New discrete and polymeric supramolecular architectures derived from dinuclear (bis-β-diketonato)copper(II) metallocycles†‡

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New examples of adducts between di- (and, in one instance, tetra-) functional nitrogen ligands and planar 'platform-like' dinuclear copper(II) complexes, [Cu_2L_2], incorporating the 1,3-aryl linked bis-β-diketonato bridging ligand 1,1′-(1,3-phenylene)-bis(4,4-dimethylpentane-1,3-dione) (H_2L) have been synthesised. The X-ray structures of six adduct species are reported. The interaction of [$Cu_2(L)_2$] with the ditopic ligand aminopyrazine (apyz) yielded the sandwich-like tetranuclear species [(Cu_2L_2(apyz))$_2$]. A variable-temperature magnetochemical investigation of this product indicated weak antiferromagnetic coupling between the (five-coordinate) copper centres, mediated by the 2-amino-pyrazine linkers. An analogous structure, [(Cu_2L_2(dabco))$_2$] (dabco = 1,4-diazabicyclo[2.2.2]octane), was generated when dabco was substituted for aminopyrazine while use of 4,4′-dipyridyl sulfide (dps) and 4,4′-(1,3-xylylene)-bis(3,5-dimethylpyrazole) (xbp) as the ditopic 'spacer' ligands resulted in polymeric species of type [Cu_2L_2(dps)]$_n$ and [Cu_2L_2(xbp)]$_n$, respectively. These latter species exist as one-dimensional chain structures in which copper(II) centres on different dinuclear platforms are linked in a 'zigzag' fashion. In contrast, with 2,2′-dipyridylamine (dpa) a discrete complex of type [Cu_2L_2(dpa)$_2$] formed in which one potential pyridyl donor from each 2,2′-dipyridylamine ligand remains uncoordinated. The use of the potentially quadruply-bridging hexamethylenetetramine (hmt) ligand as the linker unit was found to give rise to an unusual two-dimensional polymeric motif of type [($Cu_2(L^2)_2$)$_3$(hmt)$_2$]$_n$. The product takes the form of a (6,3) network, incorporating triply bridging hexamethylenetetramine units.

Introduction

The design and synthesis of both discrete and extended metallosupramolecular assemblies have been the focus of a large amount of recent chemical research since such species often display interesting molecular architectures and/or unusual properties.[1] In many such studies, emphasis has been given to systems incorporating 'classical' coordination motifs.[2] For example, very many studies have involved the interaction of bi- and polypyridyl ligand derivatives with a range of metal ions.

Despite β-diketonate ligands having played a significant role in coordination chemistry for over a century,[3] their use as structural elements in metallo-supramolecular chemistry has received

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† The HTML version of this article has been enhanced with colour images.
‡ Electronic supplementary information (ESI) available: Crystallographic details, selected bond lengths and angles and ORTEP plot of the two crystallographically independent forms of {[$Cu_2(L^2)_2$(dps)]·2THF}$_n$ and the asymmetric unit of [($Cu_2(L^2)_2$)$_3$(hmt)$_2$]$_n$. See DOI: 10.1039/b606523f

considerably less attention—even so, a number of reports of such systems have appeared.[4–9]

Mononuclear bis(β-diketonato)copper(II) centres have long been known to form adducts with nitrogen donor ligands and several structures of bis(β-diketonato)copper(II) complexes with axially coordinated nitrogen-containing heterocycles have been reported.[10] For example, the ability of bis(2,4-pentanedionato)-copper(II) to form both dimeric[11] and polymeric[12] species incorporating ditopic linker units has been documented and we have also recently synthesised [(4-(dimethylamino)pyridyl)bis(2,4-pentanedionato)copper(II)] whose X-ray structure confirms that the copper centre has a five-coordinate geometry.[13]

In an early study, aryl-linked bis-β-diketones were also shown to give rise to a variety of di- and multinuclear metal complexes, including a dicopper(II) complex of type [$Cu_2(L^1)_2$].[7] More recently, interest in these and related (functionalised) derivatives has led to the investigation of the magnetic (copper(II)–lanthanide(III)) interactions occurring between neighbouring metal centres in such species[9] as well as of the luminescence properties of particular dinuclear lanthanide(III) complexes.[5] In addition, molecular triangles,[14] squares,[15] helices[6,16,17] and tetrahedra[18] have all been obtained using such bis-β-diketone ligands.

Based on an early report that coordinately unsaturated copper(II) centres in the 1,3-substituted phenylene-bis-β-diketonato derivative, [$Cu_2(L^1)_2$], form an adduct with pyridine (although, no pure product was obtained in this case due to ready loss of pyridine from the solid complex),[7] we undertook an investigation

of the interaction of both pyridine and the stronger base 4-(dimethylamino)pyridine with dinuclear $[Cu_2(L^2)_2]$ and showed by X-ray diffraction that this 'platform' complex reacts with each of these bases to yield the corresponding adduct, $[Cu_2(L^2)_2(base)_2]$.[19] In each case the bases lie on opposite sides of the dinuclear platform such that each copper(II) attains a square-pyramidal geometry. In this study we also demonstrated that use of the difunctional base 4,4'-bipyridine (bipy) gives a similar bis-adduct in which each bipyridine unit acts as a monodentate ligand.

In contrast to the behaviour of 4,4'-bipyridine, the ditopic linker pyrazine (pyz) reacts with the coordinately unsaturated copper(II) centres in the 1,3-substituted phenylene-bis-β-diketonato derivative of type $[Cu_2(L^2)_2]$ to yield a discrete tetranuclear 'dimer of dimers' of type $[(Cu_2(L^2)_2(pyz))_2]$ in which each pyrazine links adjacent copper atoms located on different dinuclear platforms.[19] This is in contrast to early published work that showed that bis(2,4-pentanedionato)copper(II) forms a one-dimensional coordination polymer with pyrazine that incorporates alternating bis(2,4-pentanedionato)copper(II) centres and bound pyrazine moieties such that each copper centre is octahedrally coordinated.[20] In the case of $[(Cu_2(L^2)_2(pyz))_2]$, the electronic requirements of each bis(β-diketonato)copper(II) centre thus appear to be met by coordination of a single pyrazine nitrogen donor to yield the observed five-coordinate geometry.[19] Nevertheless, the 'offset' difunctional ligand trans-4,4'-azopyridine (azpy) does act as an difunctional linker between copper centres but the product has a one-dimensional 'step' polymeric structure.[19]

It needs to be noted in the above context that we have also recently reported the reaction of related trinuclear copper(II)-containing triangular platforms of type $[(Cu_3L)_3]$ ($L = L^3–L^5$) with difunctional nitrogen ligands to yield interesting new polymeric species with both step-polymeric and infinite triangular prismatic geometries.[21]

We now report an extension of the above studies based on the precursor 'platform' complex $[Cu_2(L^2)_2]$ that has resulted in formation of a range of new molecular architectures related to those just discussed. The ditopic bridging units employed in these present studies were aminopyrazine (apyz), 1,4-diazabicylco[2.2.2]octane (dabco), 4,4'-dipyridyl sulfide (dps), dipyridylamine (dpa) as well as the new bis-pyrazole system, 4,4'-(1,3-xylylene)-bis(3,5-dimethylpyrazole) (xbp) (Fig. 1). The nature of the product obtained on using the potentially tetradentate linker hexamethylenetetramine was also elucidated.

Experimental

Reagents and solvents were purchased from commercial sources and were used without further purification. Tetrahydrofuran and diethyl ether were dried over sodium wire. Low resolution, positive ion electrospray ionisation mass spectra were obtained on a Finnigan LCQ-8 spectrometer with the sample dissolved in methanol–tetrahydrofuran. UV-Vis spectra were recorded on a Cary 1E spectrophotometer as Nujol mulls; 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. Magnetic susceptibility data were collected using a Quantum Design MPMS SQUID magnetometer under an applied field of 1 T.
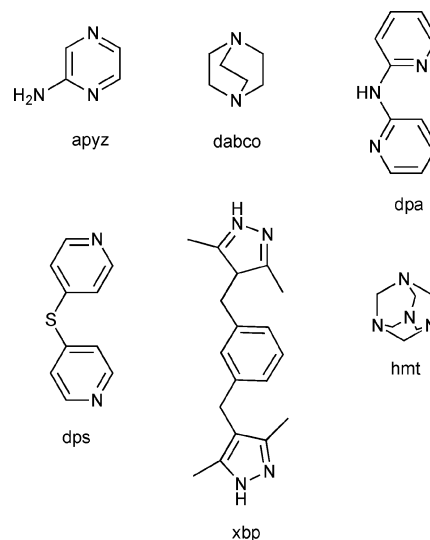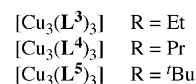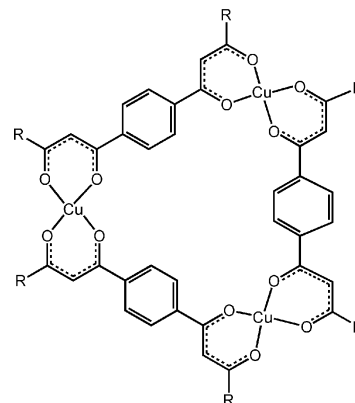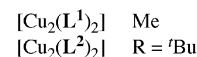

$[Cu_2(L^1)_2]$ Me
$[Cu_2(L^2)_2]$ R = ^tBu

$[Cu_3(L^3)_3]$ R = Et
$[Cu_3(L^4)_3]$ R = Pr
$[Cu_3(L^5)_3]$ R = ^tBu

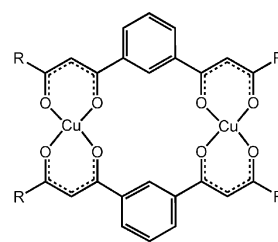**Fig. 1** Auxiliary nitrogen donor ligands employed as linker units.

The dicopper(II) complex, $[Cu_2(L^2)_2]$[19] was prepared as described previously and was dried under vacuum before use.

$[(Cu_2(L^2)_2(apyz))_2]$

A stirred solution of $[Cu_2(L^2)_2]$ (78 mg, 0.1 mmol) and aminopyrazine (10 mg, 0.1 mmol) in tetrahydrofuran (25 ml) was brought to boiling then allowed to cool. Slow diffusion of diethyl ether into the reaction mixture afforded the title compound (87 mg,

99%) as dark green crystals that were employed for the X-ray crystallographic study. Found: C, 59.85; H, 6.17; N, 4.85. Calc. for $C_{88}H_{106}Cu_4N_6O_{16}$: C, 60.12; H, 6.08; N, 4.78%. UV-Vis (solid state): 430, 600, 680 nm. FTIR (KBr): 2856, 1592, 1505, 1479, 1190, 776, 704 cm^{-1}.

[(Cu$_2$(L^2)$_2$(dabco))$_2$]

A stirred solution of [Cu$_2$(L^2)$_2$] (78 mg, 0.1 mmol) and dabco (11 mg, 0.1 mmol) in tetrahydrofuran (25 ml) was brought to boiling then allowed to cool. Slow evaporation of the reaction mixture afforded the title compound (85 mg, 95%) as bright green crystals that were employed for the X-ray crystallographic study. Found: C, 62.16; H, 6.94; N, 2.75. Calc. for $C_{92}H_{120}Cu_4N_4O_{16}$: C, 61.66; H, 6.75; N, 3.13%. ESI-MS (m/z): 1682 {M − dabco + H}$^+$, 1014 {M − dabco − [Cu$_2$(L^2)$_2$] + Na}$^+$. UV-Vis (solid state): 428, 447, 632 nm. FTIR (KBr): 2949, 1522, 1480, 1424, 1410, 1360, 1188, 774 cm^{-1}. The title complex was also prepared in a one-pot reaction from H$_2$L^2, copper(II) chloride dihydrate and dabco in tetrahydrofuran solution in the presence of sodium carbonate. Found: C, 61.55; H, 7.06; N, 3.04%.

[Cu$_2$(L^2)$_2$(dpa)$_2$]

A stirred solution of [Cu$_2$(L^2)$_2$] (78 mg, 0.1 mmol) and 2,2′-dipyridylamine (17 mg, 0.1 mmol) in tetrahydrofuran (25 ml) was brought to reflux then allowed to cool. Slow evaporation of the reaction mixture afforded the title compound as bright green crystals that were employed for the X-ray crystallographic study.

[Cu$_2$(L^2)$_2$(dps)]$_n$

A stirred solution of [Cu$_2$(L^2)$_2$] (78 mg, 0.1 mmol) and 4,4′-dipyridyl sulfide (19 mg, 0.1 mmol) in THF (10 ml) was brought to reflux and allowed to cool. Slow evaporation of the reaction mixture afforded the title compound (31 mg, 32%) as pale green crystals that were employed for an X-ray crystallographic study. Found: C, 61.63; H, 5.90; N, 3.48. Calc. for $C_{50}H_{56}Cu_2N_2O_8S$: C, 61.77; H, 5.81; N, 2.88%. UV-Vis (solid state): 447, 613 nm. FTIR (KBr): 2961, 1479, 1415, 1358, 1219, 1186, 774, 708, 685 cm^{-1}.

{[Cu$_2$(L^2)$_2$(xbp)]·1.7THF}$_n$

4,4′-(1,3-Xylylene)-bis(3,5-dimethylpyrazole) (0.11 g, 0.38 mmol) in THF (10 ml) was added to a stirred solution of [Cu$_2$(L^2)$_2$] (0.30 g, 0.38 mmol) in THF (40 ml) and the solution allowed to stand. Slow evaporation of the reaction mixture afforded the title compound as green crystals (0.25 g, 63%) that were employed for the X-ray crystallographic study. Found: C, 64.61; H, 7.11; N, 4.67. Calc. for $C_{58}H_{70}Cu_2N_4O_8$·1.7C_4H_8O: C, 64.86; H, 7.03; N, 4.67%. FTIR (KBr): 2958, 1563, 1479, 1415, 774, 490 cm^{-1}. UV-Vis (solid state): 354, 427, 606, 856 nm.

[(Cu$_2$(L^2)$_2$)$_3$(hmt)$_2$]$_n$

A solution of [Cu$_2$(L^2)$_2$] (78 mg, 0.1 mmol) in THF (3 ml) was layered upon a solution of hexamethylenetetramine (9.3 mg, 0.67 equiv) in THF (3 ml). A very small quantity of green single crystals formed within 1 week and one of these was used directly for the X-ray crystallographic study.

X-Ray structure determinations

Data for [Cu$_2$(L^2)$_2$(dpa)$_2$] were collected on a Nonius Kappa CCD with ω and ψ scans to approximately 56° 2θ at 293(2) K. Data collections were undertaken with COLLECT,[22] cell refinement with Dirax/lsq,[23] data reduction with EvalCCD.[24] Data for all other structures were collected at 150(2) K with ω scans to approximately 56° 2θ using a Bruker SMART 1000 diffractometer. Data integration and reduction were undertaken with SAINT and XPREP.[25] All structures were solved by direct methods using SIR97[26] and subsequent computations were carried out using the WinGX-32 graphical user interface.[27] Both diffractometers employed graphite-monochromated Mo-Kα radiation generated from a sealed tube (λ = 0.71073 Å). Multi-scan empirical absorption corrections were applied to the data sets using the program SADABS.[28] All structures were refined and extended with SHELXL-97.[29] In general, ordered non-hydrogen atoms with occupancies greater than or equal to 0.5 were refined anisotropically. Partial occupancy carbon atoms were refined isotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Where possible, hydrogen atoms attached to nitrogen atoms, were located in the difference Fourier map and refined with idealised geometry restraints and with isotropic thermal parameters fixed to 1.5 times the U_{eq} of the parent atom.

Crystal and structure refinement data

Crystal and structure refinement data for [(Cu$_2$(L^2)$_2$(apyz))$_2$]·3.5THF], [(Cu$_2$(L^2)$_2$(dabco))$_2$]·3.2THF·0.8H$_2$O, [Cu$_2$(L^2)$_2$(dpa)$_2$], {[Cu$_2$(L^2)$_2$(dps)]·2THF}$_n$, {[Cu$_2$(L^2)$_2$(xbp)]·2.2THF}$_n$, [(Cu$_2$(L^2)$_2$)$_3$(hmt)$_2$]$_n$ are summarised in below. ORTEP[30] depictions of the crystal structures showing the numbering schemes are provided in Figs. 2, 4–8 and S1–S2 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.‡

[(Cu$_2$(L^2)$_2$(apyz))$_2$]·3.5THF. Formula $C_{102}H_{134}Cu_4N_6O_{19.50}$, M = 2010.31, monoclinic, space group $C2/c$, a = 37.5224(17), b = 15.0477(7), c = 20.4243(9) Å, β = 117.6230(10)°, V = 10217.6(8) Å^3, D_c = 1.307 g cm^{-3}, Z = 4, crystal size 0.38 × 0.36 × 0.17 mm, colour green, habit multi-faced, temperature = 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.890 mm^{-1}, T(SADABS)$_{min,max}$ = 0.720, 0.860, $2\theta_{max}$ = 56.08°, hkl range −49 to 49, −19 to 19, −27 to 27, N = 49929, N_{ind} = 12121 (R_{merge} = 0.0400), N_{obs} = 8469 ($I > 2\sigma(I)$), N_{var} = 609, residuals: $R1(F)$ = 0.0551, $wR2(F^2)$ = 0.1769, GoF(all) = 1.023, $\Delta\rho_{min,max}$ = −0.697, 1.525 e$^-$ Å^{-3}. $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0826P)^2 + 44.0226P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[(Cu$_2$(L^2)$_2$(dabco))$_2$]·3.2THF·0.8H$_2$O. Formula $C_{104.80}H_{147.20}Cu_4N_4O_{20}$, M = 2037.23, monoclinic, space group $C2/c$, a = 37.3901(19), b = 15.7180(8), c = 20.6842(11) Å, β = 118.9230(10)°, V = 10639.8(10) Å^3, D_c = 1.272 g cm^{-3}, Z = 4, crystal size 0.58 × 0.53 × 0.31 mm, colour green, habit prism, temperature = 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.855 mm^{-1}, T(SADABS)$_{min,max}$ = 0.669, 0.767, $2\theta_{max}$ = 56.66°, hkl range −48 to 49, −20 to 20, −26 to 26, N = 51049, N_{ind} = 12554 (R_{merge} = 0.0268),

$N_{obs} = 9650$ ($I > 2\sigma(I)$), $N_{var} = 579$, residuals $R1(F) = 0.0607$, $wR2(F^2) = 0.1900$, GoF(all) = 1.024, $\Delta\rho_{min,max} = -0.743$, 1.202 e$^-$ Å^{-3}. $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0976P)^2 + 50.2320P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[Cu$_2$(L^2)$_2$(dpa)$_2$]. Formula C$_{60}$H$_{66}$Cu$_2$N$_6$O$_8$, $M = 1126.29$, triclinic, space group $P\bar{1}$, $a = 9.856(1)$, $b = 10.7020(9)$, $c = 14.693(1)$ Å, $\alpha = 96.408(9)$, $\beta = 90.624(8)$, $\gamma = 115.561(6)°$, $V = 1386.4(2)$ Å^3, $D_c = 1.349$ g cm^{-3}, $Z = 1$, crystal size 0.42 × 0.37 × 0.24 mm, colour green, habit plate, temperature = 293(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.827 mm^{-1}, T(SADABS)$_{min,max}$ = 0.7226, 0.8262, $2\theta_{max} = 52.80°$, hkl range -11 to 10, -12 to 12, -18 to 16, $N = 18019$, $N_{ind} = 4502$ ($R_{merge} = 0.0189$), $N_{obs} = 3878$ ($I > 2\sigma(I)$), $N_{var} = 349$, residuals $R1(F) = 0.0321$, $wR2(F^2) = 0.0855$, GoF(all) = 1.054, $\Delta\rho_{min,max} = -0.466$, 0.651 e$^-$ Å^{-3}. $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 1.2027P]$ where $P = (F_o^2 + 2F_c^2)/3$.

{[Cu$_2$(L^2)$_2$(dps)]·2THF}$_n$. Formula C$_{58}$H$_{72}$Cu$_2$N$_2$O$_{10}$S, $M = 1116.32$, triclinic, space group $P\bar{1}$, $a = 10.4190(9)$, $b = 15.5925(14)$, $c = 18.4105(16)$ Å, $\alpha = 99.2710(10)$, $\beta = 102.7000(10)$, $\gamma = 90.1040(10)°$, $V = 2877.5(4)$ Å^3, $D_c = 1.288$ g cm^{-3}, $Z = 2$, crystal size 0.60 × 0.38 × 0.24 mm, colour green, habit prism, temperature = 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.832 mm^{-1}, T(SADABS)$_{min,max}$ = 0.616, 0.819, $2\theta_{max} = 56.72°$, hkl range -13 to 13, -20 to 20, -24 to 24, $N = 27969$, $N_{ind} = 13270$ ($R_{merge} = 0.0311$), $N_{obs} = 8541$ ($I > 2\sigma(I)$), $N_{var} = 618$, residuals $R1(F) = 0.0668$, $wR2(F^2) = 0.1988$, GoF(all) = 1.032, $\Delta\rho_{min,max} = -0.745$, 1.062 e$^-$ Å^{-3}. $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.0867P)^2 + 5.0591P]$ where $P = (F_o^2 + 2F_c^2)/3$.

{[Cu$_2$(L^2)$_2$(xbp)]·2.2THF}$_n$. Formula C$_{66.80}$H$_{87.60}$Cu$_2$N$_4$O$_{10.20}$, $M = 1236.89$, triclinic, space group $P\bar{1}$, $a = 10.285(1)$, $b = 11.104(2)$, $c = 15.772(2)$ Å, $\alpha = 90.096(2)$, $\beta = 100.647(2)$, $\gamma = 100.187(2)°$, $V = 1741.2(4)$ Å^3, $D_c = 1.180$ g cm^{-3}, $Z = 1$, crystal size 0.48 × 0.31 × 0.10 mm, colour green, habit plate, temperature = 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.666 mm^{-1}, T(SADABS)$_{min,max}$ = 0.7392, 0.9395, $2\theta_{max} = 56.70°$, hkl range -13 to 13, -14 to 14, -20 to 20, $N = 17455$, $N_{ind} = 14663$ ($R_{merge} = 0.0205$), $N_{obs} = 11213$ ($I > 2\sigma(I)$), $N_{var} = 732$, residuals $R1(F) = 0.0670$, $wR2(F^2) = 0.1971$, GoF(all) = 1.025, $\Delta\rho_{min,max} = -0.386$, 1.343 e$^-$ Å^{-3}. $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.1327P)^2 + 0.1540P]$ where $P = (F_o^2 + 2F_c^2)/3$.

[(Cu$_2$(L^2)$_2$)$_3$(hmt)$_2$]$_n$. Formula C$_{66}$H$_{84}$Cu$_3$N$_4$O$_{12}$, $M = 1316.0472$, trigonal, space group $P\bar{3}$, $a = 18.6380(5)$, $b = 18.6380(5)$, $c = 11.5817(6)$ Å, $\gamma = 120.00°$, $V = 3484.2(2)$ Å^3, $D_c = 1.254$ g cm^{-3}, $Z = 2$, crystal size 0.48 × 0.44 × 0.13 mm, colour green, habit plate, temperature = 150(2) K, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 0.965 mm^{-1}, T(SADABS)$_{min,max}$ = 0.768, 0.882, $2\theta_{max} = 56.66°$, hkl range -24 to 24, -24 to 24, -14 to 14, $N = 34505$, $N_{ind} = 5639$ ($R_{merge} = 0.0426$), $N_{obs} = 4730$ ($I > 2\sigma(I)$), $N_{var} = 262$, residuals $R1(F) = 0.0451$, $wR2(F^2) = 0.1707$, GoF(all) = 1.236, $\Delta\rho_{min,max} = -0.285$, 1.477 e$^-$ Å^{-3}. $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum(wF_c^2)^2)^{1/2}$ all reflections; $w = 1/[\sigma^2(F_o^2) + (0.1013P)^2 + 0.9839P]$ where $P = (F_o^2 + 2F_c^2)/3$.

CCDC reference numbers 606851–606856.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606523f

Results and discussion

New examples of both discrete and polymeric adducts between di-functional nitrogen ligands (and, in one instance, a potentially tetra-functional ligand) and the planar 'platform-like' dinuclear copper(II) complex, [Cu$_2$(L^2)$_2$], have been synthesised. The synthesis of these mixed-ligand species was performed by heating a stirred solution of the dinuclear metal complex in tetrahydrofuran with the appropriate difunctional (or in one case polyfunctional) heterocyclic base. In all cases the solid state structures of the respective complexes were determined by single-crystal X-ray diffraction.

Discrete species derived from [Cu$_2$(L^2)$_2$]

The new discrete complexes [((Cu$_2$(L^2)$_2$(apyz))$_2$], [((Cu$_2$(L^2)$_2$(dpa))$_2$] and [((Cu$_2$(L^2)$_2$(dabco))$_2$] were isolated during the course of present study. For the first of these a parallel experiment to that reported earlier by us for pyrazine[19] was carried out in which the related linker aminopyrazine was substituted for pyrazine. The amino functionality in aminopyrazine introduces the possibility that coordination and hydrogen bonding might act cooperatively to stabilise the expected sandwich like product. Reaction of equimolar amounts of aminopyrazine and [Cu$_2$(L^2)$_2$] in tetrahydrofuran and subsequent cooling and diffusion of diethyl ether into the reaction mixture resulted in the crystallisation of a dark green product. The single-crystal X-ray study revealed the structure to be analogous to that of the corresponding pyrazine derivative;[19] with formation of the [2 + 2] metallocycle shown in Fig. 2. The complex has crystallographic inversion symmetry and the dinuclear subunits are somewhat distorted from planarity, with the offset linker units causing the five-coordinate copper(II) ions to lie out of the mean planes of the dinuclear components. The amino hydrogen atoms were not evident in the difference Fourier map
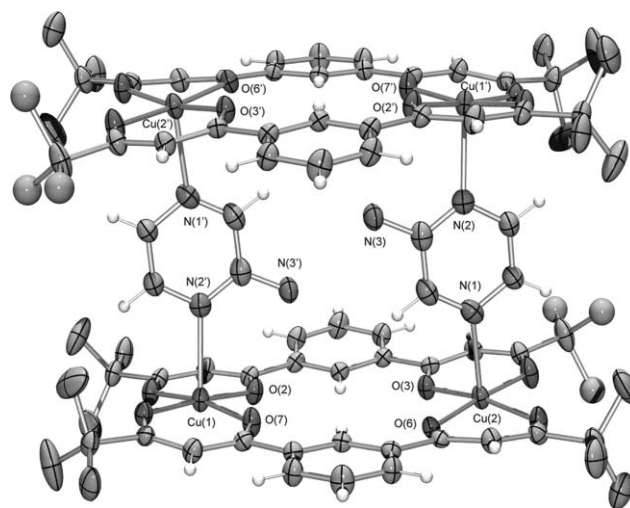
Fig. 2 ORTEP plot of [(Cu$_2$(L^2)$_2$(apyz))$_2$]·3.5THF shown with 50% probability ellipsoids. Regaons of disorder, solvate molecules and *tert*-butyl hydrogens are omitted for clarity.

and as such it is not possible to definitively define their positions. However, the distance between each amino nitrogen atom and its closest β-diketonate oxygen (N⋯O) is 3.08 Å is in keeping with a hydrogen bond being present between these atoms. Such an interaction would serve to provide a positive contribution to the overall stability of the tetranuclear species.

An investigation of the magnetic properties of $[(Cu_2(L^2)_2(apyz))_2]$ was undertaken in order to probe the possibility of magnetic interaction between pairs of copper(II) ions. Plots of reciprocal magnetic susceptibility and magnetic moment, per tetranuclear complex vs. temperature, are given in Fig. 3.
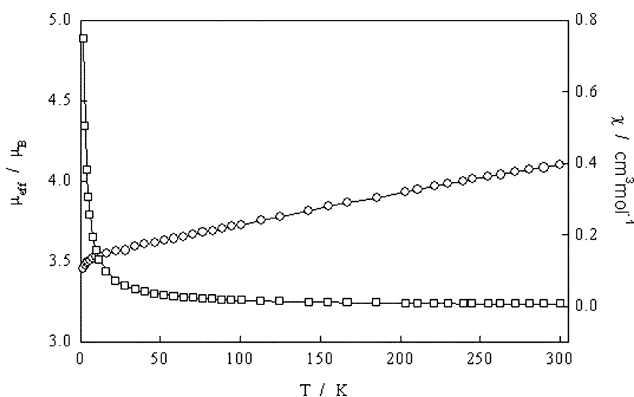

Fig. 3 Plots of reciprocal magnetic susceptibility and magnetic moment per tetranuclear complex vs. temperature.

The magnetic moment was found to decrease gradually from 4.1 μ_B (2.05 μ_B per Cu^{2+}) at 300 K to reach 3.6 μ_B at 10 K. This decreases more rapidly to 3.45 μ_B (1.72 μ_B per Cu^{2+}) at 4.2 K. This behaviour is indicative of the copper(II) centres showing weak antiferromagnetic coupling, mediated by the aminopyrazine linker units. It is noted that no coupling occurs across the benzene rings in each dinuclear component whereas, in general, pyrazine rings are weak spin couplers.[31] The overall interaction is particularly weak owing to each of the copper(II) ions being linked via a d_{z^2} orbital to the aminopyrazine bridges, while in bis-β-diketonato)copper(II) complexes the spin density typically resides in the $d_{x^2-y^2}$ orbital.[32]

In light of the successful incorporation of aminopyrazine into the above tetranuclear architecture an attempt to substitute another linker, the D_{3h}-symmetric species dabco, was undertaken. The synthetic procedure employed for $[(Cu_2(L^2)_2(pyz))_2]$ was again repeated using dabco in place of pyrazine to yield a pale green product. An X-ray crystallographic study of this product (Fig. 4) confirmed the presence of the expected tetranuclear sandwich structure, with the separation between the dinuclear building blocks being 7.26 Å.

Both dinuclear platforms in this structure are approximately planar resulting in four symmetrically arranged five-coordinate copper(II) centres. The complex has crystallographic inversion symmetry and the dabco units are rotationally disordered with alternate occupancies in 'meshed' positions.

As our studies with these dinuclear and related trinuclear platform-like complexes has so far largely featured linear (nitrogen-containing) linkers,[19,21] it was of interest to explore what effects the use of non-linear bridging ligands would have on the geometries of such species.
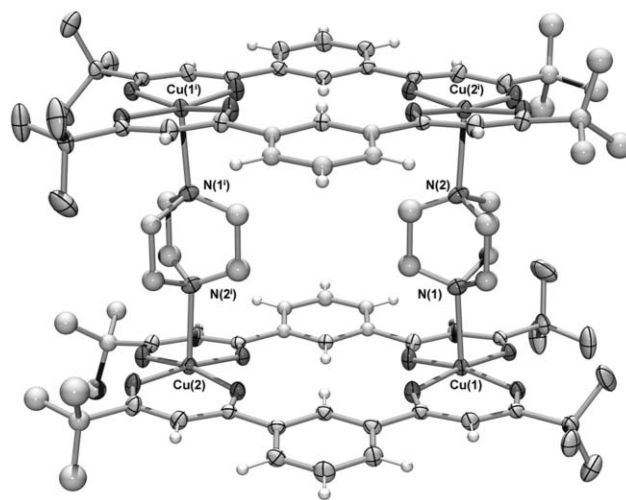
Fig. 4 ORTEP plot of $[(Cu_2(L^2)_2(dabco))_2]\cdot3.2THF\cdot0.8H_2O$ shown with 50% probability ellipsoids. Solvate molecules, regions of disorder and *tert*-butyl bound hydrogen atoms are omitted for clarity.

Unlike the linear auxiliary ligands discussed above, 2,2'-dipyridylamine (dpa) and 4,4'-dipyridyl sulfide (dps) are both non-linear and flexible. The former has been shown to act as a bidentate chelating ligand towards copper(II), palladium(II) and platinum(II) forming discrete complexes[33] and also, more recently, as a non-linear bridging ligand towards silver(I)[34] while the latter has been used as a bridging ligand between metal centres in a number of studies.[35]

Reaction of $[Cu_2(L^2)_2]$ with 2,2'-dipyridylamine in a 1:1 ratio in tetrahydrofuran yielded a bright green solution which on slow evaporation gave crystals suitable for X-ray analysis. The structure determination again showed that the dinuclear 'platform' has crystallographic inversion symmetry and is approximately planar with two 2,2'-dipyridylamine ligands coordinated *trans* with respect to each other; each copper(II) ion is again present in a square-based pyramidal arrangement (Fig. 5). Somewhat surprisingly, only one of the 2,2'-dipyridylamine pyridyl rings was found to bind to a
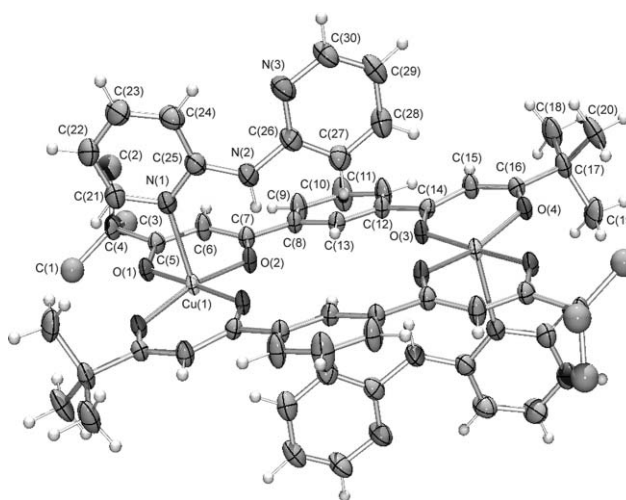

Fig. 5 ORTEP plot of $[(Cu_2(L^2)_2(dpa))_2]$ shown with 50% probability ellipsoids. Regions of disorder and disordered *tert*-butyl bound hydrogen atoms are omitted for clarity.

copper centre despite the presence of an equimolar amount of 'platform' in solution. The non coordination of the second pyridyl nitrogen is presumably influenced by the presence of a stabilising phenylene hydrogen to nitrogen interaction between the hydrogen bound to C(24) and the free electron density of the uncoordinated pyridyl nitrogen (N(3)), with the separation distance being 2.32 Å. Related to this is the observed planarity of the 2,2′-dipyridylamine ligand and the trigonal-planar arrangement of the central nitrogen (N(2)), reflecting the presence of resonance involving the pyridyl rings. There are also offset face-to-face π–π interactions present at a distance of 3.29 Å (C(23)–C(23)) between adjacent 2,2′-dipyridylamine ligands in the lattice.

One-dimensional polymeric species derived from [Cu₂(L²)₂]

The synthetic procedure employed for $[(Cu_2(L^2)_2(apyz))_2]$ was repeated using flexible 4,4′-dipyridyl sulfide (dps) instead of rigid aminopyrazine. Of course, the use of flexible components for forming supramolecular architectures typically introduces additional unpredictability into the structure adopted by such systems. Nevertheless, as pointed out elsewhere, incorporation of flexibility into supramolecular systems may allow access to topologies that cannot be attained with fully rigid systems.[36]

The X-ray structure of the green crystalline product obtained with 4,4′-dipyridyl sulfide was determined; there are two crystallographically independent forms of the product $\{[Cu_2(L^2)_2(dps)]\cdot 2THF\}_n$ (each with crystallographic inversion symmetry). The observed step-polymeric structure (Fig. 6) consists of one-dimensional chains that incorporate alternate dinuclear complex and linker units in a 1 : 1 ratio. As for the related structure incorporating *trans*-4,4′-azopyridine,[19] each dinuclear unit is attached to two adjacent units by bridging 4,4′-dipyridyl sulfide linkers which project on opposite sides of the dicopper(II) platform in a mutually *trans* fashion. The 4,4′-dipyridyl sulfide units are bound in the axial sites of each copper(II) centre such that square-pyramidal coordination once again results. The pyridyl rings subtend ∼101° angles at the sulfur atoms.
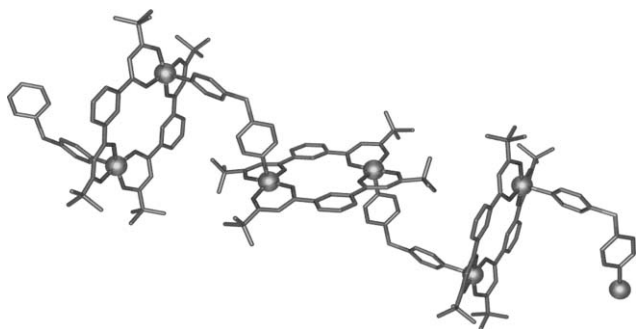
Fig. 6 Schematic representation of a fragment of a one-dimensional chain of $\{[Cu_2(L^2)_2(dps)]\cdot 2THF\}_n$. Solvate molecules are omitted for clarity. An ORTEP plot is presented as Fig. S1 in the ESI.‡

Flexible 4,4′-(1,3-xylylene)-bis(3,5-dimethylpyrazole) (xbp) was also chosen as a linker. This difunctional reagent is readily synthesised from H₂L²,[37] and has its nitrogen donor atoms separated by ∼13 Å, compared with ∼9 Å for 4,4′-dipyridyl sulfide (distances estimated from the corresponding X-ray structures).

This ditopic unit also has additional degrees of freedom compared to 4,4′-dipyridyl sulfide and the presence of the NH groups also adds further potential for hydrogen bond formation.

A related synthetic procedure to that mentioned above using 4,4′-(1,3-xylylene)-bis(3,5-dimethylpyrazole) as the linker yielded a pale green crystalline product. The structure of this product is polymeric with the bis-pyrazole units linking [Cu₂(L²)₂] units in a stepwise manner through square-pyramidal copper(II) centres (Fig. 7). The N(2) and N(3) atoms are involved in hydrogen bonding with tetrahydrofuran molecules, while a further tetrahydrofuran molecule is present in the crystal lattice.

### A two-dimensional polymeric species derived from [Cu₂(L²)₂]

In the final system investigated the effect of incorporating a new linker unit that is potentially capable of bridging more than two dinuclear components was probed. To this end, hexamethylenetetramine (hmt) was employed. The latter has four tetrahedrally oriented nitrogen donor atoms and was recently shown by us to produce chiral structures on reaction with triangular building blocks of type $[Cu_3(L^3)_3]$.[21] Mixing hexamethylenetetramine and the dinuclear complex $[Cu_2(L^2)_2]$ in tetrahydrofuran in a 2:3 molar ratio yielded bright green crystals whose X-ray structure (Fig. 8) shows a two-dimensional network in which the hexamethylenetetramine ligand acts as triply-bridging unit.

The structural fragment given on the left of Fig. 8 propagates with crystallographic three-fold symmetry with that axis passing through the unbound nitrogen atom to give a propeller-like arrangement. Each dinuclear component incorporates two five-coordinate copper(II) centres, with one hexamethylenetetramine linker coordinated on either side of the mean plane of the platform. Each layer in the network may be viewed as being composed of fused chiral hexagons, each hexagon being defined by six dinuclear platforms and six hexamethylenetetramine linker units forming infinite two-dimensional sheets which propagate in the *ab* plane. When viewed from the side, these hexagons are not planar but adopt a conformation similar to that of a cyclohexane 'chair'. Overall, the network is achiral and the hexagonal arrangement depicted on the right of Fig. 8 is best described as a (6,3) network structure.[38] Perhaps surprisingly, there appears to be essentially (see below) no residual solvent present in the central cavities of the hexagons, which extend along the *c* axis as channels running the length of the crystal. The SQUEEZE function of PLATON[39] estimated the volume of these channels to be 482.4 Å³ per unit cell or 13.8% of the total volume of the latter. However, a very small amount of residual electron density (which was estimated by PLATON to be a mere 57 e⁻ Å⁻³) was associated with the channels. Since no sensible model could be found to account for this electron density, it was not modelled-its presence may possibly reflect the existence of some disordered nitrogen molecules (perhaps originating from the cryostream) in the channels or, alternatively, the presence of a very small amount of (extremely) disordered solvent.

Concluding remarks

The above study demonstrates the use of ditopic nitrogen donor linking units for the formation of extended neutral
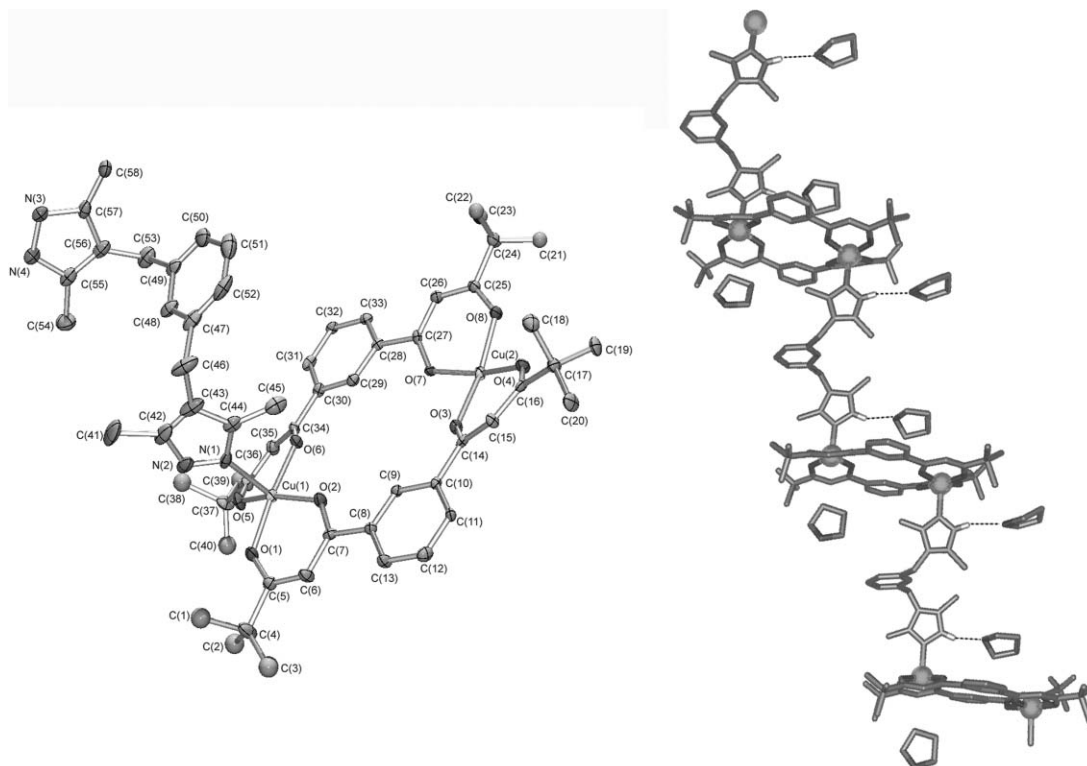
Fig. 7 ORTEP plot of $\{[Cu_2(L^2)_2(xbp)]\cdot 2.2THF\}_n$, shown with 50% probability ellipsoids (left). Solvate molecules, regions of disorder and hydrogen atoms have been omitted for clarity. Schematic representation of a fragment of a one-dimensional chain (right).
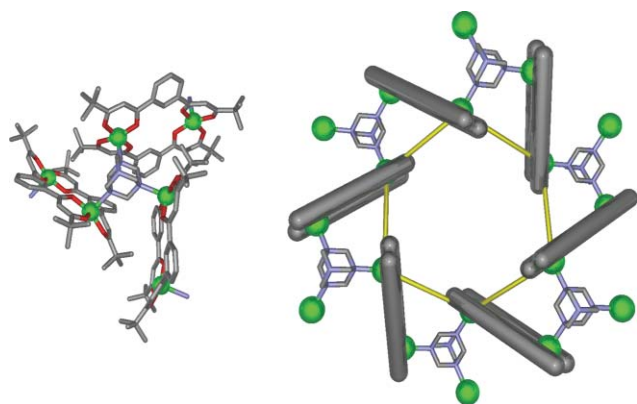
Fig. 8 Schematic representation of a fragment of $[(Cu_2(L^2)_2)_3(hmt)_2]_n$ (left) and a representation of the two-dimensional structure (right). An ORTEP plot is presented as Fig. S2 in the ESI.‡

bis-β-diketonate copper(II) systems which adopt both discrete and polymeric structures. Hexamethylenetetramine, when substituted for a ditopic linker, acted as a tritopic linker to yield an extended structure containing significant pore volume. Overall, the synthesis of these unusual di-, tetra- and multinuclear products serves to illustrate the potential of using well-defined, two-dimensional building blocks incorporating coordinately unsaturated metal centres as precursors for the preparation of new (uncharged) metallosupramolecular architectures.

Acknowledgements

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