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

Cecelia McDonald,a David W. Williams,b Priyanka Comar,c Simon J. Coles,d Tony D. Keene,a Mateusz B. Pitak,d Euan K. Brechin† and Leigh F. Jones∗a,b

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 [Cu10L4(2-aph)2(H2O)2](ClO4)4·5MeOH (1), [Cu14L4(MeOH)2.5(H2O)7.5](NO3)4·3MeOH·7H2O (2), [Cu12L8b-(MeOH)6(H2O)4](ClO4)4·4MeOH·8H2O (3), [Cu14L8(MeOH)6(H2O)2](ClO4)4·4MeOH·8H2O (4) and [Cu15O-(OH)2][Me2(L5)16(MeOH)2(H2O)2](ClO4)4·2MeOH·3H2O (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)(L4)]·H2O]n (6) comprising the pseudo macrocyclic 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.

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]5, [Fe10]6 and [Dy8]7), albeit via a more serendipitous route. In a similar vein we describe here the 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), derived from the Schiff base condensation of 2-(amino)phenylhydroxamic acid (L1H3), 5-bromo-2-hydroxy-3-methoxybenzaldehyde (for L2H3) or 2-hydroxybenzaldehyde (for L3H3), and an MeCN unit at the hydroxamate group of precursor ligand L1H3.

**Results and discussion**

To this end we present the synthesis, structural and magnetic characterisation of the cages: [Cu10L4(2-aph)2(H2O)2](ClO4)4·5MeOH (where 2-aphH2 is 2-(amino)phenylhydroxamic acid).
acid) (1), [Cu(u)14(L1)8(MeOH)2.5(H2O)7.5](NO3)4·3MeOH·7H2O (2), [Cu(u)14(L2)8(MeOH)6(H2O)6][NO3]4·6H2O (3), [Cu(u)14(L3)8
(MeOH)6(H2O)6][NO3]4·4MeOH·8H2O (4) and [Cu(u)16(OH)1
(OMe)2(L1)16(MeOH)4(H2O)2][ClO4]4·2MeOH·30H2O (5). Pro-
ligands L1H3, L2H3 and L3H3 are unknown in the literature in
terms of their synthesis and subsequent complexation.

The decametallic complex [Cu(II)10(L1)4(2-aph)2(H2O)2]
(ClO4)4·2MeOH·30H2O (1) (Fig. 1) crystallises in the mono-
clinic 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

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[u] ion arrangement within
each {Cu3} layer is best described as comprising three (dis-
torted) edge-sharing triangles whose edges are spanned by a
combination of 2 × L13− moieties and a single 2-(amino)phenyl-
hydroxamate (2-aph2−) ligand- a precursor to the formation
of the L1H3. Despite varying the reaction conditions in
1, the L13−/2-aph2− ligand combination is consistently produced, whereas
complexes 2–4 each exclusively comprise our Schiff base
ligands (L1H2, L2H2 or L3H2; vide infra). The four L13− ligands
in 1 exhibit remarkably high binding site concentrations rep-
resented by the $\eta^1\eta^3\eta^1\eta^1\mu_4$ bonding mode, while the
2-aph2− ligands display a $\eta^1\eta^1\eta^1\eta^1\mu_4$ 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 π–π
interactions are observed between their respective L13− and
2-aph2− 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 afore-
mentioned long Cu–O contacts, while the second set lie
further afield. The individual {Cu10} units in 1 pack in a brick-
work motif along the ab plane of the unit cell. These sheets

Scheme 1 General structure (right) and precursors (left) of the ligands
LxH3 (x = 1–3) utilised in this work.

Fig. 1 Polyhedral (a) and standard (b) representation of the crystal
structure in 1. All hydrogen atoms have been omitted for clarity. (c) The
inorganic core in 1. Colour code (used throughout this work): green
(Cu), red (O), blue (N), grey (C) and yellow (Cl).
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 tetracanical copper clusters. However, all bar one of these members are mixed valence \([Cu(n)]\),

while a sole mono-valent \([Cu(i)_{14}]\) cage was recently reported by Zhang and co-workers.

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 another. 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†). The \(L_1^{3–}\) and \(L_2^{3–}\) ligands in 2 and 3 respectively, utilise an equal distribution of \(\eta^2\)–\(\eta^3\)–\(\eta^4\)–\(\mu_4\)-bonding modes to construct their \(\{Cu_7\}\) units. A combination of \(\eta^3\)–\(\eta^3\)–\(\eta^3\)–\(\mu_4\)- and \(\eta^3\)–\(\eta^3\)–\(\eta^3\)–\(\mu_4\)-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 geom-

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**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.
tries. The remaining metal centres in 2 exhibit distorted octahedral geometries (i.e. Cu2 and Cu9), while a single Cu(II) centre in 4 (Cu1 and s.e.) is of a distorted square planar geometry. Terminal methanol, water and/or NO3− moieties complete the coordination spheres at many of the Cu(II) centres in 2–4.

Intramolecular interactions between terminally bound H2O 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 NO3− oxygen atoms (e.g. O47A) and juxtaposed terminally bound water protons (H42A) are also observed in 2 (O47A⋯H42A = 1.747 Å). The individual {Cu14} 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 NO3− 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 {Cu14} units and effectively connect them to one another using extensive hydrogen bonding with their terminal MeOH, H2O and NO3− ligands (e.g. O10⋯O40 = 2.544 Å and O8⋯O45 = 2.777 Å). The {Cu14} moieties in 4 arrange in superimposable rows along the c direction of the unit cell and exhibit weak inter-chain πcentroid⋯πcentroid interactions (e.g. [C43⋯C48] = 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(ClO4)2·6H2O and the L1H3 precursors 2-(amino)phenylhydroxamic acid and 2-hydroxy-3-methoxybenzaldehyde affords the complex [Cu30O(OH)4(OMe)2(L1)16(MeOH)4(H2O)2](ClO4)4·2MeOH·30H2O (5). Discounting the extremely large and numerous copper-chalcogenide14 nanoclusters known in the literature (e.g. the staggering [Cu136S56(SCH2C4H3O)24-(dpppt)10] cage; where dpppt = 1,5-bis(diphenylphosphino)pentane),15 the architecture in [Cu30] (5) represents one of the largest O-donor Cu(II) cages known and is only smaller than the complexes [K4(µ-MeOH)4][Cu(II)36(µ3-OH)32(µ-OR)8Cl6-(ndpa)8(H2O)5]{KCl6} (R is H or Me); H3ndpa = (nitrilodipropionic)
acetic acid)\(^{16}\) and \([\text{Cu}][\text{ntp}][\text{MeOH}]_2\) as a chelating ligand.\(^{17}\) Likewise terminal MeOH moieties partake in the formation of the Pac-Man-shaped \([\text{Cu}_{16}]\) superstructure (Fig. 8a and b). The central \([\text{Cu}_{16}]\) fragment may also be described as comprising two near planar \([\text{Cu}_8]\) sub-fragments which are connected by a centrally located distorted tetrahedral µ- bridging \(\text{O}^{2-}\) anion (O36; Fig. 8c). The metal centres within each \([\text{Cu}_8]\) moiety are held together via two µ-bridging \(\text{O}^{2-}\) ions (O22, O31, O45 and O57) along the four L\(^1\) ligands showing an equal distribution of \(\eta^3: \eta^1: \eta^1: \eta^1\) µ- and \(\eta^3: \eta^1: \eta^1: \eta^1\) µ-bonding modes (Fig. 9-left). This bonding mode combination is also employed by the four L\(^3\) ligands that bridge the metal centres within each of the two bowl-shaped \([\text{Cu}_7]\) layers in 5 (Fig. 8d). Interestingly, these heptanuclear inorganic core units in 5 may be described as puckered versions of the \([\text{Cu}_4]\) units observed in siblings 2-4 (Fig. 5 cf. Fig. 8d). A single µ-OMe\(^-\) ion (via O9 and O73 respectively) also aids cage formation within each heptanuclear section while two terminal \(\text{H}_2\text{O}\) 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 \([\text{Cu}_4]\) fragments are connected to the \([\text{Cu}_{16}]\) main-frame through characteristically long Cu–O contacts namely through interactions with the aforementioned µ-bridging \(\text{O}^{2-}\) ions at distances of: 2.670 Å (Cu4–O22) and 2.686 Å (Cu27–O45).

Four of the \([\text{Cu}_n]\) 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 \([\text{Cu}_n]\) metal centres within the central \([\text{Cu}_{16}]\) 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 \([\text{Cu}_7]\) moieties in 5 (\(\tau\) values ranging from 0.017 (Cu26) to 0.298 (Cu1)). Four charge balancing and crystallographically independent \(\text{ClO}_4^-\) anions lie away from the \([\text{Cu}_{30}]\) structure in 5 and are held in position by H-bond interactions with adjacent L\(^3\) ligand protons (Cl1(089A)...H360(C360) = 2.655 Å, Cl3(O66)...H40(C40) = 2.646 Å). No obvious intramolecular interactions are observed within the cage in 5. The \([\text{Cu}_{30}]\) 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.\(^{18}\) This is perhaps not surprising as ligands \(\text{L}_1\text{H}_3\), \(\text{L}_2\text{H}_4\) and \(\text{L}_3\text{H}_4\) share similarities with known metallacrown-directing ligands. Moreover, the subsequent linking of our planar units into larger architectures has precedence in metallacrown coordination chemistry.\(^{19}\) 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.

**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-

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**Fig. 8** (a) and (b) Two perspectives of the cluster in 5 as viewed in polyhedral mode. All hydrogen atoms have been omitted for clarity. (c and d) Two perspectives of the inorganic core in 5. Image d shows the three distinct near planar layers forming the core. The long Cu–O contacts linking the layers are given as thick black lines.

**Fig. 9** (left) The two distinct bonding modes exhibited by the L\(^3\) ligands in [Cu\(_{30}\)] (5). (right) Packing of the crystals in 5 as viewed along the a cell direction. All hydrogen atoms and perchlorate counter anions have been omitted for clarity.
expected coordination polymer was produced. More specifically, a methanolic reaction mixture comprising Cu(ClO$_4$)$_2$·6H$_2$O, 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 $\{\text{Cu(II)(L$_4$)}\cdot\text{H$_2$O}\}$ (6) comprising the new ligand $[\text{2-}((\text{E})-(\text{2-hydroxy-3-methoxy-phenyl})\text{methyleneamino)}\text{benzoyl}]\text{amino}\text{ethanimidate} \ (L_4\text{H}_2; \text{Fig. 10}).$ 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 ethanimidate functionality which upon Cu(II) ligation gives rise to the formation of the pseudo macrocyclic $L_4^{2-}$ 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.$^{20}$ Complex 6 crystallises in the monoclinic $C2/c$ 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 $L_4^{2-}$ 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 ethanimidate 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 $L_4^{2-}$ 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 $\{\text{Cu(L$_4$)}\}$ unit and is locked into position by three hydrogen bonding interactions with aliphatic protons (H3H) and oxygen donor atoms (O1 and O2) of the $L_4^{2-}$ 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$}\} \ (\text{in 1})$ or $\{\text{Cu$_2$}\} \ (\text{in 2, 4 and 5})$ units, whose structures may also be described as comprising edge- and vertex sharing $\{\text{Cu(n)}\}$ triangular sub-units. Moreover, these individual polymetallic layers are connected by long axial Cu–Cu contacts via filled Cu–O contacts within a filled Cu–O 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(n) 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) cm$^3$ K mol$^{-1}$ are well below their expected spin-only values of ~4.13 (1), 5.78 (2 and 4) and 12.4 (5) cm$^3$ K mol$^{-1}$ (assuming $g = 2.1$) and are indicative of strong intramolecular antiferromagnetic exchange between the Cu(n) ions within the layers of each complex. The $\chi_M T$ vs. $T$ plot for 1 shows a steady drop in its magnetic susceptibility.
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, [Cu$_{14}$] 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-hydroxymono- 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 (L$_1$H$_3$), o-[(E)-2-hydroxy-3-methoxy-5-bromophenyl)methylideneamino]benzohydroxamic acid (L$_2$H$_3$) and o-[(E)-2-hydroxyphenyl)methylideneamino]benzohydroxamic acid (L$_3$H$_3$), respectively. The end products, depending on specific reaction conditions, are the Cu(ii) cages: [Cu$_{10}$L$_1$(2-aph)$_2$(H$_2$O)$_2$][ClO$_4$]$\cdot$5MeOH (1), [Cu$_{14}$L$_1$$(\text{MeOH})_{2.5}$(H$_2$O)$_{2.5}$][NO$_3$]$_3$$\cdot$3MeOH$\cdot$7H$_2$O (2), [Cu$_{14}$L$_2$$(\text{MeOH})_4$(H$_2$O)$_{2.5}$][NO$_3$]$_3$$\cdot$6H$_2$O (3), [Cu$_{14}$L$_3$$(\text{MeOH})_4$(H$_2$O)$_{2.5}$][NO$_3$]$_4$$\cdot$4MeOH$\cdot$8H$_2$O (4) and [Cu$_{30}$L$_3$(OH)$_4$(OMe)$_2$(L)$_{16-}$(MeOH)$_4$(H$_2$O)$_{2.5}$][ClO$_4$]$_4$$\cdot$2MeOH$\cdot$3H$_2$O (5). The introduction of acetonitrile into the synthesis of 1 results in the in situ Cu(ii) mediated formation of the unexpected ligand [(2-aph)-(2-hydroxy-3-methoxy-phenyl)methylenediamino][benzoyl]amino-ethanidimide (L$_4$H$_4$) and this ligand modification gives rise to the formation of the 1D coordination polymer {[Cu$_{10-}$(L$_4$)][H$_2$O]}$_n$(6). 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 synthion 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 (Cl$_2$–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 L$_4$– 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 modelling using the SQUEEZ program. The four voids in 1 represented a total volume of 1720 Å$^3$, which equates to five MeOH solvent molecules of crystallisation per [Cu$_{14}$] cage (commensurate with microanalysis results on 1; calculated formula: 1.5MeOH cf. elemental analysis: 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–O602B, 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: 2·3MeOH·7H₂O cf. elemental analysis: 2·5H₂O).

Significant disorder in 3 was observed at Cu and was therefore modelled at 50% occupancy along with the bound L₃⁻– 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 NO₃⁻ 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 Å³) and was assumed to contain six waters of crystallisation per cage (commensurate with microanalysis results on 3; calculated formula: 3·6H₂O cf. elemental analysis: 3·6H₂O).

All non-hydrogen atoms in 4 were refined as anisotropic with the exception of one NO₃⁻ 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 Å³) and was assumed to contain four waters of crystallisation per cage (commensurate with microanalysis results on 4; calculated formula: 4·4MeOH·8H₂O cf. elemental analysis: 4·4MeOH·4H₂O).

Despite carrying out numerous collections, weak X-ray data was obtained from all crystals of complex 5 (\(R_{int} = 0.1034, \omega R_2 = 0.3398\) 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. The three channels in 5 (total void volume \(\sim 1905\) Å³) 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: 5·2MeOH·30H₂O cf. elemental analysis: 5·11H₂O).

Preparation of complexes

All reactions were performed under aerobic conditions and all reagents and solvents were used as purchased. 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. The solvothermal synthesis of 5 was carried out in a Hereaus (UT6420-Thermo Scientific) oven using spring loaded stainless steel digestion vessels (23 cm³ capacity) produced by the Parr Instrument Company. The microwave synthesis of 2 was carried in a CEM Discover® microwave reactor.

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[Cu(n)(L)_{2}(MeOH)_{2}(H_{2}O)_{3}](ClO_{4})_{4}·5MeOH (1). \quad Cu(ClO_{4})_{2}·6H_{2}O (0.25 g, 0.68 mmol), 2-(amino)phenylhydroxamic acid (0.052 g, 0.34 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.052 g, 0.34 mmol) and NaOH (0.027 g, 0.68 mmol) were dissolved in 30 cm³ 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), 1540(m), 1490(w), 1433(m), 1372(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 C₇⁹H₈₀Cl₄N₁₂O₄₃Cu₁₀·5MeOH: C 35.63 (35.27), H 3.03 (2.89), N 6.31 (6.59).

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[Cu(n)_{2}(L)_{2}(MeOH)_{2}·(H_{2}O)_{3}](NO_{3})_{4}·3MeOH·7H₂O (2). \quad Cu(NO_{3})₂·3H₂O (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 cm³ 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(NO₃)₂·3H₂O (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 cm³ 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 \(T = 110°C\), 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 C₁₁₃H₁₃₈N₂₀O₉₆Cu₁₄·2·5H₂O: C 39.56 (39.18), H 3.40 (2.96), N 7.50 (7.30).

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[Cu(n)_{2}(L)_{2}(MeOH)_{2}·(H_{2}O)_{3}](NO_{3})_{4}·6H₂O (3). \quad Cu(NO₃)₂·3H₂O (0.25 g, 1.04 mmol) was added to a 30 cm³ 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), 1447(s), 1499(m), 1346(w), 1348(s), 1328(w), 1293(m), 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),
688(w), 665(w), 633(w), 5669(m), 451(m). Elemental analysis (%) calculated (found) for C_{12}H_{22}N_{3}O_{10}Cl_{4}Cu_{3}O_{15}7(m), 1540(m), 1488(w), 1432(m), 1374(m), 1297(w), 1233(m), 2MeOH·30H_{2}O (5).

30 cm^{3} of MeOH and stirred for 4 h. The resultant dark green solution was then placed in a teflon lined stainless steel autoclave and heated at 100 °C for 24 h followed by slow cooling over a further 24 h period. Dark green X-ray quality crystals of dark green X-ray quality crystals of dihydride (0.104 g, 0.68 mmol) were dissolved in 30 cm^{3} of MeOH and stirred for 1 h. This solution was then filtered and X-ray quality crystals of

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Notes and references

Acknowledgements

LFJ would like to thank the College of Science, NUI Galway (CM), the School of Chemistry, Bangor University (DWW) and the EPSRC (National Crystallographic Service) for their support.
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