[Cr\textsubscript{III8}M\textsubscript{II6}]\textsuperscript{n+} (M\textsubscript{II} = Cu, Co) face-centred, metallosupramolecular cubes

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Introduction

Metallosupramolecular chemistry relies on the use of dynamic metal-ligand bonds for the construction of multinuclear coordination assemblies. From a design perspective, the selection of a particular metal ion can have numerous implications on the outcome of any given assembly reaction because they provide differing coordination geometry preferences, and a range of binding strengths, which often show a strong correlation with substitutional lability. Given this potential variation in metal-ion component and the capacity to readily access multitiopic ligands with differing coordination vectors, it is perhaps not surprising that this rational design approach has yielded a vast array of discrete nanostructures of varying shape, size and nuclearity. Often, the combination of highly directional metal-ligand bonding and the rigid nature of the ligand framework creates a molecular scaffold that defines the boundaries of a permanent internal cavity. These discrete void areas impart unique properties to the structure allowing for numerous applications in areas such as gas adsorption, stabilisation of reactive molecules, catalysis, biochemical and biomedical applications, separation of species from a mixture, and development of magnetic materials.

In the field of molecular magnetism the systematic exploration of ligand design, metal identity and reaction conditions is employed to build families of structurally related complexes whose subsequent physical characterisation reveals the underlying principles behind the magneto-structural relationship. Geometric and molecular symmetry, for example, defines a range of fascinating, and potentially useful low temperature physics, ranging from spin-frustrated molecules to anisotropic metal cages behaving like nanoscale magnets. Judicious ligand design is the first stage of the synthetic process, and the use of rigid ligands with fixed coordination modes allows for the construction of cages with predictable topologies, and potentially those that possess cavities capable of binding guest molecules. While the host-guest chemistry of diamagnetic coordination capsules has been widely studied and exploited, magnetic coordination capsules and the study of the interaction between magnetic hosts and guests has largely been ignored.

Recently we embarked on a new project that would enable heterometallic paramagnetic coordination cages to be accessed in a modular and predictable fashion, an approach centred around the tritopic “metallogand”, [MIII(L₄)] (HL = 1-(4-
pyridyl)butane-1,3-dione, which features a tris(acac) octahedral transition metal core pendant functionalised with three p-pyridyl donor groups (Figure 1).

In the case of the fac-isomer, the N-donor groups are aligned in a tripodal array such that the entropically-favoured smallest assembly that ensures maximum-site occupancy with a square-planar connector would be a cubic system.20 As such, we would be able to use pre-designed self-assembly to position one metallic [and paramagnetic] ion at the eight cube vertices and another at the centre of the six faces. Herein, we report the preparation and structural data of four heterometallic [CrII(CO)3]n+ molecular cubes, where MII = Cu, Co, along with a discussion of their magnetic behaviour.

Experimental section
Syntheses
1-(4-pyridyl)butane-1,3-dione (HL) and the metalloligand [CrLIII] were prepared according to previously published procedures.20,21 All reactions were performed under aerobic conditions. Solvents and reagents were used as received from commercial suppliers. Variable-temperature, solid-state direct current (dc) magnetic susceptibility and variable-temperature-and-variable-field (VTVB) magnetisation data down to $T = 2\, \text{K}$ were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet.

$[\text{Cr}_2 \text{CO}_3 \text{L}_2 \text{Cl}_2]$ (1)
To a solution of the metalloligand [CrLIII] (108 mg, 0.2 mmol) in 20 mL of dichloromethane/tetrahydrofuran (1:1 v/v) was added CoCl$_2$ (20 mg, 0.15 mmol). The solution was stirred for 14 hours, before being filtered and allowed to stand. Brown, X-ray quality crystals were obtained after room temperature evaporation of the mother liquor after 5 days. Elemental analysis (%) calculated (found): C 51.84 (51.61), H 4.20 (4.09), N 6.25 (6.54).

$[\text{Cr}_2 \text{CO}_3 \text{L}_2 \text{(SCN)}_2]$ (2)
To a solution of the metalloligand [CrLIII] (108 mg, 0.2 mmol) in 20 mL of dichloromethane/methanol (1:1 v/v) was added Co(SCN)$_2$ (35 mg, 0.2 mmol). The solution was stirred for 2 hours, before being filtered and allowed to stand. Brown, X-ray quality crystals were obtained after room temperature evaporation of the mother liquor after 5 days. Elemental analysis (%) calculated (found): C 53.63 (53.26), H 3.79 (3.51), N 4.94 (5.13). Yield = 77%.

$[\text{Cr}_3 \text{Cu}_2 \text{L}_2 \text{(H}_2\text{O})_2]_2[\text{SO}_4]_3$ (3)
To a solution of the metalloligand [CrLIII] (108 mg, 0.2 mmol) in 20 mL of dichloromethane/methanol (1:1 v/v) was added a solution of Cu(SO$_4$)$_2$·5H$_2$O (50 mg, 0.2 mmol) in 3 mL of water. The solution was stirred for 1 hour, before being filtered and allowed to stand. Green X-ray quality crystals were obtained after room temperature evaporation of the mother liquor after 5 days. Elemental analysis (%) calculated (found): C 47.33 (47.12), H 3.97 (3.83), N 6.13 (5.97). Yield = 59%.

$[\text{Cr}_3 \text{Cu}_2 \text{L}_2 \text{Cl}_2]$ (4)
To a solution of the metalloligand [CrLIII] (108 mg, 0.2 mmol) in 20 mL of dichloromethane/methanol (1:1 v/v) was added a solution of CuCl$_2$·2H$_2$O (34 mg, 0.2 mmol) in 2 mL of water. The solution was stirred for 5 minutes before being filtered and allowed to stand. Green-brown, X-ray quality crystals were obtained after room temperature evaporation of the mother liquor after 5 days. Elemental analysis (%) calculated (found): C 50.72 (50.43), H 3.78 (3.45), N 6.57 (6.64). Yield = 68%.

Crystal structure information
For compounds 1, 2 and 4 single-crystal X-ray diffraction data were collected at $T = 100\, \text{K}$ on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn 724+ detector mounted at the window of an FR-E+ Superbright MoKα rotating anode generator with HF Varimax optics (70 μm focus)22 using Rigaku Crystal Clear and CrystalsPro software23,24 for data collection and reduction. For compound 3 and [CrLIII] single crystal X-ray diffraction data were measured on a Rigaku Oxford Diffraction SuperNova diffractometer using Mo (for [CrLIII]) or Cu (for 3) radiation at $T = 120\, \text{K}$. The CrystalsPro software package was used for instrument control, unit cell determination and data reduction.25 Unit cell parameters in all cases were refined against all data. Crystal structures were solved using the charge flipping method implemented in SUPERFLIP26 (1, 2, and 4), Olex2 ([CrLIII]), or by direct methods with ShelXS (3). All structures were refined on $F^2$ by full-matrix least-squares refinements using ShelXL27 within the OLEX2 suite.28 All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were added at calculated positions and refined using a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter ($U_{eq}$) of the parent atom.

Crystal data for [CrLIII]: C$_{22}$H$_{24}$N$_2$O$_5$Cr, $M_r = 538.49$, trigonal, a = 17.6411(3) Å, $b = 17.6411(3)$ Å, $c = 27.0463(4)$ Å, $\alpha = 90.0^\circ$, $\beta = 90.0^\circ$, $\gamma = 120.0^\circ$, $V = 7289.3(2)$ Å$^3$, $\mu = 0.520$ mm$^{-1}$, $T = 120\, \text{K}$, 5148 unique reflections ($R_{int} = 0.0473$), 4803 with $F^2 > 2\sigma$, $R(F) = 0.0561$, $R_w (F^2)$, all data = 0.1096.

Crystal data for 1: C$_{22}$H$_{24}$N$_2$O$_5$Cl$_2$Cr$_8$Co$_6$, $M_r = 5375.43$, triclinic, $a = 28.265(4)$ Å, $b = 29.830(4)$ Å, $c = 31.290(5)$ Å, $\alpha = 72.023(16)^\circ$, $\beta = 71.093(15)^\circ$, $\gamma = 63.981(13)^\circ$, $V = 21995(7)$ Å$^3$, $Z = 2$, $P = 1$, $D_r = 0.812$ g/cm$^3$, $\mu = 0.526$ mm$^{-1}$, $T = 100(2)$ K, 73957 unique reflections ($R_{int} = 0.063S$), 49534 with $F^2 > 2\sigma$, $R(F) = 0.0561$, $R_w (F^2)$, all data = 0.4175.
Crystal data for 2: C_{226}H_{426}N_{12}O_{48}S_{12}Cr_{3}Co_{6}. M_r = 5106.41, tetragonal, a = 41.7282(5) Å, b = 41.7282(5) Å, c = 30.6665(7) Å, α = β = γ = 90.0 °, V = 53397.9(18) Å³, Z = 4, I4_12_22, D_c = 0.667 g/cm³, μ = 0.420 mm⁻¹, T = 100(2) K, 23556 unique reflections (R_int= 0.1250), 10357 with F² > 2σ, R(F, F² > 2σ) = 0.0457, R_w(F², all data) = 0.0941.

Crystal data for 3: C_{216}H_{324}N_{28}O_{48}S_{6}Cr_{8}Cu_{6}. M_r = 5481.79, tetragonal, a = 28.79166(19) Å, b = 28.79166(19) Å, c = 24.4854(3) Å, α = β = γ = 90.0 °, V = 20297.4(4) Å³, Z = 2, P4/n, D_c = 0.897 g/cm³, μ = 2.782 mm⁻¹, T = 120 K, 16958 unique reflections (R_int= 0.0762), 11352 with F² > 2σ, R(F, F² > 2σ) = 0.1208, R_w(F², all data) = 0.3932.

Crystal data for 4: C_{216}H_{324}N_{28}O_{48}Cl_{12}Cr_{3}Cu_{6}. M_r = 5114.68, tetragonal, a = 41.329(14) Å, b = 41.329(14) Å, c = 31.056(10) Å, α = β = γ = 90.0 °, V = 53046(40) Å³, Z = 4, I4_12_22, D_c = 0.640 g/cm³, μ = 0.486 mm⁻¹, T = 100(2) K, 23152 unique reflections (R_int= 0.1250), 11046 with F² > 2σ, R(F, F² > 2σ) = 0.0424, R_w(F², all data) = 0.1118.

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Crystallography discussion

Crystals of all samples were very sensitive to solvent loss, which resulted in rapid crystal delamination and poor quality X-ray diffraction data. To slow down this crystal degradation, crystals of compounds 1, 2 and 4 were ‘cold mounted’ on MiTeGen Micromounts™ at T = 203 K using Sigma-Aldrich Fomblin Y® LVAC (3300 mol. wt.) with the X-Temp 2³⁹ crystal cooling system attached to the microscope. This procedure protected crystal quality and permitted collection of usable X-ray data. All four structures contain large accessible voids and channels that are filled with diffuse electron density belonging to uncoordinated solvent, whose electron contribution was accounted for by the SMTBX solvent masking routine as implemented in OLEX2 software. The crystal structure of 1 exhibits a significant amount of positional disorder, whereby part of the complex adopts two positions along the C33-Co2-CI4 axis. This disorder has been modelled over two sites with a 60:40 ratio. Several geometrical constraints (DFIX, AFIX 66, FLAT) have been used to maintain sensible molecular geometry.

Crystal structures 2 and 4 (both in the tetragonal I4_12_22 space group) have been refined as two-component inversion twins with 81:19 and 58:42 ratios, respectively. Global SIMU, RIGU and DELU restraints were used to model atomic displacement parameters. For structure 3, the measured data were consistently of poor quality. This structure has been modelled as far as is reasonable and practical, given the poor quality of the data set. The ShelX weighting scheme could not be optimized. The Cu₆Cr₉ cage was identified easily from the initial structure solution and refines well without restraints. Overall the cube carries a total charge of 12+. This is balanced by six sulphate anions. Peaks in the difference map corresponding to three crystallographically inequivalent sulphate anions per asymmetric unit were identified. Of these, two are inside the cube (S2 and S3) and one (S1) is outside of the cube. The geometry of the S1 anion is the most stable, and thus S2 and S3 anions were modelled to have similar geometries to S1. S1 and S2 were refined anisotropically with displacement ellipsoid restraints; S3 was refined using an isotropic model. Each sulphate anion was modelled as half-occupied, and each is disordered around a crystallographic four-fold rotation axis so that the charges balance. Bond distance and displacement similarity restraints (SADI and RIGU) were used, as shown in the .res file embedded within the CIF shelx_res_file. Close O...O contacts between sulphate anions are flagged by PLATON; this is inevitable given the disordered nature of the anions. The copper centres are assumed to have axial aqua ligands, with the H atoms on these ligands placed for the sake of chemical completeness. The SQUEEZE routine of PLATON was used to remove the remaining electron density, corresponding to 2934 electrons per unit cell. It is not good practice to attempt to ascribe this much electron density to either of the two solvents employed, methanol and dichloromethane, or to adventitious water molecules, as the ratio of solvents cannot be established by any other means. There is one residual peak of approximately 6.6 electrons located in the centre of the cube. There is no chemically plausible model for this, given the reagents and solvents used.
Results and discussion

The heterometallic cages \([\text{Cr}^{III} \text{Rh}^{II} \text{L}_2 \text{Cl}_2] (1), [\text{Cr}^{III} \text{Rh}^{III} \text{L}_2 \text{Cl}_2] (2), [\text{Cr}^{III} \text{Cu}^{II} \text{L}_2 \text{H}_2 \text{O}]_2 \text{Cl} \text{L}_2] (3)\) and \([\text{Cr}^{III} \text{Cu}^{III} \text{L}_2 \text{Cl}_2] (4)\) were all prepared in a similar manner by addition of an \(\text{M}^{III}\) salt to the metalloligand \([\text{Cr}^{III} \text{L}_3] (\text{HL} = 1-(4\text{-pyridyl})\text{butane-1,3-dione}) in a mixed solvent system (either CH\(_2\)Cl\(_2\) / MeOH or CH\(_3\)Cl\(_2\) / THF, see the experimental section for full details). The resultant reactions were stirred for a period of 1-14 hours, before being filtered; crystals were obtained by slow evaporation of the mother liquor at room temperature over several days. All four structures (Figures 2-3) reveal a similar pseudo-cubic metallic skeleton \([\text{Cr}^{III} \text{M}^{III}]_2\)\(^{12}\) where each \(\text{M}^{III}\) \((\text{M}^{III} = \text{Co}, \text{Cu})\) ion is situated slightly above \((1.2-1.4 \text{ Å})\) the centre of a square face of approximate dimensions 12 Å, defined by four \(\text{Cr}\) ions. Each \([\text{Cr}^{III} \text{L}_3]\) corner unit consists of a six-coordinate \(\text{Cr}\) ion with regular \([\text{CrO}_6]\) octahedral geometry, with \(\text{Cr-O}\) distances between 1.86-2.01 Å and cis/trans angles in the range 85.6-94.2° and 176.3-179.5°, respectively. The face-centred linkage of each corner fragment is achieved by the coordination of the four pyridyl donors to the equatorial positions of the six-coordinate \(\text{M}^{III}\) metal ions, with \(\text{M}^{III}\) distances in the range 2-2.2 Å. For 1, 2 and 4, the remaining apical sites of each \(\text{M}^{III}\) ion are occupied by the anions present in the starting cobalt or copper salts \((\text{i.e. Cl or SCN})\) giving overall charge neutral cages. However, with 3, the apical sites are occupied by water molecules (arising from either the hydrated metal salt or from the non-dried solvent), which gives an assembly with overall +2 charge. Charge balance is maintained through the presence of a total of six \(\text{SO}_4^{2-}\) anions, four inside and two outside the cube (Figure 3). The Jahn-Teller axis of each \(\text{Cu}^{II}\) ion in 3 and 4 lies perpendicular to the face it sits in.

All four structures reveal that 1-4 crystallise as homochiral racemates, \(\text{i.e. each cube possesses eight } [\text{Cr}^{III} \text{L}_3]\) stereocentres of the same \(\Lambda\) or \(\Delta\) chirality. While it is possible that this could simply be a packing effect from a complex and dynamic diastereomeric mixture, solution-based self-sorting of assemblies that contain multimetallic stereocentres is a common,\(^{31}\) if not universal,\(^{32}\) occurrence. The energetic preference for a single diastereomer is a sign that stereoechemical information between adjacent metal vertices is efficiently transmitted through the ligand framework. In the case of 1-4, the \([\text{Cr}^{III} \text{L}_3]\) stereocentres communicate via the tetrapyridyl-\(\text{M}^{III}\) coordination motif, which exhibit pronounced propeller-like twists (rather than idealised \(\text{D}_{4h}\) symmetry). Interestingly, the sense of this twist is conserved over the six connected faces of each individual assembly; the opposite holds for connecting \([\text{Cr}^{III} \text{L}_3]\) fragments of alternate stereochemistry.

Figure 3. Metallic skeleton of the cation of complex 3 (left). The distance between nearest neighbour \(\text{Cr}^{III}\) and \(\text{Cu}^{II}\) ions is approximately 8.8 Å. The molecular structure of 3 (centre) highlighting the encapsulation of four \(\text{SO}_4^{2-}\) molecules in the internal cavity of the cage. \(\text{H}\)-atoms and external \(\text{SO}_4^{2-}\) anions have been omitted for clarity. Representation of one of the six faces of the cube (right), highlighting the coordination geometry of the \(\text{Cu}^{II}\) ion. The \(\text{Cu}^{II}\) ion is six coordinate with a \(\{\text{CuN}_6\}\) coordination sphere; the Jahn-Teller distortion lying along the \(\text{Cu-Cu}\) face, perpendicular to the face of the cube. Colour code: \(\text{Cr} = \text{green}, \text{Cu} = \text{gold}, \text{O} = \text{red}, \text{N} = \text{blue}, \text{C} = \text{black}\).

Figure 4. Representation of the available internal cavity space in complex 2. A volume of 1471 Å\(^3\) was calculated employing an outer probe of 8.0 Å and an internal probe of 1.5 Å. See reference 33 for details.
accommodated in compounds 1-4. Indeed this is in accordance with the encapsulation of four SO₄²⁻ anions, with total volume of 668 Å³, inside the cavity of complex 3 (Figure 3). Future work will focus on examining the host-guest chemistry of these cages, since their large internal cavities potentially could play host to an array of different species. For example, one can imagine constructing magnetic coordination capsules capable of hosting magnetic and/or redox-active guests, exerting control over magnetic super-exchange between metal ions in the host framework and between the host and guest.

There are several close intermolecular contacts between the cages in the extended structures of 1-4. In 1 the closest intercluster contacts are between the halide ions on one cube and the L ligands of the neighbouring cube with Cl···C distances in the range 3.6-3.9 Å, while for 2 the closest contact is between the O- and C-atoms of the L ligands, with distances as short as 3.3 Å. Similar ligand-ligand interactions also occur between the corners of the cubes in 3 and 4, but in addition the externally located SO₄²⁻ ions in 3 H-bond to the terminally bonded H₂O molecules on the M⁰ ions (O···O, 2.7 Å), directing the formation of chains of clusters along the c-axis of the cell (Figure 5).

**Magnetic studies**

Quantitatively analysing the magnetic behaviour of such large heterometallic species using traditional matrix diagonalisation techniques is non-trivial, and often impossible, due to the enormous dimensions of the associated spin-Hamiltonian matrices. For complexes 1 and 2 analysis is further hindered by the presence of the highly anisotropic octahedral Co⁰ ion. As such we do not attempt fits of the susceptibility and magnetisation data, but instead simply compare the experimental data to the detailed magnetothermal and spectroscopic investigation of the structurally similar complexes [Cr₆III₅CoV₄L₄2(H₂O)₁₂]₂(CIO₄)₁₂ (5) and [Cr₆III₅CuV₄L₄2(H₂O)₁₀(NO₃)₂](NO₃)₁₀ (6) reported in reference 20, in which computational techniques known in theoretical nuclear physics as statistical spectroscopy were employed. The dc (direct current) molar magnetic susceptibility, χM, of polycrystalline samples of complexes 1-4 were measured in an applied magnetic field, B, of 0.1 T, over the T = 5-300 K temperature range (Figure 6); where χM = M/B, and M is the magnetisation. At room temperature, the χM/T products of 1 - 2 and 3 - 4 have values of 26.3 and 17.7 cm³ mol⁻¹ K, respectively, in excellent agreement with that expected from the spin-only contributions to the magnetism of a [Cr₄III₅CoV₄L₄] unit (26.3 cm³ mol⁻¹ K) with g₄₃ = 2.00, and of a [Cr₄III₅CuV₄L₄] unit (17.6 cm³ mol⁻¹ K), with g₄₃ = 2.00 and g₄₄ = 2.15, where g₄₃, g₄₄, and g₄₅ are the g-factors of Cr₄III, CoIII and CuIV, respectively. Upon cooling, the χM/T values of 1-2 decrease continuously reaching a low temperature value of ~20 cm³ mol⁻¹ K. The behaviour of complexes 3-4 appears, at least upon initial inspection, to be somewhat different. Upon cooling, the χM/T products of both remain essentially constant down to T = 20 K, below which there is an increase to a value of ~18.5 cm³ mol⁻¹ K. Qualitatively the magnetic behaviour of 3 and 4 is straightforward: the exchange between the Cr⁰ and Cu⁰ ions is very weak and ferromagnetic in nature. One can also come to the same conclusion for compounds 1 and 2 [and 5] if one assumes the high temperature decrease in χM/T is due solely to the anisotropy of the octahedral Co⁰ ion. Indeed, the data for 5 shows a low temperature increase in χM/T which is consistent with a weakly ferromagnetic Cr⁰-Co⁰ interaction. Clearly, however, other models invoking an antiferromagnetic interaction could explain the variable temperature susceptibility. Variable-temperature-and-variable-field (VTVB) magnetisation studies are consistent with the presence of weak exchange interactions in all cases (Figure 6, bottom), with the saturation magnetic moment at T = 2 K and B = 7 T being close to that expected for a fully parallel alignment of the spins in the case of the Cr-Cu cages. For the Cr-Co cages 1 and 2 the saturation magnetic moments are lower than the ferromagnetic limit due to the large orbital contribution of the octahedral Co⁰ ion.

Figure 5. The packing of three molecules of compound 3 in the crystal, highlighting the H-bonded chains of cubes along the c-axis of the cell.

Figure 6. Plot of the χM/T product versus temperature for complexes 1-4 (top). The data for complexes 5 and 6 are added for comparison. See reference 20 for full...
Conclusions

The modular assembly of magnetic coordination capsules with internal cavities capable of hosting magnetic and redox-active guests is an under-explored field of research that can be exploited for the construction of tuneable, multifunctional molecular magnets with potential application in information storage and molecular spintronics. The ability to control and manipulate (switch on, switch off) magnetic exchange between metal ions in the host framework and between the host and guest(s) via the use of redox-active (redox) ligands in the framework of the host, and/or redox-active/paramagnetic guests held within the cavities, remains an attractive target. The construction of said capsules in a manner amenable to exohedral functionalization such that the organic sheath surrounding the capsules are easily derivatised post-synthetically to modify and tune solubility, magnetic behaviour, reactivity, stability and substrate specificity would also make the cages suitable for materials applications.

Here, the simple, modular assembly of \([\text{M}^{\text{II}}\text{M}^{\text{III}}\text{L}]_{3}\) cubes [with \(\text{M}^{\text{II}} = \text{Cr}^{2+}\) and \(\text{M}^{\text{III}} = \text{Co}^{2+}\) or \(\text{Cu}^{2+}\)] suggests that any combination of \([\text{M}^{\text{II}}\text{L}]_{3}\) metalloid/organic ligand and \(\text{M}^{\text{III}}\) salt will work, potentially resulting in an enormous family of supramolecular assemblies. The charge of the cubes varies from neutral to 12+ and is controlled by the nature of the ligand occupying the axial sites on the \(\text{M}^{\text{II}}\) ions. Ligand substitution at these sites should be trivial and may prove a gateway to accessing a variety of new cages and polymers whereby the clusters are linked via di/polytopic linker ligands. Complex 3 encapsulates four \(\text{SO}_2\text{H}_2\) ions in its central cavity (of volume ~1400 Å\(^3\)) suggesting that cationic cages may be good hosts for different guests, such as organic radicals or simple coordination compounds containing paramagnetic metal ions.

Heterometallic \(\text{Cr}^{\text{III}}\text{-Co}^{\text{II}}\) cages are surprisingly rare. Excluding organometallic and metal-metal bonded species, a search of the Cambridge Structural Database returned just a handful of hits, and the vast majority of these are derivatives of the well-known \([\text{Cr}_2\text{Co}]\text{wheels}\) of Winpenny and Timco.\(^{35}\) There are two hydroxo/alxo-bridge dimers,\(^{36}\) linear trimers and the ubiquitous triangular basic carboxylates,\(^{37}\) a \(\text{Cr}_2\text{Co}_2\) butterfly and a \(\text{Cr}_3\text{Co}\) star,\(^{38}\) and pivalate/phosphonate-bridged \(\text{Cr}_2\text{Co}_4,\text{Cr}_2\text{CO}_3\) and \(\text{Cr}_4\text{CO}_4\) cages.\(^{39}\) Heterometallic \(\text{Cr}^{\text{III}}\text{-Cu}^{\text{II}}\) complexes are similarly dominated by Manchester wheels, but here there is a little more variety with \(\text{Cr}_2\text{Cu},\text{Cr}_3\text{Cu}_2,\text{Cr}_4\text{Cu}_2\) and \(\text{Cr}_2\text{Cu}_2\) examples all being reported.\(^{40}\) Beyond these there is very little else in the literature, but a few examples of dimers, \(\text{Cr}_2\text{Cu}\) trimers, \(\text{Cr}_2\text{Cu}_2\) butterflies and one example of a \(\text{Cr}_2\text{Cu}_4\) cage.\(^{41}\) The \(\text{Cr}_2\text{Cu}_2\) and \(\text{Cr}_2\text{Cu}_4\) cages reported herein are therefore the largest such species yet reported.

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Notes and references

Crystallographic data (including structure factors) for 1-4 have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1457376-1457380. Copies of the data can be obtained, free of charge, on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk). Magnetic data has been deposited at Edinburgh Datashare: http://datashare.is.ed.ac.uk/.


