Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Neutral (bis-*β*-diketonato) iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) metallocycles: structural, electrochemical and solvent extraction studies

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Crystal Structure refinement details

$[Co_2(L^1)_2(Py)_4]\cdot 2.25CHCl_3\cdot 0.5H_2O$ (R = Pr)

Specific refinement details:

The C(1A) containing propyl group is disordered and modelled over two equal occupancy positions. One of the chloroform solvent molecules (containing C(58) is ordered and is modelled with a total occupancy of 1. The C(57A) chloroform molecule is disordered over two positions and is modelled with occupancies of 0.75 and 0.25, the latter modelled without anisotropic parameters. The C(59) containing molecule lies on a 2-fold axis (C(59) on axis) and was modelled with a total occupancy of 0.25 without anisotropic parameters. The residual density close to this position was modelled with an isotropic water molecule (occupancy 0.5). The hydrogen atoms of the water molecule could not be located in the Fourier difference map and were not modelled. The following bond length and through space distance geometric restraints were applied to the disordered chloroform molecules to facilitate a realistic refinement model: C–Cl 1.745 Å, Cl···Cl 2.88 Å.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Co(1)	2.178(3)	N(2)	Co(1)	2.178(3)
N(3)	Co(2)	2.192(5)	N(4)	Co(2)	2.191(5)
O(1)	Co(1)	2.060(2)	O(2)	Co(1)	2.049(2)
O(3)	Co(2)	2.049(3)	O(4)	Co(2)	2.039(3)
O(5)	Co(1)	2.065(3)	O(6)	Co(1)	2.050(2)
O(7)	Co(2)	2.036(3)	O(8)	Co(2)	2.055(3)

O(6)	Co(1)	O(2)	90.69(9)
O(6)	Co(1)	O(1)	178.20(10)
O(2)	Co(1)	O(1)	87.51(10)
O(6)	Co(1)	O(5)	87.04(10)
O(2)	Co(1)	O(5)	177.70(10)
O(1)	Co(1)	O(5)	94.76(10)
O(6)	Co(1)	N(2)	88.24(11)
O(2)	Co(1)	N(2)	88.80(11)
O(1)	Co(1)	N(2)	91.76(11)

O(5)	Co(1)	N(2)	90.72(11)
O(6)	Co(1)	N(1)	89.74(11)
O(2)	Co(1)	N(1)	89.68(11)
O(1)	Co(1)	N(1)	90.20(11)
O(5)	Co(1)	N(1)	90.72(11)
N(2)	Co(1)	N(1)	177.46(13)
O(7)	Co(2)	O(4)	174.96(14)
O(7)	Co(2)	O(3)	89.28(10)
O(4)	Co(2)	O(3)	88.00(11)
O(7)	Co(2)	O(8)	88.84(11)
O(4)	Co(2)	O(8)	94.17(12)
O(3)	Co(2)	O(8)	175.49(14)
O(7)	Co(2)	N(3)	90.94(13)
O(4)	Co(2)	N(3)	85.06(15)
O(3)	Co(2)	N(3)	94.52(14)
O(8)	Co(2)	N(3)	89.61(14)
O(7)	Co(2)	N(4)	94.18(14)
O(4)	Co(2)	N(4)	90.01(15)
O(3)	Co(2)	N(4)	89.08(14)
O(8)	Co(2)	N(4)	86.97(14)
N(3)	Co(2)	N(4)	173.78(14)

$[Co_2(L^1)_2(EtPy)_4]$ (R = *t*-Bu)

Specific refinement details:

The C(40) containing *t*-Bu group is modelled as disordered over two 50 % occupancy sites. The C(46) containing ethyl group is disordered over three positions and modelled with a total occupancy of 1. Some bond length and angle restraints were required to facilitate a realistic model.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Co(1)	2.1596(18)	N(2)	Co(1)	2.1974(19)
N(3)	Co(2)	2.2030(19)	N(4)	Co(2)	2.1699(18)
O(1)	Co(1)	2.0340(14)	O(2)	Co(1)	2.0412(14)
O(3)	Co(1) #1	2.0439(13)	O(4)	Co(1) #1	2.0493(14)
O(7)	Co(2) #1	2.0374(14)	O(6)	Co(2)	2.0424(14)
O(8)	Co(2) #1	2.0424(15)	O(5)	Co(2)	2.0394(14)
Co(1)	O(3) #1	2.0439(13)	Co(1)	O(4) #1	2.0493(14)
Co(2)	O(7) #1	2.0374(14)	Co(2)	O(8) #1	2.0424(15)
O(1)	Co(1)	O(2)		89.03(5)	

O(1)	Co(1)	O(3) #1	177.07(6)
O(2)	Co(1)	O(3) #1	88.63(5)
O(1)	Co(1)	O(4) #1	94.53(6)
O(2)	Co(1)	O(4) #1	176.44(5)
O(3) #1	Co(1)	O(4) #1	87.81(5)
O(1)	Co(1)	N(1)	90.11(6)
O(2)	Co(1)	N(1)	91.13(6)
O(3) #1	Co(1)	N(1)	91.69(6)
O(4) #1	Co(1)	N(1)	89.05(6)
O(1)	Co(1)	N(2)	89.31(6)
O(2)	Co(1)	N(2)	94.11(6)
O(3) #1	Co(1)	N(2)	89.11(6)
O(4) #1	Co(1)	N(2)	85.76(6)
N(1)	Co(1)	N(2)	174.72(7)
O(7) #1	Co(2)	O(5)	176.41(6)
O(7) #1	Co(2)	O(8) #1	88.39(6)
O(5)	Co(2)	O(8) #1	94.48(6)
O(7) #1	Co(2)	O(6)	88.46(6)
O(5)	Co(2)	O(6)	88.58(6)
O(8) #1	Co(2)	O(6)	175.94(6)
O(7) #1	Co(2)	N(4)	92.25(6)
O(5)	Co(2)	N(4)	90.00(6)
O(8) #1	Co(2)	N(4)	88.13(6)
O(6)	Co(2)	N(4)	94.56(6)
O(7) #1	Co(2)	N(3)	89.62(6)
O(5)	Co(2)	N(3)	88.39(6)
O(8) #1	Co(2)	N(3)	86.69(6)
O(6)	Co(2)	N(3)	90.72(6)
N(4)	Co(2)	N(3)	174.44(7)

Symmetry Operator

(#1) -x, -y, -z

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

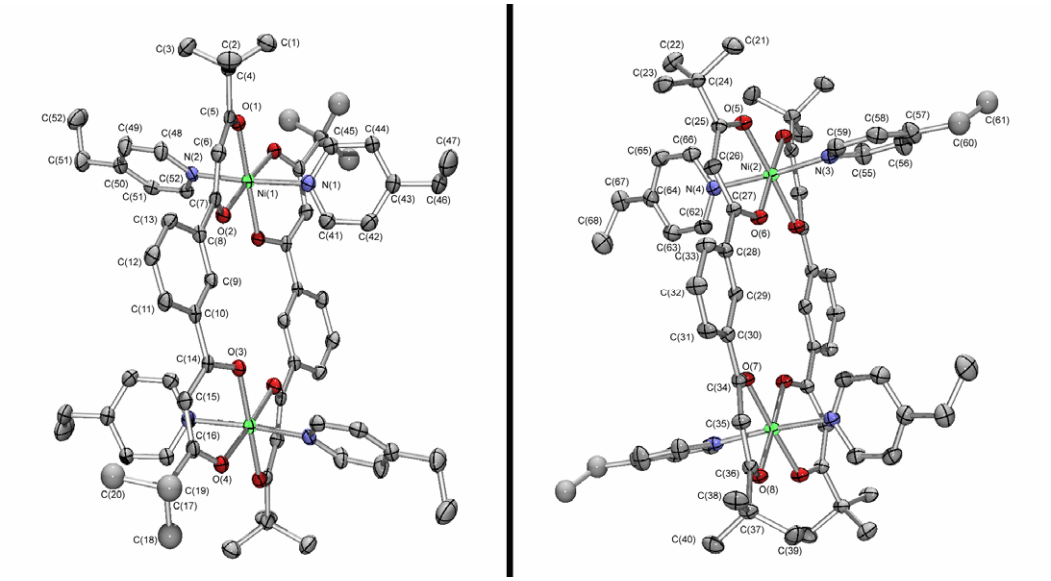

Fig. S1 ORTEP plots of the two crystallographically independent forms of $[Ni_2(\mathbf{L^1})_2(EtPy)_4]$ (R = *t*-Bu) shown with 50% probability ellipsoids. Hydrogen atoms and minor occupancy components in the regions of disorder omitted for clarity.

Specific refinement details:

The C(20) containing *t*-Bu group and the C(61) containing ethyl group are disordered over two positions each. Each was modelled with a total occupancy of 1.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Ni(1)	2.136(2)			
N(2)	Ni(1)	2.106(2)	N(3)	Ni(2)	2.097(2)
N(4)	Ni(2)	2.128(2)	O(1)	Ni(1)	2.0234(18)
O(2)	Ni(1)	2.0139(17)	O(3)	Ni(1)	2.0170(18)
O(4)	Ni(1)	2.0240(17)	O(5)	Ni(2)	2.0163(17)

O(6)	Ni(2)	2.0127(17)	O(7)	Ni(2)	2.0173(16)
O(8)	Ni(2)	2.0312(16)			

O(2)	Ni(1)	O(3)	87.08(7)
O(2)	Ni(1)	O(1)	90.46(7)
O(3)	Ni(1)	O(1)	176.90(7)
O(2)	Ni(1)	O(4)	176.47(7)
O(3)	Ni(1)	O(4)	90.17(7)
O(1)	Ni(1)	O(4)	92.22(7)
O(2)	Ni(1)	N(2)	94.13(8)
O(3)	Ni(1)	N(2)	92.04(8)
O(1)	Ni(1)	N(2)	90.01(8)
O(4)	Ni(1)	N(2)	88.18(8)
O(2)	Ni(1)	N(1)	91.05(8)
O(3)	Ni(1)	N(1)	89.75(8)
O(1)	Ni(1)	N(1)	88.41(8)
O(4)	Ni(1)	N(1)	86.73(8)
N(2)	Ni(1)	N(1)	174.60(8)
O(6)	Ni(2)	O(5)	90.96(7)
O(6)	Ni(2)	O(7)	87.18(6)
O(5)	Ni(2)	O(7)	177.74(7)
O(6)	Ni(2)	O(8)	176.87(7)
O(5)	Ni(2)	O(8)	92.13(7)
O(7)	Ni(2)	O(8)	89.72(7)
O(6)	Ni(2)	N(3)	91.57(7)
O(5)	Ni(2)	N(3)	89.73(8)
O(7)	Ni(2)	N(3)	91.61(7)
O(8)	Ni(2)	N(3)	88.98(7)
O(6)	Ni(2)	N(4)	93.53(7)
O(5)	Ni(2)	N(4)	89.23(8)
O(7)	Ni(2)	N(4)	89.60(7)
O(8)	Ni(2)	N(4)	85.99(7)
N(3)	Ni(2)	N(4)	174.82(8)

$[Zn_2(L^1)_2(EtPy)_2]$ (R = Me)

Selected Bond Lengths (Å) and Angles (°)

N(1)	Zn(1)	2.0605(17)	O(1)	Zn(1)	1.9947(14)
O(2)	Zn(1)	2.0503(14)	O(3)	Zn(1) #1	1.9828(13)
O(4)	Zn(1) #1	2.0552(14)	Zn(1)	O(3) #1	1.9828(13)
Zn(1)	O(4) #1	2.0552(14)			

O(3) #1	Zn(1)	O(1)	141.73(6)
O(3) #1	Zn(1)	O(2)	88.02(6)
O(1)	Zn(1)	O(2)	89.88(6)

O(3) #1	Zn(1)	O(4) #1	89.08(6)
O(1)	Zn(1)	O(4) #1	84.37(6)
O(2)	Zn(1)	O(4) #1	166.68(6)
O(3) #1	Zn(1)	N(1)	106.05(6)
O(1)	Zn(1)	N(1)	112.17(6)
O(2)	Zn(1)	N(1)	96.08(6)
O(4) #1	Zn(1)	N(1)	97.21(7)

Symmetry Operators

(#1) -x, -y, -z

$[Zn_2(L^1)_2(EtPy)_4]$ (R = *t*-Bu)

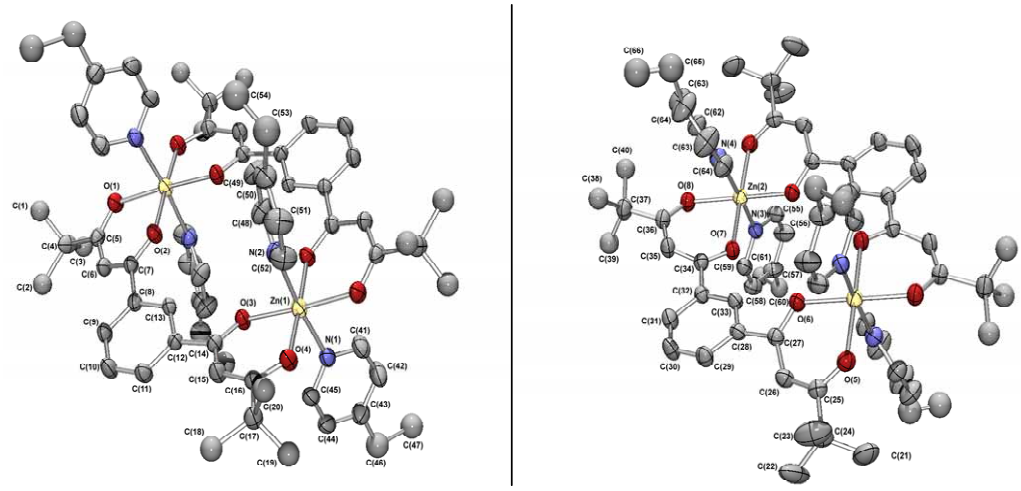

Fig. S2 ORTEP plots of the two crystallographically independent forms of $[Zn_2(\mathbf{L^1})_2(EtPy)_4]$ (R = *t*-Bu), shown with 30% probability ellipsoids. Hydrogen atoms and minor occupancy components in the regions of disorder omitted for clarity.

Specific refinement details:

The C(40) and C(20) containing *t*-Bu groups are rotationally disordered. The former was modelled over two positions and the latter over three, with a total occupancy of 1 in each case. Each of the ethyl groups is disordered. The C(53) containing group was modelled over two positions and the others over three, each with a total occupancy of 1. Some bond length and angle restraints were required to facilitate realistic positions.

Selected Bond Lengths (Å) and Angles (°)

N(1)	Zn(1)	2.288(4)			
N(2)	Zn(1)	2.197(4)	N(3)	Zn(2)	2.177(4)
N(4)	Zn(2)	2.270(4)	O(1)	Zn(1)	2.037(3)
O(2)	Zn(1)	2.040(3)	O(3)	Zn(1) #1	2.047(3)
O(4)	Zn(1) #1	2.059(3)	O(5)	Zn(2)	2.070(3)
O(6)	Zn(2)	2.055(3)	O(7)	Zn(2) #1	2.053(3)
O(8)	Zn(2) #1	2.065(3)	Zn(1)	O(3) #1	2.047(3)
Zn(1)	O(4) #1	2.059(3)	Zn(2)	O(7) #1	2.053(3)
Zn(2)	O(8) #1	2.065(3)			

O(1)	Zn(1)	O(2)	89.03(11)
O(1)	Zn(1)	O(3) #1	177.27(12)
O(2)	Zn(1)	O(3) #1	89.80(11)
O(1)	Zn(1)	O(4) #1	93.53(11)
O(2)	Zn(1)	O(4) #1	177.03(10)
O(3) #1	Zn(1)	O(4) #1	87.57(11)
O(1)	Zn(1)	N(2)	91.06(12)
O(2)	Zn(1)	N(2)	92.73(12)
O(3) #1	Zn(1)	N(2)	91.46(12)
O(4) #1	Zn(1)	N(2)	88.73(12)
O(1)	Zn(1)	N(1)	88.85(13)
O(2)	Zn(1)	N(1)	93.71(12)
O(3) #1	Zn(1)	N(1)	88.76(12)
O(4) #1	Zn(1)	N(1)	84.85(12)
N(2)	Zn(1)	N(1)	173.56(12)
O(7) #1	Zn(2)	O(6)	89.16(11)
O(7) #1	Zn(2)	O(8) #1	87.84(12)
O(6)	Zn(2)	O(8) #1	174.61(11)
O(7) #1	Zn(2)	O(5)	176.06(11)
O(6)	Zn(2)	O(5)	88.13(12)
O(8) #1	Zn(2)	O(5)	94.64(12)
O(7) #1	Zn(2)	N(3)	93.58(13)
O(6)	Zn(2)	N(3)	96.02(12)
O(8) #1	Zn(2)	N(3)	88.64(13)
O(5)	Zn(2)	N(3)	89.55(13)
O(7) #1	Zn(2)	N(4)	90.13(13)
O(6)	Zn(2)	N(4)	89.68(13)
O(8) #1	Zn(2)	N(4)	85.85(13)
O(5)	Zn(2)	N(4)	87.00(13)
N(3)	Zn(2)	N(4)	173.25(13)

Symmetry Operator

(#1) -x, -y, -z

Solvent extraction study

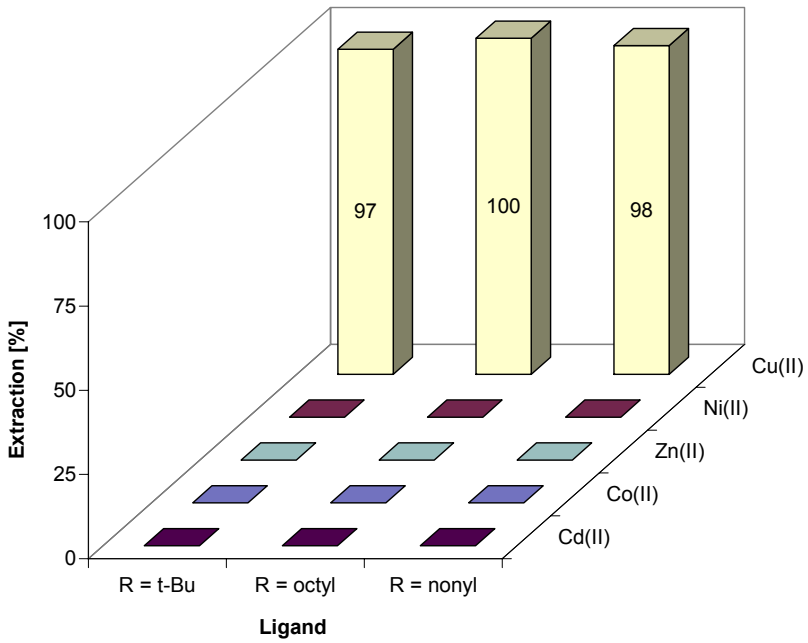

Fig. S3 Percentage of cadmium(II), cobalt(II), nickel(II), zinc(II) and copper(II) competitive extracted from the aqueous into the organic phase by $H_2\mathbf{L}^{\mathbf{1}}$ (R = *t*-Bu, octyl and nonyl). $[M(ClO_4)_2] = 1 \times 10^{-4}$ M, pH 7.8 (HEPES/NaOH buffer); $[H_2\mathbf{L}^{\mathbf{1}}] = 1 \times 10^{-3}$ M in $CHCl_3$; shaking time 24 h; T = 24 ± 1°C.