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Tetrabutylammonium aquatetrachlorooxomolybdate(V)

Chuan-De Wu, Quan-Zheng Zhang, Can-Zhong Lu,* Hong-Hui Zhuang and Jin-Shun Huang

The State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: czlu@ms.fjirsm.ac.cn

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Key indicators

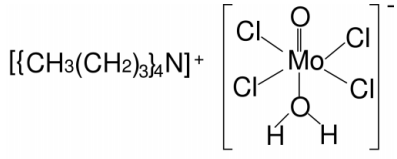
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.050
wR factor = 0.124
Data-to-parameter ratio = 19.4

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

Crystals of the title compound, $[(C_4H_9)_4N][MoOCl_4(H_2O)]$, were synthesized by the reaction of a hydrochloric acid solution of H_2MoO_4 and $[(C_4H_9)_4N]Cl$ with the reducing agent $N_2H_4{\cdot}2HCl$. The structure consists of an $[MoOCl_4(H_2O)]$ anion and a tetrabutylammonium cation. The Mo^V atom is coordinated by four chlorides, one terminal oxo and one aqua ligand in a distorted octahedral geometry. The Mo—Cl bond lengths are in the range 2.352 (2)–2.402 (1) Å, Mo—O(oxo) 1.647 (4) Å and Mo—OH_2 2.340 (4) Å. Intermolecular O—H···Cl hydrogen bond lengths are in the range 3.232–3.336 Å for O···Cl.

Comment

Molybdenum in its higher oxidation states readily forms polynuclear anionic metal–oxygen clusters and many polymolybdates with a wide variety of geometrical and electronic structures have been reported (Pope & Müller, 1991; Müller *et al.*, 1995, 1998; Müller & Serain, 2000). However, the synthesis of polymolybdates with bridging chlorine atoms is far less well developed. In the course of our work on the synthesis of chlorine-bridged polymolybdates, the title compound, (I), was unexpectedly obtained as single crystals.



(I)

The X-ray structure analysis of (I) reveals that the geometry of the $[MoOCl_4(H_2O)]^-$ anion is similar to those of its analogues (Bino & Cotton, 1979; Boorman *et al.*, 1975; Cindric *et al.*, 1996; Garner *et al.*, 1977; Junk & Atwood, 1998; Kepert *et al.*, 1997). As shown in Fig. 1, the coordination environment of the Mo atom is a distorted octahedron with the *cis* angles at Mo ranging from 80.4 (1) to 99.8 (2)°. The Mo═O bond length of 1.647 (4) Å and the Mo—O_{water} bond length of 2.340 (4) Å are typical values for terminal oxygen and aqua bond lengths to Mo. The Mo—Cl bond lengths are in the range 2.352 (2)–2.402 (1) Å, the *cis*–Cl—Mo—Cl angles are 88.3 (1)–89.1 (1)°, and the O═Mo—OH_2 angle is 177.7 (2)°, so the $[MoOCl_4(H_2O)]^-$ anion deviates only slightly from C_{4v} symmetry.

Anions are linked in pairs through O—H···Cl hydrogen bonds involving the aqua ligands (Table 2). As shown in the

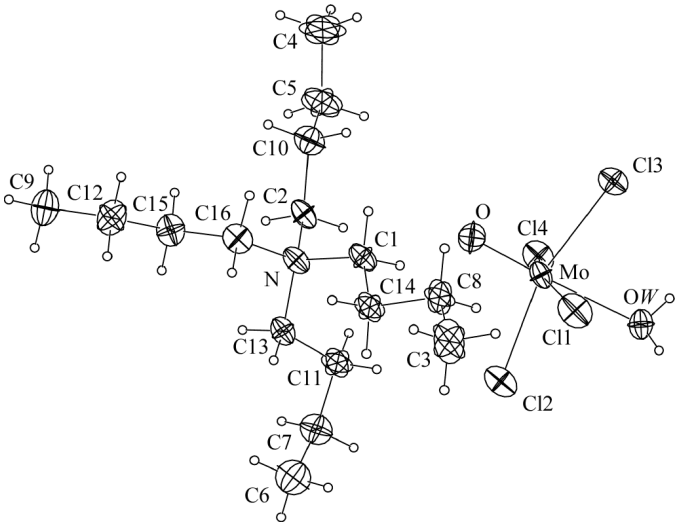


Figure 1
The cation and anion of (I) shown with 30% probability ellipsoids.

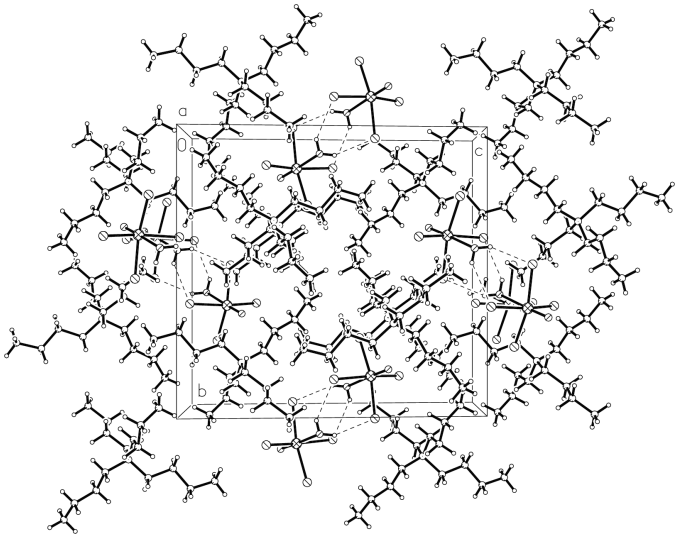


Figure 2
Packing diagram of (I), viewed down the *a* axis.

packing of the cations and anions in the crystal structure, there are no other significant interactions (Fig. 2).

Experimental

A solution of H_2MoO_4 (4.86 g, 30 mmol) in 20 ml concentrated HCl and 20 ml water was stirred with $N_2H_4{\cdot}2HCl$ (0.75 g, 7.14 mmol) for about 1 h, resulting in a green mixture. $[(C_4H_9)_4N]Cl$ (2.77 g, 10 mmol) was added and the solution was filtered. Green crystals of the title compound formed after a few days.

Crystal data

$(C_{16}H_{36}N)[MoOCl_4(H_2O)]$
M_r = 514.21
Monoclinic, $P2_1/n$
a = 9.401 (1) Å
b = 15.770 (1) Å
c = 16.845 (1) Å
β = 95.581 (1)°
V = 2485.6 (2) Å^3
Z = 4
D_x = 1.374 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3968 reflections
θ = 1.8–25.1°
μ = 0.97 mm^{-1}
T = 293 (2) K
Prism, green
0.45 × 0.20 × 0.10 mm

Data collection

SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.644, T_{max} = 0.908
8905 measured reflections
4368 independent reflections
3157 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 25.1°
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 18$
$l = -20 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.124
S = 1.15
4368 reflections
225 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 3.4179P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0010 (3)

Table 1
Selected geometric parameters (Å, °).

Mo—O	1.647 (4)	Mo—Cl4	2.358 (1)
Mo—O*W*	2.340 (4)	Mo—Cl1	2.380 (1)
Mo—Cl2	2.352 (2)	Mo—Cl3	2.402 (1)
O—Mo—O*W*	177.7 (2)	Cl2—Mo—Cl1	88.3 (1)
O—Mo—Cl2	99.8 (2)	Cl4—Mo—Cl1	162.7 (1)
O*W*—Mo—Cl2	82.48 (11)	O—Mo—Cl3	97.3 (2)
O—Mo—Cl4	99.0 (2)	O*W*—Mo—Cl3	80.4 (1)
O*W*—Mo—Cl4	81.5 (1)	Cl2—Mo—Cl3	162.9 (1)
Cl2—Mo—Cl4	89.1 (1)	Cl4—Mo—Cl3	88.6 (1)
O—Mo—Cl1	98.3 (2)	Cl1—Mo—Cl3	88.8 (1)
O*W*—Mo—Cl1	81.1 (1)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*—H*W*1···Cl1^{i}	0.84	2.61	3.338 (4)	145
O*W*—H*W*2···Cl3^{i}	0.85	2.47	3.238 (4)	151

Symmetry code: (i) $2-x, 1-y, 2-z$.

H atoms on C atoms were generated geometrically. Aqua H atoms were clearly visible in a different map and were positioned geometrically and included in the structure-factor calculations as riding atoms with fixed isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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