Propane-1,3-diammonium molybdate

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The reaction between equimolar amounts of propane-1,3-diamine and molybdenum trioxide in water led to the formation of single crystals of the title salt, $(C_3H_{12}N_2)[MoO_4]$. The asymmetric unit is comprised of one propane-1,3-diammonium cation and one molybdate anion. The latter is isolated in the structure and has a slightly distorted tetrahedral configuration. An extensive network of N—H⋯O hydrogen bonds connects anions and cations, giving rise to a compact three-dimensional packing.

3D view
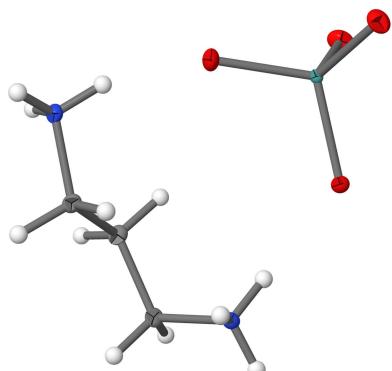
Chemical scheme
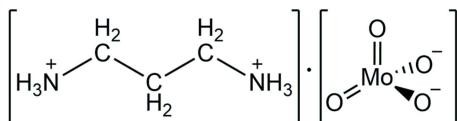
Structure description

In recent decades, oxyanions of metals from groups 5 and 6 in the periodic table (polyoxometalates, POMs) have attracted great interest in many fields (catalysis, medicine, functional materials and photochemistry) and continue to be extensively studied for energy applications (An *et al.*, 2018). This is particularly the case for molybdenum compounds which constitute suitable building blocks for the assembly of more complex and unusual structures (Süss-Fink *et al.*, 1997; Plasseraud *et al.*, 1999).

Numerous crystal structures of hetero- and polyoxidomolybdates are known from the literature (Li & Xu, 2011). For mononuclear molybdates with tetrahedral anions, the first crystal structure determination was reported for $Na_2[MoO_4]\cdot2H_2O$ (Lindqvist, 1950; Matsumoto *et al.*, 1975), followed by the potassium compound $K_2[MoO_4]$ (Gatehouse & Leverett, 1969). Ammonium salts of $[MoO_4]^{2-}$ have also been isolated in the solid state and their crystal structures determined: $(CH_6N_3)_2[MoO_4]$ (Ozeki *et al.*, 1987), $(C_6H_{14}N)_2[MoO_4]$ and $(C_{12}H_{26}N)_2[MoO_4]\cdot2H_2O$ (Thiele & Fuchs, 1979), $(C_2H_{10}N_2)[MoO_4]$ (Bensch *et al.*, 1987), $(C_4H_{12}NO)_2[MoO_4]$ (Sheikhshoaie & Ghazizadeh, 2013), $(Cy_2NH_2)_2[MoO_4]\cdot2H_2O$ (Pouye *et al.*, 2014) and $(^iPr_2NH_2)_2[MoO_4]$ (Sarr *et al.*, 2018). In this context and in continuation of our studies of interactions between organic ammo-

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Table 1
Selected geometric parameters (Å, °).

Mo—O1	1.8035 (12)	Mo—O3	1.7548 (12)
Mo—O2	1.7536 (12)	Mo—O4	1.7547 (13)
O2—Mo—O1	108.69 (6)	O3—Mo—O1	109.06 (6)
O2—Mo—O3	108.94 (6)	O4—Mo—O1	111.04 (6)
O2—Mo—O4	109.52 (6)	O4—Mo—O3	109.55 (7)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O3^{i}	0.91	1.85	2.7550 (19)	173
N1—H1$B\cdots$O1	0.91	2.00	2.8512 (18)	156
N1—H1$C\cdots$O2^{ii}	0.91	1.89	2.7670 (19)	163
N2—H2$A\cdots$O1^{iii}	0.91	1.93	2.8048 (18)	162
N2—H2$B\cdots$O1^{iv}	0.91	1.87	2.7690 (18)	170
N2—H2$C\cdots$O4	0.91	1.80	2.6808 (19)	162

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

nium cations and transition-metal or main-group metal anions (Pouye *et al.*, 2014; Diallo *et al.*, 2014), we report here the crystal structure of (C₃H₁₂N₂)[MoO₄], (I).

The asymmetric unit of (I) consists of a propane 1,3-di-ammonium cation and a molybdate anion (Fig. 1). Several crystal structures of salts containing the propane-1,3-di-ammonium dication are reported in the literature (*e.g.* Ayadi *et al.*, 2017; Kamoun *et al.*, 1992). Bond lengths and angles of the (C₃H₁₂N₂)²⁺ cation in (I) are in accordance with those reported previously for other oxidometalate salts, such as {(C₃H₁₂N₂)[Mo₃O₁₀]·2H₂O}$_n$ (Ding *et al.*, 2007) or (C₃H₁₂N₂)-[Cr₂O₇] (Trabelsi *et al.*, 2012). A search of the Cambridge Structural Database (*WebCSD*; Thomas *et al.*, 2010) revealed 30 crystal structures of salts involving the propane-1,3-di-ammonium cation associated with anions containing molybdenum. The [MoO₄]²⁻ anion in (I) exhibits a slightly distorted tetrahedral configuration. Three of the four Mo—O bond lengths (involving O2, O3 and O4; Table 1) are in the range of those reported in the literature (Bensch *et al.*, 1987; Sarr *et al.*, 2018). The fourth (involving O1; Table 1) is considerably

longer because it is the acceptor atom of three hydrogen bonds, whereas the other O atoms are involved in only one hydrogen bond each. From a supramolecular point of view, the (C₃H₁₂N₂)²⁺ cations and [MoO₄]²⁻ anions are connected *via* several N—H$\cdots$O hydrogen bonds, with $D\cdots A$ contacts ranging from 2.6808 (19) to 2.8512 (18) Å (Table 2). Each molybdate anion is surrounded by six propane-1,3-di-ammonium cations, and each of the cations is hydrogen bonded to five neighbouring anions. These interactions lead to a three-dimensional network structure (Fig. 2).

The crystal structure of the tetrathiomolybdate analog of (I), *i.e.* (C₃H₁₂N₂)[MoS₄] (Srinivasan *et al.*, 2005), is comprised of the same building units [an organic (C₃H₁₂N₂)²⁺ cation and a tetrahedral [MoS₄]²⁻ anion] but is not isotypic. However, the crystal structure of (C₃H₁₂N₂)[MoS₄] likewise is consolidated

Figure 1
The expanded asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dotted lines. [Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-1, y, z$.]
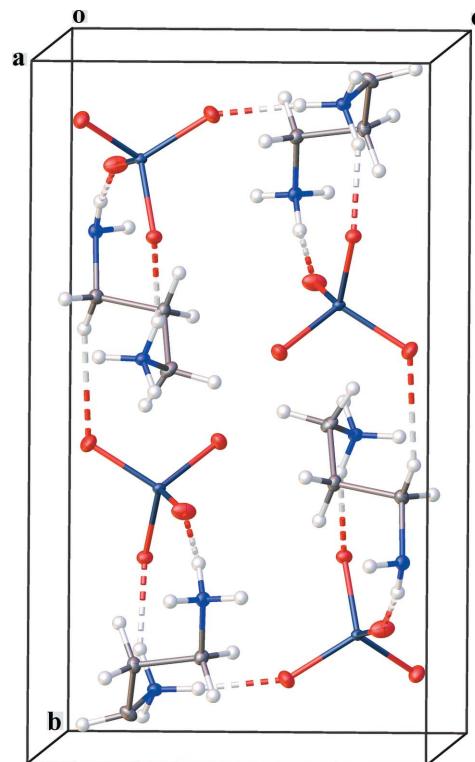

Figure 2
Partial packing diagram of (I), showing the intermolecular hydrogen-bonding scheme (dashed lines). Colour code: C dark grey, H white, O red, N blue and Mo blue metal.

Table 3
Experimental details.

Crystal data	
Chemical formula	$(C_3H_{12}N_2)[MoO_4]$
M_r	236.09
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	6.4849 (3), 14.7539 (7), 8.3224 (4)
β (°)	97.2950 (13)
V (Å^3)	789.82 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.63
Crystal size (mm)	$0.55 \times 0.45 \times 0.30$
Data collection	
Diffractometer	Bruker D8 Venture Cu
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.613, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11859, 1813, 1780
R_{int}	0.024
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.041, 1.11
No. of reflections	1813
No. of parameters	93
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.69, −0.48

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

by hydrogen bonds between the cation and the anion (here of type N—H···S).

Synthesis and crystallization

All chemicals were purchased from Sigma–Aldrich (Germany) and used without further purification. The title salt was prepared by mixing equimolar amounts of propane-1,3-diamine (0.50 g, 6.75 mmol) and molybdenum trioxide (0.97 g, 6.75 mmol) in 25 ml of water (75% yield). Colourless prismatic crystals, suitable for X-ray crystallographic analysis, were obtained by slow evaporation (10 d) at 333 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

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full crystallographic data

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Crystal data
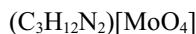
$(C_3H_{12}N_2)[MoO_4]$	$F(000) = 472$
$M_r = 236.09$	$D_x = 1.985$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.4849\ (3)$ Å	Cell parameters from 9941 reflections
$b = 14.7539\ (7)$ Å	$\theta = 2.8–27.6°$
$c = 8.3224\ (4)$ Å	$\mu = 1.63$ mm^{-1}
$\beta = 97.2950\ (13)°$	$T = 100$ K
$V = 789.82\ (6)$ Å^3	Prism, colourless
$Z = 4$	$0.55 \times 0.45 \times 0.30$ mm

Data collection

Bruker D8 Venture Cu diffractometer	$T_{min} = 0.613$, $T_{max} = 0.746$
Radiation source: sealed X-ray tube, high brilliance microfocus sealed tube, Cu	11859 measured reflections
	1813 independent reflections
QUAZAR MX multilayer optics monochromator	1780 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.024$
Detector resolution: 1024 x 1024 pixels mm^{-1}	$\theta_{max} = 27.6°$, $\theta_{min} = 2.8°$
φ and ω scans′	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)	$k = -19 \rightarrow 19$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.016$	$w = 1/[\sigma^2(F_o^2) + (0.0135P)^2 + 1.0699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.041$	
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
1813 reflections	$\Delta\rho_{max} = 0.69$ e Å^{-3}
93 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
0 restraints	

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
N1	0.8168 (2)	0.43213 (10)	0.26436 (16)	0.0097 (3)
H1A	0.810512	0.429665	0.154588	0.012*
H1B	0.855824	0.377091	0.307292	0.012*
H1C	0.911423	0.474723	0.303924	0.012*
N2	0.2514 (2)	0.27700 (9)	0.08732 (17)	0.0100 (3)
H2A	0.183145	0.271475	−0.014722	0.012*
H2B	0.157872	0.275641	0.160109	0.012*
H2C	0.342784	0.230364	0.107595	0.012*
C1	0.6079 (3)	0.45664 (11)	0.3092 (2)	0.0123 (3)
H1D	0.554783	0.510294	0.245464	0.015*
H1E	0.622845	0.473537	0.425179	0.015*
C2	0.4506 (3)	0.38039 (12)	0.2796 (2)	0.0114 (3)
H2D	0.332328	0.393725	0.340245	0.014*
H2E	0.516258	0.323603	0.324156	0.014*
C3	0.3666 (3)	0.36483 (11)	0.1021 (2)	0.0109 (3)
H3A	0.272418	0.415035	0.062280	0.013*
H3B	0.482908	0.363095	0.035692	0.013*
Mo	0.83296 (2)	0.14663 (2)	0.25817 (2)	0.00677 (6)
O1	0.96985 (18)	0.25143 (8)	0.30707 (14)	0.0106 (2)
O2	0.9652 (2)	0.08535 (8)	0.12245 (15)	0.0143 (2)
O3	0.8303 (2)	0.08287 (9)	0.43589 (15)	0.0170 (3)
O4	0.5768 (2)	0.16715 (9)	0.17004 (17)	0.0179 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0096 (6)	0.0081 (6)	0.0110 (7)	0.0003 (5)	0.0000 (5)	−0.0004 (5)
N2	0.0087 (6)	0.0110 (6)	0.0097 (6)	0.0004 (5)	−0.0009 (5)	0.0004 (5)
C1	0.0108 (7)	0.0118 (7)	0.0143 (8)	0.0019 (6)	0.0014 (6)	−0.0042 (6)
C2	0.0114 (7)	0.0135 (8)	0.0091 (7)	−0.0010 (6)	0.0005 (6)	−0.0010 (6)
C3	0.0108 (7)	0.0112 (7)	0.0104 (8)	−0.0013 (6)	−0.0005 (6)	0.0009 (6)
Mo	0.00632 (8)	0.00583 (8)	0.00786 (8)	0.00055 (4)	−0.00030 (5)	0.00027 (4)
O1	0.0102 (5)	0.0090 (5)	0.0122 (5)	−0.0007 (4)	−0.0005 (4)	0.0001 (4)
O2	0.0168 (6)	0.0135 (6)	0.0126 (6)	0.0037 (5)	0.0017 (5)	−0.0017 (5)
O3	0.0243 (7)	0.0140 (6)	0.0131 (6)	−0.0004 (5)	0.0044 (5)	0.0040 (5)
O4	0.0104 (6)	0.0145 (6)	0.0270 (7)	0.0021 (5)	−0.0051 (5)	−0.0014 (5)

Geometric parameters (Å, º)

N1—H1A	0.9100	C1—C2	1.518 (2)
N1—H1B	0.9100	C2—H2D	0.9900
N1—H1C	0.9100	C2—H2E	0.9900
N1—C1	1.494 (2)	C2—C3	1.526 (2)
N2—H2A	0.9100	C3—H3A	0.9900
N2—H2B	0.9100	C3—H3B	0.9900

N2—H2C	0.9100	Mo—O1	1.8035 (12)
N2—C3	1.493 (2)	Mo—O2	1.7536 (12)
C1—H1D	0.9900	Mo—O3	1.7548 (12)
C1—H1E	0.9900	Mo—O4	1.7547 (13)
H1A—N1—H1B	109.5	C1—C2—H2D	108.6
H1A—N1—H1C	109.5	C1—C2—H2E	108.6
H1B—N1—H1C	109.5	C1—C2—C3	114.72 (14)
C1—N1—H1A	109.5	H2D—C2—H2E	107.6
C1—N1—H1B	109.5	C3—C2—H2D	108.6
C1—N1—H1C	109.5	C3—C2—H2E	108.6
H2A—N2—H2B	109.5	N2—C3—C2	108.87 (13)
H2A—N2—H2C	109.5	N2—C3—H3A	109.9
H2B—N2—H2C	109.5	N2—C3—H3B	109.9
C3—N2—H2A	109.5	C2—C3—H3A	109.9
C3—N2—H2B	109.5	C2—C3—H3B	109.9
C3—N2—H2C	109.5	H3A—C3—H3B	108.3
N1—C1—H1D	109.0	O2—Mo—O1	108.69 (6)
N1—C1—H1E	109.0	O2—Mo—O3	108.94 (6)
N1—C1—C2	113.10 (13)	O2—Mo—O4	109.52 (6)
H1D—C1—H1E	107.8	O3—Mo—O1	109.06 (6)
C2—C1—H1D	109.0	O4—Mo—O1	111.04 (6)
C2—C1—H1E	109.0	O4—Mo—O3	109.55 (7)
N1—C1—C2—C3	−74.84 (18)	C1—C2—C3—N2	167.95 (13)

Hydrogen-bond geometry (Å, º)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$O3[i]	0.91	1.85	2.7550 (19)	173
N1—H1$B\cdots$O1	0.91	2.00	2.8512 (18)	156
N1—H1$C\cdots$O2[ii]	0.91	1.89	2.7670 (19)	163
N2—H2$A\cdots$O1[iii]	0.91	1.93	2.8048 (18)	162
N2—H2$B\cdots$O1[iv]	0.91	1.87	2.7690 (18)	170
N2—H2$C\cdots$O4	0.91	1.80	2.6808 (19)	162

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