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

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Supplementary information

General experimental details

The syntheses were carried out in Ace pressure tubes (15 cm^3), purchased from Aldrich Chemical Co., and heated in programmable ovens. The reagents used for syntheses were obtained from Aldrich Chemical Co. (sodium molybdate dihydrate) or Epsilon Chimie (H_4xdp) and used without further purification.

Powder X-ray diffraction patterns (PXRDs) were recorded on a Bruker AXS D8 Advance diffractometer with copper Kα radiation of wavelength 1.5406 Å at 298 K. Samples were placed in 0.5 mm diameter Lindemann capillaries, and measured with a 2θ range of 3-60°. The step size was 0.016° with time per step of 134.5 s. Simulated X-ray powder patterns were generated from single crystal data that were imported into PowderCell[S1] with a step size of 0.02° and time per step of 1.00 s.

TGA experiments were carried out on a Perkin Elmer TGA 4000 Thermogravimetric Analyser. The samples were heated from 45°C to 600°C at a heating rate of 10°C/min, under a flow of nitrogen (20 mL/min).

^1H NMR spectra were recorded at 298 K on a Bruker Advance 300 MHz Ultrashield NMR spectrometer. The spectra were referenced to the residual *protio* peak at δ 4.79 ppm for D_2O.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 spectrometer equipped with an ATR sampling accessory.

Synthesis of $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ 1

$Na_2MoO_4\cdot 2H_2O$ (0.120 g, 0.50 mmol) was stirred together with *p*-xylylenediphosphonic acid (H_4xdp) (0.070 g, 0.25 mmol) in 8 cm^3 deionised water. The pH of the solution was adjusted to pH 1 by dropwise addition of conc. hydrochloric acid. The acidified solution was then placed in a 15 cm^3 Ace pressure tube and heated at 120°C for 15 h. The resultant white crystalline material was thoroughly washed with deionised water (3×5 cm^3) and air-dried. Yield 0.140 g (91 %). ν/cm^{-1} 3613 (br), 3451 (br), 1629m, 1514s, 1426w, 1398w, 1258s, 1201s, 1143s, 1123s, 1093s, 987s, 928s, 850s, 815w, 737s, 592s.

The identity of the bulk compound was confirmed by PXRD, and the observed powder pattern matches that simulated from the crystal structure (Fig. S1).

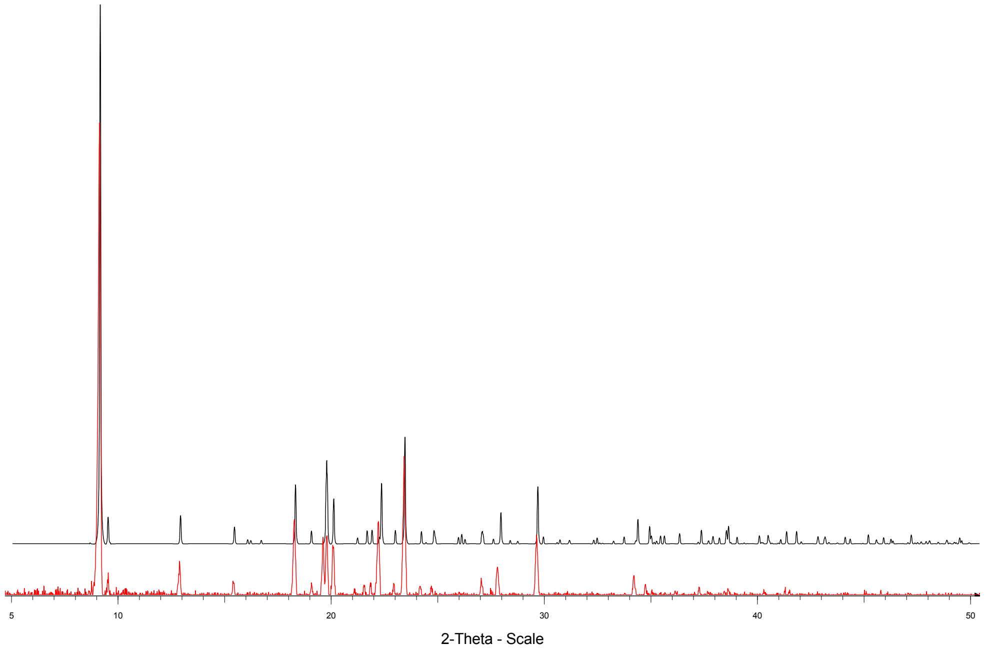

Figure S1. The PXRD pattern for $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1** with the experimental pattern shown in red and that simulated from the crystal structure in black.

Conversion of $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ 1 into $[(MoO_2)_2(xdp)]$ 2

$[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1** was converted into $[(MoO_2)_2(xdp)]$ **2** by heating *in vacuo* at 150°C for 3 h. The TGA traces of **1** and **2** are shown in Fig. S2.

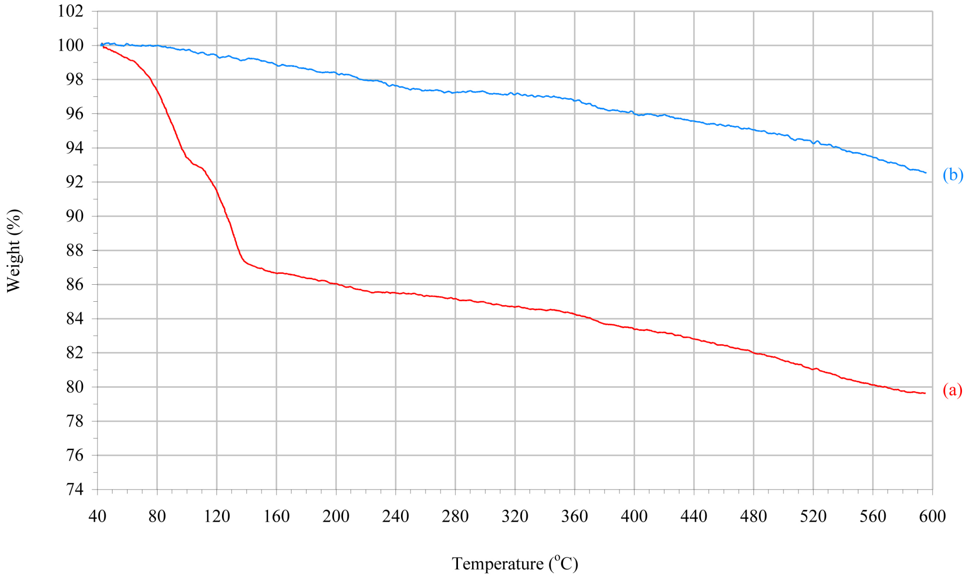

Figure S2. TGA traces for (a) $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1**, and (b) $[(MoO_2)_2(xdp)]$ **2**.

Rehydration of $[(MoO_2)_2(xdp)]$ 2 and conversion back to $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ 1

When a sample of **2** was soaked in water for 36 h it was re-converted into **1**, as shown by changes in the PXRD pattern (Fig. 2) and a change of colour. The TGA trace of the soaked sample is also identical to that of $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1** (Fig. S3).

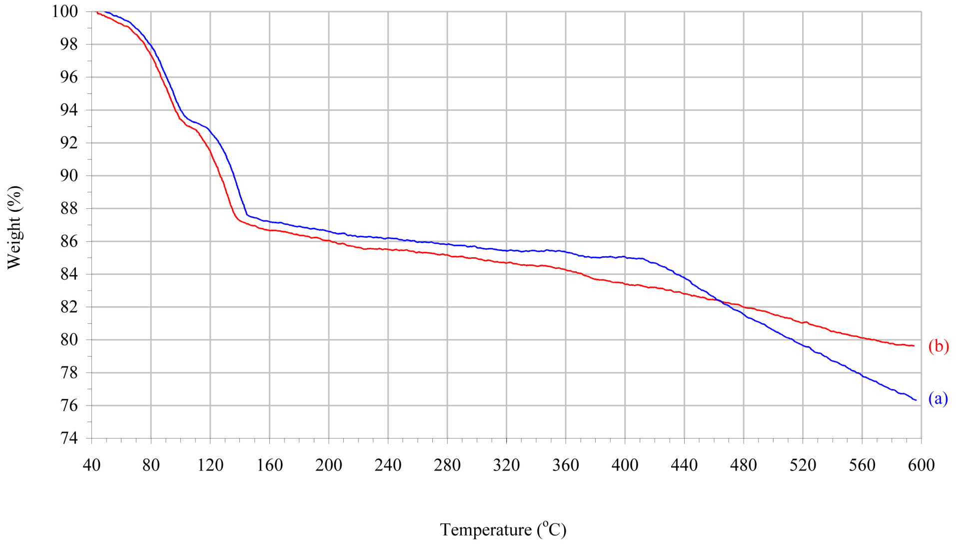

Figure S3. The TGA traces for (a) $[(MoO_2)_2(xdp)]$ **2** soaked in H_2O, and (b) $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1** as-synthesised.

Alcohol adsorption experiments with [(MoO$_2$)$_2$(xdp)] 2

Infrared spectra for samples of **2** that have been soaked in methanol or ethanol for 36 h to give **3** or **4** respectively are shown in Fig. S4, with PXRD patterns for these samples shown in Fig. S5. The TGA trace of **3** is shown in Fig. S6. Samples for NMR studies were digested using a stock solution of NaOD in D$_2$O (0.2 cm^3 40% NaOD/D$_2$O, in 1 cm^3 D$_2$O). ^{1}H NMR spectra of **3** and **4** following digestion are shown in Figs. S7 and S8.

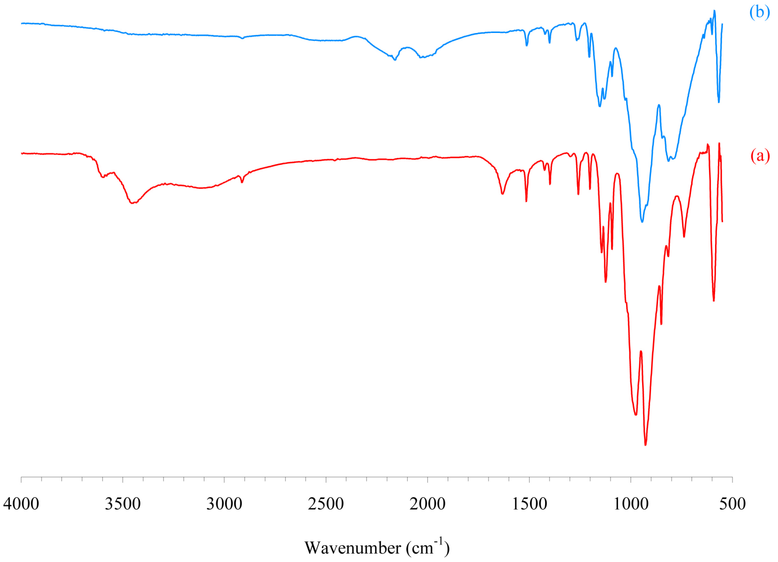

Figure S4. Infrared spectra for (a) [(MoO$_2$)$_2$(xdp)] **2** soaked in MeOH (*i.e.* **3**), and (b) [(MoO$_2$)$_2$(xdp)] **2** soaked in EtOH (*i.e.* **4**).

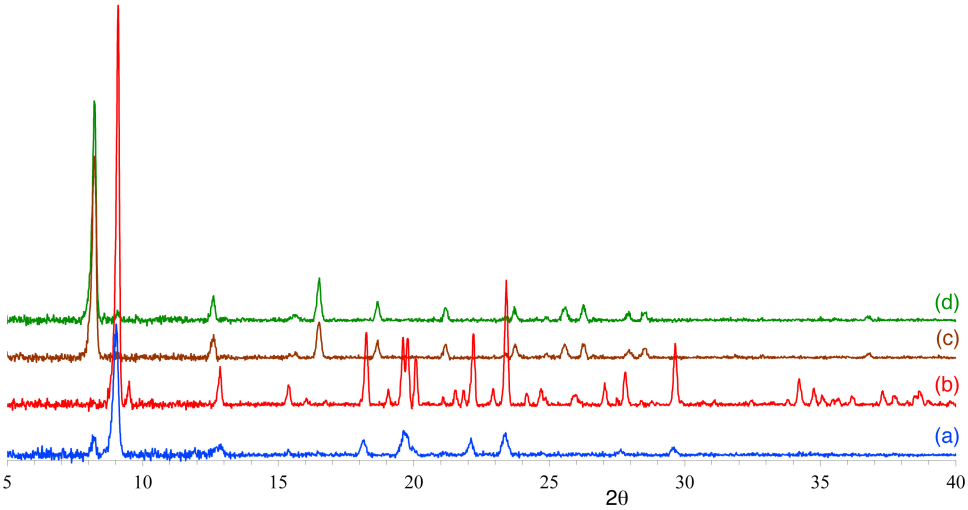

Figure S5. PXRD patterns for (a) [(MoO$_2$)$_2$(xdp)] **2** soaked in MeOH (*i.e.* **3**), (b) [(MoO$_2$)$_2$(xdp)(H$_2$O)$_2$]·2H$_2$O **1**, (c) [(MoO$_2$)$_2$(xdp)] **2** soaked in EtOH for (*i.e.* **4**), and (d) [(MoO$_2$)$_2$(xdp)] **2**.

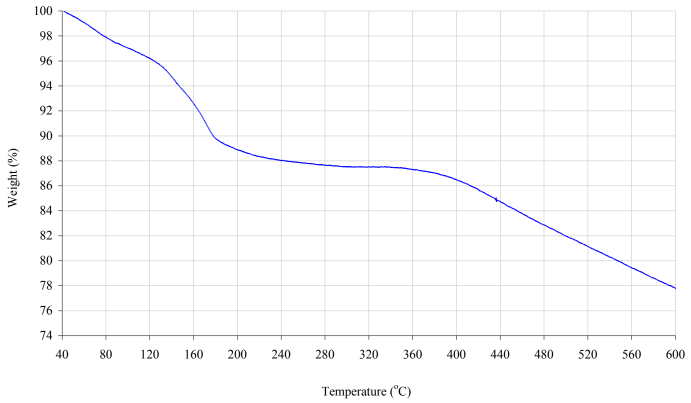

Figure S6. TGA trace for [(MoO$_2$)$_2$(xdp)] **2** soaked in MeOH (*i.e.* **3**).

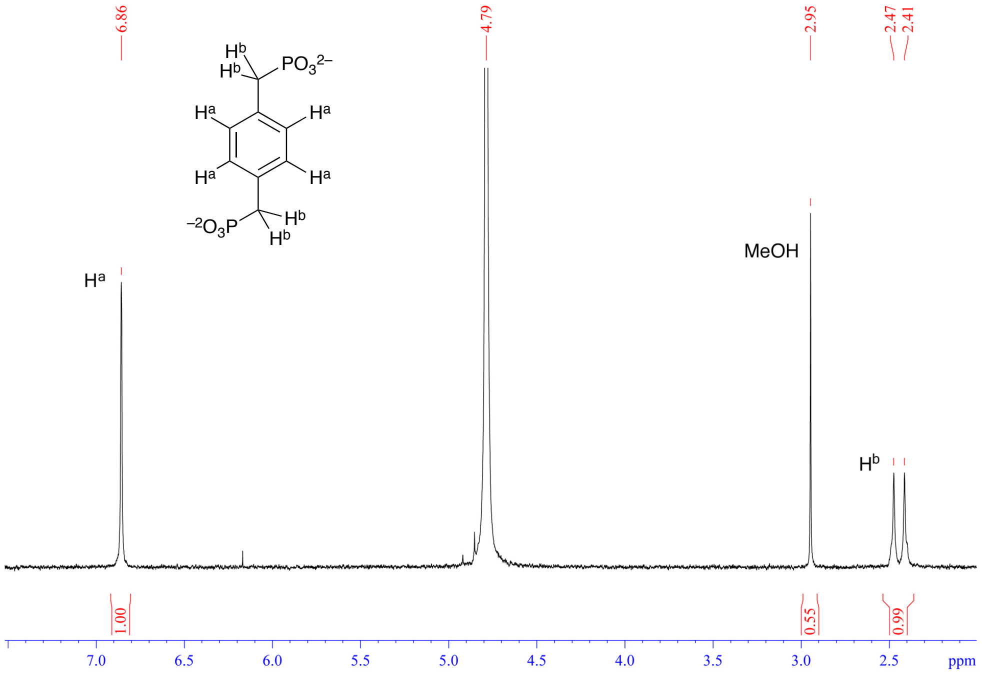

Figure S7. ^{1}H NMR spectrum of [(MoO$_2$)$_2$(xdp)] **2** after soaking in MeOH (*i.e.* **3**) followed by digestion.

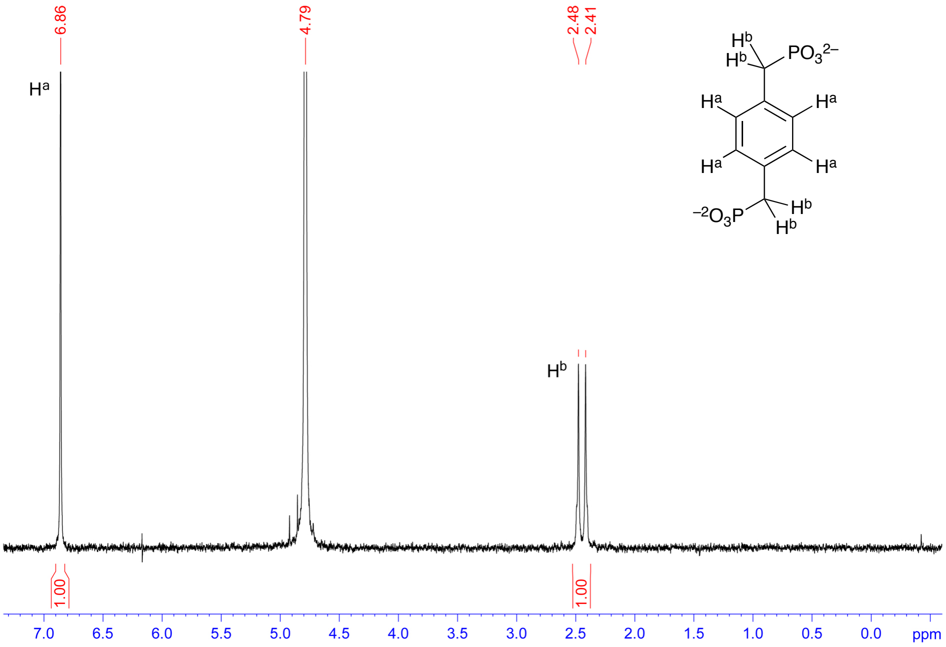

Figure S8. ^{1}H NMR spectrum of [(MoO$_2$)$_2$(xdp)] **2** after soaking in EtOH (*i.e.* **4**) followed by digestion.

Crystal structure of $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ 1

X-ray diffraction data was collected on an Oxford Diffraction Gemini diffractometer fitted with an Atlas CCD detector using Mo-Kα radiation of wavelength 0.71073 Å at 150 K. Details of the data collection, structure solution and refinement are given in Table S1. Details of the observed hydrogen bonding are given in Table S2.

The structure was solved using SHELXS-97[S2] and refined using full-matrix least squares in SHELXL-97.[S2] The final refinements were generally straightforward with all non-hydrogen atoms refined anisotropically in the final least squares run, and hydrogen atoms included at calculated positions. The hydrogen atoms attached to the water molecules were located and refined at 0.98 Å from the parent oxygen atoms. There is some evidence of disorder in the position of H7B which has not been modelled. This does, however, account for a short D-H...H-D contact involving the hydrogen atom assigned to this position. The asymmetric unit is shown in Fig. S9.

Table S1. Crystal data and structure refinement for **1**

Empirical formula	$C_4H_8MoO_7P$
Formula weight	295.01
Temperature / K	150(2)
Wavelength / Å	0.7107
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 20.8424(8)Å, α = 90°
	b = 10.6114(3)Å, β = 111.686(4)°
	c = 9.0023(4)Å, γ = 90°
Volume / $Å^3$	1850.09(12)
Z	8
Density (calculated) / g cm^{-3}	2.118
Absorption coefficient / mm^{-1}	1.595
$F(000)$	1160
Crystal size / mm	0.18 × 0.05 × 0.02
Theta range for data collection	2.97 to 27.48°
Index ranges	$-19 \le h \le 26; -13 \le k \le 13; -10 \le l \le 11$
Reflections collected	6442
Independent reflections	2111 [R(int) = 0.0278]
Reflections observed (>2σ)	1628
Data Completeness	0.996
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94878
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2111 / 4 / 134
Goodness-of-fit on F^2	0.946
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0200$ $wR_2 = 0.0405$
R indices (all data)	$R_1 = 0.0328$ $wR_2 = 0.0415$
Largest diff. peak and hole / e $Å^{-3}$	0.467 and –0.357

Table S2. Hydrogen bonds present in the structure of **1**

D–H···A	**d(D···A)/Å**	**d(H···A)/Å**	**∠DHA/°**	**Symmetry relating A to D**
O(6)–H(6A)···O(7)	2.758	1.79	173	–
O(6)–H(6B)···O(5)	3.040	2.14	153	$x, -y + 1, z - {}^{1}/_{2}$
O(6)–H(6B)···O(4)	2.981	2.35	122	$-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{1}/_{2}$
O(7)–H(7A)···O(6)	2.930	1.96	175	$x, -y + 1, z + {}^{1}/_{2}$

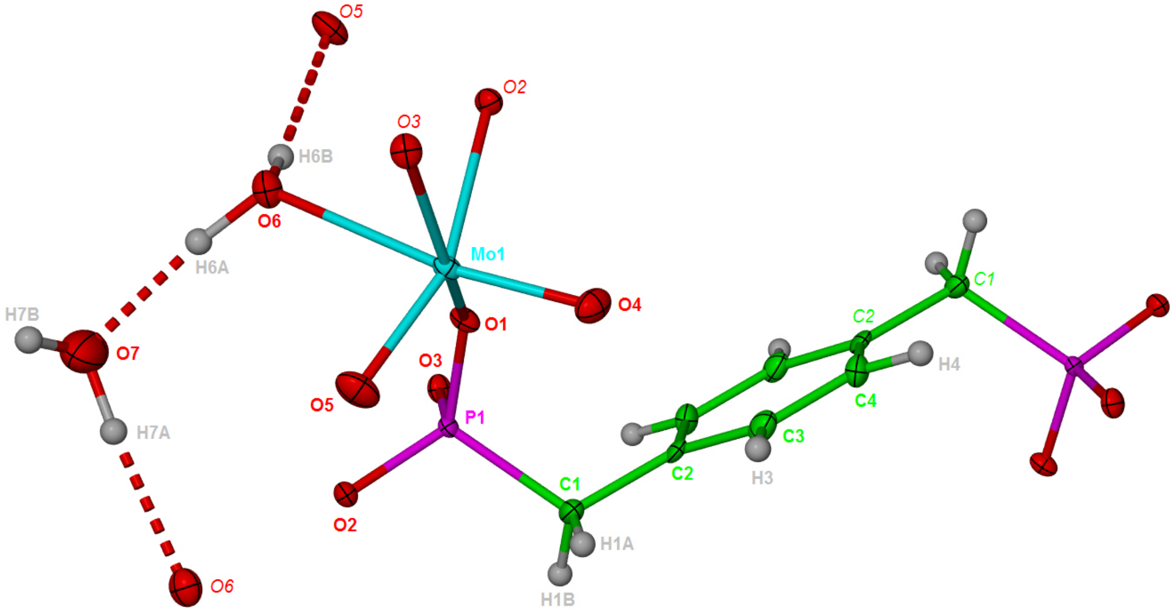

Figure S9. Asymmetric unit for $[(MoO_2)_2(xdp)(H_2O)_2]\cdot 2H_2O$ **1** showing symmetry related fragments (labelled in italics) and the major hydrogen bonding.

References

S1. W. Kraus and G. Nolzeb, *J. Appl. Cryst.*, 1996, **29**, 301.
S2. G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.