Bis(3,5-dimethylpyrazolium) bis(hydroxonium) β-octamolybdate(VI) ethanol disolvate

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The title compound, $(C_5H_9N_2)_2(H_3O)_2[Mo_8O_{26}]\cdot2C_2H_6O$, consists of centrosymmetric β-$Mo_8O_{26}^{4-}$ anions, 3,5-dimethylpyrazolium cations, H_3O^+ cations and ethanol solvent molecules, linked through hydrogen bonding into a two-dimensional network.

Comment

The structures of many compounds containing octamolybdate anions and organic cations have been investigated (Gili *et al.*, 1992; Xu *et al.*, 1999; Rarig *et al.*, 2001). One subset of these are β-octamolybdate anions combined with organic *N*-heterocyclic cations, including piperidinium (Xu *et al.*, 1994), imidazolium (Gili *et al.*, 2000), 2-ethylpyridinium (Roman *et al.*, 1982) and 3-methylpyridinium (Roman *et al.*, 1983). To date, only one structure of the γ-octamolybdate polyanion combined with pyrazolium cations has been reported, in which the cation is coovalently bound to an Mo atom (Gili *et al.*, 1999). Here, we report the synthesis and structure of the title compound, (I), by the reaction of $MoO_2(acac)_2$ (acac = acetylacetonate, $C_5H_7O_2^-$) and 3,5-dimethylpyrazole in ethanol–water solution.

(I)
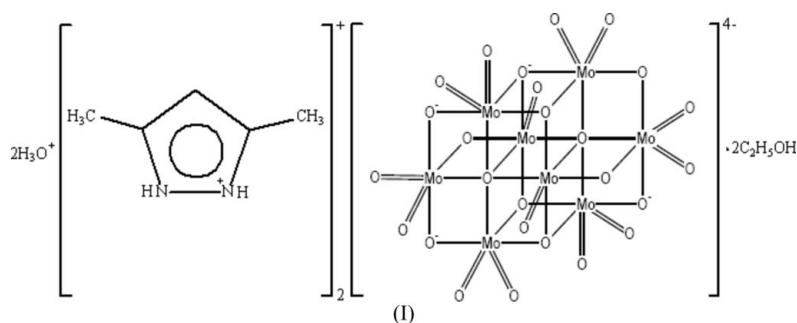
As illustrated in Fig. 1, compound (I) contains centrosymmetric $[Mo_8O_{26}]^{4-}$ anions, and 3,5-dimethylpyrazolium and hydroxonium cations, as well as ethanol solvent molecules. The octamolybdate anions show the β-configuration, which can be bisected into two $[(\mu_5$-O)$(Mo_4O_{12})]^{2-}$ subunits built up about a centre of symmetry. The Mo—O bond distances (Table 1) and angles for (I) fall within their expected ranges (Wang *et al.*, 1999).

The hydroxonium atom O1*W* and the terminal atoms O9 and O13 form intermolecular hydrogen bonds, with the O···O distances and O—H···O angles falling in the ranges 2.773 (4)–3.025 (4) Å and 116 (4)–158 (4)°, respectively (Table 2). The acute O—H···O angles correlate with bifurcated hydrogen bonds. The hydrogen-bonding network is completed by the 3,5-dimethylpyrazolium cations and ethanol molecules, to give a two-dimensional network (Fig. 2).
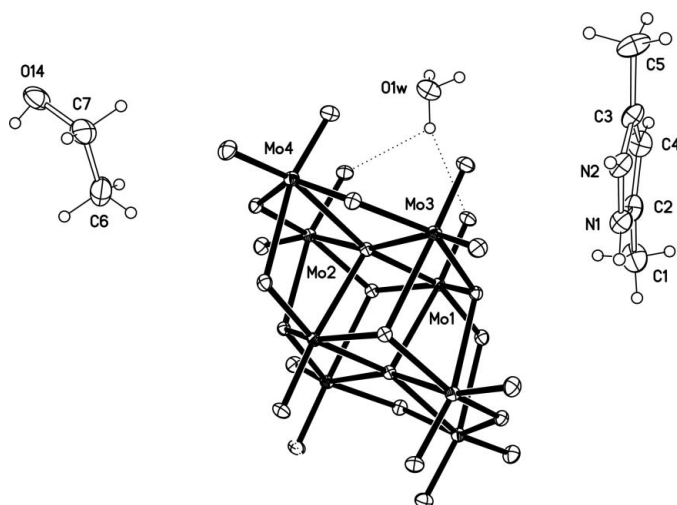
Figure 1
A view of (I), showing 30% probability displacement ellipsoids and arbitrary spheres for H atoms. Hydrogen bonds are indicated by dashed lines. The inversion centre at the central point of the octamolybdate anion generates the unlabelled atoms by the symmetry operation $(1 - x, 2 - y, 1 - z)$.

Figure 2
A packing diagram for (I), viewed along the c axis, with the octamolybdate anions shown as polyhedra. The O—H···O hydrogen bonds are denoted by dashed lines and H atoms not involved in hydrogen bonding have been omitted.

Experimental

An ethanol solution (15 ml) of $MoO_2(acac)_2$ (2 mmol) was added dropwise to an aqueous solution (15 ml) containing 3,5-dimethyl-pyrazole (2 mmol). The resulting mixture was refluxed with stirring for 1.5 h, and then cooled slowly to room temperature and filtered. Brown prismatic crystals of (I) were obtained from the solution after several days. Analysis, calculated for $C_{14}H_{36}N_4O_{30}Mo_8$: C 11.15, H 2.41, N 3.72%; found: C 11.19, H 2.44, N 3.75%.
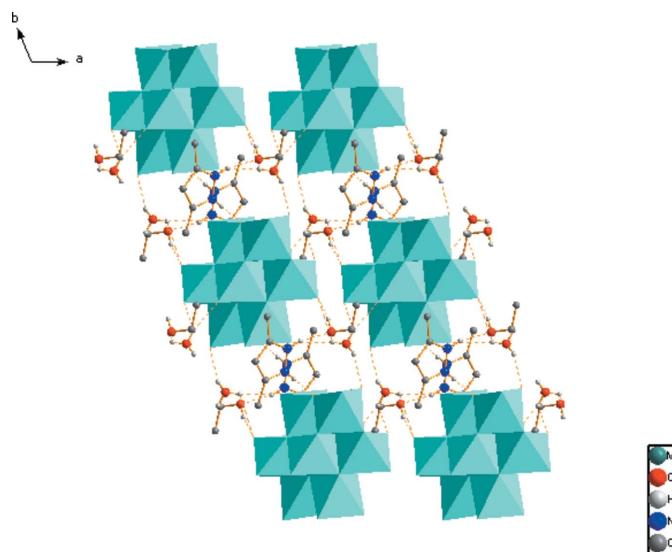
Crystal data

$(C_5H_9N_2)_2(H_3O)_2[Mo_8O_{26}]\cdot 2C_2H_6O$	$Z = 1$
$M_r = 1507.99$	$D_x = 2.547$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.9910$ (18) Å	Cell parameters from 9165
$b = 10.475$ (2) Å	reflections
$c = 11.441$ (2) Å	$\theta = 3.1–27.5°$
$\alpha = 93.72$ (3)°	$\mu = 2.57$ mm^{-1}
$\beta = 97.55$ (3)°	$T = 295$ (2) K
$\gamma = 111.96$ (3)°	Prism, brown
$V = 983.0$ (4) Å^3	$0.36 \times 0.25 \times 0.18$ mm

Data collection

Rigaku RAXIS-RAPID diffractometer	4427 independent reflections
	3936 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.016$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$\theta_{max} = 27.5°$
$T_{min} = 0.462$, $T_{max} = 0.635$	$h = -11 \rightarrow 11$
9637 measured reflections	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$+ 1.8158P]$
$wR(F^2) = 0.062$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
4427 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
274 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected bond distances (Å).

Mo1—O4	1.742 (2)	Mo3—O2	1.697 (2)
Mo1—O7	2.157 (2)	Mo3—O6	1.911 (2)
Mo1—O7^i	2.365 (2)	Mo3—O7	2.327 (2)
Mo1—O9	1.691 (2)	Mo3—O10	1.981 (2)
Mo1—O10	1.953 (2)	Mo3—O11^i	2.342 (2)
Mo1—O11	1.944 (2)	Mo3—O12	1.701 (2)
Mo2—O5	1.901 (2)	Mo4—O1	1.686 (3)
Mo2—O7	2.334 (2)	Mo4—O3	1.711 (3)
Mo2—O8	1.702 (2)	Mo4—O4^i	2.294 (2)
Mo2—O10^i	2.338 (2)	Mo4—O5	1.898 (2)
Mo2—O11	1.979 (2)	Mo4—O6	1.942 (2)
Mo2—O13	1.697 (2)	Mo4—O7	2.433 (2)

Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1W1···O13	0.85 (3)	2.29 (4)	2.773 (4)	116 (4)
O1W—H1W1···O9	0.85 (3)	2.21 (2)	3.025 (4)	158 (4)
O1W—H1W2···O3^{ii}	0.85 (4)	2.11 (4)	2.914 (4)	157 (4)
O1W—H1W3···O2^{iii}	0.85 (4)	2.22 (5)	3.044 (4)	161 (5)
O14—H14···O8^{iv}	0.85 (4)	1.84 (3)	2.654 (4)	159 (7)
N1—H1···O14^v	0.86 (4)	1.85 (4)	2.693 (6)	166 (6)
N2—H2···O6^{vi}	0.87 (5)	1.84 (5)	2.708 (4)	178 (5)

Symmetry codes: (ii) $-x, -y + 1, -z + 1$; (iii) $x - 1, y, z$; (iv) $-x, -y + 2, -z$; (v) $x + 1, y, z + 1$; (vi) $-x + 1, -y + 1, -z + 1$.

C-bound H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å, and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}$(methyl C). The H atoms of the hydroxonium O and pyrazolium N atoms were located in a difference map and refined, with O—H and N—H distance restraints of 0.85 (1) and 0.86 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O,N)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC,

2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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