

A molybdenum diphosphonate network structure exhibiting reversible dehydration and selective uptake of methanol†

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A new molybdenum diphosphonate network structure has been prepared and structurally characterised. It shows reversible dehydration, which occurs with a structural change. The dehydrated material is able to adsorb methanol but not ethanol.

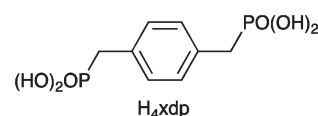
A wide range of bridging ligands has been employed in combination with metal ions to form coordination network structures.¹ Polycarboxylates are the most extensively used of these linkers² as the resultant networks are usually neutral, so don't need to include counter-ions. In addition, they are often stable to loss of included solvent molecules from the pores, thus giving rise to permanently porous materials. Despite this ubiquity, other anionic linkers such as imidazoles have also been employed to generate neutral framework structures.³

Polyphosphonates have also attracted attention as linkers, and have been used in combination with a range of metal centres to give porous materials.⁴ Phosphonates are derived from phosphonic acids, which can be deprotonated to form mono- or dianions. As a consequence, several potential products may be accessible from a particular combination of a metal and linker, depending on the pH.

Recently, we have developed an interest in semi-rigid linkers, in which a limited degree of flexibility is built into the linker in order to accommodate structural flexibility, though not enough to ensure the formation of close-packed structures. We have previously demonstrated how the introduction of methylene groups between a central aromatic ring and nitrogen donors affords a ligand capable of adopting different conformations, and that use of this in silver(i) chemistry leads to

materials that show intriguing solid state rearrangements from coordination oligomers to coordination networks.^{5,6}

p-Xylylenediphosphonate acid (H₄xdp) has methylene groups connecting the central benzene ring with phosphonic acid groups, and thus also has the potential to lead to flexible materials. Indeed, H₄xdp has previously been shown to adopt *cis* and *trans* conformations,⁷ and has been used to form network structures. For example, the Stock group have prepared a range of metal(II) compounds with the general formula [M₂(xdp)].^{8–10} Network structures have also been prepared with other metals, including gallium(III),¹¹ lanthanides¹² and vanadium(IV).¹³



Molybdophosphonates as building blocks or subunits in extended structures have also been studied,^{14,15} but there are no reports of molybdenum diphosphonates in the absence of co-ligands. We reasoned that the combination of a dioxomolybdenum(VI) fragment with a diphosphonate could give rise to interesting structures, and if these could be formed it might be possible to exploit the donor ability and/or hydrogen bonding potential of the oxo groups in the resultant networks.

The solvothermal reaction between sodium molybdate(VI) dihydrate (Na₂MoO₄·2H₂O) and H₄xdp in the presence of concentrated hydrochloric acid led to colourless crystals of [(MoO₂)₂(xdp)(H₂O)₂].2H₂O **1**, which were characterised by X-ray crystallography.† The asymmetric unit of **1** consists of a molybdenum centre which is coordinated to two oxides, a half of a xdp⁴⁻ anion (located at a crystallographic inversion centre) and a water molecule. One lattice water molecule is also present. The xdp ligand is fully deprotonated, adopting a *trans* conformation, and each phosphonate group is coordinated to molybdenum centres through all three oxygen atoms. The molybdenum(VI) centre is six-coordinate with a distorted octahedral geometry, coordinated to two oxides,

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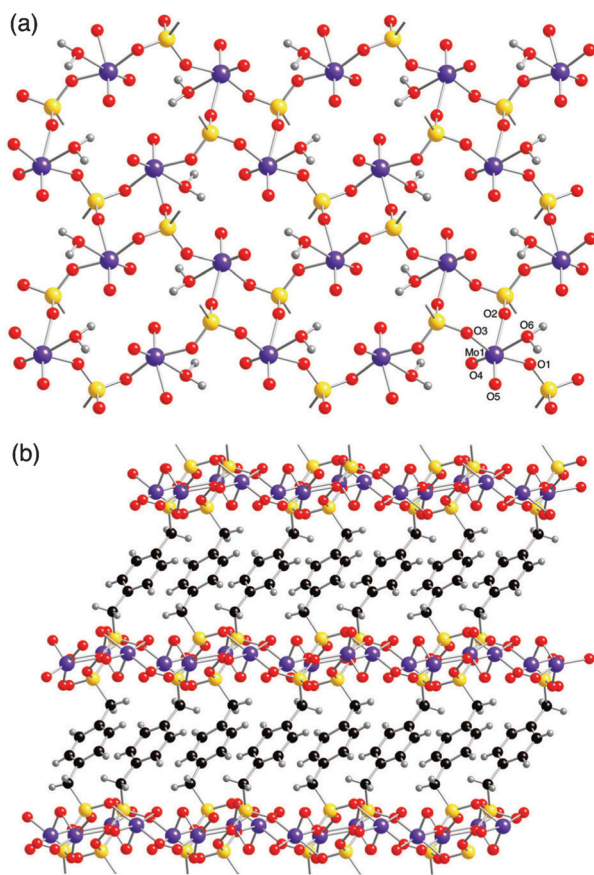
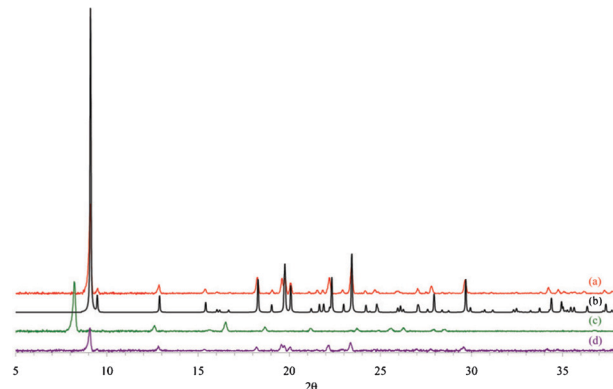
Table 1 Selected bond lengths (Å) and bond angles (°) for $[(\text{MoO}_2)_2(\text{xdp})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ **1**^a

Mo(1)–O(4)	1.6821(17)	Mo(1)–O(5)	1.6931(15)
Mo(1)–O(1)	1.9940(17)	Mo(1)–O(3)	2.0082(17)
Mo(1)–O(2)''	2.1109(15)	Mo(1)–O(6)	2.3299(18)
O(4)–Mo(1)–O(5)	104.72(8)	O(1)–Mo(1)–O(3)'	159.46(6)
O(1)–Mo(1)–O(2)''	81.21(6)	O(5)–Mo(1)–O(2)''	158.11(8)
O(4)–Mo(1)–O(6)	170.39(7)	O(3)'–Mo(1)–O(2)''	81.08(6)

^a Primed atoms generated by the symmetry operation $-x + 1/2, y + 1/2, -z + 1/2$, double primed atoms generated by the symmetry operation $x, -y + 1, z - 1/2$.

three phosphonate oxygen atoms, and a water molecule. Selected bond lengths and angles are given in Table 1.

The octahedral molybdenum units are linked by the tetrahedral phosphonate groups of the xdp ligand into sheets with the 4.8^2 topology (Fig. 1a). These sheets are pillared by the xdp linkers leading to a three-dimensional network (Fig. 1b). The structure contains channels of approximate dimensions 3.9×4.6 Å, based on the van der Waals radii of the surface atoms. In the crystal structure, however, these channels are occupied by the included water molecules, which form O–H...O hydrogen bonds with the oxygen atoms of the coordinated water molecules acting as acceptors. Further hydrogen

**Fig. 1** The structure of $[(\text{MoO}_2)_2(\text{xdp})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ **1**, showing (a) the molybdenum-phosphonate sheets, and (b) the three-dimensional network with the hydrogen atoms on the water molecules removed for clarity.**Fig. 2** PXRD traces of (a) $[(\text{MoO}_2)_2(\text{xdp})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ **1** as synthesised, (b) **1** simulated from the crystal structure, (c) **1** heated *in vacuo* at 150 °C for 3 h to convert it into $[(\text{MoO}_2)_2(\text{xdp})]$ **2**, and (d) **2** immersed in water for 36 h, to re-convert it into **1**.

bonds are present between the coordinated water molecules and the oxo ligands (Table S2, ESI[†]).

The TGA trace of the as-synthesised $[(\text{MoO}_2)_2(\text{xdp})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$ **1** (Fig. S2, ESI[†]) shows a first mass loss of 6.5% between 45 °C and 105 °C attributed to the loss of lattice water (calculated 6.1%) and then loss of a further 6.5% between 105 °C and 140 °C attributed to the loss of coordinated water (calculated 6.1%). Up to 320 °C further weight losses are relatively small, indicating that the pillaring organic residues remain intact within the framework on heating to this temperature.

On heating under vacuum for 3 hours at 150 °C, **1** is converted into the fully dehydrated compound $[(\text{MoO}_2)_2(\text{xdp})]$ **2**. This loss of water is accompanied by a colour change, from colourless to pale green. Significant differences in the PXRD patterns of **1** and **2** (Fig. 2a and 2c) are indicative of a major structural change that occurs on removal of the water molecules. Interestingly, N_2 sorption measurements revealed **2** to be non-porous, suggesting that the structural change occurs to minimise void space.

The difference between the as-synthesised compound **1** and fully dehydrated compound **2** can also be observed from their infrared spectra. Compound **1** shows two $\nu(\text{OH})$ bands at 3613 and 3451 cm^{-1} and a corresponding deformation vibration $\delta(\text{H}_2\text{O})$ at 1629 cm^{-1} . The spectrum for **2** shows the absence of these $\nu(\text{OH})$ and $\delta(\text{H}_2\text{O})$ bands and a change in the bands characteristic of the tetrahedral CPO groups observed between 1200 and 900 cm^{-1} .

To examine whether **2** can re-form **1** on hydration, a crystal-line sample of **1** was dried under vacuum at 150 °C for 3 hours to convert it into **2**, and the sample was then immersed in water for 36 hours. The pale green colour characteristic of **2** was lost in the first few hours of immersion, and the resulting product was colourless. The PXRD pattern of the sample soaked in water matches that of the as-synthesised **1**, confirming that the fully dehydrated **2** has been re-hydrated, to re-form **1** (Fig. 2d). The re-hydrated compound was also analysed by TGA and shown to be similar to that of as-synthesised **1** (Fig. S3, ESI[†]).

A number of framework structures have been previously reported that can be dehydrated and re-hydrated reversibly with a few experiencing a phase change. For example, Bourne and co-workers demonstrated reversible dehydration and re-

hydration for $(\text{Me}_2\text{NH}_2)[\text{Zn}_2(\text{Hbtc})(\text{btc})(\text{H}_2\text{O})_3]\cdot 3\text{H}_2\text{O}$ (btc = 1,3,5-benzenetricarboxylate) and explained this behaviour on the basis of breathing in the structure.^{16,17}

Qui and co-workers reported a cobalt derivative of xdp, $[\text{Co}_2(\text{H}_2\text{O})_2(\text{xdp})]$ that also underwent a reversible dehydration-rehydration process, though in this case the dehydration occurred without structural change, which was evidenced by the PXRD patterns.¹⁸ The colour of the $[\text{Co}_2(\text{H}_2\text{O})_2(\text{xdp})]$ crystals changed from pink to blue on heating, and the rehydration process was accompanied by a return of the original pink colour. This is consistent with the coordination environment of the cobalt ion changing with loss of the coordinated water, though the framework itself was retained.

For a porous adsorbent, both the cross-sectional size (usually referred to as the kinetic diameter) and the shape of the adsorbate molecule are factors affecting selective adsorption. The capacity of 2 to adsorb small molecules in addition to water (kinetic diameter 2.64 Å),¹⁹ was further investigated for methanol and ethanol which have kinetic diameters of 3.63 Å and 4.53 Å, respectively.

Samples of 2 were soaked in either methanol or ethanol for 36 hours. The colour of the sample soaked in methanol (3) changed in the first few hours from pale green to colourless, whereas the sample soaked in ethanol (4) remained pale green. The PXRD pattern of 3 showed a good match with 1, whereas the PXRD pattern of 4 showed a good match with 2 (Fig. S5, ESI†). This suggests that methanol is adsorbed, re-forming a framework analogous to that of the water-containing analogue 1, whereas ethanol is not adsorbed, presumably because of steric factors.

The TGA trace of 3 (Fig. S6, ESI†) shows a mass loss of approximately 12% up to 200 °C, which is consistent with loss of one MeOH per molybdenum centre (calc. 11.0%). In contrast, the TGA trace of 4 showed no significant mass loss before 150 °C, again consistent with no uptake of ethanol.

In order to confirm that 3 had adsorbed methanol and not water, a sample was digested using NaOD/D₂O and analysed by ¹H NMR spectroscopy. A peak for the methyl group was observed at δ 2.95 ppm (Fig. S7, ESI†), with the integral suggesting incorporation of 0.73 methanol molecules per molybdenum centre, in reasonable agreement with the value obtained from the TGA. In contrast, the ¹H NMR spectrum of 4, digested under the same conditions, revealed no evidence for inclusion of ethanol (Fig. S8, ESI†), again in agreement with the TGA results.

The NMR and TGA results, taken together, illustrate that 2 can selectively adsorb methanol but not ethanol, consistent with the smaller kinetic diameter of MeOH. Although the changes in the structure of 1 on dehydration mean that the pore size in 2 is unknown, the conversion of 2 into a 1-like structure on methanol adsorption means that the pore size in 1 can be used for comparison. As noted above, following removal of the included and coordinated water molecules, the size of the channels present in 1 is approximately 3.9 × 4.6 Å.

The breathing behaviour observed in this system is presumably a consequence of the inherent flexibility of the xdp linker, which allows the framework to undergo a reversible structural change upon dehydration to give a more dense structure. The selective

adsorption of water and methanol but not ethanol has previously been observed for $[\text{Cd}(\text{pzdc})(\text{bpe})]$ (pzdc = pyrazine-2,3-dicarboxylate, bpe = *trans*-1,2-di(4-pyridyl)ethene) and was related to the size of the channel windows.²⁰

In conclusion, we have prepared and structurally characterised a new molybdenum–diphosphonate coordination network, and shown that it can undergo reversible dehydration, which occurs with a structural change. The dehydrated material shows size-selective adsorption of alcohols, adsorbing methanol but not ethanol.

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Notes and references

‡ $\text{C}_4\text{H}_8\text{MoO}_7\text{P}$, $M = 295.01$, monoclinic, $C2/c$, $a = 20.8424(8)$ Å, $b = 10.6114(3)$ Å, $c = 9.0023(4)$ Å, $\beta = 111.686(4)^\circ$, $U = 1850.09(12)$ Å³, $Z = 8$, $D_c = 2.118$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 1.595$ mm⁻¹, final $R_1 = 0.0200$, $wR_2 = 0.0405$ for $I > 2\sigma(I)$, $R_1 = 0.0328$, $wR_2 = 0.0415$ for all data, GOF = 0.946.

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