

## The novel chain-like anion $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$ in $(\text{Hmim})_3[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]$ (mim is 1-methylimidazole)

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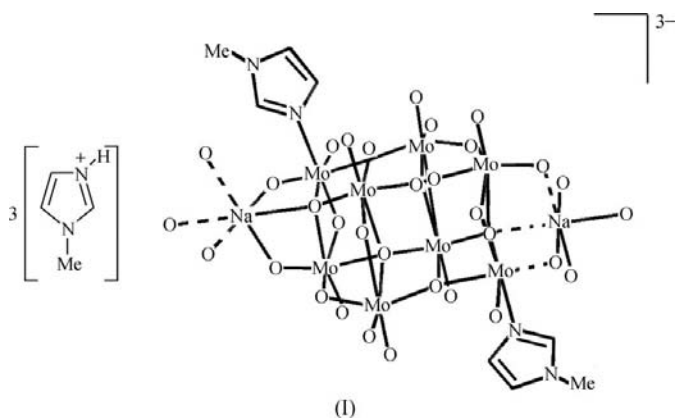
Tris(1-methylimidazolium) bis(1-methylimidazole)hexacosaoxidooctamolybdatesodium,  $(\text{C}_4\text{H}_7\text{N}_2)_3[\text{NaMo}_8\text{O}_{26}(\text{C}_4\text{H}_6\text{N}_2)_2]$ , prepared from an aqueous solution containing  $\text{Na}_2\text{MoO}_4$  and 1-methylimidazole, contains the novel chain-like anion  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$  (mim is 1-methylimidazole). The  $[\text{Mo}_8\text{O}_{26}(\text{mim})_2]^{4-}$  building unit, which lies across a center of inversion, is comprised of eight edge-sharing  $\text{MoO}_6$  and  $\text{MoO}_5(\text{N}_{\text{mim}})$  octahedra. These molybdate units are interlinked by sodium, itself exhibiting a sixfold coordination with O atoms.

### Comment

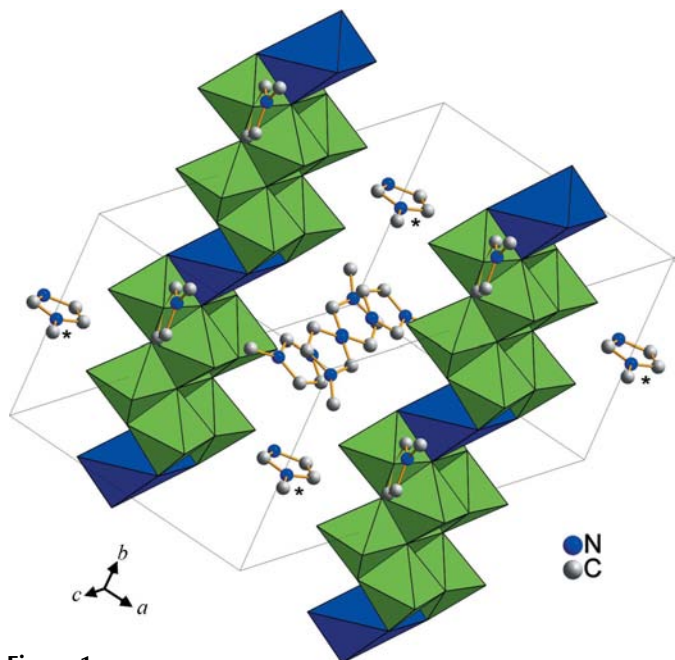
Polyoxometalates (POMs) are of particular interest because of their fascinating structures, properties and potential applications, such as catalysis, sorption and magnetism (Müller & Pope, 1991; Cheetham, 1994; Proust *et al.*, 2008). The class of materials is characterized by complex building units and a diverse chemical reactivity (Heyns *et al.*, 1991; Wang *et al.*, 1992). Molybdate-based POMs in particular have attracted a lot of attention since some of the largest inorganic clusters have been identified here, for instance,  $\text{Na}_{48}[\text{H}_x\text{Mo}_{368}\text{O}_{1032}(\text{H}_2\text{O})_{240}(\text{SO}_4)_{48}] \cdot x\text{H}_2\text{O}$ , with  $x \simeq 1000$  (Müller *et al.*, 2002). The fundamental building unit is quite often related to the well known octamolybdate  $[\text{Mo}_8\text{O}_{26}]^{4-}$ . With this study, we report a novel chain-like  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$  anion (mim is 1-methylimidazole) that is comprised of sodium-interlinked  $[\text{Mo}_8\text{O}_{26}(\text{mim})_2]^{4-}$  building units. Although alkali-metal-interlinked chains of octamolybdate units have already been identified (McCann *et al.*, 1994; Jia *et al.*, 1999; Chen *et al.*, 2005; Liu *et al.*, 2006; Yu *et al.*, 2008; Kobayashi *et al.*, 2009), the title compound, (I), when examined in detail shows some significant structural differences.

$(\text{Hmim})_3[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]$  contains the chain-like anion  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$ , which is oriented parallel to the

crystallographic *b* axis. The molybdate unit exhibits a center of inversion, resulting in only four crystallographically independent Mo sites. Between the chains, protonated methylimidazole is incorporated as the cation (Fig. 1). In detail, the



$\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$  ion is constituted of eight edge-sharing octahedra. The resulting  $[\text{Mo}_8\text{O}_{26}(\text{mim})_2]^{4-}$  units are interlinked by sodium cations to form extended chains. Here, sodium possesses sixfold coordination to the terminal O atoms of two molybdate units (Fig. 2).  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$ , or  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{N}_{\text{mim}})_2]^{3-}$  when only considering the coordinating N atom, can be compared firstly to the well-known  $\infty^1[\text{NaMo}_8\text{O}_{26}]^{3-}$  building unit (McCann *et al.*, 1994; Chen *et al.*, 2005; Liu *et al.*, 2006; Kobayashi *et al.*, 2009) and secondly to  $[\text{Mo}_8\text{O}_{28}]^{8-}$ . Both  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{N}_{\text{mim}})_2]^{3-}$  and  $\infty^1[\text{NaMo}_8\text{O}_{26}]^{3-}$  exhibit a chain-like interlinking of octamolybdate units via  $\text{Na}^+$  cations (Fig. 3). However, because of the different


**Figure 1**

The unit cell of  $(\text{Hmim})_3[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]$  with polyhedra indicating the chain-like anion  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$  (in the electronic version of the paper,  $\text{MoO}_6$  octahedra are green and  $\text{NaO}_6$  octahedra are blue). For clarity, H atoms have been omitted and the disordered 1-methylimidazolium units (indicated as \*) are shown in one position only.

stoichiometry, the (MoO<sub>6</sub>) octahedra in  $\infty^1[\text{NaMo}_8\text{O}_{26}]^{3-}$  show a higher degree of condensation. Moreover, the coordination between the octamolybdate units and sodium is different. This holds for the coordination number (sixfold and eightfold) as well as for the relative orientation of the octamolybdate unit inside the  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{N}_{\text{mim}})_2]^{3-}$  and  $\infty^1[\text{NaMo}_8\text{O}_{26}]^{3-}$  chains.  $[\text{Mo}_8\text{O}_{28}]^{8-}$ , which is also comparable to  $[\text{Mo}_8\text{O}_{26}(\text{N}_{\text{mim}})_2]^{4-}$  in the title compound, has been identified both in layer-type structures, with a direct Mo–O–Mo interlinking between the octamolybdate units (Evain *et al.*, 2006), and as an individual octamolybdate unit that is interlinked *via* hydrogen-bridge bonding only (Bharadwaj *et al.*, 1986; You *et al.*, 1989).

Regarding their coordination, the O atoms in  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$  can be divided into two types. First, one group of atoms is exclusively coordinated to molybdenum: ten terminal O atoms with bond distances (Mo–O<sub>μ</sub>) ranging from 1.700 (3) to 1.712 (4) Å; six atoms with twofold coordination and bond distances (Mo–O<sub>μ</sub>) in the range 1.746 (3)–2.394 (3) Å; two three-coordinated atoms with Mo–O<sub>μ</sub> = 1.934 (3) Å; and finally two four-coordinated atoms with Mo–O<sub>μ</sub> = 2.115 (3) Å. In the second group, the O atoms are coordinated to sodium as well as to molybdenum. Here, the ⟨Na–O⟩ distances average 2.377 (2) Å and the ⟨Mo–O<sub>Na</sub>⟩ distances average 1.729 (2) Å. All these distances, as well as the variation with increasing coordination number, are in agreement with literature data (Evain *et al.*, 2006; Bharadwaj

*et al.*, 1986; You *et al.*, 1989). Finally, two Mo centers are coordinated by 1-methylimidazole, resulting in an Mo–N bond length of 2.229 (9) Å, which is also in accordance with the literature (2.2–2.5 Å; Cotton & Ilsey, 1982; Brisdon & Woolf, 1978; Schrauzer *et al.*, 1982). On the basis of the composition of the compound, as well as with regard to coordination and bond distances, all Mo atoms exhibit an oxidation state of +6.

## Experimental

(Hmim)<sub>3</sub>[NaMo<sub>8</sub>O<sub>26</sub>(mim)<sub>2</sub>] was prepared from aqueous solutions containing water (5 ml), Na<sub>2</sub>MoO<sub>4</sub> (200 mg, 0.97 mmol) and 1-methylimidazole (1.2 ml). The resulting solution was stirred at room temperature with 30% H<sub>2</sub>O<sub>2</sub> (1.0 ml) added dropwise at 263 K. The resulting dark-red–brown solution was stirred for an additional 2–4 h. During this period, the color of the red–brown solution changed to light yellow. Finally, the solution was concentrated by evacuation and left for crystallization at room temperature. After a few weeks, rectangular transparent colorless crystals of the title compound were formed. A crystal suitable for crystal structure analysis was fixed on a glass filament and coated in perfluorinated oil (Kel-F).

### Crystal data

(C <sub>4</sub> H <sub>7</sub> N <sub>2</sub> ) <sub>3</sub> [NaMo <sub>8</sub> O <sub>26</sub> (C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> ) <sub>2</sub> ]	<i>V</i> = 2630.2 (9) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 1620.04	<i>Z</i> = 2
Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 11.692 (2) Å	<i>μ</i> = 1.95 mm <sup>−1</sup>
<i>b</i> = 10.298 (2) Å	<i>T</i> = 298 K
<i>c</i> = 22.190 (4) Å	0.4 × 0.2 × 0.2 mm
<i>β</i> = 100.12 (3)°	

### Data collection

Stoe IPDS II diffractometer	22631 measured reflections
Absorption correction: numerical ( <i>X-SHAPE</i> ; Stoe & Cie, 1999)	7219 independent reflections
<i>T</i> <sub>min</sub> = 0.393, <i>T</i> <sub>max</sub> = 0.528	5717 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.058

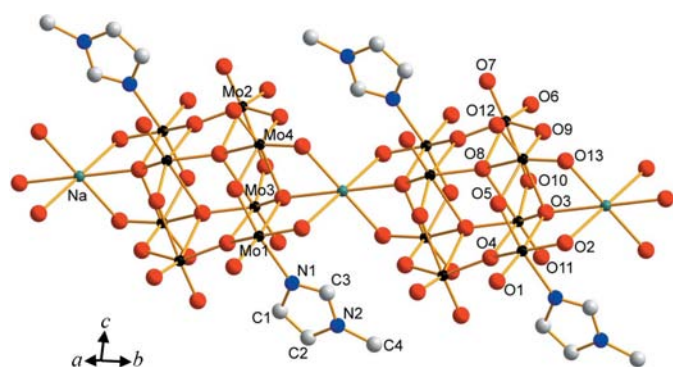
### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.040	378 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.095	H-atom parameters constrained
<i>S</i> = 0.97	Δ <i>ρ</i> <sub>max</sub> = 1.11 e Å <sup>−3</sup>
7219 reflections	Δ <i>ρ</i> <sub>min</sub> = −0.96 e Å <sup>−3</sup>

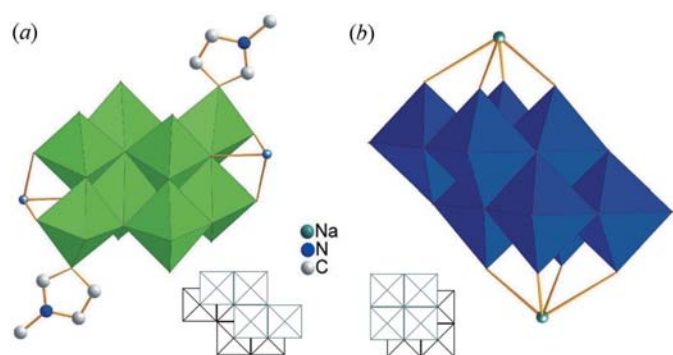
H atoms were positioned geometrically [C–H = 0.93–0.96 Å and N–H = 0.86 Å, and *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C,N)]. During structure refinement, one of the methylimidazolium cations was found to be disordered (Fig. 1). This was dealt with using split atom positions. When refining the relevant site-occupation factors, values near 0.5 were identified, and these site occupancies were subsequently fixed at 0.5.

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *pubCIF* (Westrip, 2009).

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**Figure 2**  
The chain-like anion  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{mim})_2]^{3-}$ .



**Figure 3**  
Scheme illustrating the different condensation, interlinking and Na<sup>+</sup> coordination in (a)  $\infty^1[\text{NaMo}_8\text{O}_{26}(\text{N}_{\text{mim}})_2]^{3-}$  and (b)  $\infty^1[\text{NaMo}_8\text{O}_{26}]^{3-}$ .

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3013). Services for accessing these data are described at the back of the journal.

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