

Bis(ethylenediammonium) di- μ_5 -hydrogen-phosphato-penta- μ_2 -oxo-decaoxopentamolybdenum

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Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.022

wR factor = 0.045

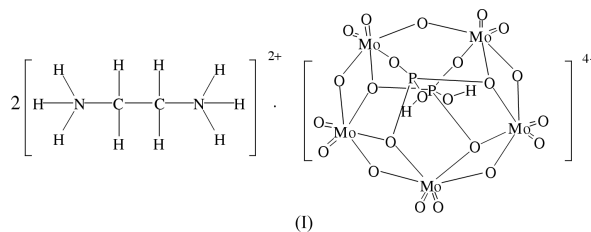
Data-to-parameter ratio = 16.1

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

The title compound, $(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]$, consists of $[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]^{4-}$ clusters with one Mo and one O atom located on a twofold rotation axis linked to $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+}$ ions. The $[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]^{4-}$ anion consists of five edge-sharing or corner-sharing MoO_6 octahedra, which adopt distorted octahedral geometry, and two corner-sharing PO_4 tetrahedra. The anion clusters are connected by hydrogen bonds with $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+}$.

Comment

Since the mid-1990s, organic-inorganic hybrid compounds have become a significant area of research for chemists, on account of their pronounced structural diversity and controllability of their chemical and physical properties (Hagrman *et al.*, 1999; Khan *et al.*, 1999). In addition, the potential applications of this type of compound in catalysis (Smith, 1988; Occelli & Robson, 1989), new functional materials (Kresge *et al.*, 1992) and biochemistry (Mann, 1993) *etc.*, have attracted much attention from materials scientists and biological chemists. A class of metal oxide clusters based on an anionic molybdenum phosphate framework has received much attention as a consequence of their potential applications in catalysis and materials science (Chen Qin & Hill, 1996). In the past few years, we have obtained several polyoxomolybdenum-phosphates, such as $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_{2.5}[\text{Mo}_5\text{O}_{15}(\text{PO}_4)(\text{HPO}_4)] \cdot 7.5\text{H}_2\text{O}$ (Lin Zhengzhong *et al.* 2002) and $\text{Na}_4 \cdot (\text{H}_3\text{O})[\text{Na}(\text{HPO}_4)_2(\text{PO}_4)_4\text{Mo}_{18}\text{O}_{49}] \cdot 16\text{H}_2\text{O}$ (Lin Zhengzhong *et al.* 2001). We have now synthesized a new compound, $(\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3)_2[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]$.



As shown in Fig. 1, the crystal structure comprises two ethylenediammonium and one $[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]^{4-}$ anion. The anion clusters are connected by extensive intermolecular hydrogen bonds involving $[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+}$. The $[\text{Mo}_5\text{O}_{15}(\text{HPO}_4)_2]^{4-}$ cluster anion can be described as a puckered ring of five edge-sharing or corner-sharing distorted $[\text{MoO}_6]$ octahedra, with two capping $[\text{HPO}_4]$ tetrahedra on each side. The five Mo atoms are coplanar. As a result of interatomic repulsion, each Mo centre displays typically

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distorted octahedral coordinations to their O-atom neighbours, with two short molybdenyl Mo=O bonds in a *cis* configuration, two long Mo—O bonds *trans* to the short bonds, and two Mo—O bonds of intermediate length. Bond-valence sum (BVS) calculations show that the Mo atom exhibits a BVS of +6. In the PO₄ tetrahedron, one of the P—O bonds is longer, which is ascribed to the P—O—H contact. The remaining three O atoms of each PO₄ are shared with five MoO₆ as common corners; thus one of the three O atoms is μ_2 -O and the other two are μ_3 -O. In the building block, each [Mo₅O₁₅(HPO₄)₂]⁴⁻ cluster is linked to two [H₃N(CH₂)₂NH₃]²⁺. The [Mo₅O₁₅(HPO₄)₂]⁴⁻ clusters are connected by [H₃N(CH₂)₂NH₃]²⁺ through hydrogen bonds to form a layer. Within the layer lie many irregular tunnels occupied by ethylenediamine. Here, the addition of the organic template ethylenediamine does not only play a structure-directing role, but also supplies charge-compensating cations; this is not a unique phenomena in the synthesis of organic-inorganic hydrid organodiamine molybdenum oxides.

Experimental

A mixture of Ti(SO₄)₂ (0.4 g, 1.67 mmol), Na₂MoO₄·2H₂O (0.6 g, 2.48 mmol), Mo (0.05 g, 0.52 mmol), H₂N(CH₂)₂NH₂ (0.2 ml, CR) and H₃PO₄ (0.5 ml, AR) in H₂O (4 ml) was sealed in a 20 ml Teflon-lined stainless steel vessel and heated at 423 K for 4 d under autogeneous pressure. After the reaction was complete, the vessel was cooled slowly to room temperature and green crystals were produced.

Crystal data

| | |
|-----------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| (C ₂ H ₁₀ N ₂) ₂ [Mo ₅ O ₁₅ (HPO ₄) ₂] | $D_x = 2.828 \text{ Mg m}^{-3}$ |
| $M_r = 1035.90$ | Mo $K\alpha$ radiation |
| Monoclinic, $C2/c$ | Cell parameters from 25 reflections |
| $a = 17.6993 (10) \text{ \AA}$ | $\theta = 12\text{--}18^\circ$ |
| $b = 10.0639 (8) \text{ \AA}$ | $\mu = 2.75 \text{ mm}^{-1}$ |
| $c = 13.7659 (10) \text{ \AA}$ | $T = 298 (2) \text{ K}$ |
| $\beta = 97.1240 (16)^\circ$ | Block, green |
| $V = 2433.1 (3) \text{ \AA}^3$ | $0.18 \times 0.16 \times 0.16 \text{ mm}$ |
| $Z = 4$ | |

Data collection

| | |
|--------------------------------------|----------------------------------------|
| Rigaku Weissenberg IP diffractometer | 2245 reflections with $I > 2\sigma(I)$ |
| ω - 2θ scans | $\theta_{\text{max}} = 27.5^\circ$ |
| 2782 measured reflections | $h = 0 \rightarrow 22$ |
| 2782 independent reflections | $k = 0 \rightarrow 13$ |
| | $l = -17 \rightarrow 17$ |

Refinement

| | |
|---------------------------------|------------------------------------------------------|
| Refinement on F^2 | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.022$ | $w = 1/[\sigma^2(F_o^2) + (0.0136P)^2]$ |
| $wR(F^2) = 0.045$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.00$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 2782 reflections | $\Delta\rho_{\text{max}} = 1.33 \text{ e \AA}^{-3}$ |
| 173 parameters | $\Delta\rho_{\text{min}} = -0.93 \text{ e \AA}^{-3}$ |

All H atoms were positioned geometrically and fixed.

Data collection: *TEXRAY* (Molecular Structure Corporation, 1999); cell refinement: *TEXRAY*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve

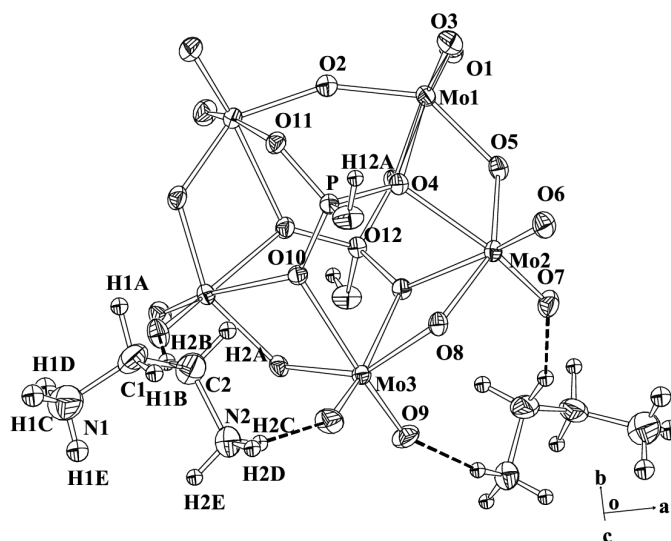


Figure 1

A perspective view of the crystal structure. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. Hydrogen bonds are shown as dashed lines.

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

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