

Synthesis and Structure of Sodium Tetraoxo Nitrido Molybdate, $\text{Na}_5\text{MoO}_4\text{N}$

Nachiappan Arumugam, Eva M. Peters, and Martin Jansen

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany

Reprint requests to Prof. Dr. M. Jansen. Fax: +49-(0)711-6891502. E-mail: m.jansen@fkf.mpg.de

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The new oxynitride of molybdenum, $\text{Na}_5\text{MoO}_4\text{N}$ was prepared from stoichiometric mixtures of the starting materials MoO_2 , Na_2O_2 and NaN_3 which were heated in a special regime up to 500 °C, and cooled down slowly. Its crystal structure was solved and refined from single crystal data (orthorhombic, $Cmcm$, $a = 991.1(2)$, $b = 574.3(1)$, $c = 1067.7(2)$ pm, $R_1 = 0.0153$, $wR_2 = 0.0427$). The structure consists of isolated $[\text{MoO}_4\text{N}]^{5-}$ rectangular pyramids which are separated by Na^+ cations. This compound is structurally related to $\text{Na}_5\text{WO}_4\text{N}$ which crystallizes in space group $Cmc2_1$.

Key words: Sodium, Molybdenum, Oxynitrides, Structure Determination

Introduction

Only few alkali oxynitride compounds of molybdenum, $\text{Na}_4\text{Mo}(\text{O,N})_4$ [1], $\text{Na}_4(\text{MoO}_2\text{N}_2)$ [1], and $\text{Na}_3\text{MoO}_3\text{N}$ [2], have been reported, so far. General preparative methods for this class of compounds were given in [1–5]. Among these, the most versatile route seems to be the reaction between the transition metal oxides and the oxides, hydroxides or amides of alkali metals under a flow of N_2 or NH_3 . Here, for the synthesis of $\text{Na}_5\text{MoO}_4\text{N}$, we have used the “azide – peroxide route”, which is similar to the azide-nitrate technique [6].

Results and Discussion

$\text{Na}_5\text{MoO}_4\text{N}$ has been obtained as highly hygroscopic light green crystals. This molybdenum oxynitride is nearly isostructural to sodium tungsten oxynitride, $\text{Na}_5\text{WO}_4\text{N}$ [7], which has been reported to crystallize in space group, $Cmc2_1$, an acentric subgroup of $Cmcm$ found by us. No change in the R -value is observed while moving from the centrosymmetric space group to the acentric one. So, in our case $Cmcm$ is more appropriate than $Cmc2_1$. By accepting larger tolerances, the local parameters [7] of $\text{Na}_5\text{WO}_4\text{N}$ would also match space group $Cmcm$.

In $\text{Na}_5\text{MoO}_4\text{N}$, the Mo atom is coordinated with four O atoms and with one N atom forming an isolated rectangular (almost square) pyramidal polyhedron. One half of the polyhedra is oriented in $[0\ 1\ 0]$

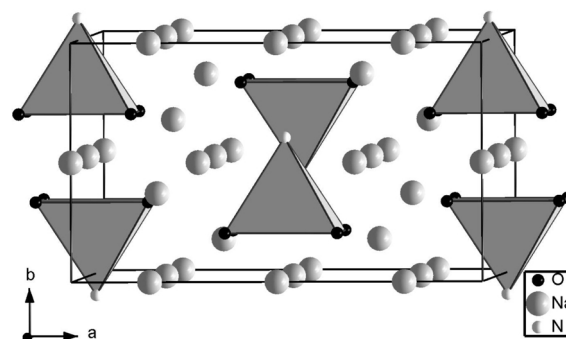


Fig. 1. Perspective view of the crystal structure of $\text{Na}_5\text{MoO}_4\text{N}$.

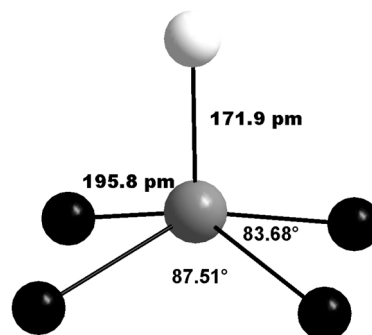


Fig. 2. The complex anion $[\text{MoO}_4\text{N}]^{5-}$.

direction while the other is oriented in the opposite direction as shown in Fig. 1. The Mo atom is located above the plane formed by the four oxygen atoms, and

Table 1. Bond lengths.

Atom	Dist. in pm	Atom	Dist. in pm
Mo(1)–N	171.9	Mo(1)–O	195.8 (4×)
Na(1)–O	227.4 (2×)	Na(1)–O	246.5 (2×)
Na(2)–O	235.4 (2×)	Na(2)–O	240.1 (2×)
Na(2)–N	242.4	Na(3)–O	223.0 (4×)

Table 2. Powder diffraction data of Na₅MoO₄N (*d* > 150.0 pm).

No.	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (pm)	<i>I</i> / <i>I</i> ₀	No.	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (pm)	<i>I</i> / <i>I</i> ₀
1	0	0	2	535.31	33.0	26	1	3	1	186.16	8.3
2	2	0	0	492.57	9.1	27	4	2	1	184.63	3.2
3	1	1	1	451.88	100.0	28	5	1	1	183.72	1.2
4	1	1	2	364.79	5.8	29	2	2	4	182.39	6.6
5	2	0	2	362.48	22.7	30	4	0	4	181.24	13.4
6	1	1	3	290.16	6.6	31	0	0	6	178.44	1.3
7	0	2	0	288.93	4.0	32	1	3	2	178.25	1.8
8	3	1	0	285.51	0.8	33	4	2	2	176.90	7.9
9	0	2	1	278.95	4.0	34	0	2	5	172.03	4.6
10	3	1	1	275.87	18.7	35	3	1	5	171.30	16.6
11	0	0	4	267.66	18.5	36	1	1	6	168.00	0.6
12	0	2	2	254.26	26.9	37	2	0	6	167.77	2.4
13	3	1	2	251.91	37.3	38	1	3	3	167.05	3.1
14	2	2	0	249.22	7.4	39	3	3	0	166.15	11.4
15	4	0	0	246.29	2.7	40	5	1	3	165.28	3.0
16	1	1	4	235.81	3.4	41	6	0	0	164.20	6.9
17	2	0	4	235.18	7.3	42	3	3	1	164.18	1.0
18	2	2	2	225.94	4.8	43	3	3	2	158.68	1.4
19	0	2	3	224.56	8.1	44	6	0	2	156.98	1.9
20	4	0	2	223.75	4.3	45	1	3	4	154.41	3.4
21	3	1	3	222.94	33.2	46	4	2	4	153.53	4.2
22	1	1	5	196.74	2.3	47	0	2	6	151.82	5.0
23	0	2	4	196.35	1.4	48	3	1	6	151.31	5.8
24	3	1	4	195.27	0.8	49	3	3	3	150.62	2.5
25	5	1	0	186.49	0.5						

the nitrogen atom occupies the apex of the square pyramid. The bond distance Mo–N (1.719 Å) is significantly shorter than the Mo–O distances (1.958 Å), *cf.* Table 1.

The three crystallographically independent sodium atoms have different coordination environments of oxygen atoms. Four oxygen atoms form an approximate tetrahedron around the sodium atom Na1, while the Na2 atom is coordinated by four oxygen atoms forming the plane, and one nitrogen atom the apex, of a rectangular pyramid. The Na3 atom is coordinated to four oxygen atoms forming a rectangular plane. The potential experienced by this sodium atom is flat in the direction perpendicular to the plane. This explains the enhanced thermal motion as reflected by the slight increase of *U*₂₂ for Na3.

From the results of the high temperature X-ray measurements it follows that the sample decomposes at 300 °C to form Na₃MoO₃N [2], as Na₂O is extracted from the oxynitride while reacting with the

Table 3. Crystallographic data and structure refinement for Na₅MoO₄N.

Crystal system	orthorhombic
Space group (No.)	<i>Cmcm</i> (63)
Lattice parameters/pm	<i>a</i> = 991.1(2), <i>b</i> = 574.3(1), <i>c</i> = 1067.7(2)
(from X-ray powder data)	
<i>Z</i>	4
Cell volume / Å ³	607.7(2)
Formula weight / g mol ^{−1}	288.90
Density calcd. / g·cm ^{−3}	3.158
Crystal colour	Light green
Crystal size, mm	0.08 × 0.1 × 0.12
Method of the refinement	Full-matrix least-squares on <i>F</i> ² , SHELXTL [8]
Parameters refined	34
<i>R</i> -Values [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0153, <i>wR</i> ₂ = 0.0427
<i>R</i> -Values (all data)	<i>R</i> ₁ = 0.0157, <i>wR</i> ₂ = 0.0429
Weight	$W = 1/[\sigma^2(F_o^2) + (0.0267 \cdot P)^2 + 0.57 \cdot P]$, where $P = (\max(F_o^2, 0) + 2 \cdot F_c^2)/3$
Δρ _{min} , ρ _{max} (e [−] Å ^{−3})	−0.84, 0.54
Diffractometer	STOE STADI 4, CCD Oxford instrument
Monochromator	Graphite
Mo–K _α Radiation, λ	0.71073 Å
Theta range for data collection	4.10 to 36.92°
Range of <i>h</i> , <i>k</i> , <i>l</i>	−13 ≤ <i>h</i> ≤ 14, −8 ≤ <i>k</i> ≤ 7, −14 ≤ <i>l</i> ≤ 14
Reflections collected	2669
Independent reflections	529 [<i>R</i> (int) = 0.0264]
Absorption coeff. mm ^{−1}	2.455
<i>F</i> (000)	544
Temperature in K	293

Table 4. Atomic coordinates and isotropic displacement parameters (pm² × 10^{−1}) for Na₅MoO₄N.

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Mo(1)	4 <i>c</i>	0	0.2086(1)	1/4	8(1)
Na(1)	8 <i>e</i>	0.1904(1)	0	0	19(1)
Na(2)	8 <i>g</i>	0.1893(1)	0.6419(2)	1/4	14(1)
Na(3)	4 <i>b</i>	0	1/2	0	33(1)
O	16 <i>h</i>	0.1366(1)	0.3030(2)	0.3723(1)	11(1)
N	4 <i>c</i>	0	0.0907(5)	1/4	24(1)

Table 5. Anisotropic displacement parameters (pm² × 10^{−1}). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Mo(1)	7(1)	7(1)	10(1)	0	0	0
Na(1)	23(1)	16(1)	18(1)	−6(1)	0	0
Na(2)	13(1)	13(1)	16(1)	0	0	2(1)
Na(3)	12(1)	57(1)	31(1)	32(1)	0	0
O	10(1)	14(1)	9(1)	0(1)	−1(1)	0(1)
N	14(1)	10(1)	49(2)	0	0	0

quartz capillary during the measurement. However, in a TGA/DTA study, run in a corundum crucible, the de-

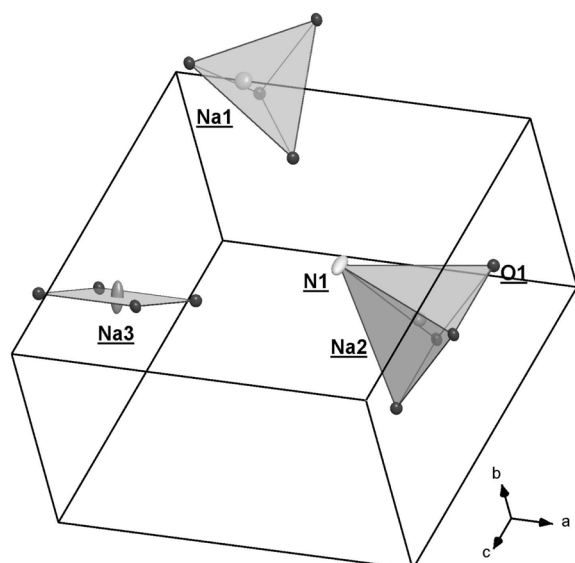


Fig. 3. Elongated thermal ellipsoid of Na3 atom along with selected Na, N and O atoms in the unit cell. The oxide and nitride anions are represented by black and white spheres, respectively.

composition temperature of the oxynitride was found to be 600 °C.

Experimental Section

Na₅MoO₄N was synthesized starting from MoO₃ (Alfa Aesar, 99%), Na₂O₂ (Riedel-de Häen, 95%) and NaN₃ (Sigma, 99.5%). The reactants were mixed in the ratio of 1:1:4 and dried under vacuum (10⁻³ mbar) at 150 °C for

12 h. Subsequently, they were finely ground, pressed as a pellet ($\varnothing = 13$ mm) under 10⁵ N, and placed under argon in a tightly closed steel container provided with a Mo inlay [6]. In a flow of dry argon, the following temperature program was applied: 25 °C → 260 °C(20 °C/h) → 380 °C(5 °C/h) → 500 °C(80 °C/h, 48 h) → 30 °C(20 °C/h). The light green crystals obtained were sealed in glass ampoules under argon atmosphere. All the preparative work with the reaction mixture was carried out in a glove box.

The X-ray investigation on powder was performed on a STOE Stadi P diffractometer with Cu K α ₁ radiation ($\lambda = 1.5406$) at room temperature using a position sensitive detector and a curved germanium monochromator in Debye-Scherrer geometry. The powder diffraction data are given in Table 2. Single crystals of Na₅MoO₄N were selected in the glove box using a 0.1 mm glass capillary and are inserted into a 0.3 mm capillary which was then sealed under dry argon. Single crystal diffraction analysis was effected on a STOE STADI 4 diffractometer coupled with a CCD Oxford instrument detector at room temperature. The crystallographic details are given in Table 3. Table 4 contains the atomic coordinates and the isotropic displacement parameters, and the anisotropic displacement parameters are listed in Table 5.

The thermal behavior of Na₅MoO₄N was investigated by using the device DTA/TGA (STA 409, Netzsch, Selb) coupled with a quadrupole mass spectrometer. The sample was heated at the rate of 10 °C/min in a corundum crucible under a flow of dry argon.

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