

Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Tm	0	0	0.35007 (1)	76.4 (4)
S	0.3026 (2)	0	$\frac{1}{4}$	97.5 (4)

Table 2. Interatomic distances (\AA)

Tm—S	2.660 (1) ($\times 3$)	S—Tm	2.660 (1) ($\times 2$)
—S	2.743 (1) ($\times 3$)	—Tm	2.743 (1) ($\times 2$)
—Tm	3.650 (1)	—S	3.547 (2) ($\times 2$)
—Tm	3.995 (1) ($\times 3$)	—S	3.683 (1) ($\times 2$)
		—S	3.852 (1) ($\times 4$)
		—S	4.100 (2) ($\times 4$)

reason is the electrostatic repulsion between Tm atoms. Owing to the face sharing of TmS₆ octahedra in Tm₂S₃-V, however, the closest Tm-Tm approach (3.65 \AA) is still shorter than in the other Tm₂S₃ modifications. The volume increase connected with the I \rightarrow V transformation is 6.2%.

Related literature. For the *P,T* phase diagram of Tm₂S₃ see Range *et al.* (1984). The only other sul-

fides with corundum-type structure are Lu₂S₃ and Yb₂S₃ (Flahaut, Domange & Pardo, 1964; Range & Leeb, 1975), a high-pressure modification of In₂S₃ (Range & Zabel, 1978), and, not yet confirmed, the so-called γ -Al₂S₃ (Flahaut, 1952).

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Diammonium Trimolybdate(VI), (NH₄)₂Mo₃O₁₀

BY KLAUS-JÜRGEN RANGE* AND ARMIN FÄSSLER

Institut für Anorganische Chemie der Universität, Universitätsstr. 31, D-8400 Regensburg, Federal Republic of Germany

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Abstract. (NH₄)₂Mo₃O₁₀, $M_r = 483.89$, orthorhombic, *Pnma*, $a = 13.182$ (2), $b = 7.589$ (2), $c = 9.286$ (2) \AA , $V = 928.95$ \AA^3 , $Z = 4$, $D_x = 3.450$ Mg m^{-3} , $\lambda(\text{Cu } K\alpha) = 1.5418$ \AA , $\mu = 34.67$ mm^{-1} , $F(000) = 912$, $T = 296$ K. The structure was refined to $R = 0.043$, $wR = 0.031$ for 848 absorption-corrected reflections. Distorted MoO₆ octahedra [Mo(1)—O = 1.72–2.24 \AA , Mo(2)—O = 1.71–2.32 \AA] are face- and edge-shared to form Mo₃O₁₀²⁻ chains along [010]. The ammonium ions are situated between the chains with N(1) in eightfold [N(1)—O = 2.77–3.39 \AA] and N(2) in tenfold coordination [N(2)—O = 2.88–3.27 \AA].

Experimental. (NH₄)₂Mo₃O₁₀ was prepared by high-pressure-high-temperature decomposition of

ammonium heptamolybdate, (NH₄)₆Mo₇O₂₄·2H₂O. Experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975), using silver as crucible material. After quenching from 0.1 GPa and 723 K the new phase was obtained. Reaction time had to exceed half an hour. A light-red crystal fragment (approx. 5 \times 5 \times 60 μm) was used for data collection on an Enraf-Nonius CAD-4 diffractometer (Cu $K\alpha$, $\lambda = 1.5418$ \AA , graphite monochromator, $T = 296$ K). Lattice parameters were refined from 2θ values of 25 reflections in the range $5.8 \leq \theta \leq 29.8^\circ$. Intensities measured for $2 \leq \theta \leq 50^\circ$; ω - 2θ -scan technique, scan width $(0.8 + 0.14 \times \tan \theta)^\circ$. Three standard reflections indicated no loss of intensity throughout data collection. An experimental correction for absorption was applied based on ψ scans; transmission factors varied between 92.8 and 99.6%. Merging of the 3231 collected intensities

* To whom correspondence should be addressed.

$[(\sin\theta_{\max})/\lambda = 0.491 \text{ \AA}^{-1}; -7 \leq h \leq 7, -9 \leq k \leq 9, 0 \leq l \leq 13]$ gave 848 unique reflections ($R_{\text{int}} = 0.029$) which were used for all calculations (program system *SHELX76*; Sheldrick, 1976).

The systematic absences for $h0l$ and $0kl$ pointed to the diffraction symbol $Pn\bar{3}a$. The results of the structure refinement showed space group $Pnma$ to be correct. The atomic positions for Mo were derived from a Patterson map, the remaining atoms were found in successive difference Fourier maps. In least-squares refinement $|F|$ magnitudes were used to refine atomic coordinates and anisotropic temperature factors of the non-H atoms. Final $R = 0.043$, $wR = 0.031$, $w = 1.61/\sigma^2$ and $(\Delta/\sigma)_{\max} < 0.01$ for 79 variables. Max. features in the final difference Fourier synthesis $+1.1, -1.4 \text{ e \AA}^{-3}$. Atomic scattering factors and f', f'' values were taken from *International Tables for X-ray Crystallography* (1974). Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969).

Final atomic coordinates and equivalent isotropic temperature factors are given in Table 1, derived interatomic distances in Table 2.† The structure (Fig. 1) consists of distorted MoO_6 octahedra which are face and edge shared to form $\text{Mo}_3\text{O}_{10}^{2-}$ chains along $[010]$. The Mo(1)—O and Mo(2)—O distances range from 1.717 to 2.243 Å and 1.714 to 2.319 Å, respectively. $\text{NH}_4(1)$ is surrounded by eight O atoms with N(1)—O distances ranging from 2.772 to 3.390 Å. $\text{NH}_4(2)$ has tenfold coordination by O [N(2)—O 2.879–3.271 Å].

Related literature. Several phases with a supposed stoichiometry $(\text{NH}_4)_2\text{O} \cdot 3\text{MoO}_3$ have been described

† Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52357 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

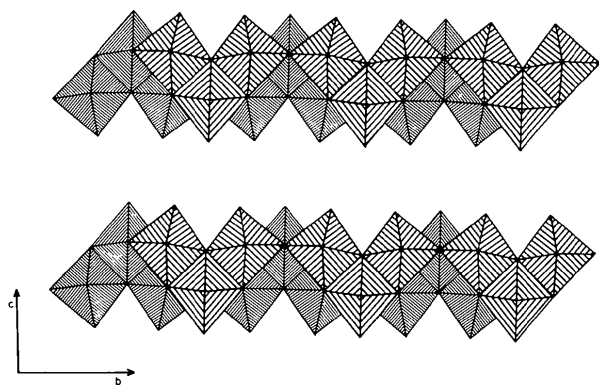


Fig. 1. Part of the crystal structure of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$, showing the $\text{Mo}_3\text{O}_{10}^{2-}$ chains along $[010]$.

Table 1. Atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^4$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mo(1)	0.40981 (5)	0.0035 (1)	0.35737 (8)	88
Mo(2)	0.11083 (8)	$\frac{1}{4}$	0.1502 (1)	89
O(1)	0.0964 (7)	$\frac{1}{4}$	0.3343 (9)	167
O(2)	0.2393 (7)	$\frac{1}{4}$	0.119 (1)	177
O(3)	0.0761 (7)	$\frac{1}{4}$	0.9103 (9)	132
O(4)	0.0751 (4)	0.511 (1)	0.0979 (6)	147
O(5)	0.2199 (4)	0.494 (1)	0.8719 (8)	180
O(6)	0.0646 (6)	$\frac{1}{4}$	0.869 (1)	129
O(7)	0.0701 (5)	0.5423 (8)	0.6773 (6)	187
N(1)	0.420 (1)	$\frac{1}{4}$	0.965 (1)	316
N(2)	0.246 (1)	$\frac{1}{4}$	0.107 (1)	307

Table 2. Interatomic distances (Å)

Mo(1)—O(5)	1.717 (5)	Mo(2)—O(1)	1.714 (9)
—O(7)	1.718 (6)	—O(2)	1.720 (9)
—O(3)	1.943 (2)	—O(4)	1.938 (7) (2 ×)
—O(6)	1.956 (1)	—O(3)	2.279 (9)
—O(4)	2.222 (6)	—O(6)	2.319 (8)
—O(4)	2.243 (5)		
N(1)—O(2)	2.77 (1)	N(2)—O(5)	2.88 (1) (2 ×)
—O(7)	2.86 (1) (2 ×)	—O(7)	2.96 (1) (2 ×)
—O(7)	2.97 (1) (2 ×)	—O(4)	3.00 (1) (2 ×)
—O(5)	3.39 (1) (2 ×)	—O(6)	3.25 (1)

in the literature (Funaki & Segawa, 1950; Schwing-Weil, 1967; Hanafi, Khilla & Askar, 1981), but only poorly characterized. Published d values do not agree with a powder pattern calculated from the present single-crystal data. The crystal structure of $(\text{NH}_4)_2\text{Mo}_3\text{O}_{10}$ is different from that of the analogous compound $\text{K}_2\text{Mo}_3\text{O}_{10}$ (Gatehouse & Levereth, 1968).

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