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Self-assembly of precursors to potential open framework alkali earth metal-organic complexes

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Experimental

Crystallisation experiments

All chemicals and solvents are commercially available and were used without further purification. Crystals of **Mg1** – **Mg6** suitable for X-ray diffraction were grown by slow evaporation of solvent at set temperatures. The substrates were weighed into vials and dissolved in appropriate solvent(s), then the vial was covered with a hole-pierced lid and the contents left to crystallise at a specific temperature. At 30°C, 40°C and 50°C, the temperature was controlled using a jacketed hot-plate and samples crystallised at 4°C were placed in the fridge. Samples crystallised at lab temperature were stored on the crystallisation shelf and subject to fluctuations, but the temperature was maintained at approximately 20 °C. All crystals were clear and colourless in appearance and displayed slight variations in morphology. PXRD shows that in each preparation, the sample is inhomogeneous and a range of phases result, except for **Mg5** and **Mg6**, for which there is good correlation between the calculated and actual PXRD patterns.

Crystals of **Mg1** and **Mg2** [$Mg(C_6H_5NO_2)_2(NO_3)_2(H_2O)_4$] (**Mg1**, cuboids, **Mg2**, platelets) were produced from a solution of $Mg(NO_3)_2.6H_2O$ and picolinic acid (molar ratio 1:1) dissolved in an equal v/v mixture of DCM and acetone and crystallised by solvent evaporation at lab temperature.

Crystals of **Mg3** [$Mg(C_6H_5NO_2)_2(NO_3)_2(H_2O)_4$] (large angular chunks) were produced from a solution of $Mg(NO_3)_2.6H_2O$ and isonicotinic acid (molar ratio 1:1) dissolved in isopropanol and crystallised by solvent evaporation at 50°C.

Crystals of **Mg4** [$Mg(C_6H_5NO_2)(NO_3)_2(H_2O)_3$] (smooth crystalline 'melt') were produced from a solution of $Mg(NO_3)_2.6H_2O$ and picolinic acid (molar ratio 2:1) dissolved in methanol and crystallised by solvent evaporation at 50°C.

Crystals of **Mg5** [$Mg(C_7H_3N_2O_4).4.5(H_2O)$] (small flat rounded platelets) were produced in a two-step process. First $Mg(NO_3)_2.6H_2O$ (21 mg, 0.0819 mmol) and 2,4-pyridinedicarboxylic acid monohydrate (15 mg, 0.0810 mmol) were dissolved in methanol and left on a hotplate at 30°C, resulting in a white crystalline powder. This was dissolved in methanol and an aqueous solution of *m*-xylylenediamine (2.41 ml, 0.0379 mol L^{-1}, 0.00810 mmol) was added, and the vial left on a hotplate at 50°C. After 1 week crystals were found floating on the surface of the solution and the vial was removed from heat.

Crystals of **Mg6** [$Mg(C_7H_3N_2O_4)_2.(H_2O)_2Mg(H_2O)_6.1.5(H_2O)$] (rectangular shards) were produced by dissolving $Mg(CO_2CH_3)_2.4H_2O$ (214 mg, 1 mmol) and 2,4-pyridinedicarboxylic acid monohydrate (167 mg, 0.9 mmol) together in water in a Teflon-lined stainless steel autoclave. The mixture was heated in an oven from ambient temperature at a rate of 0.26°C min^{-1} and maintained at 150°C for 72 hours. The autoclave was allowed to cool back to room temperature in the oven before being removed. On opening, the vial contained some white solid and small clear colourless crystals. The vial was left on the crystallisation shelf at lab temperature for 10 weeks after which there was a large homogeneous mass of clear, colourless crystalline shards.

Complex		$Mg(NO_3)_2.6H_2O$ (mass, no. moles)	Pyridine carboxylic acid P/I (mass, no. moles)	Solvent	Temp. (°C)
Mg1	(1)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
	(2)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	Methanol	50 °C
	(3)	31 mg, 0.121 mmol	(P) 30 mg, 0.244 mmol	Methanol	50 °C
	(4)	62 mg, 0.242 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
	(5)	31 mg, 0.121 mmol	(P) 30 mg, 0.244 mmol	DCM / acetone	lab temp.
	(6)	52 mg, 0.203 mmol	(P) 25 mg, 0.203 mmol	Water	50 °C
	(7)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	Acetone	lab temp.
	(8)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	Ethyl acetate / THF	lab temp.
	(9)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	4 °C
Mg2	(1)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
	(2)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
	(3)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
	(4)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.
Mg3	(1)	31 mg, 0.121 mmol	(I) 15 mg, 0.122 mmol	Isopropanol	50 °C
	(2)	31 mg, 0.121 mmol	(I) 15 mg, 0.122 mmol	Methanol / water	lab temp.
Mg4	(1)	62 mg, 0.242 mmol	(P) 15 mg, 0.122 mmol	Methanol	50 °C
	(2)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	Chloroform / water	lab temp.
	(3)	31 mg, 0.121 mmol	(P) 15 mg, 0.122 mmol	DCM / acetone	lab temp.

Table S1. Preparation conditions for **Mg1, Mg2, Mg3** and **Mg4.** P = picolinic acid, I = isonicotinic acid.[1]

[1] 3-pyridinecarboxylic acid (nicotinic acid) was also used as a starting material, however this did not result in a crystalline product displaying metal-organic ligand coordination.

Single crystal XRD

For **Mg1-Mg5**, single crystal X-ray diffraction data were collected using a Rigaku R-axis/RAPID image plate diffractometer or a Bruker Nonius Kappa CCD diffractometer, each equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected at 100 K using Oxford Cryosystems Cryostream low temperature device, except for **Mg3** which was collected at 110 K. For **Mg6**, data were recorded on an Agilent Technologies Gemini A Ultra CCD diffractometer, using monochromatic MoK_α radiation, λ = 0.71073 Å. The data were collected at 150 K and the temperature was controlled using an Oxford Diffraction Cryojet.

The data were processed using CrystalClear.[1] (Rigaku), Collect[2] with HKLDenzo and Scalepack[3] (Kappa) or CrysAlisPro[4] (Gemini). Absorption corrections were applied using SADABS[5] or ABSCOR[6]. Structure solution, followed by full-matrix least-squares refinement on F^2 was carried out using SHELX97[7], with final refinement by SHELX2013 for **Mg1**-**Mg5**) within WinGX.[8] All non-hydrogen atoms were refined anisotropically**.** H atoms were generally located in difference Fourier maps and refined isotropically; where this was not possible they were included in calculated positions where possible and/or had U_{iso} values fixed to a value of 1.5 times those of the parent atoms.

Powder XRD (PXRD)

PXRD was carried out using a Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.5406 Å). Data were collected between the 2θ angles of 5 and 50°.

Differential scanning calorimetry (DSC)

Heat flux DSC measurements were carried out using a TA instrument Q20 DSC system. A 3–5 mg sample of crystalline material was gathered from the sample vial from which single crystals were obtained. The sample was heated from ambient temperature to approximately 140°C at a rate of 10°C min^{-1}. Melting points were derived from the endotherm peak using the TA Universal Analysis software.

Hot stage Microscopy (HSM)

HSM was performed using a Mettler Toledo FP82HT hot stage instrument. A single crystal for which the unit cell had been identified was placed on a glass slide and fitted into the heating chamber. The sample was then heated at a rate of 10°C min^{-1} until the crystal appeared to have melted.

Geometric parameters in crystal structures – Magnesium complexes Mg1-Mg6

Mg1

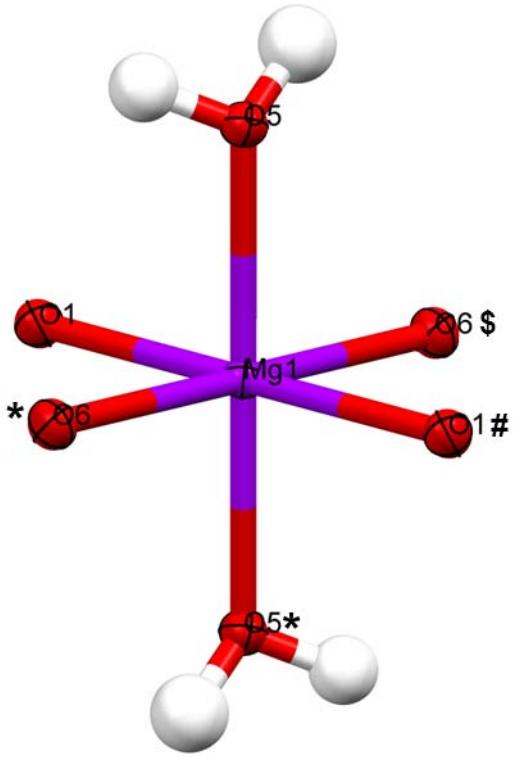

Figure S1. Octahedral environment of Mg centre in **Mg1**. Symmetry equivalent positions: $^{\$}$(-x,-y,-z), $^{\#}$(1-x,-y,-z), *(1+x,y,z)

Coordination	O-Mg-O angle (°)	Interaction	Distance (Å)
O5-Mg1-O1	92.28(3)	Mg1-O5/O5*	2.071(1)
O5-Mg1-O6$^{\$}$	95.50(3)	Mg1-O6$^{\$}$/O6*	2.063(1)
O5-Mg1-O1$^{\#}$	87.72(3)	Mg1-O1/O1$^{\#}$	2.060(1)
O5-Mg1-O6*	84.50(3)		
O1/O1$^{\#}$-Mg1-O6$^{\$}$/O6*	93.78(3)		
O6$^{\$}$/O6*-Mg-O1$^{\#}$/O1	86.22(3)		

$^{\$}$(-x,-y,-z), $^{\#}$(1-x,-y,-z), *(1+x,y,z)

Table S2. O-Mg-O bond angles and Mg-O distances in **Mg1.**

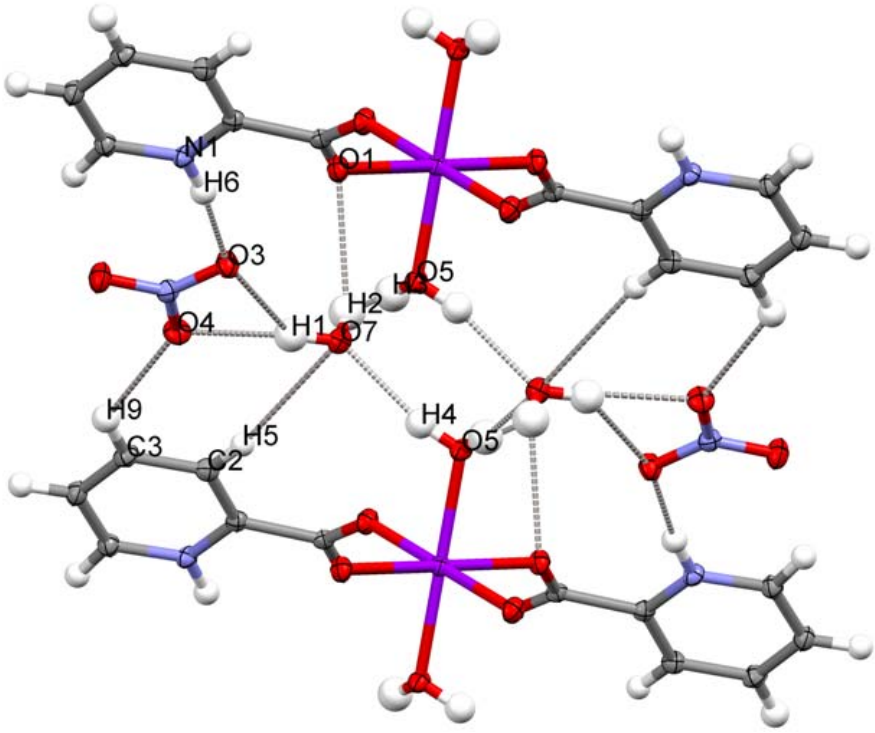

Figure S2. H-bonds between nitrate ions and water molecules connecting 1D polymers in **Mg1.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(3)	0.896(16)	1.957(16)	2.8441(13)	169.7(14)
C(5)-H(5)...O(2)	0.987(15)	2.407(15)	3.1843(15)	135.2(11)
C(5)-H(5)...O(2)#3	0.987(15)	2.492(15)	3.1043(14)	119.9(11)
O(5)-H(5A)...O(7)#4	0.826(19)	1.973(19)	2.7873(13)	168.5(17)
O(5)-H(5B)...O(7)	0.84(2)	1.94(2)	2.7759(12)	171.4(19)
O(7)-H(7A)...O(4)#1	0.851(19)	1.98(2)	2.8285(13)	175.0(18)
O(7)-H(7A)...N(2)#1	0.851(19)	2.671(19)	3.4600(13)	154.9(15)
O(7)-H(7B)...O(1)#2	0.84(2)	2.49(2)	3.0587(13)	125.7(16)
O(7)-H(7B)...O(5)#5	0.84(2)	2.21(2)	2.9790(13)	151.6(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x,-y,-z #3 -x+1,-y,-z-1

#4 -x,-y-1,-z #5 x-1,y,z

Table S3. Geometries of H-bonds in **Mg1**; atom numbering given in Figures in main text or ESI.

Mg2

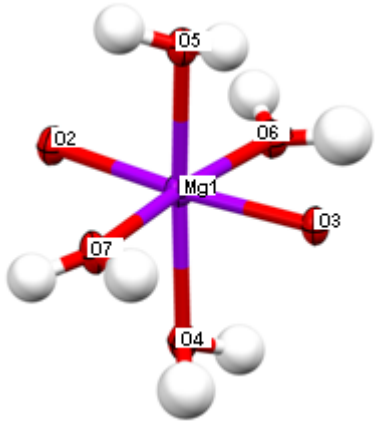

Figure S3. Octahedral environment of Mg centre in **Mg2.**

O(6)-Mg(1)-O(2)	87.00(6)	Mg(1)-O(6)	2.0459(14)
O(6)-Mg(1)-O(7)	175.27(6)	Mg(1)-O(2)	2.0529(13)
O(2)-Mg(1)-O(7)	96.60(6)	Mg(1)-O(7)	2.0693(14)
O(6)-Mg(1)-O(3)	88.31(6)	Mg(1)-O(3)	2.0728(13)
O(2)-Mg(1)-O(3)	174.91(5)	Mg(1)-O(5)	2.0941(14)
O(7)-Mg(1)-O(3)	88.19(6)	Mg(1)-O(4)	2.1059(14)
O(6)-Mg(1)-O(5)	94.57(5)		
O(2)-Mg(1)-O(5)	92.50(6)		
O(7)-Mg(1)-O(5)	88.36(6)		
O(3)-Mg(1)-O(5)	85.92(6)		
O(6)-Mg(1)-O(4)	88.86(6)		
O(2)-Mg(1)-O(4)	92.92(5)		
O(7)-Mg(1)-O(4)	87.89(6)		
O(3)-Mg(1)-O(4)	88.95(5)		
O(5)-Mg(1)-O(4)	173.73(6)		

TableS4. O-Mg-O bond angles (°; left) and Mg-O distances (Å; right) in **Mg2.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(22)-H(22)...O(14)#1	0.93(2)	2.46(2)	3.104(2)	126.7(15)
C(24)-H(24)...O(11)#2	0.94(2)	2.49(2)	3.132(2)	126.2(15)
C(24)-H(24)...O(12)#2	0.94(2)	2.64(2)	3.575(2)	172.8(17)
C(25)-H(25)...O(15)	0.923(19)	2.39(2)	3.218(2)	148.5(15)
C(25)-H(25)...O(11)#2	0.923(19)	2.659(18)	3.148(2)	113.8(14)
N(17)-H(17)...O(13)	0.92(2)	1.93(2)	2.810(2)	160.0(19)
C(31)-H(31)...O(11)	0.919(19)	2.40(2)	3.200(2)	145.7(15)
N(16)-H(16)...O(10)	0.94(2)	1.82(2)	2.735(2)	165(2)
O(6)-H(6A)...O(5)#3	0.93(3)	2.55(2)	3.0489(18)	114.1(18)
O(6)-H(6A)...O(9)	0.93(3)	1.96(3)	2.7857(18)	148(2)
O(6)-H(6B)...O(13)	0.87(2)	1.95(2)	2.7954(18)	164(2)
O(7)-H(7A)...O(10)	0.94(2)	1.73(3)	2.6671(19)	172(2)
O(7)-H(7A)...N(19)	0.94(2)	2.66(2)	3.575(2)	164(2)
O(7)-H(7B)...O(4)#4	0.85(2)	2.02(3)	2.8715(19)	175(2)
O(4)-H(4A)...O(9)#5	0.91(3)	1.80(3)	2.7093(18)	174(2)
O(4)-H(4B)...O(8)#4	0.87(3)	1.84(3)	2.6959(17)	173(3)
O(5)-H(5A)...O(8)#6	0.89(3)	1.87(3)	2.7633(19)	176(2)
O(5)-H(5B)...O(14)#3	0.87(2)	2.04(3)	2.9058(19)	172(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z #2 x+1,y,z-1 #3 -x+1,-y+1,-z #4 -x,-y+2,-z

#5 -x,-y+1,-z #6 -x+1,-y+2,-z

Table S5. Geometries of H-bonds in **Mg2.**

Mg3

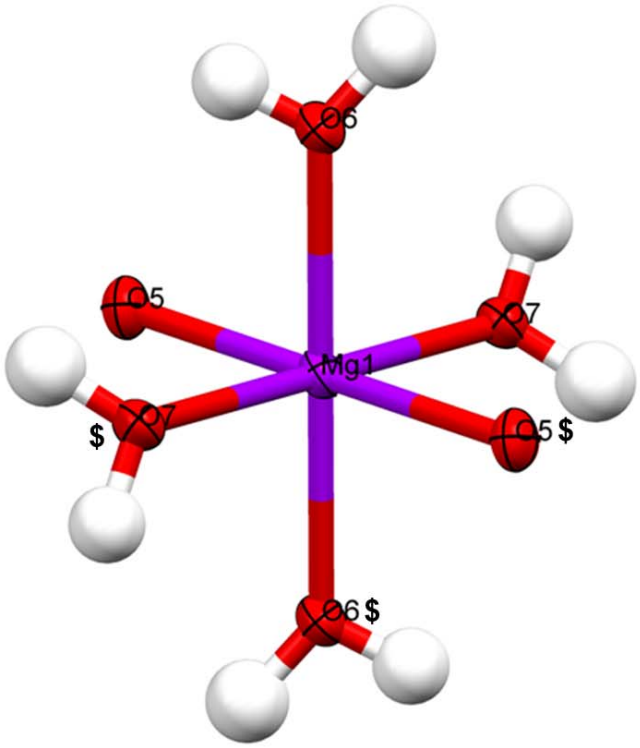

Figure S4. Octahedral environment of Mg centre in **Mg3**. Symmetry equivalent positions: $^{\$}$(-x,-y,-z)

Coordination	O-Mg-O angle (°)	Interaction	Distance (Å)
O6-Mg1-O5	89.25(4)	Mg1-O5/O5$^{\$}$	2.040(1)
O6-Mg1-O7	94.74(4)	Mg1-O6/O6$^{\$}$	2.071(1)
O6-Mg1-O5$^{\$}$	90.75(4)	Mg1-O7/O7$^{\$}$	2.089(1)
O6-Mg1-O7$^{\$}$	85.26(4)		
O5/O5$^{\$}$-Mg1-O7/O7$^{\$}$	91.46(4)		
O7/O7$^{\$}$-Mg1-O5$^{\$}$/O5	88.54(4)		

Table S6. O-Mg-O bond angles (°; left) and Mg-O distances (Å; right) in **Mg3.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)...O(4)#2	0.968(17)	2.492(18)	3.3671(17)	150.3(14)
C(4)-H(4)...O(7)#3	0.927(17)	2.619(16)	3.3048(17)	131.3(12)
C(4)-H(4)...O(3)#4	0.927(17)	2.584(16)	3.0674(17)	113.0(12)
N(2)-H(7)...O(1)#5	0.90(2)	1.85(2)	2.7322(15)	168.3(18)
N(2)-H(7)...O(3)#5	0.90(2)	2.65(2)	3.3286(16)	133.2(15)
N(2)-H(7)...N(1)#5	0.90(2)	2.60(2)	3.4556(16)	160.0(16)
O(6)-H(8)...O(2)	0.78(2)	2.11(2)	2.8849(15)	169(2)
O(6)-H(9)...O(4)#6	0.88(2)	1.81(2)	2.6837(14)	175(2)
O(7)-H(10)...O(2)#6	0.82(2)	1.94(2)	2.7453(14)	167.7(19)
O(7)-H(11)...O(1)#1	0.86(2)	1.93(2)	2.7920(14)	175.2(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y,-z+1 #3 -x,-y,-z+1

#4 -x+1,-y-1,-z+1 #5 -x,-y-1,-z+1 #6 -x+1,-y,-z

Table S7. Geometries of H-bonds in **Mg3.**

Mg4

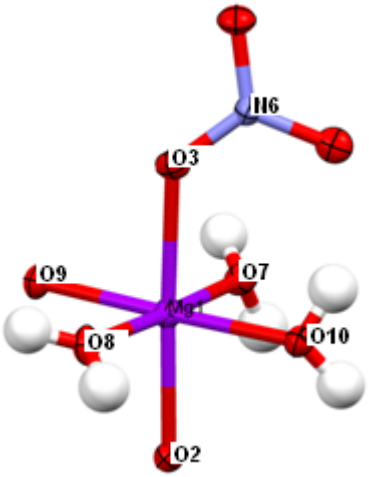

Figure S5. Octahedral environment of the Mg centre in **Mg4.**

O(9)-Mg(1)-O(8)	87.52(6)	Mg(1)-O(9)	2.0303(13)
O(9)-Mg(1)-O(7)	88.64(5)	Mg(1)-O(8)	2.0404(13)
O(8)-Mg(1)-O(10)	91.16(6)	Mg(1)-O(7)	2.0529(13)
O(7)-Mg(1)-O(10)	92.67(5)	Mg(1)-O(10)	2.0687(13)
O(9)-Mg(1)-O(2)	93.09(5)	Mg(1)-O(2)	2.0761(13)
O(8)-Mg(1)-O(2)	94.14(5)	Mg(1)-O(3)	2.1333(13)
O(7)-Mg(1)-O(2)	86.01(5)		
O(10)-Mg(1)-O(2)	88.82(5)		
O(9)-Mg(1)-O(3)	88.64(5)		
O(8)-Mg(1)-O(3)	87.09(5)		
O(7)-Mg(1)-O(3)	92.88(5)		
O(10)-Mg(1)-O(3)	89.48(5)		

Table S8. O-Mg-O bond angles (°; left) and Mg-O distances (Å; right) in **Mg4.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(10)-H(1)...O(4)	0.86(3)	1.95(3)	2.7226(19)	149(3)
O(10)-H(1)...O(5)#3	0.86(3)	2.57(3)	3.1683(18)	128(2)
O(10)-H(1)...N(6)	0.86(3)	2.67(3)	3.227(2)	124(2)
O(10)-H(3)...O(12)	0.85(3)	2.02(3)	2.8427(18)	164(3)
O(7)-H(4)...O(4)#4	0.84(3)	2.51(3)	3.1119(19)	130(2)
O(7)-H(4)...O(5)#4	0.84(3)	2.02(3)	2.8539(18)	170(2)
O(7)-H(4)...N(6)#4	0.84(3)	2.58(3)	3.358(2)	155(2)
O(7)-H(5)...O(14)#5	0.87(3)	1.88(3)	2.7330(19)	167(3)
O(8)-H(6)...O(2)#2	0.79(3)	2.14(3)	2.8668(18)	154(3)
O(8)-H(6)...O(9)#2	0.79(3)	2.64(3)	3.0741(18)	117(2)
O(8)-H(7)...O(12)#1	0.84(3)	2.64(3)	3.2852(19)	136(2)
O(8)-H(7)...O(13)#1	0.84(3)	1.96(3)	2.7894(18)	170(3)
O(8)-H(7)...N(11)#1	0.84(3)	2.61(3)	3.4195(19)	163(2)
C(17)-H(8)...O(4)#6	0.89(2)	2.42(2)	3.288(2)	162.5(16)
C(20)-H(11)...O(5)#7	0.95(2)	2.29(2)	3.156(2)	151.8(19)
N(21)-H(12)...O(14)#5	0.97(3)	1.82(3)	2.790(2)	174(2)
N(21)-H(12)...N(11)#5	0.97(3)	2.66(3)	3.527(2)	149.1(19)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y-1/2,-z+1/2 #2 -x+1/2,y+1/2,-z+1/2

#3 -x+3/2,y+1/2,-z+1/2 #4 -x+3/2,y-1/2,-z+1/2

#5 -x+1,-y+1,-z+1 #6 x-1,y,z #7 x-1/2,-y+1/2,z+1/2

Table S9. Geometries of H-bonds in **Mg4**.

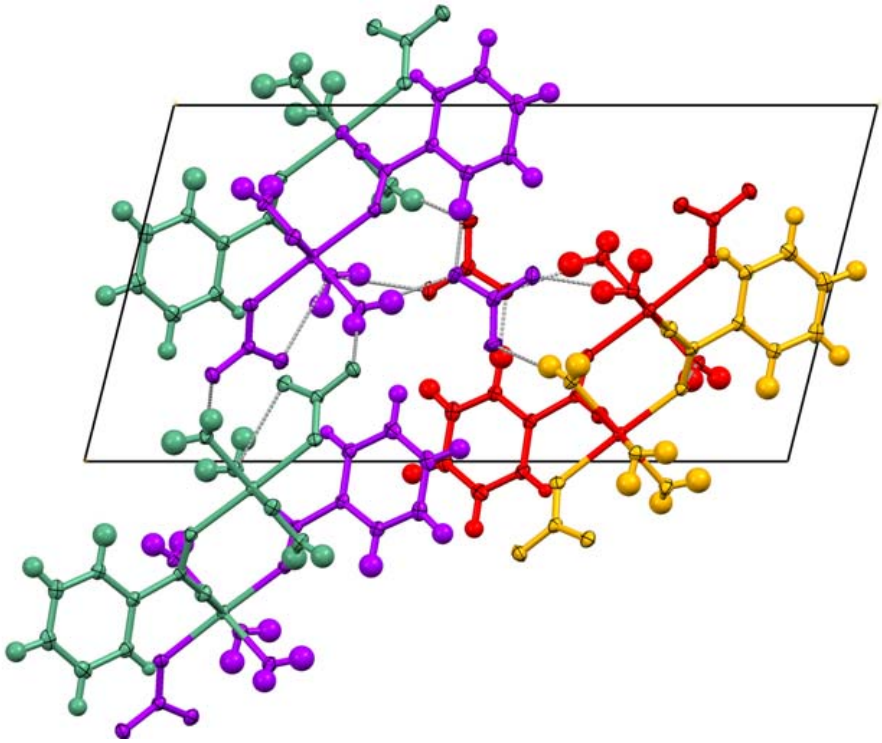

Figure S6. Global packing of **Mg4** showing H-bonding interactions that connect coordination polymers along the *a* and *c* axes.

Mg5

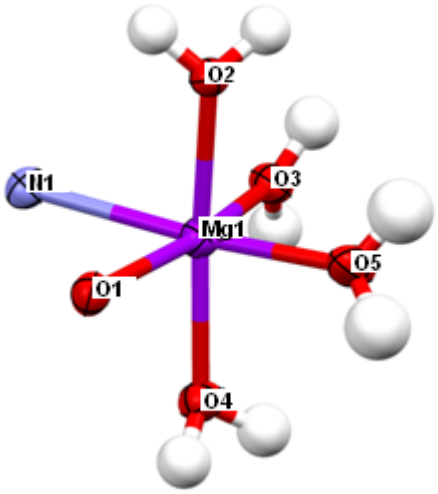

Figure S7. Octahedral environment of Mg centre in **Mg5.**

O(3)-Mg(1)-O(5)	97.58(17)	Mg(1)-O(3)	2.024(4)
O(5)-Mg(1)-O(1)	96.32(16)	Mg(1)-O(5)	2.050(4)
O(3)-Mg(1)-O(4)	88.46(14)	Mg(1)-O(1)	2.066(3)
O(5)-Mg(1)-O(4)	91.24(15)	Mg(1)-O(4)	2.067(3)
O(1)-Mg(1)-O(4)	88.00(14)	Mg(1)-O(2)	2.092(3)
O(3)-Mg(1)-O(2)	94.50(14)	Mg(1)-N(1)	2.203(4)
O(5)-Mg(1)-O(2)	83.42(14)		
O(1)-Mg(1)-O(2)	90.30(13)		
O(3)-Mg(1)-N(1)	90.65(15)		
O(1)-Mg(1)-N(1)	76.12(14)		
O(4)-Mg(1)-N(1)	97.50(14)		
O(2)-Mg(1)-N(1)	87.48(14)		

Table S10. O-Mg-O bond angles (°; left) and Mg-O distances (Å; right) in **Mg5.**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(1)-H(1)...O(3)	0.96(6)	2.66(5)	3.231(6)	119(4)
C(2)-H(2)...O(9)#2	1.04(4)	2.40(5)	3.326(9)	147(3)
C(4)-H(4)...O(9)#3	1.03(6)	2.27(6)	3.228(9)	155(5)
O(2)-H(2A)...O(7)#4	0.871(10)	1.85(3)	2.696(4)	162(8)
O(2)-H(2B)...O(1)#5	0.869(10)	1.91(4)	2.708(4)	152(7)
O(3)-H(3A)...O(2)#5	0.871(10)	1.99(3)	2.817(4)	158(7)
O(3)-H(3B)...O(8)#2	0.872(10)	1.824(19)	2.687(4)	169(8)
O(4)-H(4A)...O(5)#6	0.870(10)	2.46(5)	3.196(5)	142(7)
O(4)-H(4B)...O(7)#3	0.873(10)	1.904(12)	2.776(4)	177(7)
O(5)-H(5B)...O(8)#7	0.872(10)	1.758(13)	2.629(5)	176(7)
O(5)-H(5A)...O(6)#5	0.871(10)	1.872(12)	2.742(5)	178(8)
O(9)-H(9A)...O(4)	0.873(10)	1.89(7)	2.701(9)	154(14)
O(9)-H(9B)...O(6)#2	0.873(10)	2.00(7)	2.806(9)	153(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z #2 -x+2,y-1/2,-z+1/2 #3 -x+2,y+1/2,-z+1/2

#4 -x+2,-y,-z+1 #5 -x+1,y-1/2,-z+1/2 #6 -x+1,-y,-z

#7 x-1,-y+1/2,z-1/2

Table S11. Geometries of H-bonds in **Mg5**.

Mg6

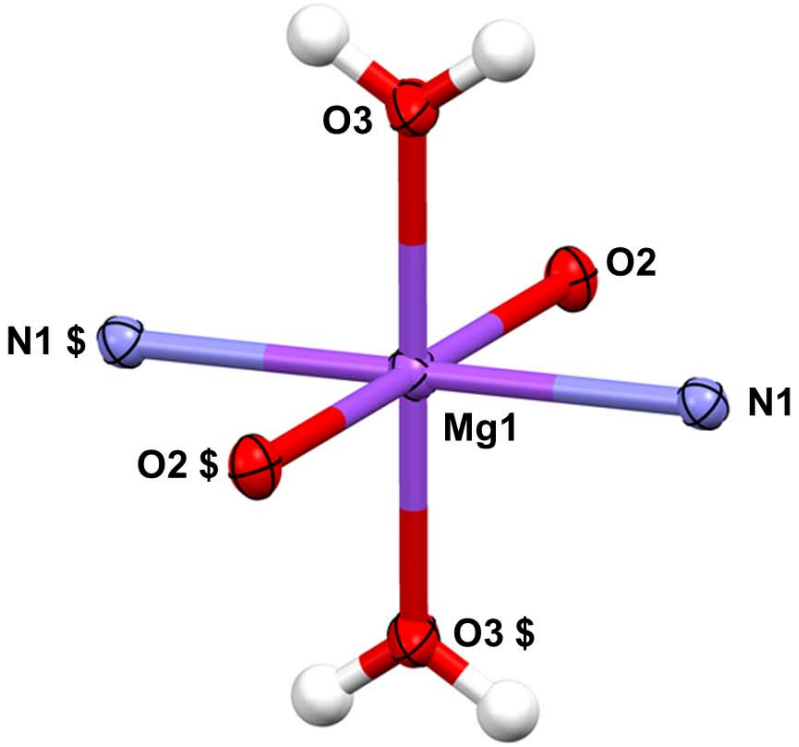

Figure S8. Octahedral environment of Mg(1) centre in **Mg6**. Symmetry equivalent positions: $^{\$}$(1-x,1-y,-z)

Coordination	O-Mg-O angle (°)	Interaction	Distance (Å)
O3/O3$^{\$}$-Mg1-O2/O2$^{\$}$	90.4(1)	Mg1-N1/N1$^{\$}$	2.191(3)
O3/O3$^{\$}$-Mg1-O2$^{\$}$/O2	89.6(1)	Mg1-O2/O2$^{\$}$	2.063(3)
O3/O3$^{\$}$-Mg1-N1/N1$^{\$}$	87.9(1)	Mg1-O3/O3$^{\$}$	2.037(3)
O3/O3$^{\$}$-Mg1-N1$^{\$}$/N1	92.1(1)		
O2/O2$^{\$}$-Mg1-N1/N1$^{\$}$	77.8(1)		
O2/O2$^{\$}$-Mg1-N1$^{\$}$/N1	102.2(1)		

Table S12. O-Mg-O bond angles and Mg-O distances of Mg(1) centre in **Mg6.**

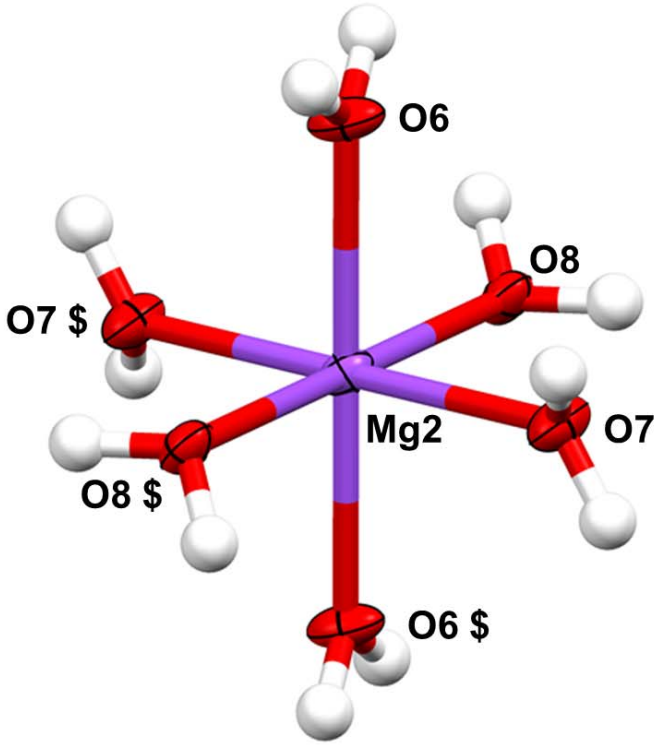

Figure S9. Octahedral environment of Mg(2) centre in **Mg6**. Symmetry equivalent positions: $^{\$}$(-x,-y,-z)

Coordination	O-Mg-O angle (°)	Interaction	Distance (Å)
O6/O6$^{\$}$-Mg2-O7/O7$^{\$}$	89.3(1)	Mg2-O6/O6$^{\$}$	2.068(3)
O6/O6$^{\$}$-Mg2-O7$^{\$}$/O7	90.7(1)	Mg2-O7/O7$^{\$}$	2.044(3)
O6/O6$^{\$}$-Mg2-O8/O8$^{\$}$	89.6(1)	Mg2-O8/O8$^{\$}$	2.065(3)
O6/O6$^{\$}$-Mg2-O8$^{\$}$/O8	90.4(1)		
O7/O7$^{\$}$-Mg2-O8/O8$^{\$}$	90.5(1)		
O7/O7$^{\$}$-Mg2-O8$^{\$}$/O8	89.5(1)		

Table S13. O-Mg-O bond angles and Mg-O distances of Mg(2) centre in **Mg6.**

D-H---A Interaction	D-H (Å)	H---A (Å)	D---A (Å)	D-H---A (°)
O6-H6A-O4	0.84(4)	1.91(4)	2.749(4)	173(4)
O6-H6B-O2	0.84(3)	1.98(3)	2.811(4)	177(3)
O7-H7A-O9	0.85(3)	1.85(3)	2.692(4)	168(4)
O7-H7B-O5	0.84(2)	1.88(2)	2.712(4)	174(3)
O8-H8A-O2	0.85(3)	2.04(3)	2.878(4)	169(3)
O8-H8B-O1	0.84(3)	1.85(3)	2.689(4)	173(3)
O9-H9A-O4	0.85(2)	1.96(2)	2.799(4)	170(4)
O10-H10A-O1	0.85(8)	2.35(8)	3.065(3)	141(7)
O10-H10B-O9	0.86(4)	1.83(5)	2.685(4)	170(7)

Table S14. Geometries of H-bonds in **Mg6** connecting $Mg(C_7H_3NO_4)_2(H_2O)_2$ units to $Mg(H_2O)_6$ and uncoordinated water molecules.

D-H---A Interaction	D-H (Å)	H---A (Å)	D---A (Å)	D-H---A (°)
O3-H3A-O5	0.84(2)	1.89(2)	2.721(4)	173(4)
O3-H3B-O4	0.84(3)	2.16(2)	2.989(4)	167(3)
O3-H3B-O5	0.84(3)	2.49(4)	3.136(4)	134(4)

Table S15. Geometries of H-bonds in Mg6 connecting $Mg(C_7H_3NO_4)_2(H_2O)_2$ units.

Powder XRD (PXRD)

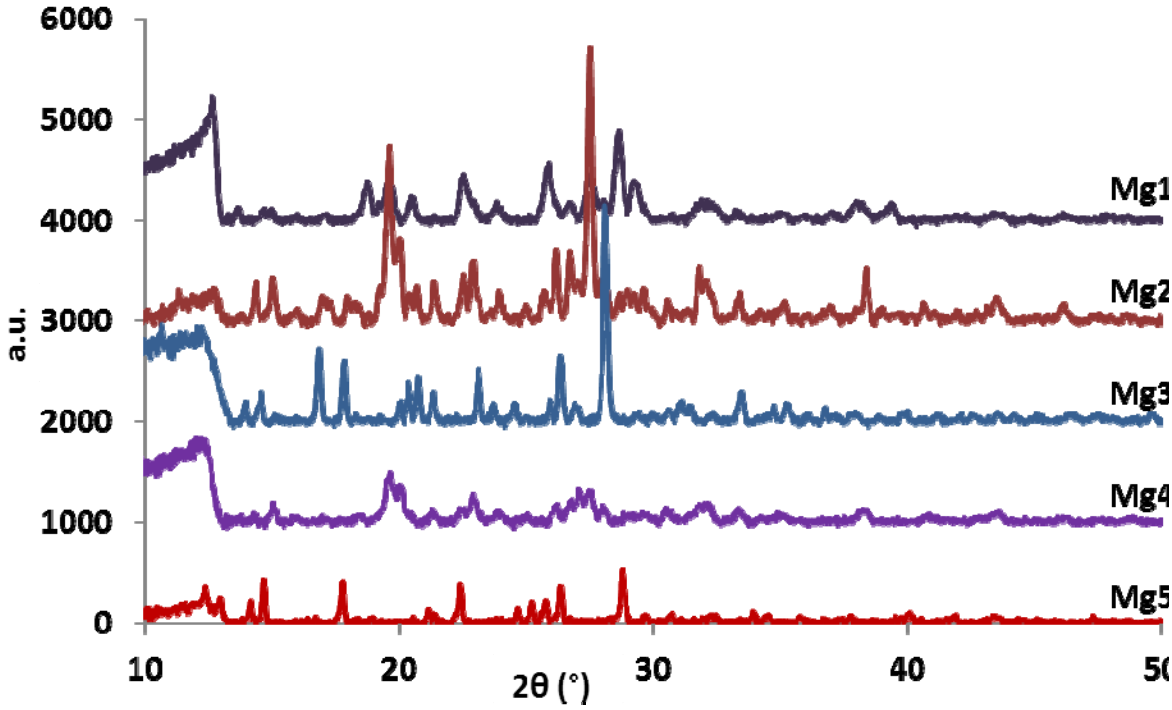

Figure S10. PXRD patterns of complexes **Mg1 – Mg5.**

Differential scanning calorimetry (DSC)

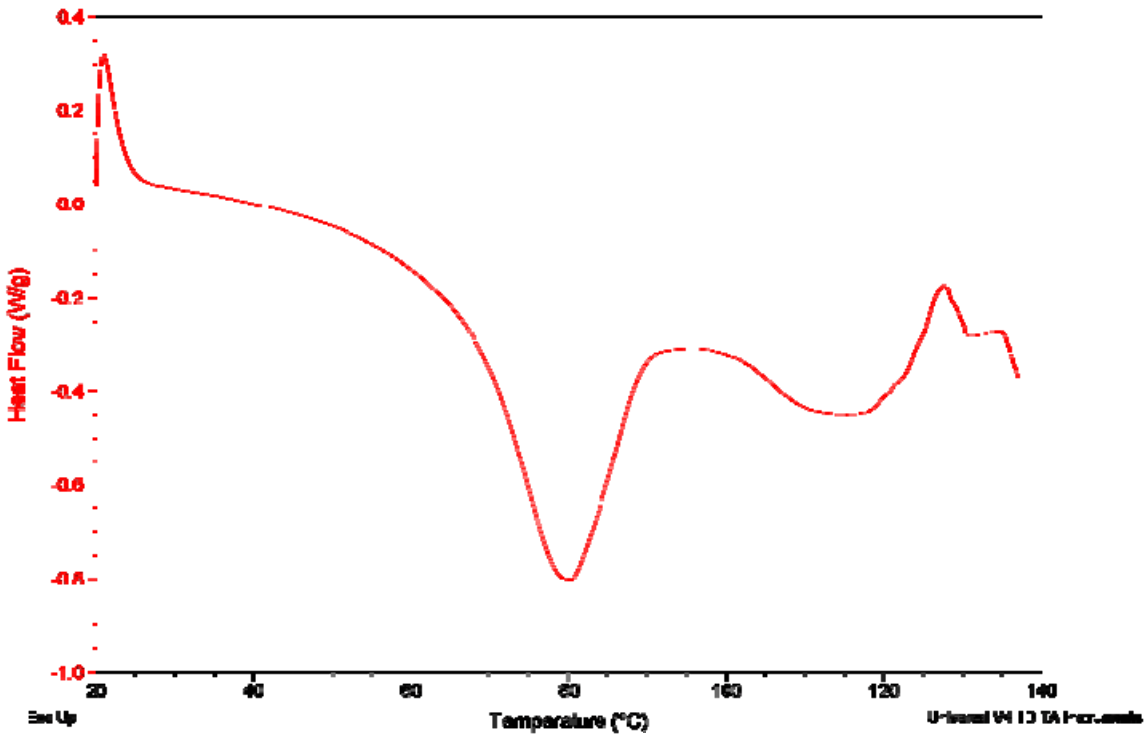

Figure S11. DSC plot of **Mg1**.

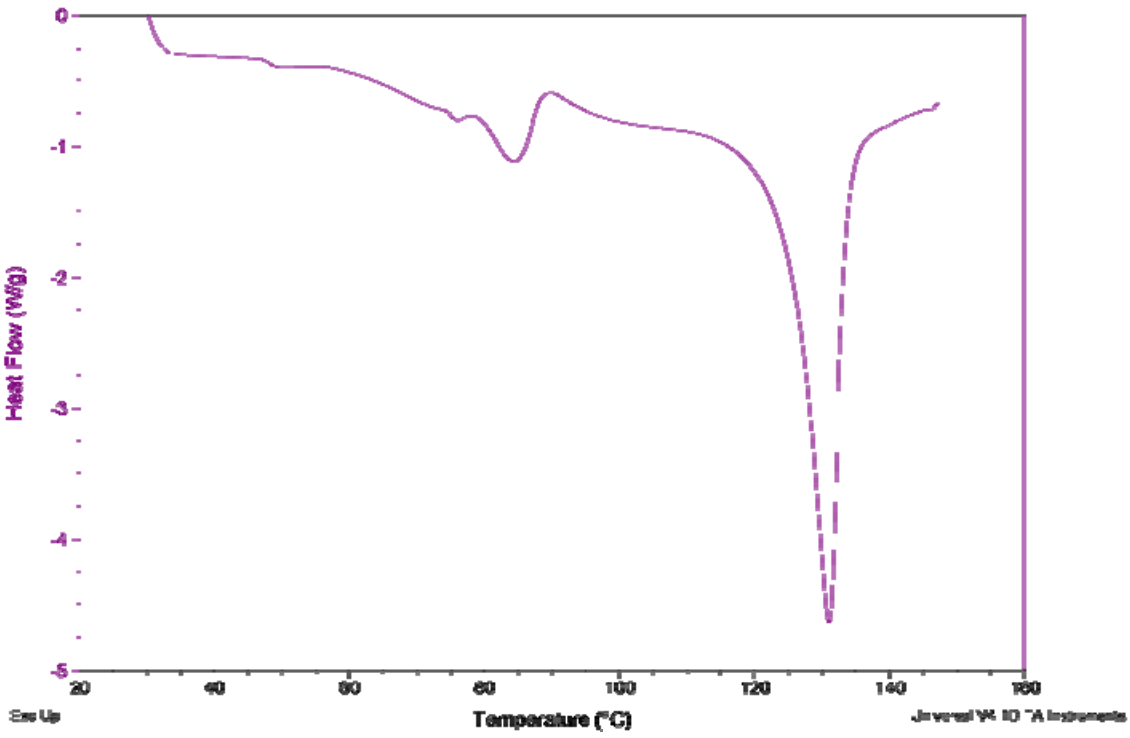

Figure S12. DSC plot of **Mg2**

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