Supplementary Material (ESI) for CrystEngComm


# A 3-dimensional coordination polymer with a fluorite structure constructed from a semi-rigid tetrahedral ligand

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## Supplementary Materials

### 1. Materials and Methods

Ligand tetrakis[4-(carboxyphenyl)oxamethyl]methane acid ($H_4L$) was prepared according to the literature (*Macromolecules*, **1999**, *32*, 4819–4825). All other reagents and solvents were commercially purchased and used without further purification. Infrared spectra were obtained on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000 – 400 $cm^{-1}$ region. Elemental analyses for C, H, and N were performed on a CHN-O-Rapid analyzer and an Elementar Vario MICRO analyzer. Magnetic susceptibility measurements for the crystalline samples were obtained with the use of a Quantum Design MPMS-XL7 SQUID magnetometer in the temperature range 1.8–300 K. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream using Pysis 1 DTA equipment with a heating rate of 20 °C/min. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 5–30°$ range with a scan speed of 0.2 sec/deg. on a Bruker D8 diffractometer with Cu Kα radiation equipped with a LynxEye detector at room temperature.

Single-crystal X-ray diffraction analysis. The suitable crystals of **1** with the dimensions *ca*. 0.20 × 0.18 × 0.18 $mm^3$ were selected for single crystal X-ray diffraction and the data were collected at 291 K on a Bruker Smart CCD diffractometer with a graphite-monochromatic Kα radiation (λ = 0.71073 Å) from an enhanced optic X-ray tube. Data reductions and absorption corrections were performed using the SAINT and SADABS software packages, respectively. The structure was solved by direct methods and refined by full matrix least-squares methods on F2 using the SHELXS-97 and SHELXL-97 programs, using atomic scattering factors for neutral atoms. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of $U_{iso}$. In the asymmetric unit, the PLATON/SQUEEZE program was used to deal with the disordered guest DMF and $H_2O$ molecules. The final structural model was refined without the guest molecules. The identity and number of the guest molecules were determined from the IR spectra, elemental analyses, and TGA data.

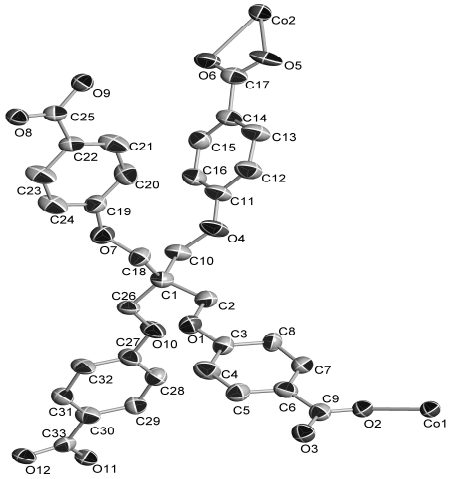


**Fig. S1**. An ORTEP drawing of the asymmetric unit (except hydrogen) of **1** with ellipsoids at 50% probability.

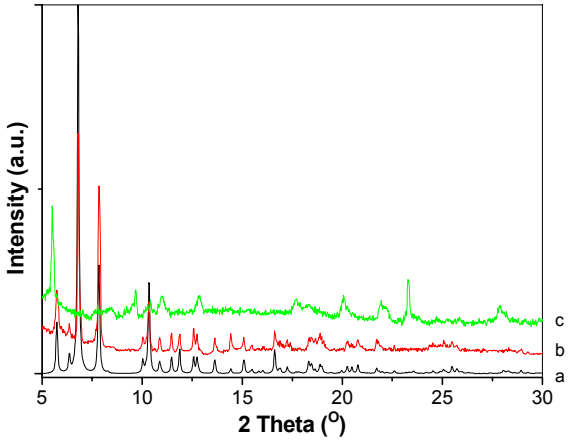


**Fig. S2**. PXRD patterns for **1**: (a) simulated (black), (b) as-synthesized (red), (c) after kept in air for weeks (green).

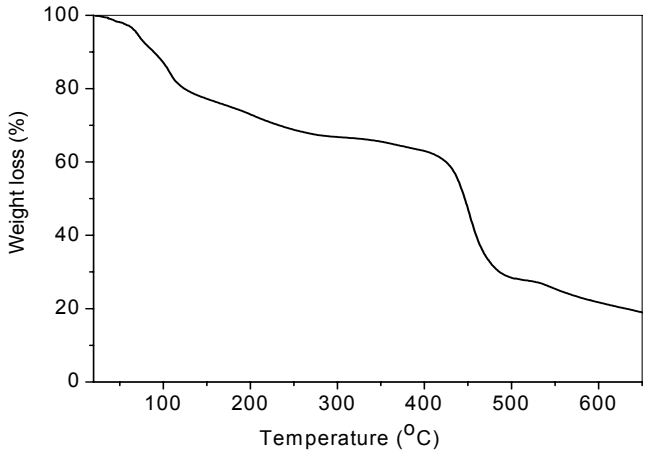


**Figure S3**. The TGA curve of compound **1**.