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Saddling up copper – new twists on a metallo-wheel†

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A unique octanuclear copper(II) cluster with a saddle-shaped structural topology has been prepared from a large, flexible polydentate ligand comprising a 4,4′-bipyridine linker bearing four pendant pyrazolate heterocycles.

Metal clusters, rings, wheels or cages are ubiquitous to many areas of chemistry and biochemistry including main group, organometallic, molecular magnetism, metallo-supramolecular and bioinorganic chemistry.[1] Particular interest in polynuclear copper clusters is fuelled by the characterisation of several unusual copper-containing metalloenzymes.[2] Cyclic metal arrays containing large numbers of spin-coupled paramagnetic metal centres are frequently synthesised from multicomponent systems in an uncontrolled "serendipitous" process that employs simple organic molecules and/or bridging ligands.[3] A more controlled approach that excludes extraneous bridging fragments can be adopted when designed polytopic ligands are employed, as then a self-assembly process proceeds through an algorithm defined by the coordination preferences of the metal ion and the steric information contained within the ligand structure.[4,5] Cyclic metal arrays and clusters assembled *via* this second approach have yet to offer the high nuclearities and magnetic phenomena associated with those formed from simpler bridging ligands.[5] This is in part due to the considerable synthetic effort required to synthesise families of polytopic ligands containing both rigid and flexible bridging groups.

Our research programme is focused towards the synthesis of multitopic ligands with two or more discrete binding domains and their coordination with metal ions for the self-assembly of magnetic chains, clusters and networks. To date we have focused our efforts on systems which ligate metals within a 4,4′-bipyridine-containing $[N_3O_2]$ macrocyclic framework[6a] as well as exploiting the coordination chemistry and reactivity of 3,3′-diamino-2,2′-bipyridine[6b] for the preparation of dicarboxamide[6c] and reactive Schiff-base bis-imine ligands.[6d] In this paper we report the synthesis of the first example of a new family of 4,4′-bipyridine tetracarboxamide ligands bearing four amide-bridged pendant heterocycles and its ability to construct a high-nuclearity copper(II) cluster.

4,4′-Bipyridyl-2,2′,6,6′-tetracarboxylic acid[7] was readily converted to the tetramide by first preparing the chloroformyl derivative that was then refluxed with the 3-amino-5-*t*-butyl pyrazole heterocycle in toluene overnight. *t*-Butyl groups were introduced to improve the solubility of the ligand in common organic solvents. Ligand **L** was characterised by multinuclear NMR, CHN microanalysis, FAB MS and X-ray diffraction.†

The crystal structure revealed that the pyrazole nitrogen atoms point into the molecular cleft (as illustrated in Fig. 1), affording two binding domains for the ligand. The pendant pyrazole groups are known to form diverse coordination

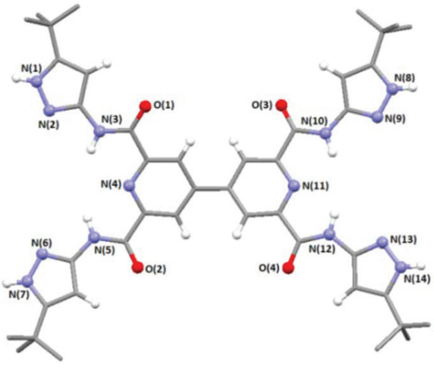

Fig. 1 Crystallographically determined structure of tetramide ligand, **L**; two H_2O and DMF molecules and the H atoms of the *t*-butyl groups are omitted for clarity.

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† Electronic supplementary information (ESI) available: Full details of the synthesis of **L** and complex **1**; crystallographic data for **L** and **1** in cif format; frozen solution EPR spectra of **1** in MeOH; UV-vis spectra of **1** in MeOH; magnetic susceptibility data for **1**. CCDC 969763 and 969764. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53267d

motifs,[8] and can potentially bind two or more metal centres in close proximity, thereby facilitating the formation of clusters (often of high nuclearity),[8f,g] and/or frameworks through judicious choice of metal ions. Slow diffusion of a methanolic solution of $CuCl_2{\cdot}2H_2O$ into a chloroform solution of **L** at room temperature afforded green plates suitable for X-ray diffraction. Crystallographic studies revealed an octanuclear cluster of stoichiometry $[Cu_8\mathbf{L}_4Cl_{16}]$.†

The coordination complex crystallises in the triclinic space group $P\bar{1}$ with one unique cluster in the asymmetric unit.† The cluster has approximate S_4 symmetry and is comprised of four ligands and eight copper centres (Fig. 2a). Unlike a number of previously reported heterocyclic amido complexes[9] the nitrogen atoms of the amide groups remain protonated and **L** coordinates the metal centres as a neutral ligand. As a consequence, it does not chelate *via* its tridentate binding pocket, but instead each polydentate ligand binds four copper centres, two in a chelate fashion and two in a monodentate manner to form a unique octanuclear complex with saddle-shaped geometry. The C–N and C–O bond lengths of the amides are in the range 1.328(6)–1.362(8) Å and 1.211(7)–1.245(5) Å respectively, consistent with a conjugated amide. The pentacoordinate geometries around the copper centres are best interpreted as intermediate between trigonal bipyramidal and square-based pyramidal; the distortion parameter, τ,[10] has calculated values in the range 0.34–0.8 ($\tau = (\theta_1 - \theta_2)/60$; in which the largest angles in the coordination sphere are designated θ_1 and θ_2 and $\tau = 0$ for square pyramidal and $\tau = 1$ for trigonal bipyramidal). Whilst Cu(2) and Cu(4) have values of 0.34 and 0.43, the remaining copper atoms have $\tau > 0.5$ and are best described as distorted trigonal bipyramidal. For these ions, the axial positions are occupied by two pyrazole nitrogens from two different ligand molecules, while the pseudo-equatorial positions are occupied by the oxygen of an amide unit and the two chloride ions. In the case of Cu(2) and Cu(4), the geometries are closer to distorted square pyramidal; the two pyrazole nitrogens are *trans* to each other in the basal plane, as are an amide oxygen and one chloride, and the coordination sphere is completed with the remaining chloride in the axial position. At each copper centre different Cu–Cl bond lengths are observed; for the Cu(2) and Cu(4) centres, the pseudo-axial bonds are longer than the equatorial bonds by approximately 1.9 Å. A similar trend is observed for the copper centres with distorted trigonal bipyramidal geometry, but the differences are generally shorter (~1.5 Å). In order for the ligand to chelate all four of its pendant arms to the copper centres, all four 4,4′-bipyridine backbones are substantially twisted when compared with the geometry adopted by the native ligand, with torsion angles in the range 41.2°–43.5° between the mean planes of their pyridyl rings.

The structure of **1** consists of a non-planar saddle-like loop comprised of eight Cu(II) centres. Although there are examples of metal complexes that adopt a saddle-type geometry,[11] this complex is unique, being the first reported octanuclear copper cluster with a saddle-shaped or closed sinusoidal conformation (Fig. 2b). The Cu⋯Cu distances around the saddle rim are in the range 7.462(1) Å–8.695(1) Å, and the distances between the apical metal centres are 13.818(1) Å and 13.135(1) Å for Cu(2)⋯Cu(6) and Cu(4)⋯Cu(8) respectively. For all eight copper centres, one chloride ion is involved in two hydrogen bonding interactions with neighbouring amide hydrogen atoms with H⋯Cl contacts in the range 2.33–2.49 Å [see ESI†]. The intermolecular Cu⋯Cu distances are long, the shortest being 10.324(1) Å between two neighbouring Cu(5) centres, but shorter than the intramolecular apical Cu⋯Cu separation. The CHN elemental analysis of **1** is consistent with the

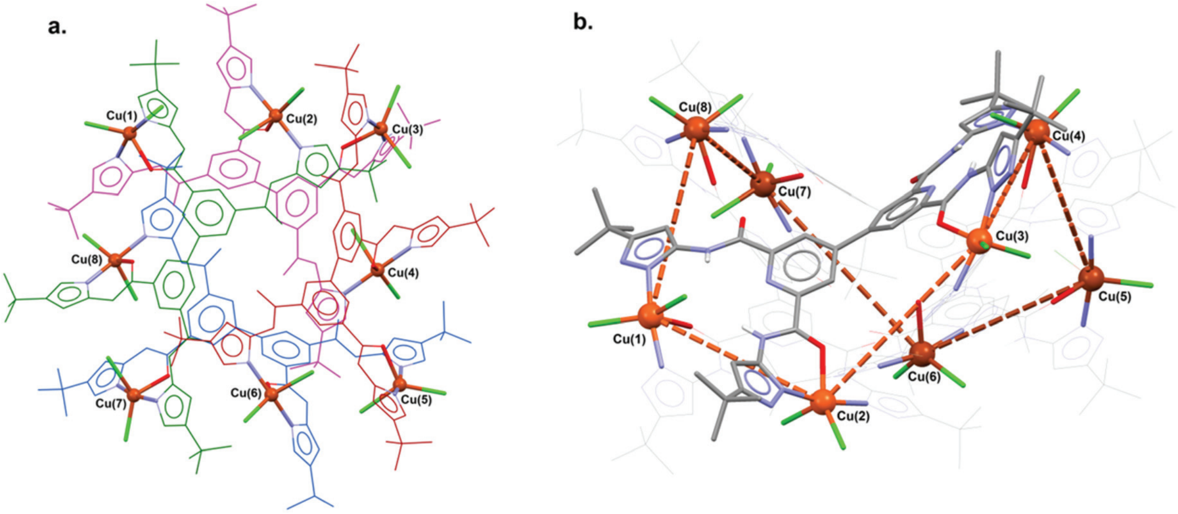

Fig. 2 (a) View of the octanuclear cluster $[Cu_8L_4Cl_{16}]$ **1** along its approximate S_4 axis with the four independent ligands shown as different colours. The coordination geometry of each unique Cu(II) centre is highlighted by capped sticks. (b) View of the cluster highlighting the saddle shape of the Cu_8 core and the coordination geometries of the eight independent Cu(II) ions. In both cases hydrogen atoms bonded to carbon are omitted for clarity. Disordered solvent was removed from the model by applying the SQUEEZE command in PLATON.† The *t*-butyl groups are disordered (only one orientation is shown).

stoichiometry $[Cu_8L_4Cl_{16}]\cdot CHCl_3\cdot 7MeOH\cdot 5H_2O$. The IR spectrum confirms the presence of amide N–H bonds, and two amide C═O stretches at 1694 and 1640 cm^{-1} can be assigned to the uncoordinated and Cu^{2+}-coordinated amide carbonyl groups respectively. FAB mass spectrometry of the cluster exhibited only fragmentation peaks; however, several of these were multi-metallic, suggesting that the cluster remains at least partially intact in solution.

The UV-Vis spectrum of **1** in DCM–MeOH† displays a maximum at $\lambda = 261$ nm ($\varepsilon = 81\,000$ M^{-1} cm^{-1}) consistent with π to π^* transitions of the bipyridine ligands; a broad absorption band at $\lambda = 797$ nm ($\varepsilon = 854$ M^{-1} cm^{-1}) is assigned to d–d transitions. Five-coordinate copper complexes typically show d–d absorptions in the range 588–769 nm when possessing a square pyramidal geometry, while trigonal bipyramidal complexes show absorption bands at longer wavelengths, typically 685–952 nm.[12] The EPR spectrum of **1** in frozen methanol solution at 77 K† revealed a near axial spectrum ($g_1 = 2.224$, $g_2 = 2.065$ and $g_3 = 2.035$). Whilst the high-field component revealed some evidence for hyperfine coupling, the features were not well resolved. Conversely the low-field features revealed a coupling of *ca.* 80 G consistent with hyperfine coupling to copper (both ^{63}Cu and ^{65}Cu have $I = 3/2$). The *g*-values give $R = 0.1875$ [according to the calculation $R = (g_2 - g_1)/(g_3 - g_2)$],[12a] reflecting a predominantly $d_{x^2-y^2}$ ground state; this is consistent with a movement from trigonal bipyramidal coordination towards square pyramidal geometry around the Cu(II) centres in MeOH solution. The magnetism of the Cu_8 cluster was examined in the temperature range 300–1.8 K. Magnetic susceptibility data reveal **1** obeys the Curie–Weiss law with $C = 3.59$ cm^3 K mol^{-1} and $\theta = -0.74$ K. The Curie constant is close to the value of 3.31 cm^3 K mol^{-1} expected for eight independent Cu(II) ions ($S = 1/2$, $g = 2.1$) with the negative Weiss constant indicating the presence of very weak antiferromagnetic interactions consistent with the absence of an efficient through-bond super-exchange pathway. The field dependence of the magnetisation at 1.8 K revealed a saturation magnetisation at 7 T of 7.61 μ_B, slightly lower than the value of 8.4 μ_B expected for eight $S = 1/2$ ions with $g = 2.1$. [A discussion of the dipolar intra- and inter-cluster exchange and magnetic modelling as a ring of eight $S = 1/2$ ions is available as ESI.†]

In conclusion we have prepared and characterised a new tetracarboxamide ligand **L** comprising a 4,4′-bipyridine backbone and pendant pyrazole heterocycles. The resultant octanuclear metallocycle formed with $CuCl_2$ is a rare example of a polynuclear cyclic array comprising more than six Cu(II) ions assembled from large, flexible polydentate organic ligands.[5,13] The closest known related complex is the octanuclear copper array assembled from a polytopic diazine ligand reported by Matthews *et al.* in 2004.[5] Following this general synthetic strategy a family of 4,4′-bipyridine ligands have been prepared and will be reported in due course. We are currently exploiting hydrothermal methodologies for the self-assembly of new cluster and metal organic framework topologies.

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