Molecular Pac-Man and Tacos: layered Cu(II) cages from ligands with high binding site concentrations†

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The in situ formation and subsequent Cu(II) ligation of the polydentate pro-ligands o-[(E)-2-hydroxy-3-methoxyphenyl)methylideneamino]benzohydroxamic acid (L1H3), o-[(E)-2-hydroxy-3-methoxy-5-bromophenyl)methylideneamino]benzohydroxamic acid (L2H3) and o-[(E)-2-hydroxyphenyl)methylideneamino]benzohydroxamic acid (L3H3), leads to the self-assembly of the cages [Cu10(L1)4(2-aph)2(H2O)2](ClO4)4·5MeOH (1), [Cu14(L1)6(MeOH)2.5(H2O)7.5](NO3)4·3MeOH·7H2O (2), [Cu12(L2)6·(MeOH)2](H2O)2](ClO4)4·6H2O (3), [Cu14(L3)6(MeOH)6(H2O)2](ClO4)4·4MeOH·8H2O (4) and [Cu30O(OH)20(MeOH)20(H2O)4](ClO4)4·2MeOH·30H2O (5). Each member comprises a highly unusual topology derived from off-set, stacked, near planar layers of polynuclear subunits connected through long Cu(II)–O contacts. The exact topology observed is dependent on the specific reaction conditions and methodologies employed. Dc magnetic susceptibility studies on 1, 2, 4 and 5 reveals strong antiferromagnetic exchange between the Cu(II) centres in all siblings. We also present the 1D coordination polymer [[Cu(II)4(L4)]·H2O]6 (6) comprising the pseudo macroyclic ligand [[(2-[(E)-2-hydroxy-3-methoxyphenyl)methylideneamino]benzoyl](aminol)ethanimidate (L4H2), which is formed upon the incorporation of an MeCN unit at the hydroxamate group of precursor ligand L1H3.

Introduction

The strategic formation and rapid metal complexation of pre-designed ligands from their ‘simpler’ organic precursors has become an important synthetic tool towards otherwise unattainable metal–ligand architectures of varying complexities. This specific process is commonly described as subcomponent self-assembly and is a subtle extension upon the field of template-directed synthesis. Although other examples are known in the literature, the Nitschke group have notably demonstrated that the Schiff base condensation of various aldehyde and amine moieties, driven by reversible C=N and M–N bond formation,1,2 are versatile precursors towards the preparation of numerous host-guest metal container complexes of varying topologies. Indeed, the process of producing a ligand ‘in situ’ in the presence of a metal ion has also benefitted the field of molecular magnetism, where a number of polymetallic transition metal cages have been produced (e.g. [Mn14], [Fe10] and [Dy8]), albeit via a more serendipitous route. In a similar vein we describe here the Cu(ii) ligation of the polydentate prolignands o-[(E)-2-hydroxy-3-methoxyphenyl)methylideneamino]benzohydroxamic acid (L1H3), o-[(E)-2-hydroxy-3-methoxy-5-bromophenyl)methylideneamino]benzohydroxamic acid (L2H3) and o-[(E)-2-hydroxyphenyl)methylideneamino]benzohydroxamic acid (L3H3; Scheme 1) – formed by the imine condensation of 2-(amino)phenylhydroxamic acid and either 2-hydroxy-3-methoxysterbenaldehyde (for L1H3), 5-bromo-2-hydroxy-3-methoxybenzaldehyde (for L2H3) or 2-hydroxybenzaldehyde (for L3H3). Here we combine two of our most recently (and successfully) employed ligands, hydroxamic acids and phenolic imines, to form moieties comprising multiple metal binding sites in order to encourage polynuclear cage formation.

Results and discussion

To this end we present the synthesis, structural and magnetic characterisation of the cages: [Cu10(L1)4(2-aph)2(H2O)2](ClO4)4·5MeOH (where 2-aphH2 is 2-(amino)phenylhydroxamic acid).
acid) 1, [Cu(n)14(L1)6(MeOH)3.5(H2O)7.5][NO3]4·3MeOH·7H2O (2), [Cu(n)14(L2)6(MeOH)6][H2O]6[NO3]4·6H2O (3), [Cu(n)14(L3)6(MeOH)6][H2O]6[NO3]4·4MeOH·8H2O (4) and [Cu(n)16(OH)11·(OMe)2(L1)16(MeOH)4(H2O)2][ClO4]4·2MeOH·30H2O (5). Pr‐
ligands L1H3, L2H3 and L3H3 are unknown in the literature.11

The decametallic complex [Cu(II)10(L1)4(2-aph)2(H2O)2](ClO4)4·2MeOH·30H2O (1) (Fig. 1) crystallises in the monoclinic C2/c space group and was formed from a methanolic solution of Cu(ClO4)2·6H2O and a 1 : 1 equimolar mixture of L1H3 precursors: 2-(amino)phenylhydroxamic acid and 2-hydroxy-3-methoxy-
benzaldehyde (Scheme 1), in the presence of a suitable base (NaOH). All pertinent crystallographic data for 1 and siblings 2–4 are given in Table S1.† The crystal structure in 1 adds to a relatively small number of discrete decametallic Cu(n) assemblies10 although a small number of wheel-like architectures are also known in the literature.11

The core in 1 comprises two near planar \{Cu3\} sheets linked in an off‐set fashion by a combination of long Cu–O contacts (Cu5–O4 = 2.777 Å) and bridging Ophen atoms (O2 from L13 ligands), resulting in its rather unusual taco-shaped arrangement (Fig. 1 and 2). The Cu(n) ion arrangement within each \{Cu3\} layer is best described as comprising three (distorted) edge-sharing triangles whose edges are spanned by a combination of 2 × L13– moieties and a single 2-(amino)phenyl-
hydroxamate (2-aph3−) ligand- a precursor to the formation of the \{Cu3\} layer. Despite varying the reaction conditions in 1, the L13−/2-aph3− ligand combination is consistently produced, whereas complexes 2–4 each exclusively comprise our Schiff base ligands (L1H3, L2H3 or L3H3; vide infra). The four L13− ligands in 1 exhibit remarkably high binding site concentrations represented by the \eta1\eta1\eta1\eta1\eta1\eta1\mu4− bonding mode, while the 2-aph3− ligands display a \eta1\eta1\eta1\eta1\eta1\mu3− bridging motif. Metal centres Cu1, Cu3 and Cu4 (and symmetry equivalent, s.e.) possess distorted square based pyramidal geometries (r = 0.36, 0.11 and 0.14 respectively), the latter two ions exhibiting long axial Cu–O contacts to the nearby ClO4− counter anions lying above the \{Cu3\} planes in 1 (Cu3–O17 = 2.440 Å, Cu4–O18 = 2.794 Å). The Cu2 centre (and s.e.) is of distorted square planar geometry although the aforementioned perchlorate anions give rise an extremely long Cu–O contact at its axial site at a distance of 2.872 Å (Cu2–O19). The Cu5 centre (and s.e.) exhibits a Jahn–Teller distorted octahedral geometry thanks to two axially elongated Cu–O bonds (Cu5–O1 = 2.231 Å and Cu5–O4 = 2.777 Å), while a terminal H2O ligand completes its coordination sphere (Cu5–O11 = 1.948 Å). Despite the close proximity of the \{Cu3\} units in 1, no formal intramolecular \pi−\pi interactions are observed between their respective L13− and 2-aph3− aromatic rings. Two sets of symmetry equivalent perchlorate counter anions maintain electroneutrality in 1, with one set directly ‘bound’ to the \{Cu10\} cage through the aforementioned long Cu–O contacts, while the second set lie further afield. The individual \{Cu10\} units in 1 pack in a brickwork motif along the ab plane of the unit cell. These sheets
then stack in parallel off-set rows along the c cell direction (Fig. 3).

The analogous complexes [Cu(n)_{14}(L_1)_{10}(MeOH)_{2.5}(H_2O)_{7.5}]^+(NO_3)_{14}·3MeOH·7H_2O (2), [Cu(n)_{14}(L_2)_{10}(MeOH)_{10}H_2O)_{9}(NO_3)_{14}·6H_2O (3) and [Cu(n)_{14}(L_3)_{10}(MeOH)_{10}H_2O)_{2}][NO_3]_{14}·4MeOH·8H_2O (4) are readily obtained via the ambient reaction of cupric nitrate hexahydrate and L_3H_3 (x = 1 (2), x = 2 (3), x = 3 (4); made in situ) in MeOH and in the presence of a suitable base. It should also be noted that the structure in 2 can also be synthesised using microwave heating (see Experimental section for details). The homovalent [Cu(n)_{14}] complexes 2-4 join an exclusive group of tetracationic copper clusters. However, all bar one of these members are mixed valence Cu(n)_{14} while a sole mono-valent [Cu(i)_{14}] cage was recently reported by Zhang and co-workers.\(^{11}\)

Akin to the structure in 1, complexes 2-4 have layered structures this time comprising the fusion of two \{Cu_7\} units (Fig. 4 and Fig. S1 and S2\(^{†}\)). The dark green crystals in 2-4 crystallise in the triclinic P\(\overline{1}\) (2), monoclinic C2/c (3) and P2_1/c (4) space groups respectively, and their contrasting symmetries are manifested (in part) by the stacking arrangements of the \{Cu_7\} units relative to one other. More specifically, the two hepta-nuclear moieties in 4 stack directly on top of one another in a pseudo superimposable fashion, while the two \{Cu_7\} layers in 2 and 3 sit at approximate right angles to one another as highlighted in Fig. 5 and S2.\(^{†}\) Apart from these obvious differences the three structures share many similarities and will be discussed in general terms from herein. The Cu(n) centres within each \{Cu_7\} unit in 2-4 comprise two triangular arrays joined by a central cupric ion (Cu1 and Cu8 in 2, Cu4 in both 3 and 4) (Fig. S6\(^{\dagger}\)). The \(L_1^{3−}\) and \(L_2^{3−}\) ligands in 2 and 3 respectively, utilise an equal distribution of \(\eta^1\eta^1\eta^1\eta^1\eta^1\mu_4^+\) and \(\eta^1\eta^1\eta^1\eta^1\eta^1\mu_4^-\) bonding modes to construct their \{Cu_7\} units. A combination of \(\eta^1\eta^1\eta^1\eta^1\eta^1\mu_4\) and \(\eta^1\eta^1\eta^1\eta^1\eta^1\mu_3\)-bridging motifs are employed by the \(L_3^{3−}\) ligands in sibling complex 4 (Fig. 6). The \{Cu_7\} planes in 2-4 are then connected by Jahn-Teller elongated axial Cu–O contacts to produce their final topologies (i.e. Cu2–O30 = 2.698 Å in 2, Cu5B–O50 = 2.855 Å in 3 and Cu7–O1 = 2.718 Å in 4) (Fig. 4). The majority of the Cu centres in 2-4 exhibit distorted square based pyramidal geo-

**Fig. 2** Alternative perspective of 1. All hydrogen atoms have been omitted for clarity.

**Fig. 3** Crystal packing in 1 as viewed along the c unit cell direction. Note: only the non-coordinated ClO_4^- counter anions are represented in space-fill mode. Hydrogen atoms have been omitted for clarity.

**Fig. 4** Polyhedral and standard representations of the crystals in 2 (a and b respectively) and 4 (d and e respectively). All hydrogen atoms have been omitted for clarity. The NO_3^- counter anions in 2 were also omitted for clarity. (c) and (f) represent the inorganic cores in 2 and 4 respectively.
Intramolecular interactions between terminally bound H$_2$O protons (H37B) and adjacent carbonyl O atoms (e.g. O6) are prevalent in the structure of 2 (O37(H37B)⋯O6 = 1.640 Å). Likewise, strong intermolecular hydrogen bonding interactions between unbound NO$_3^-$ oxygen atoms (e.g. O47A) and juxtaposed terminally bound water protons (H42A) are also observed in 2 (O47A⋯H42A = 1.747 Å). The individual {Cu$_{14}$} units in 2 arrange in superimposable rows along the a direction of the unit cell and pack along the bc plane in the familiar brickwork pattern (Fig. 7-left).

Intramolecular interactions are observed in 4 between metal bound methanol ligands with juxtaposed NO$_3^-$ anions (e.g. O21(H21)⋯O18 = 2.062 Å) as well as unbound water molecules (O43(H43)⋯O47 = 2.213 Å). These interstitial waters of crystallisation sit in-between the {Cu$_{14}$} units and effectively connect them to one another using extensive hydrogen bonding with their terminal MeOH, H$_2$O and NO$_3^-$ ligands (e.g. O10⋯O40 = 2.544 Å and O8⋯O45 = 2.777 Å). The {Cu$_{14}$} moieties in 4 arrange in superimposable rows along the c direction of the unit cell and exhibit weak inter-chain π centroid⋯π centroid interactions (e.g. [C43⋯C48]⋯[C50⋯C55] = 4.510 Å). These individual rows pack in the brickwork motif along the ab plane (Fig. 7-right), as also seen for 3 (Fig. S3†).

Solvothermal heating of a basic methanolic solution containing Cu(ClO$_4$)$_2$·6H$_2$O and the L$_1$H$_3$ precursors 2-(amino)phenylhydroxamic acid and 2-hydroxy-3-methoxybenzaldehyde affords the complex [Cu$_{30}$O(OH)$_4$(OMe)$_2$(L$_1$)$_{16}$(MeOH)$_4$(H$_2$O)$_2$](ClO$_4$)$_4$·2MeOH·30H$_2$O (5). Discounting the extremely large and numerous copper-chalcogenide$_{14}$ nanoclusters known in the literature (e.g. the staggering [Cu$_{136}$S$_{56}$(SCH$_2$C$_4$H$_3$O)$_{24}$- (dpppt)$_{10}$] cage; where dpppt = 1,5-bis(diphenylphosphino)pentane), the architecture in [Cu$_{30}$] (5) represents one of the largest O-donor Cu(II) cages known and is only smaller than the complexes [K$_4$(µ-MeOH)$_4$][Cu(II)$_{36}$(µ$_3$-OH)$_{32}$(µ-OR)$_8$Cl$_6$-(ndpa)$_8$(H$_2$O)$_5${KCl$_6$}] (R is H or Me; H$_3$ndpa = (nitrilodipropionic)-

Fig. 5 The criss-cross orientation of the {Cu$_7$} planes in 2 and 3 (a and b) as opposed to the pseudo superimposable stacking arrangement observed in 4 (c).

Fig. 6 The two different bonding modes exhibited by the L$_1^-$ ligands in 2 (top) and L$_3^-$ ligands in 4 (bottom). All hydrogen atoms have been omitted for clarity.

Fig. 7 (Left) Polyhedral packing diagram of 2 as viewed along the c unit cell axis. Only the non-coordinating NO$_3^-$ anions are shown in the space−fill mode. (Right) Polyhedral representation of the packing in 4 as viewed along the a axis of the unit cell. MeOH solvents of crystallisation are represented using the space−fill mode.

The remaining metal centres in 2 exhibit distorted octahedral geometries (i.e. Cu2 and Cu9), while a single Cu(u) centre in 4 (Cu1 and s.e.) is of a distorted square planar geometry. Terminal methanol, water and/or NO$_3^-$ moieties complete the coordination spheres at many of the Cu(u) centres in 2–4.
acetic acid\textsuperscript{16} and [Cu(n)(µ₈-Br)₂(µ₃-OH)₃(µ-OH)₄(ntp)₁₂Br₆-
(H₂O)₁₈]Br₂·81H₂O (where H₃ntp = aminopolycarboxylate nitrolotripropionic acid).\textsuperscript{17}

Complex 5 crystallises in the triclinic P\textit{i} space group and once more comprises a layered structure as observed in 1–4 (see Table S2\textsuperscript{f} for details). More specifically, a central \{Cu₃₀\}(O)–(OH)₂(L₁)\textsuperscript{12+} unit (layer 2 in Fig. 8d) forms a platform which is sandwiched between two offset \{Cu₅(OMe)-(L₁)₄(MeOH)₂(H₂O)₃\} layers (\(x = 0\) in layer 1; \(x = 2\) in layer 3; Fig. 8d) to form the Pac-Man shaped \{Cu₅₀\} superstructure (Fig. 8a and b). The central \{Cu₁₆\} fragment may also be described as comprising two near planar \{Cu₈\} sub-fragments which are connected by a centrally located distorted tetrahedral µ₄- bridging O\textsuperscript{2−} anion (O₃₆; Fig. 8c). The metal centres within each \{Cu₅₀\} moiety are held together via two µ-bridging OH\textsuperscript{−} ions (O₂₂, O₃₁, O₄₅ and O₅₇) alongside four L₁ ligands showing an equal distribution of \(\eta^1\eta^2\eta^3\eta^4\) and \(\eta^1\eta^2\eta^3\eta^1\) µ₄- and µ₃-bonding modes (Fig. 9-left). This bonding mode combination is also employed by the four L₁⁻⁻ ligands that bridge the metal centres within each of the two bowl-shaped \{Cu₇\} layers in 5 (Fig. 8d). Interestingly, these heptanuclear inorganic core units in 5 may be described as puckered versions of the \{Cu₇\} units observed in siblings 2–4 (Fig. 5 cf. Fig. 8d). A single µ-OMe⁻⁻ ion (\textit{via} O₉ and O₇₃ respectively) also aids cage formation within each heptanuclear section while two terminal H₂O ligands (O₇₅ and O₇₆) complete the coordination spheres at centres Cu₃, Cu₅ and Cu₆ respectively (Cu₃–O₇₆ = 2.570 Å, Cu₅–O₇₆ = 2.515 Å and Cu₆–O₇₅ = 2.479 Å). Likewise terminal MeOH moieties partake in the same role at centres labelled Cu₂ (Cu₂–O₇₄ = 2.544 Å), Cu₄ (Cu₄–O₁₀₂ = 2.633 Å), Cu₂₅ (Cu₂₅–O₆₁ = 2.331 Å), Cu₂₆ (Cu₂₆–O₇₃ = 2.484 Å) and Cu₂₈ (Cu₂₆–O₇₃ = 2.545 Å). The two \{Cu₇\} fragments are connected to the \{Cu₁₆\} main-frame through characteristically long Cu–O contacts namely through interactions with the aforementioned µ-bridging OH\textsuperscript{−} ions at distances of: 2.670 Å (Cu₄–O₂₂) and 2.686 Å (Cu₂₇–O₄₅).

Four of the Cu(II) centres in 5 display distorted octahedral geometry (Cu₃, Cu₄, Cu₂₇ and Cu₂₈), while the remaining twenty six metal centres exhibit distorted square planar or square based pyramidal geometries. More specifically, the majority of Cu(II) metal centres within the central \{Cu₁₆\} belt exhibit distorted square planar geometries (Cu₁₆ and Cu₂₃ centres are distorted square based pyramidal), while a distorted square based pyramidal geometry dominates within the two \{Cu₇\} moieties in 5 (\(\tau\) values ranging from 0.017 (Cu₂₆) to 0.298 (Cu1)). Four charge balancing and crystallographically independent ClO₄⁻⁻ anions lie away from the \{Cu₃₀\} structure in 5 and are held in position by H-bond interactions with adjacent L₁⁻⁻ ligand protons (Cl₁(O₈₉A)⋯H₃₆₀(C₃₆₀) = 2.655 Å, Cl₁₃(O₆₆)⋯H₄₀(C₄₀) = 2.646 Å). No obvious intramolecular interactions are observed within the cage in 5. The \{Cu₃₀\} units arrange in superimposable rows along the \(a\) unit cell direction and these chains then align using a brickwork pattern along the \(bc\) plane (Fig. 9-right)

The near planar units within all five complexes (1–5) may be described as fragments of metallacrown structures as first highlighted by Pecoraro and co-workers.\textsuperscript{18} This is perhaps not surprising as ligands L₁H₃, L₂H₃ and L₃H₃ share similarities with known metallacrown-directing ligands. Moreover, the subsequent linking of our planar units into larger architectures has precedence in metallacrown coordination chemistry.\textsuperscript{19} The deviation from planar metallacrown formation in 1–5 is presumably due to ligand driven steric effects. For instance, the puckered sheets diverging away from one another to form the taco-shaped topologies in siblings 1 and 4 and the Pac-Man configuration in 5.

\textbf{Unexpected twists}

During our synthetic investigations, we inadvertently discovered that by re-dissolving the dried solid obtained from the evaporation of the mother liquor in reactions that produced complex 1 into acetonitrile, an entirely different and un-
expected coordination polymer was produced. More specifically, a methanolic reaction mixture comprising CuClO₄·6H₂O, 2-(amino)phenylhydroxamic acid and 2-hydroxy-3-methoxybenzaldehyde was evaporated to dryness under reduced pressure and the resultant powder recrystallised from acetonitrile. We initially proposed that the addition of heat along with the solvent removal step would promote the required aldehyde-imine Schiff base coupling. The result was the 1D coordination polymer \([\text{Cu(II)}(\text{L})·\text{H}_2\text{O}]\) comprising the new ligand \([\text{L}] = \{[\text{2-[(E)-(2-hydroxy-3-methoxy-phenyl)methyleneamino]benzoyl}]-\text{amino} \}\text{ethanamide}\) (Fig. 10). This new ligand stems from the Cu(ii) mediated addition of a MeCN group at the hydroxyl position of the hydroxamate moiety, thus forming an ethanamide functionality which upon Cu(II) ligation gives rise to the formation of the pseudo macrocyclic \(\text{L}_4^{2−}\) ligand in 6 (Fig. 10). Indeed, Tolman et al. report the attachment of a MeCN functional group to a pyrazolyl ring via a Cu-mediated cycloaddition reaction, resulting in a novel heterocyclic ring system. Complex 6 crystallises in the monoclinic \(\text{C}2\text{c}\) space group and all pertinent X-ray diffraction data are given in Table S2.†

The Cu(ii) centre (Cu1) displays an almost perfect square based pyramidal geometry with a \(\tau\) value of 0.016. The equatorial positions at the Cu1 metal centre are occupied by a single chelating \(\text{L}_4^{2−}\) ligand moiety via the phenolic oxygen atom (O2), the imine nitrogen atom (N1), the nitrogen atom of the hydroxamate functional group (N2) and the nitrogen atom of the ethanamide group (N3), resulting in bond lengths ranging between 1.921 and 1.970 Å. The coordination is completed at the axial position of the Cu1 centre via the carbonyl oxygen atom (O3) of a second \(\text{L}_4^{2−}\) ligand giving a Cu1–O3′ bond length of 2.338 Å. The result is the 1D chain topology in 6 possessing an intra-chain Cu1⋯Cu1 distance of 5.220 Å. A single water of crystallisation lies near each \(\{\text{Cu(II)}\}\) unit and is locked into position by three hydrogen bonding interactions with aliphatic protons (H3H) and oxygen donor atoms (O1 and O2) of the \(\text{L}_4^{2−}\) ligands (O5⋯(H3H)N3 = 2.142 Å, O5(H5A)⋯O1 = 2.206 Å and O5(H5A)⋯O2 = 2.303 Å) (Fig. S4†). These waters of crystallisation also partake in H-bonding throughout the crystal structure in 6 (O5⋯(H5B)O5′ = 2.151 Å). The individual 1D rows in 6 propagate along the \(b\) axis of the unit cell in a superimposable manner and these rows then pack into a common brickwork motif (Fig. S5†).

**Magnetic susceptibility studies**

As described previously and illustrated in Fig. S6,† the molecular structure in 1, 2, 4 and 5 contain linked polynuclear layers of either \(\{\text{Cu}_3\}\) (in 1) or \(\{\text{Cu}_5\}\) (in 2, 4 and 5) units, whose structures may also be described as comprising edge- and vertex sharing \(\{\text{Cu}_n\}\) triangular sub-units. Moreover, these individual polymeric layers are connected by long axial Cu–O contacts via filled Cu(ii) \(d_{z^2}\) orbitals. We can therefore envisage antiferromagnetic exchange within the layers and negligible magnetic interactions between layers. In this scenario, the layers of odd numbered Cu(ii) ions would likely lead to small but magnetic ground states. Magnetic data support such an hypothesis. DC magnetic susceptibility measurements were performed on powdered microcrystalline samples of 1, 2, 4 and 5 in the 300–5 K temperature range in an applied field of 0.1 T (Fig. 11). The room temperature \(\chi_M T\) values of 2.41 (1), 3.53 (2) 3.79 (4) and 11.6 (5) cm³ K mol⁻¹ are well below their expected spin-only values of \(\sim 4.13\) (1), 5.78 (2) and 12.4 (5) cm³ K mol⁻¹ (assuming \(g = 2.1\)) and are indicative of strong intramolecular antiferromagnetic exchange between the Cu(ii) ions within the layers of each complex. The \(\chi_M T\) vs. \(T\) plot for 1 shows a steady drop in its magnetic susceptibility.

**Fig. 10** (a) ChemDraw representation and crystal structure (b) of one \([\text{Cu}(\text{II})(\text{L})]\) unit in 6 including the next bridging oxygen (O3) atom. (c) Representation of the repeating 1D structure in 6 (comprising three \([\text{Cu}(\text{II})(\text{L})]\) units). The majority of hydrogen atoms and all H₂O solvents of crystallisation were omitted for clarity.

**Fig. 11** Plots of \(\chi_M T\) vs. \(T\) for complex 1, 2, 4 and 5.
product which becomes a little more abrupt below 50 K, before reaching a value of 0.34 cm$^3$ mol$^{-1}$ K at 5 K. Likewise, [Cu14]$^+$ complexes 2 and 4 exhibit a gradual decline in their $\chi_M T$ products before reaching $T = 5$ K values of 0.96 and 1.03 cm$^3$ mol$^{-1}$ K, respectively (Fig. 11). A much more rapid decline in the magnetic susceptibility of complex 5 is shown along the entire temperature range, giving a 5 K value of 1.73 cm$^3$ K mol$^{-1}$. Despite our efforts, the complexity of the magnetic cores in these complexes, which contain multiple different exchange interaction pathways, precludes any quantitative analysis of the data.

Conclusions

The Schiff base condensation of precursors 2-(amino)phenyl-hydroxymidate and 2-hydroxy-3-methoxybenzaldehyde, 5-bromo-2-hydroxy-3-methoxybenzaldehyde or 2-hydroxybenzaldehyde in the presence of Cu(II) ions leads to the in situ formation and subsequent metal ligation of the polydentate ligands $o-[(E)-2$-hydroxy-3-methoxyphenyl]methylideneamino]-benzohydroxamic acid (L4H2), $o-[(E)-2$-hydroxy-3-methoxy-5-bromophenyl]methylideneamino]-benzohydroxamic acid (L2H3) and $o-[(E)-2$-hydroxyphenyl]methylideneamino]benzohydroxamic acid (L1H3), respectively. The end products, depending on specific reaction conditions, are the Cu(II) cages: [Cu(u)]$_{14}$L$_{14}$)$(H_2O)_2$][ClO$_4$]$_4$·5MeOH (1), [Cu(u)]$_{14}$L$_{14}$)$(MeOH)_{2n}(H_2O)_2$][NO$_3$]$_4$·3MeOH·7H$_2$O (2), [Cu(u)]$_{14}$L$_{14}$)$(MeOH)_{n}(H_2O)_2$][NO$_3$]$_4$·6H$_2$O (3), [Cu(u)]$_{14}$L$_{14}$)$(MeOH)_{2n}(H_2O)_2$][NO$_3$]$_4$·4MeOH·8H$_2$O (4) and [Cu(u)]$_{30}$O(OH)$_2$(OMe)$_8$L$_{16}$)$(MeOH)_{2n}(H_2O)_2$][ClO$_4$]$_4$·2MeOH·3O$_2$H$_2$O (5). The introduction of acetonitrile into the synthesis of 1 results in the in situ Cu(u) mediated formation of the unexpected ligand $[2-[(E)-2$-hydroxy-3-methoxy-phenyl]methylideneamino]benzoylamino]-ethanimidate (L4H2) and this ligand modification gives rise to the formation of the 1D coordination polymer $[Cu(u)_n$]$_{14}$)[ClO$_4$]$_4$·5MeOH]. Dc magnetic susceptibility studies on complexes 1, 2, 4 and 5 indicate strong antiferromagnetic exchange between nearest neighbours resulting in small, but magnetic ground states within the Cu layers and negligible inter-layer interactions in all cases. In this work, we have employed an elegant synthons previously used in the field of subcomponent self-assembly to drive the in situ formation of ligands comprising multiple metal binding sites to aid the growth of large paramagnetic cages. Work is currently underway on probing further the coordination ability of these interesting ligands with other paramagnetic metal ions. We are also currently investigating these ligands towards metal sequestration.

Experimental

Infra-red spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrometer equipped with a Universal ATR Sampling accessory (NUI Galway). Elemental analysis was carried out at the School of Chemistry microanalysis service, NUI Galway. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 5 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants. All measured complexes were set in eicosane to avoid torquing of the crystallites. All magnetic samples are collected as single-crystalline products and analysed using microanalysis and IR measurements prior to their magnetic assessment. If necessary, phase purity between cross-batches are validated using unit cell checks and IR measurements.

Crystallography

The X-ray data for crystal structures of 1–6 were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source (CCDC numbers: 1055293–1055298). Each data reduction was carried out on the CrysAlisPro software package. The crystal structures were solved by direct methods (SHELXS-97) and refined by full matrix least squares using SHELXL-97. SHELX operations were automated using the OSCAIL software package, except for crystal structures 2 and 3, where the SHELX-2013 within the OLEX2 suite was employed. All hydrogen atoms in 1–6 were assigned to calculated positions.

The unbound perchlorate in 1 (Cl2–O12–O15) was modelled as disordered over two sites and restrained using the DFIX command. The carbon atom, C1, belonging to a methoxide group on an L3$^{−}$ unit, was modelled as disordered over two sites (70:30). Residual electron density in solvent accessible voids and channels were observed in 1 that required modelled using the SQUEEZE program. The four voids in 1 represented a total volume of 1720 Å$^3$, which equates to five MeOH solvent molecules of crystallisation per [Cu14]$^+$ cage (commensurate with microanalysis results on 1; calculated formula: 1:5MeOH).

In the crystal structure of 2, four NO$_3^−$ anions have been assigned. The nitrate labelled N17–O47–O49 is disordered and modelled over two sites with a 70:30 ratio. The NO$_3^−$ moiety labelled N18–O50–O52 has been refined as fully occupied with displacement parameters refined as isotropic only. The remaining two nitrates have been split over two sites with partial occupancies arbitrarily set at half. Moreover, the atom O60A forms part of a partially occupied NO$_3^−$ anion (N20A–O60A–O61A–O62A), which shares the same site as a partially occupied water (O11) at Cu1. Likewise, the Cu6 centre is bound to a 50:50 partial occupancy comprising a NO$_3^−$ anion (N20B–O60B–O61B–O62B) and a MeOH (C201–O60C) ligand. Several DFIX/DANG restraints were used to maintain sensible geometry with respect to the disordered NO$_3^−$ and MeOH ligands in 2, while SIMU/DELU restraints were used to model displacement parameters. More specifically, the EAPD restraints were applied to atoms O60A–O62A, O60B–O62B, O60C and O47A/O47B. The crystal structure in 2 contains a large number of disordered, uncoordinated solvent molecules (H$_2$O/MeOH) located in the voids. A number of them have been successfully assigned (some as half occupied and isotropic only). The remaining highly diffused electron density...
(negligible amount) was removed using SMTBX algorithms within the OLEX2 suite, which improves the final model and led structure refinement to convergence. Elemental analysis on 2 support these residual electron density calculations although solvent loss was observed upon drying (calculated formula: \(\text{C}_2\text{H}_4\text{O}_2\text{H}_2\text{O}\) cf. elemental analysis: 2:5\(\text{H}_2\text{O}\)).

Significant disorder in 3 was observed at Cu5 and was therefore modelled at 50% occupancy along with the bound \(\text{L}^{3-}\) atoms C86–C92A. DFIX, DANG and SIMU restraints were also employed. All disorder was modelled as anisotropic where possible; however O73A/B and O103 required to remain isotropic. The SMTBX function was employed to treat diffuse solvent and the \(\text{NO}_3^{-}\) counter anions in 3. The SQUEEZE program was required to account for the residual electron density within the two independent accessible voids in 3 (total void volume = 740 Å\(^3\)) and was assumed to contain six waters of crystallisation per cage (commensurate with microanalysis results on 3; calculated formula: 3:6\(\text{H}_2\text{O}\) cf. elemental analysis: 3:6\(\text{H}_2\text{O}\)).

All non-hydrogen atoms in 4 were refined as anisotropic with the exception of one \(\text{NO}_3^{-}\) anion (N10–O17–19), which has been refined as isotropic. A DFIX restraint was also required for this anion. All solvent molecules of crystallisation located in the lattice also remained isotropic. DFIX restraints were used for MeOH solvents of crystallisation in complex 4 (C71–O42, C72–O41 and C73–O44). The SQUEEZE program was required to account for the residual electron density within the four independent accessible voids in 4 (total void volume = 360 Å\(^3\)) and was assumed to contain four waters of crystallisation per cage (commensurate with microanalysis results on 4; calculated formula: 4:4\(\text{MeOH}\) 8\(\text{H}_2\text{O}\) cf. elemental analysis: 4:4\(\text{MeOH}\) 4\(\text{H}_2\text{O}\)).

Despite carrying out numerous collections, weak X-ray data was obtained from all crystals of complex 5 (\(R_{int} = 0.1034, \text{w}\(R_2 = 0.3398\) as given in this work). All C atoms required remaining isotropic and all H atoms were placed in calculated positions. Residual electron density in solvent accessible voids and channels were observed in 5 and so were modelled using the SQUEEZE program.\(^{23}\) The three channels in 5 (total voids volume ∼1995 Å\(^3\)) contained extremely diffuse electron density and were assumed to contain numerous methanol and waters of crystallisation. CHN analysis on 5 supported these observations although significant solvent loss was observed upon drying (calculated formula: 5:2\(\text{MeOH}\) 30\(\text{H}_2\text{O}\) cf. elemental analysis: 5:11\(\text{H}_2\text{O}\)).

Preparation of complexes

All reactions were performed under aerobic conditions and all reagents and solvents were used as purchased. \textbf{Caution:} Although no problems were encountered in this work, care should be taken when manipulating the potentially explosive perchlorate and nitrate salts. 2-(Amino)phenylhydroxamic acid was synthesised using previously reported synthetic procedures.\(^{26}\) The solvothermal synthesis of 5 was carried out in a Hereaus (UT6420-Thermo Scientific) oven using spring loaded stainless steel digestion vessels (23 cm\(^3\) capacity) produced by the Parr Instrument Company. The microwave synthesis of 2 was carried in a CEM Discover® microwave reactor.

\[ \text{[Cu(II)_{14}(L_1)_{8}(\text{MeOH})_{2}2(H_2O)_{2}]([NO_3]_{4}3\text{MeOH}7\text{H}_2\text{O})} \]

\[ \text{[Cu(NO_3)_{2}3\text{H}_2\text{O}] (0.25 g, 1.04 mmol), 2-(amino)phenylhydroxamic acid (0.52 g, 0.34 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.52 g, 0.34 mmol) and NaOH (0.027 g, 0.68 mmol) were dissolved in 30 cm}^3\text{ of MeOH and stirred for 4 h. The resultant dark green solution was then filtered and aliquots of the mother liquid were then diffused with diethyl ether. Dark green X-ray quality crystals of 1 began to form after two days. The crystals were collected and air dried to give a yield of approximately 5%. FT-IR (cm}^{-1}\): 2937(w), 1605(m), 1580(m), 1543(m), 1490(w), 1433(m), 1373(m), 1298(w), 1234(m), 1183(m), 1160(w), 1078(s), 977(w), 932(m), 871(w), 853(w), 771(m), 740(m), 687(m), 651(w), 621(s), 579(m), 556(m), 536(m), 524(m), 519(s). Elemental analysis (%) calculated (found) for C\(_{71}\text{H}_{86}\text{Cl}_{2}\text{N}_{12}\text{O}_{43}\text{Cu}_{10} \cdot 1\text{5\text{MeOH}}\): C 35.63 (35.27), H 3.03 (2.89), N 6.31 (6.59).

\[ \text{[Cu(n)_{4}(L_1)_{2}(\text{MeOH})_{2}2(H_2O)_{2}]2[NO_3]_{3}\text{MeOH7H}_2\text{O}} \]

\[ \text{[Cu(NO_3)_{3}3\text{H}_2\text{O}] (0.25 g, 1.04 mmol), 2-(amino)phenylhydroxamic acid (0.08 g, 0.53 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.08 g, 0.53 mmol) and NaOH (0.042 g, 1.04 mmol) were dissolved in 30 cm}^3\text{ of MeOH and stirred for 4 h. The resultant dark green solution was then filtered and X-ray quality crystals of 2 began to form after two days. Method B: Cu(NO_3)_{3}3\text{H}_2\text{O} (0.25 g, 1.04 mmol), 2-(amino)phenylhydroxamic acid (0.08 g, 0.53 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.08 g, 0.53 mmol) and NaOH (0.042 g, 1.04 mmol) were dissolved in 15 cm}^3\text{ of MeOH in a microwave reactor vial which was stirred for 2 minutes. The glass vial was then sealed and inserted into a microwave oven reactor. The reaction was maintained at \(T = 110 \text{ °C}\), pressure = 110 psi and power = 200 W for a total of 5 min. The resultant green solution was left to cool before filtration and slow evaporation of the mother liquor gave X-ray quality crystals of 2 after two days. Both synthetic methodologies gave approximately 10% yields. FT-IR (cm}^{-1}\): 3065(w), 1607(w), 1581(m), 1541(m), 1490(w), 1457(w), 1432(m), 1372(m), 1328(m), 1233(m), 1183(m), 1100(m), 1080(w), 1027(w), 979(m), 932(m), 871(w), 854(m), 827(w), 786(m), 772(m), 740(s), 689(m), 652(m), 625(m), 586(m), 555(m), 535(m), 524(s). Elemental analysis (%) calculated (found) for C\_{113}\text{H}_{138}\text{N}_{20}\text{O}_{60}\text{Cu}_{14} (2\cdot5\text{H}_2\text{O}): \text{C} 39.56 (39.18), \text{H} 3.40 (2.96), \text{N} 7.50 (7.30).

\[ \text{[Cu(n)_{4}(L_2)_{2}(\text{MeOH})_{2}2(H_2O)_{2}]2[NO_3]_{3}6\text{H}_2\text{O}} \]

\[ \text{Cu(NO_3)_{2}3\text{H}_2\text{O} (0.25 g, 1.04 mmol) was added to a 30 \text{cm}^3 \text{ methanolic solution of 2-amino-phenylhydroxamic acid (0.078 g, 0.52 mmol) and 5-bromo-2-hydroxy-3-methoxybenzaldehyde (0.12 g, 0.52 mmol) and stirred for approximately 2 minutes. The solution became very dark green in colour. NaOH (0.04 g, 1.03 mmol) was then added and the solution stirred for a further 4 hours. The resultant solution was then filtered and X-ray quality crystals of 3 were obtained after 1 week in 15% yield. FT-IR (cm}^{-1}\): 3400(w), 29323(w), 2427(w), 1606(w), 1583(s), 1547(s), 1489(m), 1436(w), 1384(s), 1328(w), 1293(w), 1241(s), 1184(m), 1159(w), 1120(w), 1100(m), 1031(m), 980(m), 934(m), 881(w), 866(w), 841(w), 795(m), 770(w), 758(w), 720(m), \text{H} 3.40 (2.96), \text{N} 7.50 (7.30). \]
687(m), 651(m), 623(s), 557(m), 531(m), 524(m). Elemental analysis (%) calculated (found) for C_{122}H_{124}N_{20}O_{56}Cu_{14} (NO_3)_4·4MeOH·8H_2O (4). Cu(NO_3)_3·3H_2O (0.25 g, 1.04 mmol), 2-(amino)phenylhydroxamic acid (0.08 g, 0.53 mmol), salicyaldehyde (0.058 cm^3, 0.042 g, 1.04 mmol) were dissolved in 10 cm^3 of MeOH and stirred for 1 h. The resultant dark green solution was then stirred over-night (16 h), after which the solvent was removed under reduced pressure and the green solid re-dissolved in 20 cm^3 of MeCN and stirred for 5 min. NaOMe (0.073 g, 1.36 mmol) was added to the solution. The dark green solution was then stirred overnight after which the solvent was removed under reduced pressure and the green solid re-dissolved in 20 cm^3 of MeCN and stirred for 4 h. The resultant dark green solution was filtered and X-ray quality crystals of 4 were obtained from both slow evaporation and diethyl ether diffusion (total yield = 10%). FT-IR (cm^{-1}): 3404(w), 3075(w), 2928(w), 1605(m), 1578(m), 1486(m), 1463(m), 1354(m), 1297(w), 1233(m), 771(m), 737(s), 740(s), 679(s). Elemental analysis (%) calculated (found) as C_{124}H_{120}N_{20}O_{60}Br_{8}Cu_{14} (NO_3)_4·4MeOH·8H_2O (5).

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Notes and references


