Electronic Supplementary Information

New discrete and polymeric supramolecular architectures derived from dinuclear Co(II), Ni(II) and Cu(II) complexes of aryl-linked bis-*β*-diketonato ligands and nitrogen bases: synthetic, structural and high pressure studies†‡

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Crystal Structure refinement details

$[Cu_2(L^1)_2(Py)_2]\cdot Py$ (R = Me)

Specific refinement details:

The pyridine solvent molecule is disordered across and inversion site and was modelled in two positions with 50 % occupancy each.

Selected Bond Lengths (Å) and Angles (°)

Cu(1)	O(1)	1.9282(12)	Cu(1)	O(2)	1.9304(12)		
Cu(1)	O(3)	1.9326(12)	Cu(1)	O(4)	1.9496(13)		
Cu(1)	N(1)	2.2546(15)					
O(1)	Cu(1)	O(2)	93.02(5)				
O(1)	Cu(1)	O(3)	169.16(6)	O(2)	Cu(1)	O(3)	85.29(5)
O(1)	Cu(1)	O(4)	87.12(5)	O(2)	Cu(1)	O(4)	167.54(6)
O(3)	Cu(1)	O(4)	92.24(5)	O(1)	Cu(1)	N(1)	96.21(6)
O(2)	Cu(1)	N(1)	97.54(6)	O(3)	Cu(1)	N(1)	94.63(6)
O(4)	Cu(1)	N(1)	94.83(5)				

$[Cu_2(L^1)_2(EtPy)]\cdot 2EtPy$ (R = t-Bu)

Specific refinement details:

The coordinated EtPy ligands and the *t*-Bu groups are each disordered over two positions and were modelled with a total occupancy of 1.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Cu(1)	2.273(3)	O(1)	Cu(1)	1.937(2)		
O(2)	Cu(1)	1.934(2)	O(3)	Cu(1)	1.936(2)		
O(4)	Cu(1)	1.933(2)					
O(4)	Cu(1)	O(2)	170.64(11)	O(4)	Cu(1)	O(3)	92.70(9)
O(2)	Cu(1)	O(3)	86.94(9)	O(4)	Cu(1)	O(1)	86.30(9)
O(2)	Cu(1)	O(1)	92.28(10)	O(3)	Cu(1)	O(1)	169.06(11)
O(4)	Cu(1)	N(1)	93.17(11)	O(2)	Cu(1)	N(1)	96.19(11)
O(3)	Cu(1)	N(1)	92.65(11)	O(1)	Cu(1)	N(1)	98.28(11)

$[Ni_2(L^1)_2(pipi)_4]\cdot pipi$ (R = t-Bu)

Specific refinement details:

The C(19) containing *t*-Bu group is disordered over three positions and the C(22) containing *t*-Bu group is disordered over two positions. Each were modelled with a total occupancy of 1. The free pipi is disordered over two positions (one 75 % the other 25 %). The hydrogen on the 25 % occupancy pipi nitrogen could not be located in the difference Fourier map and was not modelled.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Ni(1)	2.123(3)	N(2)	Ni(1)	2.173(3)
N(3)	Ni(2)	2.145(3)	O(8)	Ni(2)	2.022(2)
N(4)	Ni(2)	2.156(3)	O(1)	Ni(1)	2.005(2)
O(2)	Ni(1)	2.023(2)	O(3)	Ni(2)	2.039(2)
O(4)	Ni(2)	2.002(2)	O(5)	Ni(1)	2.022(2)
O(6)	Ni(1)	2.026(2)	O(7)	Ni(2)	2.018(2)

O(1)	Ni(1)	O(5)	89.47(8)
O(1)	Ni(1)	O(2)	89.84(8)
O(5)	Ni(1)	O(2)	177.38(9)
O(1)	Ni(1)	O(6)	177.77(9)
O(5)	Ni(1)	O(6)	89.49(8)
O(2)	Ni(1)	O(6)	91.12(8)
O(1)	Ni(1)	N(1)	93.65(10)
O(5)	Ni(1)	N(1)	92.92(10)
O(2)	Ni(1)	N(1)	89.65(9)
O(6)	Ni(1)	N(1)	88.37(9)
O(1)	Ni(1)	N(2)	92.06(10)
O(5)	Ni(1)	N(2)	85.87(10)
O(2)	Ni(1)	N(2)	91.63(10)
O(6)	Ni(1)	N(2)	85.90(10)
N(1)	Ni(1)	N(2)	174.15(11)
O(4)	Ni(2)	O(7)	179.09(9)
O(4)	Ni(2)	O(8)	89.51(9)
O(7)	Ni(2)	O(8)	89.68(8)
O(4)	Ni(2)	O(3)	89.13(8)
O(7)	Ni(2)	O(3)	91.70(8)
O(8)	Ni(2)	O(3)	176.62(9)
O(4)	Ni(2)	N(3)	91.16(9)
O(7)	Ni(2)	N(3)	88.47(9)
O(8)	Ni(2)	N(3)	93.95(10)
O(3)	Ni(2)	N(3)	89.17(10)
O(4)	Ni(2)	N(4)	87.97(10)
O(7)	Ni(2)	N(4)	92.48(10)
O(8)	Ni(2)	N(4)	91.70(10)
O(3)	Ni(2)	N(4)	85.16(11)
N(3)	Ni(2)	N(4)	174.27(11)

Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA (º)
N(1)	H(1N)	N(5)	0.891(10)	2.188(13)	3.070(6)	170(3)
N(3)	H(3N)	N(5A)	0.886(10)	2.19(2)	3.047(14)	162(3)

$[Cu_2(L^1)_2(pipi)_2]\cdot pipi$ (R = *t*-Bu)

Specific refinement details:

The molecule is centred around a mirror plane and inversion centre such that ¼ of the molecule is in the asymmetric unit. The central phenylene ring is disordered and modelled over three equal occupancy positions (including special positions). The uncoordinated pipi is also disordered and modelled over two positions. The N-bound H could not be located on this molecule and so was not modelled.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Cu(1)	2.259(4)	O(2)	Cu(1)	1.947(2)
O(1)	Cu(1)	1.947(2)			
O(1)	Cu(1)	O(1)	87.58(13)		
O(1)	Cu(1)	O(2)	91.73(9)		
O(1)	Cu(1)	O(2)	167.47(10)		
O(1)	Cu(1)	O(2)	167.47(10)		
O(1)	Cu(1)	O(2)	91.73(9)		
O(2)	Cu(1)	O(2)	86.23(13)		
O(1)	Cu(1)	N(1)	97.38(10)		
O(1)	Cu(1)	N(1)	97.38(10)		
O(2)	Cu(1)	N(1)	95.11(10)		
O(2)	Cu(1)	N(1)	95.11(10)		

Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA (º)
N(1)	H(1N)	N(2A)	0.89(5)	2.17(3)	3.05(2)	169(5)
N(1)	H(1N)	N(2)	0.89(5)	2.56(3)	3.42(2)	161(5)

$[Co_2(L^1)_2(tmen)_2]$ (R = *t*-Bu)

Specific refinement details:

The C(19) containing *t*-Bu group is disordered and modelled over two positions with total occupancy of 1.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Co(1)	2.191(3)	N(2)	Co(1)	2.207(3)
O(1)	Co(1)	2.054(2)	O(2)	Co(1)	2.0432(19)

O(3)	Co(1)	2.054(2)	O(4)	Co(1)	2.052(2)

O(2)	Co(1)	O(4)	175.52(8)
O(2)	Co(1)	O(1)	87.54(8)
O(4)	Co(1)	O(1)	91.62(8)
O(2)	Co(1)	O(3)	89.57(8)
O(4)	Co(1)	O(3)	86.03(8)
O(1)	Co(1)	O(3)	89.79(8)
O(2)	Co(1)	N(1)	93.73(9)
O(4)	Co(1)	N(1)	90.68(8)
O(1)	Co(1)	N(1)	90.96(9)
O(3)	Co(1)	N(1)	176.65(9)
O(2)	Co(1)	N(2)	87.68(9)
O(4)	Co(1)	N(2)	93.65(9)
O(1)	Co(1)	N(2)	171.80(9)
O(3)	Co(1)	N(2)	96.83(9)
N(1)	Co(1)	N(2)	82.71(10)

$[Ni_2(L^1)_2(tmen)_2]$ (R = *t*-Bu)

Specific refinement details:

The C(19) containing *t*-Bu group is disordered and modelled over two positions with total occupancy of 1.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Ni(1)	2.143(4)	N(2)	Ni(1)	2.151(4)
O(1)	Ni(1)	2.022(3)	O(2)	Ni(1)	2.034(3)
O(3)	Ni(1)	2.030(3)	O(4)	Ni(1)	2.037(3)

O(1)	Ni(1)	O(3)	89.57(12)
O(1)	Ni(1)	O(2)	88.77(12)
O(3)	Ni(1)	O(2)	88.34(12)
O(1)	Ni(1)	O(4)	90.19(12)
O(3)	Ni(1)	O(4)	87.80(12)
O(2)	Ni(1)	O(4)	176.01(12)
O(1)	Ni(1)	N(1)	90.84(14)
O(3)	Ni(1)	N(1)	178.79(14)
O(2)	Ni(1)	N(1)	92.81(13)
O(4)	Ni(1)	N(1)	91.06(13)
O(1)	Ni(1)	N(2)	174.68(13)
O(3)	Ni(1)	N(2)	94.74(13)
O(2)	Ni(1)	N(2)	88.25(13)
O(4)	Ni(1)	N(2)	93.09(13)
N(1)	Ni(1)	N(2)	84.92(15)

$[Cu_2(L^1)_2(tmen)_2]$ (R = *t*-Bu)

Specific refinement details:

The tmen ligands are disordered over two equal occupancy positions. Each of which was modelled anisotropically with identical thermal ellipsoids.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Cu(1)	2.4237(15)	O(1)	Cu(1)	1.9279(13)
O(2)	Cu(1)	1.9338(12)	Cu(1)	O(3)	1.9294(13)
Cu(1)	O(4)	1.9302(13)			

O(1)	Cu(1)	O(3)	172.90(5)
O(1)	Cu(1)	O(4)	86.91(6)
O(3)	Cu(1)	O(4)	91.77(5)
O(1)	Cu(1)	O(2)	91.75(6)
O(3)	Cu(1)	O(2)	87.78(5)
O(4)	Cu(1)	O(2)	165.58(6)
O(1)	Cu(1)	N(1)	94.56(5)
O(3)	Cu(1)	N(1)	92.53(5)
O(4)	Cu(1)	N(1)	96.88(5)
O(2)	Cu(1)	N(1)	97.54(5)

$[Ni_2(L^1)_2(Py)_4]$·dmpip (R = *t*-Bu)

Selected Bond Lengths (Å) and Angles (°)

N(1)	Ni(1)	2.108(2)	N(2)	Ni(1)	2.123(2)
O(2)	Ni(1)	2.0205(17)	O(3)	Ni(1)	2.0094(17)
O(4)	Ni(1)	2.0097(16)	O(5)	Ni(1)	2.0120(17)

O(3)	Ni(1)	O(4)	176.48(6)
O(3)	Ni(1)	O(5)	90.14(7)
O(4)	Ni(1)	O(5)	92.14(7)
O(3)	Ni(1)	O(2)	87.08(7)
O(4)	Ni(1)	O(2)	90.63(7)
O(5)	Ni(1)	O(2)	177.22(6)
O(3)	Ni(1)	N(1)	94.23(8)
O(4)	Ni(1)	N(1)	88.52(8)
O(5)	Ni(1)	N(1)	88.29(7)
O(2)	Ni(1)	N(1)	91.96(7)
O(3)	Ni(1)	N(2)	90.32(8)
O(4)	Ni(1)	N(2)	87.10(8)
O(5)	Ni(1)	N(2)	87.80(7)
O(2)	Ni(1)	N(2)	92.16(7)
N(1)	Ni(1)	N(2)	174.01(7)

$\{[Cu_2(L^1)_2(pip)]\cdot pip\cdot 2THF\}_n$ (R = *t*-Bu)

Specific refinement details:

The N-bound hydrogens on the uncoordinated pip molecule could not be located in the difference Fourier map and were not modelled.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Cu(1)	2.265(3)		O(1)	Cu(1)	1.919(2)	
O(2)	Cu(1)	1.944(2)		O(3)	Cu(1)	1.930(2)	
O(4)	Cu(1)	1.936(2)					
O(1)	Cu(1)	O(3)	172.35(10)	O(1)	Cu(1)	O(4)	85.85(9)
O(3)	Cu(1)	O(4)	91.65(9)	O(1)	Cu(1)	O(2)	91.73(9)
O(3)	Cu(1)	O(2)	88.55(9)	O(4)	Cu(1)	O(2)	162.93(9)
O(1)	Cu(1)	N(1)	95.83(10)	O(3)	Cu(1)	N(1)	91.73(10)
O(4)	Cu(1)	N(1)	100.44(10)	O(2)	Cu(1)	N(1)	96.62(10)

Hydrogen Bond Geometry

Donor	Hydrogen	Acceptor	D-H(Å)	H-A(Å)	D-A(Å)	DHA (º)
N(1)	H(1N)	O(1T)	0.89(4)	2.32(3)	3.195(4)	167(3)

$[Cu_2(L^1)_2(mmorph)_2]$ (R = *t*-Bu)

150(2) K

Selected Bond Lengths (Å) and Angles (°)

O(1)	Cu(1)	1.9288(17)		O(2)	Cu(1)	1.9266(17)	
O(3)	Cu(1)	1.9447(17)		O(4)	Cu(1)	1.9302(18)	
N(1)	Cu(1)	2.492(2)					
O(2)	Cu(1)	O(1)	92.73(7)	O(2)	Cu(1)	O(4)	174.01(7)
O(1)	Cu(1)	O(4)	86.24(7)	O(2)	Cu(1)	O(3)	88.14(7)
O(1)	Cu(1)	O(3)	166.89(7)	O(4)	Cu(1)	O(3)	91.53(7)
N(1)	Cu(1)	O(5)	167.59(6)	O(2)	Cu(1)	N(1)	89.91(7)
O(1)	Cu(1)	N(1)	101.67(7)	O(4)	Cu(1)	N(1)	96.08(8)
O(3)	Cu(1)	N(1)	91.41(7)				

293(2) K

Specific refinement details:

The C(1) containing *t*-Bu group is disordered and modelled over two positions with a total occupancy of 1. Completeness is also slightly lower than ideal, due to crystal decay during the collection from loss of coordinated mmorph ligands at this temperature.

Selected Bond Lengths (Å) and Angles (°)

O(1)	Cu(1)	1.915(3)	O(2)	Cu(1)	1.911(3)

O(3)	Cu(1)	1.925(3)	O(4)	Cu(1)	1.922(3)
N(1)	Cu(1)	2.536(5)			

O(2)	Cu(1)	O(1)	92.53(13)
O(2)	Cu(1)	O(4)	174.06(16)
O(1)	Cu(1)	O(4)	86.44(15)
O(2)	Cu(1)	O(3)	87.96(14)
O(1)	Cu(1)	O(3)	166.28(15)
O(4)	Cu(1)	O(3)	91.65(14)
O(2)	Cu(1)	N(1)	90.82(16)
O(1)	Cu(1)	N(1)	102.42(16)
O(4)	Cu(1)	N(1)	95.12(17)
O(3)	Cu(1)	N(1)	91.28(16)

1.9 kbar

Selected Bond Lengths (Å) and Angles (°)

Cu(1)	O(4)	1.929(10)	Cu(1)	O(3)	1.895(11)
Cu(1)	N(1)	2.484(10)	Cu(1)	O(1)	1.905(13)
Cu(1)	O(2)	1.914(8)			

O(4)	Cu(1)	O(3)	90.9(4)
O(4)	Cu(1)	N(1)	96.4(4)
O(3)	Cu(1)	N(1)	91.5(4)
O(4)	Cu(1)	O(1)	86.7(5)
O(3)	Cu(1)	O(1)	166.0(3)
N(1)	Cu(1)	O(1)	102.5(4)
O(4)	Cu(1)	O(2)	173.9(3)
O(3)	Cu(1)	O(2)	88.8(4)
N(1)	Cu(1)	O(2)	89.7(3)
O(1)	Cu(1)	O(2)	92.1(4)

9.1 kbar

Selected Bond Lengths (Å) and Angles (°)

N(1)	Cu(1)	2.445(7)	O(1)	Cu(1)	1.915(8)
O(2)	Cu(1)	1.924(6)	O(3)	Cu(1)	1.917(7)
O(4)	Cu(1)	1.942(6)			

N(1)	Cu(1)	O(4)	97.2(2)
N(1)	Cu(1)	O(2)	89.2(2)
O(4)	Cu(1)	O(2)	173.6(2)
N(1)	Cu(1)	O(3)	91.3(3)
O(4)	Cu(1)	O(3)	91.5(3)
O(2)	Cu(1)	O(3)	88.3(3)
N(1)	Cu(1)	O(1)	100.9(3)
O(4)	Cu(1)	O(1)	85.8(3)

O(2)	Cu(1)	O(1)	93.0(3)
O(3)	Cu(1)	O(1)	167.7(2)