Supplementary Material for Dalton Transactions

Electronic Supplementary Material

Dinuclear bis-β-diketonato ligand derivatives of iron(III) and copper(II) and use of the latter as components for the assembly of extended metallo-supramolecular structures

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Individual crystal structure refinement details

1,1′-(1,3-phenylene)-bis-3,3-dimethylpentane-1,3-dione (**5**H_2)

In the solid state the free ligand, **5**H_2, has two-fold crystallographic symmetry (atoms C(10) and C(11) lie on the 2-fold axis) and therefore the asymmetric unit consists of one half of the ligand. The ligand is present as the enol tautomer with enol groups oriented as shown in Figure 1 (donors directed at 120° with respect to each other). As is characteristic of β-diketones, the six-membered rings incorporating the hydrogen-bonding are approximately planar. The enol planes are rotated by *ca*. 30° from the mean plane of the central benzene ring and the dihedral angle between the two enol planes is approximately 55°. These rotations almost certainly occur as a

result of steric conflict between O(2) and the C(9) hydrogen, as well as between the C(6) hydrogen and the C(11) hydrogen.

$[Cu_2(\mathbf{5})_2azpy]_n \cdot (2THF)_n$

The asymmetric unit contains fragments from two crystallographically independent polymeric chains. Each of these fragments consists of half of the repeating polymeric unit (*i.e.* $[Cu(\mathbf{5})azpy_{0.5}] \cdot (THF)$) which replicates with inversion symmetry. The pyridyl ring of the 4,4'-*trans*-azopyridine ligand comprising atoms N(1) and C(41)-C(45) is disordered and was modelled with two alternate positions, denoted A and B, with occupancy fractions of 0.8 and 0.2 respectively. The THF molecule comprising atoms O(2T) and C(5T)-C(8T) is disordered and was modelled with an alternate position comprising atoms O(3T) and C(9T)-C12(T) (occupancy fractions 0.55 and 0.45 respectively). ORTEP representations of the two crystallographically independent components of the asymmetric unit are provided in Fig. S2.

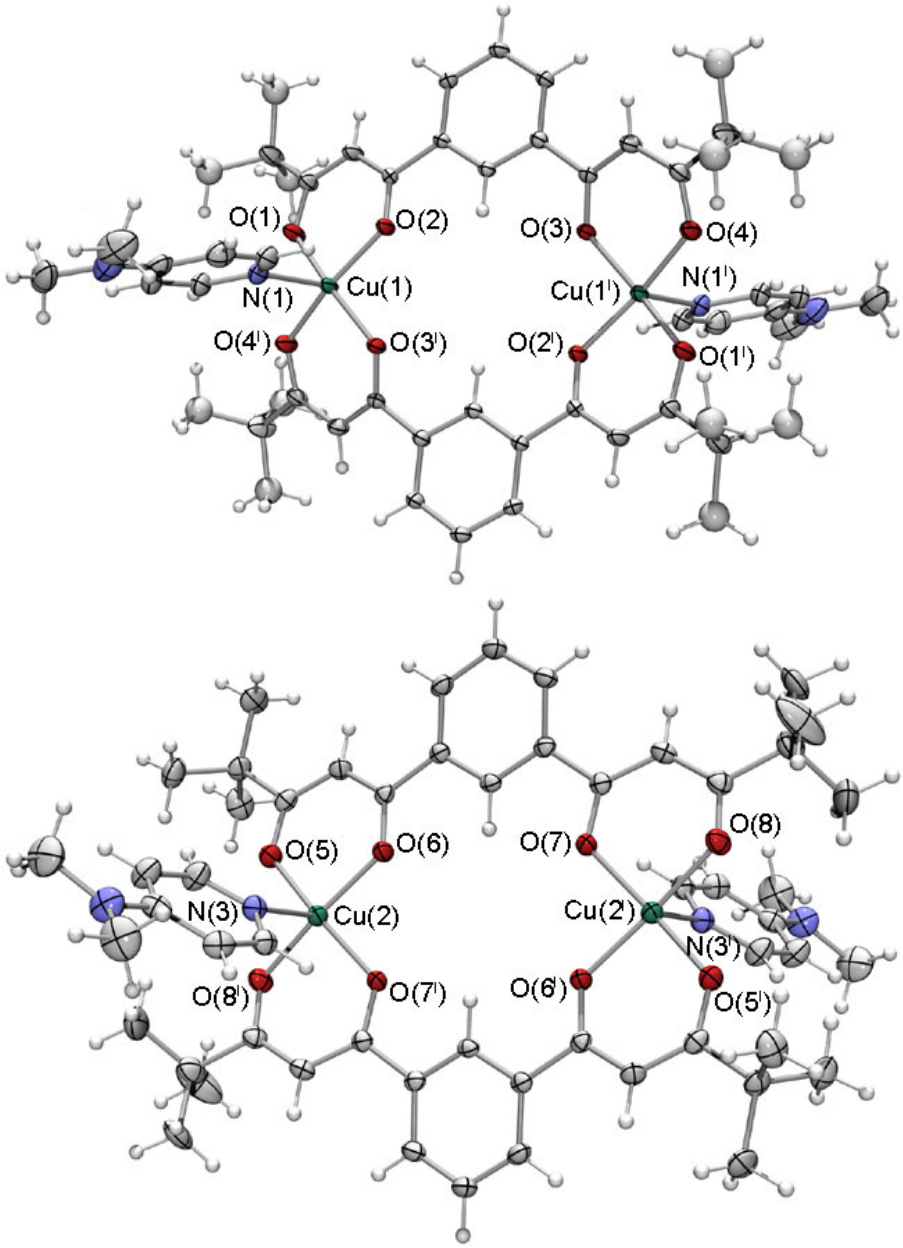

Figure S1. Illustrations of the two crystallographically independent complexes in the structure of $[Cu_2(\mathbf{5})_2(dmapy)_2]\cdot 3.25THF$. Both of the asymmetric components have crystallographic inversion symmetry (codes: ^{I} $-x + 1, -y + 1, -z$; ^{II} $-x + 1, -y, -z$). Thermal ellipsoids are drawn at the 40% probability level.

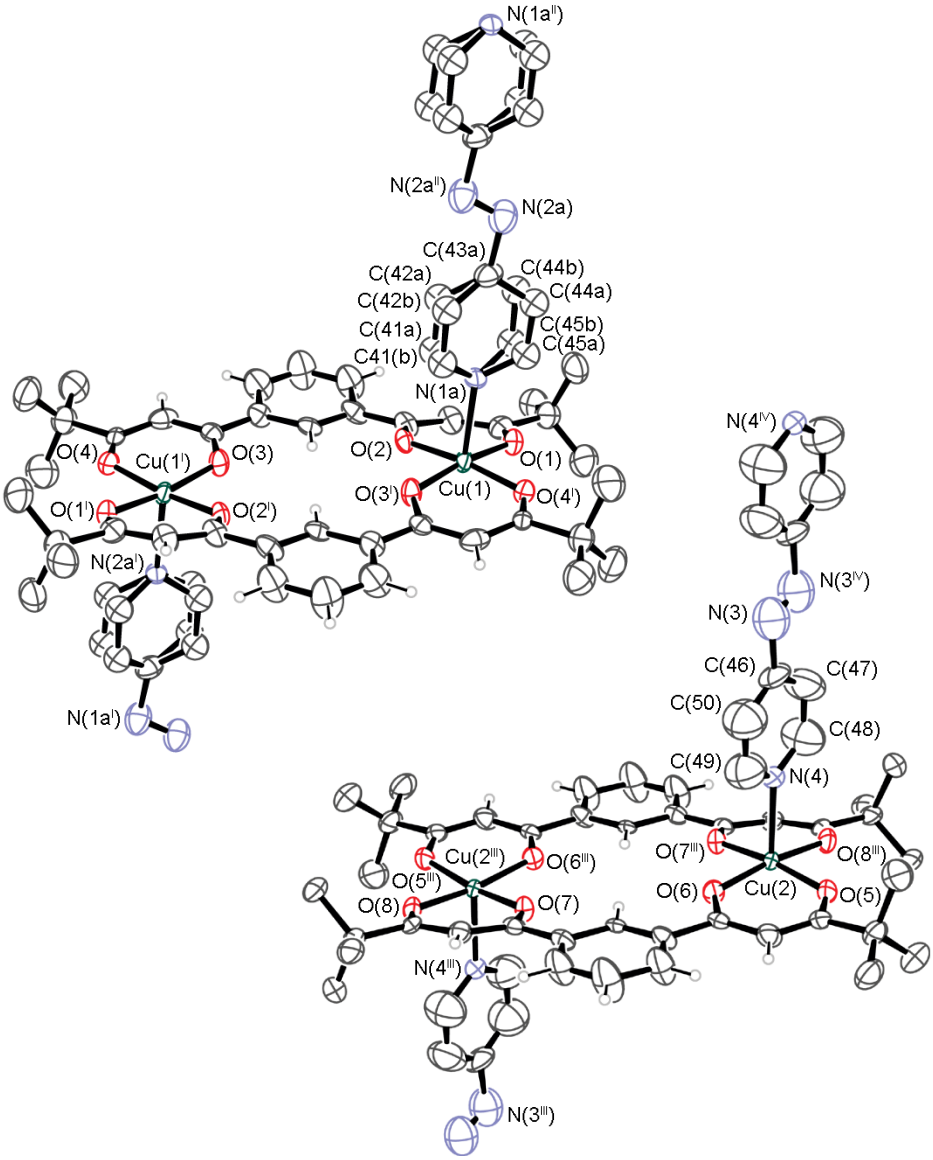

Figure S2. ORTEP representations of fragments from the two crystallographically independent polymeric chains containing $[Cu_2(\mathbf{5})_2(azpy)_2]\cdot 2THF$ units (symmetry codes: ^{I} $-x, -y+1, -z-1$; ^{II} $-x, -y+2, -z-1$; ^{III} $-x+1, -y+1, -z-2$; ^{IV} $-x+1, -y, -z-2$).

Table S1. Selected bond lengths (Å) and angles (°) for $[Fe_2(\mathbf{5}\text{-}H_2)_3]\cdot Et_2O$

$[Fe_2(\mathbf{5}\text{-}H_2)_3]\cdot Et_2O$			
Fe(1)-O(1)	1.975(2)	Fe(2)-O(3)	1.983(2)
Fe(1)-O(2)	1.981(1)	Fe(2)-O(4)	1.979(2)
Fe(1)-O(5)	2.000(2)	Fe(2)-O(7)	2.017(2)
Fe(1)-O(6)	1.9940(2)	Fe(2)-O(8)	1.988(2)
Fe(1)-O(9)	1.999(2)	Fe(2)-O(11)	1.981(2)
Fe(1)-O(10)	2.014(1)	Fe(2)-O(12)	2.002(2)
O(1)-Fe(1)-O(2)	85.70(6)	O(3)-Fe(2)-O(4)	85.97(6)
O(1)-Fe(1)-O(5)	89.09(6)	O(3)-Fe(2)-O(7)	87.00(6)
O(1)-Fe(1)-O(6)	104.25(6)	O(3)-Fe(2)-O(8)	96.84(6)
O(1)-Fe(1)-O(9)	87.42(6)	O(3)-Fe(2)-O(11)	90.09(6)
O(1)-Fe(1)-O(10)	168.78(7)	O(3)-Fe(2)-O(12)	173.64(7)
O(2)-Fe(1)-O(5)	170.19(7)	O(4)-Fe(2)-O(7)	171.10(6)
O(2)-Fe(1)-O(6)	88.46(6)	O(4)-Fe(2)-O(8)	90.26(6)
O(2)-Fe(1)-O(9)	100.54(7)	O(4)-Fe(2)-O(11)	101.23(6)
O(2)-Fe(1)-O(10)	88.10(6)	O(4)-Fe(2)-O(12)	90.41(6)
O(5)-Fe(1)-O(6)	84.77(6)	O(7)-Fe(2)-O(8)	85.18(6)
O(5)-Fe(1)-O(9)	87.50(7)	O(7)-Fe(2)-O(11)	84.21(6)
O(5)-Fe(1)-O(10)	98.33(6)	O(7)-Fe(2)-O(12)	97.08(6)
O(6)-Fe(1)-O(9)	165.86(6)	O(8)-Fe(2)-O(11)	167.00(6)
O(6)-Fe(1)-O(10)	84.90(6)	O(8)-Fe(2)-O(12)	88.39(6)
O(9)-Fe(1)-O(10)	84.53(6)	O(11)-Fe(2)-O(12)	85.49(6)

Table S2. Selected bond lengths (Å) and angles (°) for $[Cu_2(\mathbf{5}\text{-}H_2)_2(thf)_2]$ and $[Cu_2(\mathbf{5}\text{-}H_2)_2(py)_2]\cdot py$

$[Cu_2(\mathbf{5}\text{-}H_2)_2(thf)_2]$		$[Cu_2(\mathbf{5}\text{-}H_2)_2(py)_2]\cdot py$	
Cu(1)-O(1)	1.912(1)	Cu(1)-O(1)	1.931(1)
Cu(1)-O(2)	1.918(1)	Cu(1)-O(2)	1.928(1)
Cu(1)-O(3^I)	1.932(1)	Cu(1)-O(3^I)	1.929(1)
Cu(1)-O(4^I)	1.915(1)	Cu(1)-O(4^I)	1.942(1)
Cu(1)-O(5)	2.343(1)	Cu(1)-N(1)	2.278(2)
O(1)-Cu(1)-O(2)	92.70(5)	O(1)-Cu(1)-O(2)	92.93(6)
O(1)-Cu(1)-O(3^I)	171.87(5)	O(1)-Cu(1)-O(3^I)	165.90(6)
O(1)-Cu(1)-O(4^I)	85.32(5)	O(1)-Cu(1)-O(4^I)	87.58(6)
O(2)-Cu(1)-O(3^I)	89.14(4)	O(2)-Cu(1)-O(3^I)	86.05(6)
O(2)-Cu(1)-O(4^I)	172.03(5)	O(2)-Cu(1)-O(4^I)	173.29(6)
O(3^I)-Cu(1)-O(4^I)	91.78(4)	O(3^I)-Cu(1)-O(4^I)	91.82(6)
O(1)-Cu(1)-O(5)	92.90(5)	O(1)-Cu(1)-N(1)	95.63(6)
O(2)-Cu(1)-O(5)	90.91(5)	O(2)-Cu(1)-N(1)	96.53(6)
O(3^I)-Cu(1)-O(5)	94.99(4)	O(3^I)-Cu(1)-N(1)	98.46(6)
O(4^I)-Cu(1)-O(5)	96.90(4)	O(4^I)-Cu(1)-N(1)	90.08(6)

^{I} *-x*, *-y*, *-z*

^{I} *-x*, *-y*, *-z*

Table S3. Selected bond lengths (Å) and angles (°) for $[Cu_2(\mathbf{5}\text{-}H_2)_2(dmapy)_2]\cdot 3.25thf$.

$[Cu_2(\mathbf{5}\text{-}H_2)_2(dmapy)_2]\cdot 3.25thf$			
Molecule 1		Molecule 2	
Cu(1)-O(1)	1.926(3)	Cu(2)-O(5)	1.933(3)
Cu(1)-O(2)	1.941(3)	Cu(2)-O(6)	1.929(3)
Cu(1)-O(3^{I})	1.946(3)	Cu(2)-O(7^{II})	1.933(3)
Cu(1)-O(4^{I})	1.944(3)	Cu(2)-O(8^{II})	1.939(3)
Cu(1)-N(1)	2.224(4)	Cu(2)-N(3)	2.252(4)
O(1)-Cu(1)-O(2)	92.19(12)	O(5)-Cu(2)-O(6)	91.9(1)
O(1)-Cu(1)-O(3^{I})	166.1(2)	O(5)-Cu(2)-O(7^{II})	165.9(1)
O(1)-Cu(1)-O(4^{I})	84.4(1)	O(5)-Cu(2)-O(8^{II})	86.6(1)
O(2)-Cu(1)-O(3^{I})	88.6(1)	O(6)-Cu(2)-O(7^{II})	87.6(1)
O(2)-Cu(1)-O(4^{I})	165.2(2)	O(6)-Cu(2)-O(8^{II})	170.3(1)
O(3^{I})-Cu(1)-O(4^{I})	91.3(1)	O(7^{II})-Cu(2)-O(8^{II})	91.5(1)
O(1)-Cu(1)-N(1)	94.4(2)	O(5)-Cu(2)-N(3)	97.6(1)
O(2)-Cu(1)-N(1)	100.0(1)	O(6)-Cu(2)-N(3)	100.0(1)
O(3^{I})-Cu(1)-N(1)	99.1(1)	O(7^{II})-Cu(2)-N(3)	96.4(1)
O(4^{I})-Cu(1)-N(1)	94.6(2)	O(8^{II})-Cu(2)-N(3)	89.7(1)

^{I} $-x + 1, -y + 1, -z$; ^{II} $-x + 1, -y, -z$

Table S4. Selected bond lengths (Å) and angles (°) for $[Cu_2(\mathbf{5}\text{-}H_2)_2(bipy)_2]\cdot 2bipy$

$[Cu_2(\mathbf{5}\text{-}H_2)_2(bipy)_2]\cdot 2bipy$			
Cu(1)-O(1)	1.9282(14)	Cu(1)-O(4^{I})	1.9316(13)
Cu(1)-O(2)	1.9236(13)	Cu(1)-N(1)	2.3082(17)
Cu(1)-O(3^{I})	1.9331(14)		
O(1)-Cu(1)-O(2)	92.34(6)	O(3^{I})-Cu(1)-O(4^{I})	92.08(6)
O(1)-Cu(1)-O(3^{I})	167.60(6)	O(1)-Cu(1)-N(1)	95.94(6)
O(1)-Cu(1)-O(4^{I})	86.83(6)	O(2)-Cu(1)-N(1)	94.68(6)
O(2)-Cu(1)-O(3^{I})	87.61(6)	O(3^{I})-Cu(1)-N(1)	96.42(6)
O(2)-Cu(1)-O(4^{I})	174.71(6)	O(4^{I})-Cu(1)-N(1)	90.61(6)

[I] *-x*, *-y*, *-z* + 1

Table S5. Selected bond lengths (Å) and angles (°) for $[Cu_2(\mathbf{5}\text{-}H_2)_2(azpy)_2]\cdot 2THF$

$[Cu_2(\mathbf{5}\text{-}H_2)_2azpy]_n\cdot(2THF)_n$			
Molecule 1		Molecule 2	
Cu(1)-O(1)	1.975(6)	Cu(2)-O(5)	1.946(6)
Cu(1)-O(2)	1.924(5)	Cu(2)-O(6)	1.923(5)
Cu(1)-O(3^{I})	1.936(6)	Cu(2)-O(7^{III})	1.946(6)
Cu(1)-O(4^{I})	1.902(6)	Cu(2)-O(8^{III})	1.923(5)
N(1A)-Cu(1)	2.332(6)	N(4)-Cu(2)	2.325(7)
O(1)-Cu(1)-O(2)	91.1(2)	O(5)-Cu(2)-O(6)	91.9(2)
O(1)-Cu(1)-O(3^{I})	169.5(3)	O(5)-Cu(2)-O(7^{III})	171.5(3)
O(1)-Cu(1)-O(4^{I})	87.4(3)	O(5)-Cu(2)-O(8^{III})	87.7(2)
O(2)-Cu(1)-O(3^{I})	86.6(2)	O(6)-Cu(2)-O(7^{III})	86.7(2)
O(2)-Cu(1)-O(4^{I})	171.3(2)	O(6)-Cu(2)-O(8^{III})	171.0(3)
O(3^{I})-Cu(1)-O(4^{I})	93.3(2)	O(7^{III})-Cu(2)-O(8^{III})	92.3(2)
O(1)-Cu(1)-N(1A)	93.1(3)	O(5)-Cu(2)-N(4)	92.0(3)
O(2)-Cu(1)-N(1A)	97.3(2)	O(6)-Cu(2)-N(4)	96.0(2)
O(3^{I})-Cu(1)-N(1A)	97.4(2)	O(7^{III})-Cu(2)-N(4)	96.5(2)
O(4^{I})-Cu(1)-N(1A)	91.3(2)	O(8^{III})-Cu(2)-N(4)	93.0(2)

[I] *-x*, *-y* + 1, *-z* - 1; [III] *-x* + 1, *-y* + 1, *-z* - 2

Table S6. Selected bond lengths (Å) and angles (°) for $[Cu_4(\mathbf{5}\text{-}H_2)_4(pz)_2]\cdot 4THF$

$[Cu_4(\mathbf{5}\text{-}H_2)_4(pz)_2]\cdot 4THF$			
Cu(1)-O(1)	1.9240(16)	Cu(2)-O(3)	1.9160(16)
Cu(1)-O(2)	1.9222(15)	Cu(2)-O(4)	1.9295(16)
Cu(1)-O(5)	1.9200(16)	Cu(2)-O(7)	1.9278(16)
Cu(1)-O(6)	1.9346(15)	Cu(2)-O(8)	1.9227(16)
Cu(1)-N(1)	2.366(2)	Cu(2)-N(2^{I})	2.343(2)
O(1)-Cu(1)-O(2)	93.03(7)	O(3)-Cu(2)-O(4)	92.88(7)
O(1)-Cu(1)-O(5)	86.57(7)	O(3)-Cu(2)-O(7)	87.24(7)
O(1)-Cu(1)-O(6)	176.16(7)	O(3)-Cu(2)-O(8)	176.58(7)
O(2)-Cu(1)-O(5)	172.00(7)	O(4)-Cu(2)-O(7)	168.71(8)
O(2)-Cu(1)-O(6)	87.96(6)	O(4)-Cu(2)-O(8)	87.02(7)
O(5)-Cu(1)-O(6)	91.94(7)	O(7)-Cu(2)-O(8)	92.19(7)
O(1)-Cu(1)-N(1)	94.64(8)	O(3)-Cu(2)-N(2^{I})	92.53(8)
O(2)-Cu(1)-N(1)	94.38(7)	O(4)-Cu(2)-N(2^{I})	92.22(8)
O(5)-Cu(1)-N(1)	93.62(8)	O(7)-Cu(2)-N(2^{I})	99.05(8)
O(6)-Cu(1)-N(1)	88.98(7)	O(8)-Cu(2)-N(2^{I})	90.88(7)

[I] $-x + ½, -y + ½, -z + 1$