Single-crystal to single-crystal transformations in discrete solvated metalloycles: 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 diffractometer¹ using graphite monochromated Mo-Kα 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 F² using SHELXL-97⁴ within the X-Seed⁵ 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 CH₂, aromatic C and O-H groups, or 1.5 times those of their parent atoms for CH₃ 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 \([\text{Co}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\), the calculated position of the hydroxyl hydrogen atom is on the mirror plane. For \([\text{Cd}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\) 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 \([\text{Zn}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\) 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 \([\text{Co}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\) and \([\text{Cd}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\) with \( \angle \text{DHA} = 175.8^\circ \) and 175(9)\(^\circ \), respectively. For \([\text{Zn}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\) 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, \( \angle \text{DHA} \) is 153.2\(^\circ \).

3. THERMAL ANALYSIS

![Figure S1](#) a) Thermogravimetric analysis and b) differential scanning calorimetry of \([\text{Zn}_2\text{L}_2\text{Cl}_4] \cdot 2\text{MeOH}\).
4. POWDER X-RAY DIFFRACTION

Figure S2  Powder X-ray diffraction data of [Co₂L₂Cl₄]·2MeOH.

Figure S3  Powder X-ray diffraction data of [Zn₂L₂Cl₄]·2MeOH.
5. REFERENCES


