

Extended three-dimensional supramolecular architectures derived from trinuclear (bis- β -diketonato)copper(II) metallocycles†

Jack K. Clegg,^a Leonard F. Lindoy,^{*a} John C. McMurtrie^{a,b} and David Schilter^a

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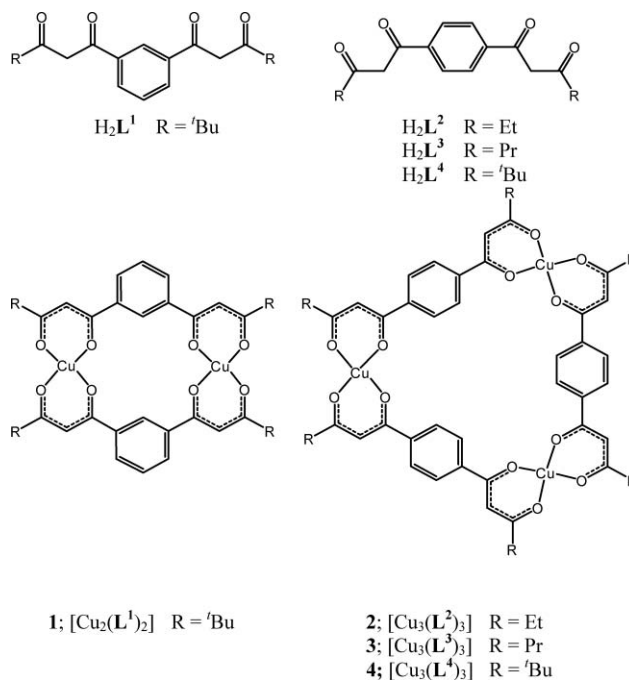
Neutral trinuclear (triangular) copper(II) complexes of type $[\text{Cu}_3\text{L}_3]$ incorporating the 1,4-aryl linked bis- β -diketonato bridging ligands, 1,1-(1,4-phenylene)-bis(butane-1,3-dione) (H_2L^2), 1,1-(1,4-phenylene)-bis(pentane-1,3-dione) (H_2L^3) and 1,1-(1,4-phenylene)-bis(4,4-dimethylpentane-1,3-dione) (H_2L^4) have been demonstrated to react with selected heterocyclic nitrogen donor bases to generate extended supramolecular architectures whose structures have been confirmed by X-ray diffraction. Thus on reaction with 4,4'-bipyridine (bipy), $[\text{Cu}_3(\text{L}^2)_3]$ yields polymeric structures of type $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot 2.75\text{THF}\}_n$ and $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot \text{bipy}\cdot 0.75\text{THF}\}_n$ while with pyrazine (pyz), $\{[\text{Cu}_3(\text{L}^2)_3(\text{pyz})]\cdot 0.5\text{THF}\}_n$ was obtained. Each of these extended structures contain alternating triangle/linker units in a one-dimensional polymeric chain arrangement in which two of the three copper sites in each triangular 'platform' are formally five-coordinate through binding to a heterocyclic nitrogen atom. Interaction of the multifunctional linker unit hexamethylenetetramine (hmt) with $[\text{Cu}_3(\text{L}^3)_3]$ afforded an unusual, chiral, three-dimensional molecular framework of stoichiometry $[\text{Cu}_3(\text{L}^3)_3(\text{hmt})]_n$. The latter incorporates the trinuclear units coordinated to three triply bridging hmt units. In marked contrast to the formation of the above structures incorporating bifunctional linker units and five-coordinate metal centres, the trinuclear platform $[\text{Cu}_3(\text{L}^2)_3]$ reacts with the stronger difunctional base 1,4-diazabicyclo[2.2.2]-octane (dabco) to yield a highly symmetric trigonal columnar species of type $\{[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3]\cdot 3\text{H}_2\text{O}\}_n$ in which each copper centre is octahedrally coordinated.

Introduction

The assembly of metal-organic frameworks is an area of much current interest because such infinite systems frequently exhibit novel molecular architectures and have potential applications as functional materials in areas that include gas storage, catalysis, zeolitic behaviour and magnetism.¹

Although β -diketone ligands and their derivatives have played a significant role in coordination chemistry for over a century,^{2,3} their incorporation into metallo-supramolecular materials has received relatively less attention than, for example, other 'classical' coordination fragments such as di- and poly-pyridyl derivatives.⁴

Nevertheless, a number of reports of β -diketone-containing metallo-supramolecular systems have appeared and prior studies have demonstrated that 1,3- and 1,4-aryl linked bis- β -diketones such as H_2L^1 and H_2L^2 – H_2L^4 give rise to a variety of di- and multinuclear metal complexes. Thus, the 1,3-aryl linked ligands tend to form dinuclear complexes on interaction with divalent metal ions; as is exemplified by the preparation of the copper(II) 'dimer' complex **1**.^{5,6}



^aCentre for Heavy Metals Research, School of Chemistry, University of Sydney, NSW, 2006, Australia

^bSchool of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, 4001, Australia

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In contrast, when such divalent metal ions are reacted with 1,4-aryl linked derivatives, neutral trinuclear metallocycles tend to form; examples are given by the copper(II) species **2–4**.⁷ Related triangular complexes have also been reported incorporating cobalt(II) and nickel(II).⁸

On reaction with trivalent metal ions, the 1,3-linked derivatives have been demonstrated to yield neutral dinuclear triple helical structures⁹ while their 1,4-linked analogues yield tetranuclear, tetrahedral-shaped (neutral) products.⁷

We have previously demonstrated that **1** can act as a dinuclear building block for the formation of a discrete tetranuclear 'dimer of dimers' on reaction with the ditopic linker unit pyrazine, while a one dimensional coordination polymer of stoichiometry $[\text{Cu}_2(\text{L}^1)_2(\text{azpy})_2]_n$ was obtained when the 'offset' linear linker, 4,4'-*trans*-azopyridine (azpy) was employed.⁶ In each case, the copper centres are five-coordinate and approximately square pyramidal, with 4,4'-*trans*-azopyridine ligands occupying axial positions such that they bridge adjacent copper(II) dimer units in a step-like arrangement. The present investigation is an extension of the above studies in which the triangular building blocks, **2–4**⁷ (rather than dinuclear species of type **1**)⁶ were employed for reaction with selected amine 'linker' units. In particular, the prospect of reacting these 'platform-like' precursors with such linking groups to form extended supramolecular structures has been explored.

Experimental

4,4'-Bipyridine, pyrazine, dabco and hexamethylenetetramine (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) were obtained from commercial sources and were used without further purification. Tetrahydrofuran and diethyl ether were dried over sodium wire. Solid state UV-Vis spectra were recorded on a Cary 1E spectrophotometer as nujol mulls spread on a filter paper; in all cases the visible region contained the 'tail' of an intense charge transfer and/or ligand absorption that extended from the UV region. FTIR (KBr) spectra were collected using a Bio-Rad FTS-7 spectrometer. The tricopper(II) complexes **2–4** were prepared as described elsewhere.⁷ These were employed for reaction with a selection (see below) of difunctional nitrogen bases. Only syntheses for those products that yielded crystals suitable for X-ray study are given below.

$[\text{Cu}_3(\text{L}^2)_3(\text{pyz})]\cdot 0.5\text{THF}]_n$

A stirred solution of **2** (61 mg, 0.06 mmol) and pyrazine (36 mg, 0.45 mmol) in tetrahydrofuran (25 ml) was brought to boiling then allowed to cool. Slow evaporation of the reaction mixture afforded the title compound (57 mg, 52%) as green crystals that were employed for the X-ray crystallographic study. The sample for microanalysis was washed with ether, crushed, and then allowed to stand in air. Found: C, 57.79; H, 5.31; N, 2.39. Calc. for $\text{C}_{54.5}\text{H}_{56}\text{N}_2\text{Cu}_3\text{O}_{12.5}$: C, 57.95; H, 5.00; N, 2.48%.

$[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3\cdot 3\text{H}_2\text{O}]_n$

To a solution of **4** (29 mg, 0.025 mmol) in tetrahydrofuran (2 ml) was added dabco (28 mg, 0.25 mmol) in tetrahydrofuran (2 ml). Slow diffusion of diethyl ether into the resulting mixture afforded the title compound (18 mg, 48%) as bright green crystals; these were employed for the X-ray crystallographic study. The sample used for microanalysis was washed with ether, crushed, and then allowed to stand in air. Found: C, 60.04; H, 7.16; N, 5.55. Calc. for $(\text{C}_{78}\text{H}_{114}\text{Cu}_3\text{O}_{15}\text{N}_6)_n$: C, 59.81; H, 7.34; N, 5.37%. UV-Vis (solid state): 421, 450, 624 nm.

$[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot 2.75\text{THF}]_n$

A stirred solution of **2** (101 mg, 0.10 mmol) and 4,4'-bipyridine (23 mg, 0.15 mmol) in tetrahydrofuran (25 ml) was brought to boiling then allowed to cool. Slow evaporation of the reaction mixture afforded the title compound as green crystals (65 mg, 53%). These were employed directly for the X-ray crystallographic study. UV-Vis (solid state): 457, 409, 550, 682 nm. FTIR (KBr): 1516, 1489, 1332, 1284, 1116, 1064, 807, 764 cm^{-1} .

$[\text{Cu}_3(\text{L}^2)_3(\text{bipy})]\cdot \text{bipy}\cdot 0.75\text{THF}]_n$

A stirred solution of **2** (61 mg, 0.06 mmol) and 4,4'-bipyridine (70 mg, 0.45 mmol) in tetrahydrofuran (25 ml) was brought to reflux then allowed to cool. Slow evaporation of the reaction mixture afforded the title compound (38 mg, 48%) as green crystals. These were employed directly for the X-ray crystallographic study. UV-Vis (solid state): 481, 631, 680 nm. FTIR (KBr): 2978, 1488, 1431, 1333, 1286, 1114, 1066, 804, 771, 449 cm^{-1} .

$[\text{Cu}_3(\text{L}^3)_3(\text{hmt})]_n$

A solution of **3** (109 mg, 0.1 mmol) in THF (3 ml) was layered upon a solution of hexamethylenetetramine (14 mg, 0.1 mmol) in THF (3 ml). Green crystals (64 mg, 70%) formed over one week. These were used directly for the X-ray crystallographic study.

X-Ray structure determinations

Data were collected at 150(2) K with ω scans to approximately 56° 2θ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP¹⁰ and subsequent computations were carried out using the WinGX-32 graphical user interface.¹¹ Multi-scan empirical absorption corrections were applied to the data using the program SADABS.¹² The structures were solved by direct methods using SIR97¹³ then refined and extended with SHELXL-97.¹⁴ In general, ordered non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Partial occupancy carbon, nitrogen and oxygen atoms were refined isotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen-bound hydrogen atoms that were structurally evident in the difference Fourier map were included and refined with bond length and angle restraints. Idealised intramolecular atom–atom distance restraints were applied to disordered solvent molecules, 'Bu, Et and Pr groups to facilitate refinement with realistic models where necessary.

Crystal data. Crystal and structure refinement data for $[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot 2.75\text{THF}]_n$, $[\text{Cu}_3(\text{L}^2)_3(\text{pyz})]\cdot \text{THF}]_n$, $[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot \text{bipy}\cdot 0.75\text{THF}]_n$, $[\text{Cu}_3(\text{L}^2)_3]\cdot 0.5\text{H}_2\text{O}]_n$, $[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3]\cdot 3\text{Et}_2\text{O}]_n$ and $[\text{Cu}_3(\text{L}^3)_3(\text{hmt})]_n$ are summarised in Table 1. ORTEP¹⁵ depictions of the crystal structures showing the numbering scheme are provided in Fig. 1 and Fig. S1–S6 in the ESI.† Where applicable, additional details relating to the X-ray crystal structure (along with tables of selected bond lengths and angles) are given in the ESI.†

CCDC reference numbers 292064–292069.

Table 1 Crystal and structure refinement data

Formula	$\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})] \cdot 2.75\text{THF}\}_n$	$\{[\text{Cu}_3(\text{L}^2)_3(\text{pyz})(\text{THF})] \cdot \text{THF}\}_n$	$\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})] \cdot \text{bipy} \cdot 0.75\text{THF}\}_n$	$[\text{Cu}_3(\text{L}^2)_3] \cdot 0.5\text{H}_2\text{O}$ $\text{C}_{48}\text{H}_{48}\text{Cu}_3\text{O}_{12} \cdot 0.5\text{H}_2\text{O}$	$[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3] \cdot 3\text{Et}_2\text{O}\}_n$ $(\text{C}_{78}\text{H}_{108}\text{Cu}_3\text{N}_6\text{O}_{12} \cdot 3\text{Et}_2\text{O})_n$	$[\text{Cu}_3(\text{L}^3)_3(\text{hm})]_n$ $(\text{C}_{60}\text{H}_{72}\text{Cu}_3\text{N}_4\text{O}_{12})_n$
Empirical formula	$\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})] \cdot 2.75\text{THF}\}_n$	$\{[\text{Cu}_3(\text{L}^2)_3(\text{pyz})(\text{THF})] \cdot \text{THF}\}_n$	$\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})] \cdot \text{bipy} \cdot 0.75\text{THF}\}_n$	$[\text{Cu}_3(\text{L}^2)_3] \cdot 0.5\text{H}_2\text{O}$	$[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3] \cdot 3\text{Et}_2\text{O}\}_n$	$[\text{Cu}_3(\text{L}^3)_3(\text{hm})]_n$
Molecular weight	1434.06	1159.68	1446.03	1016.49	1734.68	1231.23
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Cubic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P2_13$
$a/\text{\AA}$	15.0084(18)	12.571(3)	14.0012(16)	10.2001(8)	7.5941(8)	18.206(1)
$b/\text{\AA}$	15.8591(18)	13.202(3)	14.1336(16)	14.7227(12)	33.013(3)	18.206(1)
$c/\text{\AA}$	17.910(2)	19.105(4)	18.328(2)	15.3507(13)	21.558(2)	18.206(1)
$\alpha/^\circ$	112.600(2)	109.55(3)	72.259(2)	80.131(1)	90	90
$\beta/^\circ$	103.553(2)	100.89(3)	88.496(2)	87.500(1)	90.130(2)	90
$\gamma/^\circ$	101.522(2)	102.37(3)	83.084(2)	78.150(1)	90	90
$V/\text{\AA}^3$	3621.1(7)	2799.1(15)	3429.0(7)	2222.7(3)	5404.8(9)	6034.5(6)
$D_c/\text{g cm}^{-3}$	1.315	1.376	1.401	1.519	1.066	1.356
Z	2	2	2	2	2	4
Crystal size/mm	$0.599 \times 0.350 \times 0.183$	$0.33 \times 0.32 \times 0.06$	$0.36 \times 0.18 \times 0.01$	$0.21 \times 0.18 \times 0.06$	$0.65 \times 0.32 \times 0.16$	$0.21 \times 0.21 \times 0.20$
Crystal colour	Green	Green	Green	Dark green	Green	Green
Crystal habit	Prism	Plate	Plate	Prism	Prism	Tetrahedron
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
$\lambda(\text{Mo-K}\alpha)$	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	0.938	1.192	0.990	1.487	0.639	1.110
$T(\text{Empirical})_{\text{min,max}}$	0.703, 0.841	N/A	0.807, 0.990	0.809, 0.915	N/A	N/A
$2\theta_{\text{max}}/^\circ$	56.64	55.70	56.64	56.74	56.20	56.60
hkl range	–20 to 19 –21 to 20 –23 to 23	–15 to 16 –17 to 17 –24 to 24	–17 to 17 –18 to 18 –24 to 24	–13 to 13 –19 to 19 –20 to 20	–10 to 10 –42 to 42 –28 to 28	–22 to 23 –24 to 24 –24 to 23
N	35294	24786	34047	22002	52355	49783
$N_{\text{ind}} (R_{\text{merge}})$	16536 (0.0222)	21993	15835 (0.0509)	10284 (0.0309)	12961 (0.0696)	4995 (0.1051)
$N_{\text{obs}} (I > 2\sigma(I))$	13036	10179	9906	7708	8377	2903
N_{var}	799	710	874	575	486	219
$R1^a (I > 2\sigma(I)), wR2^a (\text{all})$	0.0653, 0.1961	0.1069, 0.3313	0.0537, 0.1332	0.0441, 0.1185	0.0718, 0.2029	0.0517, 0.1246
A^a, B^a	0.1326, 8.3004	0.2000, 0.0000	0.0958, 0.000	0.0794, 0.0818	0.1387, 0.0000	0.0814, 0.0000
GoF	0.992	0.974	0.923	1.032	1.021	0.900
Residual extrema/ $e \text{\AA}^{-3}$	1.743, –0.953	1.724, –2.371	0.944, –0.397	1.044, –0.500	0.726, –0.847	0.549, –0.729

^a $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ for $F_o > 2\sigma(F_o)$ and $wR2 = \{[\sum (w(F_o^2 - F_c^2))^2] / \sum [w(F_c^2)]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, $P = (F_o^2 + 2F_c^2)/3$ and A and B are listed in the crystal data information supplied.[†]

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517274h

Results and discussion

The following complex species: $\{[(\text{Cu}_3(\text{L}^2)_3)(\text{bipy})(\text{THF})] \cdot 2.75\text{THF}\}_n$, $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})] \cdot \text{bipy} \cdot 0.75\text{THF}\}_n$, $\{[(\text{Cu}_3(\text{L}^2)_3)(\text{pyz})] \cdot 4\text{THF}\}_n$, $\{[(\text{Cu}_3(\text{L}^4)_3)(\text{dabco})_3] \cdot 3\text{H}_2\text{O}\}_n$ and $[\text{Cu}_3(\text{L}^3)_3(\text{hmt})]_n$ were obtained on heating a stirred solution of the required trinuclear metal complex in tetrahydrofuran with the appropriate heterocyclic base. In each case the corresponding solid state structure was determined by single crystal X-ray diffraction.

As a preliminary to the above studies, the X-ray structure of the previously reported trinuclear 'platform' **2** was also determined. An ORTEP representation of this precursor complex is given in Fig. 1.

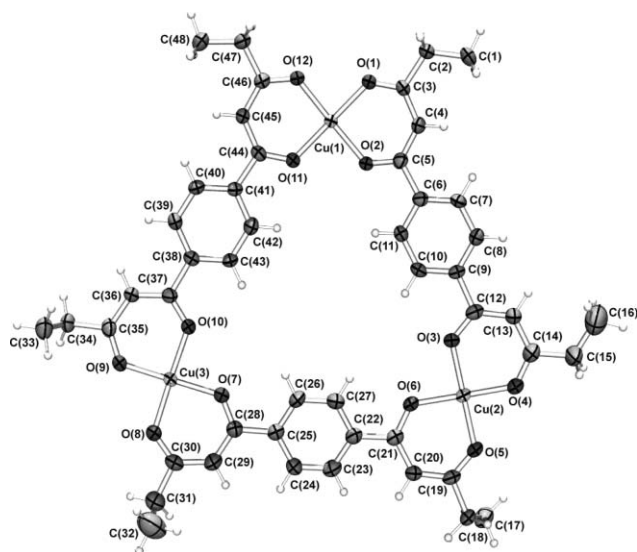


Fig. 1 ORTEP plot of $[\text{Cu}_3(\text{L}^2)_3] \cdot 0.5\text{H}_2\text{O}$, shown with 85% probability ellipsoids. Solvent molecules have been removed for clarity.

As previously found for the analogous trinuclear complex **3**,⁷ the present structure also possesses intermolecular inversion symmetry, with two triangular units occurring within the unit cell. Close contacts (2.51 Å) exist between a copper(II) ion in each triangle and a β -diketonate oxygen atom in an adjacent triangle (Cu(1) and O(2)), making this copper(II) ion formally five coordinate. A contact between Cu(3) and a π -electron sp^2 -hybrid rich carbon atom (C(36)) (3.03 Å) in a nearby triangle results in this copper existing in what may be considered a pseudo five-coordinate arrangement. Cu(2), however, has long range weak copper to sp^2 -hybridised carbon atom contacts (3.33 Å–3.34 Å between Cu(2)–C(7) and C(22) respectively). Related intermolecular interactions were observed in our previous study where copper to β -diketonate oxygen atom distances of 2.7–2.8 Å and copper to sp^2 -hybridised carbon atom distances of 3.1–3.5 Å were reported.⁷

The above triangular complex **2** was initially chosen for interaction with 4,4'-bipyridine. Thus reaction of **2** with 1.5 equivalents of 4,4'-bipyridine in tetrahydrofuran yielded green crystals on slow evaporation of the reaction solution. The product

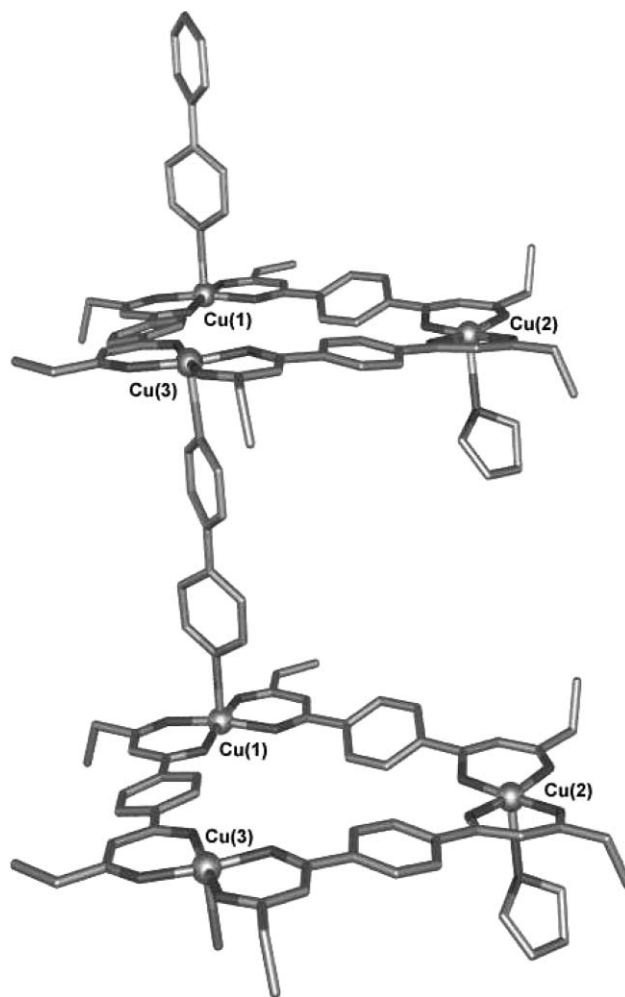


Fig. 2 A schematic representation of a fragment of the one-dimensional chain present in $\{[(\text{Cu}_3(\text{L}^2)_3)(\text{bipy})(\text{THF})] \cdot 2.75\text{THF}\}_n$. An ORTEP plot is given in the ESI.†

obtained is polymeric with repeating formula unit $\{[(\text{Cu}_3(\text{L}^2)_3)(\text{bipy})(\text{THF})] \cdot 2.75\text{THF}\}_n$, and comprises alternating triangle and bound 4,4'-bipyridine units, such that the one-dimensional step-like structure shown in Fig. 2 results. Cu(2) of each trinuclear component is not bound to a 4,4'-bipyridine linker but one of its apical coordination sites is instead occupied by a tetrahydrofuran molecule. Adjacent polymeric chains are related by crystallographic inversion symmetry and stack closely, interconnecting *via* interactions between the metal and regions of delocalised electron density of the ligands. Cu(2), for example, is formally coordinated to a THF ligand on one side while on the other there is a copper to sp^2 -hybridised carbon atom distance of 3.33 Å (Cu(2)–C(7) in the adjacent chain). The C(7)-containing ring is also rotated from the mean plane of the molecule. Similarly, the Cu(1) to C(39) distance is 3.43 Å; however, in this case there is not a significant deviation of the C(39)-containing ring from the mean plane of the triangular building block; Cu(3)–O(7) distance is 3.34 Å.

Almost certainly equilibria will occur between the precursor components and the product(s) in solution. Hence the use of an excess of linker might be expected to help promote formation of a prismatic arrangement rather than, for example, the step-like

polymer observed for the structure described above and the structure of $[\text{Cu}_2(\text{L}^1)_2(\text{azpy})]_n$ reported previously.⁶ Clearly prismatic arrangements require more linker moieties per triangular building block than occurs in the above stepped polymeric structure, with its 1 : 1 (building block: linker) stoichiometry. In view of this the synthetic procedure outlined for $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot 2.75\text{THF}\}_n$ was repeated using excess 4,4'-bipyridine.

An X-ray structure analysis of the bright green product obtained from the above procedure showed a one-dimensional step-like polymeric structure (Fig. 3) which was generally similar to that of $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot 2.75\text{THF}\}_n$ discussed above. Namely, the new product also contains alternating triangle and linker units, with those copper(II) centres that are not coordinated to 4,4'-bipyridine linkers instead being bound to tetrahydrofuran molecules. Interestingly, the use of excess 4,4'-bipyridine in this case results in the inclusion of non-coordinated 4,4'-bipyridine in the lattice. In each triangular unit, Cu(1) lies 3.4 Å from such a 4,4'-bipyridine molecule—perhaps reflecting the presence of a weak contact between the copper(II) ion and the π -electron density of the bipyridyl aromatic groups. Similar interactions appear to be present between Cu(2) and C(10) as well as between Cu(3) and C(24) with separations of 3.4–3.5 Å being observed. Edge to face π – π interactions also occur between free 4,4'-bipyridine and the C(6)- and C(22)-containing phenyl rings, in these cases the separations are 3.1–3.3 Å.

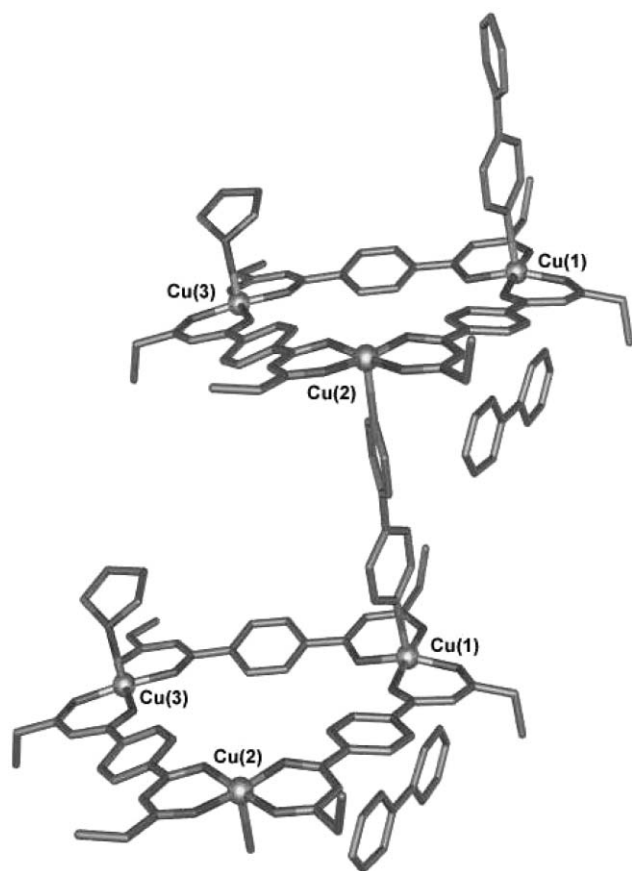


Fig. 3 A schematic representation of a fragment of a one-dimensional chain of $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot \text{bipy}\cdot 0.75\text{THF}\}_n$. An ORTEP plot is available in the ESI.†

In general terms, structures incorporating closely-packed molecular units tend to be favoured over those exhibiting large cavities. In the present context, this has implications for the possible formation of trigonal prismatic motifs. The use of 4,4'-bipyridine as the spacer would result in the incorporation of a moderately large internal void in this latter case and hence such a geometry may be destabilised relative to a more compact arrangement.¹⁶ In any case, as discussed above, the observed polymeric architectures each contain a number of weak intermolecular interactions involving copper centres which undoubtedly also help stabilise the adopted structures.

With respect to the above, the use of a shorter linking group was investigated in order to probe whether this would influence the structure adopted. In particular, it was envisaged that pyrazine, a smaller unit than 4,4'-bipyridine, might promote the generation of a triangular prismatic arrangement for the reason just mentioned. However it needs to be noted that while pyrazine is smaller, it is also a weaker base than 4,4'-bipyridine (the protonated forms of these bases have $\text{p}K_a$ values of 1.0 and 4.8, respectively).¹⁷ The synthetic procedure for the preparation of $\{[\text{Cu}_3(\text{L}^2)_3(\text{bipy})(\text{THF})]\cdot \text{bipy}\cdot 0.75\text{THF}\}_n$, was subsequently repeated with pyrazine substituted for 4,4'-bipyridine and the X-ray structure of the resulting pale green product was determined (Fig. 4). Once again, a stepped polymeric structure, similar to the structures with 4,4'-bipyridine, was obtained. However, in this case the product differs from the previous ones in that no THF molecules are bound to individual copper(II) centres. Thus, unlike both structures containing 4,4'-bipyridine, in the present compound two copper(II) sites, (Cu(1), Cu(2)), in each triangle are formally five-coordinate. The remaining centre (Cu(3)) can be considered pseudo five-coordinate, with an electron-rich β -diketonate oxygen atom from a neighbouring triangle occupying an apical position (Cu(3)–O(10), 2.69 Å), similar to the situation occurring in the structure of $[\text{Cu}_3(\text{L}^2)_3]\cdot 0.5\text{H}_2\text{O}$ discussed earlier. A relatively small separation (3.36 Å) between copper(II) centres in adjacent triangles is present. As discussed earlier, the closely-packed intercalated nature of the chains may once again be a factor aiding the stabilisation of the observed extended structural motif.

Of course, the structure of the prevalent species in solution is not necessarily mirrored by the corresponding solid state structure.¹⁶ Indeed, it is quite possible that the present system exists in solution as a mixture of discrete and polymeric species, and that the latter crystallises preferentially;¹⁸ however, in the absence of additional data it appears inappropriate to speculate further concerning this.

Given the tendency of the copper centres in the structures discussed so far to yield five-coordinate adducts, we were motivated to investigate the possibility of inducing the formation of an additional extended structure (or structures) in which the metal centres were coordinately saturated—namely, present in octahedral rather than square pyramidal environments. To this end the stronger ditopic base dabco ($\text{p}K_a = 8.19$)¹⁷ was employed in an attempt to generate such six coordination. It was also anticipated that use of this stronger base would readily disrupt the formation of weak copper to diketonato chelate ring interactions between adjacent bis(β -diketonato)Cu(II) fragments that are a feature of the polymeric crystalline structures discussed so far.

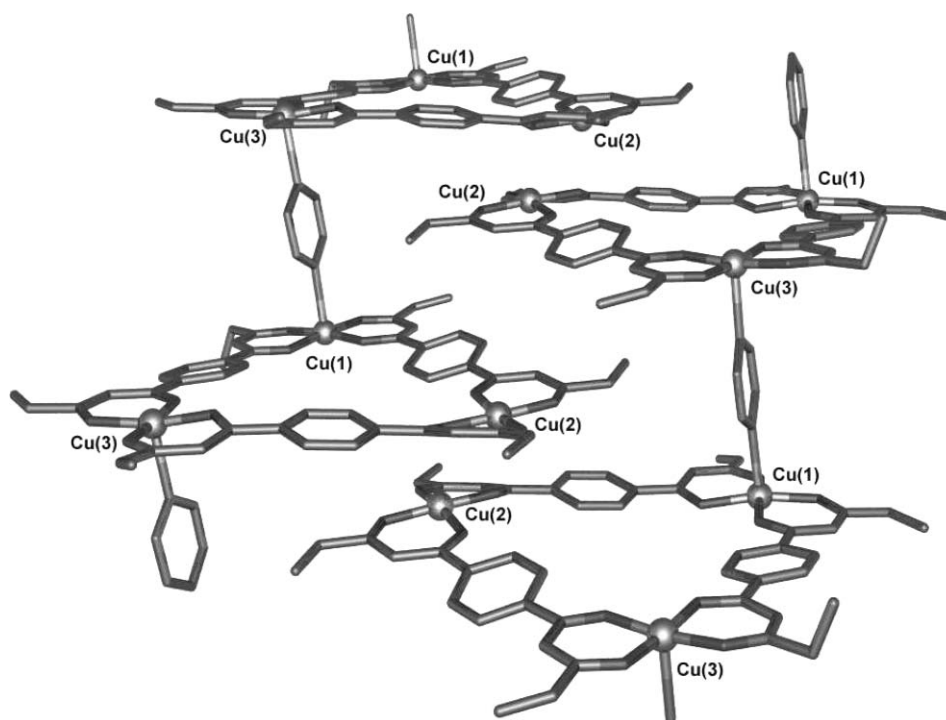


Fig. 4 A schematic representation of the close packing between two fragments of the one-dimensional chains of $\{[\text{Cu}_3(\text{L}^3)(\text{pyz})]\cdot(\text{THF})\}_n$ forming an intercalated zipper-like arrangement. An ORTEP plot is available in the ESI.†

The addition of excess dabco to a tetrahydrofuran solution of **4** yielded bright green single crystals whose X-ray structure confirmed a stoichiometry of type $\{[\text{Cu}_3(\text{L}^4)(\text{dabco})_3]\cdot 3\text{Et}_2\text{O}\}_n$. This product consists of an infinite columnar arrangement in which each copper ion is indeed six coordinate, with three dabco units per triangular complex bridging axial positions to produce an infinite one-dimensional triangular prismatic arrangement (Fig. 5). This aesthetically pleasing structure incorporates triangular channels that extend throughout the crystal lattice, with the channels being filled with disordered diethyl ether molecules. The SQUEEZE function of PLATON¹⁹ was used to estimate the void volume to be 971 Å³ per unit cell (or 18.0% of the total volume of the unit cell).

The polymeric complexes discussed above demonstrate the manner by which coordination unsaturation of the copper centres in the triangular precursors may be exploited by reaction with ditopic linker units to give extended one-dimensional polymeric species. For comparison, it was of interest to investigate the incorporation of a linker unit that is potentially capable of bridging more than two triangular units. To this end hexamethylenetetramine (hmt) was chosen for investigation. This polyfunctional base contains four tetrahedrally oriented nitrogen donor atoms. Reaction of equimolar amounts of hexamethylenetetramine and trinuclear complex **3** in THF resulted in bright green crystals of type $[\text{Cu}_3(\text{L}^3)(\text{hmt})]_n$ whose X-ray structure is given in Fig. 6.

The structure revealed an interesting neutral three-dimensional network in which both hexamethylenetetramine and **3** are present as triply-bridging units. The structural fragment shown on the left in Fig. 6 has a three-fold axis passing through the unbound nitrogen atom to give a propeller-like arrangement. Each 'triangle' incorporates three five-coordinate copper(II) centres, with three

hexamethylenetetramine linkers coordinated on one side of the mean plane of the triangle. The structure crystallises within a chiral cubic space group and there is one third of a triangular $[\text{Cu}_3(\text{L}^3)_3]$ entity in the asymmetric unit. Unlike the previous structures discussed in this report, the overall structure corresponds to a three-dimensional molecular network. If each of the triangular and hexamethylenetetramine units is defined as a trigonal linking component then the overall structure can be described topologically as a highly distorted (10,3)-*a* network arrangement with an anti-clockwise helical twist (for the particular single crystal employed for the structure determination).^{20,21} The crystal is thus optically active. Unlike the linear structures discussed earlier, there is no solvent included in the lattice and there is an absence of channels within the structure. Of the 24 previously reported structures with this topology in the Cambridge structural database,²¹ all contain planar nodes. The present arrangement differs in the respect that the three-connecting nodes (that is, the triangles and hmt) are not coordinated to the copper(II) centres in a planar manner. As a result it is not possible to use the dihedral angle between adjacent nodal planes (ω) as a measure of distortion.^{21,22} The arrangement thus corresponds to an unusual type of distortion to the (10,3)-*a* net that does not appear to have been reported previously.

Concluding remarks

In the present study the reactions of rigid nitrogen donor linking units with the trinuclear copper(II) 'platform-like' complexes **2–4** have been investigated and the results illustrate how coordination unsaturation associated with such neutral species

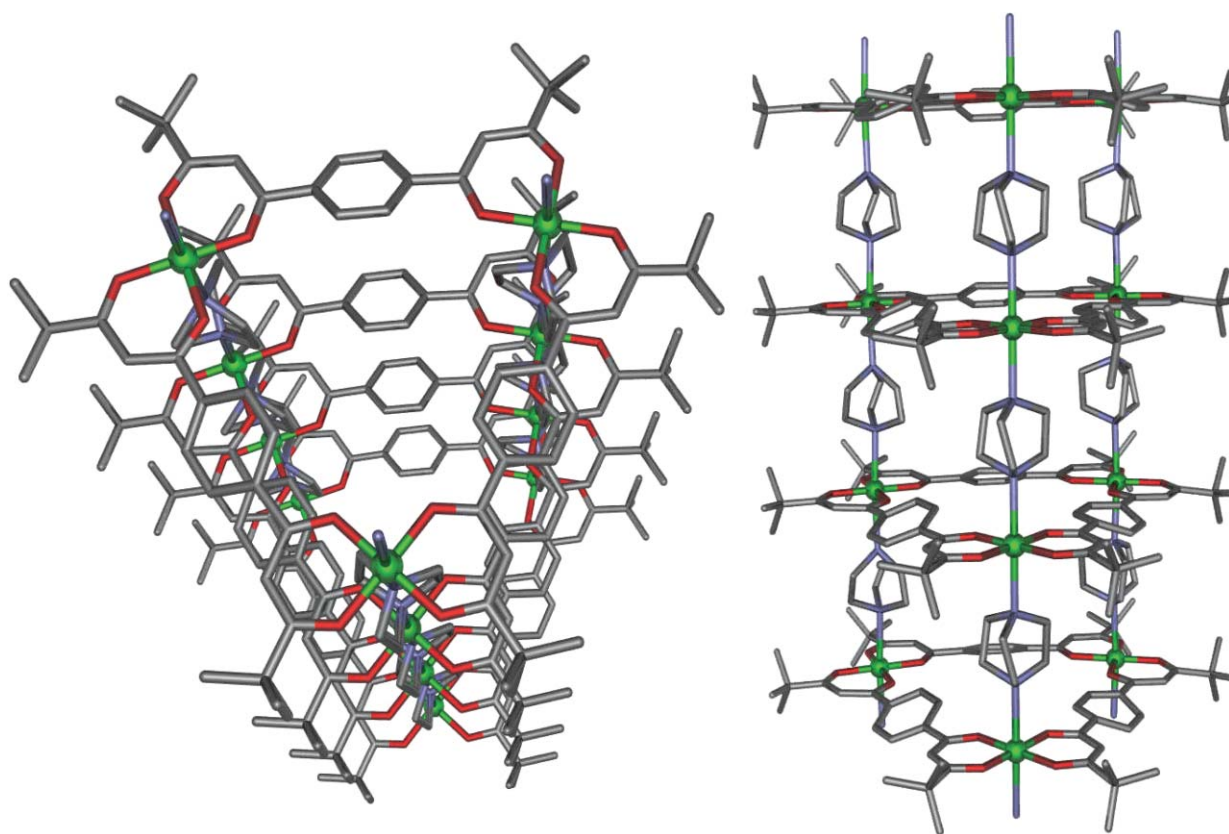


Fig. 5 Two schematic representations of a fragment of the trigonal prismatic species $\{[\text{Cu}_3(\text{L}^4)_3(\text{dabco})_3] \cdot 3\text{Et}_2\text{O}\}_n$. An ORTEP plot is available in the ESI.†

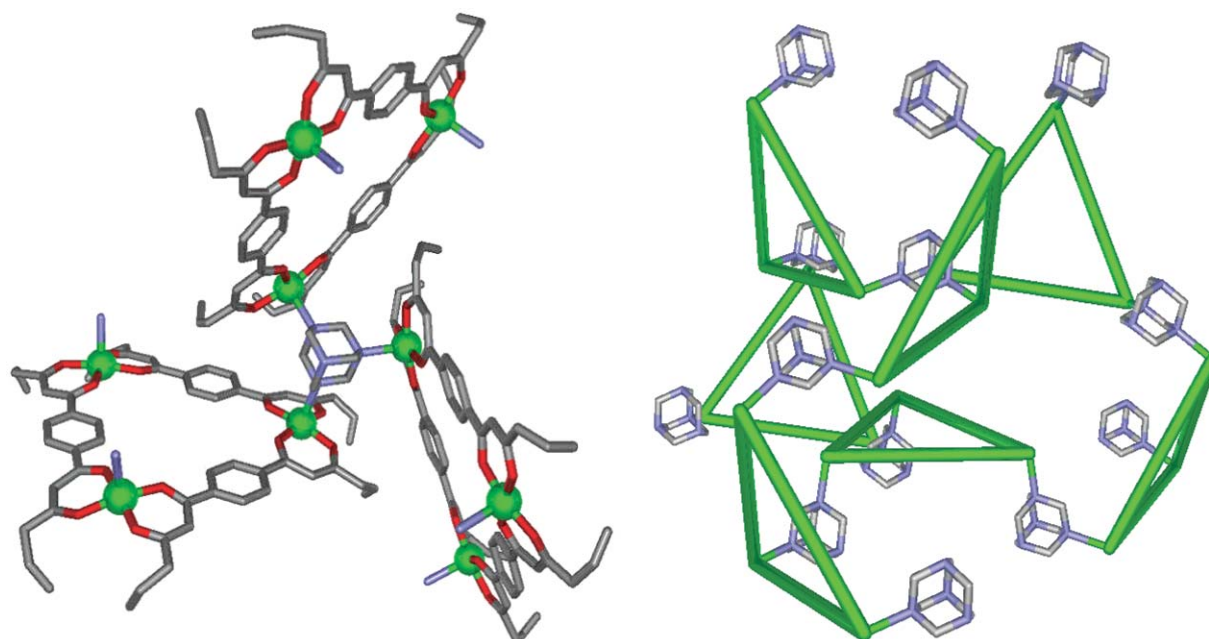


Fig. 6 Representations of fragments of the species $[\text{Cu}_3(\text{L}^3)_3(\text{hmt})]_n$. Left: view approximately down three-fold axis. Right: a portion of the three dimensional lattice with triangular metalocycles represented schematically.

may be exploited to yield a range of expanded metallo-assemblies showing unusual polymeric arrangements.

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