

Bo Liu,\* Shi Zhou, Chuan-Bi Li  
and Hong-Gang ZhangDepartment of Chemistry, Jilin Normal  
University, Siping 136000, People's Republic of  
ChinaCorrespondence e-mail:  
boliu.chem@yahoo.com.cn

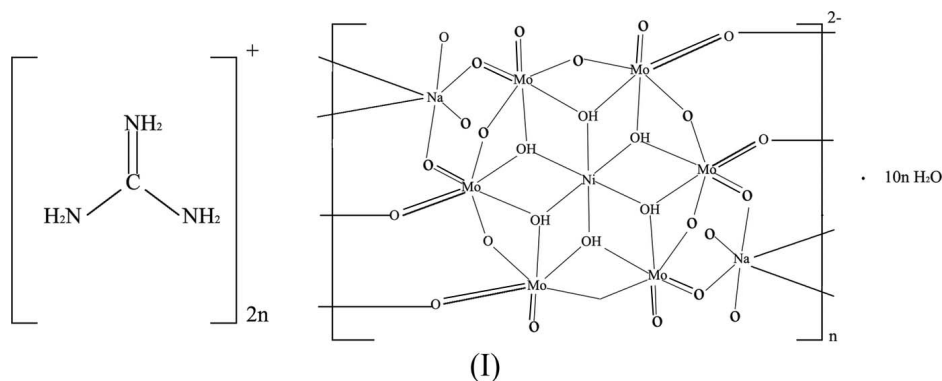
## Key indicators

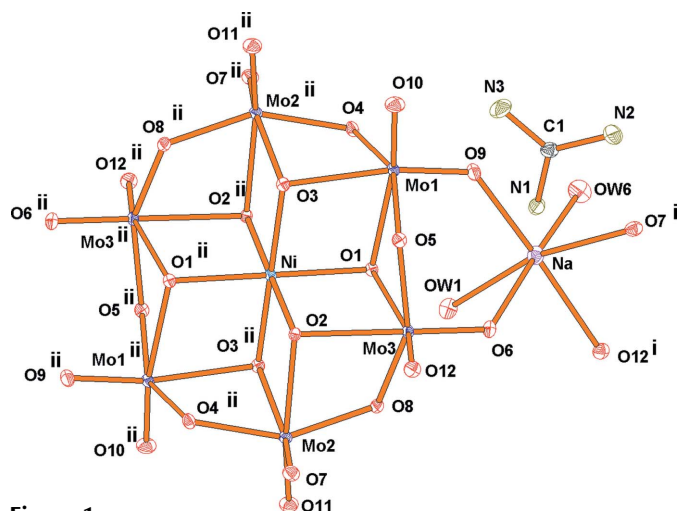
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{N}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.023  
 $wR$  factor = 0.060  
Data-to-parameter ratio = 15.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Bis(guanidinium) hexahydroxooctadeca-  
disodiohexamolybdonickelate decahydrateThe title compound,  $(\text{CH}_6\text{N}_3)_2[\text{Na}_2\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 10\text{H}_2\text{O}$ , features inversion-generated hexamolybdonickelate anions (Ni site symmetry  $\bar{1}$ ). The anions are linked by octahedrally coordinated  $\text{Na}^+$  cations into extended sheets. The guanidinium cations and uncoordinated water molecules link the sheets together *via*  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds to form a three-dimensional network. Two water molecule O atoms have site symmetry 2.

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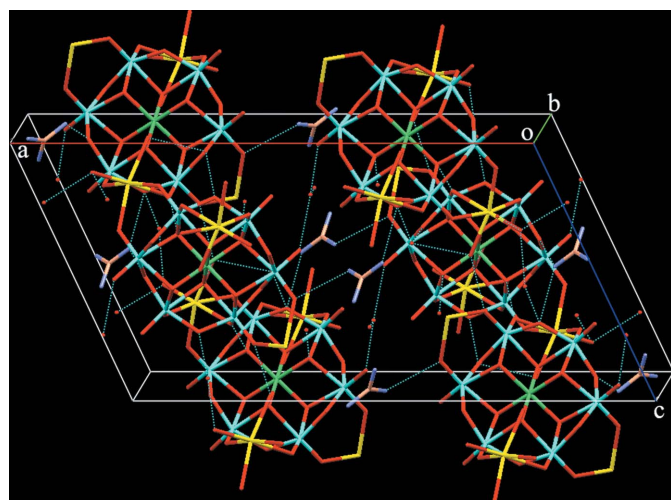
Accepted 27 October 2006

## Comment

Polyoxometallate (POM) clusters have attracted much attention due to their intriguing structural features and potential applications in catalysis, magnetism and materials science (Hill, 1998; Coronado & Gomez-Garcia, 1998; Yamase, 1998). Varying the inorganic or organic cation employed in the synthesis has been demonstrated as an efficient strategy for obtaining novel variants of this family. POMs accompanied by guanidinium cations have been reported for the hexamolybdochromate (Lee *et al.* 2003) system, but none has so far been reported with  $[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-}$  (Hasenknopf *et al.*, 2002).The title compound, (I), contains  $[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-}$  anionic clusters,  $\text{Na}^+$  cations, guanidinium cations and water molecules, as shown in Fig. 1. The anion lies on a centre of inversion and two water O atoms have site symmetry 2. The  $[\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{4-}$  cluster adopts a  $\beta$ -type Anderson structure, made up of seven edge-sharing octahedra, namely six  $\text{MoO}_6$  groups arranged hexagonally around the central  $\text{Ni}(\text{OH})_6$  octahedron (Ni site symmetry  $\bar{1}$ ). The Ni–O and Mo–O distances are in the ranges 2.021 (2)–2.049 (2) Å and 1.701 (2)–2.254 (2) Å, respectively (Table 1). Bond-valence sum calculations (Brown & Altermatt, 1985) indicate oxidation states of 5.91–6.02 for the Mo atoms and 1.89 for Ni, in agreement with the expected values of 6 and 2, respectively.



**Figure 1**  
A fragment of the polymeric structure of (I), showing the metal coordination polyhedra. Displacement ellipsoids are drawn at the 30% probability level. H atoms and uncoordinated water molecules have been omitted for clarity. [Symmetry codes: (i)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (ii)  $\frac{3}{2} - x, \frac{3}{2} - y, -z$ .]



**Figure 2**  
The packing of (I), with the donor...acceptor contacts for the hydrogen bonds shown as dotted lines. All H atoms have been omitted for clarity.

The Na<sup>+</sup> cation is bonded to four terminal O atoms from two neighbouring [Ni(OH)<sub>6</sub>Mo<sub>6</sub>O<sub>18</sub>]<sup>4-</sup> polyanions, and the other two sites are occupied by water molecules, to result in a *cis*-Na(H<sub>2</sub>O)<sub>2</sub>O<sub>4</sub> octahedron. Thus, the polyanions and Na<sup>+</sup> cations form a two-dimensional extended network. The guanidinium cations and isolated water molecules link the inorganic layers into a three-dimensional framework *via* hydrogen bonds (Table 2, Fig. 2).

### Experimental

Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (1 g, 4 mmol) was dissolved in aqueous NaOH solution (0.5 M, 25 ml) with stirring. NiSO<sub>4</sub>·6H<sub>2</sub>O (0.104 g, 0.4 mmol) and [C(NH<sub>2</sub>)<sub>3</sub>]<sub>3</sub>NO<sub>3</sub> (0.024 g, 0.2 mmol) were then added to the mixture and the pH was adjusted to about 2.7–2.8 using 4 M HCl. The

mixture was refluxed at 343 K for about 1 h and then cooled to room temperature. Slow evaporation of the solvent at room temperature led to prismatic crystals of (I) suitable for X-ray diffraction after three weeks.

### Crystal data

(CH<sub>6</sub>N<sub>3</sub>)<sub>2</sub>[Na<sub>2</sub>·Ni(OH)<sub>6</sub>Mo<sub>6</sub>O<sub>18</sub>]·10H<sub>2</sub>O  
*M<sub>r</sub>* = 1370.69  
 Monoclinic, C2/c  
*a* = 25.2247 (9) Å  
*b* = 11.6583 (4) Å  
*c* = 13.7668 (5) Å  
 $\beta$  = 114.918 (4)°

*V* = 3671.6 (3) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.480 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 $\mu$  = 2.62 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, green  
 0.28 × 0.24 × 0.18 mm

### Data collection

Bruker SMART APEXII CCD  
 area-detector diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2002)  
*T<sub>min</sub>* = 0.475, *T<sub>max</sub>* = 0.630

9516 measured reflections  
 3557 independent reflections  
 3275 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.017  
 $\theta_{max}$  = 26.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.024  
*wR* (*F*<sup>2</sup>) = 0.060  
*S* = 1.02  
 3557 reflections  
 233 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0316P)^2 + 13.3478P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{max}$  = 0.65 e Å<sup>-3</sup>  
 $\Delta\rho_{min}$  = -0.63 e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Ni—O1	2.021 (2)	Mo2—O2	2.253 (2)
Ni—O3	2.045 (2)	Mo3—O6	1.720 (2)
Ni—O2	2.049 (2)	Mo3—O12	1.721 (2)
Mo1—O10	1.701 (2)	Mo3—O8	1.933 (2)
Mo1—O9	1.723 (2)	Mo3—O5	1.946 (2)
Mo1—O4	1.939 (2)	Mo3—O1	2.207 (2)
Mo1—O5	1.972 (2)	Mo3—O2	2.254 (2)
Mo1—O3	2.217 (2)	Na—OW6	2.321 (3)
Mo1—O1	2.252 (2)	Na—O7 <sup>ii</sup>	2.379 (3)
Mo2—O11	1.707 (2)	Na—O9	2.379 (3)
Mo2—O7	1.723 (2)	Na—OW1	2.380 (3)
Mo2—O8	1.945 (2)	Na—O12 <sup>ii</sup>	2.468 (3)
Mo2—O4 <sup>i</sup>	1.948 (2)	Na—O6	2.615 (3)
Mo2—O3 <sup>i</sup>	2.227 (2)		

Symmetry codes: (i)  $-x + \frac{3}{2}, -y + \frac{3}{2}, -z$ ; (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...OW1	0.87	1.85	2.703 (3)	167
O2—H2...O6 <sup>iii</sup>	0.86	2.06	2.896 (3)	165
O3—H3...OW3 <sup>iii</sup>	0.80	1.94	2.722 (4)	164
OW1—H1WB...O12 <sup>iv</sup>	0.83	2.00	2.822 (3)	173
OW1—H1WA...OW2	0.85	2.07	2.892 (4)	165
OW2—H2WA...O8	0.89	1.92	2.786 (4)	164
OW2—H2WB...O5 <sup>ii</sup>	0.89	2.00	2.818 (3)	152
OW3—H3WA...OW6 <sup>iii</sup>	0.86	2.12	2.932 (4)	158
OW5—H5W...OW4	0.91	2.24	2.630 (11)	105
OW6—H6WA...OW5 <sup>ii</sup>	0.84	1.95	2.736 (4)	155
OW6—H6WB...OW2 <sup>v</sup>	0.82	1.95	2.754 (4)	165

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
OW6—H6WA $\cdots$ OW5 <sup>vi</sup>	0.84	1.95	2.736 (4)	155
N1—H1A $\cdots$ O5	0.86	2.17	3.017 (4)	168
N1—H1B $\cdots$ O4 <sup>vii</sup>	0.86	2.01	2.832 (4)	159
N2—H2B $\cdots$ O9 <sup>viii</sup>	0.86	2.22	2.966 (4)	145
N3—H3B $\cdots$ O7 <sup>ix</sup>	0.86	2.20	3.029 (4)	161
N3—H3B $\cdots$ O11 <sup>ix</sup>	0.86	2.81	3.243 (4)	113

Symmetry codes: (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $x, -y + 1, z - \frac{1}{2}$ ; (v)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z$ ; (vi)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (vii)  $x, -y + 1, z + \frac{1}{2}$ ; (viii)  $-x + 2, -y + 1, -z + 1$ ; (ix)  $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ .

The highly anisotropic displacement factors of OW4 and OW5 perhaps reflect unresolved positional disorder away from their modelled positions on twofold axes. All H atoms were located in difference maps and refined in their as-found relative positions using a riding model, with  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{carrier})$ .

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* (Branden-

burg, 1999); software used to prepare material for publication: *SHELXTL*.

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