

# **Crystal Engineering of Coordination Polymers Using Flexible Tetracarboxylate Linkers with Embedded Cyclohexyldiamine Cores**

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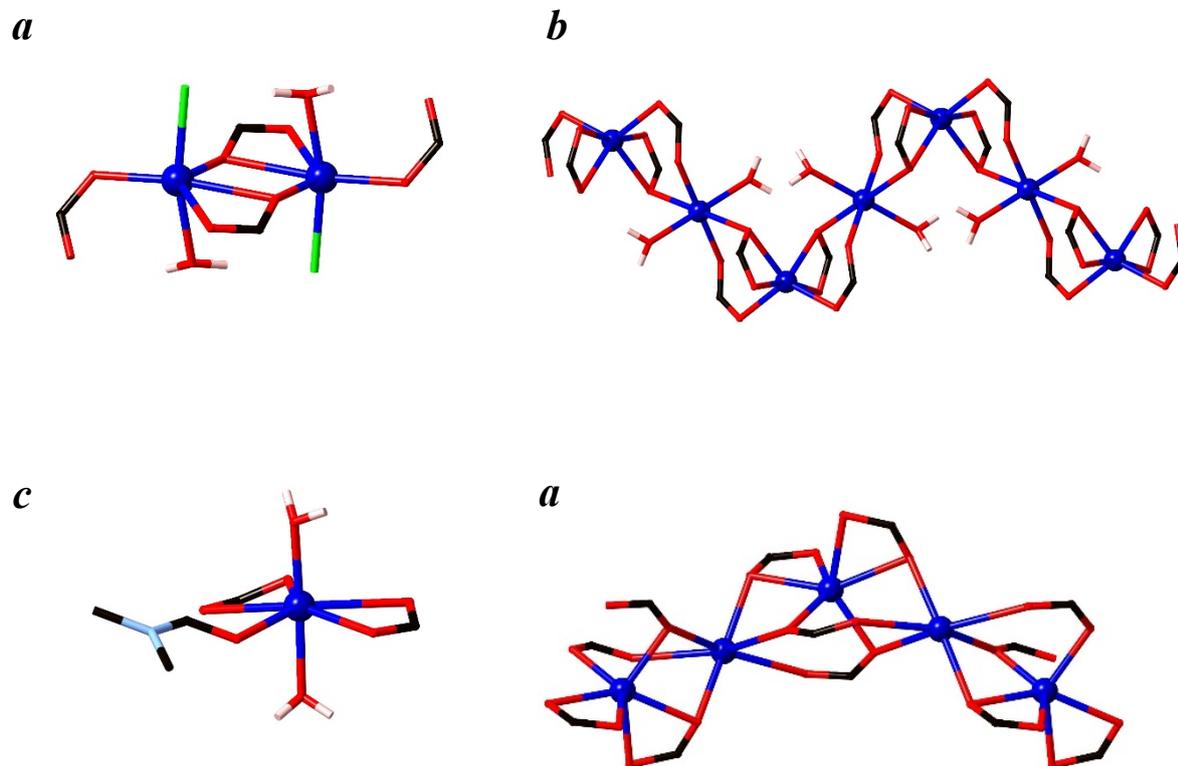
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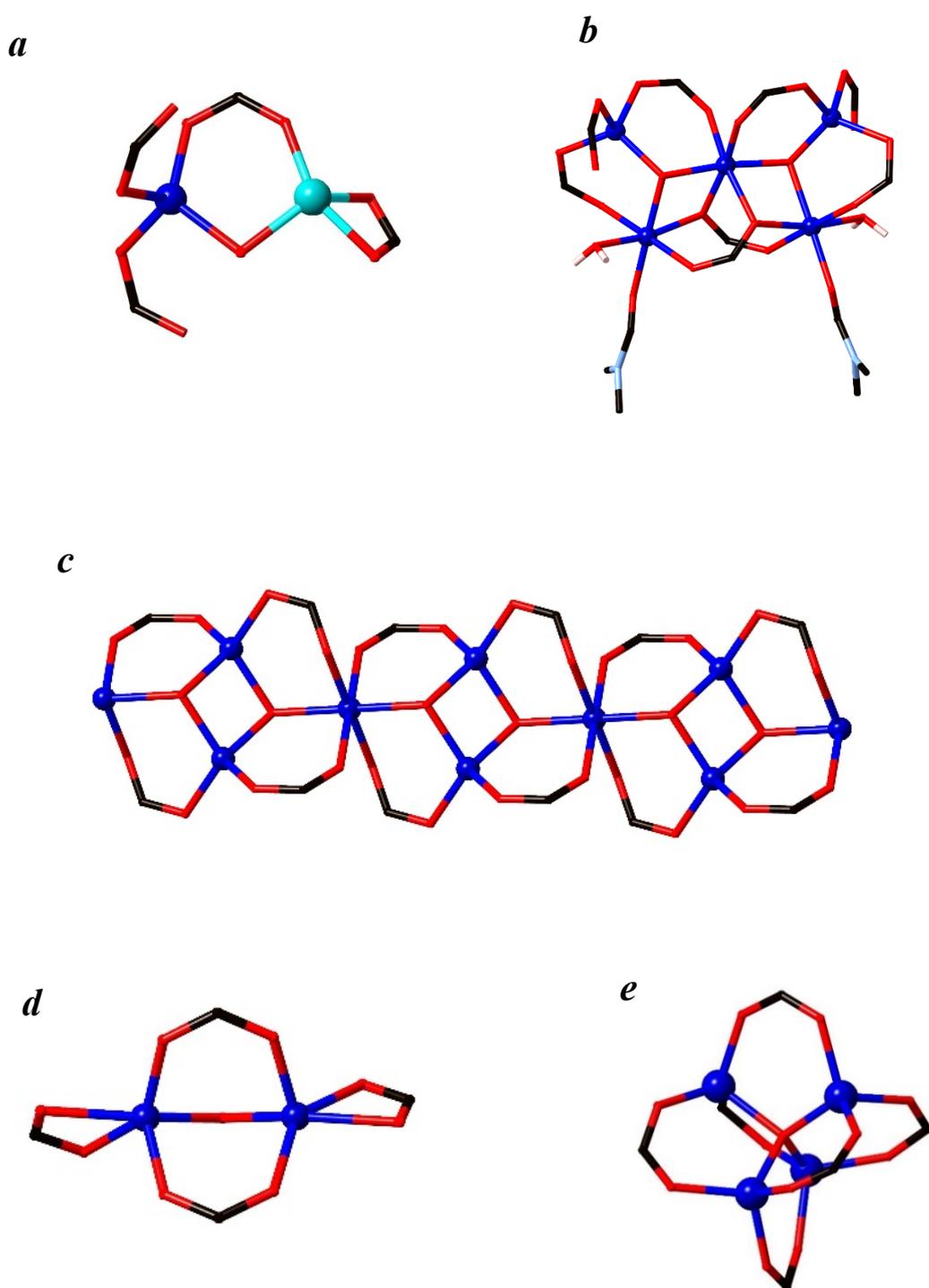
## **Electronic Supplementary Information**

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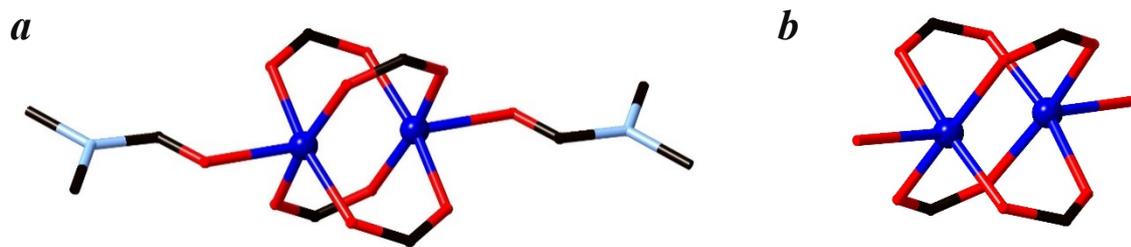
## S1 Metal Coordination Environments



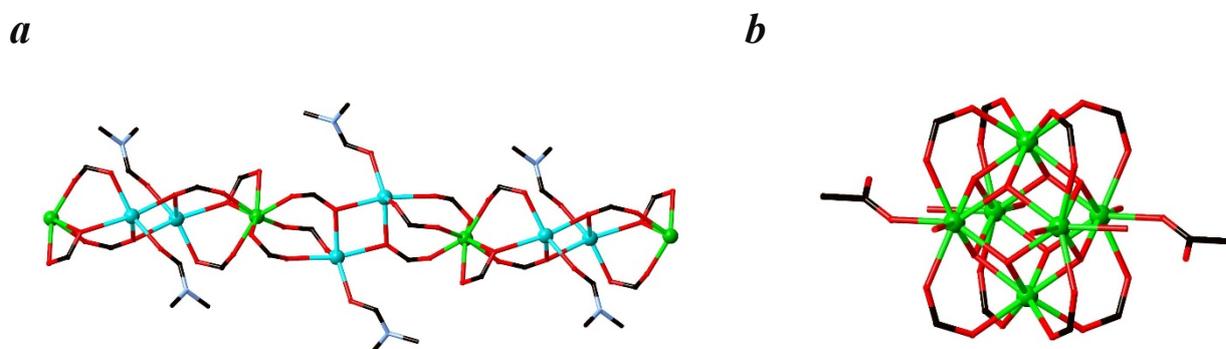
**Figure S1.1** Cadmium(II) nodes in (a) **1**, (b) **2Cd** (**2Mn** is analogous), (c) **3** and (d) **4**. Cd, deep blue; O, red; C, black; N, pale blue; Cl, green; non-water hydrogen atoms are omitted for clarity.



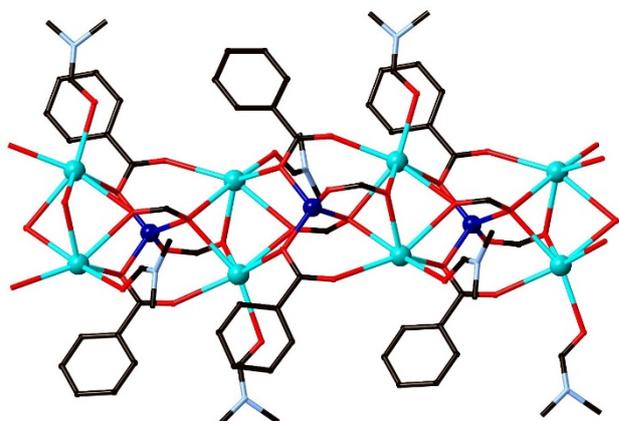
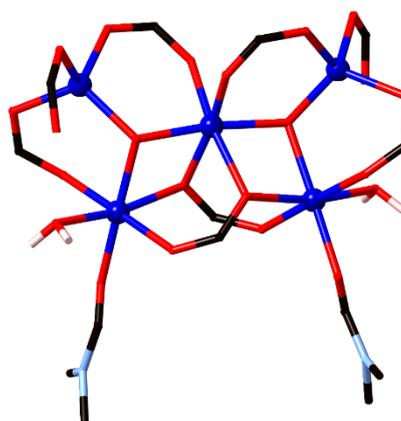
**Figure S1.2** Zinc(II) and sodium(I) bimetallic node in (a) **5** (half-occupied DMF ligand bound to Na not shown), and zinc nodes in (b) **6Zn** (**6Co** is analogous), (c) **7**, (d) **8** and (e) **9**. For clarity, only one position of the disordered oxide in **8** and the disordered node in **9** are shown. Zn, deep blue; Na, cyan; O, red; C, black; N, pale blue; non-water hydrogen atoms are omitted for clarity.



**Figure S1.3** Copper(II) nodes observed in (a) **10** and (b) **11** (only one disordered position shown). Cu, deep blue; O, red; C, black; N, pale blue; hydrogen atoms are omitted for clarity.

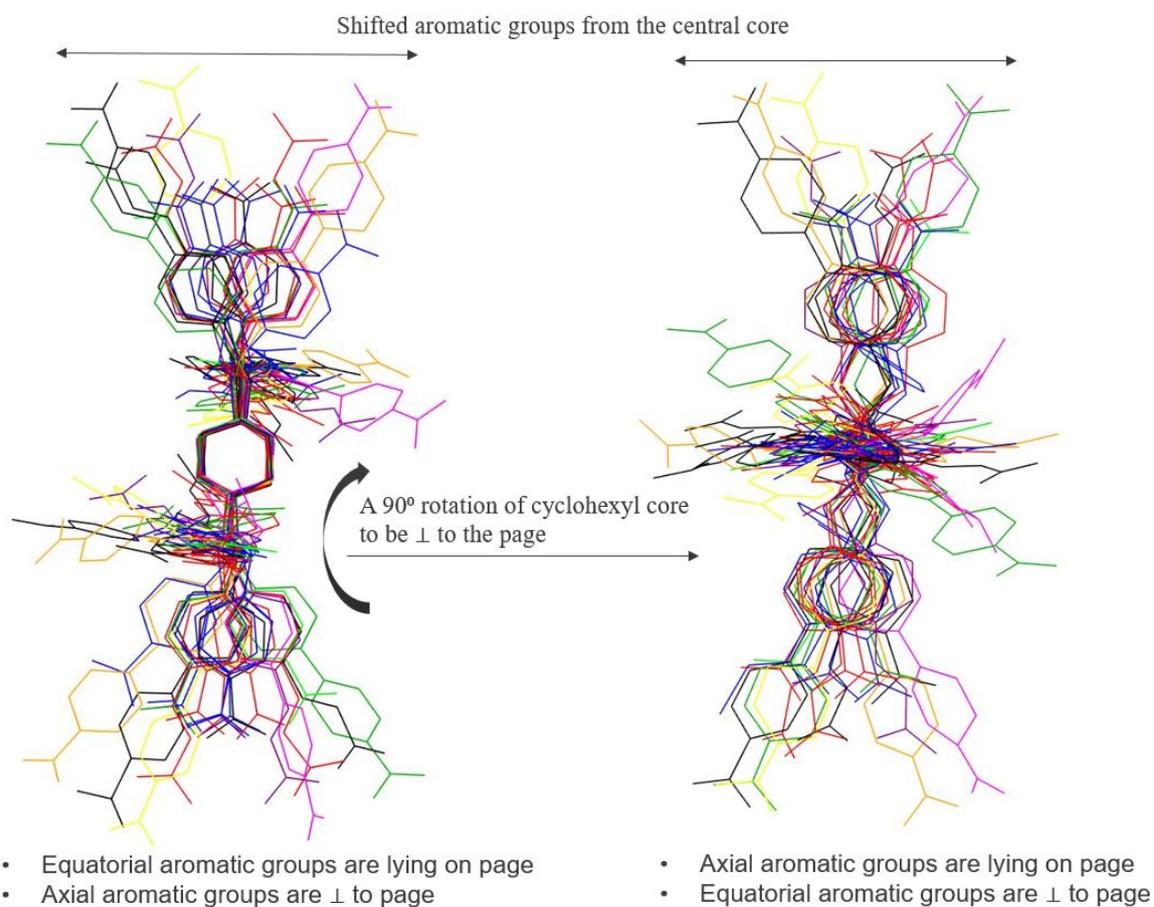


**Figure S1.4** (a) Alternating zirconium(IV) and sodium(I) nodes observed in **12**. (b)  $Zr_6$  cluster node observed in **13** (only one position of the disordered acetate is shown for clarity). Zr, green; Na, cyan; O, red; C, black; hydrogen atoms are omitted for clarity.

*a**b*

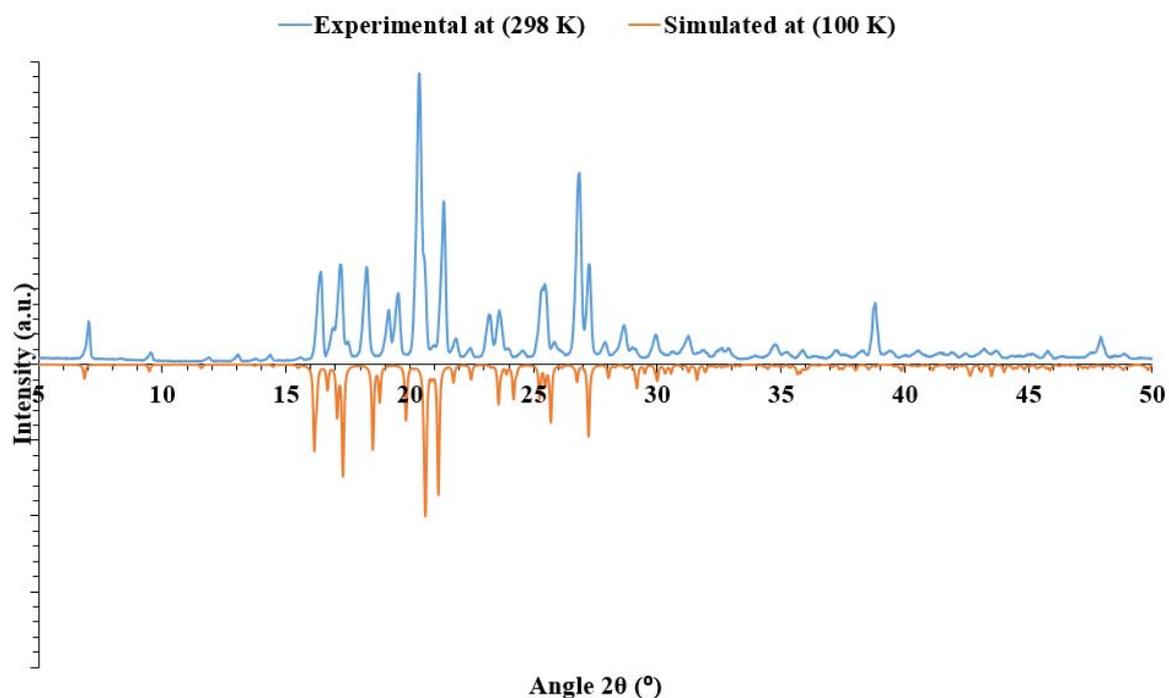
**Figure S1.5** Alternating cobalt(II) and potassium(I) nodes observed in (a) **14**; and cobalt(II) node in (b) **6Co**. Co, deep blue; K, cyan; O, red; C, black; N, pale blue; hydrogen atoms and partially occupied DMF molecule in **14** are omitted for clarity.

## S2 Structural overlay of 16 coordination polymers obtained

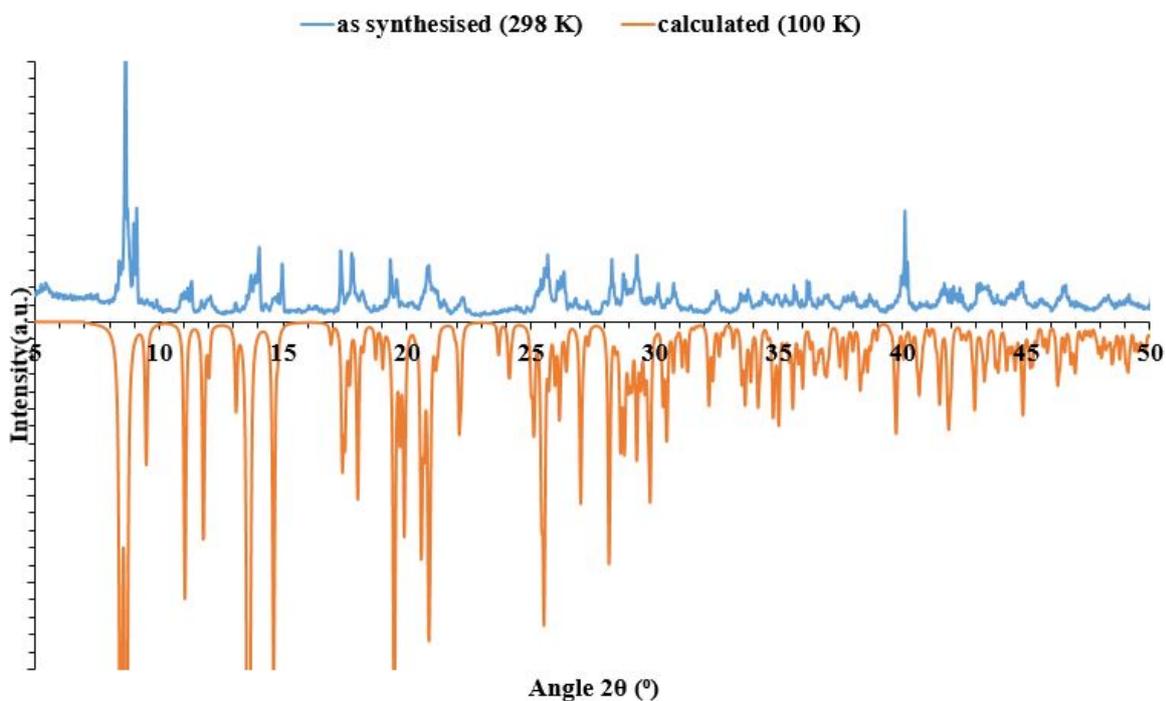


**Figure S2.** Overlay of the ligand conformations in the sixteen synthesised coordination polymers with L1 [**1**, **5**, **6Zn/Co**, **7**, **10**, **12**, **13** and **14**], L2 [**2Cd/Mn**, **8** and **11**] and L3 [**3**, **4** and **9**].

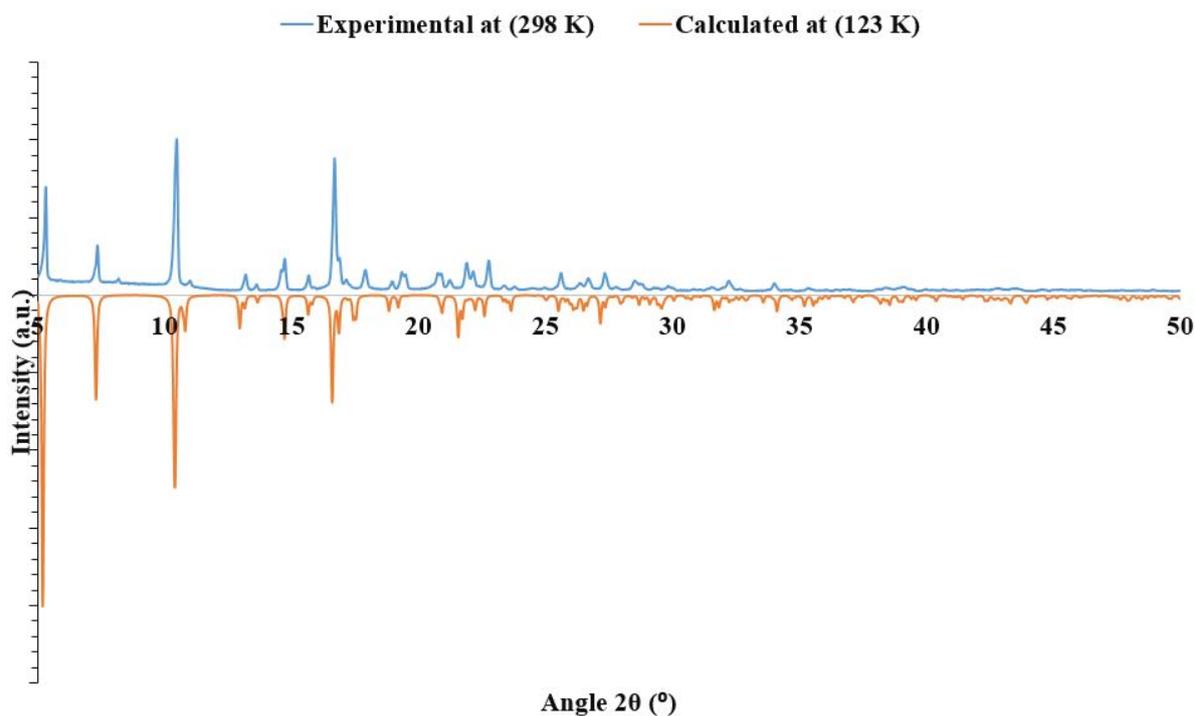
### S3 PXRD



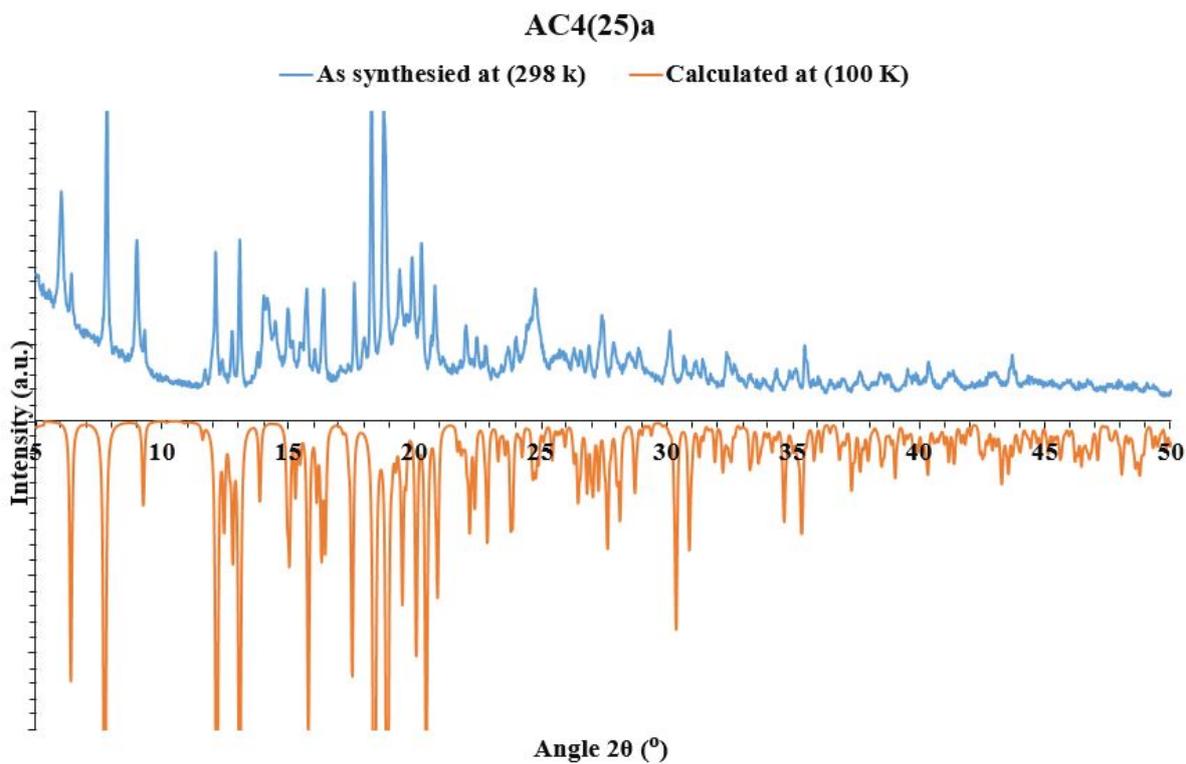
**Figure S3.1** PXRD of Me<sub>4</sub>L1 collected at room temperature compared to that calculated from the single crystal data at 100 K.



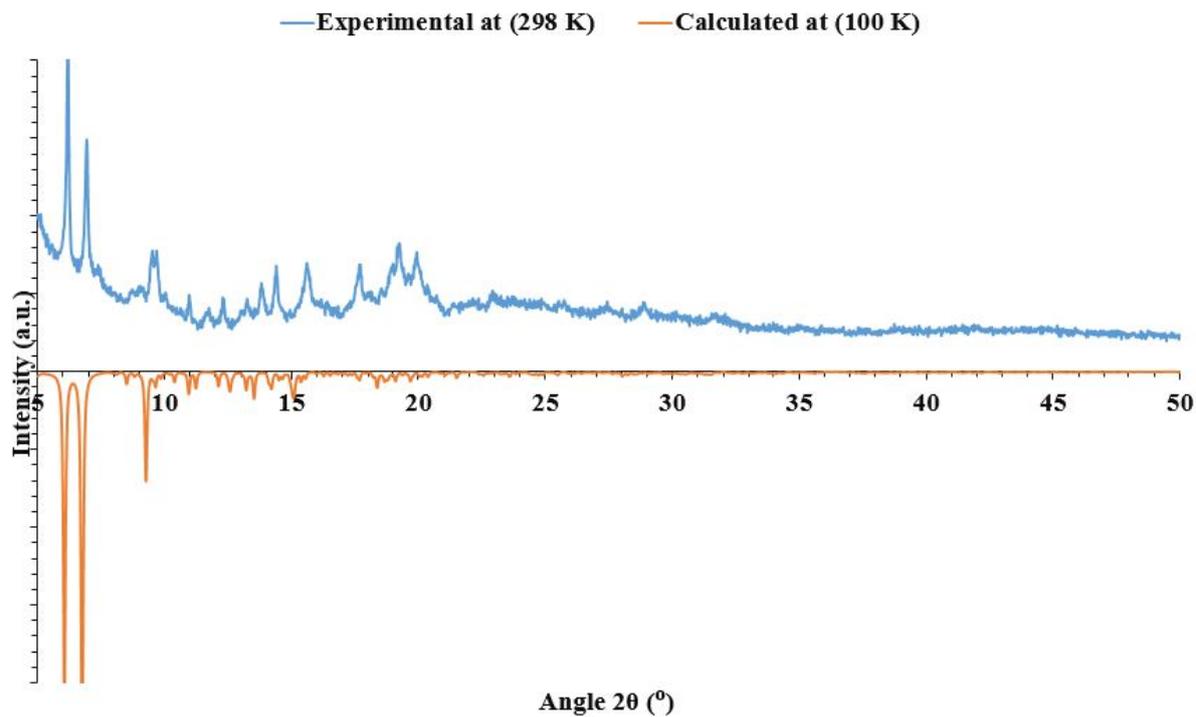
**Figure S3.2** PXRD of 1 collected at room temperature compared to that calculated from the single crystal data at 100 K.



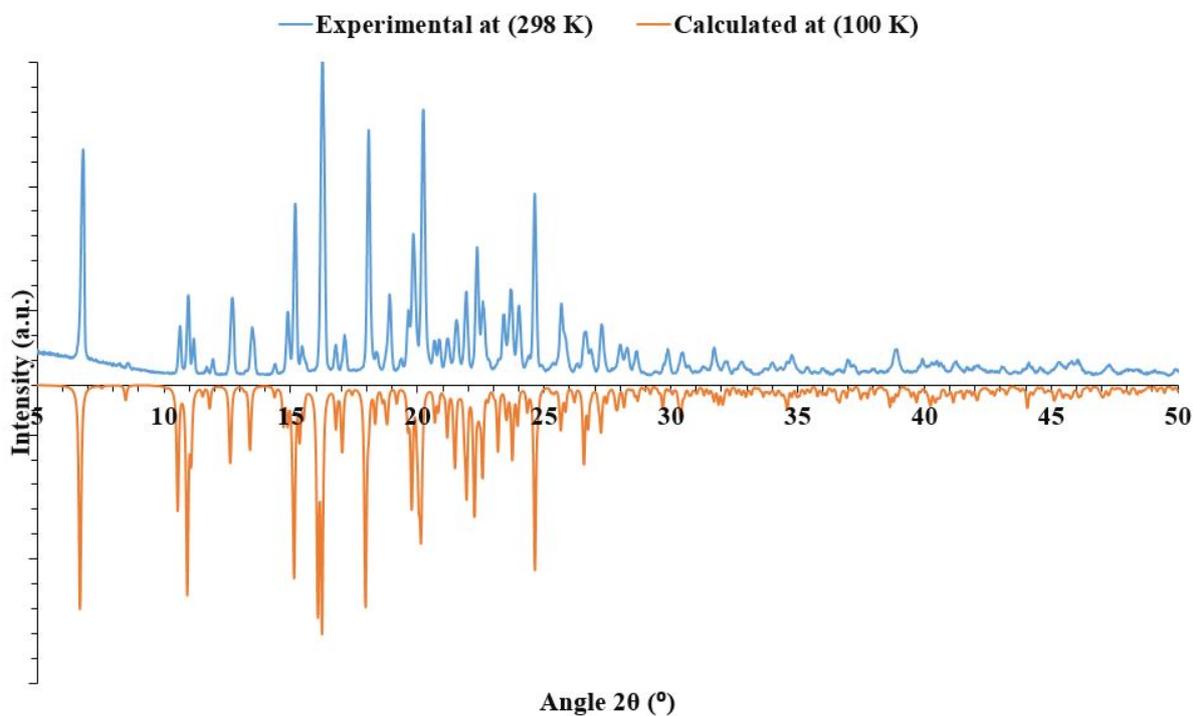
**Figure S3.3** PXRD of **2Cd** collected at room temperature compared to that calculated from the single crystal data at 123 K.



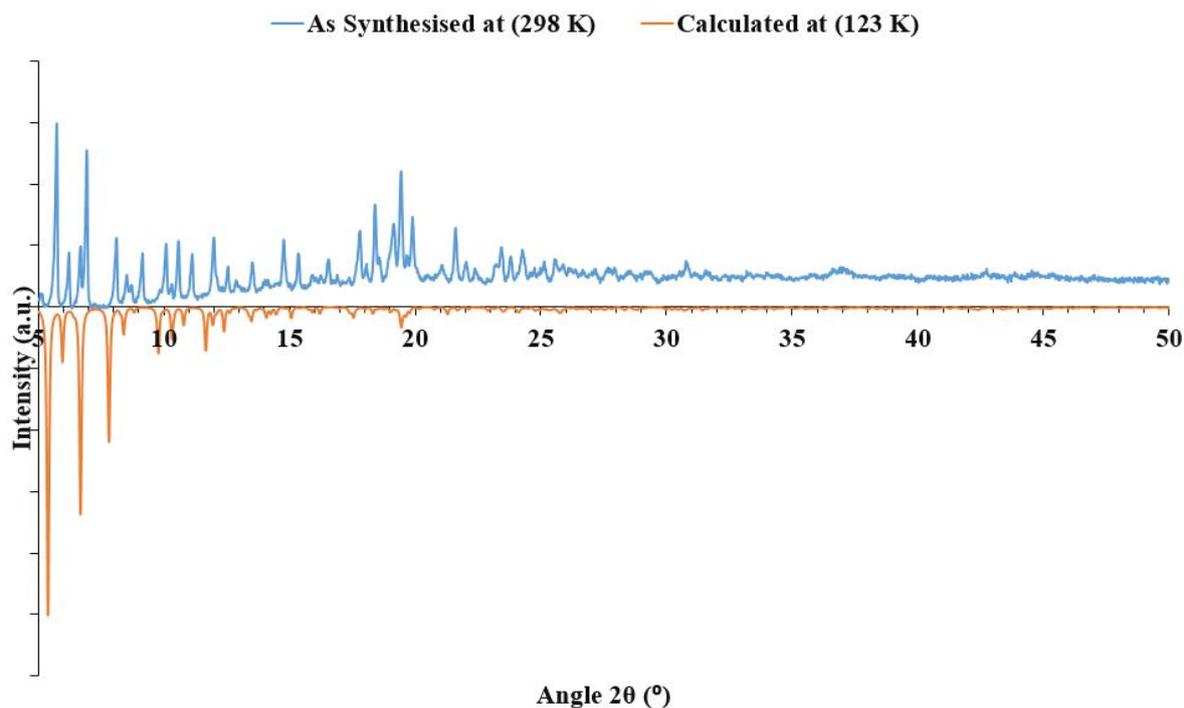
**Figure S3.4** PXRD of **3** collected at room temperature compared to that calculated from the single crystal data at 100 K.



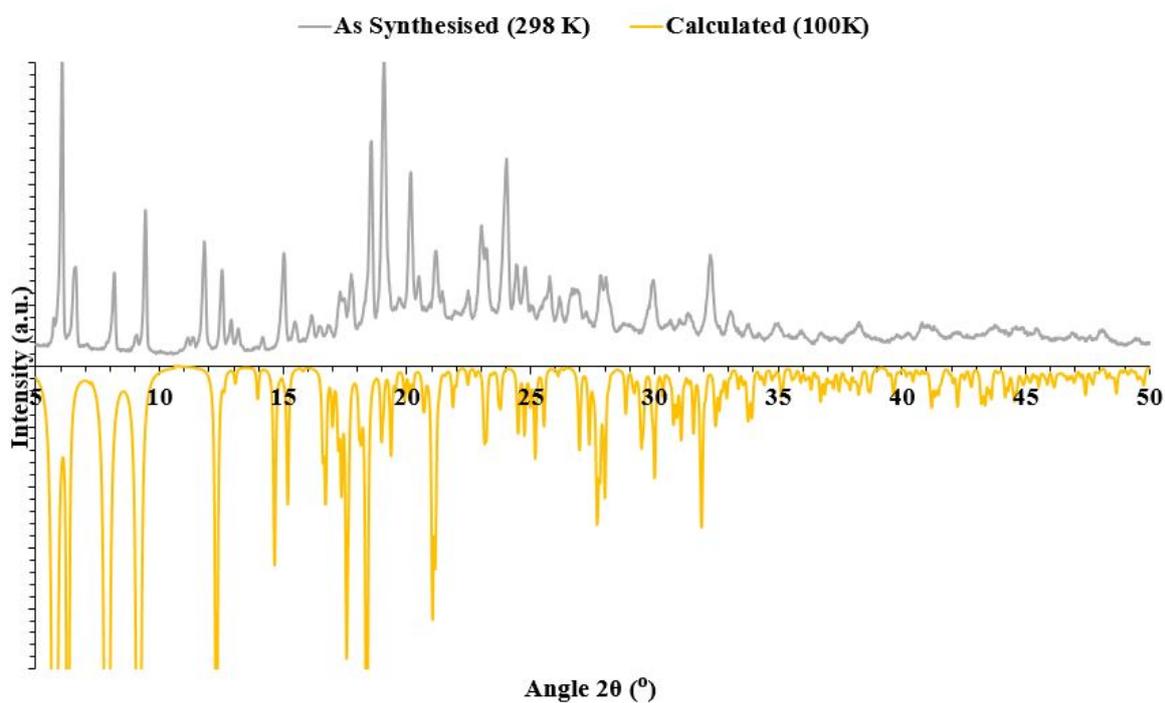
**Figure S3.5** PXRD of **4** collected at room temperature compared to that calculated from the single crystal data at 100 K.



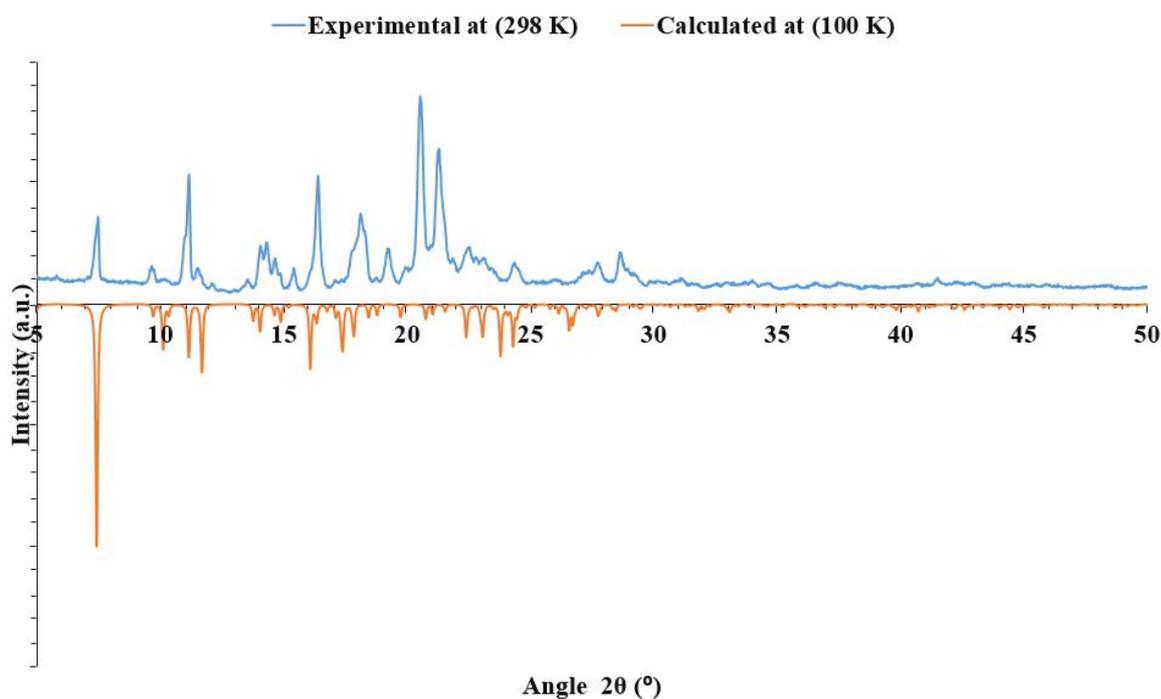
**Figure S3.6** PXRD of **5** collected at room temperature compared to that calculated from the single crystal data at 100 K.



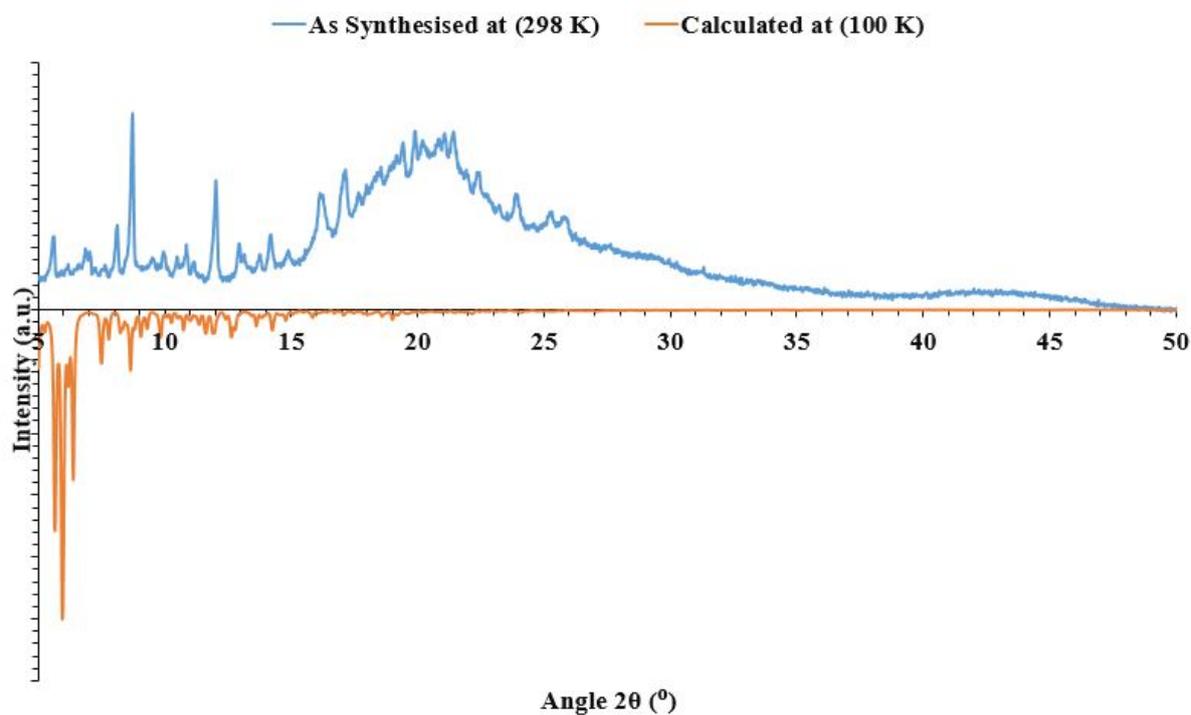
**Figure S3.7** PXR D of **6Zn** collected at room temperature compared to that calculated from the single crystal data at 123 K.



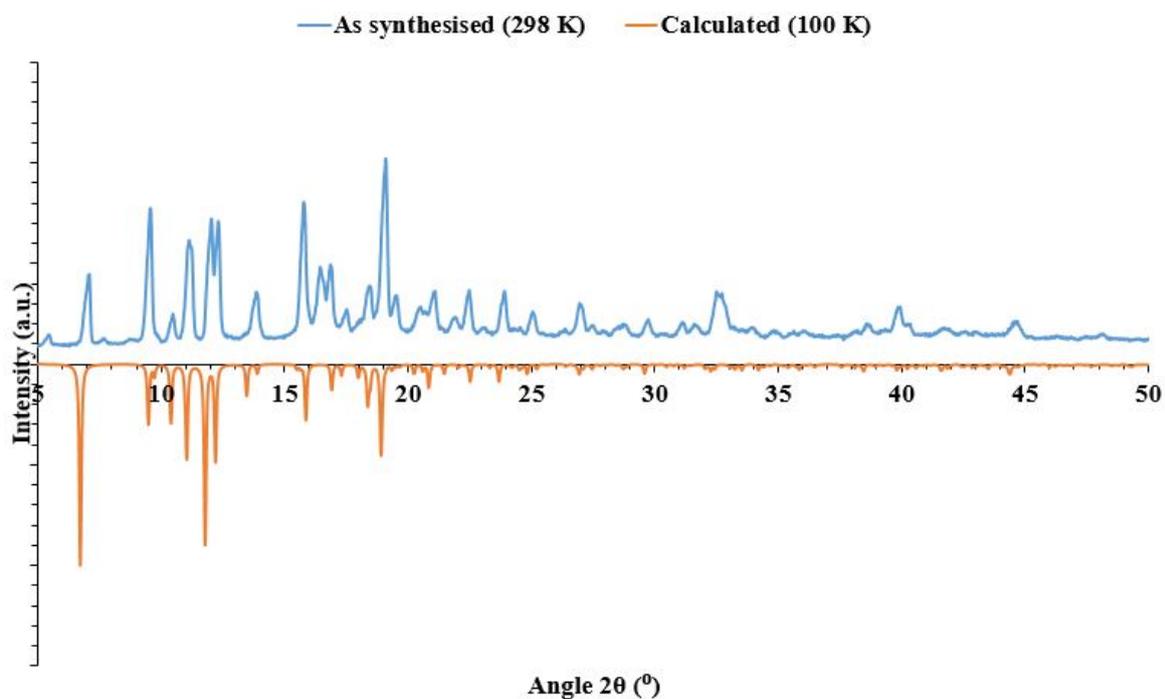
**Figure S3.8** PXR D of **7** collected at room temperature compared to that calculated from the single crystal data at 100 K.



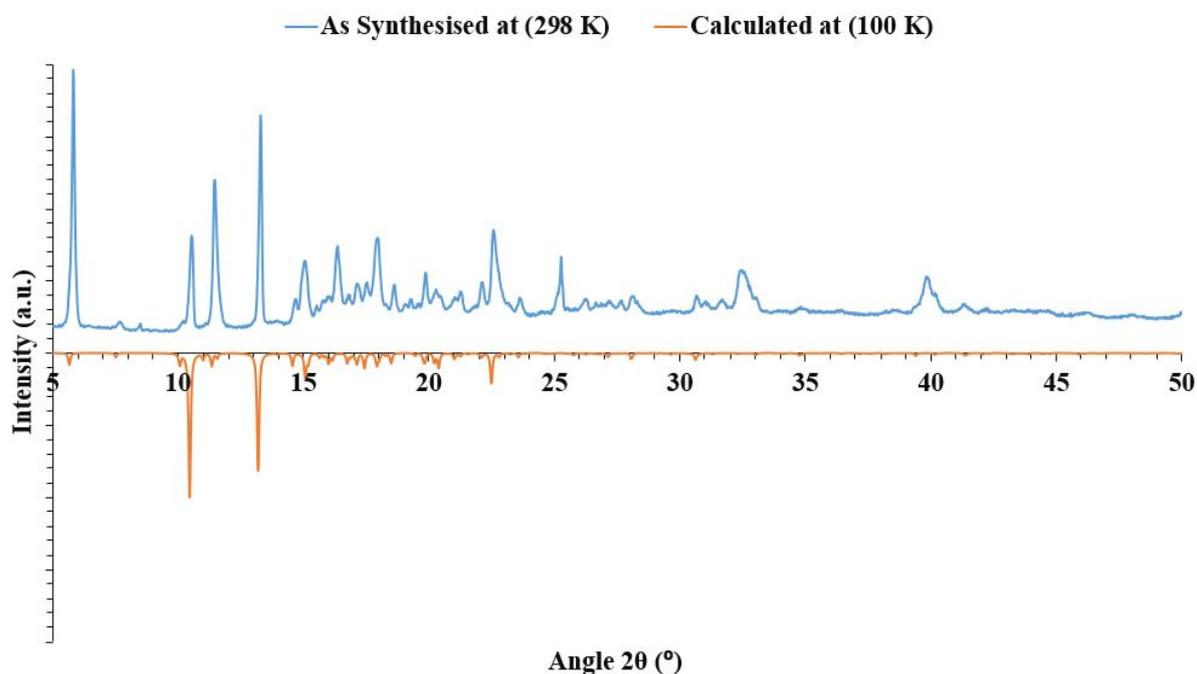
**Figure S3.9** PXRD of **8** collected at room temperature compared to that calculated from the single crystal data at 100 K.



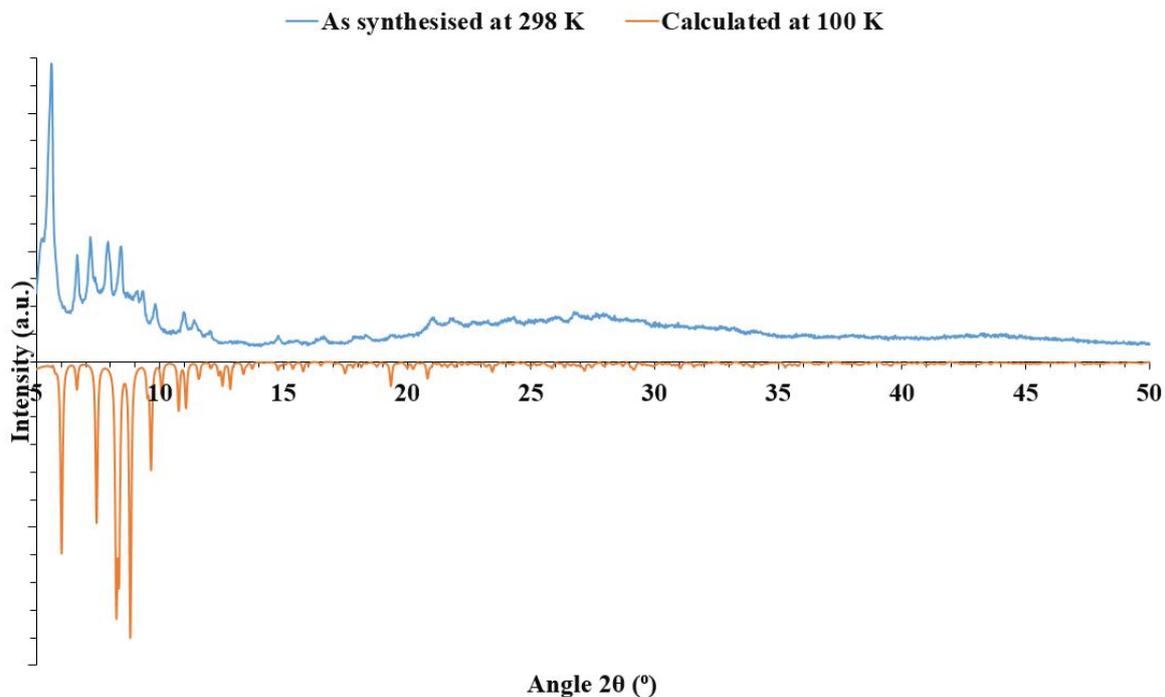
**Figure S3.10** PXRD of **9** collected at room temperature compared to that calculated from the single crystal data at 100 K.



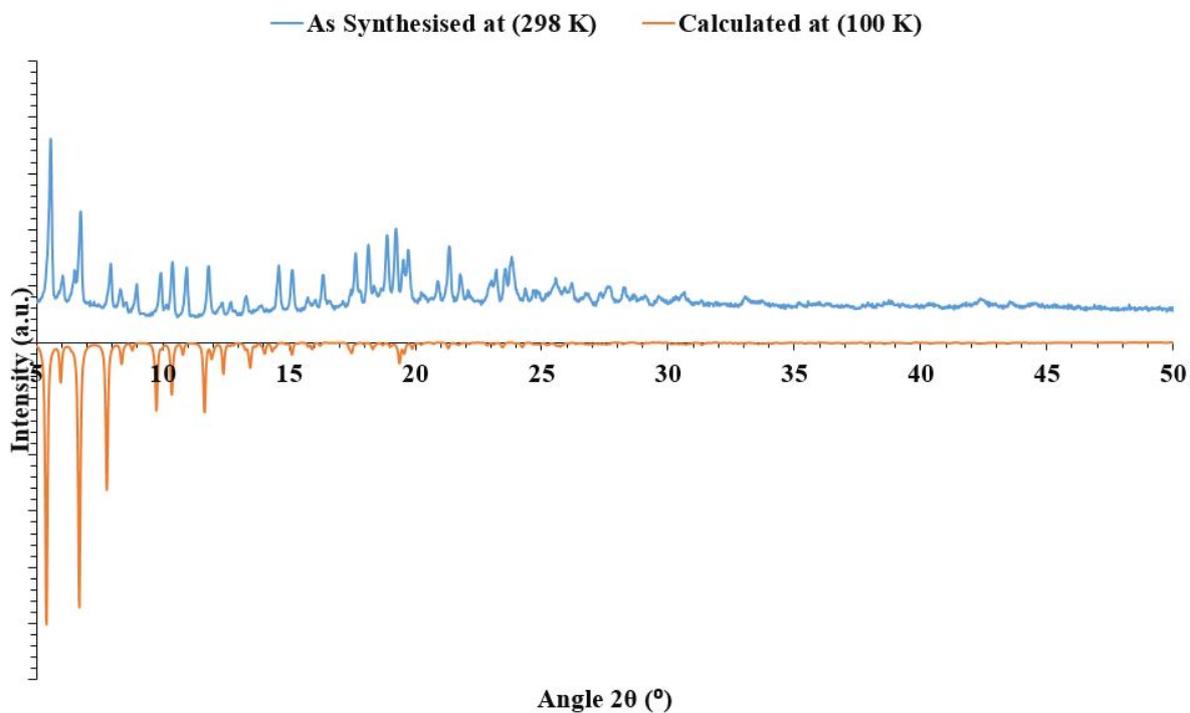
**Figure S3.11** PXRD of **10** collected at room temperature compared to that calculated from the single crystal data at 100 K.



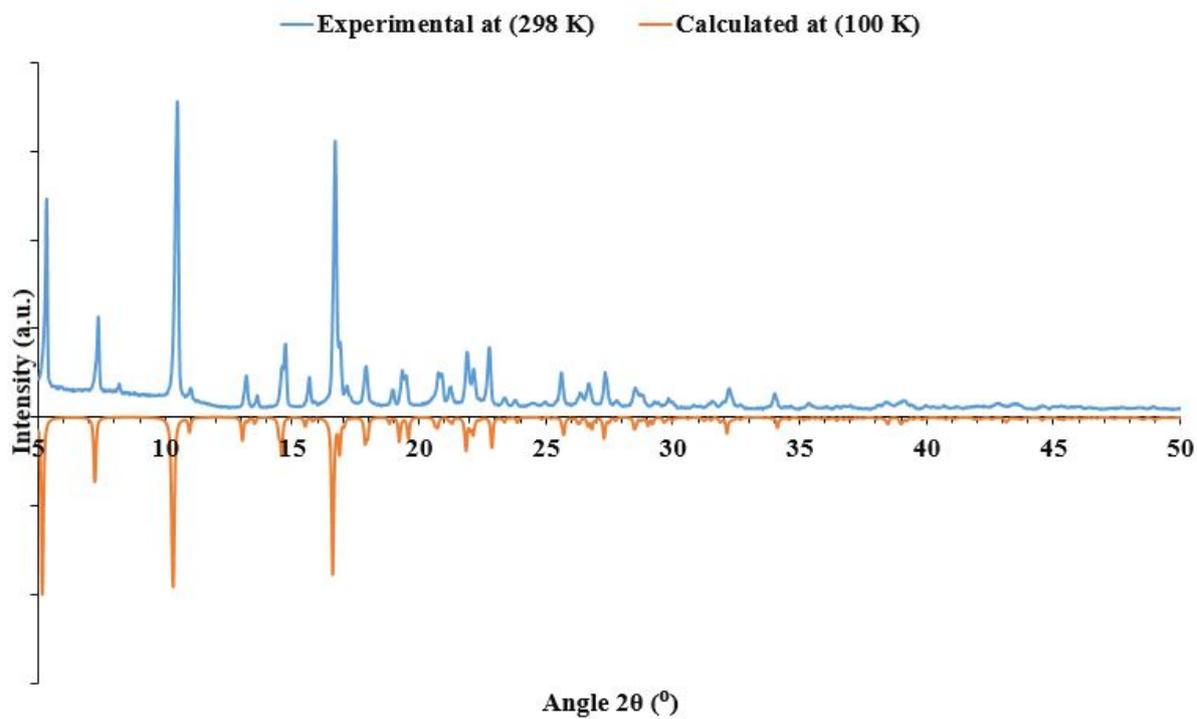
**Figure S3.12** PXRD of **11** collected at room temperature compared to that calculated from the single crystal data at 100 K.



**Figure S3.13** PXR D of **13** collected at room temperature compared to that calculated from the single crystal data at 100 K.

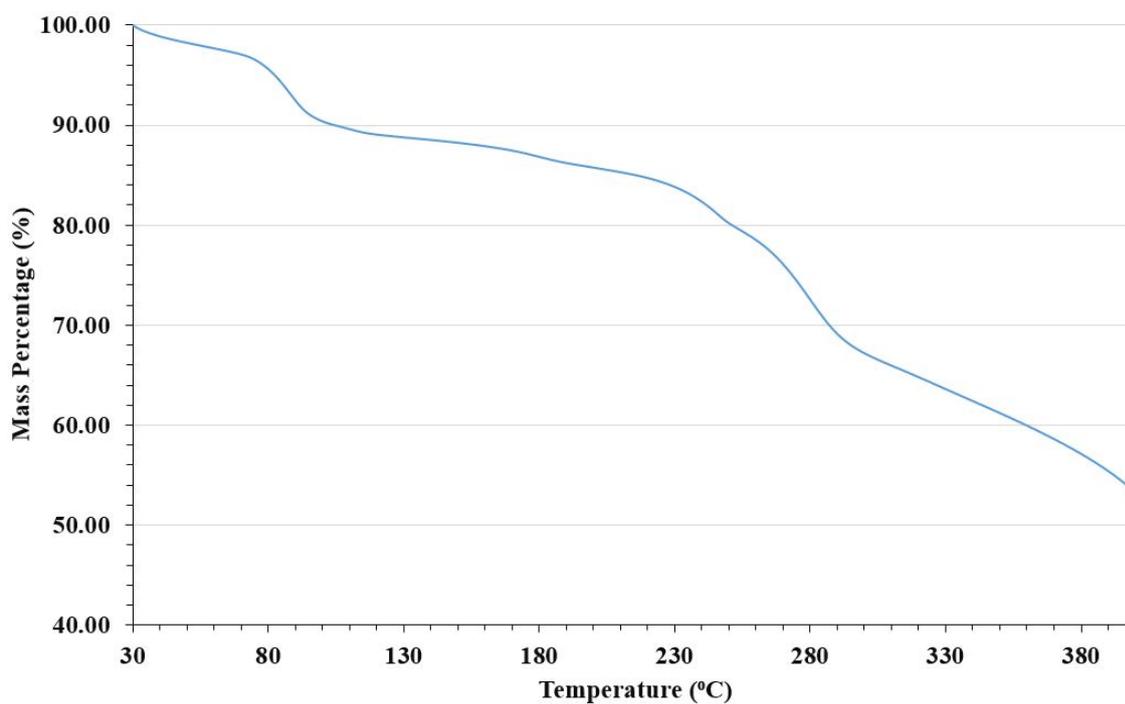


**Figure S3.14** PXR D of **6Co** collected at room temperature compared to that calculated from the single crystal data at 100 K.

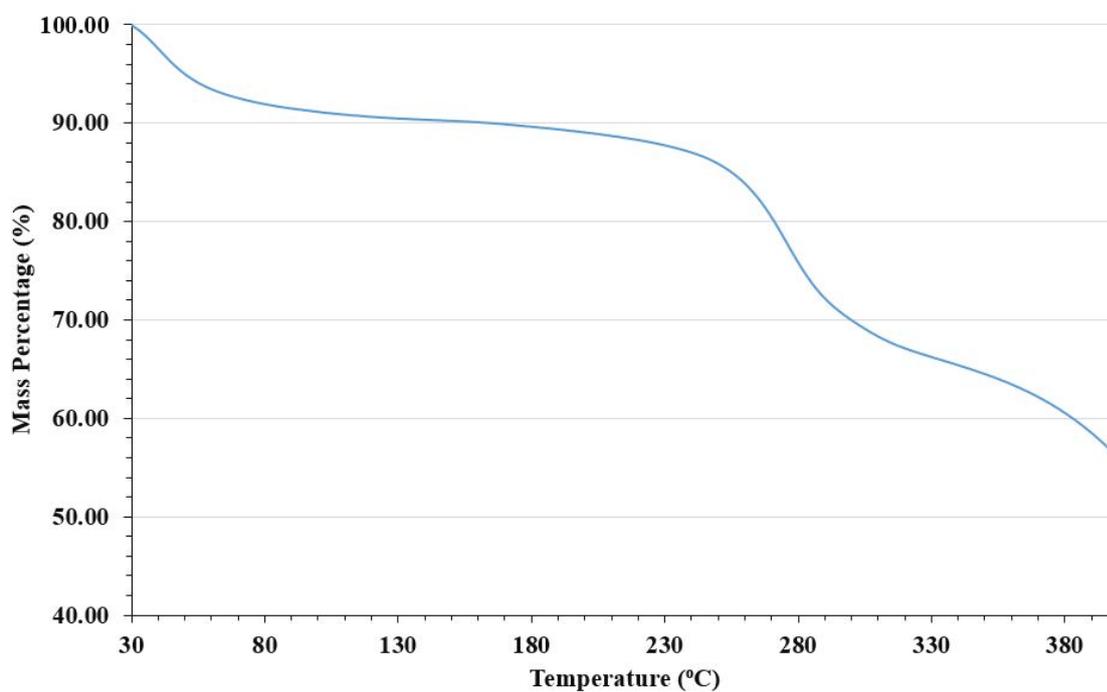


**Figure S3.15** PXRd of **2Mn** collected at room temperature compared to that calculated from the single crystal data at 100 K.

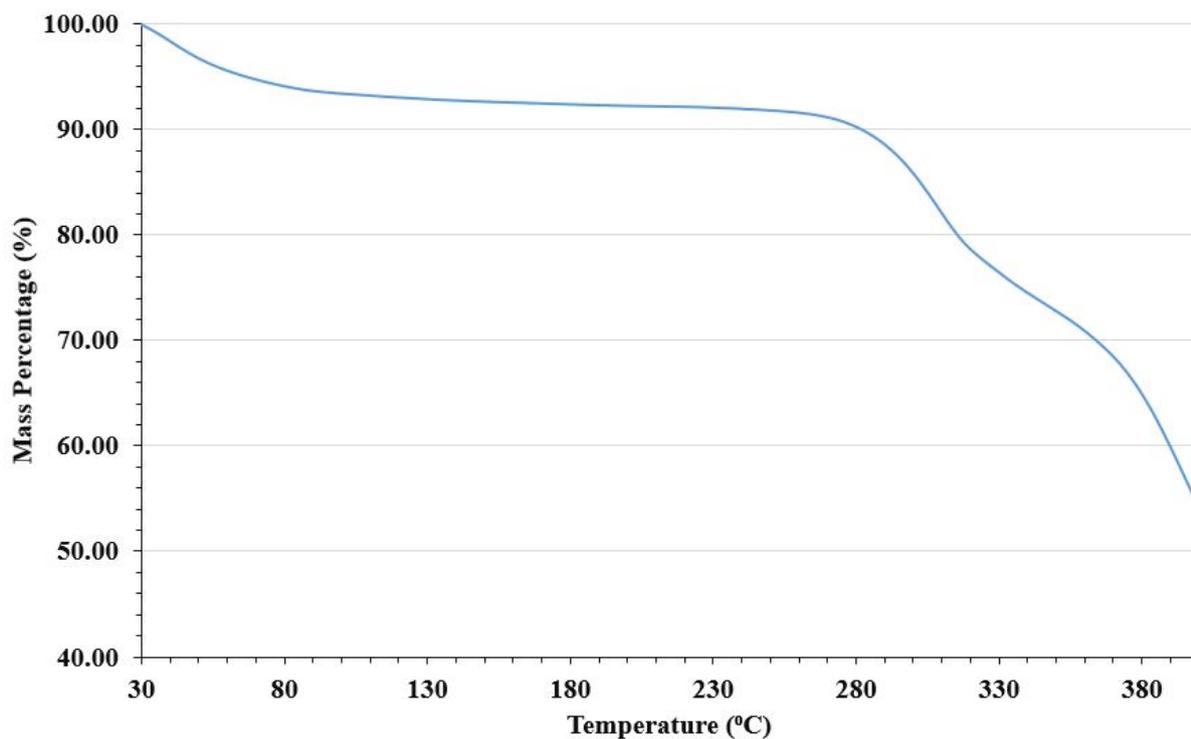
## S4 TGA



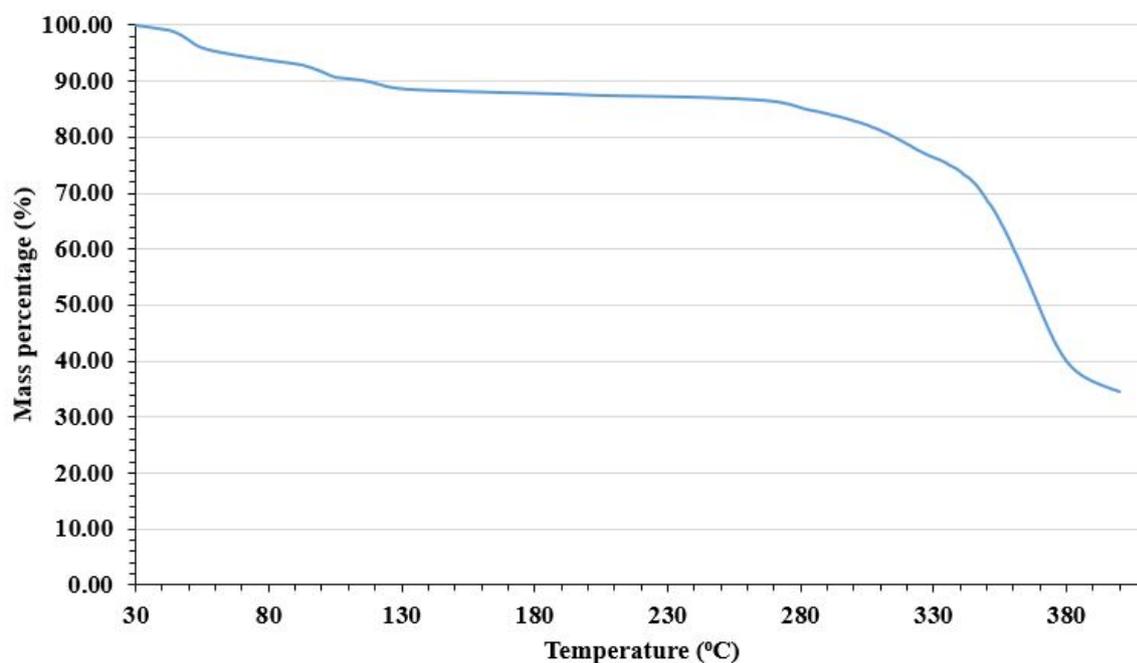
**Figure S4.1** TGA trace for  $H_6L1(Cl)_2 \cdot 5(H_2O)$  showing mass loss (11 %) corresponding to 5  $H_2O$  (calc. 11.1 % for 5 $H_2O$ ) in the range 30-122 °C.



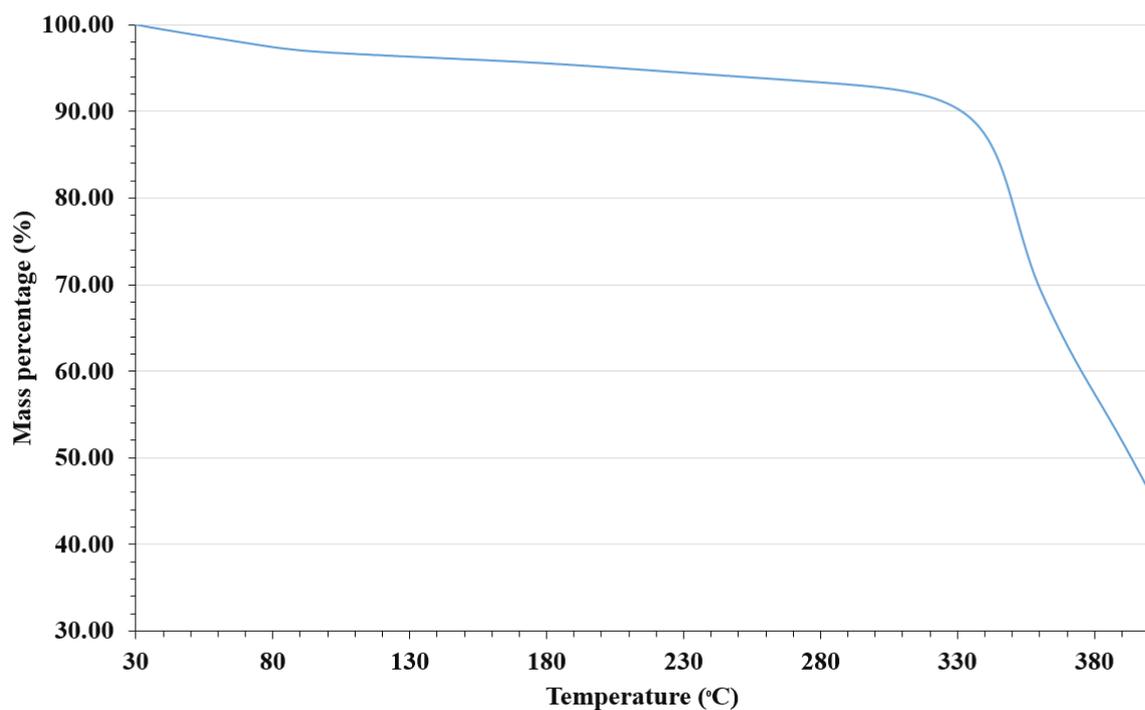
**Figure S4.2** TGA trace for  $H_6L2(Cl)_2 \cdot 8(H_2O)$  showing mass loss (10 %) corresponding to 4.6  $H_2O$  (calc. 10 % for 4.6  $H_2O$ ) in the range 30-140 °C.



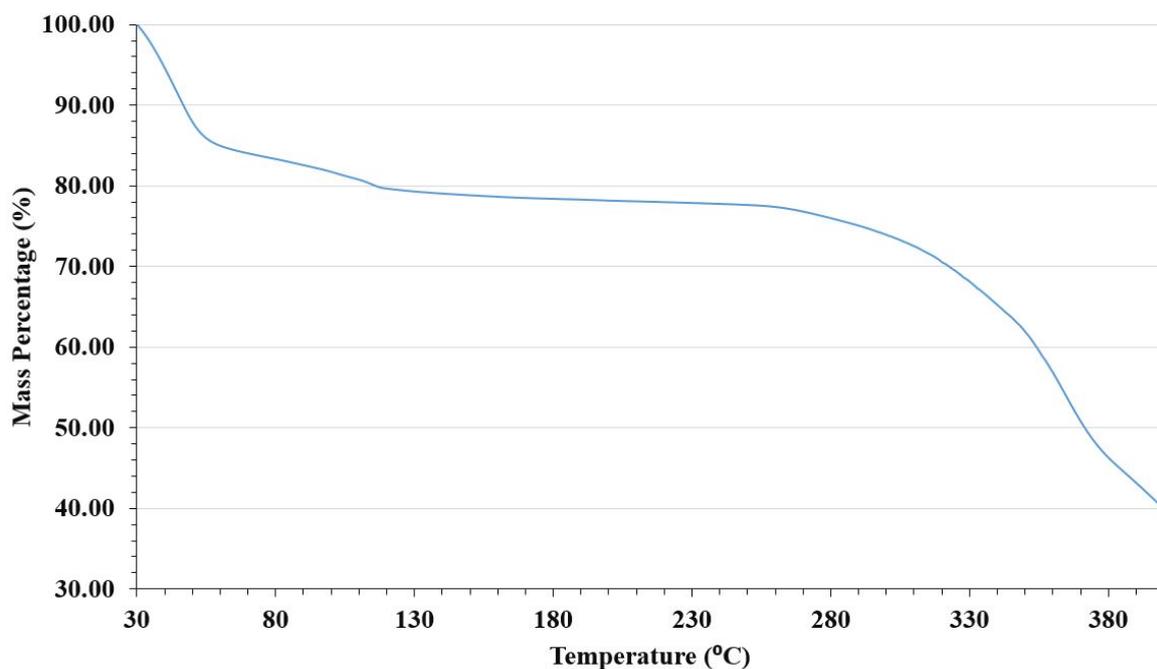
**Figure S4.3** TGA trace for  $\text{H}_6\text{L}_3(\text{Cl})_2 \cdot 7(\text{H}_2\text{O})$  showing mass loss (7 %) corresponding to 4  $\text{H}_2\text{O}$  (calc. 7 % for  $4\text{H}_2\text{O}$ ) in the range 30-130 °C.



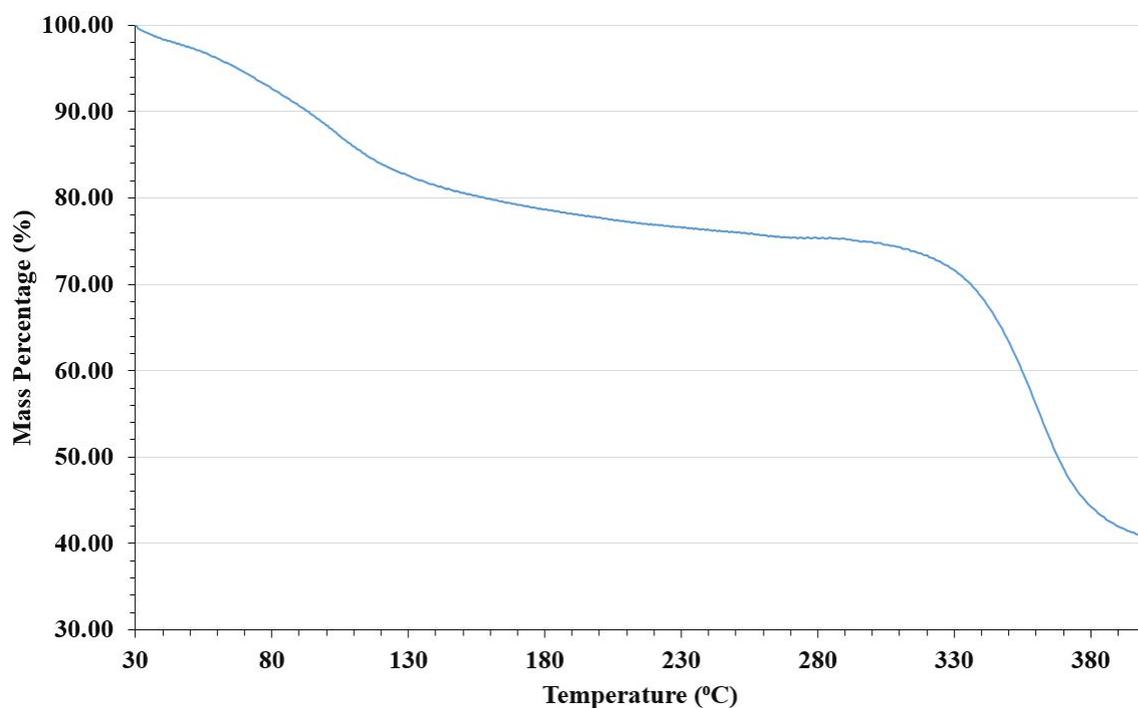
**Figure S4.4** TGA trace for **1** showing mass loss (12 %) corresponding to 7  $\text{H}_2\text{O}$  (calc. 11.78 % for 7  $\text{H}_2\text{O}$ ) in the range 30-130 °C.



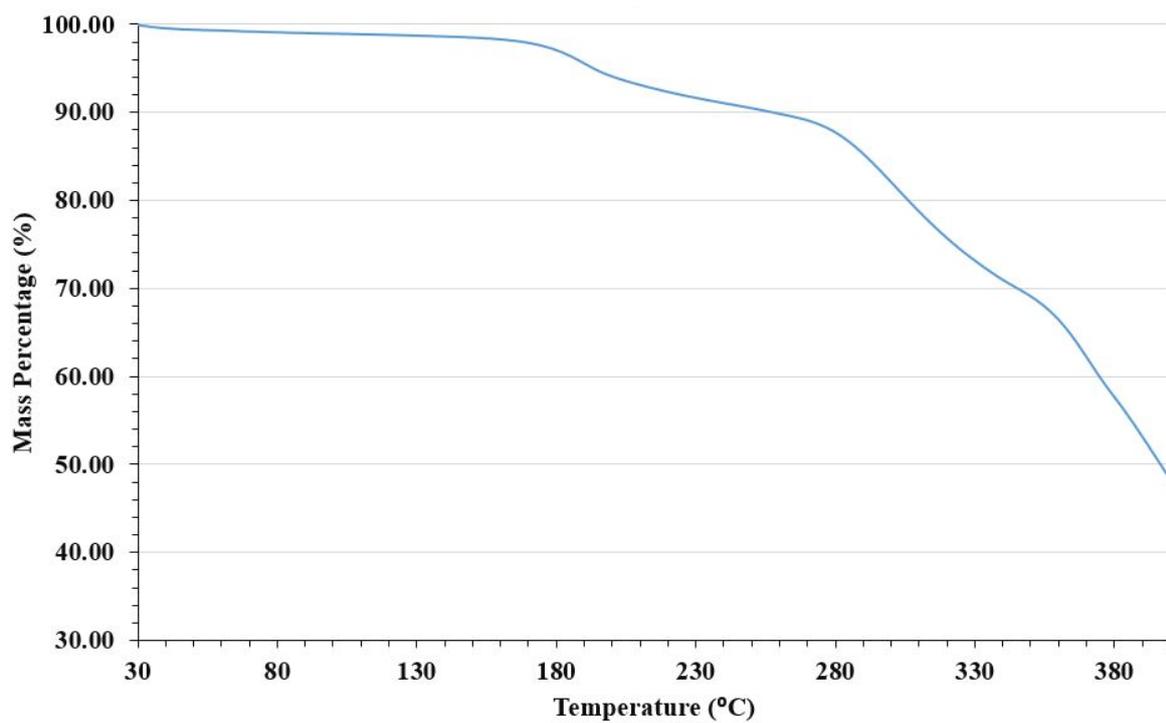
**Figure S4.5** TGA trace for **2Cd** showing mass loss (7.2 %) corresponding to 2 H<sub>2</sub>O and 0.5 DMA (calc. 7.54 % for 2 H<sub>2</sub>O and 0.5 DMA) in the range 30-298 °C.



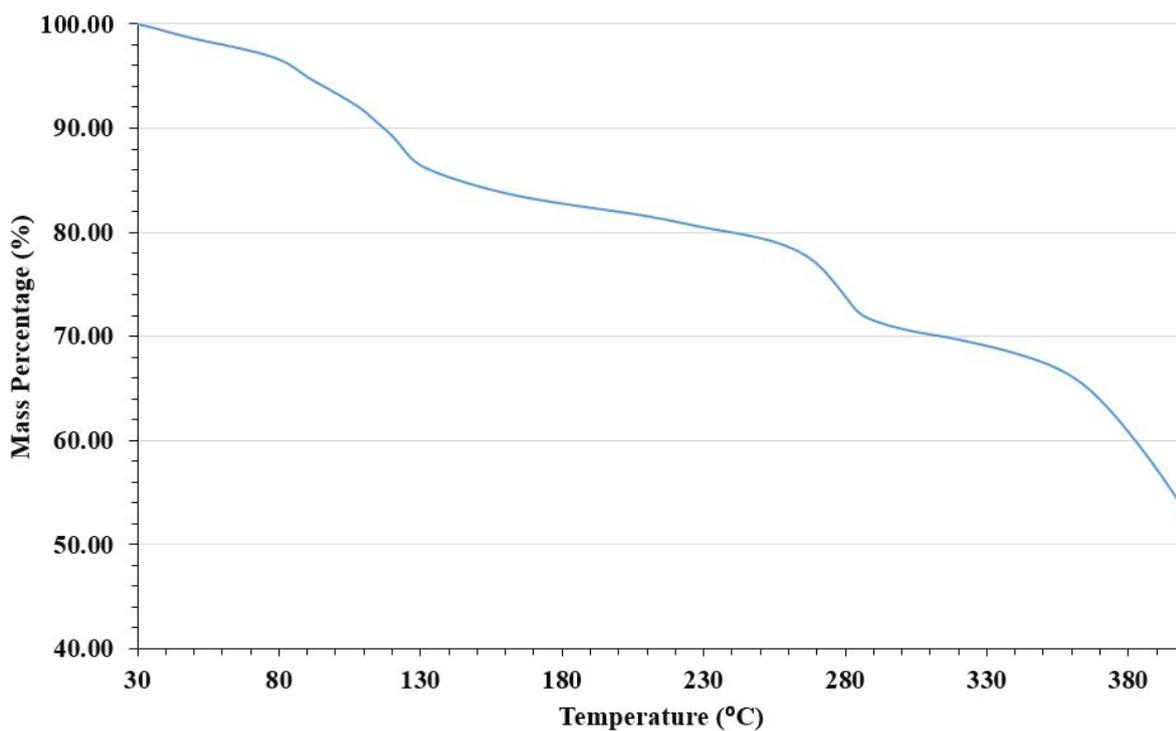
**Figure S4.6** TGA trace for **3** showing mass loss of (15 %) corresponding to 4 H<sub>2</sub>O and 2 DMF (calc. 15 % for 4 H<sub>2</sub>O and 2 DMF) in the range 85-300 °C. The rapid mass loss in the range 30-85 °C was not counted since it is due to surface hydration of the fresh sample.



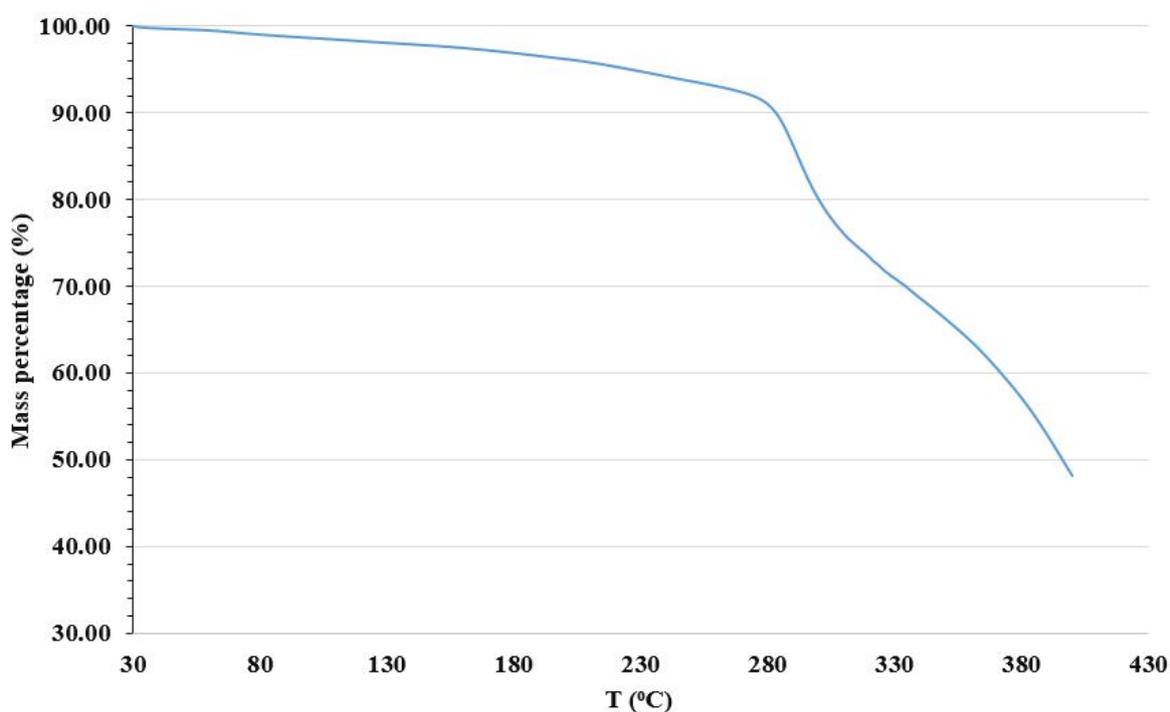
**Figure S4.7** TGA trace for **4** showing mass loss (28 %) corresponding to 16 H<sub>2</sub>O and 2 DMA (calc. 28 % for 16 H<sub>2</sub>O and 2 DMA) in the range 30-320 °C.



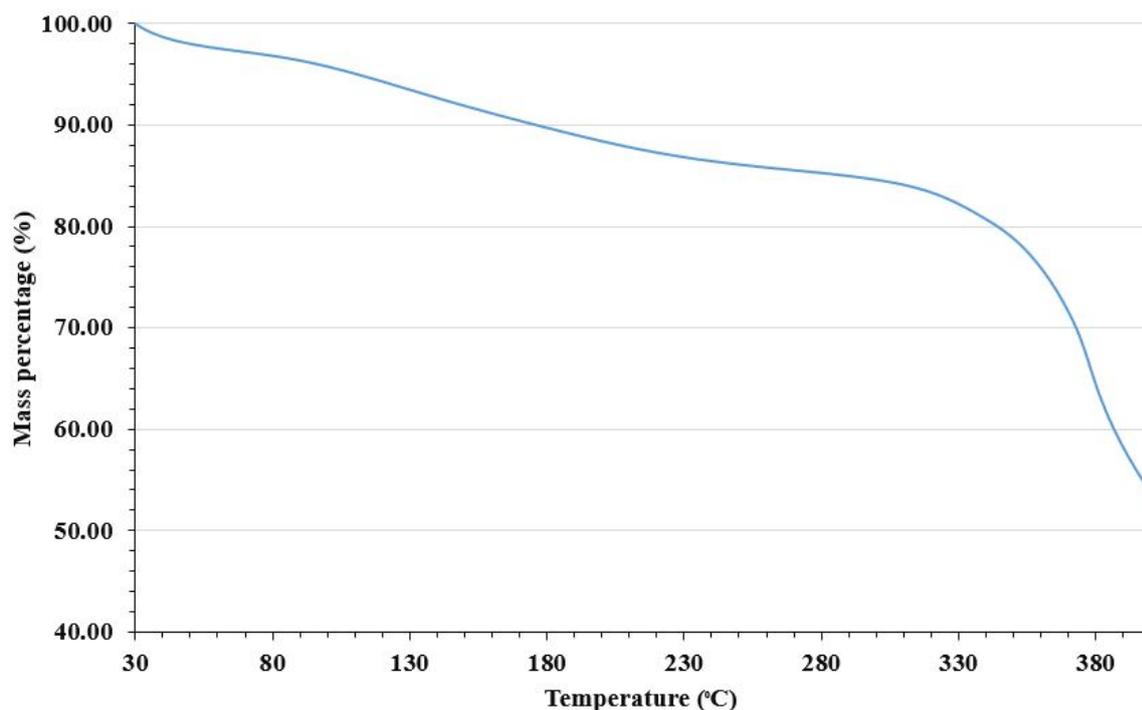
**Figure S4.8** Figure S4.8 TGA trace for **5** showing mass loss (2.5 %) corresponding to 4 H<sub>2</sub>O (calc. 2.5 % for 4 H<sub>2</sub>O) in the range 30-176 °C.



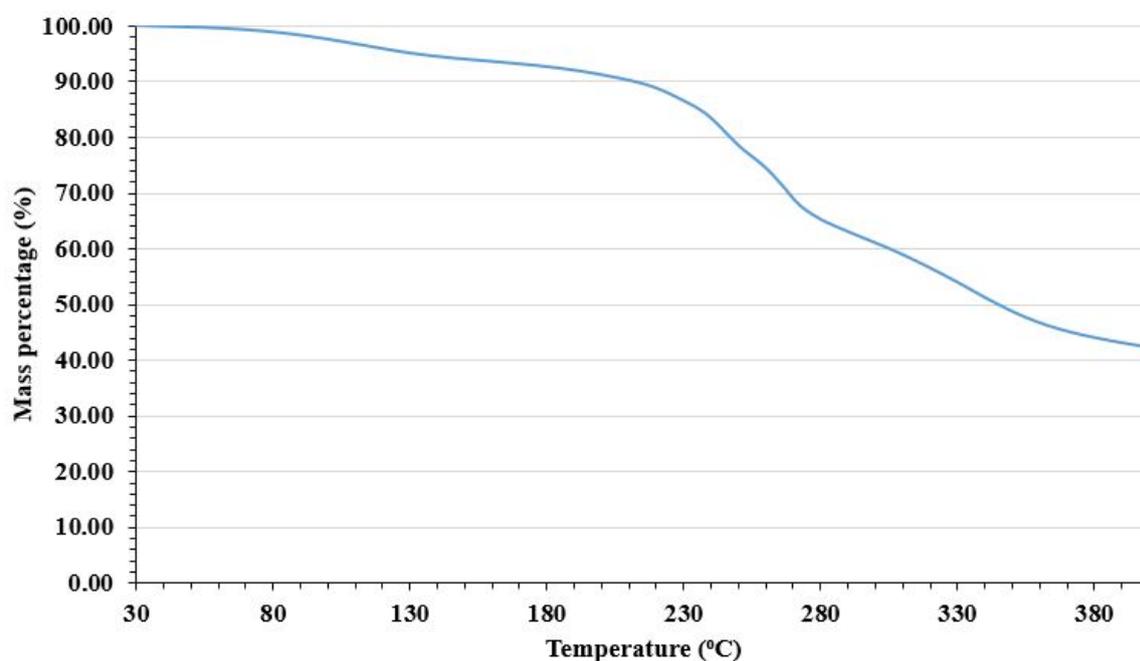
**Figure S4.9** TGA trace for **6Zn** showing mass loss (29 %) corresponding to 20 H<sub>2</sub>O and 4 DMF (calc. 28 % for 20 H<sub>2</sub>O and 4 DMF) in the range 30-290 °C.



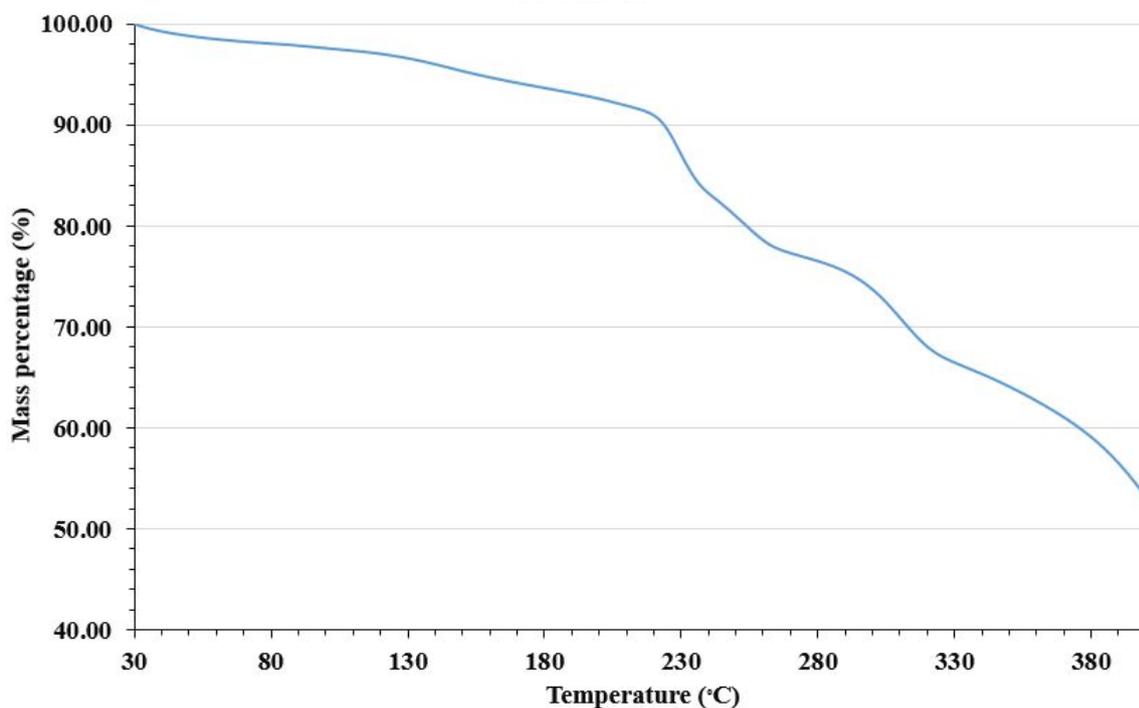
**Figure S4.10** TGA trace for **7** showing mass loss (14 %) corresponding to 2 DMF (calc. 14 % for 2 DMF) in the range 30-290 °C.



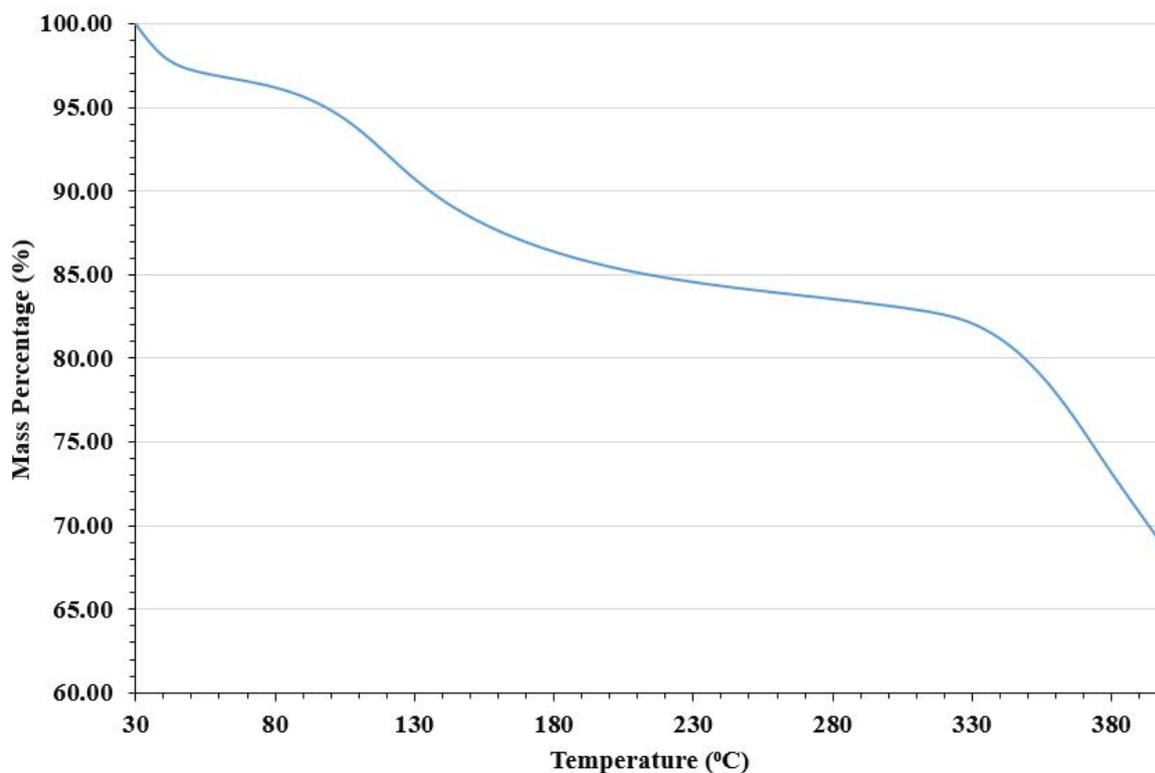
**Figure S4.11** TGA trace for **8** showing mass loss (15 %) corresponding to a 6.7 H<sub>2</sub>O and 0.5 DMF (calc. 11.4 % for 6.7 H<sub>2</sub>O and 0.5 DMF) in the range 30-320 °C.



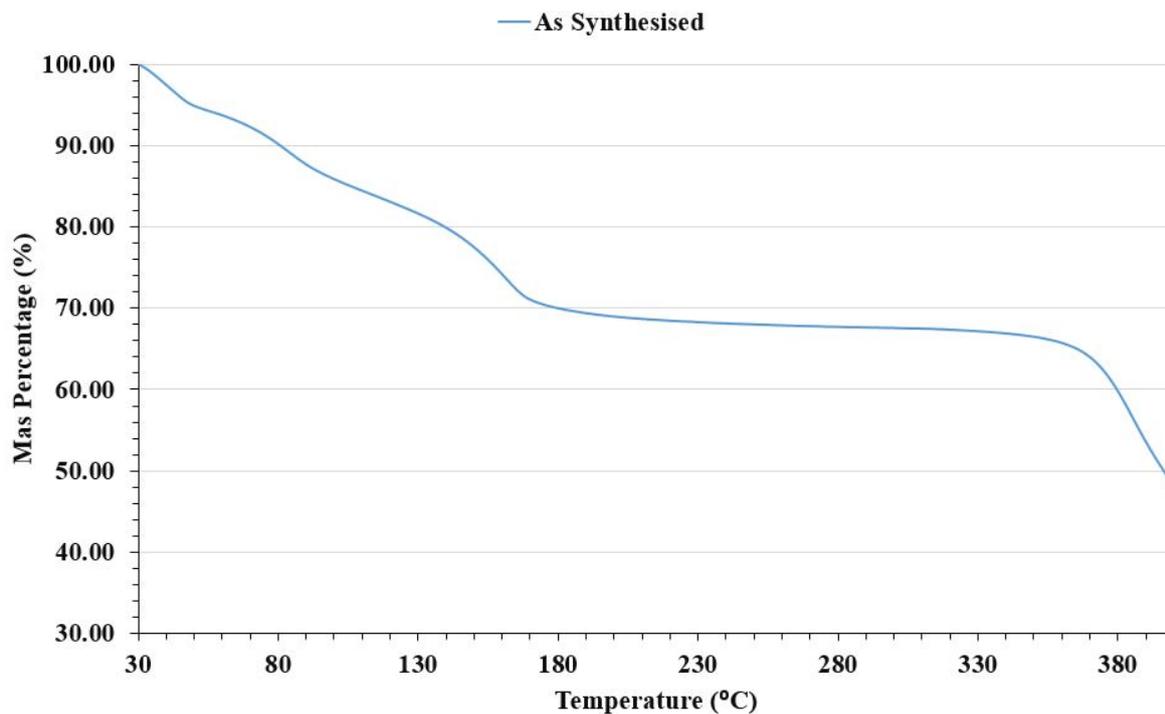
**Figure S4.12** TGA trace for **10** showing mass loss (24 %) corresponding to 3 H<sub>2</sub>O, 2 DMF and a dimethylamine (calc. 5.3 % for 3 H<sub>2</sub>O, calc. 14.3 % for 2 DMF and calc. 4.4 % for dimethylamine) in the range 30-255 °C.



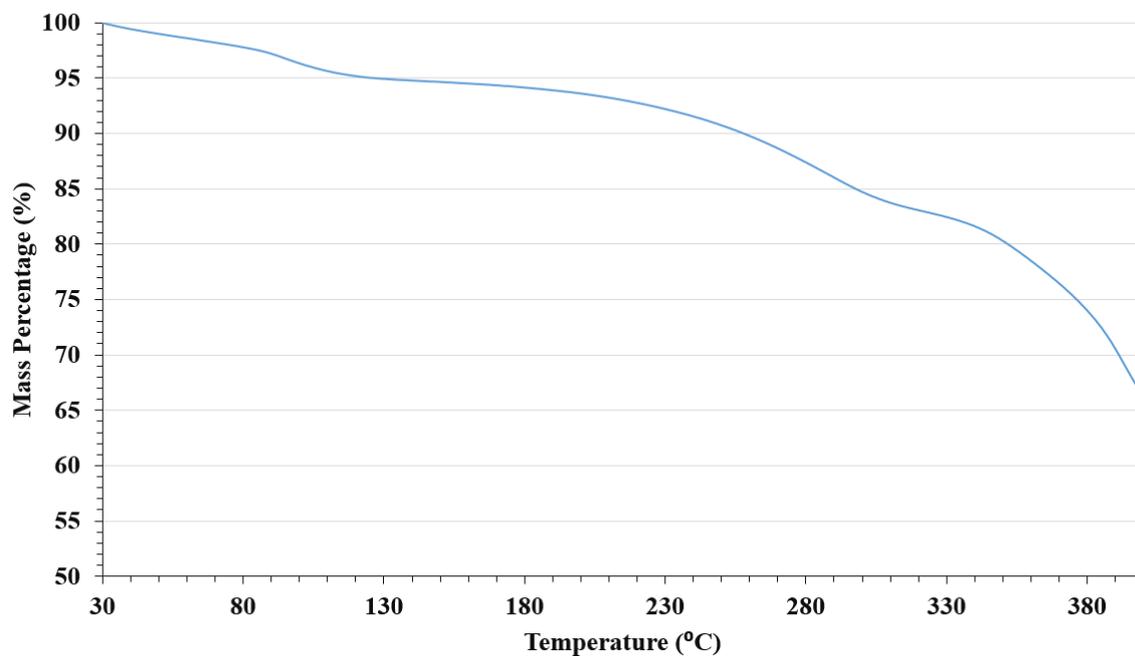
**Figure S4.13** TGA trace for **11** showing mass loss (10 %) corresponding to 5.4 H<sub>2</sub>O (calc. 10 % for 5.4 H<sub>2</sub>O) in the range 30-224 °C.



**Figure S4.14** TGA trace for **13** showing mass loss (18 %) corresponding to 16 H<sub>2</sub>O and 1.9 DMF (calc. 12 % for 16 H<sub>2</sub>O, 6 % for 1.9 DMF) in the range of 30-239 °C.



**Figure S4.15** TGA trace for **6Co** showing mass loss (32 %) corresponding to 12 H<sub>2</sub>O and 7.5 DMF (calc. 23 % for 7.5 DMF, 9 % for 12 H<sub>2</sub>O) in the range of 30-238 °C.



**Figure S4.16** TGA trace for **2Mn** showing mass loss (8.5 %) corresponding to 2 H<sub>2</sub>O and 0.5 DMA (calc. 8.5 % for 3 H<sub>2</sub>O and 0.5 DMA) in the range 30-239 °C.

## S5 Special Crystallographic Refinement Information

### $[(\text{H}_4\text{L}_2)] \cdot \text{DMF} \cdot 9.5\text{H}_2\text{O}$ (from DMF/H<sub>2</sub>O)

In ASU a half ligand was modelled as a zwitterion where the carboxyl group C23O3O4 was modelled as protonated and is hydrogen bonded to nearby carboxyl group with O2. The ligand's amine was modelled as protonated and acts as a hydrogen bonding donor to a nearby water molecule modelled with full chemical occupancy. A disordered DMF molecule was modelled with ½ chemical occupancy as part 1 and acts as a hydrogen bonding acceptor to a nearby water molecule. A nearby water molecule was modelled with ½ chemical occupancy assigned as part 0 and acts as a hydrogen bonding donor to the DMF assigned as part 1. The remaining disordered water molecules were assigned as part 2; five water molecules assigned with ½ chemical occupancy and one assigned with ¼ chemical occupancy. The hydrogen atoms were assigned to O6, O8, O9 and O13. No hydrogen atoms assigned to O7, O10, O11 and O12 due to their high disorder.

### $\text{poly} - [\text{Cd}_2\text{L}_2(\text{OH}_2)_2] \cdot \text{DMA}$ **2Cd** and $\text{poly} - [\text{Mn}_2(\text{L}_2)(\text{H}_2\text{O})_2] \cdot \text{DMA}$ **2Mn**

A dimethylacetamide molecule was disordered and modelled with ½ chemical occupancy given as part -1 since the two parts are related by symmetry; it acts as a hydrogen bond acceptor for a coordinated water molecule.

### $\text{poly} - [\text{Cd}_2(\text{L}_3)] \cdot 2\text{DMA} \cdot 16\text{H}_2\text{O}$ **4**

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.<sup>1</sup> SQUEEZE calculated a total void space per unit cell of 4992 Å<sup>3</sup> containing 894 e<sup>-</sup>, or *ca.* 224 e<sup>-</sup> per formula unit. Furthermore, thermogravimetric analysis showed a mass loss of 28 % in the range 30-230 °C. Combining these, we have tentatively assigned a solvation of 2DMA and 16H<sub>2</sub>O (which equates to 256 e<sup>-</sup> and 28% mass loss). No reasonable formula could be found for the elemental analysis.

### $\text{poly} - \{((\text{CH}_3)_2\text{NH}_2)_4[\text{Zn}_5\text{Na}_4(\text{L}_1)_4(\text{OH}_2)_4(\text{DMF})_2]\}$ **5**

A coordinated DMF to Na1 was modelled with ½ chemical occupancy. A bridging water was modelled with full chemical occupancy but the hydrogen atoms were not assigned. A full occupancy dimethyl ammonium ion was modelled and the two hydrogen atoms were assigned and act as hydrogen bonding donors to the nearby carboxylate oxygen atoms.

*poly*-[Co<sub>5</sub>(HL1)<sub>2</sub>(O)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(DMF)]·9DMF·10H<sub>2</sub>O. **6Co** and *poly*-[Zn<sub>5</sub>(HL1)<sub>2</sub>(O)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(DMF)<sub>2</sub>]·2DMF·18H<sub>2</sub>O. **6Zn**

For **6Zn**, two disordered, uncoordinated DMF molecules were successfully modelled; one acts as a hydrogen bonding acceptor to a nearby coordinated water molecule assigned with ½ chemical occupancy whereas the second DMF, modelled isotropically, was found to be trapped in the channels and assigned as ¼ chemical occupancy. Its oxygen atom, facing nearby cyclohexyl proton at a distance of 2.637 Å, was assigned with ¼ chemical occupancy. **6Co** is essentially isostructural to **6Zn** but the coordinated DMF molecule was more disordered and modelled as ½ chemical occupancy; the methyl groups were modelled as disordered across four positions with ¼ chemical occupancies. Only one uncoordinated DMF was successfully modelled isotropically with ¼ chemical occupancy; it acts as a hydrogen bond acceptor to a coordinated water molecule as in **6Zn**.

A significant region of disordered electron density exists within the voids of both structures that could not be satisfactorily modelled. Therefore, this electron density within the channels was removed and quantified using the SQUEEZE routine within PLATON.<sup>1</sup> SQUEEZE calculated a total void space per unit cell of 6005 Å<sup>3</sup> containing 1244 e<sup>-</sup> for **6Zn**. The electron density suggests the void space contains 124.4 H<sub>2</sub>O or 31.1 DMF molecules per unit cell (on the basis of 10e<sup>-</sup> per H<sub>2</sub>O or 40 e<sup>-</sup> per DMF; 15.5 H<sub>2</sub>O or 3.8 DMF per formula unit). Thermogravimetric analysis shows showing a mass loss of (29 %) corresponding to 20 H<sub>2</sub>O and 4 DMF (calc. 28.3 % for 20 H<sub>2</sub>O and 4 DMF) in the range 30-290 °C. The elemental analysis suggested a much higher solvation state that couldn't be assigned reasonably hence the TGA and crystallographic model were only considered in generating the formula. Overall, the SQUEEZE and TGA results for **6Zn** suggested a solvation of 18 H<sub>2</sub>O and 2 DMF molecules per formula unit. For **6Co** the void space and electron density were 6800 Å<sup>3</sup> and 2112 e<sup>-</sup> respectively. In addition, the TGA also showed a higher solvation state (12 H<sub>2</sub>O and 7.5 DMF / formula unit). The electron density suggests 26.4 H<sub>2</sub>O or 6.6 DMF per formula unit existing in the void space of **6Co**. Overall, the SQUEEZE, TGA and elemental analysis results for **6Co** suggested a solvation of 10 H<sub>2</sub>O and 9 DMF molecules per formula unit.

*poly*-[Zn<sub>3</sub>(L1)(OH)<sub>2</sub>]·2DMF **7**

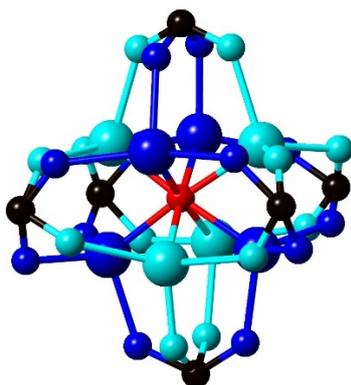
The bridging oxygen was modelled as a hydroxide where the hydrogen atom was assigned from a Q peak with residual electron density 0.48 close to the bridging oxygen. The hydrogen atom acts as a hydrogen bonding donor to a nearby DMF molecule.

### *poly*-{((CH<sub>3</sub>)NH<sub>2</sub>)[Zn<sub>2</sub>(HL<sub>2</sub>)(O)]·DMF } **8**

A bridging oxygen atom O7 was modelled as an oxide with ½ chemical occupancy and assigned as part -1 since its second half is related by symmetry. A nearby uncoordinated dimethyl ammonium ion was modelled with ½ chemical occupancy and its two hydrogen atoms were assigned and act as hydrogen bonding donors to the bridging oxide ion O7 and the nearby carboxylate oxygen O4. No hydrogen atoms were assigned to the methyl group of dimethyl ammonium ion due to the disorder of the nitrogen atom. The ligand amine was assigned with a hydrogen atom with ½ chemical occupancy in order to charge balance with the dimethyl ammonium ion. A non-coordinated DMF molecule was successfully modelled with ½ chemical occupancy. It lies in the channels and faces a nearby aromatic hydrogen atom at a distance of 2.483 Å.

### *poly*-[Zn<sub>8</sub>(L<sub>3</sub>)<sub>3</sub>(O)<sub>2</sub>]·16DMF **9**

In ASU three ligands and two zinc clusters were modelled with highly disordered benzoate moieties of the linkers and the two zinc clusters. The first zinc cluster with O1 oxide is disordered as 50 % occupancy for each zinc ion modelled in two positions. The second zinc cluster with O2 oxide is disordered as 25 % and 75 % occupancy for each zinc ion modelled in two positions. The carboxyl groups coordinated to the first zinc cluster with O1 oxide were modelled as disordered with 50 % occupancies whereas the carboxyl groups coordinated to the second zinc cluster with O2 oxide were modelled as 25 % and 75 % except one assigned with 20 % and 80 %. The disorder of the aromatic rings was modelled with occupancies that best fit the electron density, being either 50:50, 35:65 or 25:75. Data quality was limited despite several attempts to collect better data, due to the highly porous nature of his framework, with the resolution limited to 1.06 Å. Therefore, the non-hydrogen atoms were refined anisotropically and ISOR restraints were applied.



**Figure S5.1** The disordered zinc cluster model showing part 1 zinc and oxygen atoms in cyan and part 2 zinc and oxygen atoms in deep blue. The carbons and oxide are shown in black and red respectively.

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.<sup>1</sup> SQUEEZE calculated a total void space per unit cell of 16054 Å<sup>3</sup> containing 4018 e<sup>-</sup>. The electron density suggest the void space contains 100.45 DMF molecules per unit cell (on the basis of 40e<sup>-</sup> per DMF; 16.7 DMF per formula unit).

### *poly*-[Cu<sub>2</sub>(L2)(OH<sub>2</sub>)<sub>2</sub>] **11**

The data were collected for a small blue plate of compound **11** at the MX2 beamline of the Australian Synchrotron, which exhibited poor diffraction at high angles. All attempts to collect better quality data were unsuccessful. Both cinnamate groups were found to be disordered over two positions, as were the copper atoms and the water ligands of the paddlewheel cluster. All disordered atoms were refined at 50% occupancy, and the disorder combined with the poor data quality meant that all disordered atoms except the copper atoms were refined isotropically. No hydrogen atoms were assigned to the disordered water ligands.

### *poly*-[Zr<sub>6</sub>(HL1)<sub>2</sub>(O)<sub>8</sub>(CH<sub>3</sub>COO)<sub>2</sub>(OH<sub>2</sub>)<sub>6</sub>] **13**

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.<sup>1</sup> SQUEEZE calculated a total void space per unit cell of 8173 Å<sup>3</sup> containing 933 e<sup>-</sup>. The electron density suggests that the void

space contains 93.3 H<sub>2</sub>O or 23.3 DMF molecules per unit cell (on the basis of 10e<sup>-</sup> per H<sub>2</sub>O or 40 e<sup>-</sup> per C<sub>3</sub>H<sub>7</sub>NO; 23 H<sub>2</sub>O or 5.8 DMF per formula unit).

## References

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