

Tetraethylammonium aquatetrachloro-oxomolybdate(V),  $[\text{Et}_4\text{N}][\text{MoOCl}_4(\text{H}_2\text{O})]$ Simon J. Hibble,\*  
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## Key indicators

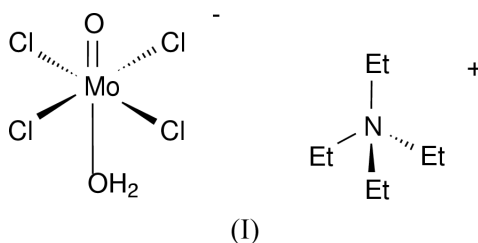
Single-crystal X-ray study  
 $T = 293 \text{ K}$   
Mean  $\sigma(\text{Mo}-\text{O}) = 0.003 \text{ \AA}$   
Disorder in solvent or counterion  
 $R$  factor = 0.031  
 $wR$  factor = 0.028  
Data-to-parameter ratio = 14.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound contains  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$  distorted octahedral anions with a short Mo—O bond of length 1.641 (3) Å *trans* to the  $\text{H}_2\text{O}$  group. These units are linked by hydrogen bonds between the  $\text{H}_2\text{O}$  group and chlorines of neighbouring anions to form infinite chains. Charge balance is achieved by  $[\text{Et}_4\text{N}]^+$  cations which exhibit twofold disorder.

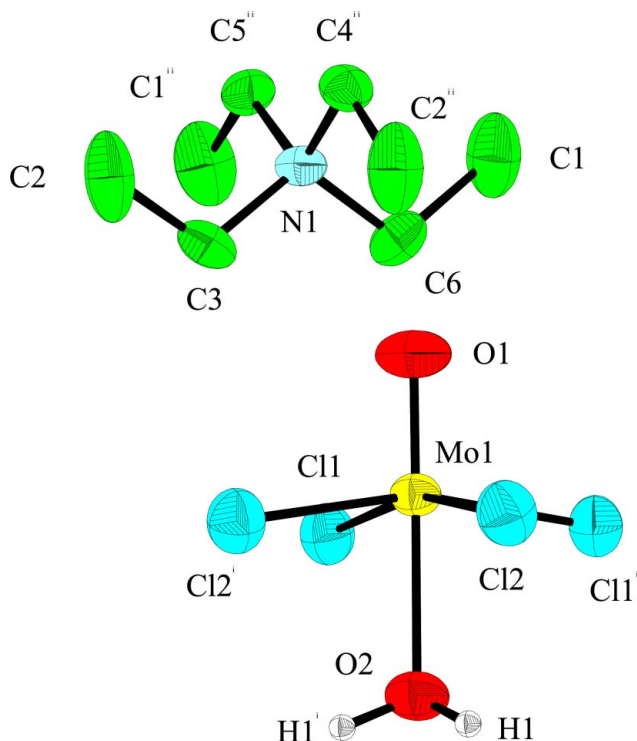
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## Comment

As part of our continuing work on the use of chemical excision to obtain information on the structural units present in amorphous  $\text{MoS}_3$  (Hibble *et al.*, 2001), we have characterized the products formed on reaction of amorphous  $\text{MoS}_3$  with concentrated hydrochloric acid, followed by precipitation in the presence of the tetraethylammonium cation. Other workers previously identified, from IR data, one product of this reaction as the complex ion  $[\text{Mo}_3\text{S}_7\text{Cl}_6]^{2-}$  (Weber *et al.*, 1995). In our reaction, we also found this ion present in the orange-brown solid  $[\text{Et}_4\text{N}][\text{H}_9\text{O}_4][\text{Mo}_3\text{S}_7\text{Cl}_6]$ , as confirmed by single-crystal X-ray diffraction. After partial solvent evaporation, a second crop of crystals was formed comprising further  $[\text{Et}_4\text{N}][\text{H}_9\text{O}_4][\text{Mo}_3\text{S}_7\text{Cl}_6]$  and the bright-green title product,  $[\text{Et}_4\text{N}][\text{MoOCl}_4(\text{H}_2\text{O})]$ , (I).



The crystal structure of  $[\text{Et}_4\text{N}][\text{MoOCl}_4(\text{H}_2\text{O})]$  contains  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$  anions, which deviate only slightly from  $C_{4v}$  ( $4m$ ) symmetry, charge balanced by tetrahedral  $[\text{Et}_4\text{N}]^+$  cations, which are disordered over two positions related by a mirror plane through N1. The Mo1—O1 bond is very short, consistent with it having multiple-bond character. We associate this molybdenum-oxo group with the observed intense IR stretching vibration at  $992 \text{ cm}^{-1}$ . An  $\text{OH}_2$  group is bonded *trans* to O1, leading to a long Mo1—O2 bond. The presence of hydrogen is confirmed by its location in difference Fourier maps and observation of vibrations in the IR spectrum at  $3458$  and  $1612 \text{ cm}^{-1}$  consistent with O—H stretching and  $\text{OH}_2$  bending modes, respectively. There are two crystallographically distinct Cl atoms completing the coordination sphere around Mo1. The  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$  anions are linked together through  $\text{O}2\text{H}\cdots\text{Cl}1$  hydrogen bonds to form infinite



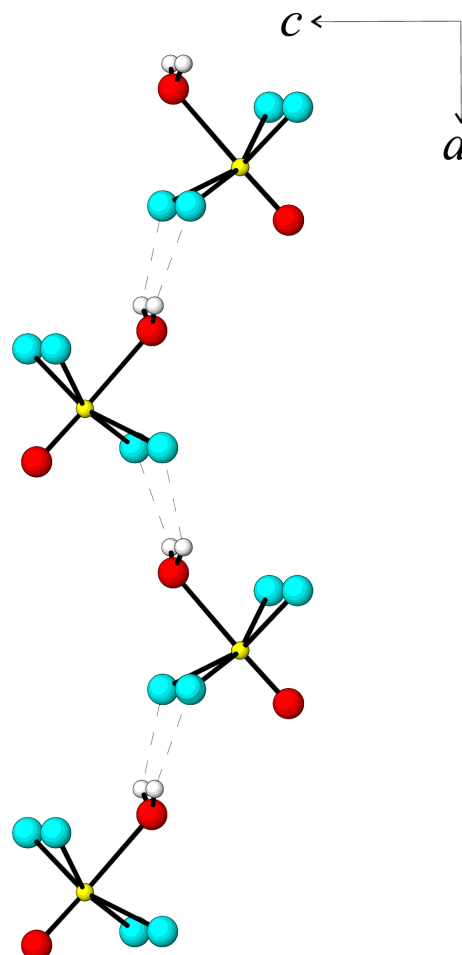
**Figure 1**  
Local coordination of atoms in  $[\text{Et}_4\text{N}][\text{MoOCl}_4(\text{H}_2\text{O})]$  (50% probability displacement ellipsoids). Only one of the two symmetry-related possibilities for the disordered  $[\text{Et}_4\text{N}]^+$  cation is shown. [Symmetry codes: (i)  $x, 3/2-y, z$ ; (ii)  $x, 1/2-y, z$ .]

chains along the  $a$  axis, slightly weakening and lengthening the  $\text{Mo1}-\text{Cl1}$  bond compared to the  $\text{Mo1}-\text{Cl2}$  bond.

The structure of the aquatetrachlorooxomolybdate(V) anion,  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$ , has been reported previously, occurring as the sole anion in a number of compounds. It occurs as isolated units [in (azonia-18-crown-6) monohydrate clathrate aquaoxotetrachloromolybdate(V) (Atwood *et al.*, 1996) and tetraphenylarsonium aquatetrachlorooxomolybdate(V) (Garner *et al.*, 1977)], in pairs linked by  $\text{O}-\text{H}\cdots\text{Cl}$  bonds [in (18-crown-6) hydroxonium clathrate aquatetrachlorooxomolybdate(V) (Atwood *et al.*, 1996), 3,5-di-*tert*-butyl-1,2-oxathiolium aquatetrachlorooxomolybdate(V) (Cindric *et al.*, 1996) and (12-crown-4) monohydrate oxonium monohydrate oxonium aquatetrachlorooxomolybdate(V) (Sergienko, Ilyukhin *et al.*, 1991)], and in chains linked by  $\text{O}-\text{H}\cdots\text{O}$  bonds [in (15-crown-5) oxonium monohydrate clathrate aquatetrachlorooxomolybdate(V) (Junk & Atwood, 1998) and bis(ethylenedithio)tetrathiafulvalene aquatetrachlorooxomolybdenum(V) (Kepert *et al.*, 1997)], as well as in chains linked by  $\text{O}-\text{H}\cdots\text{Cl}$  bonds similar to those observed here [in (18-crown-6) hydroxonium aquatetrachlorooxomolybdate(V) (Sergienko, Minacheva *et al.*, 1991)].

## Experimental

Amorphous  $\text{MoS}_3$  was prepared from a solution of 1.0 g of  $(\text{NH}_4)_2\text{MoS}_4$  in water (30 ml), degassed with nitrogen, which was treated with 12 *M* HCl (2 ml) whilst stirring (Müller *et al.*, 1993;



**Figure 2**  
Linking of  $[\text{MoOCl}_4(\text{H}_2\text{O})]^-$  units via  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bonds to form infinite chains along the  $a$  axis.

Weber *et al.*, 1995). The dark-brown precipitate was filtered off and washed several times with  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CS}_2$  (for removal of sulfur), and  $\text{Et}_2\text{O}$ , in turn, and dried *in vacuo*. Single crystals of (I) were obtained as follows: amorphous  $\text{MoS}_3$  (0.65 g) was suspended in 12 *M* HCl (35 ml). The reaction mixture was refluxed under  $\text{N}_2$  for 1 h and gravity filtered whilst still hot.  $\text{Et}_4\text{NCl}$  (0.5 g) was added to the yellow-green filtrate and the solution placed in the freezer at 253 K for 10 d, after which time a small amount of an orange-brown solid had precipitated. The solution was concentrated by slow evaporation to approximately 90% of the original volume and, after cooling, it was returned to the freezer for a further 14 d. Approximately equal quantities of the orange-brown plate-shaped crystals of  $[\text{Et}_4\text{N}][\text{H}_3\text{O}_4][\text{Mo}_3\text{S}_7\text{Cl}_6]$  and bright-green needle-like crystals of (I) were isolated and easily separated. Single-crystal X-ray diffraction confirmed their compositions and structures. IR data were also recorded from KBr discs.

### Crystal data

$(\text{C}_8\text{H}_{20}\text{N})[\text{MoOCl}_4(\text{H}_2\text{O})]$   
 $M_r = 402.01$   
 Orthorhombic,  $Pnma$   
 $a = 10.9913$  (3) Å  
 $b = 12.6073$  (5) Å  
 $c = 11.4222$  (3) Å  
 $V = 1582.78$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.687$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 1886 reflections  
 $\theta = 5.1-27.5^\circ$   
 $\mu = 1.48$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, bright green  
 $0.15 \times 0.15 \times 0.15$  mm

Data collection

Nonius KappaCCD diffractometer	1886 independent reflections
2 $\theta$ / $\omega$ scans	1402 reflections with $I > 3\sigma(I)$
Absorption correction: multi-scan (DENZO SCALEPACK;	$R_{\text{int}} = 0.022$
Otwinowski & Minor, 1997)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.801$ , $T_{\text{max}} = 0.801$	$h = -14 \rightarrow 14$
10 054 measured reflections	$k = -16 \rightarrow 16$
	$l = -14 \rightarrow 14$

Refinement

Refinement on $F$	Weighting scheme: Chebychev
$R = 0.031$	polynomial with 3 parameters
$wR = 0.028$	(Carruthers & Watkin, 1979),
$S = 1.15$	0.213, 0.0203 and $-0.0593$
1402 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
100 parameters	$\Delta\rho_{\text{max}} = 0.38 \text{ e } \text{\AA}^{-3}$
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{\text{min}} = -0.49 \text{ e } \text{\AA}^{-3}$

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Mo1—Cl1	2.3827 (9)	N1—C5	1.530 (6)
Mo1—Cl2	2.3654 (9)	N1—C6	1.524 (6)
Mo1—O1	1.641 (3)	C1—C5	1.553 (4)
Mo1—O2	2.351 (3)	C1—C6	1.556 (4)
O2—H1	0.86 (3)	C2—C3	1.559 (4)
N1—C3	1.534 (6)	C2—C4	1.561 (4)
N1—C4	1.537 (6)		
Cl1—Mo1—Cl1 <sup>i</sup>	87.41 (4)	Cl2—Mo1—O1	97.75 (9)
Cl1—Mo1—Cl2	163.75 (4)	Cl1—Mo1—O2	82.60 (7)
Cl1—Mo1—Cl2 <sup>i</sup>	89.44 (3)	Cl2—Mo1—O2	81.19 (7)
Cl2—Mo1—Cl2 <sup>i</sup>	89.15 (5)	O1—Mo1—O2	178.5 (1)
Cl1—Mo1—O1	98.47 (9)		

Symmetry code: (i)  $x, \frac{3}{2} - y, z$ .

**Table 2**  
Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H1 $\cdots$ Cl1 <sup>i</sup>	0.86 (3)	2.61 (3)	3.332 (3)	142 (3)

Symmetry code: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} - z$ .

The C, N and H atoms of the amine cation and the H atom of the water molecule were located in difference Fourier maps. The fractional coordinates of the water H atom were refined with the isotropic

displacement parameter fixed at  $0.05 \text{ \AA}^2$ . The  $[\text{Et}_4\text{N}]^+$  cation was modelled as disordered over two symmetry-related sites. The H atoms of the amine cation were placed geometrically during the final refinement procedure and constrained to ride on their parent C atoms, with  $U_{\text{iso}}$  fixed at  $0.05 \text{ \AA}^2$ .

Data collection: COLLECT (Nonius, 1997); cell refinement: DENZO SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO SCALEPACK; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 1996); molecular graphics: ATOMS (Shape Software, 1998); software used to prepare material for publication: CRYSTALS.

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