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Hierarchical assembly of discrete copper(II) metallo-structures from pre-assembled dinuclear (bis- β -diketonato)metallo-cycles and flexible difunctional co-ligands†‡

Jack K. Clegg,^{a,b} Feng Li,^{a,c} Katrina A. Jolliffe,^a Leonard F. Lindoy,^{*a} George V. Meehan,^d Simon Parsons,^{e,f} Peter A. Tasker^e and Fraser J. White^{e,f}

The sequential interaction of preformed $[\text{Cu}_2(\text{L}^1)_2(\text{THF})_2]$ (where H_2L^1 is 1,1-(1,3-phenylene)-bis(4,4-dimethylpentane-1,3-dione) incorporating a 1,3-phenylene linker between its two β -diketone domains) and $[\text{Cu}_2(\text{L}^4)_2]\cdot 2\text{H}_2\text{O}$ (where H_2L^4 is 1,1-(4,4'-oxybiphenylene)-bis(4,4-dimethylpentane-1,3-dione) incorporating a flexible oxybiphenylene linkage between the two β -diketone groups) with the potentially difunctional aliphatic non-planar co-ligands, *N*-methylpiperazine (mpip), *N,N'*-dimethylpiperazine (dmpip) and 1,4-thiomorpholine (thiomorph) is reported. A series of extended molecular assemblies exhibiting a range of di- and tetranuclear assemblies were obtained and their X-ray structures determined. Dinuclear $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2]\cdot 2\text{mpip}$ incorporates two 5-coordinate, square pyramidal metal centres as does tetranuclear $\{[\text{Cu}_2(\text{L}^1)_2(\text{dmpip})_2]\cdot 2\text{dmpip}$. In contrast, dinuclear $[\text{Cu}_2(\text{L}^1)_2(\text{dmpip})_4]\cdot \text{dmpip}$ and $\{[\text{Cu}_2(\text{L}^1)_2(\text{thiomorph})_4]\cdot 3\text{thiomorph}$ each contain two 5-coordinate and two 6-coordinate centres. Each of $[\text{Cu}_2(\text{L}^4)_2(\text{THF})_2]\cdot 2\text{THF}$ and $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$ incorporate only 5-coordinate metal centres, with the latter complex forming a one-dimensional hydrogen bonded ribbon-like structure directed along the crystallographic *a*-axis. In keeping with the documented tendency for the smallest, least strained assembly to form in supramolecular self-assembly processes, the incorporation of the flexible "oxy" linkage between the 4,4'-linked phenylene rings of H_2L^3 results in generation of a dinuclear $[\text{Cu}_2\text{L}_2]$ species rather than a trinuclear (triangular) $[\text{Cu}_3\text{L}_3]$ species of the type formed by the more rigid bis- β -diketonato ligand analogue in which the biphenylene rings separating the β -diketone domains are directly coupled in their 4,4' positions.

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Introduction

There has been increasing interest in the design and assembly of discrete^{1–3} and polymeric⁴ metal–organic architectures due to their often unusual properties and topologies^{5–7} as well as

their potential applications in catalysis, molecular separation and storage technologies.^{8,9} Despite considerable advances in the development of such materials, their synthesis to yield predictable multinuclear architectures still often remains a challenge.³ We, and others, have found that ligands incorporating more than one β -diketone motif react with selected metal ions to yield an array of metallo-supramolecular architectures with the products in many instances exhibiting a significant degree of predictability.^{1,3,10} Structures generated with these ligands include helicates,^{11–14} tetrahedra,^{15,16} boxes,¹⁷ capsules¹⁸ and an unprecedented universal 3-ravel;¹⁴ for example, the well defined coordination vectors of ligands $\text{L}^{1–3}$ produce neutral planar metallocyclic species of type $[\text{M}_2(\text{L}^1)_2]$ (**1**)^{11,13,19–21} $[\text{M}_3(\text{L}^2)_3]$ (**2**)^{16,22} and the larger $[\text{M}_3(\text{L}^3)_3]$ (**3**)^{23,24} upon reaction with selected divalent transition metals.

The di- and trinuclear complexes of types 1–3 have been demonstrated to act as building blocks in a hierarchical self-assembly strategy to form extended structures by reaction with suitable difunctional co-ligands.²⁵ Some of the resulting

^aSchool of Chemistry, F11, The University of Sydney, NSW 2006, Australia.

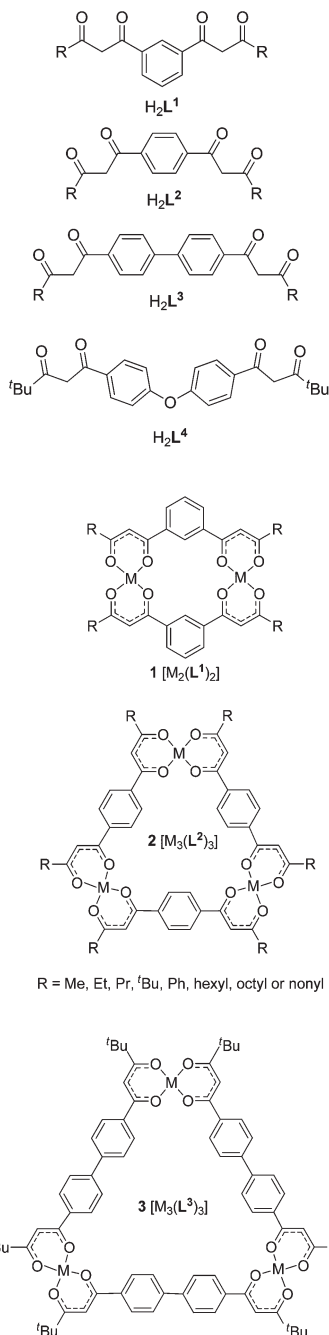
E-mail: l.lindoy@chem.usyd.edu.au

^bSchool of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane St Lucia, QLD 4072, Australia^cSchool of Science and Health, University of Western Sydney, Locked Bag 1797, Penrith, NSW 2751, Australia^dSchool of Pharmacy and Molecular Sciences, James Cook University, Townsville, QLD 4814, Australia^eSchool of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, UK^fCentre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, EH9 3JZ, UK

†Celebrating 300 years of Chemistry at Edinburgh.

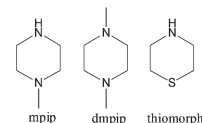
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materials have been shown to be permanently porous and capable of selective gas sorption, and their synthesis provides an alternative to conventional 'one-pot' preparations of metal-organic frameworks (MOFs). Importantly, this synthetic approach engenders a degree of predictability to the resulting architecture as the properties of the particular building block are transcribed onto the final extended assembly.²³



Here we present an extension of our previous investigations involving the interaction of co-ligands with the dinuclear copper(II) complexes of type **1** (R = ^tBu). Specifically, we now report the interaction of [Cu₂(L¹)₂(THF)₂] with the flexible aliphatic non-planar bridging ligands, *N*-methylpiperazine (mpip), *N,N'*-dimethylpiperazine (dmpip) and 1,4-thiomorpholine

(thiomorph). We also report the reaction of the extended flexible ligand, H₂L⁴,¹⁴ with copper(II) under basic conditions to yield a new metallocyclic precursor derivative. A comparative investigation of the interaction of this latter product with each of the above three co-ligands is also described.



The use of the above non-planar conformationally flexible co-ligands, while perhaps increasing the degree of uncertainty regarding the geometry of the final product,⁷ was nevertheless considered likely to allow access to further types of metallo-assemblies that may be unavailable with rigid 'linear' co-ligands of the type often employed (for example, 4,4'-bipyridine).²⁶ Further, the use of such non-planar co-ligands incorporating different donors (namely, secondary *versus* tertiary amines *versus* thioethers) also gives the potential for 'tuning' the coordination geometry adopted by the metal²⁷ and hence influence the outcome of the self-assembly process.

The aim of the present study was twofold. First, to investigate the nature of the copper(II)-containing assemblies generated with the above non-linear flexible co-ligands and secondly to probe the effect of insertion of the flexible oxy bridge between the biphenylene rings of H₂L³ (to yield H₂L⁴) on the nature of the resulting complex formed with copper(II).

Experimental

All reagents and solvents were purchased from commercial sources. Tetrahydrofuran (THF) was pre-dried over sodium wire before use. H₂L⁴ and [Cu₂(L¹)₂(THF)₂] were prepared and characterised as described previously.^{13,14}

Complex synthesis

Crystalline samples used for microanalysis were first crushed and then allowed to stand in air prior to analysis. As observed previously for related complex species, in some cases the adduct complexes rapidly lost their axial ligands on removal from the reaction solution. When this occurred, a crystal of the product was transferred quickly to the diffractometer, cooled in the cryostream, and the structure determined in the absence of further characterisation of the complex.

[Cu₂(L⁴)₂·2H₂O. H₂L⁴ (100 mg, 0.24 mmol) in dry THF (40 ml) was added to NaHCO₃ (1.0 g, 0.012 mol) in dry THF (10 ml). The mixture was stirred for 1 h before copper(II) chloride dihydrate (40 mg, 0.24 mmol) in dry THF (40 ml) was added dropwise. The mixture was stirred overnight, during which time the colour changed to deep-green. The mixture was filtered and the filtrate was allowed to undergo slow evaporation to yield plate-like green crystals. The product was washed with diethyl ether and then dried in air prior to analysis. Yield: 110 mg, 92%. Found: C, 62.14; H, 5.88. Calc. for

$C_{52}H_{56}Cu_2O_{10} \cdot 2H_2O$: C, 62.20; H, 6.02. A crystal isolated from the mother liquor and used directly for the X-ray structure determination produced a structure of composition $[Cu_2(L^4)_2(THF)_2] \cdot 2THF$.

$[Cu_2(L^1)_2(mpip)_2] \cdot mpip$, $[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot 0.5dmpip$ and $[\{Cu_2(L^1)_2\}_2(thiomorph)_4] \cdot 3thiomorph$. $[Cu_2(L^1)_2(THF)_2]$ (9.23 mg, 0.01 mmol) was dissolved in a warm solution (5 ml) of the appropriate co-ligand. The mixture was brought to reflux, filtered and allowed to cool slowly. Slow evaporation of the filtrate resulted in crystals that were used directly for the X-ray studies (see below).

$[Cu_2(L^1)_2(mpip)_2] \cdot mpip$. Yield 9.6 mg (89%), green crystals. Found: C, 60.73; H, 7.78; N, 7.84. Calc. for $C_{50}H_{72}Cu_2O_8N_4 \cdot C_5H_{12}N_2$: C, 60.92; H, 7.81; N, 7.75%. A crystal isolated from the mother liquor and used directly for the X-ray structure determination gave the composition $[Cu_2(L^1)_2(mpip)_2] \cdot 2mpip$ ($R = ^tBu$).

$[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot 0.5dmpip$. Yield 9.8 mg (95%), green crystals. Found: C, 61.83; H, 7.78; N, 6.08. Calc. for $C_{104}H_{152}Cu_4O_{16}N_8 \cdot 0.5C_6H_{14}N_2$: C, 61.79; H, 7.71; N, 6.07%. A crystal isolated from the mother liquor and used directly for the X-ray structure determination gave a composition of $[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot dmpip$ ($R = ^tBu$).

$[\{Cu_2(L^1)_2\}_2(thiomorph)_4] \cdot 3thiomorph$. A small number of unstable dark green crystals suitable for X-ray crystallography were grown by slow evaporation of the reaction mixture. These were used directly for the crystallographic study. No accurate yield was recorded or additional characterisation performed.

$[\{Cu_2(L^1)_2\}_2(dmpip)_2] \cdot dmpip \cdot 5H_2O$ and $[Cu_2(L^4)_2(mpip)_2] \cdot 2H_2O$. A 10-fold excess of the appropriate linking unit (1 mmol) was added to a warm stirred tetrahydrofuran solution (40 ml) of $[Cu_2(L^1)_2(THF)_2]$ (96 mg, 0.1 mmol) or $[Cu_2(L^4)_2] \cdot 2H_2O$ (100 mg, 0.1 mmol). The mixture was brought to reflux before cooling to room temperature and subsequent filtration. Slow evaporation of the filtrate in each case resulted in crystals suitable for X-ray analysis (see below).

$[Cu_2(L^1)_2\}_2(dmpip)_2] \cdot dmpip \cdot 5H_2O$. Yield 80 mg (90%), bright green crystals. Found: C, 58.86; H, 7.09; N, 4.33. Calc. for $C_{92}H_{124}Cu_4N_4O_{16} \cdot C_6H_{14}N_2 \cdot 5H_2O$: C, 58.89; H, 7.47; N, 4.21%. A crystal isolated from the mother liquor and used directly for the X-ray structure determination gave the composition $[\{Cu_2(L^1)_2\}_2(dmpip)_2] \cdot 2dmpip$ ($R = ^tBu$).

$[Cu_2(L^4)_2(mpip)_2] \cdot H_2O$. The small number of crystals obtained from the slow evaporation of the mother liquor were in this case highly unstable to solvent loss. These were used directly for the crystallographic study. No accurate yield was recorded or additional characterisation performed.

Crystallography

X-ray structural data for $[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot dmpip$ and $[Cu_2(L^1)_2(mpip)_2] \cdot 2mpip$ were collected with ω and ψ scans to approximately $56^\circ 2\theta$ using either a Bruker SMART 1000 diffractometer or a Bruker APEX diffractometer employing graphite-monochromated Mo-K α radiation generated from a sealed tube (0.71073 Å).²⁸ All other data were collected to approximately $56^\circ 2\theta$ with ω and ψ scans on a Bruker-Nonius APEX2-

X8-FR591 diffractometer employing graphite-monochromated Mo-K α radiation generated from a rotating anode (0.71073 Å).²⁹ Data were collected at 150 K. Multi-scan empirical absorption corrections were applied to the data set using the program SADABS.³⁰ Data integration and reduction were undertaken with SAINT and XPREP^{28,29} and subsequent computations were carried out using the WinGX-32 graphical user interface.³¹ The structures were solved by direct methods using SIR97.³² Data were refined and extended with SHELXL-97 and SHELXL-13.³³ In general, non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen and nitrogen-bound hydrogen atoms were first located in the difference Fourier map before refinement with bond length and angle restraints as required to facilitate realistic modelling. The crystallographic data are summarised in Table 1 and specific refinement details for each structure, where required, are given below.

Specific refinement details:

$[Cu_2(L^4)_2(THF)_2] \cdot 2THF$. The solvent THF molecules are disordered and were modelled over two equal occupancy positions with identical thermal parameters.

$[Cu_2(L^1)_2(mpip)_2] \cdot 2mpip$. The C(1)-containing tertiary butyl group is disordered over three positions. The phenyl rings are disordered over two positions as is the non-coordinated mpip solvent molecule. The latter required the use of bond length restraints to facilitate realistic modelling.

$[Cu_2(L^4)_2(mpip)_2] \cdot H_2O$. The C(1)-containing tertiary butyl group was modelled as disordered over two equal occupancy positions with identical thermal parameters. The water molecule is disordered over three positions. The associate hydrogen atoms could not be located in the difference Fourier map and were not modelled.

$[\{Cu_2(L^1)_2\}_2(dmpip)_2] \cdot 2dmpip$. The C(21) and C(38)-containing tertiary butyl groups are disordered over two positions. The Cu(1) centre is also slightly positionally disordered and was modelled over two positions (0.8 and 0.2 occupancy) with identical thermal parameters. In addition, there is a substantial volume of smeared electron density present in the lattice which could not be successfully modelled. This region was treated with the SQUEEZE³⁴ function of PLATON.³⁵

$[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot dmpip$. The C(40)-containing tertiary butyl group is disordered and was modelled over two positions.

$[\{Cu_2(L^1)_2\}_2(thiomorph)_4] \cdot 3thiomorph$. Both the C(18) and C(21)-containing tertiary butyl groups are disordered over two positions and each was modelled with identical thermal parameters. The encapsulated thiomorpholine ligand is disordered across a symmetry position in two equal occupancy positions.

Results and discussion

In our previous investigations we have demonstrated that a variety of nitrogen bases bind to the apical positions of the metal centres in complexes of type 1–3 to form both discrete

Table 1 Crystallographic data

Compound	[Cu ₂ (L ⁴) ₂ (THF) ₂]. 2THF	[Cu ₂ (L ¹) ₂ (mpip) ₂]. 2mpip (R = ^t Bu)	[Cu ₂ (L ⁴) ₂ (mpip) ₂]. H ₂ O	{[Cu ₂ (L ¹) ₂](dmpip) ₂ }. 2dmpip (R = ^t Bu)	{[Cu ₂ (L ¹) ₂](dmpip) ₄ }. dmpip (R = ^t Bu)	{[Cu ₂ (L ¹) ₂](thiomorph) ₄ }. 3thiomorph (R = ^t Bu)
Formula of refinement model	C ₆₈ H ₈₈ Cu ₂ O ₁₄	C ₆₀ H ₉₆ Cu ₂ N ₈ O ₈	C ₆₂ H ₈₄ Cu ₂ N ₄ O ₁₂	C ₁₀₄ H ₁₅₂ Cu ₄ N ₈ O ₁₆	C ₁₁₀ H ₁₆₆ Cu ₄ N ₁₀ O ₁₆	C ₁₀₈ H ₁₅₉ Cu ₄ N ₇ O ₁₆ S ₇
Molecular weight	1256.46	1184.52	1204.41	2024.49	2138.69	2289.99
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.9410(10)	10.3419(7)	6.9360(10)	11.2682(7)	11.3608(9)	10.9829(14)
<i>b</i> /Å	10.158(2)	10.8858(7)	11.1150(10)	14.7975(11)	14.4945(11)	16.4829(16)
<i>c</i> /Å	21.762(3)	16.9362(11)	21.390(2)	16.8090(12)	17.5171(13)	16.6407(16)
α /°	99.090(7)	93.828(4)	81.725(3)	96.891(5)	78.648(1)	103.377(7)
β /°	98.182(7)	103.808(3)	87.872(3)	90.581(4)	80.525(1)	96.601(8)
γ /°	105.622(5)	118.268(3)	75.093(3)	110.732(4)	79.962(1)	94.052(7)
<i>V</i> /Å ³	1637.5(4)	1594.32(18)	1576.9(3)	2598.1(3)	2759.3(4)	2896.5(5)
<i>D</i> _c /g cm ⁻³	1.274	1.234	1.268	1.294	1.287	1.313
<i>Z</i>	1	1	1	1	1	1
Crystal size/mm	0.15 × 0.15 × 0.1	0.75 × 0.61 × 0.4	0.38 × 0.18 × 0.05	0.30 × 0.30 × 0.05	0.40 × 0.35 × 0.30	0.30 × 0.30 × 0.25
Crystal colour	Green	Blue	Green	Green	Green	Green
Crystal habit	Block	Prism	Plate	Plate	Prism	Block
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (MoK α)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ /mm ⁻¹	0.712	0.723	0.735	0.873	0.826	0.913
<i>T</i> (SADABS) _{min,max}	0.866001, 1.0000	0.529, 0.749	0.7700, 1.0000	0.553243, 1.0000	0.826276, 1.0000	0.844953, 1.0000
2θ _{max} /°	46.65	80.28	46.79	56.56	56.81	61.04
<i>hkl</i> range	-8 8, -10 11, -24 24	-18 18, -19 17, -29 30	-7 7, -12 12, -23 23	-14 14, -19 19, -22 22	-15 14, -19 18, -23 23	-15 15, -23 23, -23 23
<i>N</i> _{obs} (<i>N</i> _{var})	19 394 (376)	60 175 (499)	18 451 (371)	50 072 (534)	27 310 (678)	10 9984 (631)
<i>N</i> _{ind} (<i>R</i> _{merge})	4654 (0.0490)	18 307 (0.0348)	4560 (0.0424)	12 681 (0.0744)	12 766 (0.0214)	17 540 (0.0559)
<i>N</i> _{obs} - (<i>I</i> > 2 σ (<i>I</i>))	3470	11 818	3723	6204	10 336	11 805
<i>R</i> ₁ - (<i>I</i> > 2 σ (<i>I</i>)), <i>wR</i> ₂ - (all)	0.0518, 0.1389	0.0563, 0.1730	0.0691, 0.1696	0.0854, 0.2741	0.0333, 0.0925	0.0524, 0.1344
GoF	1.071	1.038	1.197	1.080	1.011	1.029
Residual extrema/e Å ⁻³	-0.424, 0.707	-0.988, 0.980	-0.784, 0.856	-1.079, 1.009	-0.274, 0.430	-1.943, 1.422

and extended structures. In particular, we have found that the use of flexible co-ligands such as piperidine, 1,4-piperazine and *N*-methylmorpholine resulted in a diverse range of structures.²¹ As intimated already, this tendency likely reflects the low energetic barriers for conformer interchange available to such ligand systems.³⁶ The presence of sp³-hybridised NH amine groups also gives the possibility for such groups to act as a hydrogen bond donors.

Six new complexes were synthesised in the present study: $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2] \cdot 2\text{mpip}$, $[\{\text{Cu}_2(\text{L}^1)_2\}_2(\text{dmpip})_2] \cdot \text{dmpip} \cdot 5\text{H}_2\text{O}$, $[\{\text{Cu}_2(\text{L}^1)_2\}_2(\text{dmpip})_4] \cdot 0.5\text{dmpip}$, $[\{\text{Cu}_2(\text{L}^1)_2\}_2(\text{thiomorph})_4] \cdot 3\text{thiomorph}$, $[\text{Cu}_2(\text{L}^4)_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2] \cdot 2\text{H}_2\text{O}$.

$[\text{Cu}_2(\text{L}^1)_2(\text{THF})_2]$ was dissolved in neat hot *N*-methylpiperazine (mpip) and the solution was allowed to cool and slowly evaporate to yield large green prismatic crystals of $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2] \cdot 2\text{mpip}$ (Fig. 1). The X-ray structure of this product showed that each mpip ligand binds to a copper(II) centre through its secondary amine group, rather than *via* the more basic tertiary amine group – presumably reflecting steric influences taking precedence over electronic considerations.³⁷ Each of the metal centres is five-coordinate. The nitrogen ligands are orientated mutually *anti* to each other across the plane of the $[\text{Cu}_2(\text{L}^1)_2]$ building block.

Both the coordinated and the solvate mpip molecules are present in chair conformations in which the methyl group of each mpip occupies an equatorial position; the coordinated bases have their nitrogen-bound hydrogen orientated axially, contrasting with the free base where the corresponding proton is orientated equatorially. The orientation of the coordinated secondary amine enables it to act as an intermolecular hydrogen bond donor to the secondary amine acceptor of a *N*-methylpiperazine lattice molecule. This, in turn acts as an intermolecular hydrogen bond donor towards adjacent coordinated β -diketonato oxygen atoms. The overall arrangement of this structure is equivalent to that found in the analogous pyridine and 4-ethylpyridine derivatives if the hydrogen

bonding in the present assembly is ‘replaced’ by the corresponding π - π interactions in each of the other products.^{13,21}

The addition of *N,N'*-dimethylpiperazine (dmpip) to $[\text{Cu}_2(\text{L}^1)_2(\text{THF})_2]$ in tetrahydrofuran results in an immediate colour change from deep to bright green. Slow evaporation of the reaction solution gave plate-like green crystals. This product (Fig. 2) has five-coordinate copper(II) centres with two planar dinuclear metalocyclic units bridged by two dmpip ligands such that the overall structure is a discrete tetranuclear architecture similar to those previously reported by us using dabco and pyrazine as bridging ligands.^{13,20} However, in contrast to these previous structures, the present structure is somewhat ‘stepped’ resulting from the presence of the chair conformation of the respective bound dmpip ligands. This results in the mean planes of the two dinuclear platforms being separated by 6.35 Å – considerably less than occurs in the tetranuclear analogues incorporating ‘linear’ dabco (7.73 Å) or pyrazine (7.5 Å) as the bridging co-ligands.

Intriguingly, when neat dmpip was used as a solvent rather than the mixed dmpip-THF solvent employed in the synthesis of $[\{\text{Cu}_2(\text{L}^1)_2\}_2(\text{dmpip})_2] \cdot 2\text{dmpip}$, a different product of similar stoichiometry resulted. The X-ray analysis of this product (Fig. 3) shows that the overall structure is again a discrete tetranuclear assembly with two dinuclear platforms linked by two bridging dmpip ligands. Each of the coordinated and solvent dmpip molecules adopts a chair conformation with the methyl groups in the equatorial positions. Somewhat surprisingly, the structure contains both five- and six-coordinate copper centres. The sixth coordination site of two of the copper centres is occupied by a monodentate dmpip co-ligand. The six-coordinate copper centres (Cu(1)-N(1), 2.7916(16) Å; Cu(1)-N(3), 2.9337(15) Å) have significantly elongated axial bond lengths compared to the five-coordinate centres (Cu(2)-N(4), 2.3942(14) Å) reflecting the presence of significant Jahn-Teller distortion.

In contrast to the mpip and dmpip ligands, 1,4-thiomorpholine (thiomorph) contains two donor atom types as well as

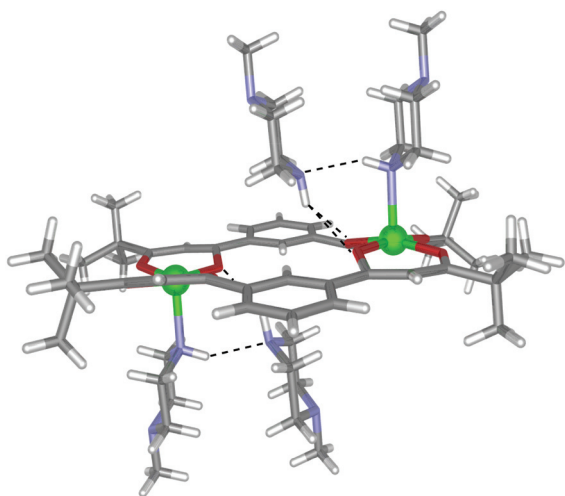


Fig. 1 Schematic representation of the X-ray structure of $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2] \cdot 2\text{mpip}$. Dashed lines represent hydrogen bonds.

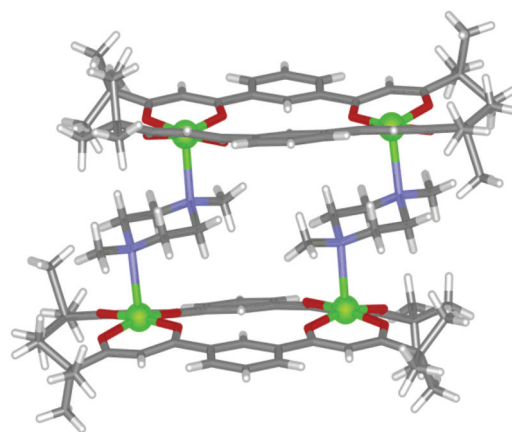


Fig. 2 Schematic representation of the X-ray structure of $[\{\text{Cu}_2(\text{L}^1)_2\}_2(\text{dmpip})_2] \cdot 2\text{dmpip}$. Disorder is removed and solvate dmpip molecules are not shown for clarity.

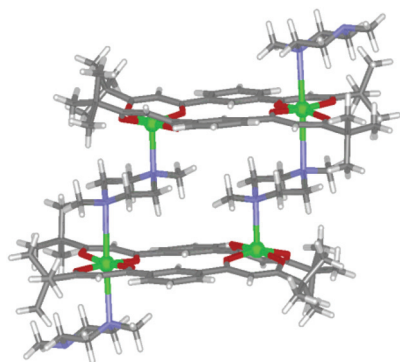


Fig. 3 Schematic representation of the X-ray structure of the second dmpip complex of stoichiometry $\{Cu_2(L^1)_2\}_2(dmpip)_4-dmpip$. The solvate dmpip molecule is not shown for clarity.

having the potential to act as both a hydrogen-bonding donor and acceptor. Without *N*-methyl groups this ligand should also experience little steric hindrance towards metal ion binding. While a thioether sulfur donor might perhaps be expected to coordinate more weakly to copper(II) than nitrogen or oxygen donor atoms, such sulfur donor binding is still well documented for copper(II).^{38–40}

Addition of thiomorph to a THF solution of $[Cu_2(L^1)_2(THF)_2]$, resulted in the formation of green crystals suitable for X-ray analysis. In contrast to the dmpip derivatives discussed above, the formation of identical crystals was also observed (and confirmed by unit cell analysis) when neat thiomorph was employed for their preparation. The resulting structure (Fig. 4) is quite similar to that obtained for $[\{Cu_2(L^1)_2\}_2(dmpip)_4] \cdot 2dmpip$.

Once again, the structure is a tetranuclear metalocycle composed of two dinuclear planar units linked by two thiomorpholine ligands. Two of the copper(II) centres are five-coordinate, while the other two are six-coordinate. Each bound apical site in the five-coordinate centres is occupied by a secondary nitrogen atom from the thiomorpholine ligand while the axial sites in the six-coordinate centres are respectively

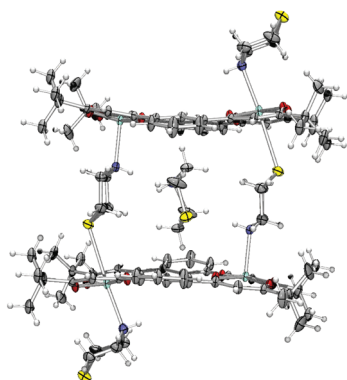


Fig. 4 ORTEP representation of the crystal structure of $[thiomorphC\{Cu_2(L^1)_2\}_2(thiomorph)_4] \cdot 2thiomorph$ shown with 50% probability ellipsoids. Regions of disorder and two thiomorph solvate molecules are removed for clarity.

bound to one thioether sulfur and one nitrogen, the latter nitrogen donor arising from a monodentate thiomorpholine molecule bound “outside” (exo) of the tetranuclear motif. All of the thiomorph molecules adopt chair conformations. The amine donors in the thiomorph bridges each coordinate through an axially directed lone pair, while the monodentate bound amines are orientated equatorially with respect to their heterocyclic ring.

Each exo co-ligand also acts as an intramolecular hydrogen bond donor towards adjacent coordinated β -diketonato oxygens as well as a intramolecular hydrogen bond donor to an uncoordinated thiomorpholine solvent molecule within the lattice. In this case the bridging amine also acts as an intermolecular hydrogen bond donor that binds to an uncoordinated thiomorpholine molecule which is encapsulated within the cavity of the tetranuclear assembly. The complex can thus be described as $[thiomorphC\{Cu_2(L^1)_2\}_2(thiomorph)_4]$. The encapsulation of the guest molecule is in keeping with the cavity within the tetranuclear structure being larger than in the corresponding structures discussed above. Namely, the two platforms are separated (mean plane–mean plane) by 7.94 Å (Cu(1)–Cu(2)) whereas, for example, the corresponding separation in $[Cu_2(L^1)_2(dmpip)_2] \cdot 2dmpip$ is 7.10 Å and 7.01 Å for $\{Cu_2(L^1)_2\}_2(dmpip)_4 \cdot dmpip$. As expected, the Cu(2)–S(1) bond length (3.1263(8) Å) is considerably elongated relative to the Cu–N bond lengths. The copper–nitrogen bond length for the six-coordinate copper centre is (Cu(2)–N(2), 2.410(2) Å) and is also longer than at the five-coordinate centre (where Cu(1)–N(1), 2.313(2) Å). All the axial bond lengths are in accord with Jahn–Teller distortion being present.

As mentioned already, L^4 , with its 4,4'-oxybiphenylene spacer, is more flexible than L^{1-3} . Reaction of H_2L^4 with copper(II) chloride in tetrahydrofuran under basic conditions initially yielded green plate-like crystals whose microanalysis corresponded to $[Cu_n(L^4)_n] \cdot nH_2O$. The X-ray structure of the tetrahydrofuran adduct, obtained by slow evaporation of the filtrate from the above preparation, is presented in Fig. 5. The complex is a discrete dinuclear metalocycle, $[Cu_2(L^4)_2(THF)_2] \cdot 2THF$, with the copper(II) ions bridged by two doubly deprotonated L^4 ligands, with each of the latter ‘bent’ about their flexible bridges. Each copper(II) centre is 5-coordinate with a square pyramidal geometry. Four β -diketonato oxygen atoms occupy the basal plane of each metal ion with an apical position being occupied by a THF molecule. The THF molecules are arranged mutually *anti* to each other across the plane of the molecule in a manner similar to that found in $[Cu_2(L^1)_2(THF)_2]$.¹³ There is a separation of 12.53 Å between the metal centres (this is ~ 5.1 Å larger than occurs in $[Cu_2(L^1)_2(THF)_2]$ (R = *t*Bu), ~ 2.5 Å larger than found in $[Cu_3(L^2)_3]$ (R = Pr)¹⁶ but ~ 2.5 Å smaller than occurs in $[Cu_3(L^3)_3]$.²³

Interestingly, incorporation of the flexible “oxy” linkage between the 4,4'-linked phenylene rings of H_2L^3 results in generation of a dinuclear $[Cu_2L_2]$ species rather than a trinuclear (triangular) $[Cu_3L_3]$ species as observed with H_2L^3 . This is in keeping with the well documented tendency (ascribed to

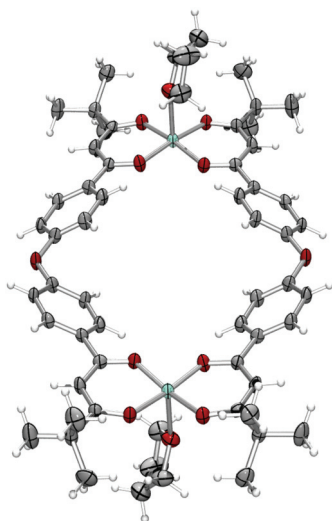


Fig. 5 ORTEP representation of the X-ray structure of $[\text{Cu}_2(\text{L}^4)(\text{THF})_2]\cdot 2\text{THF}$ shown with 50% probability ellipsoids. The solvate THF molecules have been removed for clarity.

entropy considerations)^{38,41} that supramolecular self-assembly processes often giving rise to the smallest least-strained structure where alternative structural homologues appear feasible.

Repeating the same synthetic procedure employed for $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2]\cdot 2\text{mpip}$ but with $[\text{Cu}_2(\text{L}^4)_2]\cdot 2\text{H}_2\text{O}$ in place of $[\text{Cu}_2(\text{L}^1)_2(\text{THF})_2]$ as the dinuclear precursor, resulted in the formation of highly unstable green crystals of formula $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$. The X-ray structure (Fig. 6), reveals some significant differences relative to the structure of $[\text{Cu}_2(\text{L}^1)_2(\text{mpip})_2]\cdot 2\text{mpip}$ (Fig. 1). Once again the mpip ligands are orientated mutually *anti* with respect to the plane of the dinuclear metallocycle; however, in $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$ the mpip ligand coordinates through its tertiary nitrogen rather than through the secondary amine as occurs in the previous structure.

Reflecting the increased steric demands of the tertiary amine, the Cu(1)–N(1) bond length in $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$ is elongated at 2.403(5) Å compared to that in the previous structure (2.2609(15) Å).

Again the mpip ligand adopts the expected chair conformer with the methyl group in an equatorial position and the N-bound hydrogen in the axial position hydrogen bonding to disordered water molecules in the lattice and coordinated

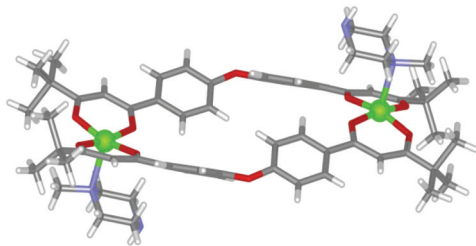


Fig. 6 Schematic representation of the X-ray structure of $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$. Disordered water molecules removed for clarity.

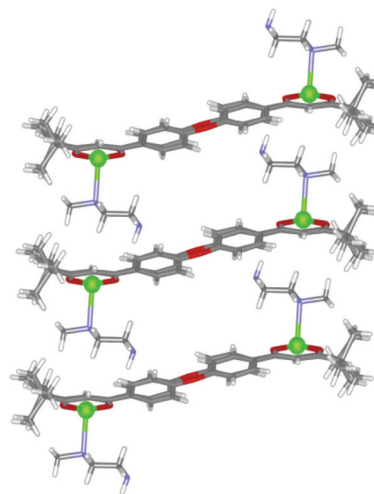


Fig. 7 Schematic representation of part of the crystal packing in the X-ray structure of $[\text{Cu}_2(\text{L}^4)_2(\text{mpip})_2]\cdot \text{H}_2\text{O}$. Disordered water molecules are removed for clarity.

oxygen atoms in adjacent complexes – resulting in the formation of a one-dimensional ribbon-like polymeric arrangement (Fig. 7) that extends along the crystallographic *a*-axis.

Conclusions

The hierarchical synthetic approach of using preformed ‘platform’ complexes for interaction with non-planar, potentially bifunctional co-ligands has resulted in the generation of a range of diverse structures incorporating dinuclear and tetranuclear copper(II) assemblies incorporating five- or six-coordinate copper centres. At least in part, the structural diversity observed in the present study reflects the respective conformational flexibility of mpip, dmpip and thiomorph, aided in turn by the mixture of donor types presented along this co-ligand series. It is also noteworthy that the introduction of a flexible ether linkage in the backbone of H_2L^3 to form H_2L^4 results in generation of a dinuclear Cu_2L_2 metallocycle rather than a trinuclear Cu_3L_3 (triangle). This result clearly exemplifies the commonly observed tendency in supramolecular chemistry for self assembly processes to generate the smallest least-strained structure that is available to the system.

Further studies on these and related metallo-assemblies, including a high pressure solid state investigation, are ongoing and will be reported in due course.

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