

Engineering porosity in a chiral heteropolyoxometalate-based framework: the supramolecular effect of benzenetricarboxylic acid†

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A chiral heteropolyoxometalate-based framework, synthesised using a planar aromatic tri-acid included as a guest, contains partially filled 1D channels and exhibits reversible water sorption capabilities.

Polyoxometalates (POMs) have been investigated in a vast number of studies due to their attractive electronic¹ and molecular properties² that give rise to a variety of applications in diverse fields such as catalysis,³ medicine,⁴ or materials science.⁵ Heteropolyoxometalates (HPOMs) are of special interest for the engineering of novel framework structures since they combine high stability with extensive structural variety⁶ and application as superacidic catalysts.⁷ Because of their possible practical use in enantioselective catalysis and separation, a considerable amount of research has focused on the synthesis of enantiomerically pure HPOM materials. Several different synthetic approaches have been reported in the literature, many of which convert Keggin and Dawson–Wells HPOMs or lacunary fragments thereof into chiral compounds.^{8,9} Recently, An *et al.* reported that an open framework with helical channels can be obtained by coordinating a chiral Cu–amino-acid complex to a {BW₁₂}–Keggin unit.¹⁰

The approach reported here is based on our previous observations which indicate that POMs strongly interact with bulky organic amines as these can “shrink-wrap” the anionic clusters and effectively yield new supramolecular arrangements.¹¹ In addition, the dimeric {Mo₆}₂ cluster was considered as a suitable building block since it is known to form 1D frameworks,¹² 2D layered structures¹³ and 3D open networks¹⁴ by incorporating organic counterions such as protonated amines in the lattice. Further, the use of an organic multifunctionalised acid with multiple hydrogen-bonding sites was expected to facilitate the formation of novel framework arrangements since several examples of POMs interacting with organic acids are known in the literature.¹⁵ However, key to the successful synthesis of the material was our recent discovery that {Mo₆}₂ dimers can be synthesised at ambient temperature and pressure, allowing for a highly improved reaction control compared to the standard hydrothermal synthesis.¹⁶

The work described herein reports the first synthesis and characterisation of a porous {Mo₆}₂-based hybrid framework which features chiral channels that are occupied by the aromatic

triacid 1,3,5-benzenetricarboxylic acid (BTC). The title compound, (C₁₅H₂₈N₂)₄(C₉H₆O₆)₁[H₁₅Mo₁₂NaO₆₂P₈]·10H₂O (**1**), is obtained by a multi-step synthetic procedure that involves precipitation and redissolving precursor materials along with precise control of pH.‡ Single crystal X-ray diffractometry§ showed that the framework of **1** is based on the inorganic dimeric polyoxomolybdenum(v) phosphate anion [H₁₅Mo₁₂NaO₆₂P₈]⁸⁻ (= **1a**, {Mo₆}₂, see Fig. 1) which has been extensively discussed in previous work.^{12–14,16}

To the best of our knowledge, **1** represents the first example of a microporous chiral framework based on heteropolyoxomolybdates. The framework is made up of chiral diprotonated (–)-sparteine cations and {Mo₆}₂ polyanions which are connected *via* hydrogen bonding and attractive electrostatic interactions, see Fig. 2. Each {Mo₆}₂-dimer is shielded by four (–)-sparteine cations which form N–H···O hydrogen bonds to the cluster anion (minimum distance *d*_{N–H···O} = 2.67 Å). The structure is further reinforced by a complex network of hydrogen-bonded water molecules. This hybrid framework arrangement results in chiral channels along the crystallographic *a* axis, which are occupied by BTC and water molecules. Remarkably, the ‘guest’ BTC molecules exhibit occupancies of only 50% and therefore indicate that the structure contains vacancies which offer interesting possibilities for the uptake of suitable guest molecules. The BTC motif here is also unusual since it is interacting with the network *via* non-coordinative, supramolecular interactions, and these are rarely found in metalloid environments which allow for hydrogen bonding inside the channels. Also, although it is not possible to

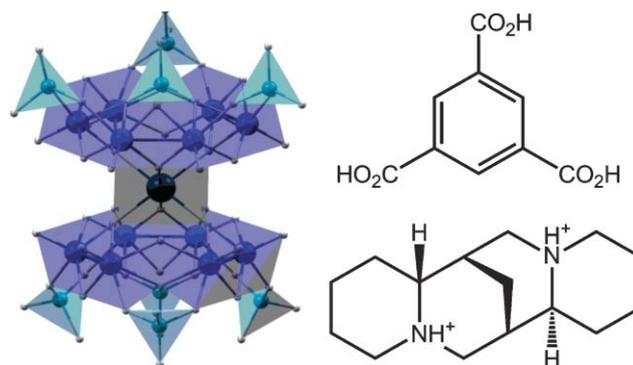


Fig. 1 Building blocks used in the synthesis of compound **1**. **LHS:** Polyhedral representation of the dimer {Mo₆}₂ (**1a**): blue octahedra: MoO₆; light blue tetrahedra: PO₄; dark blue octahedron: NaO₆. Blue spheres: Mo, dark blue sphere: Na, light blue spheres: P, small white spheres: O. **RHS: Top:** 1,3,5-benzenetricarboxylic acid, (H₃BTC). **Bottom:** di-protonated (–)-sparteine. This colour scheme will be used throughout the text.

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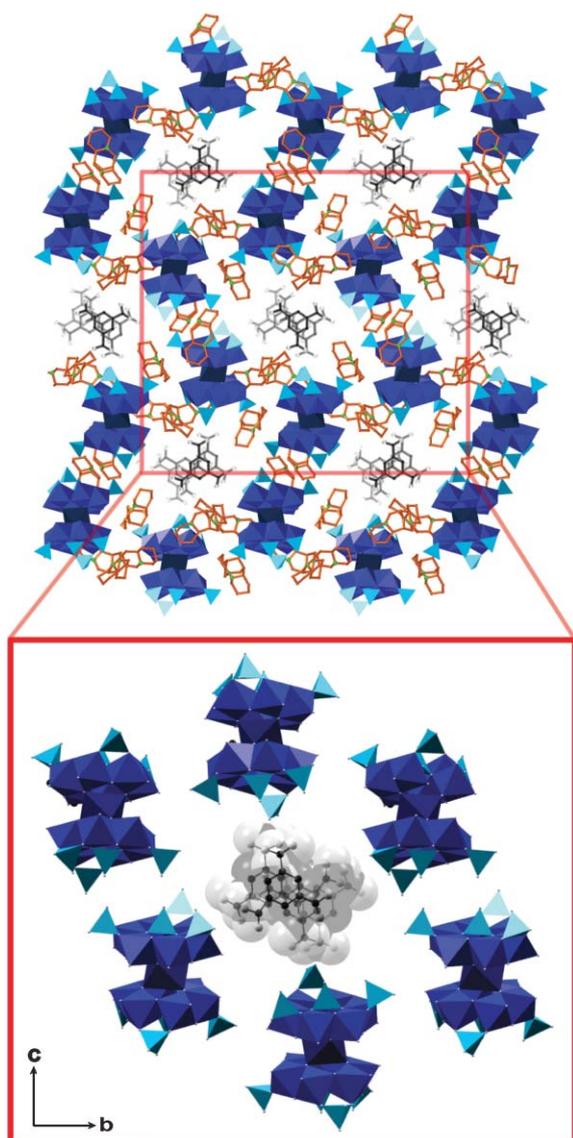


Fig. 2 **Top:** Representation of the crystal lattice of **1** along the crystallographic *a* axis. The (–)-sparteine cations are highlighted in brown and show the chiral environment into which the BTC is bound. **Bottom:** Illustration of the hexagonal 1D channels in **1**. The staggered arrangement of the BTC molecules is clearly visible. Sparteine and water molecules are omitted for clarity.

distinguish the protonation state of the BTC as either H_3BTC , $(\text{H}_2\text{BTC})^{1-}$, $(\text{H}_1\text{BTC})^{2-}$, $(\text{BTC})^{3-}$, certainly one interpretation, based on the available structural evidence and the infra-red data, would suggest the BTC exists as $(\text{H}_2\text{BTC})^{1-}$, $(\text{H}_1\text{BTC})^{2-}$ as indicated by the presence of peaks at 1715 and 1635 cm^{-1} (these are indicative of protonated and deprotonated carboxylates); the protons are transferred to the cluster anion.¹⁷ Further, the partially occupied BTC groups are aligned in a parallel fashion and form pillared structures which are held together by π - π stacking interactions between the particular aromatic rings, see Fig. 3. The minimum distance observed between two adjacent phenyl ring centroids is 4.16 \AA .

A detailed analysis of the HPOM building block in **1** shows that the anion is made up of two planar hexanuclear rings, each formed

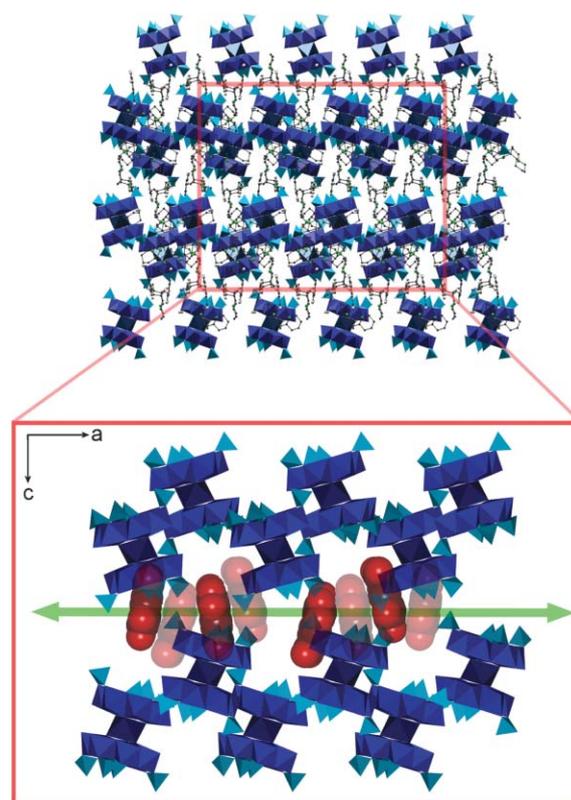


Fig. 3 Representation of the BTC-filled channels in **1**. **Top:** View along the crystallographic *b* axis. **Bottom:** Cross-section through the channels. Emphasised in red, space-filling representation: stacked BTC molecules. The green arrow indicates the directionality of the channels. Sparteine and water molecules are omitted for clarity.

by six edge-sharing MoO_6 octahedra with alternating bonding ($\sim 2.6\text{ \AA}$) and non-bonding ($\sim 3.6\text{ \AA}$) Mo–Mo distances. Three peripheral and one central PO_4 tetrahedra are located in the outer coordination sphere of each $\{\text{Mo}_6\}$ monomer. These four phosphates bridge the non-bonding Mo–Mo groups and thereby provide structural stability for the cluster. The dimer is formed by linking two $\{\text{Mo}_6\}$ -rings *via* one central sodium ion which is coordinated octahedrally by three oxygen atoms of each $\{\text{Mo}_6\}$ group, hence the two Mo_6 rings are arranged in a staggered fashion. Characteristically for the reduced Mo^{V} species, each MoO_6 octahedron features one free apex with short Mo–O distances of *ca.* 1.6 \AA . Larger Mo–O distances (*ca.* 1.95 \AA) are found for the μ_2 -oxygen bridges between two bonded Mo centres. The longest Mo–O distances were observed for the oxygen bridges between the non-bonded Mo–Mo central ions with Mo– μ_2 -O distances of *ca.* 2.1 \AA and Mo– μ_3 -O bond lengths of *ca.* 2.3 \AA .

In effect, these BTC stacks act as supramolecular templates for the 1D channels which run along the crystallographic *a* axis and give rise to the formation of hexagonal pores with dimensions of *ca.* $19 \times 9\text{ \AA}$. Initial thermogravimetric experiments indicated that the bulk material contains *ca.* 50% more water than determined by single crystal XRD. Subsequent thermogravimetric water sorption experiments were undertaken to study the porosity of the material, see Fig. 4, top.

The TGA studies revealed that the water molecules in **1** can be desorbed by heating a sample to $100\text{ }^\circ\text{C}$ to a constant weight. In

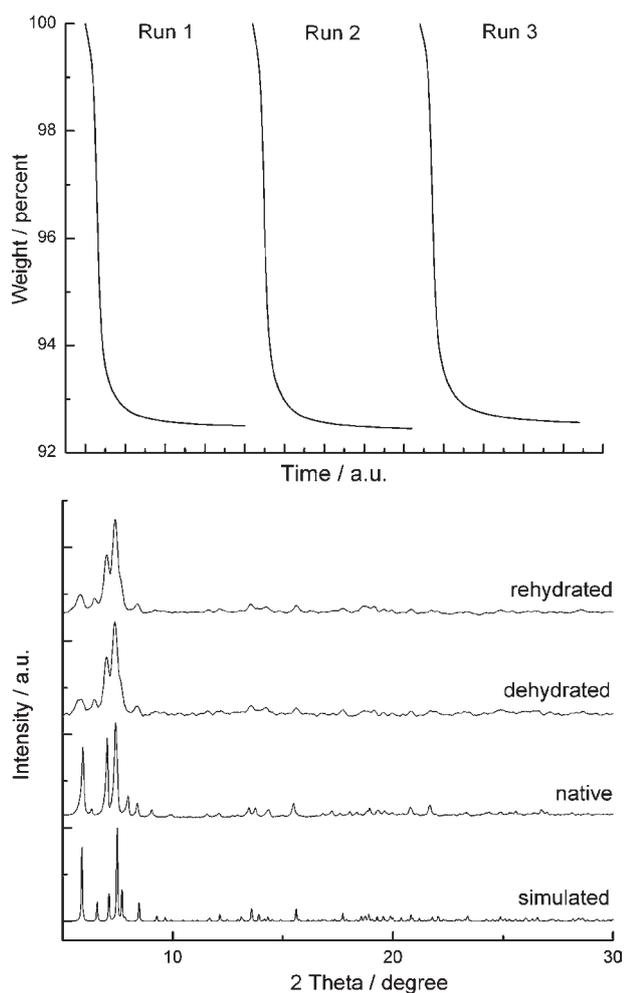


Fig. 4 Top: TGA water desorption showing three consecutive runs with a weight loss of 7.5 wt.%. Bottom: Powder X-ray diffraction patterns of **1** as simulated from single crystal XRD (123 K), native material, after dehydration and after rehydration (room temperatures).

addition, the water can be re-adsorbed by exposing the material to ambient atmosphere for 24 h. It was shown that the material desorbs 7.5 wt.% of crystal water and within 24 h can re-adsorb a similar amount of water from the atmosphere. This procedure was repeated several times to demonstrate the reversibility of the process. Further, the stability of the material was investigated by powder X-ray diffractometry which indicated that the material retains its crystallinity after several water desorption and re-adsorption cycles, see Fig. 4, bottom.

In conclusion, we were able to obtain a novel heteropolyoxometalate-based hybrid material with chiral channels which are partially occupied by mobile BTC molecules. It was further shown that the material is truly porous and exhibits reversible water sorption capabilities. The nature of the BTC is interesting; it is only partially occupied yet it appears to have a structural role defining the channels. This leads to one interpretation that the BTC appears to be acting as a 'meta-template', each crystallographic position being only partially occupied within the structure, yet still providing structural stability. This is interesting since BTC and related spacers have received a massive amount of attention as coordinative components for the assembly of metal organic

frameworks (MOFs)¹⁸ so this work provides an interesting contrast.¹⁹ Future work will aim towards the synthesis of polyoxometalate-based porous functional materials with a focus on real applications such as enantioselective adsorption, sequestration and enantioselective catalysis. In addition, attempts to both confirm and exploit the 'meta-templation' effects of sterically rigid carboxylic acid spacers with acidic building blocks including other polyoxometalates will also be made to see if this approach can be extended still further.

Notes and references

‡ Synthesis of **1**: 1.33 g (5.49 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 100 ml of a saturated aqueous 1,3,5-benzenetricarboxylic acid solution. 0.5 ml H_3PO_4 (9%) and 1.25 g (2.96 mmol) of (–)-sparteine sulfate pentahydrate were added, and the immediately formed white precipitate was redissolved by adjusting the pH to ca. 8 using a concentrated aqueous NaOH solution. The pH was then lowered to 4.0 using H_3PO_4 (9%) and 1.00 g (5.70 mmol) of $\text{Na}_2\text{S}_2\text{O}_4$ was added. The pH was lowered to 3.5 with H_3PO_4 (9%). After stirring for 2 h, the mixture was filtered and after three days, red crystals of **1** were isolated. Yield: 0.344 g (0.094 mmol, 20.6% based on Mo). Characteristic IR-bands: 3435(m, b), 2947(m), 1715(m), 1635(m), 1468(m), 1263(m), 1065(s), 966(s), 743(m). Elemental analysis for the dehydrated material, $\text{C}_{69}\text{H}_{133}\text{N}_8\text{O}_{68}\text{Na}_1\text{Mo}_{12}\text{P}_8$ (calculated values in brackets, solvated waters lost): C: 23.44 (23.12), H: 3.91 (3.74), N: 2.96 (3.13)%.

§ Crystallographic data: $(\text{C}_{15}\text{H}_{28}\text{N}_2)_4(\text{C}_9\text{H}_6\text{O}_6)_1[\text{H}_{15}\text{Mo}_{12}\text{NaO}_{62}\text{P}_8] \cdot 10\text{H}_2\text{O}$, $M = 3765.02$, orthorhombic, space group $P2_12_12_1$, $a = 14.5405(3)$, $b = 25.0846(3)$, $c = 38.3524(8)$ Å, $V = 13988.8(4)$ Å³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.229$ cm⁻¹, 47099 reflections collected, 22764 unique ($R_{\text{int}} = 0.0716$) which were used in all calculations; structure solution and refinement were done using WINGX.²⁰ Final $R1 = 0.0649$ and $wR2 = 0.1652$ (all data). CCDC 622128. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613808j

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