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Single-crystal to single-crystal transformations in discrete solvated metallocycles: the role of the metal ion

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1. MATERIALS AND METHODS

Thermogravimetric analysis and differential scanning calorimetry were performed on a TA Instruments Q500 thermogravimetric analyser and a Q100 differential scanning calorimeter using a heating rate of 5 °C.min^{-1} under a nitrogen atmosphere with a 50 ml.min^{-1} flow rate. X-ray powder diffraction experiments were carried out on a PANalytical instrument using Cu-Kα radiation (λ = 1.5418 Å).

2. SINGLE-CRYSTAL X-RAY DIFFRACTION

Intensity data were collected on a Bruker SMART Apex CCD diffractometer[1] using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The temperature of the crystals was controlled using an Oxford Cryostream Cooler. Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT.[2] Where necessary, systematic errors in the intensity data were corrected for using SADABS.[3] The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97.[4] In most cases, all non-hydrogen atoms were located using either of these methods. All ordered non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on F^2 using SHELXL-97[4] within the X-Seed[5] environment. Where appropriate, the hydrogen atoms were placed in calculated positions using riding models and assigned isotropic thermal parameters 1.2 times those of their parent atoms for CH_2, aromatic C and O-H groups, or 1.5 times those of their parent atoms for CH_3 groups. In special cases, hydrogen atoms were located in difference electron density maps and their isotropic thermal

parameters were refined freely. In the case of $[Co_2\mathbf{L}_2Cl_4]\cdot 2MeOH$, the calculated position of the hydroxyl hydrogen atom is on the mirror plane. For $[Cd_2\mathbf{L}_2Cl_4]\cdot 2MeOH$ the hydrogen atom was placed on the mirror plane and refined freely with a loose restraint on the O–H distance; an acceptable standard uncertainty was obtained in this manner. For $[Zn_2\mathbf{L}_2Cl_4]\cdot 2MeOH$ the hydroxyl hydrogen atom was also placed on the mirror plane, but the O–H···Cl geometry needed to be constrained in order to keep it there during refinement. Using this procedure, nonsensical standard uncertainties were obtained, and it was thus necessary to use a calculated model that requires an equal occupancy disorder of the hydrogen atom on either side of the (010) mirror plane. In considering the O–H···Cl^- angle, excellent directionality is implied for the hydrogen bonds in both $[Co_2\mathbf{L}_2Cl_4]\cdot 2MeOH$ and $[Cd_2\mathbf{L}_2Cl_4]\cdot 2MeOH$ with ∠DHA = 175.8º and 175(9)º, respectively. For $[Zn_2\mathbf{L}_2Cl_4]\cdot 2MeOH$ this is not the case since the O–H bond and the H···Cl^- interactions are not in the *ac* plane. In the disordered model, ∠DHA is 153.2º.

3. THERMAL ANALYSIS

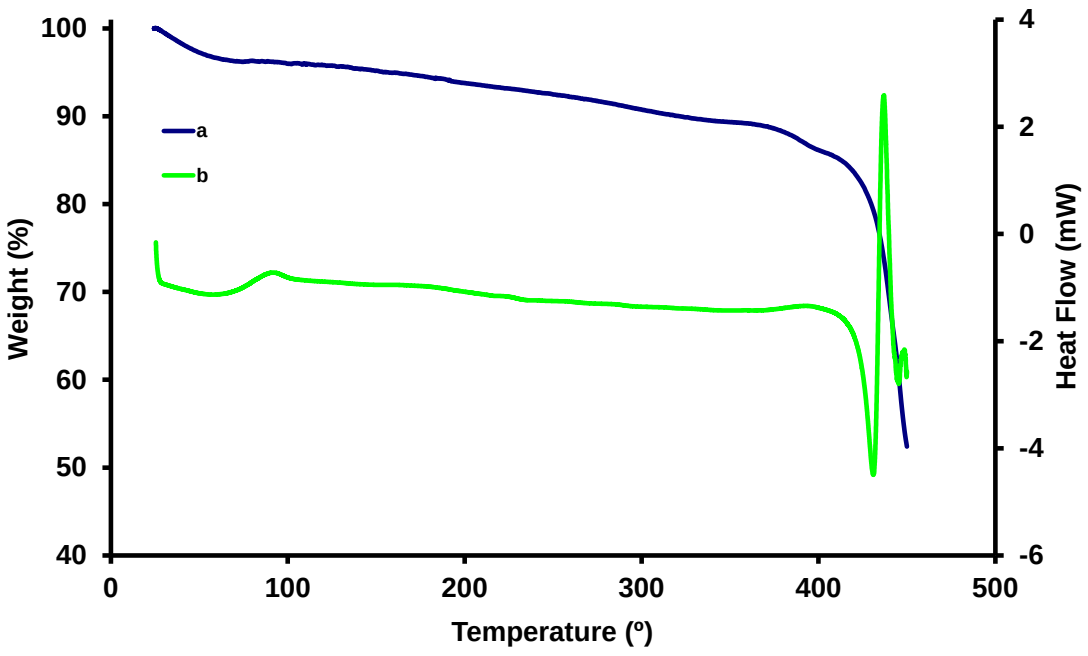

Figure S1 a) Thermogravimetric analysis and b) differential scanning calorimetry of $[Zn_2\mathbf{L}_2Cl_4]\cdot 2MeOH$.

4. POWDER X-RAY DIFFRACTION

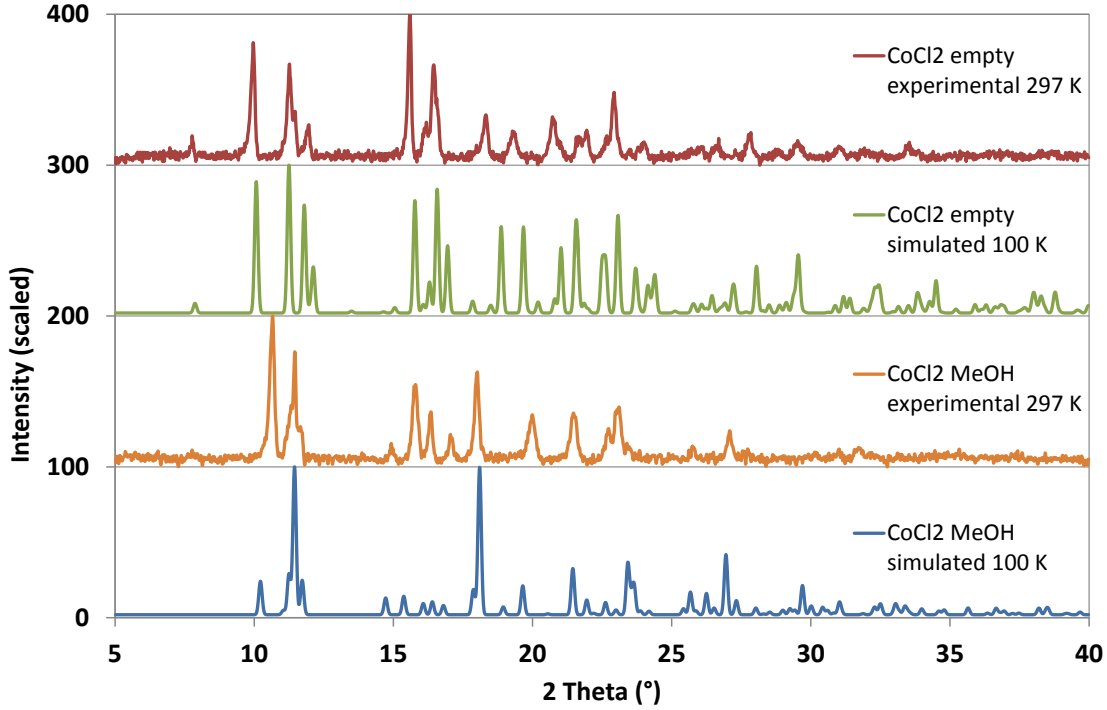

Figure S2 Powder X-ray diffraction data of $[Co_2\mathbf{L}_2Cl_4]\cdot 2MeOH$.

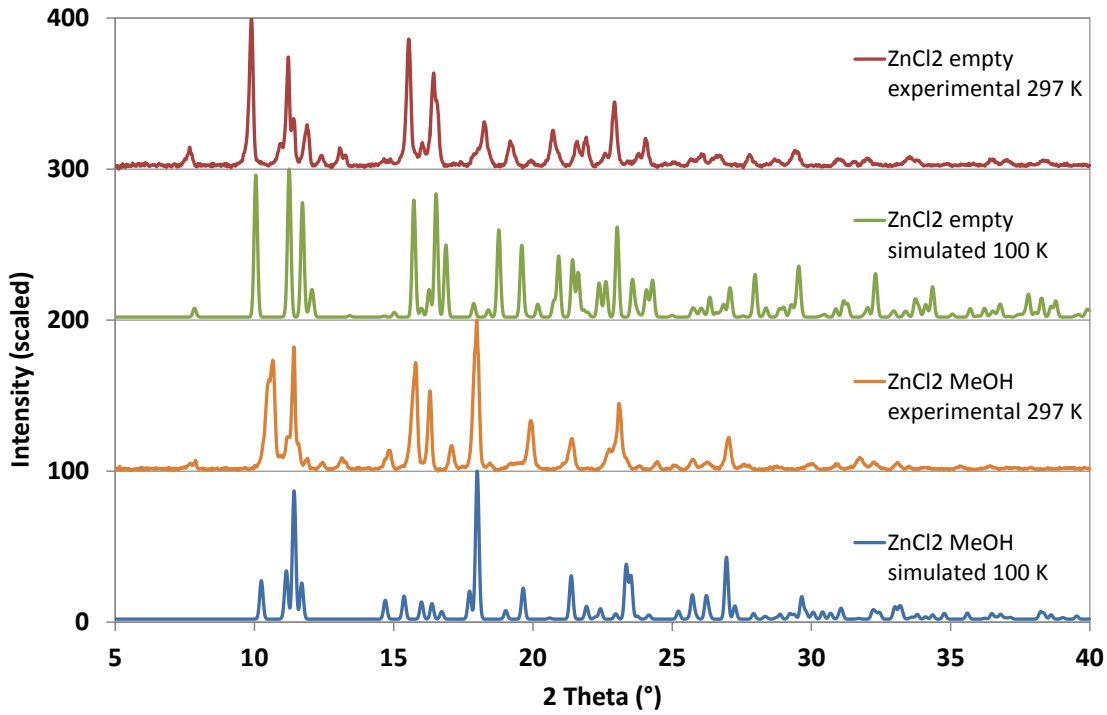

Figure S3 Powder X-ray diffraction data of $[Zn_2\mathbf{L}_2Cl_4]\cdot 2MeOH$.

5. REFERENCES

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