A manganese molybdenum phosphate with a tunnel: hydrothermal synthesis, structure and catalytic properties of $(NH_3CH_2CH_2NH_3)_{10}$-$(H_3O)_3(H_5O_2)Na_2[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4]$-$[MnMo_{12}O_{24}(OH)_6(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$

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A manganese molybdenum phosphate, $(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)Na_2[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4][MnMo_{12}O_{24}(OH)_6(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$, has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. The structure of this compound may be considered to be two $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$ units bonded together by a manganese atom, although several P–O groups are not protonated on account of coordination to a Na^+ cation. One-dimensional tunnels were formed in the solid. A probe reaction of the oxidation of acetaldehyde with H_2O_2 using this compound as catalyst was carried out in a liquid–solid system, showing that the manganese molybdenum phosphate has high catalytic activity in the reaction.

The synthesis of organic and/or inorganic solid-state materials with pore or tunnel structures are receiving increasing interest in materials science owing to their applications to catalysis, sorption, and electrical conductivity.[1–3] A number of structurally complex solid-state inorganic materials have been prepared by hydrothermal syntheses and high temperature solid-state syntheses.[4,5] In particular, a new class of solid-state materials consisting of metal oxide clusters based on anionic molybdenum phosphate frameworks have received much attention as a consequence of their potential applications in catalysis and materials science.[6–11] The molybdenum phosphates are structurally very diverse and include examples of one-dimensional polymers,[12] two-dimensional layered materials,[13] and three-dimensional solids prepared both at high temperatures[14] and under hydrothermal conditions.[5] To obtain structurally diverse and microporous solid-state materials, many experimental results showed that organic templates play a key role in the solid structure formation. High temperature preparation, however, precludes the use of water and organic templates. Hydrothermal synthesis has the advantage of reactions performed at low temperatures, so that organic molecules can be used as templates and water as the reaction medium. In order to explore the hydrothermal synthetic method of incorporating more than one d-block element into molybdenum phosphate frameworks a reasonable number of examples have to be synthesised and structurally characterized. Previously, we have synthesized several mixed valence polyoxometalates,[15,16] but they were prepared in solution and without the incorporation of other transition elements. To our knowledge, the preparation of first-row transition metal–molybdenum–phosphates by hydrothermal syntheses have been rarely reported.[17–21]

In this paper, we report the hydrothermal synthesis and structural characterization of a novel manganese molybdenum phosphate, $(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)$-$Na_2[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4][MnMo_{12}O_{24}$-$(OH)_6(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$ **1**. Compound **1** represents the first structurally characterized example of a manganese molybdenum phosphate with both tunnel structure and crystallographically different $Mn[Mo_6P_4]_2$ clusters. The two kinds of tunnels are formed by the linkage of the Na^+ cations with the $[MnMo_{12}O_{24}(OH)_6(PO_4)_4(HPO_4)_4]^{12-}$ cluster, in which two $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$ ($\equiv [Mo_6P_4]$) units are bonded together with a manganese atom. The catalytic activity of compound **1** has been explored by means of a probe reaction of the oxidation of acetaldehyde with H_2O_2.

Experimental

Hydrothermal synthesis

Compound **1** was prepared by hydrothermal techniques. A mixture of $MnSO_4\cdot H_2O$, Na_2MoO_4, Mo, H_3PO_4, $H_2N(CH_2)_2NH_2$ and H_2O in the mole ratio of 1.0 : 5.0 : 1.0 : 10 : 8.0 : 250 was sealed in a 18 cm^3 Teflon lined reactor which was kept at 250 °C for 51 h. Deep brown-red crystals of **1** were isolated (yield 82% based on Mo) by filtration and washing with water. The water and ethylenediamine content were determined by TGA and DSC analysis of the sample. Elemental analysis (ICP-AES) showed that the mole ratio of Mn : P : Mo was 1 : 8 : 12.

X-Ray crystallographic determination

A deep brown-red crystal with dimensions of $0.52 \times 0.46 \times 0.24$ mm was mounted on a glass fiber. X-Ray data were collected with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K on a Siemens P4 diffractometer in the range of $1.75 < \theta < 23.04°$ using an ω scan technique. A semi-empirical

Table 1 Crystal data and structure refinement

Molecular formula	$C_{20}H_{150}Mn_2Mo_{24}N_{20}Na_2O_{138}P_{16}$
M	5833.54
T/K	293
λ/Å	0.71073
Space group	$P\bar{1}$
Crystal system	Triclinic
a/Å	12.047(2)
b/Å	14.647(3)
c/Å	21.254(4)
α/°	80.68(2)
β/°	83.04(3)
γ/Å	76.34(3)
V/Å^3	3582.7(12)
Z	1
μ/mm^{-1}	2.513
F(000)	2834
Reflections collected	12026
Independent reflections	9981($R_{int} = 0.0711$)
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0502$, $wR2 = 0.1254$
R indices (all data)	$R1 = 0.0583$, $wR2 = 0.1292$

absorption correction was applied based on ψ-scans for selected reflections. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL software.[22] As sensible anisotropic parameters could not be obtained for the sodium atom, an isotropic refinement was made so as to achieve a satisfying thermal parameter for the sodium atom. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement are summarized in Table 1. CCDC reference number 440/132. See http://www.rsc.org./suppdata/nj/1999/1041/ for crystallographic files in .cif format.

Catalytic reaction

Catalytic reaction was carried out in a 50 mL three-neck flask equipped with a reflux condenser. The three-neck flask was charged with 5.70 mL (0.05 mole) of 40% acetaldehyde solution, then 10 mL of 30% H_2O (0.10 mole) were pipetted into the solution. When the solution was heated to 333 K, powdered compound **1** (0.1 g) was added to the solution. After 3 h at this temperature, the reaction was stopped and the catalyst was separated. Standard NaOH solution was used to titrate the reactant solution. The formation rate of the produced acetic acid (mmol per g of catalyst h^{-1}) was measured to assess the activity of the catalyst.

Results and discussion

Description of the crystal structure

The structure of **1** determined by single-crystal X-ray diffraction, revealed the anionic dimers $Mn[Mo_6O_{12}(OH_3)(PO_4)_2(HPO_4)_2]_2$ **1a**, sodium cations, ethylenediamine and lattice water molecules. Selected bond lengths are collected in Table 2. A polyhedral representation of the anionic dimers **1a**, a portion of the structure of **1** and a simplified representation of **1** are shown in Fig. 1, 2 and 3, respectively. The structure of **1a** may be considered to be two $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$($\equiv[Mo_6P_4]$) units linked by an octahedral Mn^{2+}, although several P–O groups are not protonated on account of their coordination to a Na^+ cation. Each $[Mo_6P_4]$ cluster consists of a Mo_6 ring of six edge-sharing MoO_6 octahedra with alternating long ($\approx$3.60 Å) and short ($\approx$2.58 Å) Mo–Mo contacts, the latter suggesting direct Mo–Mo single bonds. A central phosphate group bridges the ring internally, and three phosphate groups bridge each long Mo–Mo contact externally, as shown in Fig. 2. Structurally, all of phosphate tetrahedra are corner-sharing with the corresponding molybdenum octahedra. Such $[Mo_6P_4]$ cluster units have been previously found in several compounds containing molybdenum phosphates.[17–21,23] In the case of $[Et_4N]_6$-$[Na_{14}Mo_{24}P_{17}O_{97}(OH)_{31}]\cdot xH_2O$, which was hydrothermally synthesized by Haushalter and co-workers,[23] the Mo–Mo bond lengths (2.59 Å) and non-bonding Mo···Mo contacts (3.55 Å) are comparable with those in compound **1**.

Table 2 Selected bond lengths (Å)

Mo1–O38	1.689(8)	Mo1–O27	1.927(8)
Mo1–O45	1.964(7)	Mo1–O28	2.063(8)
Mo1–O26	2.118(7)	Mo1–O44	2.251(7)
Mo1–Mo8	2.577O(15)	Mn1–O35	2.246(7)
Mn1–O42	2.246(7)	Mn1–O45	2.272(7)
P3–O40	1.521(9)	P3–O49	1.535(9)
P3–O28	1.563(8)	P3–O58	1.508(9)
P7–O62	1.494(10)	P7–O61	1.542(10)
P7–O31	1.515(9)	P7–O34	1.547(8)
Na–O22	2.248(10)	Na–O62	2.225(11)
Na–O60	2.315(11)	Na–OW1[a]	2.41(2)
Na–O14	2.867(10)	Na–O10	2.271(10)

[a] Oxygen atom from water molecule.

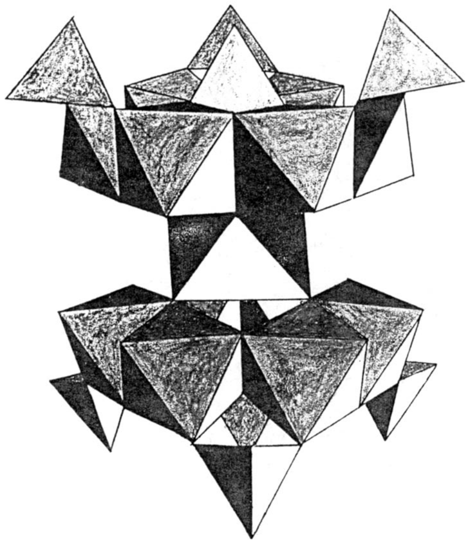

Fig. 1 Polyhedral representation of the $Mn[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]_2$ dimers in complex **1**, showing two $[Mo_6O_{12}(OH)_3(PO_4)_2(HPO_4)_2]^{7-}$ units linked by an octahedral Mn^{2+}.

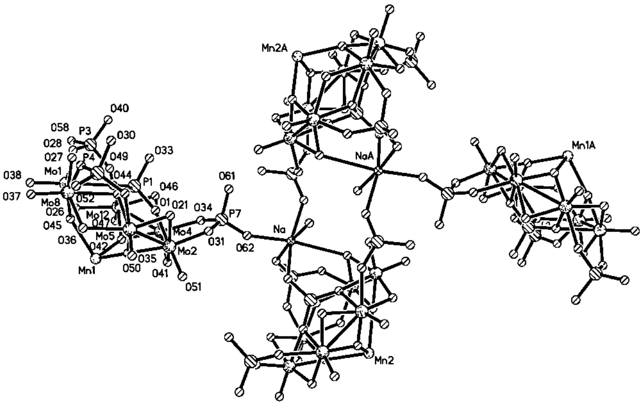

Fig. 2 ORTEP[27] view of a main portion of complex **1**, showing how the two $Mn(1)[Mo_6P_4]_2$ and the two $Mn(2)[Mo_6P_4]_2$ are associated by bonding with two Na^+ cations. They are approximately situated on a plane layer. A $[Mo_6P_4]$ part of $Mn(1)[Mo_6P_4]_2$ or of $Mn(2)[Mo_6P_4]_2$ is not drawn.

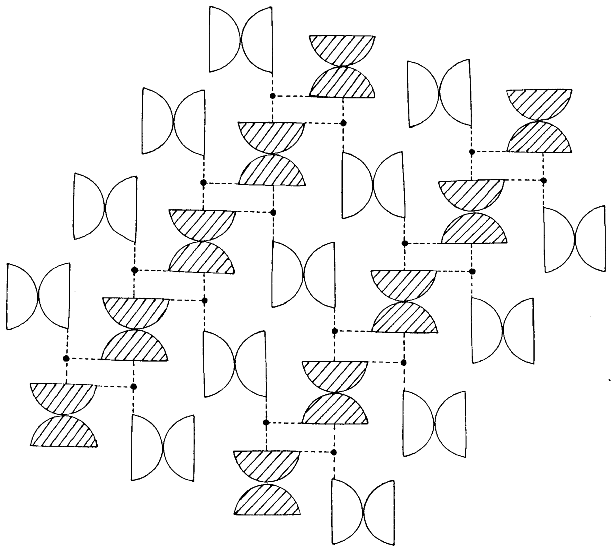

Fig. 3 Simplified schematic representation of the structure of **1**, in which the two-dimensional linkages of Na^+ cations, $Mn(1)[Mo_6P_4]_2$ and $Mn(2)[Mo_6P_4]_2$ are situated on the (100) plane layer. The $Mn(1)[Mo_6P_4]_2$ clusters are represented as blank double-semicircles, the $Mn(2)[Mo_6P_4]_2$ as striped double-semicircles, and the Na^+ cations as black circles.

This formulation for compound **1** assumes, based on the observed geometry and the bond valence sum (BVS)[24] for the oxygen atoms of P–O bonds (see Table 3), that several bridging oxygen atoms from the Mo_6 ring and the terminal OH groups on the PO_4 groups, including the central PO_4 groups, except those which are linked to the Na^+ cations, are protonated. The bond valence sum calculations, based on the observed Mo–O and Mn–O bond lengths, show the Mo to be in the +5 and Mn in the +2 oxidation state. The bond valence sums (BVS) for some oxygen atoms, those with BVS values in the range of 1.1–1.4, indicate that they are hydroxyl oxygen atoms in view of the bond valence contribution of ~0.80 for an O–H bond. Hence, the formula for compound **1** becomes $(NH_3CH_2CH_2NH_3)_{10}(H_3O)_3(H_5O_2)Na_2$-$[MnMo_{12}O_{24}(OH)_6(PO_4)_4(PO_3OH)_4]$ $[MnMo_{12}O_{24}(OH)_6$-$(PO_4)_6(PO_3OH)_2]\cdot 9H_2O$. In compound **1** each Mo^{5+} cation has a distorted octahedral configuration with an apical Mo–O bond at a length of ≈1.68 Å, and five other Mo–O bonds at lengths ranging from ≈1.92 to ≈2.25 Å. These bond lengths are comparable with those found in $[(CH_3)_4N]_2[NH_4]_2\cdot[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]\cdot nH_2O$ and $[(CH_3)_4N](H_3O)_2[Zn_3Mo_{12}O_{30}\ (HPO_4)_2\ (H_2PO_4)_6]\cdot 11.5H_2O$.[17,18]

In addition, two types of $Mn[Mo_6P_4]_2$ clusters in compound **1** are not crystallographically identical, indicated as $Mn(1)[Mo_6P_4]_2$ **2** and $Mn(2)[Mo_6P_4]_2$ **3** respectively. The main difference between the two clusters is that in **2** only one oxygen atom from one P–O group in each $[Mo_6P_4]$ coordinates with one Na^+ while in **3** two oxygen atoms from different P–O groups in each $[Mo_6P_4]$ coordinate to two Na^+ cations (see Fig. 2). Moreover, two anions of **2** and two anions of **3** are associated by bonding through two Na^+ cations, as shown in Fig. 2. On the whole the two Na^+ cations are crystallographically identical. Another difference between **2** and **3** is their arrangement in the crystal lattice: they are oriented in two different directions which are almost perpendicular to each other. As shown in Fig. 2, each Na^+ cation is coordinated by six O atoms from four P–O groups, a water molecule, and an oxo-bridge shared by Mo atoms with a Mo–Mo single bond. The most unusual feature of **1** is that the one-dimensional tunnel along the *a*-axis is formed in the solid of **1**. As the linkages of two Na^+ cations with four $Mn[Mo_6P_4]_2$ are situated on the (100) plane layer, the infinite plane layers are stacked parallel along the *a* axis to constitute a three-dimensional crystal structure, resulting in the formation of two kinds of one-dimensional tunnel along the *a* axis. A small tunnel is surrounded by two Na^+ cations and two $Mn(2)[Mo_6P_4]_2$ anions (see Fig. 3), with a tunnel bore diameter of *ca.* 6.26 Å based on the Na–Na distance. The other tunnel in the aperture with a “__|‾‾” shape is surrounded by four Na^+ cations, two **2** anions, and two **3** anions (see Fig. 3). This “__|‾‾” shaped tunnel is filled with ethylenediamine molecules and water molecules, which may be removed by heating. Futhermore, these plane layers are interconnected in-sheet (axial) through multipoint hydrogen bonding between the ethylenediamine nitrogen atoms and the cluster oxygen atoms. This feature is supported by both the distances between the nitrogen and oxygen atoms (ranging from 2.69 to 3.02 Å) and the result of DSC thermal analysis that a large endothermic effect occurs in the release of the ethylenediamine molecules. An investigation on the microporous properties of this material are in progress. Since it is difficult to determine the positions of the additional protons in **1**, ten protons are assumed to associate with five ethylenediamine molecules.[25] Another four protons are assigned to five water molecules, in which two water molecules are linked *via* H^+ by hydrogen bonding to form a $[H_5O_2]^+$ ion (the distance between the two oxygen atoms is 3.145 Å) and three more water molecules with three associated protons constitute three H_3O^+ ion. These assumptions are based on the charge balance requirement and on chemical reason. The IR spectrum of compound **1** in which there are characteristic bonds (3485, 3181 and 1521 cm^{-1}) for the protonated ethylenediamine, also supports this assumption.

Interestingly, in compound **1**, the $Mn[Mo_6P_4]_2$ cluster is much the same as that reported in Lightfoot's work[20] on the synthesis of $[(CH_3)_4N][Mn_2Mo_6O_{12}(OH)_4(PO_4)(HPO_4)$-$(H_2PO_4)_2]_4\cdot H_2O$, although these two compounds were

Table 3 Bond valence sums for oxygen atoms

O1	1.879	O2	1.856	O3	1.996	O4	1.756
O5	2.013	O6	1.080	O7	1.985	O8	1.071
O9	1.898	O10	1.602	O11	1.760	O12	1.753
O13	1.853	O14	1.801	O15	1.102	O16	1.922
O17	1.891	O18	1.930	O19	1.777	O20	1.789
O21	1.676	O22	1.598	O23	1.730	O24	1.241
O25	1.755	O26	1.076	O27	1.789	O28	1.787
O29	1.268	O30	1.105	O31	1.965	O32	1.293
O33	1.350	O34	1.828	O35	2.043	O36	1.102
O37	1.755	O38	1.723	O39	1.765	O40	1.289
O41	1.106	O42	2.021	O43	1.784	O44	1.865
O45	1.965	O46	1.796	O47	1.823	O48	1.847
O49	1.908	O50	1.681	O51	1.755	O52	1.425
O53	1.765	O54	1.713	O55	1.221	O56	1.909
O57	1.751	O58	1.342	O59	1.904	O60	1.512
O61	1.225	O62	1.615				

prepared from different Mo sources and organic templates. In comparison with the Mn–O bond lengths of MnO_6 octahedra in $[(CH_3)_4N][Mn_2Mo_6O_{12}(OH)_4(PO_4)(HPO_4)(H_2PO_4)_2]_4 \cdot H_2O$, the MnO_6 octahedra in compound **1** have slightly greater structural distortion.

IR spectrum and TGA-DSC thermal analysis

The IR spectrum of compound **1** exhibited a strong band at 951 cm^{-1}, characteristic of ν(Mo=O), and features at 732 and 1039 cm^{-1} associated with ν(Mo–O–M) and ν(P–O), respectively. The features at 3485, 3181 and 1521 cm^{-1} are characteristic of the protonated ethylenediamine, while other strong features at 3210 and 1627 cm^{-1} are assigned to water molecules. Thermogravimetric analysis (TGA) of compound **1**, carried out under N_2 with a heating rate of 10 °C min^{-1}, showed a first weight loss of 3.5% in the temperature range 98–225 °C and a second weight loss of 9.1% in the temperature range 290–460 °C. These two weight losses correspond to the release of water molecules (calculated value 3.6%) and ethylenediamine molecules (calculated value 8.7%), respectively. Compound **1** continued to lose weight gradually up to 600 °C, the highest temperature measured. The result of the DSC thermal analysis showed two endothermic events in which the temperatures of the first peak ($\Delta H_1 = 47.6$ J g^{-1}) was 151 °C and that of the second peak ($\Delta H_2 = 905.5$ J g^{-1}) 376 °C. The two endothermic events respectively correspond to the two release processes of the water molecules and the ethylenediamine molecules. Noteworthy, the large endothermic effect in the second release process implies the occurrence of hydrogen bonding between the nitrogen atom from the ethylenediamine and the oxygen atom from the anion. This is in agreement with the N–O average distance (2.83 Å) determined from the single crystal X-ray diffraction data. However, it is very difficult to localize the accurate orientations of these hydrogen bonds in the crystal structure, because these hydrogen bonds are formed in various directions and in large numbers.

Catalytic test

To investigate the oxidative catalytic activity of compound **1**, we performed a probe reaction of the oxidation of acetaldehyde with H_2O_2 using compound **1** as catalyst. Under the above mentioned experimental conditions, compound **1** has a catalytic activity of 55.5 mmol acetic acid per g catalyst per hour, while $Ni_2Al–CO_3$, *i.e.* clay catalyst $Ni_{0.70}Al_{0.30}(OH)_2 \cdot 0.15CO_3 \cdot 0.86H_2O$, has an activity of 8.0 mmol acetic acid per g catalyst per hour.[26] The difference in activity is a seven-fold increase for compound **1** over $Ni_2Al–CO_3$. The catalytic selectivity for acetic acid was nearly 100%. This suggests that compound **1** may become an oxidative catalyst of high activity in some organic syntheses.

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