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Butane-1,4-diammonium diphosphopentamolybdate: a new inorganic–organic hybrid solid

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A new inorganic–organic hybrid, bis(utane-1,4-diammonium) bis(hydrogenphosphato)pentamolybdate monohydrate, $(C_4H_{14}N_2)_2[Mo_5O_{15}(H_2PO_4)_2]\cdot H_2O$, has been determined. The structure contains the molecular ion $[Mo_5O_{15}(HPO_4)_2]^{4-}$ built of an Mo_5 oxo-anion ring capped by two protonated PO_4 tetrahedra linked by means of edge and corner sharing. A complex hydrogen-bonding network involving interactions between the organic counter-cation sand inorganic anions is observed.

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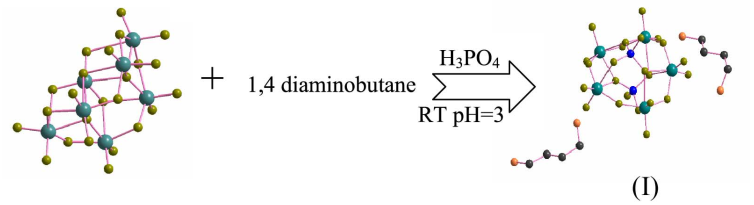
Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.005 Å
R factor = 0.027
wR factor = 0.075
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Phophomolybdates with the anionic group $[Mo_5P_2O_{23}]$ were initially described by Strandberg (1973). The basic structure consists of edge- and corner-sharing MoO_6 octahedra, forming an Mo_5O_{15} ring capped by PO_4 tetrahedra. Several workers (Müller *et al.*, 1998; Pope & Müller, 1994, 1991) have contributed to the significant growth of the structural aspects of polyoxomolybdates, phosphomolybdates and organophosphonates by the templating effect of various structure-directing organic molecules. We have been investigating the formation of several fully oxidized and reduced molybdate and phosphomolybdate structures from aqueous solution in the presence of tetramethylammonium, hexamethylenetetramine, morpholine, 1,3,5-triazine and triethanolamine (Duraisamy *et al.*, 1999). In order to rationalize the influence of dinitrogen organic molecules on the structures of hybrid solids based on polyoxomolybdates, a series of systematic reactions were performed under self-assembly conditions by the acidification of aqueous ammonium molybdate solution



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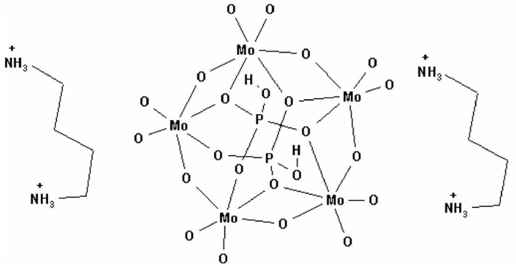

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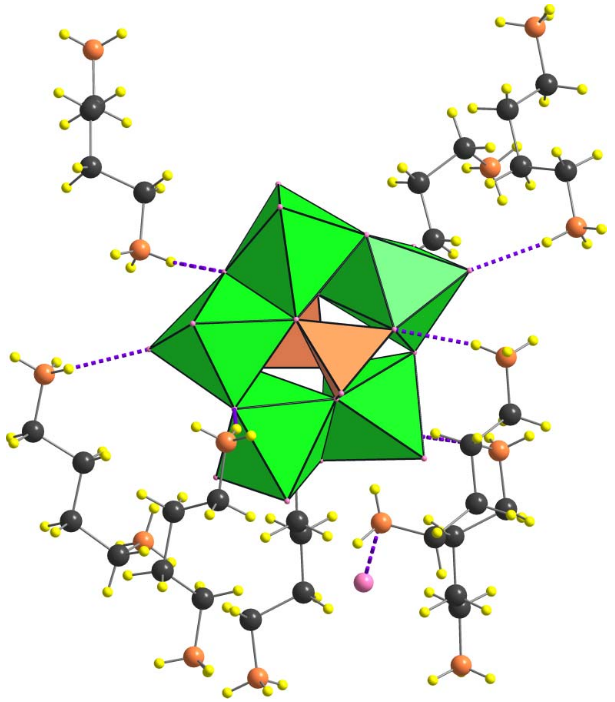

Figure 1
Polyhedral view of the diphosphopentamolybdate cluster and its hydrogen-bond interactions (dashed lines) with the butane-1,4-diammonium cations and water molecules.

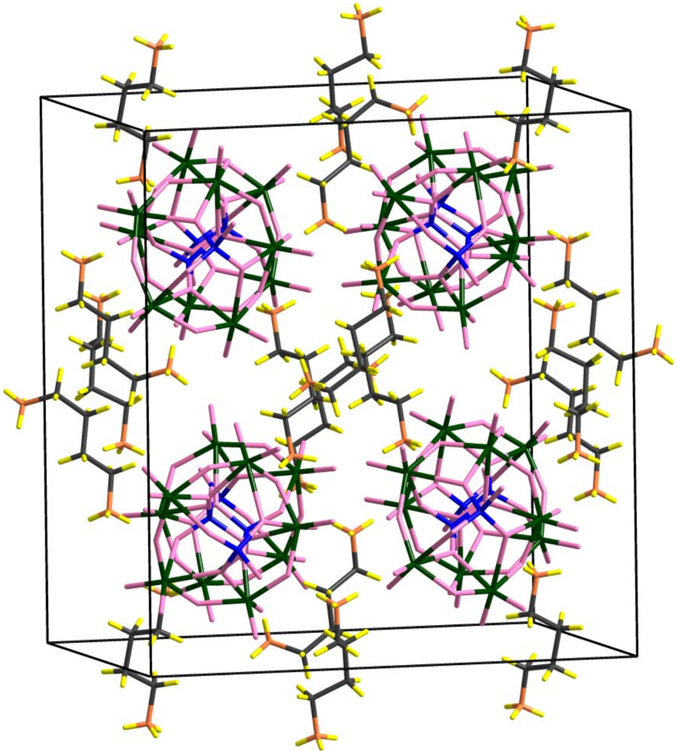

Figure 2
The packing arrangement of (I).

using H_3PO_4 in the presence of several dinitrogen organic molecules. During our investigation, we observed the formation of the title compound in the presence of 1,4-diaminobutane.

Single-crystal X-ray analysis shows that the title compound contains the anion $[Mo_5O_{15}(HPO_4)_2]^{4-}$. The cluster anion possesses the basic structural unit Mo^5O^{15}, capped by two HPO_4 tetrahedra as reported by Strandberg (1973). The two diprotonated butane-1,4-diammonium ions, $[NH_3C_4H_8NH_3]^{2+}$, provide charge compensation to the cluster anions and hold them through electrostatic interaction. Of the two diprotonated organic cations, one is involved in hydrogen bonding with a cluster O atom, while the other exhibits hydrogen bonding with both a cluster O atom and the water molecule (Fig. 1). An interesting structural feature of the title compound is the way the counter-cations and inorganic fragments are packed in the unit cell. A perspective view of the packing is shown in Fig. 2.

Experimental

A colorless aqueous solution was obtained from a mixture of ammonium heptamolybdate (0.676 g, 4 mmol) and 1,4-diaminobutane (0.352 g, 4 mmol). The pH of the solution was adjusted to ~3 by the addition of orthophosphoric acid (85%) and the solution was then heated in a microwave oven for 2 min for complete dissolution. Colorless prismatic crystals of the title compound (~0.823 g) appeared after 4 d.

Crystal data

$(C_4H_{14}N_2)_2[Mo_5O_{15}(H_2PO_4)_2]\cdot H_2O$
$M_r = 1110.02$
Orthorhombic, *Pbca*
$a = 19.4776$ (16) Å
$b = 14.0453$ (11) Å
$c = 21.1035$ (17) Å
$V = 5773.3$ (8) Å^3
$Z = 8$
$D_x = 2.554$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8918 reflections
$\theta = 2.4$–$28.3°$
$\mu = 2.33$ mm^{-1}
$T = 273$ (2) K
Block, colorless
0.35 × 0.20 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.571$, $T_{max} = 0.752$
41 302 measured reflections

5372 independent reflections
5289 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 25.5°$
$h = -23 \rightarrow 23$
$k = -16 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.075$
$S = 1.28$
5372 reflections
420 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 6.1694P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -1.42$ e Å^{-3}

H atoms were located in a difference Fourier map and then constrained in the refinement (N—H = 0.83–0.98 Å, O—H = 0.82–1.0 Å and C—H = 0.85–1.05 Å). The deepest hole in the difference map was located 0.55 Å from atom Mo3.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998) and *DIAMOND* (Klaus, 1999); software used to prepare material for publication: *SHELXTL*.

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