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Heterometallic Cages

$[\text{Cr}^\text{III}_{8}\text{M}^\text{II}_{6}]^{12+}$ Coordination Cubes ($\text{M}^\text{II} = \text{Cu}, \text{Co}$)**

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Abstract: $[\text{Cr}^\text{III}_{8}\text{M}^\text{II}_{6}]^{12+}$ ($\text{M}^\text{II} = \text{Cu}, \text{Co}$) coordination cubes were constructed from a simple $[\text{Cr}^\text{III}_{8}\text{L}_{6}]$ metalloligand and a “naked” $\text{M}^\text{II}$ salt. The flexibility in the design proffers the potential to tune the physical properties, as all the constituent parts of the cage can be changed without structural alteration. Computational techniques (known in theoretical nuclear physics as statistical spectroscopy) in tandem with EPR spectroscopy are used to interpret the magnetic behavior.

Molecules containing exchange-coupled paramagnetic metal ions represent a class of materials with potential applications across a breadth of scientific disciplines, with particular recent focus on information storage, quantum computation, and molecular spintronics. The bottom-up design of magnetic materials for such applications is attractive, as molecules are inherently monodisperse, reproducible, orientable, and chemically tuneable. Synthetic strategies that target magnetic coordination compounds span the entire spectrum from the serendipitous self-assembly of coordinatively flexible metal ions and organic ligands capable of bridging in multiple ways, through to the design of structurally predictable cages using rigid linker ligands in combination with metal precursors that possess a limited number of coordination sites free for reaction. This ‘rational design’ strategy has also been widely utilized for the preparation of numerous diamagnetic coordination capsules, the interest in these systems stemming from host–guest chemistry that has been exploited for catalysis, drug delivery, or the stabilization of reactive intermediates. Heterometallic coordination capsules have also been accessed using preprogrammed self-assembly approaches, occasionally using one-pot, self-sorting strategies with thermodynamically orthogonal metal–ligand motifs, or more commonly through a stepwise approach that takes advantage of kinetically robust intermediate complexes that possess pendant donor tectons, often referred to as metallocalixarenes. However, only a handful of these heterometallic systems possess paramagnetic centers, and even fewer have been reported to display intramolecular magnetic exchange.

Herein we discuss the structures and magnetic properties of the heterometallic cages $[\text{Cr}^\text{III}_{8}\text{Cu}^\text{II}_{4}(\text{H}_2\text{O})_{12}(\text{NO}_3)_2]_8$ and $[\text{Cr}^\text{III}_{8}\text{Co}^\text{II}_{4}(\text{H}_2\text{O})_{12}(\text{ClO}_4)_2]_8$, which were built using the simple metalloligand $[\text{Cr}^\text{III}_{8}\text{L}_{6}]$ (HL = 1-(4-pyridyl)butane-1,3-dione) and the metal salts Cu(NO$_3$)$_2$$\cdot$3H$_2$O and Co(ClO$_4$)$_2$$\cdot$6H$_2$O, respectively. The metallic skeleton of both cages (Figure 1, see also Figures S1 and S2 in the Supporting Information) describes a simple $[\text{Cr}^\text{III}_{8}\text{M}^\text{II}_{6}]^{12+}$ cube with the Cr$^{III}$ ions of the $[\text{Cr}^\text{III}_{8}\text{L}_{6}]$ metalloligands occupying the corners of the cube, and the M$^{II}$ ions capping the square faces. The former are six-coordinate and in regular

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Figure 1. Molecular structure of the cation of 1. Color code: Cr = green, Cu = light blue, O = red, N = blue, C = black. The terminally bound oxygen atoms originate from both water and nitrate molecules (see text for details).
in complex 2 (Figure S1) the face-capping CoII ions possess the same, albeit regular, octahedral [CoN4O2] geometry with Co–O bonds in the range 2.04–2.12 Å. Here, all the terminally coordinated ligands are water molecules. In the solid state, the cations of 2 pack in a brickwork-like fashion (Figure S3) with the closest intercage contacts being between the corners of neighboring cubes through a plethora of close contacts, primarily mediated by the L ligands: CH–O ≈ 3.1 Å; CH–N ≈ 3.6 Å; CH–CH, ≈ 4.0 Å; O–O, 4.3 Å; CH–CH2, 4.5 Å. The twelve charge-balancing ClO4− anions, and solvent molecules of the crystallization, are again located both within the cage cavity and in the void spaces between the cubes.

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The direct current (d.c.) molar magnetic susceptibility, \(\chi_m\), of polycrystalline samples of complexes 1 and 2 were measured in an applied magnetic field, \(B\), of 0.1 T, over the 5–280 K temperature range (Figure 2, where \(g = M/B\), and \(M\) is the magnetization). At 280 K, the \(\chi_mT\) products of 1 and 2 have values of 17.7 and 26.3 cm³ mol⁻¹ K⁻¹, respectively. These values are in excellent agreement with those expected from the spin-only contributions to the magnetism of a [CrIII12CuII] unit (17.6 cm³ mol⁻¹ K⁻¹), with \(g_Cr = 2.00\) and \(g_Cu = 2.15\), and of a [CrIII12CuII] unit (26.3 cm³ mol⁻¹ K⁻¹), with \(g_Cr = Scu = 2.00\), where \(g_Cr\) and \(g_Cu\) are the isotropic g-factors of CrIII and CuII, respectively. Upon cooling, the \(\chi_mT\) product of 1 remains essentially constant down to 30 K, below which a fast increase is observed, reaching 19.1 cm³ mol⁻¹ K⁻¹ at 5 K. This behavior is indicative of weak ferromagnetic exchange interactions. Upon cooling, the \(\chi_mT\) product of 2 decreases continuously, reaching a plateau value of 21.5 cm³ mol⁻¹ K⁻¹ at 8 K, before slightly increasing upon further cooling to 21.7 cm³ mol⁻¹ K⁻¹ at 5 K. The analysis of this behavior is complicated by the combination of the ligand-field splitting of the CoII ion and weak exchange interactions. The tetragonal symmetry ligand field of the [Co(py)3(H2O)2] site removes the degeneracy of the \(T_{1g}\) term, breaking it into \(E_g\) and \(A_{2g}\) terms, with the latter lower in energy [16]. Spin-orbit coupling (SOC) then further removes the degeneracy of the \(A_{2g}\) term, breaking it into two Kramers doublets, the energy splitting of which can be parameterized as a zero-field splitting (D) of the \(A_{2g}\) term. The fact that the high temperature \(\chi_mT\) product of 2 agrees well with the expected spin-only value supports the dominance of the axial ligand field splitting over SOC.

For the quantitative interpretation of the magnetic properties of 1 and 2, we used two limiting models: 1) with \(D_m = 0\) and \(J_{Cr-M} \neq 0\) (an isotropic model) and 2) with \(J_{Cr-M} = 0\) and \(D_m \neq 0\), where \(M = Cu\) or \(Cr\), and \(J_{Cr-M}\) is the isotropic exchange parameter between Cr and M centers (where \(M = Cu\) for 1 and Co for 2). In both limiting models, we neglected the single-ion anisotropy of CrIII, \(D_{Cr}\), as this is usually of the order of 1 cm⁻¹. [17] Given that \(D_{Cr} = 0\), we only applied the isotropic model for the analysis of 1. We started with the isotropic model for both 1 and 2. To describe the magnetic properties we used the following isotropic spin-Hamiltonian (1)

\[
\hat{H}_{iso} = J_{Cr-M} \sum_{i \neq j} \hat{s}_i \cdot \hat{s}_j + \hat{s}_i \cdot \mu_B \hat{B} \sum_i \hat{s}_i \quad (1)
\]

with \(i\) running over all constitutive metal centers, \(\hat{s}\) a spin operator, \(\mu_B\) the Bohr magneton, \(\hat{B}\) the applied magnetic field, and \(g\) the isotropic g-factor common to both Cr and M. Modelling the data using traditional matrix diagonalization is impractical for 1 and impossible for 2, because of the large
The isotropic Heisenberg Hamiltonian (1) applied to these spin systems permits the calculation of relevant thermodynamic properties. We calculated the temperature-dependent magnetic susceptibility of CoII using the bivariate moments of (1), that is, those obtained from statistical spectroscopy methods. The lack of structure prevents any further analysis. Spectra of 2 are also broadened but structured (Figure 3), resembling those of [CrIII L4] with noticeable shifts in resonance fields and new resonances at around 1400 mT (at W-band) because of the CoII sites. This implies |JCr-Co| < |DCo|, the matrix dimension of 2 is far too large for simulation using the full Cr-Co spin system, while the weak exchange limit precludes handling the problem by low-energy subspace methods. We attempted to model the spectra of 2 as a simple CoII dimer, of which the parameters for CrIII are defined experimentally from [CrIII L4], and those for CoII are fixed from the “isolated” SCo = 3/2 CoII model (Figure 2). We also fixed the relative orientation of the principal axes of the DCo and DCo ZFS tensors to 54.7°, which is the angle between the C2 (face-normal, defining the unique axis of CoII in 2) and C3 (body-diagonal, defining the unique axis of CrIII in 2) axes of a cube. Thus, the only variable is JCr-Co. The calculated spectra were very sensitive to small JCr-Co (e.g. Figure S7), and we could reproduce the experimental resonances reasonably with JCr-Co = −0.3 cm−1 (Figure 3, bottom, and S7). Note that the determined JCr-Co value is not that of 2 but for the fictitious CrIII CoII dimer. The isotropic exchange parameter, JCr-Co of 2 is likely smaller in magnitude.

Variable-temperature-and-variable-field (VTVB) magnetization studies of complexes 1 and 2 (Figure S8) were consistent with weak exchange in both cases. For 1, the saturation magnetic moment of 30.8 µB at 5 T and 2 K, was as expected for full spin alignment. In the case of 2, the magnetic moment was also 30.8 µB at 5 T and 2 K. If only the lower Kramers doublet of CoII (which has µM = 4, µM = 4, µM = 2)
The large internal cavity suggests that the cage could play host to different species, and indeed one can imagine constructing cages offering enormous scope for tuning their physical properties. The corner ions can potentially be any M\text{III} ion that can adopt a square-planar, square-pyramidal, or octahedral geometry. The 12+ charge on the cage suggests that the anions can be varied and can be innocent or non-innocent, and the solvent bonded terminally to the M\text{III} ions should be easily replaced, thus allowing the attachment of a host of different species and/or the assembly of the cubes into higher-order structures.

The internal cavity suggests that the cage could play host to different species, and indeed one can imagine constructing magnetic coordination capsules capable of hosting magnetic and/or redox-active guests, exerting control over (switching on and off) magnetic exchange between metal ions in the host framework and between the host and guest(s). Post-synthetic exohedral functionalization and simple changes to ligand design will also allow the modification of the magnetic properties, but additionally can be manipulated to tune solubility, reactivity, stability, and substrate specificity.

**Keywords:** EPR spectroscopy · heterometallic cages · magnetometry · molecular magnetism · transition metals

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