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**Introduction**

Interest in the magnetic behaviour of polymeric complexes of CuII can be traced back to studies of copper acetate in the 1950s and the subsequent magneto-structural correlations developed for [Cu4] dimers bridged by hydroxides, halides and azides. Later studies examined larger, more complex structures such as [Cu3] triangles, [Cu4] cubes, [Cu8] chains and heterometallic species containing transition metal or lanthanide metal centres. Many of these studies revealed fascinating magnetic behaviours, such as the spin frustration prevalent in equilateral triangles which represent the simplest molecular analogues of the kagome lattice, a topology also of relevance in multicopper oxidases.

A search of the Cambridge Structural Database (CSD) reveals there are several hundred homometallic O/N-bridged CuII clusters deposited that possess a nuclearity of two or more, with the largest being [Cu16]4− reported in 2004. However, as nuclearity increases this number decreases significantly – for example there are less than twenty with a nuclearity of twenty or more. A seemingly ideal ligand framework for housing the Jahn–Teller (JT) distorted octahedral CuII ion is p-Bu-calix[4]arene (H4TBC[4]; Fig. 1A), its tetraphenolic pocket being perfectly suited to accommodating four short equatorial bonds. Despite this, the success of H4TBC[4] in the coordination chemistry of the JT distorted octahedral MnIII ion, there are just three homometallic CuII compounds known. The first two, [Cu16(OH)4(TBC[4])4Cl2(dmso)5.5(EtOH)j.5][CuCl2] (1)

![Fig. 1](https://example.com/image.png)

**Fig. 1** Single crystal X-ray structures of H4TBC[4] (A) and H8L (B). Colour code C = grey, O = red, H = white.
X-ray crystallography

Diffraction data for 4 were collected on a Bruker D8 diffractometer equipped with a PHOTON 100 detector and operating with synchrotron radiation (0.7749 Å). Crystal data for 4 (CCDC 2101166): C_{14}H_{30}S_{5}Cu_{16}N_{25.5}O_{68.5}, M = 7095.88 g mol⁻¹, triclinic, space group P1 (no. 2), a = 21.4369(9) Å, b = 21.9078(9) Å, c = 22.0660(9) Å, α = 105.396(3)°, β = 111.468(2)°, γ = 95.527 (3)°, V = 9067.1(7) Å³, Z = 1, T = 100(2) K, μ(synchrotron) = 1.251 mm⁻¹, Dcalc = 1.300 g cm⁻³, 56 519 reflections measured (4.312° ≤ θ ≤ 47.784°), 21 580 unique (Rint = 0.0705, Rsig = 0.0826) which were used in all calculations. The final R1 was 0.0566 (I > 2σ(I)) and wR2 was 0.1551 (all data).

Magnetic data

Magnetic susceptibility and magnetisation data were collected on a powdered microcrystalline sample of 4 using a Quantum Design PPMS Dynacool. Susceptibility data were collected in the T = 2–300 K range under and applied magnetic field, B = 0.1 T. Magnetisation data were collected in the T = 2–10 K and B = 0.3–9.0 T ranges. A unit cell check was performed prior to measurement.

EPR spectroscopy

EPR spectra were measured on powder and solution (CH₂Cl₂/toluene) samples of 4, at 10 and 20 K and over the 0–1.8 T field range, on a Bruker EMXPlus spectrometer.

Computational details

Density functional theory in conjunction with the broken symmetry approach has been used to estimate the magnetic exchange interactions in complex 4 employing Gaussian 09. The hybrid B3LYP functional22 together with Ahlrichs TZV basis set for was used for the Cu atoms, the SVP basis set for O and N atoms, and the SV basis set for C and H atoms.23 This methodology has been shown to reproduce experimental magnetic exchange interactions accurately.24

Results and discussion

Reaction of H₈L with Cu(NO₃)₂·3H₂O and Me-deaH₂ in a basic dmf/MEOH mixture affords single crystals of formula [Cu_{16}(L)₂(Me-dea)₂(µ₂-NO₃)₂(µ₂-OH)₆(µ₄-OH)₆(dmff)₃,₅(MeOH)₂,H₂O₂] (H₂L)-16dmf·4H₂O (4, Fig. 3 and 4), following slow evaporation of the mother liquor. The crystals were found to be in a triclinic cell and structure solution was carried out in the space group P1. The asymmetric unit (ASU) comprises half of the formula.

The metallic skeleton describes a tetracapped (Cu₁–2 and symmetry equivalent) square prism (Cu₃–6) in which the ‘upper’ and ‘lower’ square faces (as drawn in Fig. 4B) are edge-capped by a {Cu₂₂} (Cu₇–8) moiety. The Cu ions in the upper and lower faces of the square prism are connected to each other by four µ-OH ions to form a [Cu₂(OH)₄]¹²⁻ central unit (Fig. S1†). The four face-capping Cu ions are housed in the polyenohlic pockets of the two fully deprotonated bis-calix-
ene ligands whose O-atoms further bridge to the Cu ions in the square prism (Cu3–Cu6; Fig. S1 and S2†). The L8⁻ ligands thus wrap around the four square faces of the prism in the ‘equatorial’ plane (as drawn in Fig. 1A), completely encapsulating the [Cu₈(OH)₄]²⁺ central unit. The ‘upper’ and ‘lower’ faces of the prism are connected to the {Cu₂} edge-cap by a µ₄-bridging NO₃⁻ ion which connects Cu₃–4 to Cu₇–8. The latter are further bridged to each other and the Cu ions on the vertices of the square prism by two Me-dea²⁻ ligands that bond in two different ways. The first µ₃-bridges, using one O-arm (O16) to link between Cu⁷–Cu₈ and the other (O17) to link between Cu₈ and Cu₆ in the square prism. The second chelates to Cu⁷ with one O-arm terminally coordinated (O15) and one arm (O14) bridging to Cu₄ in the square prism.

The Cu ions (Cu₁–2) that sit in the tetraphenolic pocket of L₈⁻ are square planar {CuO₄} with a fifth, longer contact to a disordered molecule of dmf that fills the calixarene cavity. The Cu ions in the square prism (Cu₃–6) are all five coordinate and in distorted square pyramidal geometry, the remaining sites on Cu₃ and Cu₅ being occupied by dmf/H₂O molecules. The Cu ions in the edge-capping {Cu₂} moiety (Cu₇, Cu₈) bonded to the Me-dea²⁻ ligands are five-coordinate, square pyramidal {CuO₄N}, and four-coordinate, square planar {CuO₃N}, respectively.

The complex displays numerous intra- and inter-molecular H-bonding interactions (Fig. S₃–S₆†). The water molecule bonded to Cu₅ is H-bonded to two O-atoms of the nitrate anion (O₁₉…O₁₂/O₁₁, ~2.83–3.01 Å). O₁₂ is also H-bonded to a µ-OH ion (O₁₂…O₉, ~2.95 Å), and the third O-atom in the nitrate anion (O₁₃) is H-bonded to a dmf molecule bonded to
Cu₃ (O₁₃⋯O₁₈, ~3.00 Å). There is also a complex H-bonding network in the region of one of the two Me-dea²⁻ co-ligands. The O-atom (O₁₅) belonging to the Me-dea²⁻ ligand supporting Cu⁷ is H-bonded to a H₂O molecule of crystallisation (O₁₅⋯O₂₁, ~2.62 Å). The latter is also interacting with the lower-rim oxygen atom of the co-crystallised H₆L₂⁻ ligand (O₂₁⋯O₂₆, ~2.72 Å). Upon symmetry expansion, it is possible to appreciate the importance of this network of H-bonds as it dictates the way compound 4 and the co-crystallised molecules pack, through the formation of H-bonded chains (Fig. S3–S6†).

The [Cu₁₆] cluster is surrounded at its four 'corners' by co-crystallised H₆L₂⁻. This doubly deprotonated molecule affords overall charge balance, and although there are waters of crystallisation present (and therefore potentially OH⁻ counter anions), we favour the presence of this dianion for two reasons. (1) The inter-molecular interactions discussed above; (2) refinement suggests each TBC[4] moiety in H₆L₂⁻ is singly deprotonated, consistent with the highly acidic nature of H₄TBC[4] hydroxyl groups reported in literature.²⁵ The clusters are well isolated from each other, with the closest Cu---Cu distance being >12 Å between the Cu₈ ions of distinct molecules. A search of the CSD shows that there are a total of thirteen [Cu₁₆⁺] clusters known, none of which have a topology similar to 4.²⁶

A comparison of the metallic skeletons of [Cu₉], [Cu₁₃] and [Cu₁₆] (Fig. 5) shows some striking similarities. [Cu₉] is a tricapped trigonal prism in which the square faces are all capped by a Cu ion housed in the pocket of a TBC[4] moiety with halide/nitrate anions capping the upper/lower triangular faces. [Cu₁₃] is a centred, tetracapped square prism in which the 'equatorial' square faces are all capped by a Cu ion housed in the pocket of a TBC[4] moiety with nitrate anions capping the upper/lower triangular faces. [Cu₁₆] has a structure analogous to [Cu₁₃] but without the central Cu ion, and with two additional {Cu₂} edge-capping moieties introduced through the presence of a co-ligand. These structural similarities reflect the dominant, structure-directing influence of the calix[4] arene ligands.

Magnetic measurements

Direct current magnetic susceptibility (χ) studies were performed on a polycrystalline sample of 4 over the temperature range T = 2–300 K, in an applied magnetic field B = 0.1 T (Fig. 6), where χ = M/B and M is the magnetisation. At 300 K, the χT value of 5.9 cm³ mol⁻¹ K is below the expected value for

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Fig. 5 A comparison of the metallic skeletons of [Cu₉] (1–2, A and B), [Cu₁₃] (3, C and D) and [Cu₁₆] (4, E and F). The central, distorted Cu ion in [Cu₁₃] has been removed to aid comparison. [Cu₉] describes a tricapped trigonal prism, [Cu₁₃] a (centred) tetracapped square prism, and [Cu₁₆] a tetracapped square prism containing two additional (Cu₂) edge-caps. The Cu ions in the prisms are in light blue, those housed in the tetraphenolic calixarene pocket in green and the edge-caps in pink.
spin-only contributions to the susceptibility for a [Cu\(^{II}\)] \(_n\) unit (7.26 cm\(^3\) mol\(^{-1}\) K, \(g = 2.2\); 6.00 cm\(^3\) mol\(^{-1}\) K, \(g = 2.0\)). Upon cooling, the \(\chi T\) product decreases rapidly until approximately \(T = 10\) K where it reaches 1.1 cm\(^3\) mol\(^{-1}\) K, wherefrom it increases upon further cooling reaching a value of 1.5 cm\(^3\) mol\(^{-1}\) K at 2 K. The data are therefore suggestive of the presence of competing exchange interactions, in agreement with the range of Cu–O–Cu angles present, and previous magnetostuctural correlations developed for smaller O-bridged Cu\(^{II}\) clusters.\(^{1-6}\)

The quantitative interpretation of the temperature dependence of the \(\chi T\) product of 4 was performed by numerically fitting the experimental data to the full matrix representation of spin-Hamiltonian (1), of dimension 65,536 by 65,356, by use of the Levenberg–Marquardt algorithm.\(^ {27}\)

\[
\hat{H} = \mu_B B \sum_i g_i S_i - 2 \sum_{i > j} J_{ij} S_i \cdot S_j
\]  

(1)

where the indices refer to the constituent Cu\(^{II}\) ions, \(\mu_B\) is the Bohr magneton, \(g\) is the \(g\)-factor, \(S\) is a spin operator and \(J_{ij}\) is the bilinear pairwise isotropic exchange interaction parameter.

Based on the structure of 4, four different isotropic exchange parameters could be considered to fit the experimental temperature dependence of the \(\chi T\) product (Fig. 6, insets).

We employed irreducible tensor operator algebra to block-diagonalise the matrix representation of spin-Hamiltonian (1),\(^ {28}\) fixing the \(g\) factor for all Cu\(^{II}\) centres to \(g = 2\), affording only the four different isotropic exchange parameters as free fit parameters. This resulted in very good agreement with the experimental data with the best-fit parameters \(J_1\), \(J_2\) and \(J_3\) being strongly antiferromagnetic (AF), ca. \(-70\) to \(-100\) cm\(^{-1}\), and \(J_4\) being ferromagnetic (F), ca. \(+20\) cm\(^{-1}\). However, all these exchange parameters are strongly correlated, with only the correlation coefficients between \(J_4\) and the others being less than 95%. Use of a single exchange parameter fails to satisfactorily reproduce the experimental data at all temperature regimes. Use of a model containing two different exchange parameters \(J_1 = J, J_4 = J’\) (Fig. 6, insets) results in a very good agreement with the experimental data (Fig. 6), with \(J = -122 \pm 12\) cm\(^{-1}\) and \(J’ = 22 \pm 8\) cm\(^{-1}\), with a correlation coefficient of 87%. With these best-fit parameters the ground spin-state of 4 is an \(S = 1\) spin-state, with excited \(S = 0, 0\) and 2 states lying 23, 35 and 46 cm\(^{-1}\) above the ground state, respectively, followed by a quasi-continuum of states (Fig. 7). We note that the exchange constant in the [Cu\(_{12}\)] prism of 4 is similar to the values found in [Cu\(_{11}\)] (3), which are all AF and in the range \(-66 \leq J \leq -84\) cm\(^{-1}\).\(^ {19}\) Employing the same isotropic model to fit the VTVB magnetisation data of 4 was not possible. This is because the VTVB magnetisation of 4 presents significant nesting (Fig. S7†) when plotted against \(B/T\), which indicates anisotropy splittings of the same order of magnitude as the experimental conditions (\(T = 2\) to 10 K and \(B = 1\) to 9 T). Given that individual Cu\(^{II}\) centres are devoid of anisotropy (bar the \(g\)-factor), the observed anisotropy splittings can only originate (within the spin-Hamiltonian formalism) from magnetic exchange.\(^ {29}\) The experimental data do not allow for the determination of these exchange contributions to anisotropy.

Given the relatively well-isolated \(S = 1\) ground state evidenced by the magnetic data and modelling, we attempted to probe this state by EPR spectroscopy at low temperatures. Spectra measured at 10 K and over the 0–1.8 T magnetic field range, at both X- and Q-band frequencies, only gave weak signals that could be attributed to small amounts of monomeric Cu\(^{II}\) species. This indicates that the zero-field splitting (ZFS) of the \(S = 1\) state is significantly larger than the microwave frequencies applied. In order to estimate the ZFS, attempts were made to fit the VTVB magnetisation data to an isolated \(S = 1\) model: while these fits were not entirely satisfactory (Fig. S7†) they indicate an axial ZFS parameters \((D)\) of several cm\(^{-1}\). This would be consistent with 4 being EPR silent.

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**Fig. 6** Experimental \(\chi T\) versus \(T\) data for 4 measured in the \(T = 2–300\) K temperature range in an applied field, \(B = 0.1\) T.

**Fig. 7** Energy spectrum of 4 calculated from the fit of the susceptibility data, as described in the text. The ground spin-state of 4 is an \(S = 1\) spin-state, with excited \(S = 0, 0\) and 2 states lying 23, 35 and 46 cm\(^{-1}\) above the ground state.
under the measurement conditions. Given the lack of single-ion ZFS for Cu$^{II}$, the origin of such a ZFS must lie in anisotropic components of the exchange interaction.\(^{29}\) Although a ZFS in the region of several cm\(^{-1}\) would be unusual for a Cu cluster, the project coefficients of anisotropic exchange are larger for lower total spins,\(^{28}\) which may provide an explanation given that the ground state of 4 is the lowest possible total spin. It is more usual for Cu clusters to either give rise to a diamagnetic ground state or a high spin state, so there are few data to compare this against.

### Theoretical studies

In order to analyse the sign and magnitude of the exchange interactions in more detail we have constructed three pentametallic models (4A, 4B, 4C) and one bimetallic model (4D) based on the X-ray structure of 4 to determine twelve exchange interactions (Fig. S8\(^{\dagger}\)). These are given in Table S2\(^{\dagger}\) and consist of ten antiferromagnetic interactions in the range \(-3.9 < J < -55.7\) cm\(^{-1}\), and two weakly ferromagnetic interactions in the range \(+2.6 < J < +6.9\) cm\(^{-1}\). The strongest antiferromagnetic exchange occurs between Cu2 (face-cap) and Cu4 (vertex) mediated by a single µ-OH bridge with a Cu−O−Cu angle of \(\sim 131^o\). The second strongest antiferromagnetic exchange interaction is between Cu3 (vertex) and Cu4 (vertex) mediated via a single µ-OH bridge with a Cu−O−Cu angle of \(\sim 126^o\). The two ferromagnetic exchange interactions occur between Cu1 (face cap) and Cu3 (vertex) mediated by µ-OH/µ-OPh bridges with an average Cu−O−Co angle of \(\sim 96^o\) and a Cu−O−Cu−O dihedral angle of \(\sim 24^o\), and between Cu6 (vertex) and Cu8 (edge-cap) mediated by µ(O(NO\(_3\))/OR groups with an average Cu−O−Co angle of \(\sim 98^o\) and a Cu−O−Cu−O dihedral angle of \(\sim 17^o\). A detailed examination of the structure reveals that the sign and magnitude of J strongly depends on both the Cu−O−Cu angle and the Cu−O−Cu−O dihedral angle.\(^{30}\) Large Cu−O−Cu angles lead to strong antiferromagnetic exchange whose magnitude decreases with decreasing angle (Fig. S9\(^{\dagger}\)). The switch to ferromagnetic occurs at a Cu−O−Cu angle of \(\sim 97−99^o\).\(^{1,8}^{,8}\) A large Cu−O−Cu−O dihedral angle in conjunction with a small Cu−O−Cu angle results in accidental orbital orthogonality (a counter complementarity effect arising from the presence of two different bridging ligands) which leads to a weak ferromagnetic interaction. DFT calculated spin density analysis (Fig. S10–S13\(^{\dagger}\)) suggests strong spin delocalisation with spin densities on the Cu$^{II}$ ions of between 0.391−0.673. The bridging hydroxides/phenolic O-atoms have the largest spin density among the coordinating atoms, consistent with the strongest antiferromagnetic exchange through these moieties. The pattern of calculated exchange interactions (Table S2\(^{\dagger}\)) and the spin density analysis therefore strongly suggests the presence of spin frustration between the face-capping Cu ions housed in the calixarene polyphenolic pockets and the Cu ions at the vertices of the square prism. The small spin density of the N-atom of the nitrate points to a small, near-negligible, exchange through the Cu−O−N−O−Cu pathway (Fig. S14\(^{\dagger}\)).

### Conclusions

The reaction between Cu(NO\(_3\))\(_2\)·3H\(_2\)O and 2,2′-bis-p′-Bu-calix[4] arene (H\(_2\)L) in a basic dmf/MeOH mixture and in the presence of the co-ligand Me-dea\(_2\) results in the formation of the complex [Cu\(_{16}\)(H\(_2\)O)\(_2\)](Me-dea\(_2\))(H\(_2\)O\(_2\))\(_2\)(dmf)\(_2\)(MeOH)(H\(_2\)O\(_2\))\(_2\) (H\(_2\)L)-16dmf-4H\(_2\)O. Its metallic skeleton describes a tetra-capped square prism, [Cu\(_{12}\)], with two additional edge-capping [Cu\(_4\)] units introduced by the co-ligand sitting above and below the “upper” and “lower” square faces. The cage structure is held together internally via a combination of bridging hydroxides and nitrates, and externally by the two bis-p′-Bu-calix[4]arenes. The structural similarity of [Cu\(_{16}\)] to [Cu\(_{12}\)], a centred, tetra-capped square prism also built with H\(_2\)L (in the absence of co-ligands), and [Cu\(_8\)], a tri-capped trigonal prism built with H\(_4\)TBC[4], reflects the dominant structure-directing role played by the calix[n]arene ligands. Magnetic susceptibility measurements reveal strong antiferromagnetic exchange interactions between neighbouring Cu$^{II}$ ions within the central [Cu\(_{12}\)] tetra-capped square prism and between the Cu$^{II}$ ions in the prism and the caps (\(J = -122 \pm 12\) cm\(^{-1}\)), and strong ferromagnetic exchange between the Cu$^{II}$ ions in the caps (\(J' = +22 \pm 8\) cm\(^{-1}\)), leading to a ground state of \(S = 1\). DFT calculations reveal a strong dependence of J on both the Cu−O−Cu and O−Cu−O−Cu angles, and suggest significant spin frustration in the central [Cu\(_{12}\)] tetra-capped square prism. Magnetisation and EPR data suggest the presence of significant ZFS in the S = 1 ground state, originating from anisotropic components of the exchange interaction. It will be interesting to examine the effect of extending the bridge length between the H\(_4\)TBC[4] moieties in bis-calix[4]arene ligands and/or of increasing the size of the calix[n]arene macrocyclic, e.g. to p′-Bu-calix[8]arene, on cage nuclearity and topology. Expansion into Cu-4f chemistry also promises the discovery of some interesting cages. This work is currently in progress.

### Author contributions

LRBW, MC performed the synthetic chemistry and measured the magnetic data. LRBW and SP fitted the magnetic data. SJT/SJD collected and solved the XRD data. AB, MS and EJLM collected and analysed the EPR data. MKS performed theoretical calculations. SJD and EKR conceived the idea. All authors wrote/edited the manuscript.

### Conflicts of interest

There are no conflicts to declare.

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Notes and references


