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Bis(iminodiethylenediammonium) di-μ_5-hydrogenphosphato-pentamolybdate(VI) tetrahydrate

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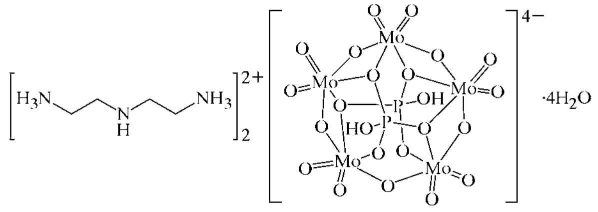
The crystal structure of the title compound, $(C_4H_{15}N_3)_2[Mo_5O_{15}(HPO_4)_2]\cdot4H_2O$, is made up of $[Mo_5O_{15}(HPO_4)_2]^{4-}$ clusters, iminodiethylenediammonium cations and solvent water molecules. The $[Mo_5O_{15}(HPO_4)_2]^{4-}$ cluster, with approximate C_2 symmetry, can be considered as a ring formed by five distorted edge- and corner-sharing MoO_6 octahedra, capped on both poles by a hydrophosphate tetrahedron. There exist N—H$\cdots$O, O—H$\cdots$N and C—H$\cdots$O hydrogen bonds between the organic ammonium groups and the clusters, with interatomic N$\cdots$O distances ranging from 2.675 (3) to 2.999 (3) Å, and C$\cdots$O distances ranging from 3.139 (5) to 3.460 (5) Å.

Comment

Over the past few decades, polyoxometallates have been found to be extremely versatile inorganic building blocks for the construction of organic–inorganic hybrid materials, owing to the wide range of their topological properties and potential applications in catalysis, photochemistry, electrochromism and magnetism (Braun *et al.*, 1999). An important class of metal oxide cluster based on molybdenum phosphate anions has been attracting much attention owing to the novel structures and unusual properties of these compounds (Guo & Liu, 2003); typical examples include $(NH_4)_2[(CH_3)_4N]_2[Fe_2Mo_{12}O_{30}(H_2PO_4)_6(HPO_4)_2]$ (Meyer & Haushalter, 1993), $(H_2en)_3[P_2Mo_5O_{23}]\cdot6H_2O$ (en is ethylenediamine; Aranzabe *et al.*, 1997), $[H_2en]_2[\{Cu(en)(H_2O)\}Mo_5P_2O_{23}]\cdot4H_2O$ (Lu *et al.*, 1998), $(H_2en)_{10}(H_3O)_3(H_5O_2)Na_2[MnMo_{12}O_{24}(OH)_6(PO_4)_4(HPO_4)_4][MnMo_{12}O_{24}(OH)_6(PO_4)_6(HPO_4)_2]\cdot9H_2O$ (Xu *et al.*, 1999), $(C_4H_{12}N_2)_{0.5}[Co(en)_3][(Mo_5O_{15})(HPO_4)_2]$ (He *et al.*, 2004), $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]$ (bpy is 2,2′-bipyridine; Finn *et al.*, 2001) and $(H_2bpy)_{0.5}\{[Ni(H_2O)_5][Ni(Hbpy)(H_2O)_4[Mo_5P_2O_{23}]\}$ (Lu *et al.*, 2005). Compared with ethylenediamine or pyridine templates, the hybrid materials containing diethylenetriamine (tren) or its ammonium cation remain largely unexplored (Lin *et al.*, 2003). We report here the hydrothermal synthesis and crystal structure of the title novel organic–inorganic hybrid, *viz.* $(H_2tren)_2[Mo_5O_{15}(HPO_4)_2]\cdot4H_2O$, (I).



(I)

The crystal structure of (I) is made up of $[Mo_5O_{15}(HPO_4)_2]^{4-}$ anionic clusters, $(H_2tren)^{2+}$ cations and solvent water molecules. As shown in Fig. 1, the $[Mo_5O_{15}(HPO_4)_2]^{4-}$ cluster has approximate C_2 symmetry, with atoms Mo4 and O12 lying on the axis. The five MoO_6

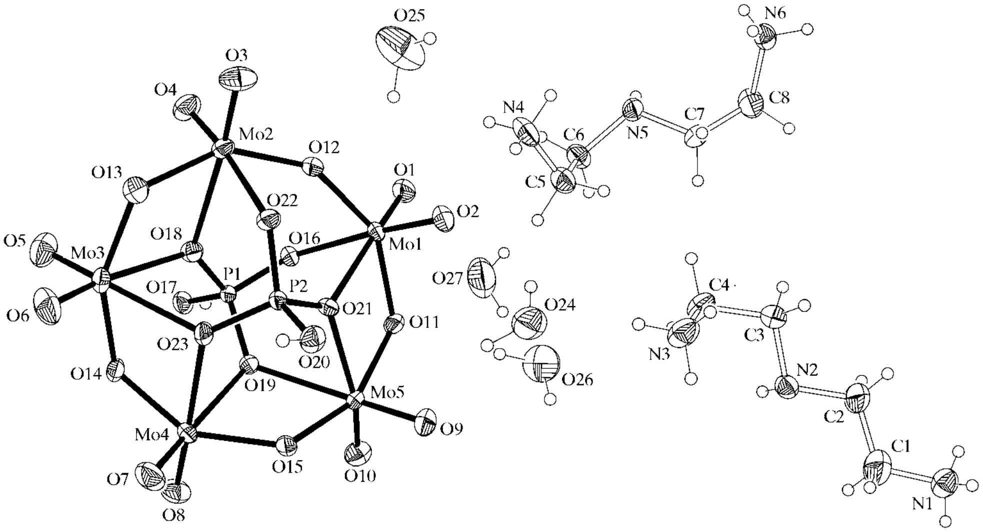


Figure 1
The asymmetric unit in (I), showing the atom-labeling scheme and 50% probability displacement ellipsoids.

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octahedra in the cluster aggregate in a compact edge-sharing or corner-sharing arrangement to form a ring with two PO_4 tetrahedra coordinated above and below the ring. The Mo_5 ring is nearly planar, with a mean least-squares deviation of 0.2238 Å, an interatomic distance between atoms P1 and P2 of 3.8024 (11) Å, and an orientation of the P1$\cdots$P2 vector with respect to the ring of 84.5 (2)°. Each hydrophosphate subunit has one terminal OH group and three bridging O atoms shared with the molybdenum ring, where one of these oxo groups adopts the μ_2-bridging mode, linking one molybdenum and one phosphorus site, and the other two adopt the μ_3-bridging mode, linking two molybdenum sites and one phosphorus site. The five MoO_6 octahedra can be classified into two groups, *viz.* (i) the corner-sharing octahedra around atoms Mo1 and Mo2, each of which has two terminal O atoms (O_t), two bridging atoms, O_b, shared by two molybdenum sites, one $O\mu_2$ atom and one $O\mu_3$ atom, and (ii) the edge-sharing octahedra surrounding atoms Mo3, Mo4 and Mo5, each of which has two O_t, two O_b and two $O\mu_3$ atoms. Different types of O atoms have different Mo—O bond distances [Mo—O_t = 1.706 (2)–1.734 (2) Å, Mo—O_b = 1.914 (2)–1.960 (2) Å, Mo—$O\mu_2$ = 2.216 (2)–2.217 (2) Å and Mo—$O\mu_3$ = 2.183 (2)–2.440 (2) Å; Table 1]. These bond distances are in accordance with those observed in $(C_6H_{11}NH_3)_5H(P_2Mo_5O_{23})\cdot4H_2O$ (Wang *et al.*, 2004) and $(H_2bpy)_{0.5}\{[Ni(H_2O)_5][Ni(Hbpy)(H_2O)_4][Mo_5P_2O_{23}]\}$ (Lu *et al.*, 2005). The PO_4 tetrahedra exhibit distorted geometry, with P—O bond distances ranging from 1.514 (2) to 1.568 (2) Å and O—P—O bond angles of between 106.32 (12) and 110.99 (12)°, which are in agreement with values reported previously (Aranzabe *et al.*, 1997). Valence sum calculations (Brown & Altermatt, 1985) demonstrate that all Mo atoms in (I) have valence sums ranging from 5.835 to 5.987, with an average value of 5.925, very close to the ideal value of 6 for Mo^{VI}. Atoms O17 and O20 have valence sums of 1.208 and 1.225, respectively, which suggests that both of the terminal O atoms of the PO_4 tetrahedra are protonated.

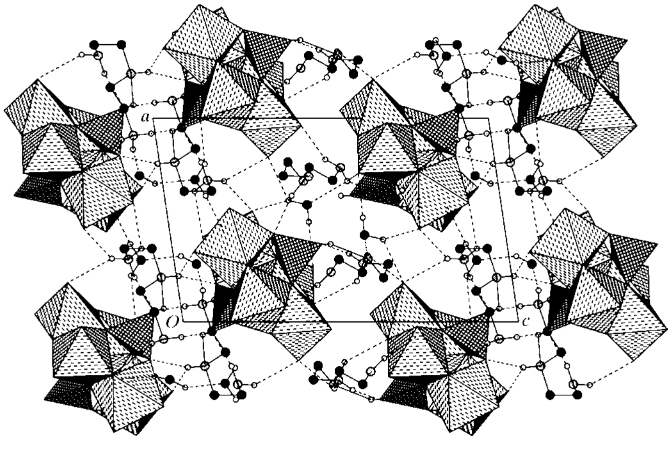

Figure 2
A packing view of (I) along the *b* axis, showing the arrangement of the $[Mo_5O_{15}(HPO_4)_2]^{4-}$ clusters (polyhedra), the $(H_2tren)^{2+}$ cations and the solvent water molecules in the crystal structure. The dashed lines denote the hydrogen-bonding interactions, and H atoms not involved in such interactions have been omitted for clarity.

The arrangement of the $[Mo_5O_{15}(HPO_4)_2]^{4-}$ clusters, the $(H_2tren)^{2+}$ cations and the solvent water molecules in the crystal structure of (I) along the *b* axis is demonstrated in Fig. 2, which shows the extensive hydrogen bonding. As listed in Table 2, N—H$\cdots$O and O—H$\cdots$N hydrogen bonds between the organic ammonium groups and the clusters have interatomic N$\cdots$O distances ranging from 2.675 (3) to 2.999 (3) Å and hydrogen-bond angles from 124 to 173°. There also exist C—H$\cdots$O hydrogen bonds between the CH groups of the organic cations and the O atoms from the clusters, with C$\cdots$O distances between 3.139 (5) and 3.460 (5) Å, and hydrogen-bond angles between 122 and 160°. These hydrogen bonds hold the $[Mo_5O_{15}(HPO_4)_2]^{4-}$ clusters and the $(H_2tren)^{2+}$ cations in (I) together into a three-dimensional supramolecular network, where the solvent water molecules occupy the interstices, forming N—H$\cdots$O and O—H$\cdots$O hydrogen bonds with the geometric parameters 2.890 (4)–3.113 (5) Å and 118 (3)–175 (5)°.

Experimental

Compound (I) was synthesized hydrothermally under autogenous pressure in a 17 ml Teflon-lined stainless steel autoclave with a fill factor of approximate 40%. A mixture of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, Nd_2O_3, H_3PO_4, diethylenetriamine and water in the molar ratio 1:1:2.8:1.15:333 was heated at 393 K for 6 d. After slow cooling to ambient temperature, colorless block-shaped crystals of (I) were obtained. The crystals were filtered off, washed with distilled water and dried in a desiccator at ambient temperature (yield *ca* 60% based on molybdenum). The pH value of the reactive system increased from 3.42 before heating to 3.68 at the end of the reaction. The strong band at 952 cm^{-1} in the IR spectrum is assigned to the Mo—O_t stretching vibrations, and the bands at 892, 775 and 676 cm^{-1} are related to the Mo—O—Mo vibrations, while the characteristic bands at 1091 and 1025 cm^{-1} are attributed to the P—O vibrations. Bands ranging from 1330 to 1268 cm^{-1} are characteristic of C—N and C—C bonds of the organic groups. Analysis calculated for $C_8H_{40}Mo_5N_6O_{27}P_2$: C 8.13, H 3.27, N 6.98, P 5.20, Mo 40.11%; found: C 8.05, H 3.36, N 7.12, P 5.08, Mo 40.03%.

Crystal data

$(C_4H_{15}N_3)_2[Mo_5O_{15}(HPO_4)_2]\cdot4H_2O$
M_r = 1194.10
Triclinic, $P\overline{1}$
a = 10.3497 (14) Å
b = 10.9934 (15) Å
c = 15.751 (2) Å
α = 95.650 (6)°
β = 95.734 (6)°
γ = 111.408 (5)°
V = 1642.4 (4) Å^3
Z = 2
D_x = 2.415 Mg m^{-3}
Mo *K*α radiation
μ = 2.06 mm^{-1}
T = 294 (2) K
Block, colorless
0.16 × 0.12 × 0.08 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.734, T_{max} = 0.852
25131 measured reflections
6733 independent reflections
6371 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.5°
3 standard reflections every 150 reflections intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.092$
$S = 1.03$
6733 reflections
462 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.165P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.93$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O1	1.706 (2)	Mo3—O13	1.960 (2)
Mo1—O2	1.723 (2)	Mo3—O18	2.183 (2)
Mo1—O12	1.916 (2)	Mo3—O23	2.366 (2)
Mo1—O11	1.956 (2)	Mo4—O7	1.733 (3)
Mo1—O16	2.216 (2)	Mo4—O8	1.734 (2)
Mo1—O21	2.332 (2)	Mo5—O9	1.721 (2)
Mo2—O3	1.715 (2)	Mo5—O10	1.723 (2)
Mo2—O4	1.729 (2)	P1—O16	1.514 (2)
Mo3—O5	1.703 (3)	P1—O17	1.538 (2)
Mo3—O6	1.724 (3)	P1—O19	1.559 (2)
Mo3—O14	1.939 (2)	P1—O18	1.564 (2)
O12—Mo1—O11	147.57 (9)	O16—P1—O17	110.55 (12)
O12—Mo2—O13	145.57 (9)	O16—P1—O18	106.32 (12)
O14—Mo3—O13	152.91 (9)	O17—P1—O18	110.79 (12)
O14—Mo4—O15	147.18 (9)	O20—P2—O22	110.62 (12)
O15—Mo5—O11	154.08 (9)	O20—P2—O23	110.99 (12)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17—H17···N5^{i}	0.82	2.27	2.906 (4)	135
O20—H20···N2^{ii}	0.82	2.02	2.675 (3)	137
N1—H1*C*···O6^{ii}	0.89	2.04	2.868 (4)	154
N1—H1*D*···O7^{iii}	0.89	1.90	2.784 (4)	173
N1—H1*E*···O9^{iv}	0.89	2.27	2.867 (4)	124
N2—H2*C*···O22^{v}	0.90	1.95	2.822 (3)	162
N3—H3*C*···O24	0.89	2.25	3.107 (4)	163
N3—H3*D*···O15^{ii}	0.89	2.31	2.996 (4)	134
N3—H3*E*···O20^{ii}	0.89	1.89	2.731 (4)	157
N4—H4*C*···O2	0.89	2.18	2.930 (4)	142
N4—H4*D*···O1	0.89	2.26	2.851 (4)	124
N4—H4*E*···O17^{vi}	0.89	1.84	2.720 (4)	168
N5—H5*C*···O4^{vii}	0.90	2.08	2.778 (4)	134
N6—H6*D*···O27^{vi}	0.89	1.86	2.726 (5)	163
N6—H6*E*···O11^{vi}	0.89	2.38	2.999 (3)	127
N6—H6*E*···O16^{vi}	0.89	2.06	2.852 (4)	147
N6—H6*C*···O17^{vii}	0.89	1.97	2.792 (3)	153
O24—H24*A*···O9	0.96 (2)	2.06 (2)	2.914 (4)	148 (4)
O24—H24*B*···O2	0.96 (2)	2.07 (2)	2.890 (4)	143 (3)
O24—H24*B*···O8^{vi}	0.96 (2)	2.39 (3)	2.967 (4)	118 (3)
O25—H25*A*···O12	0.96 (4)	1.97 (4)	2.896 (5)	162 (5)
O26—H26*A*···O11	0.96 (4)	2.11 (5)	3.072 (4)	175 (5)
O26—H26*B*···O13^{v}	0.96 (2)	1.82 (2)	2.771 (4)	173 (3)
O27—H27*A*···O25^{vii}	0.94 (4)	1.75 (3)	2.632 (7)	151 (5)
O27—H27*B*···O13^{v}	0.95 (4)	2.26 (3)	3.113 (5)	148 (5)

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+1$; (iii) $x+1, y-1, z$; (iv) $-x+1, -y, -z+1$; (v) $x, y-1, z$; (vi) $x+1, y, z$; (vii) $-x+1, -y+1, -z$.

While the H atoms attached to C, N and hydroxy O atoms were placed in calculated positions, those on water molecules were located in a difference Fourier map and then refined with the O—H distances restrained to 0.96 (4) Å and the H—O—H angles restrained to 104.4 (4)°. All H atoms were included in the refinement with U_{iso}(H) values of $1.2U_{eq}$(parent atom).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1987); cell refinement: *TEXSAN* (Molecular Structure Corporation, 1987); data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3012). Services for accessing these data are described at the back of the journal.

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