inorganic compounds

Redetermination of diammonium thiomolybdate

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In contrast to the previous structure determinations of the title structure, $(NH_4)_2[MoS_4]$, the present determination at 173 K localized the positions of the H atoms. The title structure belongs to the β-K_2SO_4 family and all the ions are located on crystallographic mirror planes. The ions are held together by N—H···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 β-K_2SO_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

$(NH_4)_2[MoS_4]$	V = 812.32 (7) Å^3
M_r = 260.26	Z = 4
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
a = 9.5867 (4) Å	μ = 2.55 mm^{-1}
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 (*MULABS*; Spek, 2009; Blessing, 1995)	859 independent reflections
	833 reflections with $I > 2\sigma(I)$
T_{min} = 0.569, T_{max} = 0.767	R_{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	
S = 1.19	
859 reflections	$\Delta\rho_{max}$ = 0.51 e Å^{-3}
61 parameters	$\Delta\rho_{min}$ = −0.88 e Å^{-3}
6 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S1^i	0.86 (2)	2.76 (4)	3.491 (3)	144 (6)
N1—H1B···S1^{ii}	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^{iii}	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
N1—H1C···S3^{iv}	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N1—H1C···S3^{iv}	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N2—H2C···S3^v	0.88 (2)	2.65 (3)	3.405 (2)	144 (4)
N2—H2A···S3^{vi}	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
N2—H2A···S3^{vii}	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) $x+1, y, z$; (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).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Fábry, J. & Pérez-Mato, J. M. (1994). *Phase Trans.* **499**, 193–229.
Herzog, S., Gustav, K. & Strähle, J. (1981). *Handbuch der Präparativen Chemie*, Vol. 3, edited by G. Brauer, pp. 1551–1552. Stuttgart: Ferdinand Enke Verlag.
Lapasset, J., Chezau, N. & Belougne, P. (1976). *Acta Cryst.* B**32**, 3087–3088.
Schäfer, H., Schäfer, G. & Weiss, A. (1964). *Z. Naturforsch. Teil B*, **19**, 76.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2001). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.

supplementary materials

Redetermination of diammonium thiomolybdate

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Comment

The crystal structure of the title compound, $(NH_4)_2MoS_4$, 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 β-K_2SO_4 family (Fábry & Pérez-Mato, 1994). The anions and cations are held together by N—H⋯S hydrogen bonds forming a three-dimensional network involving all H atoms.

Experimental

The ammonium tetrathiomolybdate $(NH_4)_2MoS_4$ was synthesized by the reaction from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with H_2S in the presence of NH_3 (Herzog *et al.*, 1981) as shown by the equation:

$(NH_4)_6Mo_7O_{24} + 28\ H_2S + 8\ NH_3 \rightarrow 7(NH_4)_2MoS_4 + 24\ H_2O.$

H_2S was bubbled for 30 minutes through a solution of 4.94 g (4.0 mmol) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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 $(NH_4)_2MoS_4$ were grown from the reaction solution at ambient temperature. The crystals are pleochroic, changing colour from red to green according to the view angle.

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 0.878Å 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 $[NH_4]^+$, K was the possibly heaviest atom in the structure, and the structures have been determined with R-factor ⟨ 0.03.
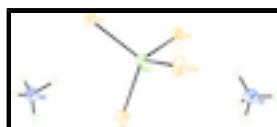
Figures

Fig. 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

$(NH_4)_2[MoS_4]$	$F(000) = 512$
$M_r = 260.26$	$D_x = 2.128$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 14093 reflections
$a = 9.5867$ (4) Å	$\theta = 2.7$–26.4°
$b = 6.9451$ (4) Å	$\mu = 2.55$ mm^{-1}
$c = 12.2005$ (5) Å	$T = 173$ K
$V = 812.32$ (7) Å^3	Plate, dark green
$Z = 4$	$0.25 \times 0.24 \times 0.11$ mm

Data collection

Stoe IPDS II two-circle diffractometer	859 independent reflections
Radiation source: fine-focus sealed tube	833 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.072$
ω scans	$\theta_{max} = 25.9°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (MULABS; Spek, 2009; Blessing, 1995)	$h = -11 \rightarrow 11$
$T_{min} = 0.569$, $T_{max} = 0.767$	$k = -8 \rightarrow 8$
14872 measured reflections	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.060$	$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 0.2462P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.19$	$(\Delta/\sigma)_{max} < 0.001$
859 reflections	$\Delta\rho_{max} = 0.51$ e Å^{-3}
61 parameters	$\Delta\rho_{min} = -0.88$ e Å^{-3}
6 restraints	Extinction correction: SHELXL97 (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Primary atom site location: structure-invariant direct methods	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 ($\mathring{A}^2$)

	x	y	z	$U_{iso}*/U_{eq}$
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 ($\mathring{A}^2$)

	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 ($\mathring{A}$, °)

Mo1—S3[i]	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[i]—Mo1—S3	108.13 (3)	H1A—N1—H1B	118 (6)
S3[i]—Mo1—S2	109.30 (2)	H1A—N1—H1C	107 (4)
S3—Mo1—S2	109.30 (2)	H1B—N1—H1C	110 (3)
S3[i]—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 codes: (i) x, $−y+3/2$, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S1^{ii}	0.86 (2)	2.76 (4)	3.491 (3)	144 (6)
N1—H1B···S1^{iii}	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^{i}	0.88 (2)	2.87 (3)	3.497 (3)	129 (3)
N1—H1C···S3^{iv}	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N1—H1C···S3^{iv}	0.88 (2)	2.76 (3)	3.550 (3)	150 (4)
N2—H2C···S3^{v}	0.88 (2)	2.65 (3)	3.405 (2)	144 (4)
N2—H2A···S3^{vi}	0.88 (2)	2.76 (2)	3.481 (2)	140 (1)
N2—H2A···S3^{vii}	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: (ii) *x*+1, *y*, *z*; (iii) *x*+1/2, *y*, −*z*+1/2; (i) *x*, −*y*+3/2, *z*; (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.

Fig. 1