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# $NaAl(MoO_4)_2$: a rare structure type among layered yavapaiite-related $AM(XO_4)_2$ compounds

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**Key indicators**

Single-crystal X-ray study
$T$ = 293 K
Mean $\sigma$(Al–O) = 0.002 Å
$R$ factor = 0.016
$wR$ factor = 0.043
Data-to-parameter ratio = 17.0

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

$NaAl(MoO_4)_2$, sodium aluminium dimolybdate(VI), represents a rare pseudo-orthorhombic structure type among $AM(XO_4)_2$ compounds with yavapaiite-related sheet structures. It is isostructural with $NaFe(MoO_4)_2$. Infinite (001) sheets composed of $AlO_6$ octahedra, corner-linked to $MoO_4$ tetrahedra, are separated by eight-coordinated Na atoms. Average Na—O, Al—O and Mo—O bond lengths are 2.648, 1.890, and 1.762 Å, respectively. All atoms are on general positions except for Na and Al (both of which have site symmetry $\overline{1}$).

## Comment

The crystal structures of both natural and synthetic kröhnkite [$Na_2Cu(SO_4)_2\cdot 2H_2O$]-type oxy-salts and related compounds are currently being investigated and classified (Fleck & Kolitsch, 2003, Fleck, Kolitsch & Hertweck, 2002, Fleck, Kolitsch, Hertweck, Giester *et al.*, 2002). In our recent research (Fleck & Kolitsch, 2003), we also provide a brief review of related yavapaiite [$KFe(SO_4)_2$]-type sheet structures of $AM(XO_4)_2$ compounds, including a discussion of the rod group symmetry of the underlying kröhnkite-chain building unit. 12 different space groups have been found for these sheet structures (Fleck & Kolitsch, 2003). The previously unknown structure of $NaAl(MoO_4)_2$, reported here, is isotypic to that of $NaFe(MoO_4)_2$, and represents a rare structure type among these 12 types. [Note that previously reported space group symmetries for $\alpha$-$NH_4Fe(CrO_4)_2$ ($P2_1$; structure determination by Gravereau *et al.*, 1977) and $CsTa(PO_4)_2$ ($P\overline{1}$; structure determination by Nikolaev *et al.*, 1983) are obviously incorrect and should be revised to $P2_1/n$ and $C2/m$, respectively; for details, see Fleck & Kolitsch, 2003.]

$NaAl(MoO_4)_2$ and other related alkali metal(III) molybdates(VI) and tungstates(VI) have attracted interest due to a series of observed ferroelastic phase transitions (*e.g.* Dudnik *et al.*, 1976; Otko *et al.*, 1978, 1979, 1997; Zapart & Zapart, 1993; Maczka, Kojima & Hanuza, *et al.*, 1999; Maczka, Hanuza *et al.*, 1999; Hermanowicz *et al.*, 2000; Maczka *et al.*, 2001). On cooling, the space-group symmetry is lowered from $P\overline{3}m1$ to $C2/c$, $C2/m$ or $P\overline{1}$. The low-temperature modifications are ferroelastic and, on heating, transform into the paraelastic $P\overline{3}m1$ high-temperature modification. In some crystals, transitions to simultaneously incommensurate and ferroelastic phases have been reported.

Klevtsov *et al.* (1975) reported that single crystals of the molybdates $NaM(MoO_4)_2$ ($M$ = Al, Cr, Fe) are all monoclinic at room temperature, with space group $C2/c$ or $Cc$. For $NaAl(MoO_4)_2$, the unit-cell parameters $a$ = 9.59, $b$ = 5.37, $c$ = 13.14 Å and $\beta$ = 90.1° were given (Klevtsov *et al.*, 1975). Subsequently, somewhat contradictory reports on the space-

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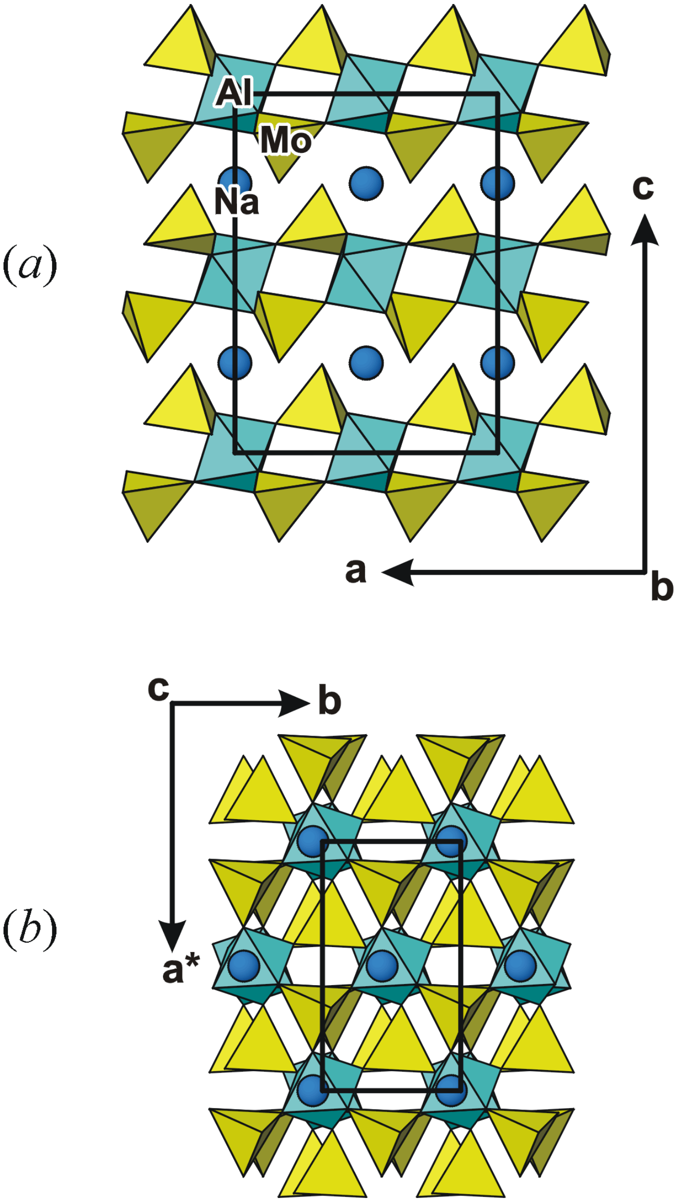

**Figure 1**
The layered crystal structure of $NaAl(MoO_4)_2$ in views (*a*) along [010] and (*b*) along [001]. $AlO_6$ octahedra are corner-connected to $MoO_4$ tetrahedra to form sheets separated by eight-coordinated Na atoms (dark-blue spheres). The pseudo-orthorhombic unit cell is outlined.

group symmetry of these three molybdates were published. The crystal structure of $NaFe(MoO_4)_2$ was determined by Klevtsova (1975) and refined in space group $C2/c$ to $R = 0.094$ [note that this structure is not included in the current edition (ICSD_021) of the ICSD (Belsky *et al.*, 2002)] In contrast, Dudnik *et al.* (1986) suggested that $NaFe(MoO_4)_2$ has space group $C2/m$, a conclusion based on studies using polarized-light microscopy and X-ray diffraction. Sinyakov *et al.* (1978) assumed, on the basis of group-theoretical considerations, that the room-temperature ferroelastic modifications of both $NaAl(MoO_4)_2$ and $NaFe(MoO_4)_2$ are isostructural with the ferroelastic phase of $KFe(MoO_4)_2$, and therefore would have space group $P2_1/c$ [the paraelastic high-temperature phase of

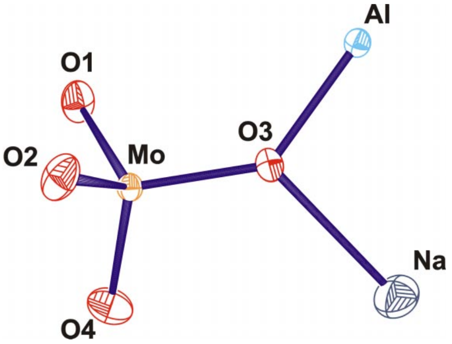

**Figure 2**
View of the seven atoms in the asymmetric unit of $NaAl(MoO_4)_2$, shown with ellipsoids at the 70% probability level.

$KFe(MoO_4)_2$ has space group $P\bar{3}c1$; Klevtsova & Klevtsov, 1970]. However, a different space group was also reported for ferroelastic $KFe(MoO_4)_2$; Otko *et al.* (1984) suggested space group $C2/m$ for this compound, and a pseudo-orthorhombic unit cell with cell parameters related to those of $NaAl(MoO_4)_2$. From detailed spectroscopic evidence, Maczka, Kojima & Hanuza (1999) and Maczka, Hanuza *et al.* (1999) concluded that $NaAl(MoO_4)_2$ has space group $C2/c$ at room temperature.

The present structure determination of the title compound at room temperature confirms the pseudo-orthorhombic unit cell reported by Klevtsov *et al.* (1975). It also shows that the compound is centrosymmetric, with space group $C2/c$, and isotypic to $NaFe(MoO_4)_2$ (Klevtsova, 1975). The crystal structure of $NaAl(MoO_4)_2$ is formed by infinite sheets composed of $AlO_6$ octahedra, corner-linked to slightly distorted $MoO_4$ tetrahedra (Figs. 1 and 2). These sheets are stacked parallel to (001) and are separated from each other by eight-coordinated interlayer Na atoms (Fig. 1). Average Na—O, Al—O and Mo—O bond lengths are 2.648, 1.890, and 1.762 Å, respectively.

Bond-valence sums for the Na, Al and Mo atoms, calculated using the parameters of Brese & O'Keeffe (1991), are 0.94, 3.15 and 5.94 v.u. (valence units). Although the longest Na—O bond, Na—O2 at 2.9957 (17) Å, seems very weak, it must be considered as a bond because it increases the bond-valence sum of the $Na^+$ cation from 0.866 to 0.944 v.u.. The four O atoms O1—O4 have bond-valence sums of 2.04, 2.05, 2.09, and 1.80 v.u., respectively. Although atom O4 seems to be somewhat underbonded, the bond distance Mo—O4 is the shortest of all four Mo—O bonds; however, according to experience, proposed bond-valence parameters for Mo—O bonds are not flexible enough to describe distorted $Mo^{VI}O_x$ polyhedra.

$NaAl(MoO_4)_2$ is isostructural with neither $NaAl(SO_4)_2$ [monoclinic, $C2/m$, Pannetier *et al.* (1972); ICDD-PDF 27-631; yavapaiite-type structure, but not refined yet], nor $KAl(MoO_4)_2$ (trigonal, $P\bar{3}m1$; Klevtsova & Klevtsov, 1970), nor $K(Cr_{0.8}Al_{0.2})(MoO_4)_2$ (monoclinic, $C2/c$; Sedello & Müller-Buschbaum, 1994), although the latter has the same space group. The atomic arrangement of $NaAl(MoO_4)_2$ represents one of 12 structure types found by Fleck & Kolitsch

(2003) for sheet structures identical or closely related to that of yavapaiite, $KFe(SO_4)_2$ (Graeber & Rosenzweig, 1971). Evidently, the different size ratios of the cations and anions in $AM(XO_4)_2$ compounds result in both flexible stretching of the sheets and enlargements of the interlayer spacings to accommodate the interlayer cation, thereby producing a large number of different, although topologically similar, crystal structure types. For a more detailed discussion of the 12 individual types, the reader is referred to Fleck & Kolitsch (2003).

High-temperature Raman studies on $NaAl(MoO_4)_2$ (Maczka, Kojima & Hanuza, 1999) have shown that it does not transform into the paraelastic $P\overline{3}m1$ modification up to its melting point, although the monoclinic distortion from the parent trigonal structure is relatively small at high temperatures, and increases continuously with decreasing temperature. This is in agreement with earlier data by Dudnik *et al.* (1976), who observed optically biaxial behavior up to 873 K, and Velikodnyi & Trunov (1977), who stated that $NaAl(MoO_4)_2$ at high temperatures is possibly orthorhombic but can be indexed as monoclinic. A determination of the unit-cell parameters of $NaAl(MoO_4)_2$ at 100 K during the present study indicated no symmetry change in the structure. As expected from the previous observations of Maczka, Kojima & Hanuza (1999), the monoclinic distortion has slightly increased upon cooling below room temperature: at 100 K the monoclinic angle has widened to a value of 90.3°.

## Experimental

Crystals of the title compound were grown by heating a mixture of $Na_2CO_3$, $Al_2O_3$ and $MoO_3$ placed in a platinum crucible to 993 K, keeping at this temperature for 20 h and cooling at a rate 2 K $h^{-1}$ to ambient temperature. The composition of the mixture corresponded to a 1:1 ratio between $NaAl(MoO_4)_2$ and the $Na_2Mo_2O_7$ solvent. The grown colorless, translucent to transparent crystals of pseudo-hexagonal block shape were separated from the solidified solvent by washing in hot water. All crystals were found to be non-merohedrally twinned, albeit to a variable degree. For the structure refinement, a nearly untwinned crystal fragment was used.

### *Crystal data*

$NaAl(MoO_4)_2$
$M_r = 369.85$
Monoclinic, $C2/c$
$a = 9.621$ (2) Å
$b = 5.339$ (1) Å
$c = 13.146$ (3) Å
$\beta = 90.01$ (3)°
$V = 675.3$ (2) Å$^3$
$Z = 4$
$D_x = 3.638$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1065 reflections
$\theta = 2.0$–30.0°
$\mu = 3.91$ mm$^{-1}$
$T = 293$ (2) K
Irregular fragment, colorless
0.07 × 0.06 × 0.02 mm

### *Data collection*

Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.771$, $T_{\max} = 0.926$
1863 measured reflections
986 independent reflections
959 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$
$\theta_{\max} = 30.0°$
$h = -13 \rightarrow 13$
$k = -7 \rightarrow 7$
$l = -18 \rightarrow 18$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.043$
$S = 1.14$
986 reflections
58 parameters
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.50$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.17$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0068 (4)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Na—O3$^{\rm i}$ | 2.3789 (16) | Al—O1$^{\rm iv}$ | 1.9040 (13) |
| Na—O4$^{\rm ii}$ | 2.5440 (19) | Mo—O4 | 1.7164 (17) |
| Na—O2$^{\rm iii}$ | 2.6744 (17) | Mo—O1 | 1.7575 (14) |
| Na—O1$^{\rm iv}$ | 2.9957 (17) | Mo—O2 | 1.7789 (14) |
| Al—O2$^{\rm v}$ | 1.8776 (14) | Mo—O3 | 1.7946 (14) |
| Al—O3$^{\rm vi}$ | 1.8874 (13) | | |
| O2$^{\rm v}$—Al—O3$^{\rm vi}$ | 87.92 (6) | O4—Mo—O1 | 106.85 (8) |
| O2$^{\rm vii}$—Al—O3$^{\rm vi}$ | 92.08 (6) | O4—Mo—O2 | 109.59 (8) |
| O2$^{\rm v}$—Al—O1$^{\rm iv}$ | 90.74 (6) | O1—Mo—O2 | 110.45 (7) |
| O2$^{\rm vii}$—Al—O1$^{\rm iv}$ | 89.26 (6) | O4—Mo—O3 | 108.84 (7) |
| O3$^{\rm vi}$—Al—O1$^{\rm iv}$ | 90.87 (6) | O1—Mo—O3 | 109.91 (6) |
| O3—Al—O1$^{\rm iv}$ | 89.13 (6) | O2—Mo—O3 | 111.09 (7) |

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

The deepest hole in the difference map is at a distance of 0.87 Å from the Mo site.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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