isotropic nature of a tetrahedral d⁵ centre.³⁴ Similar analyses were performed on the remaining host-guest complexes. For complex 3, the J_{Fe-Ni} and J_{Ni-Ni} interactions are found to be −0.073 cm⁻¹ and −0.074 cm⁻¹, respectively (Table 2). Note that J_{Fe-Ni} is stronger than J_{Mn-Ni}: a closer examination of the spin densities computed on the Cl atoms of 2 and 3 reveals stronger delocalisation of the spin density in 3 compared to that in 2 facilitating stronger exchange interactions. This is correlated to the shorter Fe-Cl distance (2.20 Å) in 3 compared to the Mn-Cl distance (2.38 Å) in 2. The CASSCF/NEVPT2 computed D values for the guest ions in complexes 2–4 are small. Indeed, they are smaller than the energy separation between the spin state energies arising from the exchange interaction.

A similar situation is observed for complex 4 with [FeBr₄]⁻ as the guest. In this case the host-guest antiferromagnetic exchange is larger (−0.085 cm⁻¹) than for 2 and 3. The spin density on the Fe^{III} ion is significantly reduced due to strong spin delocalisation on to the electronegative Cl⁻ and Br⁻ ions in 3 and 4 (Table S6). Interestingly, in complexes 5 and 6, where [CoCl₄]²⁻ and [CoBr₄]²⁻ are the guest molecules, J_{Co-Ni} was found to be weakly ferromagnetic from DFT calculations (+0.012 and +0.025 cm⁻¹, respectively; Table 2). The sign of J_{Co-Ni} is contrary to experiment, albeit both the magnitude of the exchange and the absolute difference in the exchange is extremely small. Thus, both experiment and theory point to the presence of extremely weak exchange in this instance, and we note that these particular J values are at the limit of what DFT can accurately reproduce. More importantly, the D_{Co} values determined from ab initio methods are −6.64 cm⁻¹ (5) and −3.96 cm⁻¹ (6), three orders of magnitude higher than the energy separation between the exchange-coupled spin states, i.e., |D| > J. The MS level separations, i.e., the gap between the ±3/2 and ±1/2 microstates for Co^{II} are much larger (≈2|D|) and close to 13 cm⁻¹ and 8 cm⁻¹, respectively. Deviation from ideal T₅ symmetry is well-known to result in a significant D value for tetrahedral Co^{II} ions.³⁵–³⁸
For complex 7, the orbital degeneracy of the tetrahedral Ni$^{II}$ ion precluded convergence of the DFT calculations and thus no host-guest $J_{Ni-Ni}$ exchange coupling could be estimated. NEVPT2 calculations yield a $D$ value of $+214 \text{ cm}^{-1}$ for $[\text{NiCl}_4]^{2-}$, a value much larger than that estimated from experimental susceptibility and magnetisation data. The origin of this very large anisotropy can be explained from the NEVPT2-LFT orbital splitting pattern of the pseudo-$T_d$ $[\text{NiCl}_4]^{2-}$ complex shown in Fig. 5. Here the first four excited states contribute strongly to the large positive $D$ value, and arise primarily from the $d_{xy} \rightarrow d_{yz}/d_{xz}$ and $d_{x^2-y^2} \rightarrow d_{yz}/d_{xz}$ electronic excitations (Table S7). CASSCF/NEVPT2 calculations carried out on the DFT optimised $[\text{NiCl}_4]^{2-}$ geometry yield a similar value, $D = +210 \text{ cm}^{-1}$. We have also computed the deformation energy of $[\text{NiCl}_4]^{2-}$ inside the cage. This is calculated as the difference in energy between the DFT optimised structure and the single-point energy calculated on the guest $[\text{NiCl}_4]^{2-}$. This is estimated to be $18.6 \text{ kJ mol}^{-1}$, which indicates a small structural distortion upon encapsulation.

In complex 8, the exchange interactions between Ni-Ni and Ni-Cu ions are rather similar, $J_{Ni-Ni} = -0.064 \text{ cm}^{-1}$ and $J_{Ni-Cu} = -0.066 \text{ cm}^{-1}$. The spin ground state is $S = 1/2$ (BS3, Fig. S45). Due to strong spin delocalisation from the Cu$^{II}$ ion onto its four Br$^{-}$ ions the spin density value on the metal ion reduces to just 0.39.

The theoretically determined spin-Hamiltonian parameters have been used to simulate the experimental susceptibility and magnetisation data (Fig. S46–S47). During simulation, we adopted three different spin-Hamiltonians to describe the magnetic properties for the eight complexes. For complexes 1–4 and 8 both the metal ions in the host cage and in the guest anions are found to be completely isotropic — the zfs / $D$ values of the Mn$^{II}$, Fe$^{III}$ and Ni$^{II}$ (cage) centres are very small and comparable to the $J$ values (i.e. $D \approx J$). For these five species, spin-Hamiltonian (4) was employed for simulation. All give very good agreement with the experimental data (Fig. S46). For complex 8, the g-factors for the Cu$^{II}$ ion from the NEVPT2 level of theory, $g_x = 1.633$, $g_y = 2.126$ and $g_z = 4.078$ are overestimated. This is a well-known problem in the literature for Cu$^{II}$. Higher electron correlation, higher reference space and/or ligand orbital inclusion, should be taken into consideration. We have therefore performed multi-reference CI (MRCI) calculations in combination with the CASSCF wavefunction to obtain the final g-factors, $g_x = 1.945$, $g_y = 2.470$ and $g_z = 2.879$ ($g_{iso}= 2.43$), which remain anisotropic due to mixing with the bromide orbitals. Simulation of the susceptibility and magnetisation data shows excellent agreement with the experimental data (Fig. S47).
Hamiltonian (5) to simulate the experimental data, given the simplicity of the model (Fig. S46). Instead of using $J$ values for the Co$^{II}$ ion, ground state effective g-factors for individual Kramers pairs are used as $S = 1/2$ pseudo-spins (Ising Hamiltonian; Table 2). This produces a very nice simulation of the experimental data, given the simplicity of the model (Fig. S46–47). Note that the simulations are unaffected by the sign of the $J_{Ni-Co}$ exchange. For complex 7, which contains the highly anisotropic [NiCl$_4$]$^{2-}$ guest anion, we have used spin-Hamiltonian (6) in which all exchange interactions are neglected, since $D_{Ni} >> J$ [the inclusion of any reasonable $J_{host-guest}$ value does not affect the simulation]. Note that the g-factors obtained from the NEVPT2 method for [NiCl$_4$]$^{2-}$ are overestimated, as expected for

Table 2. Comparison of experimental and computational spin-Hamiltonian parameters for complexes 1–8.

| $Exp J$ (cm$^{-1}$) | $Cal J$ (cm$^{-1}$) | $Exp |D|$ (cm$^{-1}$) | $Cal D$ (cm$^{-1}$) | $Exp$ g-factors/$g_{iso}$ | $Calc.$ g-factors/$g_{iso}/g_\nu g_\alpha g_\beta g_\gamma$
|----------------|----------------|----------------|----------------|----------------|----------------|
| 1
| $J_{host}$ = -0.078 (No MX: guest – fixed for Z–8)
| $J_{Ni} = -0.062$
| 1.575 (fixed for Z–8)
| -2.25 (E/D = 0.15) for Ni$^{III}$
| 2.13
| $g_{eff} = 2.165, 2.171, 2.184$
| 2
| $J_{host}$ = -0.041
| $J_{Ni} = -0.11$
| $J_{host}$ = -0.090
| Neglected for Mn$^{III}$
| -0.002 (E/D = 0.08) for Mn$^{III}$
| $g_{eff} = 2.00$ for Mn
| 3
| $J_{host}$ = -0.068
| $J_{Ni} = -0.073$
| $J_{host}$ = -0.074
| Neglected for Fe$^{III}$
| 0.01 (E/D = 0.26) for Fe$^{III}$
| $g_{eff} = 2.00$ for Fe
| 4
| $J_{host}$ = -0.084
| $J_{Ni} = -0.085$
| $J_{host}$ = -0.073
| Neglected for Fe$^{III}$
| -0.07 (E/D = 0.16) for Fe$^{III}$
| $g_{eff} = 2.00$ for Fe
| 5
| $J_{host}$ = -0.005
| $J_{Ni} = +0.12$
| $J_{host}$ = -0.079
| (Co) 2.37
| (E/D = 0.30) for Co$^{III}$
| Co: $g_{eff} = 1.557, 2.086, 6.619$
| 6
| $J_{host}$ = -0.001
| $J_{Ni} = +0.025$
| $J_{host}$ = -0.076
| (Co) 6.30
| (E/D = 0.17) for Co$^{III}$
| Co: $g_{eff} = 1.038, 1.234, 6.993$
| 7
| $J_{host}$ = -0.476
| $J_{Ni} = -0.78$
| -
| (Ni) 85.5
| (E/D = 0.26) for Ni$^{II}$
| Ni: $g_{eff} = 3.493, 2.864, 1.689$
| 8
| $J_{host}$ = -0.062
| $J_{Ni} = -0.066$
| $J_{host}$ = -0.064
| Neglected for Cu$^{II}$
| -
| (Cu) 2.00
| Cu: $g_{eff} = 2.43$

For complexes 5 and 6, the $D$ parameters of Co$^{III}$ are small but still much larger than the spin state energies / $J$ values (i.e. $|D| > J$). In these two cases, we have used spin-Hamiltonian (5) to simulate the experimental susceptibility and magnetisation data. Instead of using $D$ values for the Co$^{III}$ ion, ground state effective g-factors for individual Kramers pairs are used as $S = 1/2$ pseudo-spins (Ising Hamiltonian; Table 2). This produces a very nice simulation of the experimental data, given the simplicity of the model (Fig. S46–47). Note that the simulations are unaffected by the sign of the $J_{Ni-Co}$ exchange.
the highly anisotropic Ni$^{III}$ ion. Simulation of susceptibility and magnetisation data is given in Fig. S47 and shows good agreement with the experimental data, albeit of a slightly larger magnitude.

Conclusions

The tetrahedral cage [OTf\(\subset\)Ni$^{III}$L$_6$](OTf)$_7$ (1) can be synthesised from the one pot reaction of Ni(OTf)$_2$ and quaterpyridine (L) in acetonitrile. The analogous host-guest complexes, [M$^{III}$X$_6$\(\subset\)Ni$_4$L$_4$](OTf)$_9$ = MnCl$_2$$^{-}$ (2), CoCl$_2$$^{-}$ (5), CoBr$_2$$^{-}$ (6), NiCl$_2$$^{-}$ (7) and CuBr$_2$$^{-}$ (8), [M$^{III}$X$_6$\(\subset\)Ni$_4$L$_4$](OTf)$_7$ = FeCl$_2$$^{-}$ (3) and FeBr$_2$$^{-}$ (4) are formed from 1 by the selective exchange of the encapsulated triflate anion. The complexes can also be formed and interconverted through single-crystal-to-single-crystal transformations. Magnetic susceptibility and magnetisation data show that the magnetic exchange interactions between metal ions in the host complex, and between host and guest, are of comparable magnitude and antiferromagnetic in nature. Theoretically derived values for the exchange are in close agreement with experiment and reveal that large spin densities on the electronegative X-atoms of certain MX$_4$$^{-}$ guest molecules leads to stronger host-guest magnetic exchange interactions. For the tetrahedral Co$^{III}$ guests, the anisotropy is small but still much larger than the magnitude of exchange coupling between host-host and host-guest. The orbital degeneracy of the tetrahedral Ni$^{III}$ ion and the very large zfs that results makes accurate estimation of $J_{Ni-Ni}$ exchange and $D_{Ni(tet)}$ in (7) rather difficult, as reflected in the large differences in the results obtained between experiment and theory.

What is clear, however, is that the encapsulation of paramagnetic guests inside dia/paramagnetic cages can be very useful in an array of potential applications. These include sensing and switching, the encapsulation and stabilisation of highly anisotropic (and/or air- and moisture-sensitive) magnetic molecules and the organisation (and/or dilution) of magnetic molecules within ordered, solution-stable structural matrices. To date, surface deposition of magnetic molecules has proved problematic, since in the vast majority of cases structural/magnetic integrity is compromised hindering application. Encapsulation of metal complexes such as spin-crossover species, single-ion magnets (SIMs) or electron spin based qubits within a dia/paramagnetic cage whose exohedral organic skeleton is easily derivatised may prove to be an interesting option. The cage acting both as a surface anchor and a protective coating for the magnetic molecule. Although only relatively small changes to the geometries of the MX$_4$$^{-}$ guests were observed here, this work also suggests that the deliberate distortion/construction of magnetic molecules through encapsulation within the confines of a sterically restricted cavity of a coordination cage may offer an alternative route to producing highly unusual/anisotropic SIMs with specific geometries, tailored ligand fields, and targeted symmetries. In turn, such species may display a breadth of fascinating structures and magnetisation relaxation dynamics that may not exist outwith the cage.

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Supporting Information

Exploiting Host-Guest Chemistry to Manipulate Magnetic Interactions in Metallosupramolecular $M_4L_6$ Tetrahedral Cages

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## Contents

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1 Materials and Methods

Unless stated otherwise, all reagents and solvents were purchased from Alfa Aesar, VWR, Fluorochem or Sigma Aldrich and used without further purification. Where the use of anhydrous solvent is stated, drying was carried out using a solvent purification system manufactured by Glass Contour. Column chromatography was carried out using Geduran Si60 (40–63 μm) as the stationary phase and TLC was performed on precoated Kieselgel 60 plates (0.20 mm thick, 60F254, Merck, Germany) and observed under UV light at 254 nm or 365 nm. All reactions were carried out under air, unless stated otherwise.

All $^1$H and $^{13}$C NMR spectra were recorded on either a 500 MHz Bruker AV III equipped with a DCH cryo-probe (Ava500), a 500 MHz Bruker AV IIIHD equipped with a Prodigy cryo-probe (Pro500), a 600 MHz Bruker AV IIIHD equipped with a TCI cryo-probe (Ava600) or a 400 MHz Bruker AV III equipped with BBFO+ probe (Ava400) at a constant temperature of 300 K. Chemical shifts are reported in parts per million (ppm). Coupling constants ($J$) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, q = quartet, t = triplet, d = doublet, s = singlet, app. = apparent. Where required, peak assignments were confirmed through a range of two-dimensional techniques including, correlated spectroscopy (COSY), nuclear Overhauser effect spectroscopy (NOESY), heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC).

MS of the compounds was performed on a Synapt G2 (Waters, Manchester, UK) mass spectrometer or a Q-ToF (Micromass UK Ltd), using a nano-electrospray ionization source (ESI), controlled using Masslynx v4.1 software. All the scans in the experimental are for positive ions. Crystals of the samples were dissolved in acetonitrile at 50 μM. Prior to analysis, instruments were calibrated using a solution of sodium iodide (2 mg/mL) in 50:50 water:isopropanol. Capillary voltages were adjusted between 1.5 and 2.5 kV to optimize spray quality, while the sampling cone and the extraction cone voltage were minimised to reduce breakdown of the assemblies. Source temperature was set at 80 °C. The data was analysed using the MassLynx v4.1 software.
Magnetisation measurements were carried out on a Quantum Design SQUID MPMS-XL magnetometer at The University of Edinburgh, operating between 1.8 and 300 K for DC applied magnetic fields ranging from 0 to 5 T. Some measurements were made on the MPMS3 magnetometer at The University of Glasgow, operating between 1.8 and 300 K for DC applied magnetic fields ranging from 0 to 7 T.
2 Synthesis

Tetrahalometallates

All tetrahalometallates were prepared based on previously published methods.\(^1\)

\(M = \text{Mn, Fe, Co, Ni and Cu}, \ X = \text{Cl and Br}.\)

Anion \(X\) matched in the synthesis i.e. \(\text{MX}_2\) and \(\text{Et}_4\text{NX} = \text{CoCl}_2\) and \(\text{Et}_4\text{NCl}\). \(\text{MX}_2\) (3 mmol) was dissolved in \(\text{EtOH}\) (30 mL) and stirred, \(\text{Et}_4\text{NX}\) (9 mmol) was then added and stirred at room temperature for 1 hour. The precipitate was then filtered and washed with cold \(\text{EtOH}\) (3 \(\times\) 10 mL) and \(\text{Et}_2\text{O}\) (3 \(\times\) 10 mL). The product was then dried under vacuum to yield the product. Yields in excess of 80%.

2,2\(^{':5',5''':2'',2'''}\)-Quaterpyridine (L)

\[
\begin{align*}
\text{ZnBr} & \quad + \quad \text{Brbpy} \\
\text{Pd(PPh}_3)_4, \text{THF, N}_2, \text{RT, 16 h} & \quad \rightarrow \\
\text{Br} & \quad \text{Brbpy} \\
\text{i) NiCl}_2, \text{PPh}_3, \quad 50^\circ\text{C, 2 h} & \quad \rightarrow \\
\text{Zn, RT, 2 h} & \quad \rightarrow \\
\text{Brbpy, 16 h} & \quad \rightarrow \\
\end{align*}
\]

5-bromo-2,2\(^1\)-bipyridine (Brbpy)

The following procedure is based on a previously published method.\(^2\)

To a flame dried flask, 5-bromo-2-iodopyridine (11.36 g, 40 mmol) and \(\text{Pd(PPh}_3)_4\) (0.462 g, 0.4 mmol) were added. Vacuum and \(\text{N}_2\) was cycled three times before the addition 2-pyridyl zinc bromide in \(\text{THF}\) (0.5 M, 100 mL, 50.0 mmol). The resulting mixture was purged with \(\text{N}_2\) for 15 minutes and then stirred at room temperature for 16 hours. A beige suspension formed to which 0.25 M EDTA/1 M NaOH (200 mL) and saturated \(\text{Na}_2\text{CO}_3\) solution (100 mL) was added and stirred for 30 minutes. The resulting mixture was extracted with \(\text{CH}_2\text{Cl}_2\) (4 \(\times\) 200 mL). The combined organic phases were dried over anhydrous \(\text{MgSO}_4\). Solvent was then removed \textit{in vacuo} and
the crude product was purified by silica flash column (Hexane with 5–10% EtOAc) to give the title compound as a white solid. Yield = 8.46 g (90%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 8.72 (d, J = 2.3 Hz, 1H), 8.67 (d, J = 4.7 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 8.32 (d, J = 8.5 Hz, 1H), 7.94 (dd, J = 8.5, 2.4 Hz, 1H), 7.82 (td, J = 7.8, 1.8 Hz, 1H), 7.33 (ddd, J = 7.6, 4.8, 1.1 Hz, 1H).

2,2':5',5'':2'',2''''-Quaterpyridine (L)

To a flame dried flask, NiCl$_2$ (2.33 g, 18 mmol) and PPh$_3$ (1.78 g, 6.8 mmol) were added and the vacuum and N$_2$ was cycled three times. Anhydrous DMF (100 mL) was then added and the mixture was heated at 50 °C until the mixture became dark blue (30 minutes–2 hours). Once cooled to room temperature Zn dust (1.21 g, 18.5 mmol) was added and stirred until dark brown (30 min–2 hours). A solution of dried Brbpy (4.00 g, 17 mmol) in anhydrous DMF (50 mL) was added to the reaction mixture via cannula and left to stir at room temperature for 16 h. The solvent was removed in vacuo and an EDTA (10 eq.)/NaOH (40 eq.) solution (400 mL) and CH$_2$Cl$_2$ (200 mL) was added and stirred for 16 h. The mixture was separated, and the aqueous phase was further extracted with CH$_2$Cl$_2$ (3 × 200 mL). The combined organic phases were dried over anhydrous MgSO$_4$, filtered and solvent removed in vacuo. The crude product was suspended in CH$_3$CN (50 mL) and heated to boil. Once cooled the yellow crystalline solid was filtered under vacuum and dried with Et$_2$O to yield the title product. Yield = 2.22 g (84%). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ (ppm): 9.00 (dd, J = 2.4, 0.8 Hz, 2H, H$_g$), 8.72 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H, H$_a$), 8.55 (dd, J = 8.2, 0.8 Hz, 2H, H$_e$), 8.47 (dt, J = 8.0, 1.0 Hz, 2H,H$_b$), 8.10 (dd, J = 8.2, 2.4 Hz, 2H, H$_f$), 7.86 (app. td, J = 7.8, 1.8 Hz, 2H, H$_c$), 7.35 (ddd, 7.6, 4.8, 1.2 Hz, 2H, H$_d$).
Host-Guest Complexes

\[ [\text{OTf} \subset \text{Ni}^{II} \cdot \text{L}_6] \cdot (\text{OTf})_7 \, (1) \]

\( \text{L} \) (46.6 mg, 0.15 mmol) and \( \text{Ni(OTf)}_2 \) (35.7 mg, 0.1 mmol) were suspended in \( \text{CH}_3\text{CN} \) (6.0 mL) in a microwave vial. The vessel was sealed and heated at 90 °C for 1 day. The orange solution was filtered and crystallisations were set up by vapour diffusion in THF yielding dark orange X-ray quality crystals. Yields varied between 60–80%.

ESI-MS (\( m/z \)): 1495 (2+), 947 (3+), 673 (4+), 509 (5+), 399 (6+), 321 (+7).

\[ [\text{M}^{II/III} \cdot \text{X}_4 \subset \text{Ni}^{II} \cdot \text{L}_6] \cdot (\text{OTf})_{6/7} \, (2–8) \]

In preparation of the host-guest complexes, the synthesis of 1 was repeated, however, before crystallisations were set up the guests were added in \( \text{CH}_3\text{CN} \) (3 mL) and stirred for 5 minutes. Crystallisations via vapour diffusion were set up in \( \text{Et}_2\text{O} \) and THF (THF yielded larger crystals). Yields varied between 60–80%. Due to the large voids in the structure containing solvent of crystallisation, elemental analysis could not be performed accurately.
[Mn\textsuperscript{II}Cl\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (2)

[Et\textsubscript{4}N]\textsubscript{2}[Mn\textsuperscript{II}Cl\textsubscript{4}] (12.0 mg, 0.025 mmol) was added and the resultant solution became light orange in colour. Yielded orange X-ray quality crystals. ESI-MS (m/z): 1445 (2+), 913 (3+), 648 (4+), 489 (5+), 382 (6+).

[Fe\textsuperscript{III}Cl\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{7} (3)

[Et\textsubscript{4}N][Fe\textsuperscript{III}Cl\textsubscript{4}] (9.0 mg, 0.025 mmol) was added and the resultant solution became dark orange in colour. Yielded red X-ray quality crystals. ESI-MS (m/z): 1520 (2+), 963 (3+), 685 (4+), 518 (5+), 407 (6+), 328 (7+).

[Fe\textsuperscript{III}Br\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{7} (4)

[Et\textsubscript{4}N][Fe\textsuperscript{III}Br\textsubscript{4}] (13.0 mg, 0.025 mmol) was added and the resultant solution became red in colour. Yielded dark red X-ray quality crystals. ESI-MS (m/z): 1608 (2+), 1023 (3+), 740 (4+), 554 (5+), 437 (6+), 353 (7+).

[Co\textsuperscript{II}Cl\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (5)

[Et\textsubscript{4}N]\textsubscript{2}[Co\textsuperscript{II}Cl\textsubscript{4}] (12.0 mg, 0.025 mmol) was added and the resultant solution became green in colour. Yielded green X-ray quality crystals. ESI-MS (m/z): 1447 (2+), 915 (3+), 649 (4+), 489 (5+), 383 (6+).

[Co\textsuperscript{II}Br\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (6)

[Et\textsubscript{4}N]\textsubscript{2}[Co\textsuperscript{II}Br\textsubscript{4}] (16.0 mg, 0.025 mmol) was added and the resultant solution became light orange in colour. Yielded light green X-ray quality crystals. ESI-MS (m/z): 1536 (2+), 974 (3+), 693 (4+), 525 (5+), 413 (6+).

[Ni\textsuperscript{III}Cl\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (7)

[Et\textsubscript{4}N]\textsubscript{2}[Ni\textsuperscript{III}Cl\textsubscript{4}] (12.0 mg, 0.025 mmol) was added and the resultant solution became green in colour. Yielded light green X-ray quality crystals. ESI-MS (m/z): 1446 (2+), 914 (3+), 649 (4+), 489 (5+), 383 (6+).

[Cu\textsuperscript{III}Br\textsubscript{4}⊂Ni\textsuperscript{II}L\textsubscript{6}](OTf)\textsubscript{6} (8)

[Et\textsubscript{4}N]\textsubscript{2}[Cu\textsuperscript{III}Br\textsubscript{4}] (16.0 mg, 0.025 mmol) was added and the resultant solution became dark green in colour. Yielded dark green X-ray quality crystals. ESI-MS (m/z): 1537 (2+), 975 (3+), 694 (4+), 526 (5+), 413 (6+).
3 Single-Crystal-to-Single-Crystal Transformation of $1 \leftrightarrow 5$

Fig. S1 - a) Crystals of $1$ in EtOH. b) Crystals of $1$ with 5 equivalents of $[\text{Et}_4\text{N}]_2\text{CoCl}_4$ in EtOH added. Picture taken after 30 minutes, with a colour change evident. c) After two hours at room temperature the crystals have changed colour from yellow-brown to green single crystal XRD confirms transformation to complex $5$. d) Crystals of $5$ formed from the initial SCSC soaked in a saturated EtOH solution of $[\text{nBu}_4\text{N}][\text{OTf}]$ after 4 hours at 40 °C. Single crystal XRD confirms complete transformation to complex $1$, as also indicated from the colour change back to yellow-brown.
4 Mass Spectrometry

\([\text{Ni}^{II}_4\text{L}_6](\text{OTf})_8 \text{ (1)}\)

**Fig. S2** - Mass spectrum of 1. Red dots indicating the charge states of the cage from +7 on the left to +2 on the right.

\[\text{[OTf=Ni}_4\text{L}_6](\text{OTf})_2^{5+}\]

**Fig. S3** - The observed +5 charge state for 1. Black line indicates the experimental pattern and the red line indicating the modelled.
Fig. S4 - Mass spectrum of 2. Red dots indicating the charge states of the cage from +6 on the left to +2 on the right, blue dots are of complex 1.

Fig. S5 - The observed +6 charge state for 2. Black line indicates the experimental pattern and the red line indicating the modelled.
$$[\text{Fe}^{\text{III}}\text{Cl}_4\subset\text{Ni}^{\text{II}}\text{L}_6](\text{OTf})^7 (3)$$

**Fig. S6** - Mass spectrum of 3. Red dots indicating the charge states of the cage from +7 on the left to +2 on the right.

**Fig. S7** - The observed +6 charge state for 3. Black line indicates the experimental pattern and the red line indicating the modelled.
[Fe\textsuperscript{III}Br\textsubscript{4}□Ni\textsuperscript{II}L\textsubscript{6}](OTf\textsubscript{7}) (4)

Fig. S8 - Mass spectrum of 4. Red dots indicating the charge states of the cage from +7 on the left to +2 on the right, blue dots are of complex 1.

[Fe\textsuperscript{III}Br\textsubscript{4}□Ni\textsuperscript{II}L\textsubscript{6}](OTf\textsubscript{2})\textsuperscript{5+}

Fig. S9 - The observed +5 charge state for 4. Black line indicates the experimental pattern and the red line indicating the modelled.
[Co\textsuperscript{II}Cl_4\textsubscript{4}Ni\textsuperscript{II}L_6](OTf)_6 (5)

**Fig. S10** - Mass spectrum of 5. Red dots indicating the charge states of the cage from +6 on the left to +2 on the right.

**Fig. S11** - The observed +5 charge state for 5. Black line indicates the experimental pattern and the red line indicating the modelled.
$[\text{Co}^{II}\text{Br}_4\subset\text{Ni}^{II}\text{L}_6](\text{OTf})_6$ (6)

**Fig. S12** - Mass spectrum of 6. Red dots indicating the charge states of the cage from +6 on the left to +2 on the right.

**Fig. S13** - The observed +6 charge state for 6. Black line indicates the experimental pattern and the red line indicating the modelled.
\[ \text{[Ni}^{II}\text{Cl}_4\subset \text{Ni}^{II}_4\text{L}_6](\text{OTf})_6 \ (7) \]

Fig. S14 - Mass spectrum of 7. Red dots indicating the charge states of the cage from +6 on the left to +2 on the right, blue dots are of complex 1.

Fig. S15 - The observed +6 charge state for 7. Black line indicates the experimental pattern and the red line indicating the modelled.
[Cu\textsuperscript{II}Br\textsubscript{4}Ni\textsuperscript{II}L\textsubscript{6}]^{6+} (8)

**Fig. S16** - Mass spectrum of 8. Red dots indicating the charge states of the cage from +6 on the left to +2 on the right.

**Fig. S17** - The observed +6 charge state for 8. Black line indicates the experimental pattern and the red line indicating the modelled.
5 Crystallography

General Remarks

\([\text{OTf} \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_7 \) (1), \([\text{Fe}^{III}_4 \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_7 \) (3), \([\text{Fe}^{III}_4 \text{Br}_4 \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_7 \) (4) and \([\text{Co}^{III}_4 \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_6 \) (5).

Single crystal X-ray diffraction data for samples 1, and 3–5 were collected using a Rigaku Oxford Diffraction SuperNova diffractometer with CuKα (1 and 5) and MoKα (3 and 4) radiation. An Oxford Cryosystems Cryostream 700+ low temperature device was used to maintain a crystal temperature of 120.0 K (1, 3 and 4) and 250.0 K (5). The CrysAlisPro software package was used for instrument control, unit cell determination and data reduction.

The structures were solved using ShelXT\(^4\) employing the Intrinsic Phasing solution method through Olex2\(^5\) as the graphical interface. The model was refined with ShelXL\(^6\) using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were calculated geometrically and refined using the riding model. The RIGU restraint was applied to all triflate anions to appropriately model atomic displacement parameters.

All crystal structures contain large accessible voids that are filled with diffuse electron density belonging to disordered solvent, whose electron contribution was masked using the SQUEEZE\(^7\) routine of PLATON\(^8\). This missing solvent is included in the total formula, triggering checkCIF alerts which should be ignored.

\([\text{Mn}^{II}_4 \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_6 \) (2), \([\text{Ni}^{II}_4 \subset \text{Ni}^{III}_4 \text{L}_6](\text{OTf})_6 \) (7) and \([\text{Cu}^{II}_4 \text{Br}_4 \subset \text{Ni}^{II}_4 \text{L}_6](\text{OTf})_6 \) (8).

Single crystal X-ray diffraction data for 2, 7 and 8 were collected remotely\(^9\) at Diamond Light Source, beamline I19-1,\(^10\) under beam time award CY22240. An Oxford Cryosystems Cryostream 700+ low temperature device was used to maintain a crystal temperature of 100.0 K (2 and 8) and 120.0 K (7). The diffraction patterns were indexed with Xia2\(^11\)–\(^13\). The structures were solved, refined, and disordered solvent masked as mentioned for 1 and 3–5.
Single crystal X-ray diffraction data for 6 were collected using a Rigaku FRE+ diffractometer with MoKα radiation. An Oxford Cryosystems Cryostream 700+ low temperature device was used to maintain a crystal temperature of 100.0 K. The structures were solved, refined, and disordered solvent masked as mentioned for 1 and 3–5.
Table S1 - Single crystal X-ray data for complexes 1–4.

|      | 1                  | 2                      | 3                  | 4                  |
|------|--------------------|------------------------|--------------------|--------------------|
| **Formula** | C_{132}H_{88}F_{24}Ni_{26}O_{24}S_{8} | C_{128}H_{94}Cl_{16}Mn_{24}Ni_{24}O_{18}S_{6} | C_{151}H_{128}Cl_{21}Fe_{36}Ni_{24}O_{27}S_{7} | C_{147.5}H_{122}Br_{2}Fe_{0.5}Ni_{24}O_{25}S_{7.5} |
| **M (g mol⁻¹)** | 3369.60 | 3188.11 | 3830.73 | 3815.73 |
| **Crystal Colour** | Orange | Light brown | Dark red | Dark red |
| **Crystal system** | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| **Space group** | C2/c | C2/c | C2/c | C2/c |
| **a (Å)** | 31.7631(4) | 32.5915(13) | 31.6627(5) | 31.3026(3) |
| **b (Å)** | 20.3760(3) | 19.6893(7) | 20.3859(2) | 20.5660(2) |
| **c (Å)** | 26.2656(4) | 26.8651(12) | 26.5585(4) | 26.4213(3) |
| **α (°)** | 90 | 90 | 90 | 90 |
| **β (°)** | 114.2627(18) | 116.807(3) | 114.491(2) | 112.8120(10) |
| **γ (°)** | 90 | 90 | 90 | 90 |
| **V (Å³)** | 15497.7(4) | 15386.7(11) | 15600.4(4) | 15678.8(3) |
| **Z** | 4 | 4 | 4 | 4 |
| **Z’** | 0.5 | 0.5 | 0.5 | 0.5 |
| **ρcalc (g cm⁻³)** | 1.444 | 1.376 | 1.631 | 1.616 |
| **μ (mm⁻¹)** | 2.438 | 0.751 | 0.833 | 1.236 |
| **T (K)** | 120.0 | 100.0 | 120.0 | 120.0 |
| **F(000)** | 6832 | 6460.0 | 6932.0 | 7760.0 |
| **Measured Reflections** | 156152 | 29061 | 238777 | 242243 |
| **Independent Reflections (Rint)** | 16138(0.0786) | 3672 (0.1060) | 14267(0.0552) | 14855(0.0536) |
| **Reflections [I > 2σ(I)]** | 13435 | 3008 | 12312 | 12951 |
| **Data / Restraints / Parameters** | 16138 / 216 / 911 | 3672 / 77 / 402 | 14267 / 197 / 1006 | 14855 / 656 / 1179 |
| **R_p** | 0.1254(0.1363) | 0.2397(0.2527) | 0.0655(0.0749) | 0.0729(0.0820) |
| **wR_p** | 0.3432(0.3525) | 0.5481(0.5660) | 0.1774(0.1864) | 0.2032(0.2106) |
| **Goodness-of-fit** | 2.759 | 5.029 | 1.042 | 1.068 |
| **CCDC Number** | 2024431 | 2024429 | 2024434 | 2024432 |
Table S2 - Single crystal X-ray data for complexes 5–8.

|   | 5                        | 6                        | 7                        | 8                        |
|---|-------------------------|-------------------------|-------------------------|-------------------------|
| Formula                      | C_{138}H_{105}Cl_6CoF_{18}N_{28}Ni_4O_{19}S_6 | C_{138}H_{105}Cl_6CoF_{18}N_{28}Ni_4O_{19}S_6 | C_{154}H_{126}Cl_6CoF_{18}N_{28}Ni_4O_{19}S_6 | C_{154}H_{126}Br_4CuF_{18}N_{28}Ni_4O_{19}S_6 |
| M (g mol\(^{-1}\))           | 3429.42                  | 3194.96                  | 3766.63                  | 3374.55                  |
| Crystal Colour               | Dark green               | Light brown              | Light green              | Dark green               |
| Crystal System               | Monoclinic               | Monoclinic               | Monoclinic               | Monoclinic               |
| Space Group                  | P2\(_1\)/n               | P2\(_1\)/c               | C2/c                    | C2/c                    |
| a (Å)                        | 20.4016(3)               | 31.1965(6)               | 31.8614(3)               | 33.6581(8)               |
| b (Å)                        | 29.7181(6)               | 18.5947(3)               | 20.2670(2)               | 19.3004(5)               |
| c (Å)                        | 26.8106(6)               | 28.7563(6)               | 26.4739(3)               | 27.7984(9)               |
| α (°)                        | 90                       | 90                       | 90                       | 90                       |
| β (°)                        | 91.1568 (18)             | 110.013 (2)              | 114.7730 (10)            | 119.638 (2)              |
| γ (°)                        | 90                       | 90                       | 90                       | 90                       |
| V (Å\(^3\))                  | 16251.9 (5)              | 15673.9 (5)              | 15521.9 (3)              | 15695.6 (8)              |
| Z                            | 4                        | 4                        | 4                        | 4                        |
| Z’                           | 1                        | 1                        | 0.5                      | 0.5                      |
| ρ\(_{calc}\) (g cm\(^{-3}\)) | 1.402                    | 1.354                    | 1.612                    | 1.428                    |
| μ (mm\(^{-1}\))              | 3.379                    | 1.723                    | 0.781                    | 1.643                    |
| T (K)                        | 250.0 (10)               | 100.0 (2)                | 100.0                    | 120.0                    |
| F(000)                       | 6980.0                   | 6436.0                   | 7000.0                   | 6764.0                   |
| Measured Reflections         | 294893                   | 670814                   | 94775                    | 49607                    |
| Independent Reflections (R\(_{int}\)) | 17006.0 (0.1547)       | 35971.0 (0.0697)         | 14171.0 (0.0404)         | 6192.0 (0.0617)          |
| Reflections [I > 2σ (I)]     | 14654                    | 23303                    | 11094                    | 5165                     |
| Data / Restraints / Parameters | 17006 / 2169 / 1962     | 35971 / 0 / 1750         | 14171 / 108 / 990        | 6192 / 747 / 678         |
| R\(^1\)                      | 0.1312 (0.1392)          | 0.0744 (0.1120)          | 0.1274 (0.1396)          | 0.1602 (0.1669)          |
| [I > 2σ (I)] (all)           | wR\(^2\)                | 0.3722 (0.3828)          | 0.1485 (0.1673)          | 0.3680 (0.3778)          | 0.4648 (0.4780)          |
| Goodness-of-fit              | 1.712                    | 1.025                    | 3.070                    | 2.397                    |
| CCDC Number                  | 2024435                  | 2023466                  | 2024430                  | 2024433                  |

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## Data Tables

### Table S3 - Ni₆ and MX₄ bond length and angle ranges for complexes 1–8

|     | Ni–N Bond Lengths (Å) | N–Ni–N cis (°) | N–Ni–N trans (°) | M–X Bond Lengths (Å) | X–M–X (°) |
|-----|-----------------------|----------------|------------------|-----------------------|-----------|
| T1  | 2.052(4)–2.134(4)     | 77.87(14)–100.56(15) | 170.75(16)–175.70(15) |                       |           |
| T2  | 2.03(3)–2.17(3)       | 76.4(12)–99.8(12)   | 170.3(11)–175.8(12)  | 2.378(12)–2.383(12)   | 105.9(6)–113.4(4) |
| T3  | 2.057(2)–2.128(3)     | 78.19(9)–99.89(9)   | 171.52(10)–175.37(10)| 2.1946(8)–2.2060(7)  | 106.32(4)–112.33(3) |
| T4  | 2.055(4)–2.131(4)     | 77.85(16)–100.74(16)| 171.37(16)–175.62(16)| 2.3415(18)–2.3511(18)| 105.29(11)–112.99(5) |
| T5  | 2.050(3)–2.130(3)     | 78.10(14)–102.28(13)| 170.56(13)–176.60(13)| 2.272(3)–2.281(3)    | 104.99(13)–114.28(11) |
| T6  | 2.053(5)–2.105(4)     | 78.20(18)–100.00(2) | 171.59(19)–173.85(19)| 2.4034(8)–2.4242(8)  | 107.05(3)–111.07(3) |
| T7  | 2.059(5)–2.131(5)     | 78.4(2)–100.3(2)    | 170.6(2)–175.4(2)   | 2.257(4)–2.262(4)    | 101.7(2)–117.66(12) |
| T8  | 2.051(9)–2.077(14)    | 77.3(6)–100.5(6)    | 171.0(5)–176.6(6)   | 2.584(7)–2.359(5)    | 107.25(10)–117.8(3) |

### Table S4 - Pore volumes, diameters and average window diameters of complexes 1–8. Calculated using pywindow.¹⁴

|     | Pore Volume /Å³ | Pore Diameter /Å | Average Window Diameter /Å |
|-----|-----------------|-----------------|---------------------------|
| T1  | 62.6            | 4.9             | 3.4                       |
| T2  | 67.9            | 5.1             | 3.6                       |
| T3  | 68.7            | 5.1             | 3.6                       |
| T4  | 68.0            | 5.1             | 3.6                       |
| T5  | 64.2            | 5.0             | 3.6                       |
| T6  | 80.8            | 5.4             | 3.3                       |
| T7  | 62.5            | 4.9             | 3.4                       |
| T8  | 70.6            | 5.1             | 3.5                       |
Table S5 - Close intermolecular interactions of complexes 1–8 between the cages, ions and solvent of crystallisation.

|       | Guest···Cage | External Ions | External Solvent |
|-------|--------------|---------------|------------------|
| T1    | O/F···H−Ar ≈ 2.52 | F···H−Ar = 2.67 (OTf···Cage) | H₂C−H···C−Ar = 2.85 (MeCN···Cage) |
|       |               | O···H−Ar = 2.46 (OTf···Cage) | N···H−Ar = 2.56 (MeCN···Cage) |
| T2    | Cl···H−Ar ≈ 2.95 | F···H−Ar = 2.37 (OTf···Cage) | – |
|       |               | O···H−Ar = 2.50 (OTf···Cage) |                      |
| T3    | Cl···H−Ar ≈ 2.99 | F···H−Ar = 2.53 (OTf···Cage) | H₂C−H···C−Ar = 2.85 (MeCN···Cage) |
|       |               | O···H−Ar = 2.54 (OTf···Cage) | N···H−Ar = 2.57 (MeCN···Cage) |
| T4    | Br···H−Ar = 3.03 | F···H−Ar = 2.50 (OTf···Cage) | HC−H···Br = 2.78 (THF···Br) |
|       |               | O···H−Ar = 2.53 (OTf···Cage) | O···H−Ar = 2.60 (THF···Cage) |
|       |               | O···H−CH = 2.59 (OTf···THF) | HC−H···H−Ar = 2.59 (THF···Cage) |
|       |               | F···H−CH = 2.48 (OTf···THF) |                      |
| T5    | Cl···H−Ar ≈ 2.99 | F···H−Ar = 2.54 (OTf···Cage) | H₂C−H···C−Ar = 2.56 (THF···Cage) |
|       |               | O···H−Ar = 2.53 (OTf···Cage) | HC−H···H−Ar = 1.93 (THF···Cage) |
|       |               | O···H−CH = 2.57 (OTf···THF) | H₂C−H···H−Ar = 1.75 (MeCN···Cage) |
|       |               | F···H−CH = 2.62 (OTf···THF) | N···H−Ar = 2.63 (MeCN···Cage) |
| T6    | Br···H−Ar = 3.04 | F···H−Ar = 2.54 (OTf···Cage) | HC−H···Br = 2.90 (THF···Br) |
|       |               | O···H−Ar = 2.47 (OTf···Cage) | N···H−Ar = 2.58 (MeCN···Cage) |
|       |               | O···H−CH₂ = 2.60 (OTf···MeCN) |                      |
|       |               | F···H−CH₂ = 2.45 (OTf···MeCN) |                      |
| T7    | Cl···H−Ar ≈ 2.86 | F···H−Ar = 2.54 (OTf···Cage) | H₂C−H···H−Ar = 2.18 (MeCN···Cage) |
|       |               | O···H−Ar = 2.52 (OTf···Cage) | H₂C−H···C−Ar = 2.83 (MeCN···Cage) |
|       |               | O···H−Ar = 2.52 (OTf···Cage) | N···H−Ar = 2.53 (MeCN···Cage) |
| T8    | Br···H−Ar ≈ 3.00 | F···H−Ar = 2.11 (OTf···Cage) | – |
Structures and Packing

[OTf$\subset$Ni$^{III}$L$_6$](OTf)$_7$ (1)

Fig. S18 - (a)-(b) Orthogonal views of complex 1 down a vertex of the cage and through the portal, the triflate anion guest is positionally disordered within the cage, with the O and F atoms point towards the portals/H atoms in the ligand framework. (c) Side-view of 1 highlighting the connectivity of the ligand in the cage. Colour code: Colour code: Ni = orange, N = blue, C = grey, H = white, O = red, F = light green, S = yellow.
Fig. S19 - (a) Close intermolecular interactions (thin red bonds) between the O and F atoms of the encapsulated triflate anion and the H atoms of L in the cage framework. And (b) Two [Ni(\(L_1\))_6]^{8+} tetrahedra of 1, thin red bonds indicating some of the close intermolecular interactions from external triflate anions and solvent of crystallisation linking neighbouring cages. Orange bonds used to highlight the adjacent tetrahedra. Colour code as Fig.S18.
Fig. S20 - Packing of 1 (C2/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated triflate followed by a row of triflate anions connecting the cages. Colour code as Fig. S18.
[Mn$^{II}$Cl$_4$Ni$^{II}$L$_6$](OTf)$_6$ (2)

Fig. S21 - (a)-(b) Orthogonal views of complex 2 down a vertex of the cage and through the portal, illustrating the position of the [MnCl$_4$]$^{2-}$ guest which sits as an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 2 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S18, Cl = green, Mn = mauve.
**Fig. S22** - Packing of 2 (C2/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated $[\text{MnCl}_4]^{2-}$ followed by a row of triflate anions connecting the cages. Colour code as Fig. S21.
[Fe$^{III}$Cl$_4$Ni$^{II}$L$_6$](OTf)$_7$ \( (3) \)

**Fig. S23** - (a)-(b) Orthogonal views of complex 3 down a vertex of the cage and through the portal, illustrating the position of the [FeCl$_4$]$^-$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 3 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S18, Cl = green, Fe = purple.
Fig. S24 - Packing of 3 (C2/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated [FeCl$_4$]$^-$ followed by a row of triflate anions connecting the cages. Colour code as Fig. S23.
[Fe$^{III}$Br$_4$\(\subset\)Ni$^{II}$L$_6$](OTf)$_7$ (4)

Fig. S25 - (a)-(b) Orthogonal views of complex 4 down a vertex of the cage and through the portal, illustrating the position of the [FeBr]$^-$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 4 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S23, Br = dark green.
Fig. S26 - Packing of 4 (C2/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated [FeBr₄]$^-$ followed by a row of triflate anions connecting the cages. Colour code as Fig. S25.
[Co$^{II}\text{Cl}_4\text{Ni}^{II}\text{L}_6$](OTf)$_6$ (5)

**Fig. S27** - (a)-(b) Orthogonal views of complex 5 down a vertex of the cage and through the portal, illustrating the position of the [CoCl$_4$]$^{2−}$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 5 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S18, Cl = green, Co = pink.
Fig. S28 - Packing of 5 \( (P2_1/n) \) viewed down the a-axis, illustrating the alternating rows of cages with an encapsulated \([\text{CoCl}_4]^{2-}\) followed by a row of triflate anions connecting the cages. Colour code as Fig. S27.
[Co$$^{II}$$Br$_4$$\subset$$Ni$$^{II}$$L_6$](OTf)$_6$ (6)

Fig. S29 - (a)-(b) Orthogonal views of complex 6 down a vertex of the cage and through the portal, illustrating the position of the [CoBr$_4$]$^{2-}$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 6 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S27, Br = dark green.
**Fig. S30** - Packing of 6 \((P2_1/c)\) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated \([\text{CoBr}_4]^{2-}\) followed by a row of triflate anions connecting the cages. Colour code as Fig. S29.
Fig. S31 - (a)-(b) Orthogonal views of complex 7 down a vertex of the cage and through the portal, illustrating the position of the [NiCl$_4$]$^{2-}$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (Fig. 2a and b in main text). Side-view of 7 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S18, Cl = green.
Fig. S32 - Packing of 7 (C\textsubscript{2}/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated [NiCl\textsubscript{4}]\textsuperscript{2-} followed by a row of triflate anions connecting the cages. Colour code as Fig. S31.
Fig. S33 - (a)-(b) Orthogonal views of complex 8 down a vertex of the cage and through the portal, illustrating the position of the $[\text{CuBr}_4]^{2-}$ guest which sits in an inverted tetrahedron with respect to the host cage, with the halide ions pointing out of the cage portals. (c) Side-view of 8 highlighting the connectivity of the ligand in the cage. Colour code: Same as Fig. S18, Br = dark green, Cu = dark red.
**Fig. S34** - Packing of 8 (C2/c) viewed down the b-axis, illustrating the alternating rows of cages with an encapsulated [CuBr₄]²⁻ followed by a row of triflate anions connecting the cages. Colour code as Fig. S33.
6 Magnetometry

**Fig. S35** - Reduced magnetisation plot of 1 in the 2–7 K temperature range and 0–5 T field range, highlighting weak anisotropy by the limited nesting of the curves.

**Fig. S36** - Reduced magnetisation plot of 2 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.
**Fig. S37** - Reduced magnetisation plot of 3 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.

**Fig. S38** - Reduced magnetisation plot of 4 in the 3–7 K temperature range and 0–5 T field range, highlighting weak anisotropy by the limited nesting of the curves.
Fig. S39 - Reduced magnetisation plot of 5 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.

Fig. S40 - Reduced magnetisation plot of 6 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.
Fig. S41 - Reduced magnetisation plot of 7 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.

Fig. S42 - Reduced magnetisation plot of 8 in the 2–7 K temperature range and 0–7 T field range, highlighting weak anisotropy by the limited nesting of the curves.
7 Computational Details

*Ab initio* method: All single point multi-configuration SCF calculations were carried on the X-ray geometries using the ORCA 4.0.1 program code.\textsuperscript{15} Spin-Hamiltonian (SH) parameters were computed from CASSCF/NEVPT2 methodology. NEVPT2 (N-electron valence state perturbation theory) calculations were performed in combination with the CASSCF (complete active space self-consistent field) wavefunction to recover the dynamic electron correlation. While calculating the on-site SH parameters on certain paramagnetic ions the remaining paramagnetic centres were masked with diamagnetic ions (*e.g.* Zn\textsuperscript{II}). While calculating the SH parameters on the guest molecule, the host cage atoms were replaced with CHELPG charges obtained from UKS/BP86 DFT calculations. Douglas-Kroll-Hess Hamiltonian (second-order) was considered for the scalar relativistic corrections. DKH- version of contracted def2- basis sets- DKH-def2-TZVP for the Cu, Ni, Co, Fe, Mn, Cl and Br atoms; DKH-def2-TZVP(-f) for N and DKH-def2-SVP for the rest of the atoms were used during the calculations. For the starting orbitals a UKS/BP86 DFT calculation was performed and the resulting quasi-restricted orbitals (QROs) were used in the following configuration interaction step. Active space was chosen as CAS(n,5), where \( n \) is the number of electrons in the valence d-orbitals of the metals. The active orbitals were optimised with 5 doublets for Cu(II), 10 triplets and 15 singlets for Ni(II), 10 quartets and 40 doublets for Co(II); 1 sextet and 24 quartets for Fe(III) and Mn(II) species. Spin-orbit coupling effects were included from the quasi-degenerate perturbation theory (QDPT) approach with spin-orbit mean field (SOMF) operator. Final spin-Hamiltonian parameters such as \( g \)-factors, \( D \) and \( E \) parameters were determined from effective Hamiltonian approach (EHA).\textsuperscript{16}

*DFT* method: To obtain magnetic exchange interactions between the paramagnetic metal centres, single point Density Functional Theory (DFT) calculations were performed on the X-ray structures using the Gaussian 09 program.\textsuperscript{17} Broken symmetry methodology was employed using the fragmentation method to obtain the magnetic coupling constants.\textsuperscript{18} The unrestricted B3LYP functional was used with Ahlrich’s all electron triple zeta valence (TZV) basis set for all atoms.\textsuperscript{19,20} Wavefunction reoptimisation was performed after the SCF convergence to check the stability of the wavefunction. Geometry optimisation was also carried out for the anionic [NiCl\(_4\)]\textsuperscript{2-} guest with the B3LYP/TZVP level of theory and basis set to compare the change in
geometry and zero-field splitting before and after the insertion to the cage. The isotropic coupling constant $J$ was computed from the following pairwise interaction formula.\textsuperscript{21}

$$J = \frac{E_{BS} - E_{HS}}{2(2S_1S_2 + S_2)}$$
Table S6 - Spin density values obtained from the uB3LYP/TZV level of theory on the metal ions in complexes 1–8 (excluding complex 7).

| Complexes 1-8 (Excluding complex 7) | HS Spin density ($\rho^\alpha-\rho^\beta$) | BS1 Spin density ($\rho^\alpha-\rho^\beta$) | BS2 Spin density ($\rho^\alpha-\rho^\beta$) | BS3 Spin density ($\rho^\alpha-\rho^\beta$) |
|------------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Ni1, Ni2, Ni3, Ni4                | 1.64, 1.65, 1.64, 1.65           | -1.64, 1.65, 1.64, 1.65         | -1.64, 1.65, 1.64, 1.65         | -1.64, 1.65, 1.64, 1.65         |
| Ni1, Ni2, Ni3, Ni4, Mn            | 1.63, 1.65, 1.63, 1.65, 4.70     | 1.63, 1.65, 1.63, 1.65, -4.70   | -1.63, 1.65, 1.63, 1.65, 4.70   | -1.63, -1.65, 1.63, 1.65, 4.70  |
| Ni1, Ni2, Ni3, Ni4, Fe            | 1.64, 1.65, 1.64, 1.65, 3.85     | 1.65, 1.65, 1.65, 1.65, -3.85   | -1.65, 1.65, 1.64, 1.65, 3.85   | -1.65, 1.65, -1.65, 1.65, 3.85  |
| Ni1, Ni2, Ni3, Ni4, Fe            | 1.64, 1.65, 1.64, 1.65, 3.76     | 1.65, 1.65, 1.65, 1.65, -3.76   | -1.65, 1.65, 1.64, 1.65, 3.76   | -1.65, 1.65, -1.65, 1.65, 3.76  |
| Ni1, Ni2, Ni3, Ni4, Co            | 1.65, 1.65, 1.65, 1.65, 2.59     | 1.65, 1.65, 1.65, 1.65, -2.59   | -1.65, 1.65, 1.65, 1.65, 2.59   | -1.65, 1.65, -1.65, 1.65, 2.59  |
| Ni1, Ni2, Ni3, Ni4, Cu            | 1.65, 1.66, 1.66, 1.65, 0.39     | 1.65, 1.66, 1.66, 1.65, -0.39   | -1.65, 1.66, 1.66, 1.65, 0.39   | -1.65, -1.66, 1.66, 1.65, 0.39  |
Fig. S43 - High spin and four broken symmetry spin density plots for complex 1 obtained from the uB3LYP/TZV level of theory. The iso-surface cut-off was chosen to be 0.006 e/Bohr$^3$. 
Fig. S44 High spin and four broken symmetry spin density plots for complex 2 obtained from the uB3LYP/TZV level of theory. The iso-surface cut-off was chosen to be 0.006 e/Bohr³.
Table S7 - Multi-determinant electronic configurations and their respective contributions towards the $D$ and $E$ parameters for the $[\text{NiCl}_4]^2$ guest in complex 7.

| [NiCl$_4$]$^2$ ligand field states | NEVPT2 transition energies (cm$^{-1}$) | Electronic configuration | Contribution to $D$ (cm$^{-1}$) | Contribution to $E$ (cm$^{-1}$) |
|------------------------------------|-------------------------------------|-------------------------|--------------------------|--------------------------|
| 1                                  | 0.0                                 | $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xy})^2(d_{yz})^1(d_{xz})^1$ (86%) | 0.0                      | 0.0                       |
| 2                                  | 619                                 | $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xy})^1(d_{yz})^2(d_{xz})^1$ (47%) | 143.8                    | 143.7                     |
| 3                                  | 1495                                | $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xy})^1(d_{yz})^2(d_{xz})^1$ (29%) | 73.7                     | -73.6                     |
| 4                                  | 2703                                | $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xy})^1(d_{yz})^2(d_{xz})^2$ (26%) | 61.8                     | -61.6                     |
| 5                                  | 3778                                | $(d_{x^2-y^2})^2(d_{z^2})^2(d_{xy})^1(d_{yz})^2(d_{xz})^2$ (24%) | 46.3                     | 46.0                       |
**Fig. S45** - High spin and four broken symmetry spin density plots for complex 8 obtained from the uB3LYP/TZV level of theory. The iso-surface cut-off was chosen to be 0.006 e/Bohr$^3$. 
Fig. S46 - Comparison of experimental (black symbols) and theoretically computed (blue lines) $\chi T$ vs $T$ and $M$ vs $B$ data for complexes 1-6.
Fig. S47 - Comparison of experimental (black symbols) and theoretically computed (blue lines) $\chi T$ vs $T$ and $M$ vs $B$ data for complexes 7 and 8
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