Electronic Supplementary Information (ESI)

Alkyl linker effects on the coordination topology of ditopic di(2-pyridylmethyl)amine carboxylate ligands with Zn^{II} and Cu^{II} perchlorates: polymers *vs* macrocycles

Kiattipoom Rodpun,[a] Allan G. Blackman,[b,c] Michael G. Gardiner,[d] Eng Wui Tan,[b] Carla J. Meledandri[a] and Nigel T. Lucas*[a]

[a]*MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, P.O. Box 56, Dunedin 9054, New Zealand.*

E-mail: nlucas@chemistry.otago.ac.nz

[b]*Department of Chemistry, University of Otago, Dunedin 9054, New Zealand, P.O. Box 56, Dunedin 9054, New Zealand.*

[c]*School of Applied Sciences, Auckland University of Technology, Private Bag 92006, Auckland 1142, New Zealand.*

[d]*School of Chemistry, University of Tasmania, Private Bag 75, Hobart 7001, Australia.*

Table S1 Mass spectrometry data of M^{2+}:**CnCOOH** solutions with different ratios of metal ion to ligand. Assigned elemental formulas for complexes are shown alongside measured and (calculated) *m/z* values.

Ratios of M^{2+}:**CnCOOH** in solutions = **1:2**

Ligand / **M^{2+}**	**C3COOH** ($C_{16}H_{19}N_3O_2$)	**C4COOH** ($C_{17}H_{21}N_3O_2$)	**C5COOH** ($C_{18}H_{23}N_3O_2$)	**C7COOH** ($C_{20}H_{27}N_3O_2$)	**C10COOH** ($C_{23}H_{33}N_3O_2$)	**C11COOH** ($C_{24}H_{35}N_3O_2$)
Zn^{2+}	[Zn(**C3COO**)]$^+$ 348.0672 (348.0690)	[Zn(**C4COO**)]$^+$ 362.0813 (362.0847)	[Zn(**C5COO**)]$^+$ 376.0961 (376.1003)	[Zn(**C7COO**)]$^+$ 404.1275 (404.1316)	[Zn(**C10COO**)]$^+$ 446.1765 (446.1786)	[Zn(**C11COO**)]$^+$ 460.1955 (460.1942)
Cu^{2+}	[Cu(**C3COO**)]$^+$ 347.0764 (347.0795)	[Cu(**C4COO**)]$^+$ 361.0867 (361.0952)	[Cu(**C5COO**)]$^+$ 375.1088 (375.1108)	[Cu(**C7COO**)]$^+$ 403.1387 (403.1421)	[Cu(**C10COO**)]$^+$ 445.1835 (445.1891)	[Cu(**C11COO**)]$^+$ 459.1957 (459.2047)

Ratios of M^{2+}:**CnCOOH** in solutions = **1:1**

Ligand / **M^{2+}**	**C3COOH** ($C_{16}H_{19}N_3O_2$)	**C4COOH** ($C_{17}H_{21}N_3O_2$)	**C5COOH** ($C_{18}H_{23}N_3O_2$)	**C7COOH** ($C_{20}H_{27}N_3O_2$)	**C10COOH** ($C_{23}H_{33}N_3O_2$)	**C11COOH** ($C_{24}H_{35}N_3O_2$)
Zn^{2+}	[Zn(**C3COO**)]$^+$ 348.0678 (348.0690)	[Zn(**C4COO**)]$^+$ 362.0827 (362.0847)	[Zn(**C5COO**)]$^+$ 376.0971 (376.1003)	[Zn(**C7COO**)]$^+$ 404.1288 (404.1316)	[Zn(**C10COO**)]$^+$ 446.1795 (446.1786)	[Zn(**C11COO**)]$^+$ 460.1923 (460.1942)
Cu^{2+}	[Cu(**C3COO**)]$^+$ 347.0774 (347.0795)	[Cu(**C4COO**)]$^+$ 361.0828 (361.0952)	[Cu(**C5COO**)]$^+$ 375.1052 (375.1108)	[Cu(**C7COO**)]$^+$ 403.1396 (403.1421)	[Cu(**C10COO**)]$^+$ 445.1828 (445.1891)	[Cu(**C11COO**)]$^+$ 459.1918 (459.2047)

Ratios of M^{2+}:**CnCOOH** in solutions = **2:1**

Ligand / **M^{2+}**	**C3COOH** ($C_{16}H_{19}N_3O_2$)	**C4COOH** ($C_{17}H_{21}N_3O_2$)	**C5COOH** ($C_{18}H_{23}N_3O_2$)	**C7COOH** ($C_{20}H_{27}N_3O_2$)	**C10COOH** ($C_{23}H_{33}N_3O_2$)	**C11COOH** ($C_{24}H_{35}N_3O_2$)
Zn^{2+}	[Zn(**C3COO**)]$^+$ 348.0657 (348.0690)	[Zn(**C4COO**)]$^+$ 362.0820 (362.0847)	[Zn(**C5COO**)]$^+$ 376.0979 (376.1003)	[Zn(**C7COO**)]$^+$ 404.1274 (404.1316)	[Zn(**C10COO**)]$^+$ 446.1743 (446.1786)	[Zn(**C11COO**)]$^+$ 460.1935 (460.1942)
Cu^{2+}	[Cu(**C3COO**)]$^+$ 347.0741 (347.0795)	[Cu(**C4COO**)]$^+$ 361.0824 (361.0952)	[Cu(**C5COO**)]$^+$ 375.1081 (375.1108)	[Cu(**C7COO**)]$^+$ 403.1386 (403.1421)	[Cu(**C10COO**)]$^+$ 445.1862 (445.1891)	[Cu(**C11COO**)]$^+$ 459.1924 (459.2047)

a) M^{2+} and **CnCOO**$^-$ are used as abbreviations for a metal ion and deprotonated ion of **CnCOOH** respectively.
b) M^{2+} was added as a perchlorate salt.

Table S2 Volumes of the solutions used for the Job plots.

Solution	Mole fraction of **CnCOOH**	Volume of 0.010 M **CnCOOH** / μL	Volume of 0.010 M $Cu(ClO_4)_2 \cdot 6H_2O$ / μL
1	0.1	300	2700
2	0.2	600	2400
3	0.3	900	2100
4	0.4	1200	1800
5	0.5	1500	1500
6	0.6	1800	1200
7	0.7	2100	900
8	0.8	2400	600
9	0.9	2700	300

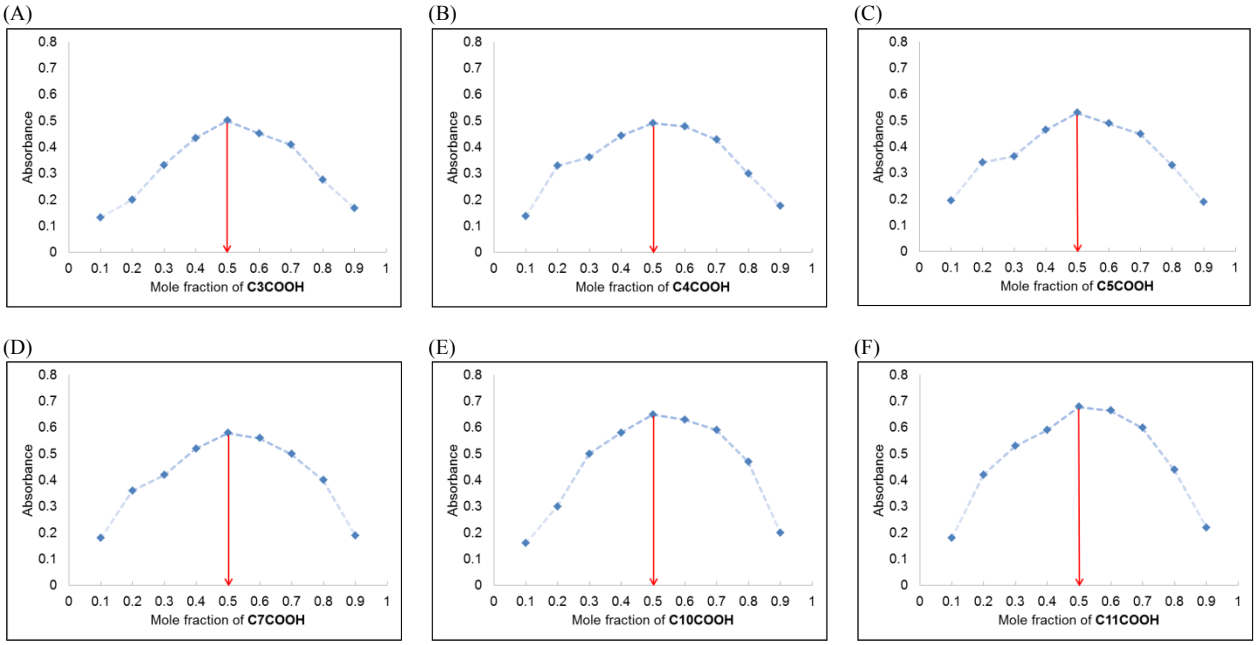

Figure S1 Job plots at 650 nm for Cu^{II} complexes of **CnCOOH**: (A) the plot of **C3COOH**, (B) the plot of **C4COOH**, (C) the plot of **C5COOH**, (D) the plot of **C7COOH,** (E) the plot of **C10COOH** and (F) the plot of **C11COOH**.

X-ray crystal structure determinations

Special conditions/variations to the general procedure are given below:

1: The perchlorate anion is disordered and has been modelled over three orientations refining to the occupancies 0.55/0.23/0.22. A region adjacent to the perchlorate contains disordered solvent which was modelled as 3.5 water molecules at four sites; the water was modelled at three positions at two sites, and in two positions at the remaining two sites. The water oxygen occupancies were chosen based on potential H-bonded pathways involving the perchlorate anions and also equalisation of U_{iso} values. The hydrogen atoms of the lattice water molecules could not be located from the difference Fourier map and have been omitted from the model. Restraints were applied to the disordered perchlorate to ensure similar bond lengths, angles and displacement parameters.

2: The asymmetric unit contains a Zn coordination polymer tetramer, along with four perchlorate anions and two lattice water molecules. One of the C_4-alkyl chains and associated carboxylate are disordered and have been modelled over two positions refining to 0.55/0.45 occupancies. Restraints ensured the two alkyl chain conformations had similar and sensible geometrical parameters. Two of the perchlorate anions are disordered and were modelled over two orientations, refining to equal occupancies; restraints were utilised in the refinement. One of the two lattice water molecules refined to half occupancy. The hydrogen atoms of the aqua ligands (one per Zn) and latter water could not be clearly located from the difference Fourier map and were omitted from the model.

4: The perchlorate anion appeared to be rotationally disordered and was modelled over two orientations at a single site, refining to 0.77/0.23 occupancies. The lattice also contains a disordered molecule of methanol which was modelled over two orientations, refining to 0.55/0.45 occupancies. Restraints were applied to the disordered perchlorate and methanol moieties.

5: One of the perchlorate anions is disordered and was modelled over two sites, refining to equal occupancies; restraints were applied across the two components. The hydrogen atoms of the lattice water molecules could not be located from the difference Fourier map and have been omitted from the model.

6: The hydrogen atoms of the lattice water molecules could not be located from the difference Fourier map and have been omitted from the model.

7: The asymmetric unit contains one cationic Zn-carboxylate complex at a two-fold axis generating the Zn_2L_2 macrocycle. The C_7 alkyl chain linking the amine and carboxylate is disordered and was modelled over three orientations refining to 0.35/0.35/0.3 occupancies and was a restrained refinement. The perchlorate anion is disordered and was modelled over two sites, refining to equal occupancies; the perchlorate is rotationally disordered at one site and was modelled with two equal orientations with the use of restraints.

8: All crystals investigated diffracted weakly and only low resolution data could be collected. Additionally, the crystals slowly lost crystallinity due to solvent loss. One perchlorate anion is well ordered, however, the remaining three perchlorate anions are disordered with only two half occupancy anions being located at a further two sites. The contents of the remaining voids between the complexes could not be effectively modelled and have been treated as a diffuse contribution to the overall scattering using SQUEEZE/PLATON (A. L. Spek). Restraints were applied across the pyridyl rings, the alkyl chains and perchlorate anions. The hydrogen atoms of the aqua ligands could not be located from the difference Fourier map and have been omitted from the model.

9: A low data completio operating under rotation data collection with a fixed detector and affects some high angle data. One perchlorate anion is rotationally disordered and was modelled over two orientations, refining to equal occupancies. Restraints were applied to the disordered perchlorate to ensure similar bond lengths, angles and displacement parameters. The hydrogen atoms of the lattice water molecules could not be located from the difference Fourier map and have been omitted from the model.n ratio is due to the limitations of the instrument available at the Australian Synchrotron.

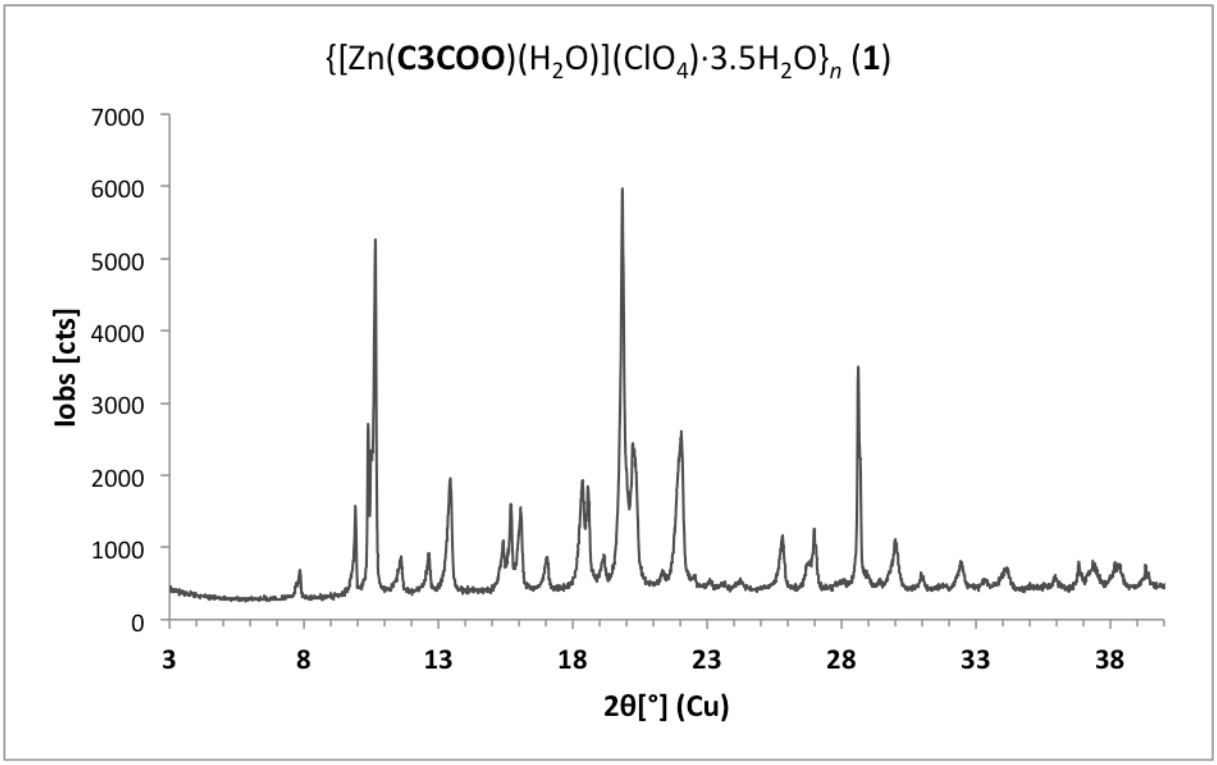

Figure S2 Powder X-ray diffraction measured from **1**.

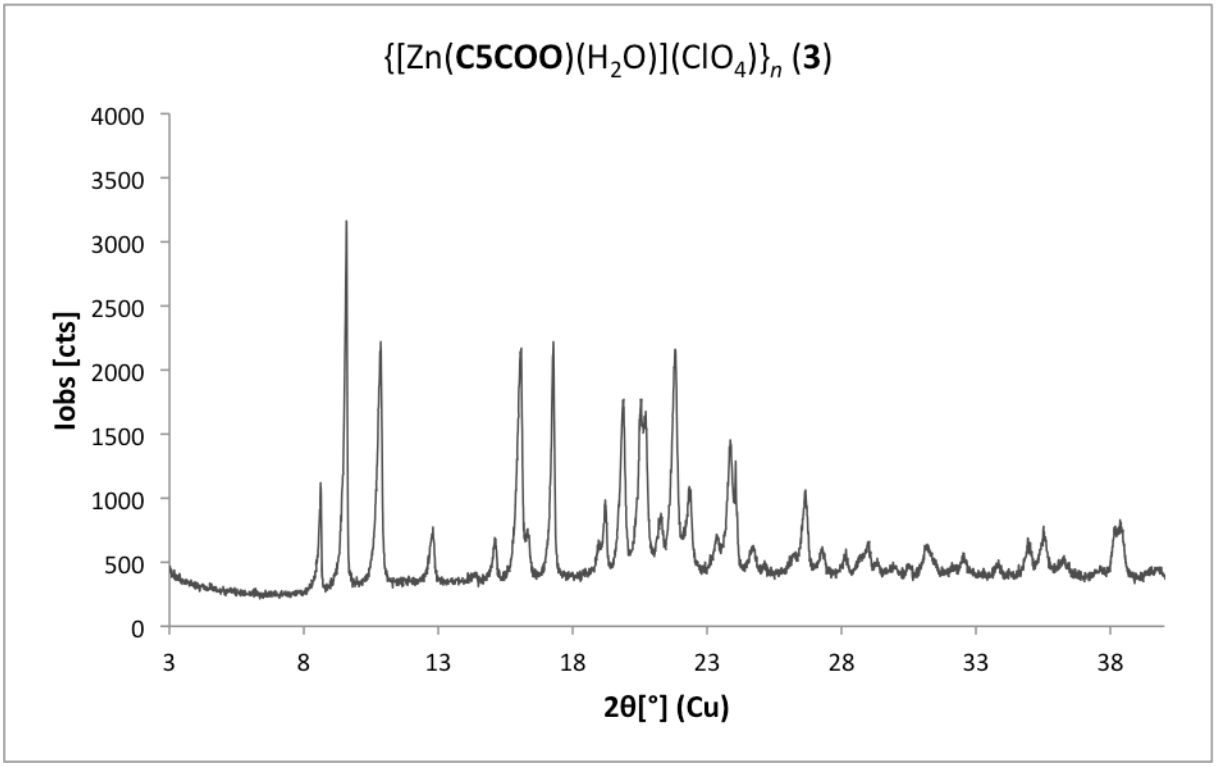

Figure S3 Powder X-ray diffraction measured from **3**.

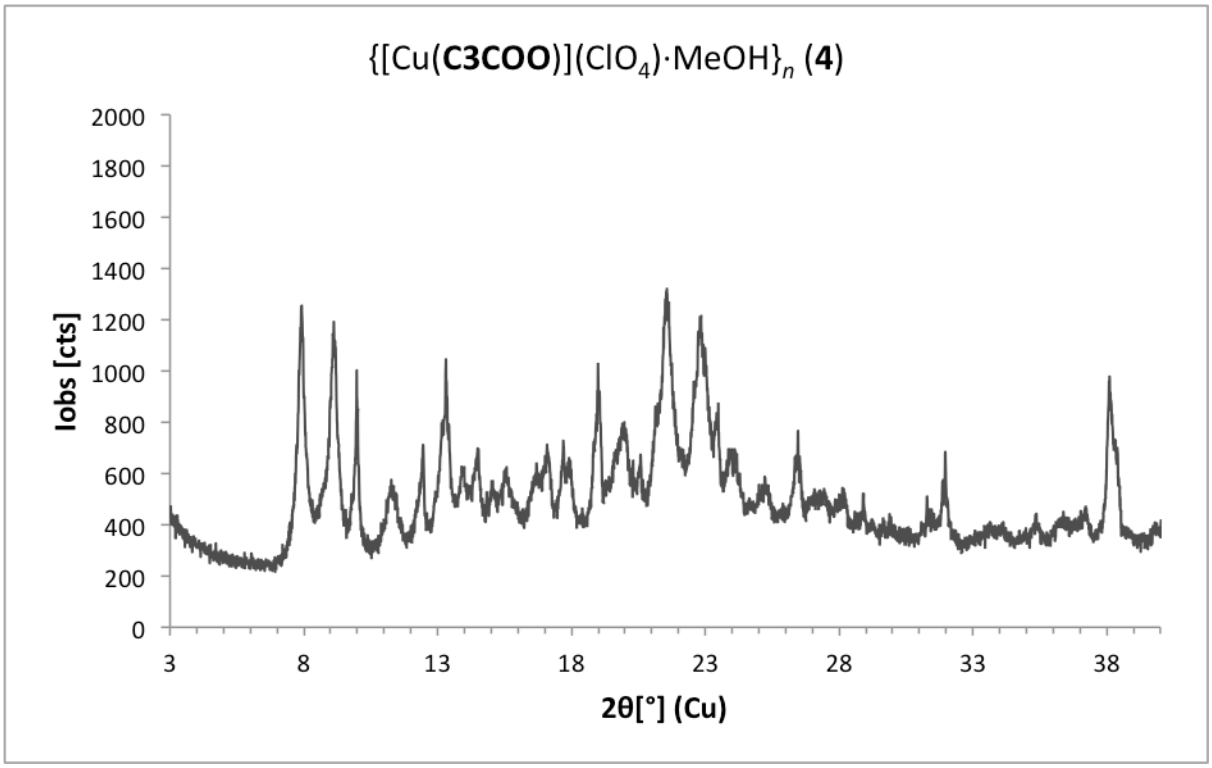

Figure S4 Powder X-ray diffraction measured from **4**.

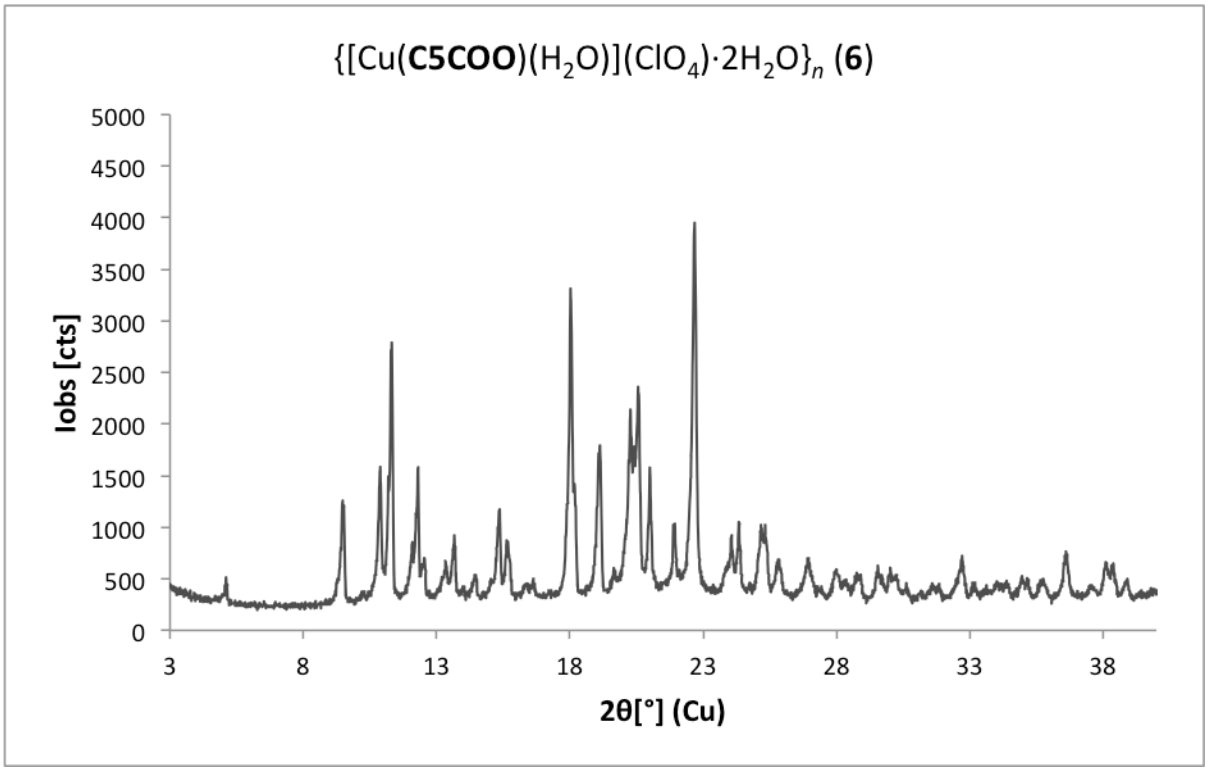

Figure S5 Powder X-ray diffraction measured from **6**.

Table S3 Bond lengths (Å), angles (°) and geometries for Zn^{II} coordination polymers of **1**, **2** and **3**.

Complexes	{[Zn(**C3COO**)(H_2O)](ClO_4)·3.5H_2O}$_n$ **(1)**	{[Zn(**C4COO**)(H_2O)](ClO_4)·1.5H_2O}$_n$ **(2)**		{[Zn(**C5COO**)(H_2O)](ClO_4)}$_n$ **(3)**
CCDC No	**1037287**	**1037288**		**1037289**
Bonds				
Zn–N pyridine	Zn1–N1 2.112(3) Zn1–N2 2.109(3)	Zn1–N11 2.122(5) Zn1–N12 2.117(5)	Zn3–N31 2.086(5) Zn3–N32 2.055(5)	Zn1–N1 2.0795(14) Zn1–N2 2.0847(14)
		Zn2–N21 2.095(5) Zn2–N22 2.122(5)	Zn4–N41 2.102(4) Zn4–N42 2.118(5)	
Zn–N tertiary	Zn1–N3 2.170(3)	Zn1–N13 2.163(4)	Zn3–N33 2.190(4)	Zn1–N3 2.1939(14)
		Zn2–N23 2.183(5)	Zn4–N43 2.205(4)	
Zn–O carboxylate	Zn1–O1* 2.001(3)	Zn1–O21 2.067(13) Zn1–O22 2.090(9)	Zn3–O41 2.111(4) Zn3–O42 2.241(4)	Zn1–O1* 2.0968(12) Zn1–O2* 2.2714(12)
		Zn2–O31 2.115(4) Zn2–O32 2.221(4)	Zn4–O11* 2.144(3) Zn4–O12* 2.184(4)	
Zn–O aqua	Zn1–O3 2.022(2)	Zn1–O13 2.114(4)	Zn3–O33 2.110(4)	Zn1–O3 2.1159(12)
		Zn2–O23 2.139(4)	Zn4–O43 2.131(4)	
H-Bonds				
	H31···O2 1.86(3)	–		–
Angles				
N pyridine–Zn–N tertiary	N1–Zn1–N3 79.09(11) N2–Zn1–N3 79.19(11)	N11–Zn1–N13 78.51(17) N12–Zn1–N13 79.55(17)	N31–Zn3–N33 79.88(88) N32–Zn3–N33 79.16(17)	N1–Zn1–N3 80.87(5) N2–Zn1–N3 79.63 (5)
		N21–Zn2–N23 78.87(19) N22–Zn2–N23 78.66(19)	N41–Zn4–N43 77.61(16) N42–Zn4–N43 78.55(17)	
N pyridine–Zn–N pyridine	N1–Zn1–N2 156.85(12)	N11–Zn1–N12 158.04(18)	N31–Zn3–N32 158.65(18)	N1–Zn1–N2 159.12(5)
		N21–Zn2–N22 157.35(18)	N41–Zn4–N42 156.02(16)	
O carboxylate–Zn–O carboxylate		O21–Zn1–O22 64.0(3)	O41–Zn3–O42 60.37(15)	O1*–Zn1–O2* 60.02(4)
		O31–Zn2–O32 60.93(14)	O11*–Zn4–O12* 60.88(14)	
O carboxylate–Zn–O aqua	O1–Zn1–O3 99.16(10)	O21–Zn1–O13 95.7(3) O22–Zn1–O13 159.6(2)	O41–Zn3–O33 99.46(15) O42–Zn3–O33 159.81(14)	O1*–Zn1–O3 98.62(5) O2*–Zn1–O3 157.70(5)
		O31–Zn2–O23 93.60(15) O32–Zn2–O23 154.52(14)	O11–Zn4–O43 91.90(14) O12–Zn4–O43 152.76(13)	
Geometries	Zn1: distorted square pyramid ($\tau = 0.10$)	Zn1: distorted octahedron	Zn3: distorted octahedron	Zn1: distorted octahedron
		Zn2: distorted octahedron	Zn4: distorted octahedron	

*symmetry equivalent atom (see text and figures for details)

Table S4 Selected bond lengths (Å), angles (°) and geometries for Cu^{II} coordination polymers of **4, 5** and **6**.

Complexes	{[Cu(**C3COO**)](ClO_4)·MeOH}$_n$ **(4)**	{[Cu(**C4COO**)(H_2O)](ClO_4)·2H_2O}$_n$ **(5)**	{[Cu(**C5COO**)(H_2O)](ClO4)·2H_2O}$_n$ **(6)**
CCDC No	**1037290**	**1037291**	**1037292**
Bonds			
Cu–N pyridine	Cu1–N1 1.977(3) Cu1–N2 1.985(3)	Cu1–N11 1.986(5) Cu1–N12 1.987(5) Cu2–N21 1.991(4) Cu2–N22 1.981(4)	Cu1–N1 1.971(3) Cu1–N2 1.987(3)
Cu–N tertiary	Cu1–N3 2.042(3)	Cu1–N13 2.013(5) Cu2–N23 2.038(4)	Cu1–N3 2.027(4)
Cu–O carboxylate	Cu1–O1* 1.982(3) Cu1–O2 2.181(3) Cu1–O2* 2.622(2)	Cu1–O11* 1.956(4) Cu1–O12* 2.649(5) Cu2–O21* 1.983(4) Cu2–O22* 2.485(4)	Cu1–O1* 1.956(3) Cu1–O2* 2.714(3)
Cu–O aqua	–	Cu1–O13 2.338(3) Cu2–O23 2.391(3)	Cu1–O3 2.269(3)
Angles			
N pyridine–Cu–N tertiary	N1–Cu1–N3 83.86(13) N2–Cu1–N3 82.98(13)	N11–Cu1–N13 82.85(19) N12–Cu1–N13 84.01(19) N21–Cu2–N23 82.80(18) N22–Cu2–N23 83.15(18)	N1–Cu1–N3 83.96(16) N2–Cu1–N3 82.85(19)
N pyridine–Cu–N pyridine	N1–Cu1–N2 162.94(14)	N11–Cu1–N12 166.82(19) N21–Cu2–N22 165.88(19)	N1–Cu1–N2 166.8(2)
O carboxylate–Cu–O carboxylate	O1*–Cu1–O2* 55.13(9) O1*–Cu1–O2 89.42(10)	O11*–Cu1–O12* 55.3(2) O21*–Cu2–O22* 57.5(1)	O1*–Cu1–O2* 53.5(1)
O carboxylate–Cu–O aqua	–	O11*–Cu1–O13 96.33(15) O12*–Cu1–O13 151.2(1) O21*–Cu2–O23 93.58(13) O22*–Cu2–O23 151.1(1)	O1*–Cu1–O3 105.06(13) O2*–Cu1–O3 158.0(1)
Geometries	Cu1: distorted octahedron	Cu1: distorted octahedron Cu2: distorted octahedron	Cu1: distorted octahedron

*symmetry equivalent atom (see text and figures for details)

Table S5 Selected bond lengths (Å), angles (°) and geometries for Zn^{II} macrocycles of **7**, **8** and **9**.

Complexes	$\{[Zn(\mathbf{C7COO})(H_2O)][ClO_4)]\}_2$ **(7)**	$\{[Zn_2(\mathbf{C10COO})_2(H_2O)_2](ClO_4)_2 \cdot 3H_2O \cdot MeOH\}_4$ **(8)**		$\{[Zn_2(\mathbf{C11COO})_2(H_2O)_2](ClO_4)_2[Zn_2(\mathbf{C11COO})_2](ClO_4)_2 \cdot H_2O\}_n$ **(9)**	
CCDC No	**1037293**	**1037294**		**1037295**	
Bonds					
Zn–N pyridine	Zn1–N1 2.093(4) Zn1–N2 2.055(4)	Zn1–N11 2.069(13) Zn1–N12 2.139(15)	Zn3–N31 2.060(12) Zn3–N32 2.118(13)	Zn1–N11 2.057(4) Zn1–N12 2.098(4)	Zn3–N31 2.062(4) Zn3–N32 2.094(4)
				Zn2–N21 2.121(4) Zn2–N22 2.100(4)	Zn4–N41 2.067(4) Zn4–N42 2.047(4)
		Zn2–N21 2.084(13)	Zn4–N41 2.072(13)		
Zn–N tertiary	Zn1–N3 2.230(6)	Zn2–N22 2.083(13)	Zn4–N42 2.084(12)	Zn1–N13 2.172(4)	Zn3–N33 2.219(4)
				Zn2–N23 2.174(4)	Zn4–N43 2.235(4)
		Zn1–N13 2.235(16)	Zn3–N33 2.224(14)		
Zn–O carboxylate	Zn1–O1* 1.978(4)	Zn2–N23 2.252(17)	Zn4–N43 2.227(16)	Zn1–O11 2.158(3) Zn1–O12 2.199(4)	Zn3–O31* 2.054(3) Zn3–O32 2.016(3)
				Zn2–O21 2.191(3) Zn2–O22 2.150(3)	Zn4–O41* 2.057(3) Zn4–O42 2.009(3)
		Zn1–O11* 2.178(13)	Zn3–O31* 2.161(12)		
Zn–O aqua	Zn1–O3 2.067(5)	Zn1–O12* 2.195(12)	Zn3–O32* 2.273(13)	Zn1–O13 2.121(3)	
				Zn2–O23 2.112(3)	
Angles		Zn2–O21 1.985(12)	Zn4–O41* 1.966(12) Zn4–O42* 2.564(12)		
N pyridine–Zn–N tertiary	N1–Zn1–N3 78.87(19) N2–Zn1–N3 78.9(2)	Zn1–O13 2.118(14) Zn2–O23 2.146(12)	Zn3–O33 2.047(11) Zn4–O43 2.136(11)	N11–Zn1–N13 81.37(17) N12–Zn1–N13 79.86(16)	N31–Zn3–N33 79.63(14) N32–Zn3–N33 79.27(14)
				N21–Zn2–N23 79.27(14) N22–Zn2–N23 80.21(15)	N41–Zn4–N43 79.28(13) N42–Zn4–N43 80.61(14)
		N11–Zn1–N13 78.4(6)	N31–Zn3–N33 80.8(5)		
N pyridine–Zn–N pyridine	N2–Zn1–N1 114.84(18)	N12–Zn1–N13 77.3(6)	N32–Zn3–N33 76.9(6)	N11–Zn1–N12 160.70(18)	N31–Zn3–N32 148.06(14)
				N21–Zn2–N22 158.82(15)	N42–Zn4–N41 147.81(15)
		N21–Zn2–N23 81.6(6)	N41–Zn4–N43 78.0(6)		
O carboxylate–Zn–O carboxylate	–	N22–Zn2–N23 80.2(6)	N42–Zn4–N43 79.2(5)	O11–Zn1–O12 60.36(12)	O31*–Zn3–O32 97.28(12)
				O21–Zn2–O22 60.55(12)	O41*–Zn4–O42 96.41(12)
		N11–Zn1–N12 111.7(6)	N31–Zn3–N32 110.4(5)		
O carboxylate–Zn–O aqua	O1*–Zn1–O3 96.97(18)	N21–Zn2–N22 111.5(6)	N41–Zn4–N42 110.9(6)	O11–Zn1–O13 103.11(13) O12–Zn1–O13 163.41(13)	
				O21–Zn2–O23 101.73(12) O22–Zn2–O23 162.28(12)	
Geometries	Zn1: distorted trigonal bipyrimid ($\tau = 0.63$)	Zn1: distorted octahedron	Zn3: distorted octahedron	Zn1: distorted octahedron	Zn3: distorted square pyramid ($\tau = 0.21$)
		Zn2: distorted square pyramid ($\tau = 0.49$)	Zn4: distorted square pyramid ($\tau = 0.44$)	Zn2: distorted octahedron	Zn4: distorted square pyramid ($\tau = 0.24$)

*symmetry equivalent atom (see text and figures for details)