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Key indicators

Single-crystal X-ray study
 T = 296 K
 Mean $\sigma(C-C)$ = 0.016 Å
 R factor = 0.047
 wR factor = 0.118
 Data-to-parameter ratio = 13.2

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

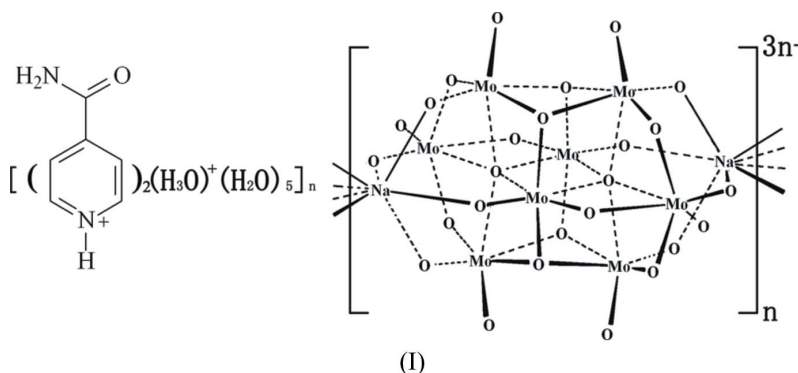
**Poly[bis(4-formamidopyridinium) hydronium
 hexacosaoxosodiooctamolybdate pentahydrate]**

The title compound, $\{(C_6H_7N_2O)_2(H_3O)[NaMo_8O_{26}] \cdot 5H_2O\}_n$, features centrosymmetric oxomolybdate anions $[Mo_8O_{26}]^{4-}$ (site symmetry $\bar{1}$). These are linked by Na^+ cations (site symmetry $\bar{1}$), yielding chains which are connected by hydrogen bonds into a three-dimensional network.

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Comment

Polyoxometalate clusters have attracted much attention for their intriguing structural features and potential application in catalysis, magnetism, medicinal chemistry and materials science (Hill, 1998; Coronado & Gomez-Garcia, 1998; Yamase, 1998). As for the syntheses of novel polyoxometalates, variation of the organic cation employed in the synthesis has been demonstrated as an efficient strategy. The introduction of organic cations can improve their properties. Among the reported syntheses of polyoxometalates, organic amide-containing ligands were rarely used, although organic amides have proved to be useful in forming supramolecular complexes with relevance to biological systems (Bhogala *et al.*, 2004; Qin *et al.*, 2003). Therefore, to enrich the family of organic amide-containing polyoxometalates, the title compound, (I), was successfully synthesized by choosing sodium molybdate and isonicotinamide (inta) as starting materials.



The structure determination revealed the formula $[(\text{Hinta})_2(H_3O)(NaMo_8O_{26})(H_2O)_5]_n$. The asymmetric unit consists of a sodium ion on an inversion centre, an $[Mo_4O_{13}]^{2-}$ subunit, a protonated isonicotinamide cation, a half-protonated water molecule and two additional molecules of water of crystallization (Fig. 1). Based on bond-valence sum calculations, the presence of H_3O^+ was assumed. The centrosymmetric $[Mo_8O_{26}]^{4-}$ anion consists of eight MoO_6 units. All Mo atoms within the $[Mo_8O_{26}]^{4-}$ clusters have distorted octahedral environments (Table 1). The O atoms within the

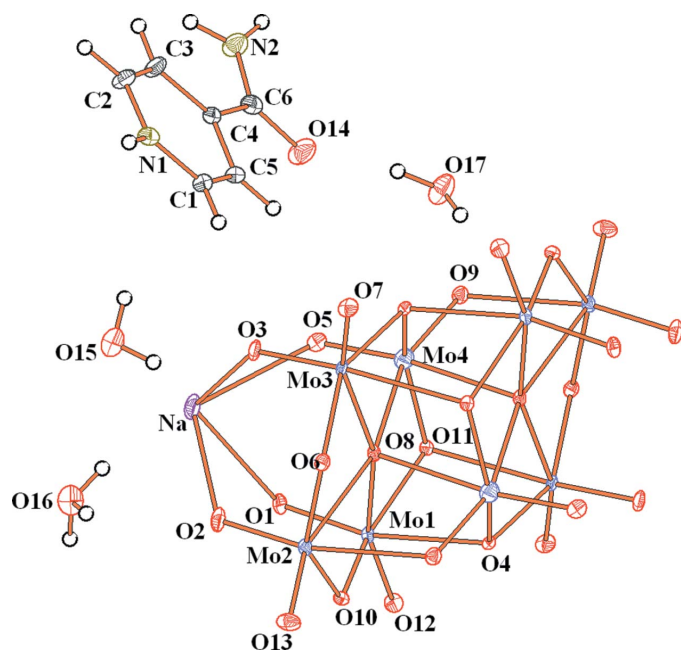


Figure 1
The contents of the structure. Displacement ellipsoids are drawn at the 30% probability level [unlabelled atoms related to labelled atoms by $(2-x, 1-y, 1-z)$].

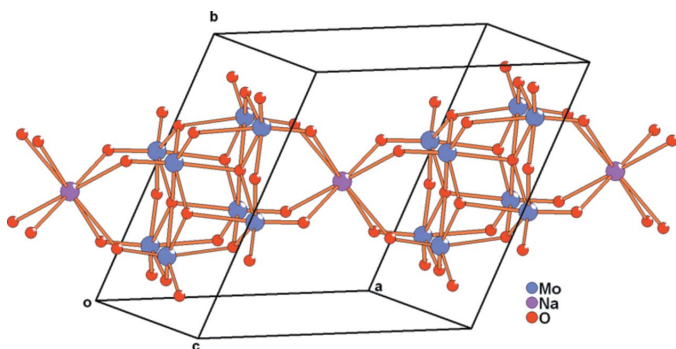


Figure 2
A view of the one-dimensional chain structure in the title compound.

$[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters can be divided into four sets according to their bonding feature, namely, terminal O atoms with Mo—O distances of 1.639 (6)–1.716 (6) Å, bi-bridging O atoms with Mo—O distances of 1.729 (6)–2.298 (5) Å, tri-bridging oxygen with Mo—O distances of 1.921 (6)–2.316 (5) Å, and penta-bridging oxygen with Mo—O distances of 2.212 (5)–2.425 (5) Å. All Mo—O bond distances are within the expected values. Bond valence sum calculations (Brown & Altermatt, 1985) showed that the oxidation state of all the Mo atoms is in the range 5.909–6.010, which agrees with the expected value of 6 for Mo atoms in the $[\text{Mo}_8\text{O}_{26}]^{4-}$ building block. The neighbouring $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters are connected by Na ions to form an infinite one-dimensional chain (Fig. 2). By hydrogen bonding between the clusters and the organic cations, a three-dimensional network is obtained (Fig. 3). The detailed hydrogen-bonding parameters are summarized in Table 2. Thus, the title compound can be considered as a three-

dimensional supramolecular complex stabilized by hydrogen-bonding interactions.

Experimental

All the analytically pure reagents and solvents were purchased from Siping Chemical Reagent Company and used without further purification. Na_2MoO_4 (1 g) was dissolved in a water/dimethylformamide (25 ml, 5:1) mixture with stirring. Isonicotinamide (0.12 g) was added to the transparent solution and the pH was adjusted to about 2.4 by adding 4 M HCl. The mixture was stirred at 333 K for about 1 h and then cooled to room temperature; the solution was filtered into a 50 ml beaker. Slow evaporation of the solvent at room temperature led to prismatic crystals of the title compound suitable for X-ray diffraction after one month.

Crystal data

$(\text{C}_6\text{H}_7\text{N}_2\text{O})_2(\text{H}_3\text{O})[\text{Mo}_8\text{NaO}_{26}] \cdot 5\text{H}_2\text{O}$
 $M_r = 1561.89$
 Triclinic, $P\bar{1}$
 $a = 9.2223$ (5) Å
 $b = 9.8307$ (5) Å
 $c = 11.7818$ (6) Å
 $\alpha = 87.1615$ (8)°
 $\beta = 74.7298$ (8)°

$\gamma = 63.9588$ (7)°
 $V = 923.14$ (8) Å³
 $Z = 1$
 $D_x = 2.809$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 2.76$ mm⁻¹
 $T = 296$ (2) K
 Prism, light yellow
 $0.26 \times 0.25 \times 0.16$ mm

Data collection

Bruker SMART APEX-II CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.442$, $T_{\max} = 0.605$
 (expected range = 0.467–0.640)

4918 measured reflections
 3537 independent reflections
 2925 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.118$
 $S = 1.06$
 3537 reflections
 268 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 17.5658P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.02$ e Å⁻³
 $\Delta\rho_{\min} = -2.54$ e Å⁻³

Table 1

Selected bond lengths (Å).

Mo1—O1	1.705 (5)	Mo3—O8	2.270 (5)
Mo1—O12	1.710 (6)	Mo3—O11 ⁱ	2.311 (5)
Mo1—O10	1.896 (5)	Mo4—O5	1.639 (6)
Mo1—O11	1.977 (5)	Mo4—O9	1.729 (6)
Mo1—O8	2.250 (5)	Mo4—O4 ⁱ	1.920 (5)
Mo1—O4	2.316 (5)	Mo4—O11	1.938 (5)
Mo2—O13	1.702 (6)	Mo4—O8	2.212 (5)
Mo2—O2	1.709 (6)	Mo4—O8 ⁱ	2.311 (5)
Mo2—O10	1.921 (6)	Na—O1 ⁱⁱ	2.466 (6)
Mo2—O6	1.925 (6)	Na—O1	2.466 (6)
Mo2—O9 ⁱ	2.298 (5)	Na—O5 ⁱⁱ	2.525 (6)
Mo2—O8	2.425 (5)	Na—O5	2.525 (6)
Mo3—O7	1.709 (6)	Na—O3	2.674 (6)
Mo3—O3	1.716 (6)	Na—O3 ⁱⁱ	2.674 (6)
Mo3—O6	1.904 (5)	Na—O2	2.874 (7)
Mo3—O4 ⁱ	1.984 (5)	Na—O2 ⁱⁱ	2.874 (7)

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$.

Table 2

 Hydrogen-bond geometry (\AA , $^\circ$).

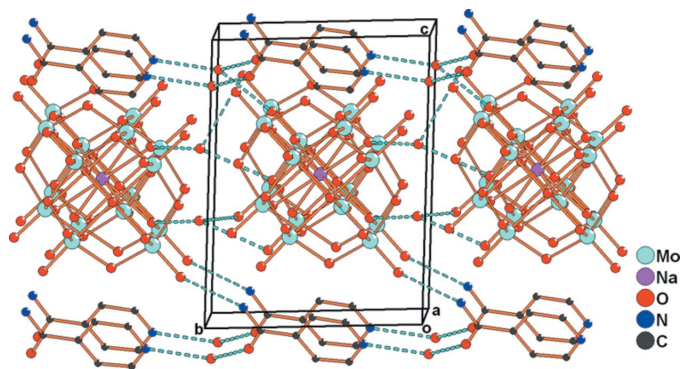
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O15-H1W\cdots O6^{iii}$	0.85	2.20	2.861 (9)	135
$O16-H3W\cdots O5^{ii}$	0.85	2.63	2.926 (10)	102
$O16-H5W\cdots O14^{ii}$	0.85	2.35	3.178 (13)	165
$O16-H3W\cdots O15$	0.85	2.31	2.891 (12)	126
$O16-H4W\cdots O7^{iii}$	0.85	2.22	2.933 (10)	142
$O16-H4W\cdots O12^{iv}$	0.85	2.30	2.978 (10)	138
$O17-H7W\cdots O9$	0.85	2.07	2.870 (10)	156
$N1-H1\cdots O17^{iv}$	0.86	1.84	2.700 (12)	177
$N2-H2N\cdots O12^v$	0.89	2.33	3.193 (11)	166
$N2-H1N\cdots O13^{vi}$	0.94	2.13	3.058 (11)	168

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

Carbon-bound H atoms were placed at calculated positions ($C-H = 0.93 \text{ \AA}$) and were allowed to ride on the carrier C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. All other H atoms were located in a Fourier map and refined in their as-found positions with a riding model with $U_{iso}(H) = 1.2U_{eq}(O,N)$. To balance the charge, the occupancy of H3W was assigned as 0.5. The highest peak and deepest hole are found close to Mo3 and Mo4, at distances of 0.28 and 0.42 \AA , respectively.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Figure 3

The three-dimensional supramolecular arrangement of the title compound. (Hydrogen bonds are displayed as dashed lines and all H atoms have been omitted.)

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