

Synthesis and crystallographic characterisation of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$

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A mononuclear complex of composition $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ has been prepared and characterised crystallographically.

Keywords: MOF; CPO-27; mononuclear; hydrogen bonding; reflux;

Coordination polymers and metal-organic frameworks (MOFs) are currently of much interest as gas storage and release materials.[1,2] One series that has received particular attention is the CPO-27-M (M = Mg,[3] Mn,[4] Fe,[5] Co,[6] Ni [7] or Cu [8]) or M-MOF-74 (M = Zn [9]) family of materials, due to their high stability to solvent loss, comparatively large pore sizes, and ability to maintain structural integrity upon removal of coordinated solvent molecules.[2,10] The desolvation of this family of compounds generates metal centres with vacant coordination sites, onto which gas adsorbents such as NO ,[11] CO ,[12] CO_2 ,[13,14] H_2S ,[15,16] H_2 [2,7] and C_2H_2 [12,17] may be bound. The CPO-27-Mg structure has particularly good properties for the adsorption of CO_2 . [13,14]

The excellent gas adsorption and gas storage properties of CPO-27 MOFs, has led to a rise in interest in the details of their synthesis. A particular goal of these studies is to understand the conditions required to get consistent crystallisation of the target materials and has to minimise potential impurity phases.[18] For example, it is known that, under solvothermal conditions, increasing the pH of the CPO-27-M (M = Mg [3] or Mn [4]) reaction mixture affords a separate, non-porous coordination framework of composition $\text{M}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_2$ (M = Mg [3] or Mn [19]) that the authors denote as CPO-26-M. A recent study on the effect of pH on the one-pot reflux synthesis of CPO-27-M describes attempts to prepare CPO-27-Mg using a 2:1 ratio of $\text{NaOH}:\text{H}_4\text{dhtp}$, however they report that no solid product could be obtained from this reaction system.[20] Herein we report the synthesis of a crystalline material of composition $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ that may be obtained by lowering the amount of NaOH in reaction mixtures that is normally used to prepare CPO-27-Mg by the reflux method.[18]

All reagents were obtained from commercial sources and were used without further purification.

Synthesis of $\text{Mg}(\text{H}_2\text{dhtp}) \cdot \text{H}_2\text{O}$: A solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (11.4 g, 44.4 mmol) in water (49 mL) and ethanol (24 mL) was added dropwise to a stirred solution of 2,5-dihydroxyterephthalic acid (3.83 g, 19.3 mmol) in aqueous sodium hydroxide (0.5 M, 77.4 mL, 38.7 mmol) over a period of four minutes. The resulting solution was heated to reflux for 24 hours. The solution was cooled to room temperature and an initial yellow solid collected via filtration, washed with hot ethanol and allowed to dry overnight yielding a yellow powder (CPO-27-Mg, 0.846 g, 2.0 mmol, 10%). The brown mother liquor was allowed to stand at room temperature for a further 3 days, over which time brown crystals (4.145 g, 12.6 mmol, 65% yield) formed as the solvent slowly evaporated. Elemental Analysis Calcd. for $\text{C}_8\text{H}_{16}\text{MgO}_{12}$ C: 29.24, H: 4.91, Found C: 29.30 H: 4.95%.

Crystallography: The crystal was coated in protective oil prior to mounting on a loop. Single crystal data [21] were collected at 173 K on a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics and Rigaku XtaLAB P200 diffractometer system ($\lambda = 0.71075 \text{ \AA}$). Powder X-ray diffraction patterns were collected using $\text{Cu K}\alpha_{1,2}$ radiation on a Rigaku Miniflex 600 diffractometer. Absorption corrections were applied using multi-scan methods in CrystalClear.[22] The structure solution was obtained using SHELXT [23] and refined by full matrix on F^2 using SHELX-2014 [24] within the WinGX [25] suite. All full occupancy non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Aromatic hydrogen atoms were included at their geometrically estimated positions. Hydrogen atoms belonging to free and coordinated water molecules were fixed at a distance of

0.90 Å from the oxygen atom and 1.47 Å from the other hydrogen bound to the same oxygen atom, and their thermal displacement parameters linked to that of the oxygen to which they are bound.

Crystals of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ were prepared as a by-product from a reflux synthesis attempt to make CPO-27-Mg. An initial yellow solid formed as the reaction mixture was cooled to room temperature, and PXRD analysis showed that this solid was CPO-27-Mg. Due to the poor yield of this reaction, the mother liquor was allowed to stand undisturbed for three days, over which time the novel compound $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ formed in good yield (65%). Details of the crystallographic structure determination are presented in the experimental section.

Crystals of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ consist of a mononuclear $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5$ unit in which five water molecules and a monodentate $\text{H}_2\text{dhtp}^{2-}$ anion are coordinated to an octahedral Mg^{2+} centre (Fig. 1). A list of the Mg-O bond distances and O-Mg-O angles is presented in Table S.1. One water molecule of crystallisation is also present. The intact phenolic -OH groups participate in intramolecular hydrogen bonds to the carboxylate oxygen atoms.

The mononuclear units are arranged into columns that extend parallel to the *b*-axis (Fig. 1). Within each column, the $\text{Mg}(\text{H}_2\text{O})_5$ units lie on the two outer edges, whilst the H_2dhtp units are directed towards the centre of the column. The H_2dhtp units interdigitate with each other, stacking in an ABAB fashion along the length of the column. Adjacent H_2dhtp anions participate in offset π - π interactions, with close contact C-C separations of 3.35 Å to 4.0 Å and close contact C-O separations of 3.42 Å to 3.43 Å.

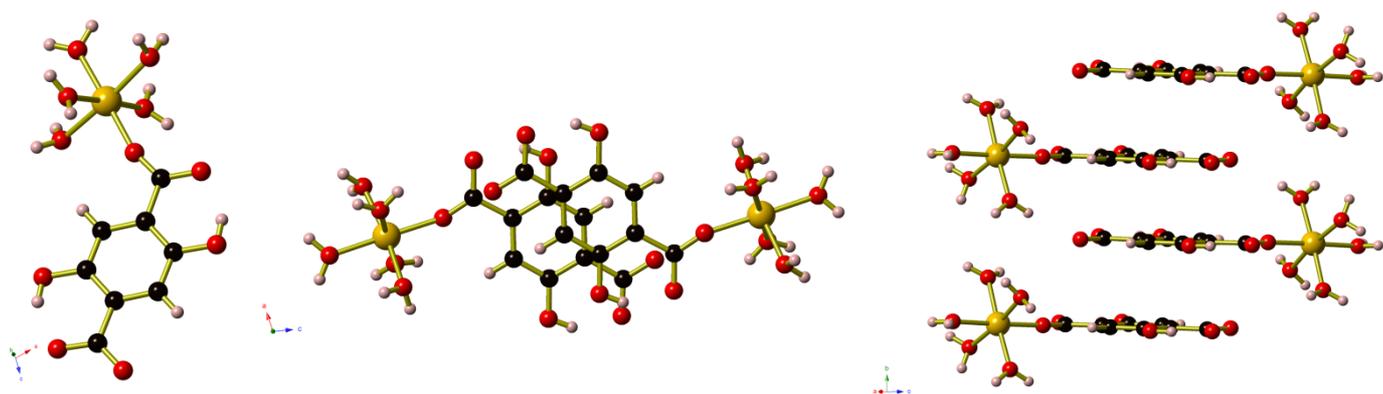
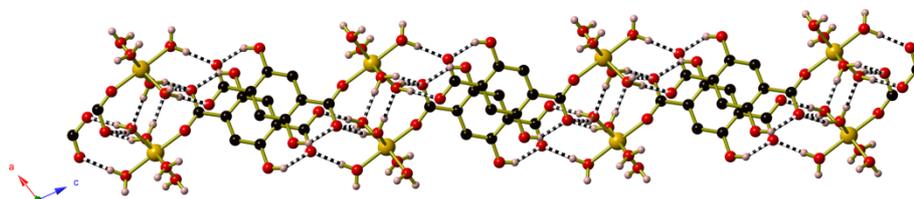


Fig. 1. **a)** The mononuclear $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5$ unit in $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$. The columns of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5$ units as viewed **b)** parallel to and **c)** perpendicular to the direction of the column.

Hydrogen bonding interactions between the coordinated water molecules and carboxylate oxygen atoms cross-link the columns to form hydrogen-bonded sheets that extend parallel to the (1 0 1) plane (Fig. 2). Further hydrogen bonds between the coordinated water molecules and phenolic hydroxyl groups connect the mononuclear units into a complex 3D hydrogen-bonded framework (Fig. 3). The non-coordinated water molecules occupy the spaces between these sheets, and participate in hydrogen bonds with three mononuclear $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5$ units belonging to two different sheets. A list of the hydrogen bond lengths and angles is provided in Table S.2.

a)



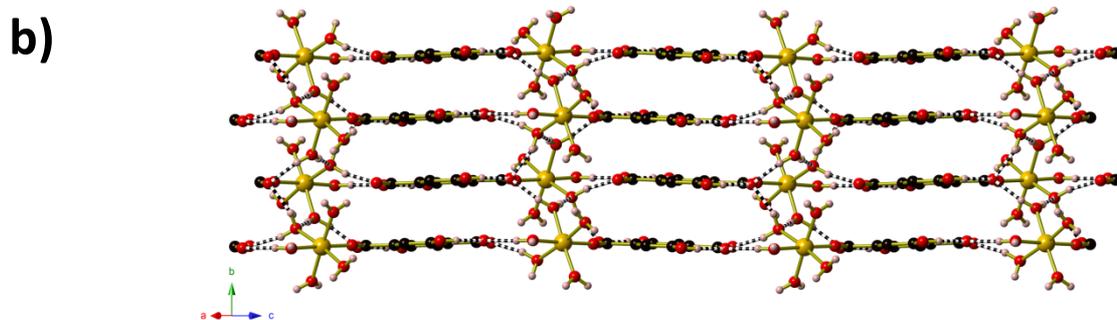


Fig. 2. The hydrogen-bonded sheets of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5$ units as views **a)** along the edge of the sheet and **b)** perpendicular to the plane of the sheet. Hydrogen bonds are depicted as black-and-white striped bonds. Aromatic hydrogen atoms have been omitted for clarity.

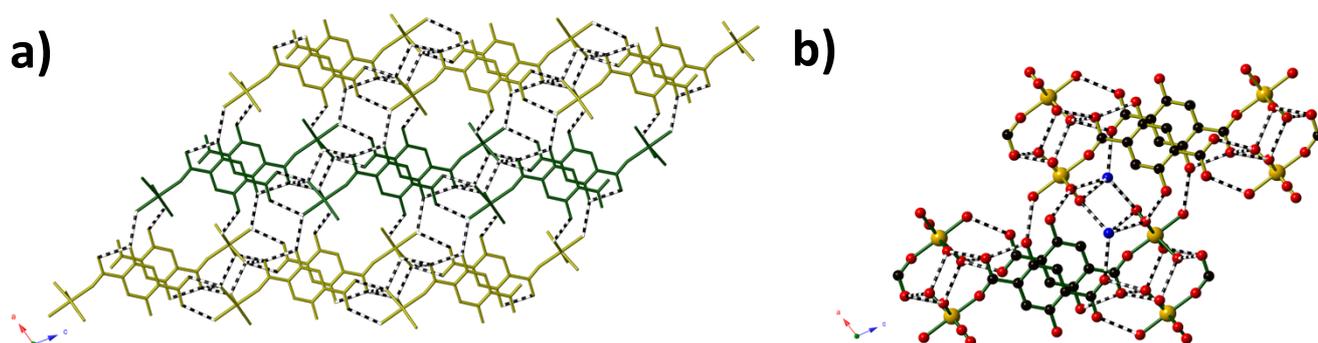


Fig. 3. View along the *a*-axis of the hydrogen-bonded network of $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$. **a)** The full network. Non-coordinated water molecules and hydrogen atoms have been omitted for clarity. **b)** The location of the water molecules (shown in blue) within the hydrogen-bonded framework. One hydrogen-bonded sheet is highlighted using green bonds.

This material is, to the best of our knowledge, the first non-polymeric Mg-dhtp coordination compound to be reported. A search of the Cambridge Crystallographic Data Centre reveals 5 different coordination polymers derived from magnesium and the di-anion of 2,5-dihydroxyterephthalate, in addition to the aforementioned CPO-26-Mg and CPO-27-Mg, all of which contain a three-dimensional coordination framework. One was prepared from DMF,[26] one from DMF in the presence of NEt_3 ,[27] and one from aqueous DMA,[28] whilst the remaining two were prepared from DMA or aqueous *N*-methyl pyrrolidone.[29] This is the first example of a material prepared from a predominately aqueous solution.

A novel mononuclear coordination complex of composition $\text{Mg}(\text{H}_2\text{dhtp})(\text{H}_2\text{O})_5 \cdot \text{H}_2\text{O}$ has been prepared by reflux of $\text{Mg}(\text{NO}_3)_2$ and H_4dhtp in the presence of NaOH.

This work was funded by the British Heart Foundation (NH/11/8/29253) and the EPSRC (EP/K005499/1) (EP/K503162/1). CCDC 1432662 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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