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

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Specific details for [(Cu$_2$(L^2)$_2$(apyz))$_2$]·3.5(THF)]

The amine groups on the azpy ligands are disordered over two positions with 0.8 and 0.2 occupancies respectively. The hydrogen atoms on these groups could not be located in the Fourier difference map. The THF solvent molecules in the structure are disordered. The O(1TA) containing molecule was modelled with 0.4 occupancies, the O(1TB) containing molecule with 0.6 occupancies, the O(2T) containing molecule was modelled

with 0.5 occupancies and the O(3T) was modelled with 0.25 occupancies, bringing the

total to 3.5 THF molecules per 'dimer or dimers'. Bond length restraints were necessary

to facilitate realistic geometries. Despite careful treatment larger than ideal U_{eq} ratios

resulted. This and the non-integer number of solvent molecules present in the structure is

presumably due to solvent loss during the mounting process. One tertiary butyl group is

rotationally disordered and was modelled over three positions with a total occupancy of

1.

Table S1. Selected bond lengths (Å) and angles (°)for $[(Cu_2(L^2)_2(apyz))_2] \cdot 3.5(THF)]$

N(1)	Cu(2)	2.355(3)			
N(2)	Cu(1)[1]	2.358(3)	O(1)	Cu(1)	1.933(2)
O(2)	Cu(1)	1.922(2)	O(3)	Cu(2)	1.923(2)
O(4)	Cu(2)	1.922(2)	O(5)	Cu(2)	1.923(2)
O(6)	Cu(2)	1.928(2)	O(7)	Cu(1)	1.933(2)
O(8)	Cu(1)	1.917(2)	Cu(1)	N(2)[1]	2.358(3)
O(8)	Cu(1)	O(2)			175.37(11)
O(8)	Cu(1)	O(1)			86.48(10)
O(2)	Cu(1)	O(1)			92.74(10)
O(8)	Cu(1)	O(7)			92.63(10)
O(2)	Cu(1)	O(7)			87.25(10)
O(1)	Cu(1)	O(7)			168.80(12)
O(8)	Cu(1)	N(2)[1]			93.02(11)
O(2)	Cu(1)	N(2)[1]			91.58(11)
O(1)	Cu(1)	N(2)[1]			92.58(11)
O(7)	Cu(1)	N(2)[1]			98.62(12)
O(4)	Cu(2)	O(3)			92.99(10)
O(4)	Cu(2)	O(5)			86.01(11)
O(3)	Cu(2)	O(5)			168.72(12)
O(4)	Cu(2)	O(6)			175.78(12)
O(3)	Cu(2)	O(6)			88.31(10)
O(5)	Cu(2)	O(6)			91.93(10)
O(4)	Cu(2)	N(1)			95.14(12)
O(3)	Cu(2)	N(1)			97.15(11)
O(5)	Cu(2)	N(1)			94.13(12)
O(6)	Cu(2)	N(1)			88.67(11)

Symmetry Operators

(1) -x+1/2, -y+1/2, -z

Specific details for [(Cu$_2$(L^2)$_2$(dabco))$_2$]·3.2(THF)·0.8(H$_2$O)

The dabco ligands are rotationally disordered over two positions and were modelled with

a total occupancy of 1.   The O(1T) containing THF solvent molecule was modelled with

0.2 occupancy and two water molecules of total occupancy 0.8 were modelled in the

vicinity of this molecule. The hydrogen atoms on the water molecules could not be

located in the Fourier difference map and were not modelled. The phenyl ring is

disordered over two positions with a total occupancy of 1. One tertiary butyl group is

rotationally disordered and was modelled over two positions with a total occupancy of 1.

Bond length and angle restraints, including a FLAT command, were necessary to

facilitate realistic geometries in regions of disorder.

Table S2. Selected bond lengths (Å) and angles (°) for
[(Cu$_2$(L^2)$_2$(dabco))$_2$]·3.2(THF)·0.8(H$_2$O)

Cu(1)	O(6)	1.930(2)	Cu(1)	O(2)	1.930(2)
Cu(1)	O(5)	1.934(2)	Cu(1)	O(1)	1.939(2)
Cu(1)	N(1)	2.347(3)	Cu(2)	O(3)	1.931(2)
Cu(2)	O(7)	1.931(2)	Cu(2)	O(8)	1.932(3)
Cu(2)	O(4)	1.940(2)	Cu(2)	N(2)[1]	2.337(3)

O(6)	Cu(1)	O(2)	87.80(10)
O(6)	Cu(1)	O(5)	91.82(10)
O(2)	Cu(1)	O(5)	172.22(11)
O(6)	Cu(1)	O(1)	166.82(11)
O(2)	Cu(1)	O(1)	91.93(10)
O(5)	Cu(1)	O(1)	86.67(10)
O(6)	Cu(1)	N(1)	95.72(11)
O(2)	Cu(1)	N(1)	93.29(11)
O(5)	Cu(1)	N(1)	94.48(11)
O(1)	Cu(1)	N(1)	97.45(11)
O(3)	Cu(2)	O(7)	87.81(10)
O(3)	Cu(2)	O(8)	166.74(12)
O(7)	Cu(2)	O(8)	91.88(10)

O(3)	Cu(2)	O(4)	91.79(10)
O(7)	Cu(2)	O(4)	172.39(12)
O(8)	Cu(2)	O(4)	86.76(11)
O(3)	Cu(2)	N(2)[1]	95.63(11)
O(7)	Cu(2)	N(2)[1]	93.35(11)
O(8)	Cu(2)	N(2)[1]	97.62(11)
O(4)	Cu(2)	N(2)[1]	94.26(12)

Symmetry Operator
(1) -x+1/2, -y+1/2, -z

Specific details for [Cu₂(L²)₂(dpa)₂]

One of the tertiary butyl groups is rotationally disordered and was modelled over two positions with a total occupancy of 1. Despite the acceptable R factor of this structure the completeness is low. Initial indications suggested that the crystal was of higher symmetry and data was collected in a monoclinic space group rather than triclinic. More than 18000 reflections were collected, however, completeness to 50° 2θ is less than ideal. Unfortunately, when this was notice the opportunity had passed for recollection. The data/parameter ratio is still greater than 11. A reasonable amount of confidence can be had in the structure presented.

Table S3. Selected bond lengths (Å) and angles (°) for [Cu₂(L²)₂(dpa)₂]

O(1)	Cu(1)	1.9288(15)			
O(2)	Cu(1)	1.9239(15)	O(3)	Cu(1)[1]	1.9239(15)
O(4)	Cu(1)[1]	1.9284(15)	N(1)	Cu(1)	2.352(2)
Cu(1)	O(3)[1]	1.9239(15)	Cu(1)	O(4)[1]	1.9283(15)

O(3)[1]	Cu(1)	O(2)	85.95(6)
O(3)[1]	Cu(1)	O(4)[1]	92.76(6)
O(2)	Cu(1)	O(4)[1]	165.68(7)
O(3)[1]	Cu(1)	O(1)	176.73(7)
O(2)	Cu(1)	O(1)	92.69(7)
O(4)[1]	Cu(1)	O(1)	87.83(7)
O(3)[1]	Cu(1)	N(1)	92.95(7)
O(2)	Cu(1)	N(1)	101.95(7)
O(4)[1]	Cu(1)	N(1)	92.36(7)
O(1)	Cu(1)	N(1)	90.24(7)

Symmetry Operator

(1) -x, -y, -z

Specific details for $\{[Cu_2(L^3)_2(bipy)]\cdot 5(DCM)\}_n$

Each of the DCM molecules is disordered and is modelled over two positions each with a

total occupancy of 1. The large residual peaks in close proximity to the copper(II) ion is

presumably due to inadequate absorption correction due to the large crystal size rather

than inadequate modelling.

**Table S4.** Selected bond lengths (Å) and angles (°) for $\{[Cu_2(L^3)_2(bipy)]\cdot 5(DCM)\}_n$

N(1)	Cu(1)	2.314(4)			
O(1)	Cu(1)	1.909(4)	O(2)	Cu(1)	1.931(4)
O(3)	Cu(1)[1]	1.924(4)	O(4)	Cu(1)[1]	1.917(4)
Cu(1)	O(4)[1]	1.917(4)	Cu(1)	O(3)[1]	1.924(4)
O(1)	Cu(1)	O(4)[1]			87.49(16)
O(1)	Cu(1)	O(3)[1]			173.92(15)
O(4)[1]	Cu(1)	O(3)[1]			91.10(16)
O(1)	Cu(1)	O(2)			91.37(15)
O(4)[1]	Cu(1)	O(2)			165.31(16)
O(3)[1]	Cu(1)	O(2)			88.50(16)
O(1)	Cu(1)	N(1)			92.42(15)
O(4)[1]	Cu(1)	N(1)			102.14(16)
O(3)[1]	Cu(1)	N(1)			93.66(15)
O(2)	Cu(1)	N(1)			92.54(15)

Symmetry Operator
(1) -x+1/2, -y+1/2, -z

Specific details for {[Cu$_2$(L^2)$_2$(dps)]·2(THF)}$_n$

Three of the four tertiary butyl groups are rotationally disordered and were modelled in

two positions, each with a total occupancy of 1. The two THF solvent molecules are also

disordered and were modelled over two positions each with a total occupancy of 1.
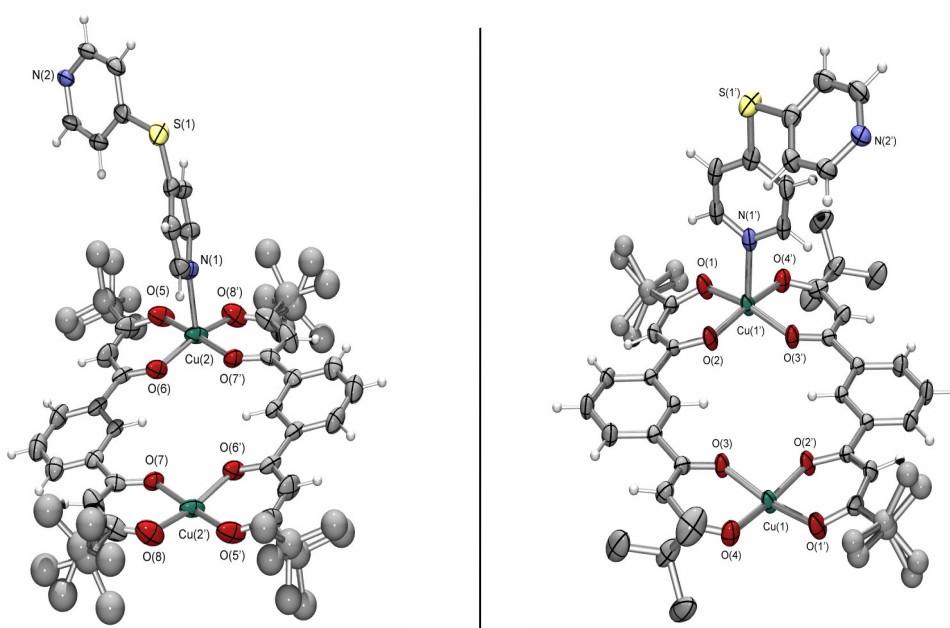
Figure S1: ORTEP plot of the two crystallographically independent forms of

{[Cu$_2$(**L**^{2})$_2$(dps)]·2THF}$_n$ shown with 50 % probability ellipsoids. Solvate molecules and

tertiary butyl bound hydrogen atoms are omitted for clarity. Symmetry operators used to

generate equivalent atoms: ^{i}-x, -y, -z

Table S5. Selected bond lengths (Å) and angles (°) for {[Cu$_2$(**L**^{2})$_2$(dps)]·2(THF)}$_n$

N(1)	Cu(1)		2.244(4)	N(2)	Cu(2)	2.254(4)
O(1)	Cu(1) ^{1}		1.938(3)	O(2)	Cu(1) ^{1}	1.937(3)
O(3)	Cu(1)		1.936(3)	O(4)	Cu(1)	1.929(3)
O(5)	Cu(2)		1.938(3)	O(6)	Cu(2)	1.924(3)

O(7)	Cu(2) [1]	1.932(3)	O(8)	Cu(2) [1]	1.898(4)
Cu(1)	O(2) [1]	1.937(3)	Cu(1)	O(1) [1]	1.938(3)
Cu(2)	O(8) [1]	1.898(4)	Cu(2)	O(7) [1]	1.932(3)

C(102)	S(1)	C(107)	101.3(2)
O(4)	Cu(1)	O(3)	91.82(11)
O(4)	Cu(1)	O(2) [1]	170.93(13)
O(3)	Cu(1)	O(2) [1]	88.35(11)
O(4)	Cu(1)	O(1) [1]	86.11(12)
O(3)	Cu(1)	O(1) [1]	166.23(15)
O(2) [1]	Cu(1)	O(1) [1]	91.57(11)
O(4)	Cu(1)	N(1)	95.26(13)
O(3)	Cu(1)	N(1)	95.42(12)
O(2) [1]	Cu(1)	N(1)	93.75(13)
O(1) [1]	Cu(1)	N(1)	98.32(14)
O(8) [1]	Cu(2)	O(6)	164.65(15)
O(8) [1]	Cu(2)	O(7) [1]	93.31(15)
O(6)	Cu(2)	O(7) [1]	88.25(12)
O(8) [1]	Cu(2)	O(5)	85.31(17)
O(6)	Cu(2)	O(5)	91.92(14)
O(7) [1]	Cu(2)	O(5)	175.34(15)
O(8) [1]	Cu(2)	N(2)	97.44(15)
O(6)	Cu(2)	N(2)	97.73(14)
O(7) [1]	Cu(2)	N(2)	92.81(12)
O(5)	Cu(2)	N(2)	91.77(14)

Symmetry Operator

(1) -x, -y, -z

Specific details for $\{[Cu_2(L^2)_2(xbp)]\cdot 2.2(THF)\}_n$

The structure was refined in $P1$ with an inversion twin component (BASF 0.53538)

despite *Platon* [PLATON, Spek, A.L., *Acta Cryst.*, 1990, **A46**, C-34] indicating an

apparent fit of 80 % to $P\bar{1}$. Refinement in $P\bar{1}$ results in a significant increase in the

amount of disorder present in the structure, including a 50 % disorder component in the

entire xbp ligand. This disorder is not present in the lower symmetry space group. The

thermal parameters also refine well in $P1$, suggesting the correct choice of space group.

Three of the tertiary butyl groups are rotationally disordered and were modelled over two positions with a total occupancy of 1 each. There are three disordered THF solvent molecules present in the lattice. One was modelled over two positions with a total occupancy of 1. The second was modelled over two positions with a total occupancy of 0.7 and the third was modelled over two positions with a total occupancy of 0.5, bringing the total number of THF molecules modelled to 2.2. The non-integer number of solvent molecules is presumably due to solvent loss during the mounting process, which is consistent with the analytical results obtain after drying. The hydrogen atoms on C(41) were modelled as rotationally disordered over two positions. Bond length and angle restraints were necessary to facilitate realistic geometries in regions of disorder.

Table S6. Selected bond lengths (Å) and angles (°) for $\{[Cu_2(\mathbf{L^2})_2(xbp)]\cdot 2.2(THF)\}_n$

N(1)	Cu(1)	2.239(6)			
N(3)	Cu(2)[1]	2.238(6)			
O(1)	Cu(1)	1.925(5)	O(2)	Cu(1)	1.963(5)
O(3)	Cu(2)	1.936(5)	O(4)	Cu(2)	1.953(5)
O(5)	Cu(2)	1.939(5)	O(6)	Cu(2)	1.926(5)
O(7)	Cu(1)	1.943(5)	O(8)	Cu(1)	1.943(5)
Cu(2)	N(3)[1]	2.238(6)			

O(1)	Cu(1)	O(7)	172.0(3)
O(1)	Cu(1)	O(8)	86.9(3)
O(7)	Cu(1)	O(8)	91.4(2)
O(1)	Cu(1)	O(2)	92.2(2)
O(7)	Cu(1)	O(2)	86.7(2)
O(8)	Cu(1)	O(2)	159.4(2)
O(1)	Cu(1)	N(1)	94.0(2)
O(7)	Cu(1)	N(1)	93.9(2)
O(8)	Cu(1)	N(1)	101.6(2)
O(2)	Cu(1)	N(1)	98.9(2)
O(6)	Cu(2)	O(3)	87.4(2)
O(6)	Cu(2)	O(5)	91.9(2)
O(3)	Cu(2)	O(5)	166.0(2)
O(6)	Cu(2)	O(4)	164.3(2)

| O(3)	Cu(2)	O(4)	91.9(2)
O(5)	Cu(2)	O(4)	85.1(2)
O(6)	Cu(2)	N(3) [1]	97.0(2)
O(3)	Cu(2)	N(3) [1]	95.7(2)
O(5)	Cu(2)	N(3) [1]	98.3(2)
O(4)	Cu(2)	N(3) [1]	98.7(2)

Symmetry Operator

(1) x, y, z

Specific details for $[(Cu_2(L^2)_2)_3(hmt)_2]_n$

The SQUEEZE function of *Platon* [PLATON, Spek, A.L., *Acta Cryst.*, 1990, **A46**, C-34] estimated the volume of these channels to be 482.4 $Å^3$ per unit cell or 13.8 % of the total volume of the unit cell which is presumably filled with disordered nitrogen molecules, as no sensible model could be found for the small amount of residual electron density present, which *Platon* estimated to be a mere 57 $e^- Å^{-3}$, it was not modelled, which resulted in a higher than ideal residual electron peak max/min ratio.
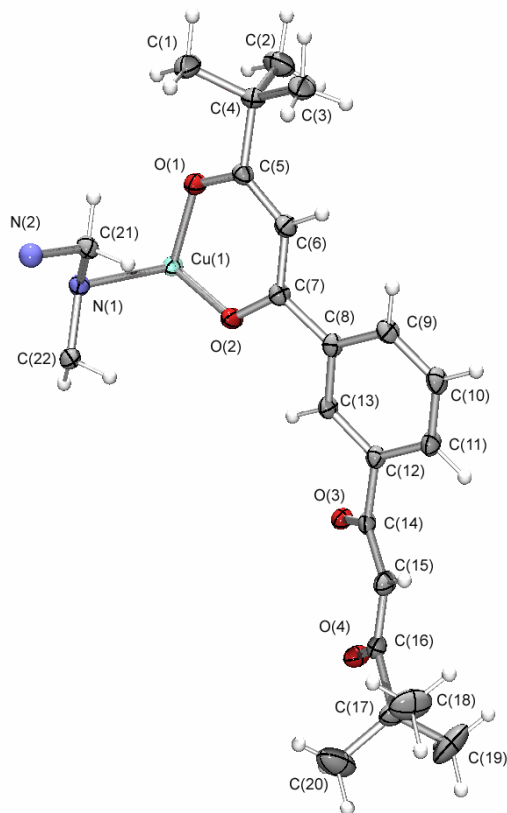
Figure S2: ORTEP plot of the asymmetric unit of $[(Cu_2(\mathbf{L^2})_2)_3(hmt)_2]_n$ shown with 50 %

probability ellipsoids.

Table S7. Selected bond lengths (Å) and angles (°) for $[(Cu_2(\mathbf{L^2})_2)_3(hmt)_2]_n$

O(1)	Cu(1)	1.9353(18)	O(2)	Cu(1)	1.9288(19)
O(3)	Cu(1)[1]	1.9345(18)	O(4)	Cu(1)[1]	1.9186(19)
Cu(1)	O(4)[1]	1.9186(19)	Cu(1)	O(3)[1]	1.9345(18)
Cu(1)	N(1)	2.346(2)	N(1)	C(22)[2]	1.474(3)
N(2)	C(21)[3]	1.459(3)	N(2)	C(21)[2]	1.459(3)

O(4)[1]	Cu(1)	O(2)	160.55(9)
O(4)[1]	Cu(1)	O(1)	85.75(8)
O(2)	Cu(1)	O(1)	91.25(8)
O(4)[1]	Cu(1)	O(3)[1]	92.74(8)
O(2)	Cu(1)	O(3)[1]	89.00(8)
O(1)	Cu(1)	O(3)[1]	176.15(8)
O(4)[1]	Cu(1)	N(1)	100.38(8)
O(2)	Cu(1)	N(1)	99.02(8)

O(1)	Cu(1)	N(1)	94.59(8)
O(3) [1]	Cu(1)	N(1)	89.16(8)

Symmetry Operators
(1) -x, -y, -z   (3) -y, x-y, z   (2) -x+y, -x, z