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Tetraammonium hexahydrogen hexamolybdonickelate(II) tetrahydrate, $(NH_4)_4[H_6NiMo_6O_{24}]\cdot 4H_2O$

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(Ni–O) = 0.006 Å
H-atom completeness 1%
R factor = 0.053
wR factor = 0.137
Data-to-parameter ratio = 18.5

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

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Crystals of the title compound, $(NH_4)_4[H_6NiMo_6O_{24}]\cdot 4H_2O$ containing the well known *B*-type Anderson–Evans heteropolyoxometalate, were obtained by recrystallization of powder $(NH_4)_4[H_6NiMo_6O_{24}]\cdot nH_2O$. The anion has the Ni atom at an inversion center and has close to $\overline{3}m$ symmetry, with Ni—O bond lengths in the range 2.046 (5)–2.052 (6), Mo—O bond lengths in the ranges 1.701 (6)–1.720 (6), 1.932 (6)–1.954 (7) and 2.216 (6)–2.258 (5) Å.

Comment

The *B*-type Anderson–Evans structure heteropolyoxoanions, $[H_6X^{n}Mo_6O_{24}]^{(6-n)-}$ (X: Co^{2+}, Co^{3+}, Ni^{2+}, Fe^{3+}) (Anderson, 1937; Tsigdinos, 1978) do not usually form crystals suitable for structure determination. The reason is that the effective packing is disturbed by six undissociated H atoms bound to O atoms in XO_6. As a result, they form a plate-like powder. However, single crystals suitable for the structure determination, such as $K_3[H_6CoMo_6O_{24}]\cdot 14H_2O$, were obtained by careful recrystallization. The title crystals were also obtained by recrystallization, as reported in the early part of last century (Hall, 1907). However, an X-ray study has not been reported. Fig. 1 shows the structure of the $[H_6NiMo_6O_{24}]^{4-}$ polyanion. The anion has an inversion center and is close to having D_{3d} ($\overline{3}m$) symmetry. All atoms, except for the central Ni^{II} atom, are located on general positions of the space group.

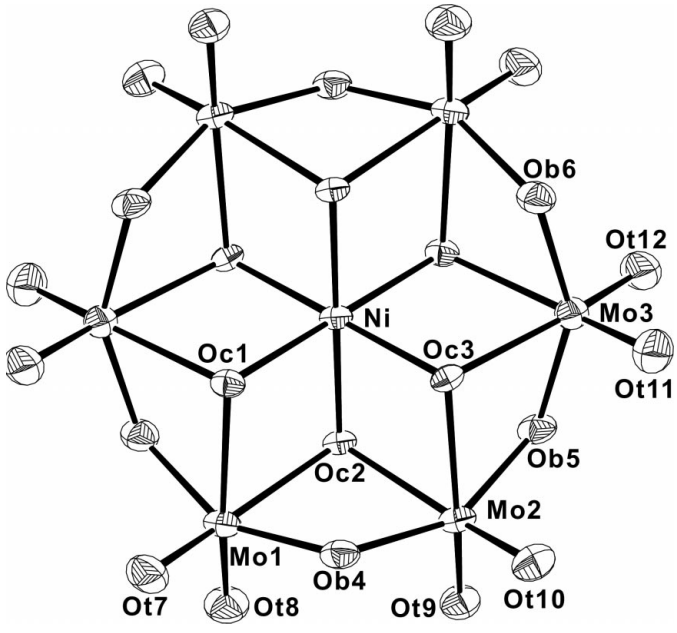

Figure 1
The polyanion structure in $(NH_4)_4[H_6NiMo_6O_{24}]\cdot 4H_2O$. H atoms are not shown. Displacement ellipsoids are shown at the 50% probability level.

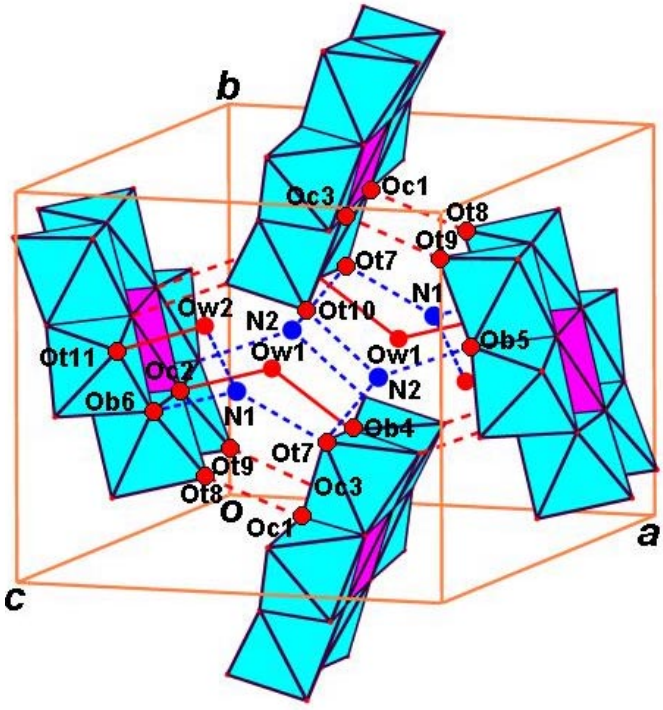

Figure 2
The unit-cell packing with hydrogen bonding.

The Ni atom lies on the inversion center of the polyanion. The labelling of the O atoms in the polyanion is the same as in the previous report (Lee & Joo, 2000). Six non-acidic H atoms in the $[H_6NiMo_6O_{24}]^{4-}$ polyanion are bound to six central O*c* atoms surrounding the Ni^{II} atom, as they are in the Anderson–Evans structure heteropolyoxoanions containing Cu^{2+} (Ito *et al.*, 1989), Al^{3+} (Lee *et al.*, 1991), Co^{3+} (Nolan *et al.*, 1998; Lee *et al.*, 2001), Cr^{3+} (Perloff, 1970) and Rh^{3+} (Ozawa *et al.*, 1991). The average *X*—O distances (and ionic radii: Shannon, 1976) in the $[H_6X^{n+}Mo_6O_{24}]^{(8-n)-}$ polyanion are 1.90 (Al^{3+}, 0.675), 1.906 (Co^{3+}, 0.685), 1.975 (Cr^{3+}, 0.755), 2.021 (Rh^{3+}, 0.805), 2.06 (Cu^{2+}, 0.87) and 2.049 (Ni^{2+}, 0.83) Å. These values show that the distances increase according to ionic radii. The Mo—O*b* and the Mo—O*t* distances were not affected by the nature of the heteroatoms.

Water molecules and ammonium ions were distinguished by the hydrogen bonding and interatomic distances. Two ammonium ions cannot be nearer to each other than 3.7 Å (Siemons & Templeton, 1954). In the first instance, atoms O*w*1 and N1 were assigned using these results.

A packing diagram of the unit cell is shown in Fig. 2. A list of all hydrogen-bond distances within 2.95 Å is given in Table 2. The H atom of O*c*2 does not contribute to the inter-anion hydrogen bonding, but it forms a strong hydrogen bond with O*w*1. All water molecules and ammonium ions contribute to hydrogen bonding with each other or with the O atoms in the polyanion. Except for the two direct inter-anion hydrogen bonds, O*c*1—O*t*8 and O*c*3—O*t*9, the other hydrogen bonds between the anions occur indirectly through H_2O or NH_4. The title compound crystal structure is stabilized by this hydrogen bonding.

Experimental

The title compound was obtained by recrystallization of a powder of $(NH_4)_4[H_6NiMo_6O_{24}]\cdot nH_2O$ at pH 5.35. The powder was obtained by the reaction of $(NH_4)_4[Mo_7O_{24}]\cdot 4H_2O$ with $Ni(NO_3)$. Elemental analysis, calculated: N 4.79 H 2.57%; found: N 4.78 H 2.59%.

Crystal data

$(NH_4)_4[H_6NiMo_6O_{24}]\cdot 4H_2O$
M_r = 1168.63
Monoclinic, $P2_1/a$
a = 11.994 (3) Å
b = 11.131 (2) Å
c = 11.384 (9) Å
β = 109.31 (8)°
V = 1434.3 (12) Å^3
Z = 2
D_x = 2.706 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
θ = 9.5–10.5°
μ = 3.29 mm^{-1}
T = 298 (2) K
Octagonal plate, pale blue
0.25 × 0.19 × 0.10 mm

Data collection

Stoe & Cie Stadi4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-SHAPE*; Stoe amp; Cie, 1996)
T_{min} = 0.542, T_{max} = 0.849
3290 measured reflections
3290 independent reflections
2448 reflections with $I > 2\sigma(I)$
θ_{max} = 27.6°
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: 4.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.137
S = 1.13
3290 reflections
178 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 13.3268P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.11 e Å^{-3}
$\Delta\rho_{min}$ = −1.33 e Å^{-3}

Table 1
Selected geometric parameters (Å).

Ni—O*c*2	2.046 (5)	Mo2—O*b*4	1.946 (6)
Ni—O*c*3	2.047 (6)	Mo2—O*b*5	1.952 (6)
Ni—O*c*1	2.052 (6)	Mo2—O*c*2	2.216 (6)
Mo1—O*t*7	1.712 (7)	Mo2—O*c*3	2.252 (5)
Mo1—O*t*8	1.720 (6)	Mo3—O*t*12	1.708 (7)
Mo1—O*b*6^{i}	1.935 (6)	Mo3—O*t*11	1.718 (7)
Mo1—O*b*4	1.954 (7)	Mo3—O*b*5	1.932 (6)
Mo1—O*c*2	2.228 (6)	Mo3—O*b*6	1.949 (6)
Mo1—O*c*1	2.258 (5)	Mo3—O*c*1^{i}	2.245 (6)
Mo2—O*t*9	1.701 (6)	Mo3—O*c*3	2.254 (6)
Mo2—O*t*10	1.717 (7)		

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

Table 2
Hydrogen-bonding $D\cdots A$ distances (Å).

O*c*1···O*t*8^{i}	2.844 (8)	N1···O*b*6	2.69 (1)
O*c*3···O*t*9^{i}	2.908 (8)	N1···O*t*7^{iii}	2.86 (1)
O*w*1···O*c*2^{ii}	2.726 (8)	N1···O*w*2^{vi}	2.90 (2)
O*w*1···O*b*4^{iii}	2.774 (9)	N1···O*w*2^{vii}	2.92 (2)
O*w*2···O*t*12	2.86 (1)	N2···O*b*5	2.71 (1)
O*w*2···O*t*11^{iv}	2.90 (1)	N2···O*t*10^{viii}	2.87 (1)
O*w*2···N1^{v}	2.90 (2)	N2···O*t*7^{ix}	2.91 (1)
O*w*2···N1^{iv}	2.92 (1)		

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

Data collection: *Stadi*4 (Stoe & Cie, 1996); cell refinement: *Stadi*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97-2 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97-2 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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