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Bis[tris(2-ammonioethyl)amine] bis(pentafluorido-oxidomolybdate) difluoride monohydrate

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Key indicators

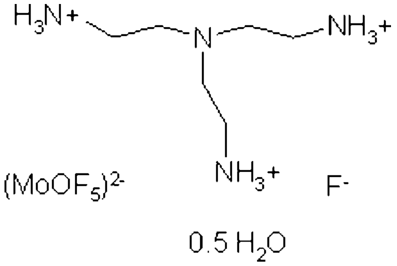
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.007 Å
R factor = 0.048
wR factor = 0.111
Data-to-parameter ratio = 18.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The first fluoridooxidomolybdate of tris(2-aminoethyl)amine (tren), bis[tris(2-ammonioethyl)amine] bis(pentafluorido-oxidomolybdate) difluoride monohydrate, $(C_6H_{21}N_4)_2[MoOF_5]_2F_2\cdot H_2O$, was obtained by solvothermal synthesis using microwave heating from the reaction of molybdenum oxide, tris-2-(aminoethyl)amine, aqueous HF and ethanol at 463 K for 1 h. The structure consists of $[MoOF_5]^{2-}$ octahedra, isolated fluoride ions, water molecules and triprotonated tren cations. Cohesion is ensured by a network of hydrogen bonds.

Comment

Bentrup *et al.* (1999) intensively explored numerous chemical systems by solvothermal routes, including an organic amine, HF and metallic cations such as aluminium, iron and manganese. More recently, several research groups have provided new examples of structures with zero-, one-, two- or three-dimensional inorganic networks with aluminium (Harlow *et al.*, 1999), uranium (Francis *et al.*, 1999), zirconium (Gerasimenko *et al.*, 1996), scandium (Stephens *et al.*, 2006) and berylium (Gerrard *et al.*, 2003). To date, very few hybrid molybdate fluorides are known. Leimkuhler *et al.* (1989) reported several new isolated clusters such as $Mo_2F_6O_4(H_2O)$, $Mo_2F_4O_4$ and Mo_4O_{12} associated with quaternary ammonium cations. Only one amine-templated fluoridomolybdate has been reported (Giese *et al.*, 1994). Its structure consists of isolated MoF_7 polyhedra, hydrogen bonded to hexamethylpiperidinium cations.



(I)

The structure of a new molybdate fluoride $(H_3tren)_2[MoOF_5]_2F_2\cdot H_2O$, (I), obtained in the MoO_2–tren–HF_{aq}–EtOH system [tren is tris-2-(aminoethyl)amine], is presented. It is built up from $[MoOF_5]^{2-}$ and isolated F^- anions, triprotonated tren cations and water molecules (Fig. 1). As a consequence of the presence of one short Mo—O distance [1.640 (4) Å], the $MoOF_5$ octahedron is distorted. Mo—F distances range from 1.892 (3) to 2.083 (3) Å, in good agreement with literature values (Leimkuhler *et al.*, 1989). The isolated fluoride F6 ions, associated by hydrogen bonds to four $—NH_3^+$ groups of four tren cations, adopt a tetrahedral

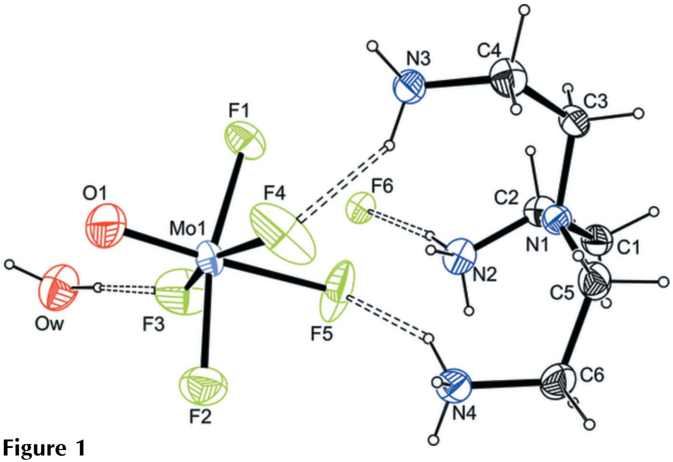


Figure 1
ORTEP-3 view (Farrugia, 1997) of water molecules, $(H_3tren)^{3+}$ cation, F^- and $[MoOF_5]^{2-}$ anions in the title compound. Displacement ellipsoids are shown at the 50% probability level. Double dashed lines indicate hydrogen bonds.

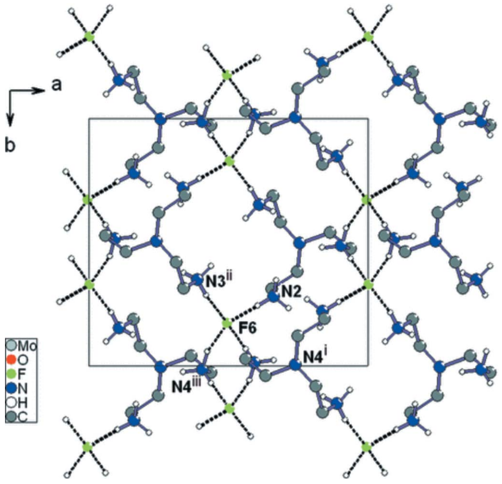


Figure 2
Environment of the isolated fluoride ion in the title compound. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$.]

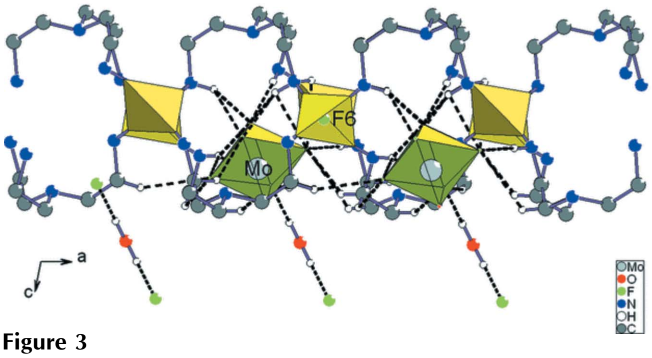


Figure 3
A view along [001] of the title compound, showing the layers separated by water molecules.

coordination (Fig. 2). Together with these isolated fluoride anions, the $MoOF_5$ octahedra, also connected to four $–NH_3^+$ groups of four tren cations, build infinite layers between which water molecules are located (Fig. 3).

Experimental

The title compound was prepared under hydrothermal conditions at 463 K for 1 h using Teflon autoclaves installed in a CEM microwave oven (MDS 2100). The starting materials were: molybdenum oxide (MoO_2), tris(2-aminoethyl)amine (96%, Aldrich), HF (40%) and ethanol in the molar ratio 1:0.5:5:170. The resulting crystalline products were washed with ethanol and dried in air. Single crystals suitable for X-ray diffraction were selected using an optical microscope.

Crystal data

$(C_6H_{21}N_4)_2[MoF_5O]_2F_2\cdot H_2O$
$M_r = 768.39$
Monoclinic, $C2/c$
$a = 12.9666$ (8) Å
$b = 11.3068$ (6) Å
$c = 19.7260$ (13) Å
$\beta = 100.939$ (2)°
$V = 2839.5$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.99$ mm^{-1}
$T = 298$ (2) K
0.10 × 0.06 × 0.03 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.92$, $T_{max} = 0.98$
30643 measured reflections
4103 independent reflections
2225 reflections with $I > 2\sigma(I)$
$R_{int} = 0.112$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.111$
$S = 1.00$
3260 reflections
174 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	1.640 (4)	Mo1—F3	1.927 (3)
Mo1—F2	1.892 (3)	Mo1—F1	1.967 (3)
Mo1—F4	1.908 (3)	Mo1—F5	2.083 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···F5^i	0.89	2.40	3.153 (6)	143
N2—H2*A*···F3^i	0.89	2.44	3.255 (6)	153
N2—H2*A*···F2^i	0.89	2.50	3.016 (5)	118
N2—H2*B*···F6	0.89	1.77	2.647 (5)	170
N2—H2*C*···F5	0.89	1.91	2.708 (5)	148
N3—H3*A*···F1^{ii}	0.89	1.89	2.783 (5)	177
N3—H3*B*···F6^{ii}	0.89	1.78	2.662 (4)	172
N3—H3*C*···F4	0.89	2.06	2.847 (5)	146
N4—H4*A*···F6^{iii}	0.89	1.80	2.654 (4)	160
N4—H4*B*···F6^i	0.89	1.79	2.678 (4)	177
N4—H4*C*···F5	0.89	1.95	2.766 (5)	151
O1*W*—H1*W*···F3	0.91 (3)	1.78 (3)	2.689 (5)	180 (8)

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

H atoms of amine cations were located applying geometrical constraints which imply equal distances and angles to the central

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atom. H atoms of water molecules were found in Fourier maps and the O—H distances were constrained to be 0.89 Å. H atoms were refined with a common isotropic displacement parameter. In the refinement, the weak data with $\theta > 27.5°$, which are largely responsible for the high value of $R_{\rm int}$, were not used.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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