# Coordination polymers of a bis-isophthalate bridging ligand with single molecule magnet behaviour of the $Co^{II}$ analogue

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## SUPPORTING INFORMATION

## S1. Magnetic data of 1Co

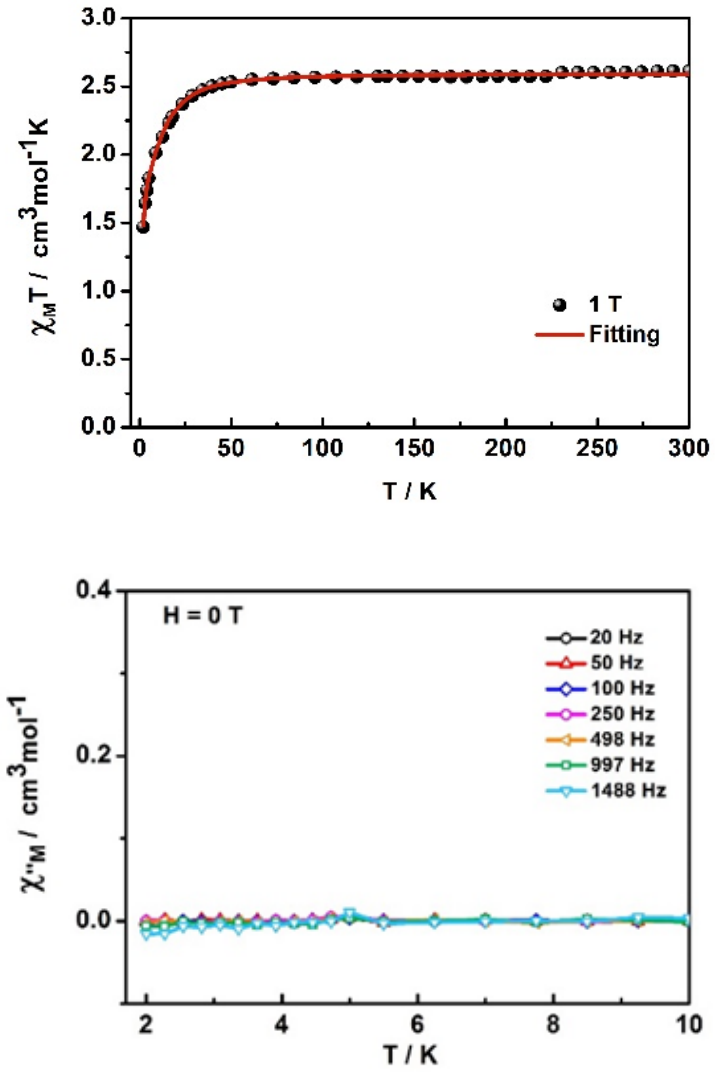


**Figure S1.** (a) Plot of $\chi_M T$ *vs.* T using an applied dc magnetic field of 1 T with the best fit shown. (b) AC $\chi''_M$ *vs.* temperature at different frequencies in the absence of a dc magnetic field.

## S2. PXRD for 1Co, 1Cd, 1Zn & 2

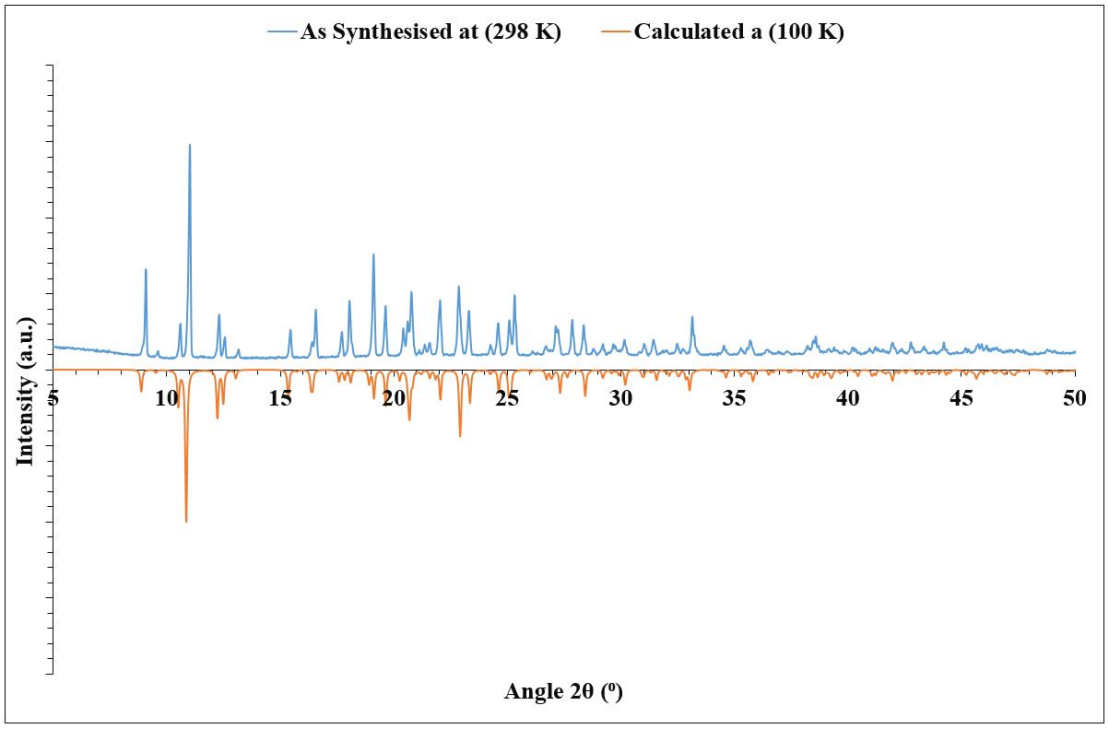


**Figure S2.1.** PXRD of *poly*-[Co($H_2$L)]·4.5$H_2$O (**1Co**) collected at room temperature compared to that calculated from the single crystal data at 100 K.

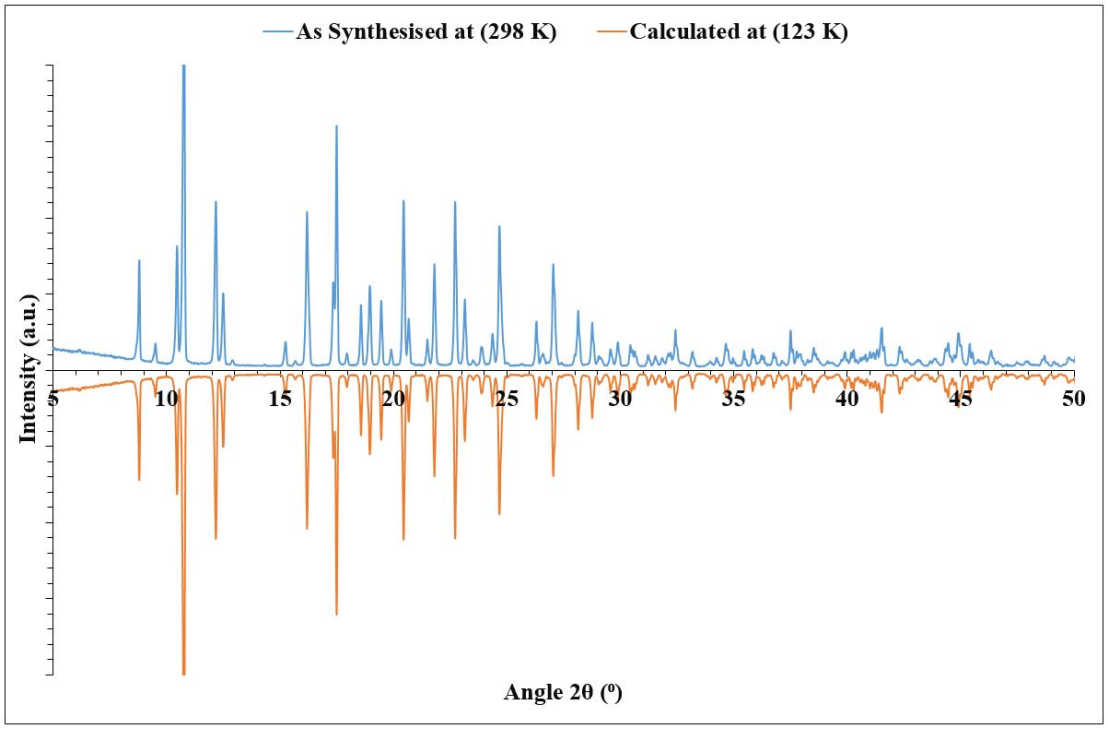


**Figure S2.2.** PXRD of *poly*-[Cd($H_2$L)]·4.5$H_2$O (**1Cd**) collected at room temperature compared to that calculated from the single crystal data at 100 K.

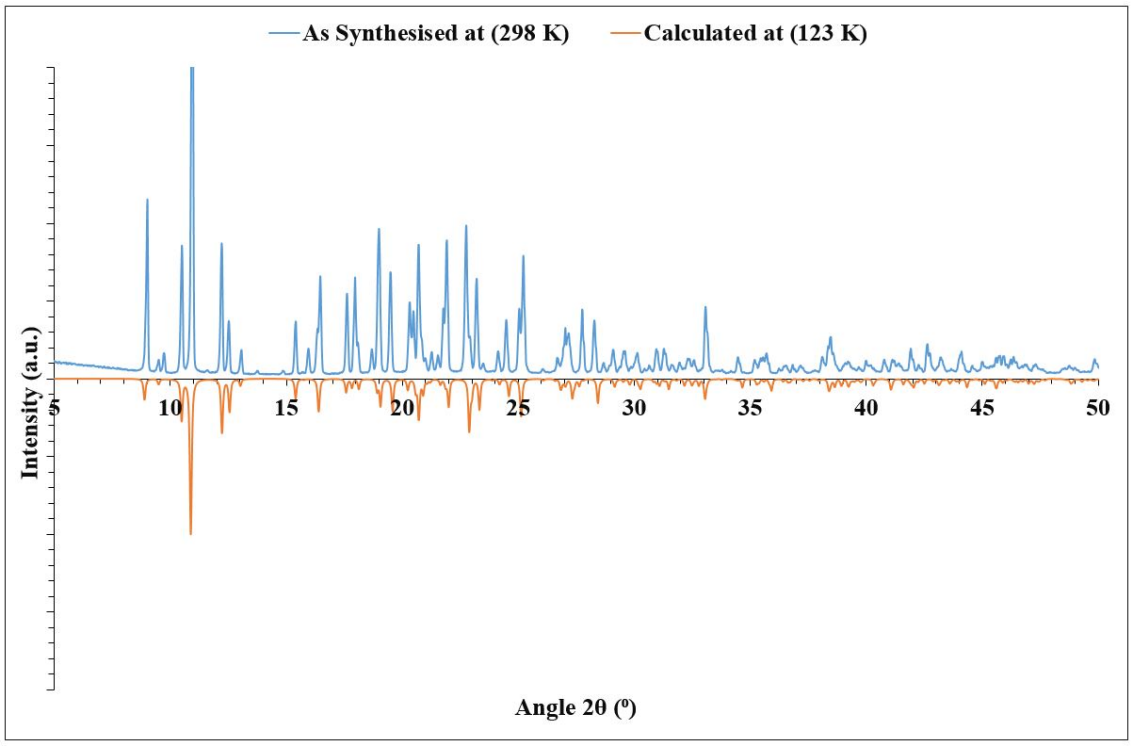


**Figure S2.3.** PXRD of *poly*-[Zn($H_2L$)]·4.5$H_2O$ (**1Zn**) collected at room temperature compared to that calculated from the single crystal data at 100 K.

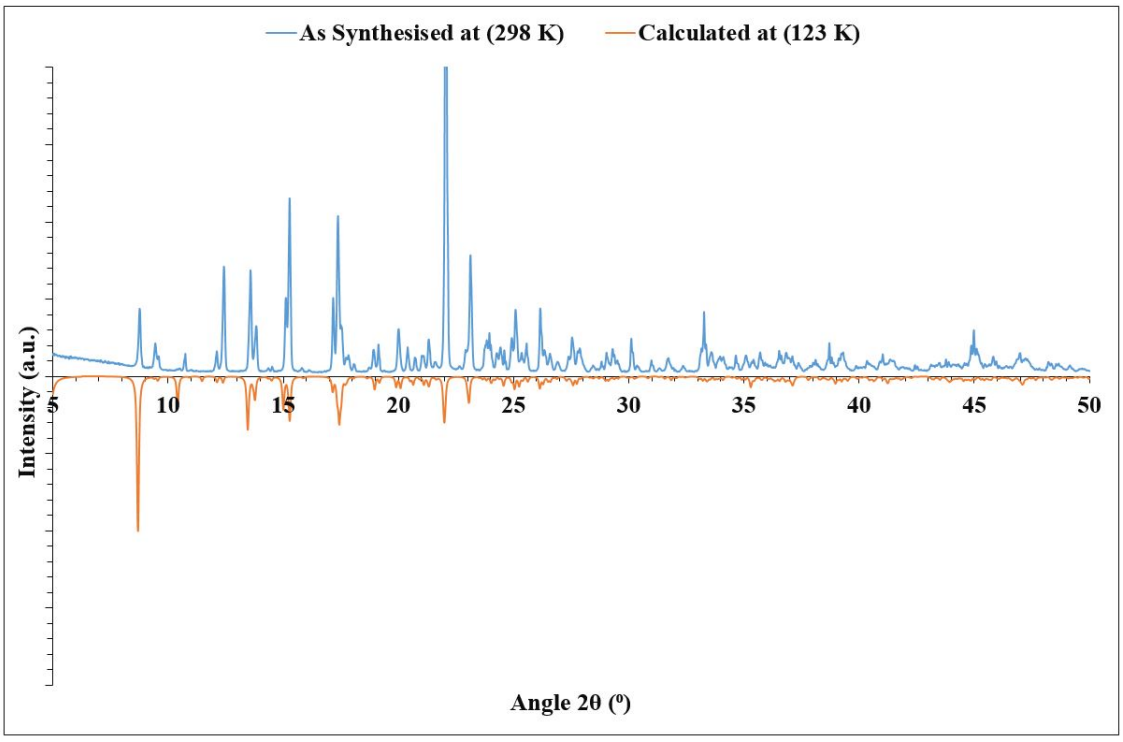


**Figure S2.4.** PXRD of *poly*-[Cd($H_2L$)($OH_2$)]·DMF·7$H_2O$ (**2**) collected at room temperature compared to that calculated from the single crystal data at 100 K.

## S3. TGA for $(H_6L)Cl_2{\cdot}5H_2O$, 1Co, 1Cd, 1Zn & 2

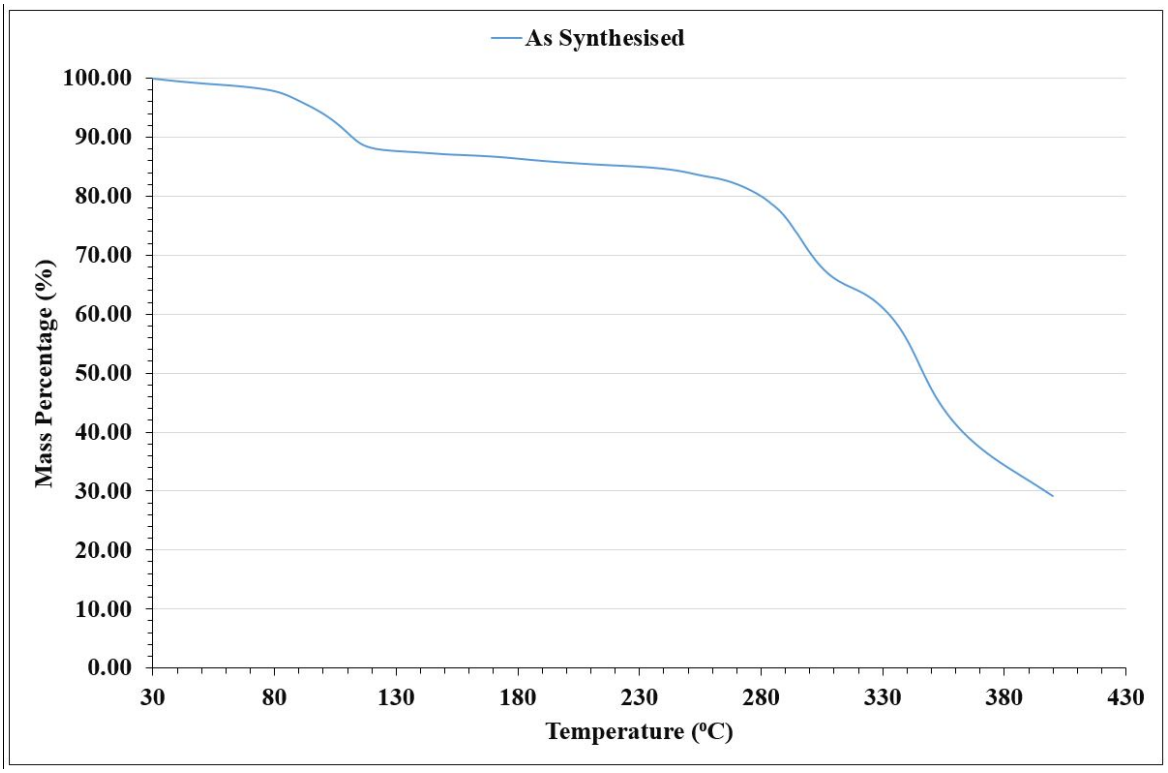


**Figure S3.1.** TGA trace for $(H_6L)Cl_2{\cdot}5H_2O$ showing mass loss (13 %) corresponding to 3.9 x $H_2O$ (calc. 16 % for $5H_2O$) in the range 30-130 °C.

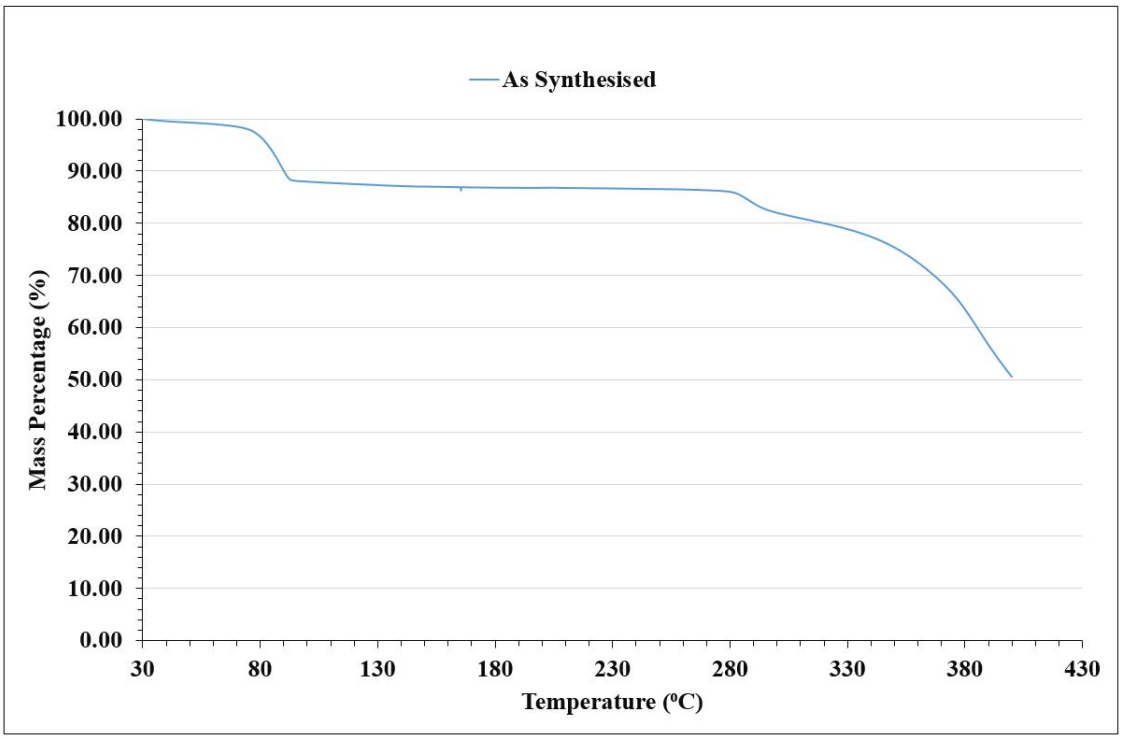


**Figure S3.2.** TGA trace for *poly*-[Co($H_2$L)]·4.5$H_2$O (**1Co**), showing mass loss (12 %) corresponding to 3.9 x $H_2$O (calc. 13.8 % for 4.5$H_2$O) in the range 30-93 °C.

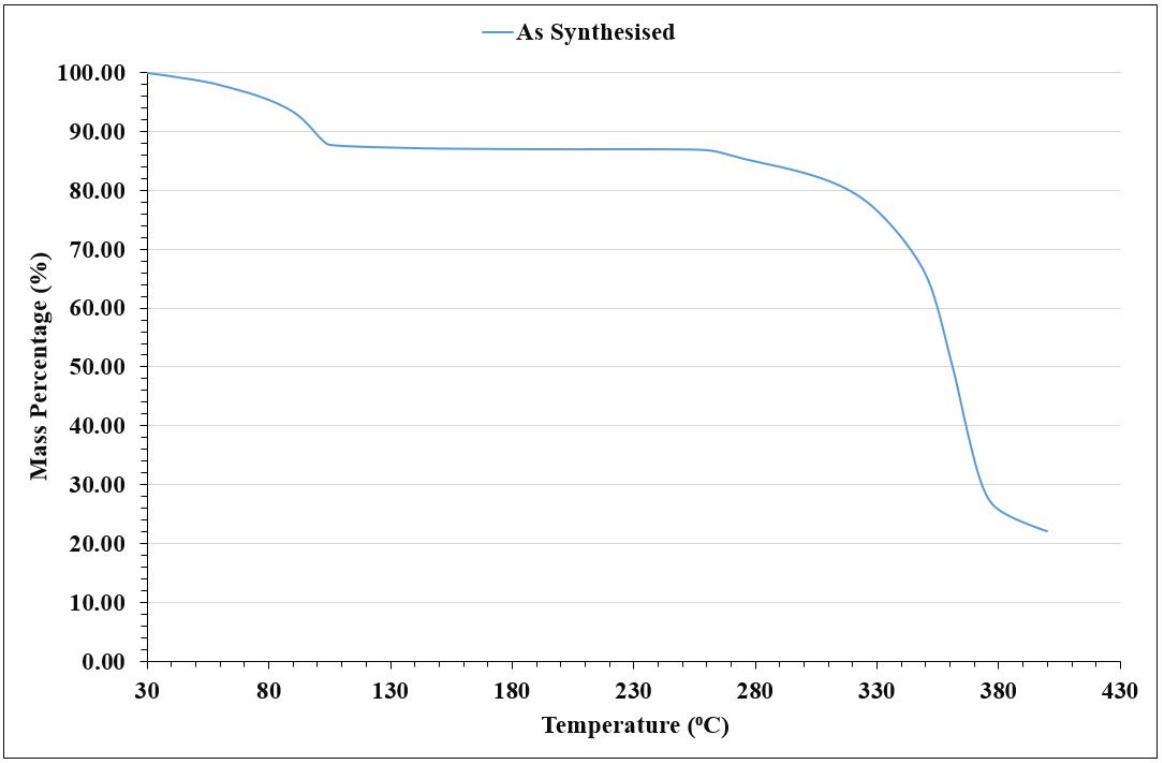


**Figure S3.3.** TGA trace for *poly*-[Cd($H_2$L)]·4.5$H_2$O (**1Cd**) showing mass loss (13 %) corresponding to 4.1 x $H_2$O (calc. 12.6% for 4$H_2$O) in the range 30-107 °C.

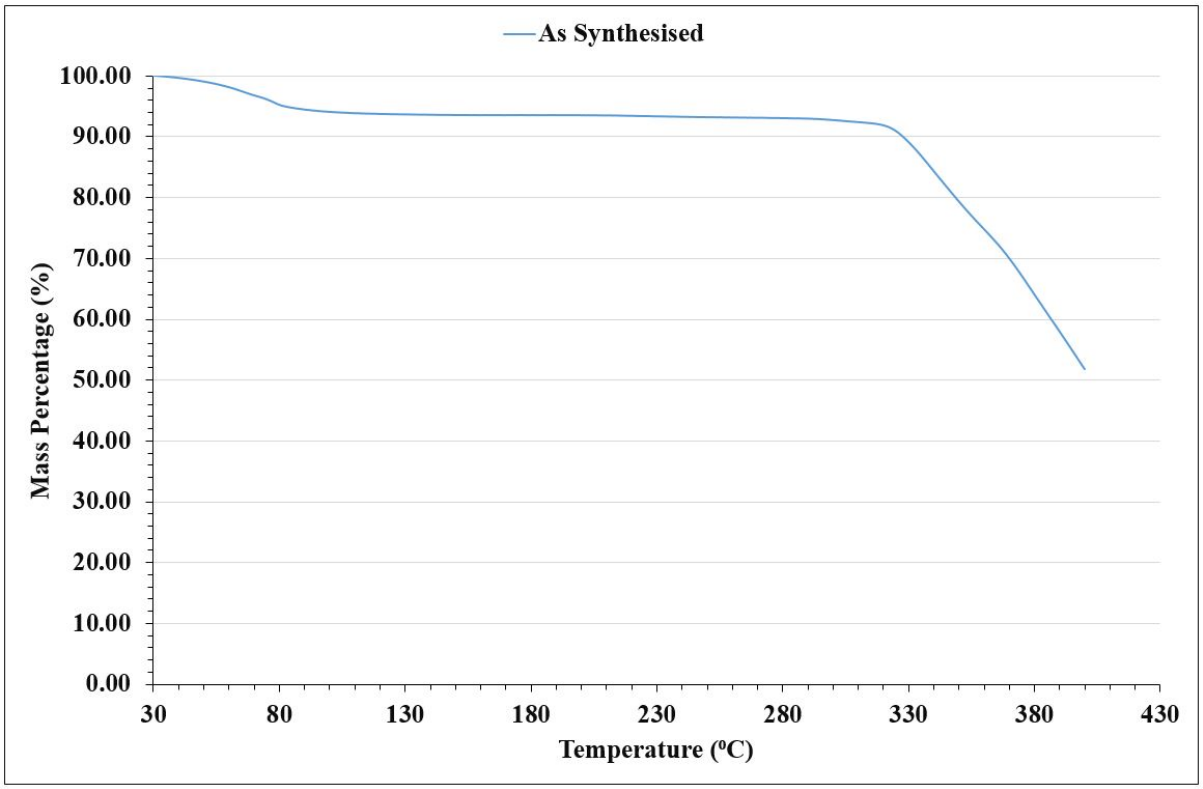


**Figure S3.4.** TGA trace for *poly*-[Zn($H_2L$)]·4.5$H_2O$ (**1Zn**) showing mass loss (7 %) corresponding to 1.9 x $H_2O$ (calc. 14.7% for 4$H_2O$) in the range 30-93 °C.

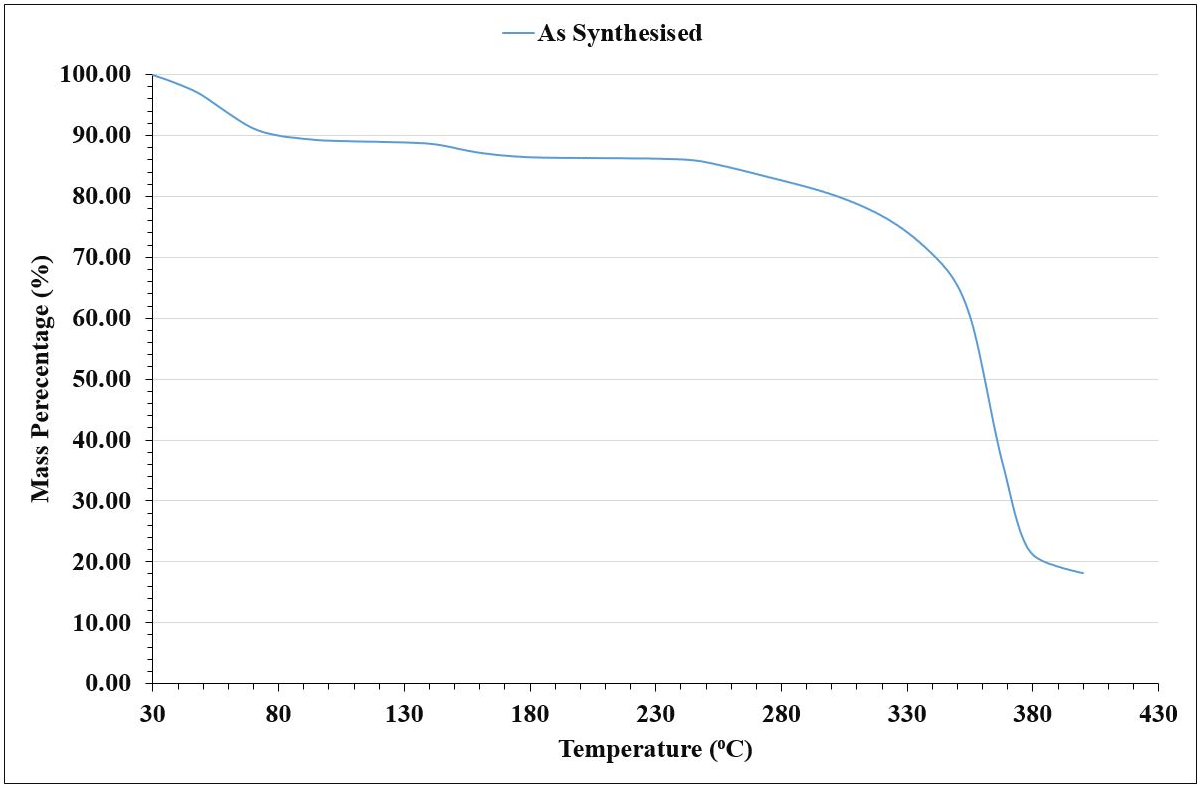


**Figure S3.5.** TGA trace for *poly*-[Cd($H_2L$)($OH_2$)]·DMF·7$H_2O$ (**2**) showing mass loss (10 %) corresponding to 3.5 x $H_2O$ (calc. 5.7 % for 2$H_2O$) in the range 30-93 °C.

## S4. Special Crystallographic Refinement Information

***poly*-[M($H_2$L)]·4.5$H_2$O (1Co, 1Zn, 1Cd)**

**1Co** and **1Zn** are isostructural, with water accurately located in the structures (4.5 per formula unit). The structure of **1Cd** is also essentially isostructural, apart from some disorder due to the presence of a minor component of the other stereoisomer at the N1 position; the two stereoisomer positions were modelled in a fixed 2:1 ratio, including the occupancies of the water molecule positions hydrogen bonded to the corresponding N-H orientations (total occupancy = 1.0). No protons were assigned to these disordered water molecules. Two other fully occupied water positions were also modelled, however unlike **1Co** and **1Zn**, further water positions could not be modelled well. Instead, the remaining disordered electron density within the voids was removed and quantified using the SQUEEZE routine within PLATON.[1] SQUEEZE calculated a total void space per unit cell of 157 $Å^3$ containing 67$e^-$. These values suggest a maximum of 8.7 water molecules per unit cell (assuming 18 $Å^3$ per non-hydrogen atom; 2.1 per formula unit) or 6.6 water molecules per unit cell (on the basis of 10$e^-$ per $H_2O$; 1.65 per formula unit). This approximates well to the same overall degree of solvation as **1Co** and **1Zn**, and thus was it was assigned as such. Notably, the TGA and microanalysis results are also in relatively close agreement to the solvation of **1Co** and **1Zn**, allowing for sample handling. TGA showed a mass loss of 13% in the range 30-107 $^0$C which corresponds to 4.1 water molecules per formula unit, while microanalysis results suggested a value of four water molecules per formula unit.

***poly*-[Cd($H_2$L)($OH_2$)]·DMF·7$H_2$O (2)**

Whilst one water molecule could be located from the Fourier difference map, a significant region of disordered electron density exists within the voids that could not be satisfactorily modelled. Therefore, this electron density within the channels was removed and quantified using the SQUEEZE routine within PLATON.[1] SQUEEZE calculated a total void space per unit cell of 398 $Å^3$ containing 197 $e^-$. These values, and consideration of the TGA and elemental analysis results, suggest an additional 2 DMF and 12 water molecules per unit cell (assuming 18 $Å^3$ per non-hydrogen atom) or 1 DMF and 6 water molecules per formula unit. While the thermogravimetric analysis and microanalysis results suggest a lower overall degree of solvation, it is likely that some included solvent was lost prior to analysis.

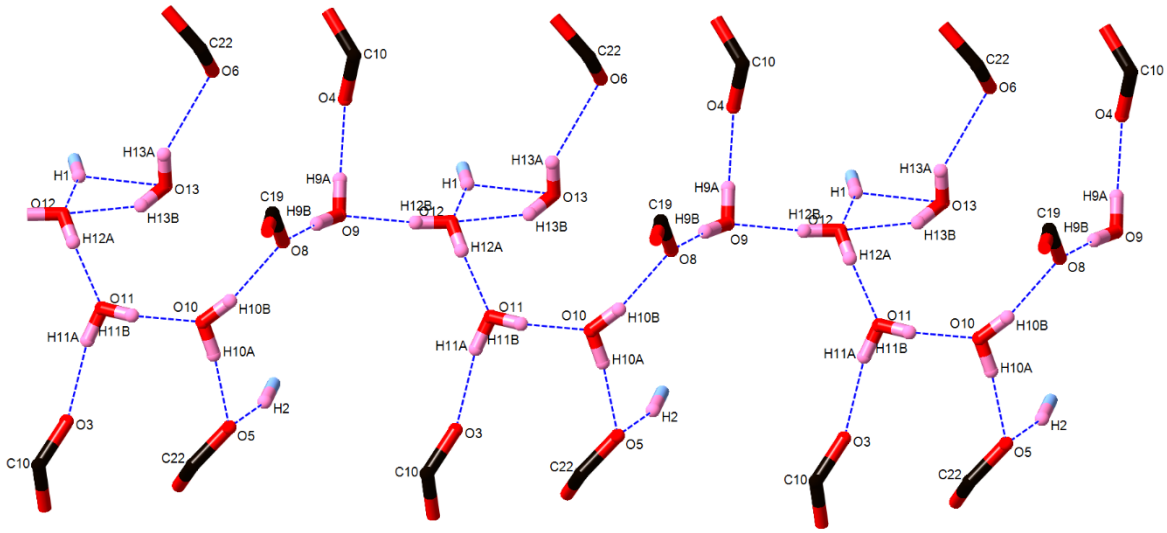


**Figure S4.1.** H-bonding chain in the 1D channels of **1Co** with selected atoms labelled. C, H, N, O are in black, pink, blue and red, respectively.

**Table S4.1.** H-bonding table with distances and angles between the hydrogen donors and acceptors in **1Co.***

| **D-H···A** | **D-H (Å)** | **H···A (Å)** | **D···A (Å)** | **D-H···A (°)** |
|---|---|---|---|---|
| N1-H1···O12[a] | 1.00 | 1.81 | 2.770(5) | 159.5 |
| N1-H1···O13 | 1.00 | 2.30 | 2.957(15) | 122.6 |
| N2-H2···O5[a] | 1.00 | 1.69 | 2.656(4) | 162.1 |
| O9-H9A···O4[b] | 0.85 | 1.97 | 2.808(4) | 169.4 |
| O9-H9B···O8 | 0.85 | 1.91 | 2.748(4) | 167.4 |
| O10-H10A···O5[c] | 0.85 | 1.96 | 2.798(4) | 167.2 |
| O10-H10B···O8 | 0.85 | 1.89 | 2.728(4) | 166.6 |
| O11-H11A···O3[d] | 0.85 | 2.00 | 2.835(5) | 167.3 |
| O11-H11B···O10 | 0.85 | 1.91 | 2.756(5) | 172.5 |
| O12-H12A···O11 | 0.85 | 1.87 | 2.717(5) | 170.7 |
| O12-H12B···O9[e] | 0.85 | 1.95 | 2.773(5) | 162.4 |
| O13-H13A···O6[a] | 0.85 | 2.32 | 3.030(12) | 141.6 |
| O13-H13B···O12[a] | 0.85 | 1.88 | 2.594(13) | 140.4 |

* Symmetry operations: a: 1-x, 1-y, z-1/2; b: x-1/2, -y, z; c: x-1/2, 1-y, z; d: x-1, y+1, z; e: x, y+1, z.

**Table S4.2.** H-bonding table with distances and angles between the hydrogen donors and acceptors in **1Zn.***

| **D-H···A** | **D-H (Å)** | **H···A (Å)** | **D···A (Å)** | **D-H···A (°)** |
|---|---|---|---|---|
| N1-H1···O12[a] | 0.98 | 1.82 | 2.759(10) | 159.9 |
| N2-H2···O5[a] | 0.98 | 1.70 | 2.647(9) | 160.5 |
| O9-H9A···O4[b] | 0.87(2) | 1.9630(14) | 2.822(7) | 170(10) |
| O9-H9B···O8 | 0.75(13) | 2.06(14) | 2.778(9) | 162(13) |
| O10-H10A···O5[c] | 0.85 | 1.99 | 2.821(8) | 166.8 |
| O10-H10B···O8 | 0.85 | 1.89 | 2.731(7) | 168.3 |
| O11-H11A···O3[d] | 0.85 | 1.96 | 2.796(9) | 166.4 |
| O11-H11B···O10 | 0.85 | 1.92 | 2.751(11) | 165.8 |
| O12-H12A···O9[e] | 0.85 | 1.94 | 2.763(9) | 162.5 |
| O12-H12B···O11 | 0.85 | 1.93 | 2.703(11) | 150.5 |
| O13-H13A···O12 | 0.85 | 1.82 | 2.667(16) | 172.2 |

* Symmetry operations: a: 1-x, 1-y, z-1/2; b: x+1/2, 2-y, z; c: x+1/2, 1-y, z; d: x+1, y-1, z; e: x, y-1, z.

**Table S4.3.** H-bonding table with distances and angles between the hydrogen donors and acceptors in **1Cd.***

| **D-H···A** | **D-H (Å)** | **H···A (Å)** | **D···A (Å)** | **D-H···A (°)** |
|---|---|---|---|---|
| N1A-H1A···O11A | 1.00 | 1.84 | 2.77(3) | 153.4 |
| N1B-H1BA···O11B | 1.00 | 1.80 | 2.670(18) | 143.8 |
| N2-H2···O5[a] | 1.00 | 1.71 | 2.673(4) | 160.8 |
| O9-H9A···O8[b] | 0.87 | 1.89 | 2.733(7) | 163.4 |
| O9-H9B···O4 | 0.87 | 1.97 | 2.832(5) | 172.3 |
| O10-H10A···O8[c] | 0.84(3) | 1.87(5) | 2.692(8) | 165(14) |
| O10-H10B···O5 | 0.90(2) | 1.9692(15) | 2.839(6) | 161(6) |

* Symmetry operations: a: 1-x, 1-y, z-1/2; b: x+1/2, -y, z; c: x+1/2, 1-y, z.

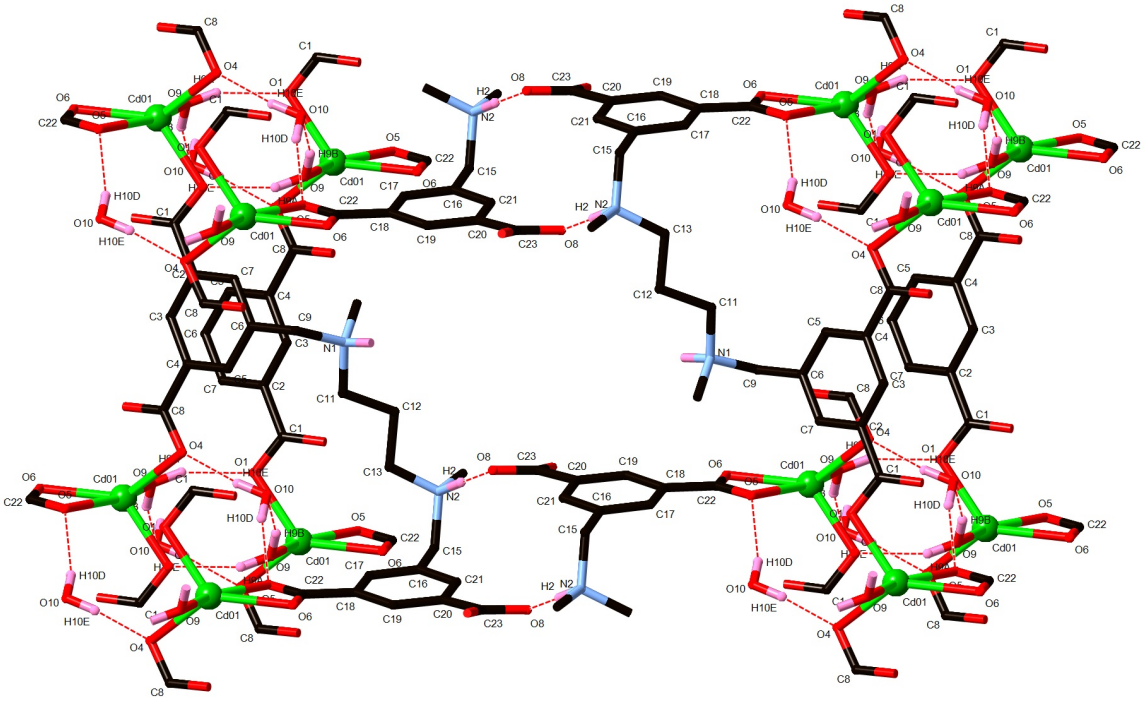

**Figure S4.2.** H-bonding chain in **2Cd** with selected atoms label. Cd, C, H, N, O are in green, black, pink, blue and red respectively.

**Table S4.4.** H-bonding table with distances and angles between the hydrogen donor and acceptor of **2Cd.**

| D-H···A | D-H (Å) | H···A (Å) | D···A (Å) | D-H···A (°) |
|---|---|---|---|---|
| N2-H2···O8[a] | 1.00 | 1.72 | 2.712(3) | 173.0 |
| O9-H9A···O1[b] | 0.87 | 1.94 | 2.758(2) | 155.6 |
| O9-H9B···O10 | 0.87 | 1.88 | 2.717(3) | 159.3 |
| O10-H10E···O4[c] | 0.85 | 1.98 | 2.787(2) | 158.8 |
| O10-H10D···O5[c] | 0.85 | 2.05 | 2.865(2) | 160.3 |

* Symmetry operations: a: 1-x, 2-y, 1-z; b: -x, -y, 2-z; c: -x, 1-y, 2-z

| **Compound reference** | **1Co** | **1Zn** | **1Cd*** | **2Cd*** |
|---|---|---|---|---|
| **Chemical formula** | $CoC_{23}H_{33}N_2O_{12.5}$ | $ZnC_{23}H_{33}N_2O_{12.5}$ | $CdC_{23}H_{33}N_2O_{12.5}$ | $CdC_{26}H_{47}N_3O_{17}$ |
| **Formula mass** | 596.44 | 602.88 | 649.91 | 786.06 |
| **Crystal system** | Orthorhombic | Orthorhombic | Orthorhombic | Triclinic |
| **Space group** | $Pca2_1$ | $Pca2_1$ | $Pca2_1$ | $P$-1 |
| $a$ / Å | 19.850(4) | 19.8716(4) | 20.4570(3) | 8.1599(2) |
| $b$ / Å | 9.2680(19) | 9.3173(2) | 9.3200(2) | 10.2806(2) |
| $c$ / Å | 14.146(3) | 14.1140(4) | 14.1950(2) | 18.7575(5) |
| $\alpha$ / ° | 90 | 90 | 90 | 82.5340(10) |
| $\beta$ / ° | 90 | 90 | 90 | 83.4680(10) |
| $\gamma$ / ° | 90 | 90 | 90 | 84.8720(10) |
| **Volume / Å$^3$** | 2602.4(9) | 2613.20(11) | 2706.41 (8) | 1545.62(6) |
| **Temperature / K** | 100(2) | 123.00(13) | 100.00(10) | 123(2) |
| **λ / Å** | 0.71075 | 1.54184 | 0.7109 | 0.71073 |
| $Z$ | 4 | 4 | 4 | 2 |
| $\rho_{calc}$ / g cm$^{-1}$ | 1.522 | 1.532 | 1.595 | 1.689 |
| $\mu$ / mm$^{-1}$ | 0.729 | 1.917 | 0.874 | 0.792 |
| $F$(000) | 1248 | 1260 | 1332 | 816 |
| 2$\theta$ range/° | 4.104 to 63.608 | 8.9 to 154.478 | 4.372 to 63.634 | 2.202 to 52.738 |
| **Reflns. measured** | 42785 | 14457 | 47704 | 21209 |
| **Indep. reflns.** | 7506 | 4541 | 7394 | 6323 |
| **Reflns. obs. ($I > 2\sigma(I)$)** | 6652 | 4026 | 7280 | 5867 |
| **Data/restraints/parameters** | 7506/1/369 | 4541/5/372 | 7394/30/372 | 6323/0/331 |
| **GOOF on $F^2$** | 1.092 | 1.090 | 1.066 | 1.083 |
| $R_{int}$ | 0.0560 | 0.0881 | 0.0207 | 0.0212 |
| $R_1(I > 2\sigma(I))$ | 0.0398 | 0.0586 | 0.0329 | 0.0263 |
| $wR(F^2)$ $(I > 2\sigma(I))$ | 0.0924 | 0.1481 | 0.0892 | 0.0702 |
| $R_1$ (all data) | 0.0491 | 0.0671 | 0.0333 | 0.0292 |
| $wR(F^2)$ (all data) | 0.0970 | 0.1551 | 0.0896 | 0.0757 |
| **CCDC no.** | 1968824 | 1968825 | 1968826 | 1968827 |

**Table S5.** Crystallographic and refinement parameters for all compounds. * Data treated using the SQUEEZE routine of PLATON. [1]

## References

1. A. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 9-18.