

## Redetermination of diammonium thiomolybdate

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 Key indicators: single-crystal X-ray study;  $T = 173$  K; mean  $\sigma(\text{Mo}-\text{S}) = 0.001$  Å;  $R$  factor = 0.022;  $wR$  factor = 0.060; data-to-parameter ratio = 14.1.

In contrast to the previous structure determinations of the title structure,  $(\text{NH}_4)_2[\text{MoS}_4]$ , the present determination at 173 K localized the positions of the H atoms. The title structure belongs to the  $\beta$ - $\text{K}_2\text{SO}_4$  family and all the ions are located on crystallographic mirror planes. The ions are held together by  $\text{N}-\text{H}\cdots\text{S}$  hydrogen bonds (some of which are bifurcated), forming a three-dimensional network. One of the N atoms has nine contacts to the S atoms shorter than 4 Å, and the other has ten.

### Related literature

For preparation of the title compound, see: Herzog *et al.* (1981). For structures of the  $\beta$ - $\text{K}_2\text{SO}_4$  family, see: Fábry & Pérez-Mato (1994). For other structure determinations of the title compound, see: Lapasset *et al.* (1976); Schäfer *et al.* (1964). For a description of the Cambridge Structural Database, see: Allen (2002).

### Experimental

#### Crystal data

$(\text{NH}_4)_2[\text{MoS}_4]$	$V = 812.32(7)$ Å <sup>3</sup>
$M_r = 260.26$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 9.5867(4)$ Å	$\mu = 2.55$ mm <sup>-1</sup>
$b = 6.9451(4)$ Å	$T = 173$ K
$c = 12.2005(5)$ Å	$0.25 \times 0.24 \times 0.11$ mm

#### Data collection

Stoe IPDS II two-circle diffractometer	14872 measured reflections
Absorption correction: multi-scan ( <i>MULABS</i> ; Spek, 2009; Blessing, 1995)	859 independent reflections
$T_{\min} = 0.569$ , $T_{\max} = 0.767$	833 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.072$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.060$	$\Delta\rho_{\text{max}} = 0.51$ e Å <sup>-3</sup>
$S = 1.19$	$\Delta\rho_{\text{min}} = -0.88$ e Å <sup>-3</sup>
859 reflections	
61 parameters	
6 restraints	

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{S1}^{\text{i}}$	0.86 (2)	2.76 (4)	3.491 (3)	144 (6)
$\text{N1}-\text{H1B}\cdots\text{S1}^{\text{ii}}$	0.88 (2)	2.92 (5)	3.607 (3)	135 (5)
$\text{N1}-\text{H1B}\cdots\text{S3}$	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
$\text{N1}-\text{H1B}\cdots\text{S3}^{\text{iii}}$	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
$\text{N1}-\text{H1C}\cdots\text{S3}^{\text{iv}}$	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
$\text{N1}-\text{H1C}\cdots\text{S3}^{\text{iv}}$	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
$\text{N2}-\text{H2C}\cdots\text{S3}^{\text{v}}$	0.88 (2)	2.65 (3)	3.405 (2)	144 (4)
$\text{N2}-\text{H2A}\cdots\text{S3}^{\text{vi}}$	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
$\text{N2}-\text{H2A}\cdots\text{S3}^{\text{vii}}$	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
$\text{N2}-\text{H2B}\cdots\text{S1}$	0.88 (2)	2.61 (4)	3.414 (3)	153 (6)
$\text{N2}-\text{H2B}\cdots\text{S2}$	0.88 (2)	2.70 (6)	3.250 (3)	122 (5)

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

Data collection: *X-Area* (Stoe & Cie, 2001); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2179).

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## supporting information

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## Redetermination of diammonium thiomolybdate

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### S1. Comment

The crystal structure of the title compound,  $(\text{NH}_4)_2\text{MoS}_4$ , previously determined using Weissenberg exposures (Schäfer *et al.*, 1964) and using a point detector diffractometer (Lapasset *et al.*, 1976) has been redetermined at low temperature since the two previous structure determinations did not include the positions of the H atoms.

The crystal structure belongs to the  $\beta$ - $\text{K}_2\text{SO}_4$  family (Fábry & Pérez-Mato, 1994). The anions and cations are held together by N—H $\cdots$ S hydrogen bonds forming a three-dimensional network involving all H atoms.

### S2. Experimental

The ammonium tetrathiomolybdate  $(\text{NH}_4)_2\text{MoS}_4$  was synthesized by the reaction from  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  with  $\text{H}_2\text{S}$  in the presence of  $\text{NH}_3$  (Herzog *et al.*, 1981) as shown by the equation:



$\text{H}_2\text{S}$  was bubbled for 30 minutes through a solution of 4.94 g (4.0 mmol)  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 50 ml aqueous ammonia. At first the reaction solution became yellow then the colour changed from yellow towards red. The red colour indicated the end of the reaction (Herzog *et al.*, 1981). X-ray quality crystals of  $(\text{NH}_4)_2\text{MoS}_4$  were grown from the reaction solution at ambient temperature. The crystals are pleochroic, changing colour from red to green according to the view angle.

### S3. Refinement

Hydrogen atoms were located in a difference Fourier map and refined isotropically. The N—H distances were restrained to 0.878 (20) Å. The value 0.878 Å has been retrieved from the structures XUDGET, TERNOT, TEJMUQ, TEJMOK, KOLKAY, KEVVEN, ICOMUI contained in the Cambridge Crystallographic Database (Version 5.31; Allen, 2002). The condition of the search in the Cambridge Crystallographic Database: The structures contained  $[\text{NH}_4]^+$ , K was the possibly heaviest atom in the structure, and the structures have been determined with R-factor  $< 0.03$ .

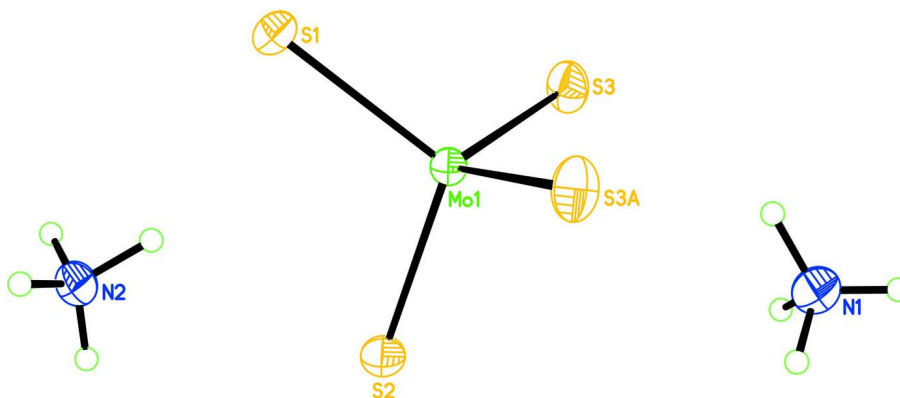


Figure 1

A view of the three molecules in the asymmetric unit of the title compound, with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level and the H atoms are shown as small spheres of arbitrary radii.

### diammonium thiomolybdate

#### Crystal data

$(\text{NH}_4)_2[\text{MoS}_4]$

$M_r = 260.26$

Orthorhombic,  $Pnma$

Hall symbol:  $-P\ 2ac\ 2n$

$a = 9.5867\ (4)\ \text{\AA}$

$b = 6.9451\ (4)\ \text{\AA}$

$c = 12.2005\ (5)\ \text{\AA}$

$V = 812.32\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 512$

$D_x = 2.128\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 14093 reflections

$\theta = 2.7\text{--}26.4^\circ$

$\mu = 2.55\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Plate, dark green

$0.25 \times 0.24 \times 0.11\ \text{mm}$

#### Data collection

Stoe IPDS II two-circle  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*MULABS*; Spek, 2009; Blessing, 1995)

$T_{\min} = 0.569$ ,  $T_{\max} = 0.767$

14872 measured reflections

859 independent reflections

833 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 25.9^\circ$ ,  $\theta_{\min} = 2.7^\circ$

$h = -11 \rightarrow 11$

$k = -8 \rightarrow 8$

$l = -14 \rightarrow 15$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.060$

$S = 1.19$

859 reflections

61 parameters

6 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.2462P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.51\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.88\ \text{e \AA}^{-3}$

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0173 (13)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Mo1	0.25414 (2)	0.7500	0.42734 (2)	0.01490 (16)
S1	0.03014 (7)	0.7500	0.38769 (6)	0.0229 (2)
S2	0.28425 (9)	0.7500	0.60460 (7)	0.0246 (2)
S3	0.35338 (5)	0.49616 (7)	0.35742 (5)	0.0259 (2)
N1	0.6660 (3)	0.7500	0.3880 (2)	0.0257 (6)
H1A	0.746 (4)	0.7500	0.355 (5)	0.072 (19)*
H1B	0.590 (4)	0.7500	0.347 (4)	0.089 (19)*
H1C	0.665 (5)	0.850 (5)	0.433 (3)	0.114 (18)*
N2	-0.0471 (3)	0.7500	0.6609 (2)	0.0223 (5)
H2A	-0.002 (5)	0.7500	0.723 (3)	0.09 (2)*
H2B	0.003 (6)	0.7500	0.600 (3)	0.10 (2)*
H2C	-0.097 (5)	0.644 (5)	0.656 (4)	0.114 (16)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Mo1	0.0146 (2)	0.0149 (2)	0.0152 (2)	0.000	0.00038 (8)	0.000
S1	0.0161 (4)	0.0297 (4)	0.0228 (4)	0.000	-0.0034 (3)	0.000
S2	0.0214 (4)	0.0349 (4)	0.0175 (4)	0.000	-0.0024 (3)	0.000
S3	0.0235 (3)	0.0196 (3)	0.0346 (3)	0.00079 (18)	0.0062 (2)	-0.0074 (2)
N1	0.0235 (14)	0.0268 (14)	0.0267 (15)	0.000	-0.0028 (11)	0.000
N2	0.0219 (13)	0.0258 (13)	0.0193 (13)	0.000	0.0030 (10)	0.000

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Mo1—S3 <sup>i</sup>	2.1773 (5)	N1—H1B	0.88 (2)
Mo1—S3	2.1773 (5)	N1—H1C	0.883 (19)
Mo1—S2	2.1818 (9)	N2—H2A	0.88 (2)
Mo1—S1	2.2013 (8)	N2—H2B	0.88 (2)
N1—H1A	0.86 (2)	N2—H2C	0.879 (19)
S3 <sup>i</sup> —Mo1—S3	108.13 (3)	H1A—N1—H1B	118 (6)
S3 <sup>i</sup> —Mo1—S2	109.30 (2)	H1A—N1—H1C	107 (4)
S3—Mo1—S2	109.30 (2)	H1B—N1—H1C	110 (3)
S3 <sup>i</sup> —Mo1—S1	109.885 (19)	H2A—N2—H2B	117 (5)

S3—Mo1—S1	109.885 (19)	H2A—N2—H2C	109 (3)
S2—Mo1—S1	110.30 (3)	H2B—N2—H2C	103 (3)

Symmetry code: (i)  $x, -y+3/2, z$ .

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...S1 <sup>ii</sup>	0.86 (2)	2.76 (4)	3.491 (3)	144 (6)
N1—H1B...S1 <sup>iii</sup>	0.88 (2)	2.92 (5)	3.607 (3)	135 (5)
N1—H1B...S3	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
N1—H1B...S3 <sup>i</sup>	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
N1—H1C...S3 <sup>iv</sup>	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N1—H1C...S3 <sup>iv</sup>	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N2—H2C...S3 <sup>v</sup>	0.88 (2)	2.65 (3)	3.405 (2)	144 (4)
N2—H2A...S3 <sup>vi</sup>	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
N2—H2A...S3 <sup>vii</sup>	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
N2—H2B...S1	0.88 (2)	2.61 (4)	3.414 (3)	153 (6)
N2—H2B...S2	0.88 (2)	2.70 (6)	3.250 (3)	122 (5)

Symmetry codes: (i)  $x, -y+3/2, z$ ; (ii)  $x+1, y, z$ ; (iii)  $x+1/2, y, -z+1/2$ ; (iv)  $-x+1, y+1/2, -z+1$ ; (v)  $-x, -y+1, -z+1$ ; (vi)  $-x+1/2, y+1/2, z+1/2$ ; (vii)  $-x+1/2, -y+1, z+1/2$ .