Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Interaction of an extended series of *N*-substituted di(2-picolyl)amine derivatives with copper(II). Synthetic, structural, magnetic and solution studies

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Crystallography

1. $[Cu(2)(\mu\text{-}Cl)]_2(PF_6)_2$

Table S1. Selected Bond Lengths (Å) and Angles (º) for $[Cu(\mathbf{2})(\mu\text{-}Cl)]_2(PF_6)_2$

Cl(1)	Cu(1)	2.2396(7)	Cu(1)	N(2)	1.989(2)
Cu(1)	N(3)	1.992(2)	Cu(1)	N(1)	2.022(2)
N(2)	Cu(1)	N(3)		166.41(9)	
N(2)	Cu(1)	N(1)		83.29(10)	
N(3)	Cu(1)	N(1)		83.14(9)	
N(2)	Cu(1)	Cl(1)		96.74(8)	
N(3)	Cu(1)	Cl(1)		96.84(7)	
N(1)	Cu(1)	Cl(1)		174.76(6)	

2. $[Cu(3)(\mu\text{-}Cl)]_2(PF_6)_2\cdot 0.5CH_2Cl_2$

Table S2. Selected Bond Lengths (Å) and Angles (º) for $[Cu(\mathbf{3})(\mu\text{-}Cl)]_2(PF_6)_2\cdot 0.5CH_2Cl_2$

N(1)	Cu(1)	1.987(9)	N(2)	Cu(1)	2.032(9)
N(3)	Cu(1)	1.964(9)	Cl(1)	Cu(1)	2.250(3)
N(3)	Cu(1)	N(1)		164.7(4)	
N(3)	Cu(1)	N(2)		82.1(4)	
N(1)	Cu(1)	N(2)		82.6(4)	
N(3)	Cu(1)	Cl(1)		97.2(3)	
N(1)	Cu(1)	Cl(1)		98.0(3)	
N(2)	Cu(1)	Cl(1)		173.9(3)	

3. $[Cu(6)(H_2O)(ClO_4)_2]\cdot 0.625H_2O$

Table S3. Selected Bond Lengths (Å) and Angles (º) for $[Cu(\mathbf{6})(ClO_4)_2(H_2O)]\cdot 0.5H_2O$

N(1)	Cu(1)	1.9758(17)	N(2)	Cu(1)	2.0279(16)
N(3)	Cu(1)	1.9838(17)	N(4)	Cu(2)	1.9759(17)
N(5)	Cu(2)	2.0357(16)	N(6)	Cu(2)	1.9729(17)
O(1)	Cu(1)	2.5043(16)	O(5)	Cu(1)	2.5195(15)
O(9)	Cu(1)	1.9677(16)	O(11)	Cu(2)	2.3527(15)
O(15)	Cu(2)	2.6598(16)	O(19)	Cu(2)	1.9714(16)
O(9)	Cu(1)	N(1)		95.34(7)	
O(9)	Cu(1)	N(3)		97.81(7)	
N(1)	Cu(1)	N(3)		165.92(7)	
O(9)	Cu(1)	N(2)		176.68(7)	
N(1)	Cu(1)	N(2)		83.14(7)	
N(3)	Cu(1)	N(2)		83.97(7)	
O(9)	Cu(1)	O(1)		77.23(6)	

N(1)	Cu(1)	O(1)	84.21(6)
N(3)	Cu(1)	O(1)	103.57(6)
N(2)	Cu(1)	O(1)	99.66(6)
O(9)	Cu(1)	O(5)	86.99(6)
N(1)	Cu(1)	O(5)	97.54(6)
N(3)	Cu(1)	O(5)	78.21(6)
N(2)	Cu(1)	O(5)	96.13(6)
O(1)	Cu(1)	O(5)	164.21(5)
O(19)	Cu(2)	N(6)	96.42(7)
O(19)	Cu(2)	N(4)	96.24(7)
N(6)	Cu(2)	N(4)	166.37(7)
O(19)	Cu(2)	N(5)	168.88(7)
N(6)	Cu(2)	N(5)	84.00(7)
N(4)	Cu(2)	N(5)	82.60(7)
O(19)	Cu(2)	O(11)	86.64(7)
N(6)	Cu(2)	O(11)	100.00(6)
N(4)	Cu(2)	O(11)	85.76(6)
N(5)	Cu(2)	O(11)	104.26(6)
O(19)	Cu(2)	O(15)	82.20(7)
N(6)	Cu(2)	O(15)	82.25(6)
N(4)	Cu(2)	O(15)	94.51(6)
N(5)	Cu(2)	O(15)	86.86(6)
O(11)	Cu(2)	O(15)	168.81(5)

Table S4. Hydrogen Bonding Geometry for [Cu(**6**)$(ClO_4)_2(H_2O)]\cdot 0.5H_2O$

D	H	A	D-H (Å)	H-A (Å)	D-A (Å)	DHA (º)
O(9)	H(1O)	O(20)[2]	0.890(11)	1.771(6)	2.640(2)	165(2)
O(9)	H(2O)	O(3)	0.890(17)	2.187(17)	2.844(2)	130.1(18)
O(9)	H(2O)	O(10)[1]	0.890(17)	2.46(2)	2.882(8)	109.8(16)
O(19)	H(3O)	O(20)	0.890(15)	1.904(12)	2.708(2)	149(2)
O(19)	H(4O)	O(10)[2]	0.890(17)	1.733(15)	2.491(8)	141(2)
O(19)	H(4O)	O(16)[2]	0.890(17)	2.285(10)	3.109(3)	154(2)
O(20)	H(5O)	O(8)[2]	0.890(16)	1.983(9)	2.829(2)	158(2)
O(20)	H(5O)	Cl(2)[2]	0.890(16)	2.992(14)	3.7222(18)	140.5(18)
O(20)	H(6O)	O(7)	0.890(12)	1.960(12)	2.842(2)	170(2)
O(20)	H(6O)	O(6)	0.890(12)	2.594(19)	3.171(2)	123.3(17)
O(20)	H(6O)	Cl(2)	0.890(12)	2.749(10)	3.5711(18)	154.2(19)

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

4. [Cu_2(8)Cl_2]

Table S5. Selected Bond Lengths (Å) and Angles (º) for [Cu_2(**8**)Cl_2]

Cu(1)	N(30)	2.0043(19)	Cu(1)	N(20)	2.015(2)
Cu(1)	N(1)	2.0620(17)	Cu(1)	Cl(3)	2.2498(7)
Cu(1)	Cl(2)	2.5370(9)			

N(30)	Cu(1)	N(20)	161.69(8)
N(30)	Cu(1)	N(1)	81.67(7)
N(20)	Cu(1)	N(1)	80.35(8)
N(30)	Cu(1)	Cl(3)	98.64(6)
N(20)	Cu(1)	Cl(3)	97.21(6)
N(1)	Cu(1)	Cl(3)	160.95(5)
N(30)	Cu(1)	Cl(2)	93.21(6)
N(20)	Cu(1)	Cl(2)	91.29(6)
N(1)	Cu(1)	Cl(2)	93.36(5)
Cl(3)	Cu(1)	Cl(2)	105.62(3)

5. [Cu_2(9+H)(μ-OCH_3)$_2$(H_2O)](ClO_4)$_3$·$C_4H_{10}O$

Table S6. Selected Bond Lengths (Å) and Angles (º) for [Cu_2(**9**+H)(μ-OCH_3)$_2$(H_2O)](ClO_4)$_3$·$C_4H_{10}O$

Cu(1)	O(1)	1.917(3)	Cu(1)	O(2)	1.919(3)
Cu(1)	N(33)	2.004(4)	Cu(1)	N(26)	2.018(4)
Cu(1)	O(5)	2.824(4)	Cu(1)	Cu(2)	3.0195(10)
Cu(2)	O(1)	1.933(3)	Cu(2)	O(2)	1.934(3)
Cu(2)	N(40)	1.995(4)	Cu(2)	N(47)	2.017(4)
Cu(2)	O(100)	2.474(4)			

O(1)	Cu(1)	O(2)	76.93(14)
O(1)	Cu(1)	N(33)	170.93(16)
O(2)	Cu(1)	N(33)	94.45(16)
O(1)	Cu(1)	N(26)	99.04(16)
O(2)	Cu(1)	N(26)	174.80(16)
N(33)	Cu(1)	N(26)	89.73(17)
O(1)	Cu(1)	O(5)	87.55(14)
O(2)	Cu(1)	O(5)	82.78(14)
N(33)	Cu(1)	O(5)	94.20(16)
N(26)	Cu(1)	O(5)	93.85(16)
O(1)	Cu(1)	Cu(2)	38.52(10)
O(2)	Cu(1)	Cu(2)	38.57(10)
N(33)	Cu(1)	Cu(2)	132.63(12)
N(26)	Cu(1)	Cu(2)	137.56(12)
O(5)	Cu(1)	Cu(2)	86.59(10)
O(1)	Cu(2)	O(2)	76.21(14)

O(1)	Cu(2)	N(40)	167.02(16)
O(2)	Cu(2)	N(40)	92.41(16)
O(1)	Cu(2)	N(47)	99.11(16)
O(2)	Cu(2)	N(47)	173.02(15)
N(40)	Cu(2)	N(47)	91.62(17)
O(1)	Cu(2)	O(100)	88.49(15)
O(2)	Cu(2)	O(100)	89.15(16)
N(40)	Cu(2)	O(100)	97.69(17)
N(47)	Cu(2)	O(100)	95.96(18)
O(1)	Cu(2)	Cu(1)	38.15(10)
O(2)	Cu(2)	Cu(1)	38.22(10)
N(40)	Cu(2)	Cu(1)	129.82(13)
N(47)	Cu(2)	Cu(1)	136.53(12)
O(100)	Cu(2)	Cu(1)	91.24(11)

Table S7. Hydrogen Bond Geometries for $[Cu_2(\mathbf{9}+H)(\mu\text{-}OCH_3)_2(H_2O)](ClO_4)_3{\cdot}C_4H_{10}O$

D	H	A	D-H(Å)	H-A(Å)	D-A(Å)	DHA(º)
O(100)	H(101)	O(8A)[1]	0.92(6)	2.07(5)	2.818(8)	139(6)
O(100)	H(102)	O(5)	0.90(4)	2.037(16)	2.932(7)	173(6)
N(12)	H(12)	N(19)	0.91(3)	1.82(3)	2.724(6)	176(5)

Symmetry Operator: (1) -x, -y, -z

Table S8. π–π Separations (Å) and angles (°) for $[Cu_2(\mathbf{9}+H)(\mu\text{-}OCH_3)_2(H_2O)](ClO_4)_3{\cdot}C_4H_{10}O$

Cg	**Cg**	**Cg···Cg [Å]**	**β[º]**
Cg1[a]	Cg2[b]	3.30[c]	24

[a]Cg1 is the (Cu1–O1–Cu2–O2) ring centroid; [b]Cg2 is the (N2–C1–N4–C5–N6–C3) ring centroid. [c]Perpendicular separation is 2.76 Å. For a discussion of Cg···Cg distances and the angle β see: C. Janiak, Dalton Trans, (2000) 3885.

Table S9. Aryl–Cu(II) bond lengths (Å) and angles (°) of $[Cu_2(\mathbf{9}+H)(\mu\text{-}OCH_3)_2(H_2O)]^{3+}$

Cg	Metal	Cg···M [Å]	β[°]
Cg2[a]	Cu1	3.53[b]	39
Cg2	Cu2	3.67[c]	40

[a]Cg2 is the (N2–Cl–N4–C5–N6–C3) ring centroid. [b]Perpendicular separation is 2.72 Å. [c]Perpendicular separation is 2.73 Å.