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Bis[benzidinium(1−)] pentamolybdate

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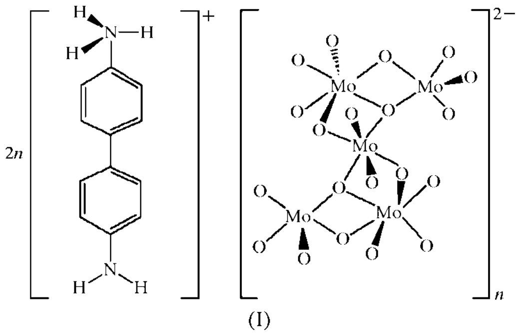
The title compound, $\{(C_{12}H_{13}N_2)_2[Mo_5O_{16}]\}_n$, was synthesized under hydrothermal conditions. The structure contains a two-dimensional layer, constructed from $[(Mo_4O_{14})_n]^{4n-}$ chains linked through MoO_6 octahedra, which lie across twofold axes. The $[(Mo_4O_{14})_n]^{4n-}$ chain consists of $[Mo_4O_{14}]^{4-}$ clusters connected to one another by sharing their MoO_5 square-pyramidal and MoO_6 octahedral vertices in an *anti* disposition. The layers are linked by the cation, to which they are connected *via* N—H···O hydrogen bonds.

Comment

From a structural point of view, Mo atoms are easy to condense into clusters, such as Mo_2O_6 (Quintal & Nogueira, 2001), Mo_4O_{13} (Hagrman & Zubieta, 1998), Mo_5O_{15} (Burkholder & Zubieta, 2001; Finn & Zubieta, 2001), Mo_6O_{19} (Strong *et al.*, 2000; Wang *et al.*, 2003), Mo_7O_{22} (Zapf *et al.*, 1997) and Mo_8O_{26} (Hagrman & Zubieta, 1999), up to giant polyoxomolybdates from the 'basket' Mo_{116} anion (Müller, Polarz & Das, 1999) to the capped cyclic Mo_{248} anion (Müller, Shah & Bögge, 1999). Polymolybdates are thus amongst the most complex compounds containing oxide polyanions, this complexity being a result of the flexible coordination of molybdenum, for example, fourfold (MoO_4, tetrahedron), fivefold (MoO_5, square pyramid) or sixfold (MoO_6, octahedron). Inorganic frameworks constructed from Mo/O polyhedra and exhibiting discrete structures, one-dimensional chains (Xu *et al.*, 2003), two-dimensional layers (Calin & Sevov, 2003) or three-dimensional open structures (Wu & Lu, 2002) have been reported recently.



(I)

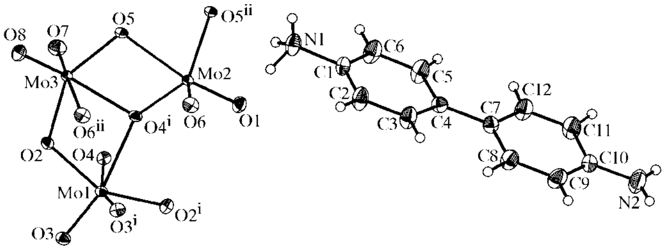


Figure 1
The molecular components of the title compound, with the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, 1 - y, 1 - z$.]

However, the structural design of organic–inorganic hybrid materials based on molybdenum oxides remains a challenge in solid-state chemistry. One approach to the design of novel materials is the introduction of organic molecules as structure-directing components to change the inorganic microstructure. As a continuation of our attempts to construct new molybdates using common Mo/O clusters as fundamental building blocks, we recently demonstrated the strategy in the design of the new compound $(C_{12}H_{13}N_2)_2[Mo_5O_{16}]$, (I), containing monoprotonated benzidine. Although a large number of organodiamines have been used as structure-directing components in the design of organic–inorganic hybrid materials, to the best of our knowledge, this is the first time that benzidine has been used.

The title compound is composed of $C_{12}H_{13}N_2^{+}$ cations and $[Mo_5O_{16}]^{2-}$ anions (Fig. 1). There are three kinds of crystallographically independent molybdenum sites in the Mo_5O_{16} polyoxomolybdate unit. The Mo1 octahedron is completed by two doubly bridging O atoms, two μ_3-O atoms and two

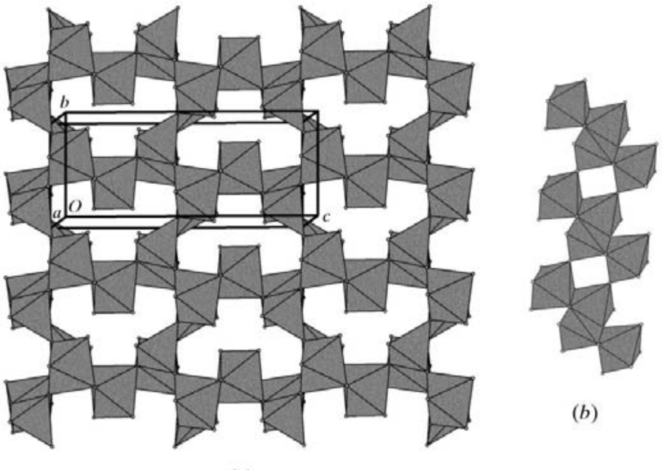


Figure 2
(*a*) The structure of the two-dimensional layer, viewed down the *b* axis, and (*b*) a view of the structure of the $[(Mo_4O_{14})_n]^{4n-}$ chains.

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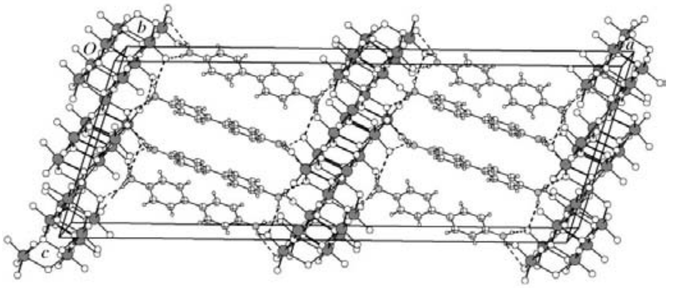

Figure 3
A packing diagram of the title compound, viewed down the *b* axis, showing N—H···O hydrogen bonds. The broken lines indicate hydrogen-bonding interactions.

terminal O atoms, with Mo1—O bond distances in the range 1.7167 (15)–2.2445 (14) Å and O—Mo1—O bond angles in the range 90.58 (6)–147.71 (9). The Mo2 square pyramid involves three μ_3-O atoms and two terminal O atoms, with Mo2—O bond distances in the range 1.7056 (16)–2.1936 (14) Å and O—Mo2—O bond angles in the range 102.93 (8)–157.16 (7). The Mo3 octahedron involves two μ_3-O atoms, two terminal O atoms and two doubly bridging O atoms, with Mo3—O bond distances in the range 1.6877 (16)–2.4800 (16) Å and O—Mo3—O bond angles in the range 98.14 (7)–144.11 (6) (Table 1).

The structure contains a two-dimensional layer, which is constructed from molybdenum oxide chains, $[(Mo_4O_{14})_n]^{4n-}$, linked through MoO_6 octahedra (Fig. 2*a*). The Mo1 atoms lie on twofold axes, and the $[(Mo_4O_{14})_n]^{4n-}$ chains lie on each side of the Mo1 octahedron and are connected to it through edge-sharing modes. The $[(Mo_4O_{14})_n]^{4n-}$ chain is composed of $[Mo_4O_{14}]^{4-}$ clusters, which can be described in terms of binuclear Mo_2O_8 subunits of edge-sharing MoO_5 square pyramids and MoO_6 octahedra, linked through corner-sharing of oxo groups in an *anti* disposition (Fig. 2*b*).

The benzidine cations participate in a number of N—H···O hydrogen bonds (Table 2) and the cations thereby link adjacent sheets, so forming a pillared-layer framework (Fig. 3).

Additionally, there is a π–π stacking interaction between near-parallel benzidine molecules at (x, y, z) and $(-\frac{1}{2} - x, -\frac{1}{2} - y, z)$; the ring separation is *ca* 3.48 (3) Å, which is close to the sum of the van der Waals radii of two C atoms (Bondi, 1964).

Experimental

Compound (I) was synthesized under hydrothermal conditions. A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.309 g, 0.25 mmol), $CdCl_2\cdot 2.5H_2O$ (0.144 g, 0.50 mmol), benzidine (0.069 g, 0.375 mmol) and H_2O (10 ml) was stirred mechanically at room temperature in air at pH 5.0. The mixture was then transferred to and sealed in a 37.5 ml Teflon-lined reactor and heated at 443 K for 3 d. After cooling to room temperature, red prismatic crystals were isolated. The IR spectrum of (I) exhibits characteristic bands at 3368 and 1497 cm^{-1} for the terminal N—H (NH_3) stretch and at 3660–3382 cm^{-1} for the O—H stretch. The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern based on the present crystal structure, indicating the phase purity of the sample. Thermogravimetric analysis (TGA) was performed in air from 303 to 1273 K, with a heating rate of 10 K min^{-1}. The TGA of (I) exhibits no weight loss below 623 K; there is only one step (623–773 K) for loss of the organodiamine, where the weight loss is 33.3% (calculated 33.5%).

Crystal data

$(C_{12}H_{13}N_2)_2[Mo_5O_{16}]$
$M_r = 1106.19$
Monoclinic, $C2/c$
$a = 38.5070$ (3) Å
$b = 5.6800$ (3) Å
$c = 14.2961$ (8) Å
$\beta = 108.366$ (2)°
$V = 2967.6$ (2) Å^3
$Z = 4$
$D_x = 2.476$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4134 reflections
$\theta = 1.5$–28.3°
$\mu = 2.14$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.25 × 0.15 × 0.10 mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.687$, $T_{max} = 0.807$
11 442 measured reflections
3681 independent reflections
3535 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 28.3°$
$h = -48 \rightarrow 50$
$k = -7 \rightarrow 5$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.049$
$S = 0.90$
3681 reflections
274 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 12.9482P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mo1—O3	1.7167 (15)	Mo2—O5	2.1936 (14)
Mo1—O2	1.9572 (14)	Mo3—O7	1.6877 (16)
Mo1—O4	2.2445 (14)	Mo3—O8	1.7177 (15)
Mo2—O6	1.7056 (16)	Mo3—O2	1.9155 (14)
Mo2—O1	1.7094 (15)	Mo3—O5	1.9933 (14)
Mo2—O4^{i}	1.8669 (14)	Mo3—O4^{i}	2.1514 (14)
Mo2—O5^{ii}	1.9606 (14)	Mo3—O6^{iii}	2.4800 (16)
O3—Mo1—O2	95.16 (6)	O1—Mo2—O5	157.16 (7)
O2—Mo1—O2^{i}	147.71 (9)	O7—Mo3—O2	101.91 (7)
O3—Mo1—O4	90.58 (6)	O8—Mo3—O5	98.14 (7)
O6—Mo2—O1	102.93 (8)	O2—Mo3—O5	144.11 (6)
O1—Mo2—O4^{i}	103.07 (7)		

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···O8^{iv}	0.85 (4)	2.26 (4)	3.043 (3)	155 (4)
N1—H1C···O2^{v}	0.86 (3)	1.95 (3)	2.797 (3)	168 (3)
N1—H1A···O1	0.96 (3)	1.92 (3)	2.816 (3)	153 (3)
N1—H1A···O7^{i}	0.96 (3)	2.59 (3)	3.289 (3)	130 (2)
N2—H2A···O7^{vi}	0.868 (19)	2.42 (3)	3.147 (3)	142 (4)
N2—H2A···O8^{vi}	0.868 (19)	2.56 (3)	3.289 (3)	142 (4)
N1—H1B···O8^{ii}	0.81 (5)	2.41 (5)	3.037 (3)	135 (4)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $-x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $-x, y - 1, \frac{1}{2} - z$; (vi) $x - \frac{1}{2}, -\frac{1}{2} - y, z - \frac{1}{2}$.

All the H atoms were clearly visible in difference maps and their positional and displacement parameters were refined independently, giving C—H distances of 0.86 (3)–0.95 (3) Å and N—H distances of 0.81 (5)–0.96 (3) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1318). Services for accessing these data are described at the back of the journal.

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