

## The crystal and molecular structure of bis(tetramethylammonium) hexamolybdate(VI)

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The crystal structure of the title compound,  $C_8H_{24}N_2Mo_6O_{19}$ , was determined by single crystal X-ray diffraction technique. The crystals are trigonals, space group P-3c1, with  $a = b = 10.0176(11)\text{\AA}$ ,  $c = 14.089(2)\text{\AA}$ ,  $\gamma = 120^\circ$ ,  $V = 1224.4(3)\text{\AA}^3$ ,  $Z = 2$ . The structure was solved by direct methods and refined by least-squares methods to a Final  $R = 0.0316$  for 1114 observed reflections with  $I > 2\sigma(I)$ . In hexamolybdate anion, six  $MoO_6$  distorted octahedra are fused together so that they all share a common vertex. O atoms are of three types: central, terminal and bridging, bonded to six, one and two Mo atoms, respectively. The crystallographic data of the structure was deposited with the Cambridge Data Center as No. CCDC 199679.

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### 1 Introduction

Multinuclear complexes may be considered as intermediate states of aggregation, between molecule and extended solid. They are thus a convenient starting point for studying the models for chemical bonding [1]. The title compound was obtained as one product of the hydrolysis and oxidation of  $(CH_3)_4N[MoOCl_4F]$ , which prepared by fluoride addition to  $MoOCl_4$  with  $(CH_3)_4NF$  [2]. The crystal structure was determined in order to identify this product.

The tetrachlorooxomolybdate(VI),  $MoOCl_4$  and tetramethylammonium fluoride,  $(CH_3)_4NF$  were synthesized according to published procedures [3, 4]. Tetrachlorooxomolybdate(VI) (0.9 gr., 3.54 mmol) was dissolved in dry acetonitrile (15ml) in a glove box under the argon atmosphere. To this red solution stoichiometric amount of powdered tetramethylammonium fluoride (0.329 gr., 3.54 mmol) was added with stirring. The color of solution changed from red to phosphorus green immediately. By passing oxygen from this solution, the color changed from green to white and then to pale yellow. The precipitate filtered, washed with MeCN and dried. Yield: 0.5 gr. (0.49 mmol, 83%).

### 2 Experimental

The compound was crystallized by thermal gradient method by use of branched pyrex tube that filled with acetonitrile after two weeks. A pale yellow crystal of size  $0.3 \times 0.3 \times 0.2$  mm was used for intensity data collection at 120(2) K temperature on a "Bruker SMART 1000 CCD area detector" diffractometer. The intensity data were collected with in the range  $2.35^\circ \leq \theta \leq 30.01^\circ$ , using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073\text{\AA}$ ). Accurate unit cell parameters and orientation matrix for data collection were obtained from least-squares refinements. Intensities of 9405 reflections were measured, from which 1114 reflections

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with  $I > 2\sigma(I)$  were used in the refinement. The relevant crystallographic data for the title compound are listed in Table 1. The crystallographic data of the structure described in this paper was deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 199679. Copies of this data are available free of charge from the following address: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: teched@chemcrs.cam.ac.uk).

**Table 1** Crystal data for the title compound.

Empirical formula	C <sub>8</sub> H <sub>24</sub> N <sub>2</sub> Mo <sub>6</sub> O <sub>19</sub>
Formula weight	1027.92
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Trigonal
Space group	P-3c1
Unit cell dimensions	a=10.0176(11) Å    α=90° b=10.0176(11) Å    β =90° c=14.089(2) Å      γ=120°
Volume	1224.4(3) Å <sup>3</sup>
Z	2
Density (calculated)	2.788 Mg/m <sup>3</sup>
Absorption coefficient	3.065 mm <sup>-1</sup>
F(000)	980
Crystal size	0.3 × 0.3 × 0.2 mm <sup>3</sup>
Theta range for data collection	2.35 to 30.01°
Index ranges	-14 ≤ h ≤ 13, -11 ≤ k ≤ 14, -19 ≤ l ≤ 16
Reflections collected	9405
Independent reflections	1205 [R(int)=0.0373]
Completeness of theta = 30.01°	99.9%
Absorption correction	Semi-empirical from equivalents
Max. And min. transmission	0.648 and 0.403
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1205 / 0 / 54
Goodness-of-fit on F <sup>2</sup>	1.046
Final R indices [(for 1114 rfln with I>2sigma(I))]	R1=0.0296, wR2=0.0619
R indices (all data)	R1=0.0316, wR2=0.0626
Largest diff. peak and hole	1.150 to -1.184 e. Å <sup>-3</sup>

### 3 Structure analysis

The structure have been solved by direct methods and refined by full-matrix- least squares techniques on F<sup>2</sup>. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atom was assigned an isotropic thermal parameter R, R<sub>w</sub> with a goodness of fit on F<sup>2</sup> of 1.046 are 0.0296 and 0.0619 respectively.  $W^1 = [\sigma^2(F_0^2) + (0.0156P)^2 + 8.5100P]$  where  $P = (F_0^2 + 2F_c^2)/3$ . The final difference density map showed a maximum peak and hole of 1.150 and - 1.184 e. Å<sup>-3</sup>. Corrections for the Lp as well as the empirical correction for absorption using the SADABS programs were applied. All structural calculations were carried out by using the SHELXTL V. 5.10 structure determination software [5]. The atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup>×10<sup>3</sup>) with estimated standard deviations for atoms except H are listed in Table 2. Selected bond lengths and bond angles are given in Table 3 and 4 respectively. Selected torsion angles (°) for anion (e.s.d 's are in parentheses) are listed in Table 5. ORTEP diagram and a perspective view of the packing in the unit cell are shown in figure 1 and 2 respectively.

**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{CH}_3)_4\text{N}]_2[\text{Mo}_6\text{O}_{19}]$ , with estimated standard deviations for atoms except H. U (eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

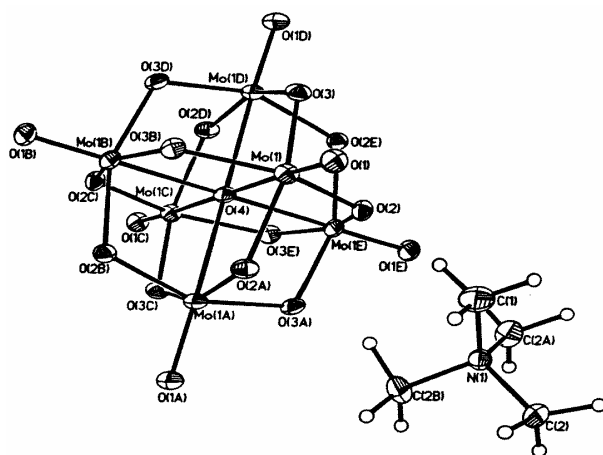
Atom	$x$	$y$	$z$	U(eq)
Mo(1)	7835(1)	9134(1)	955(1)	16(1)
O(1)	6228(3)	8544(3)	1613(2)	20(1)
O(2)	7151(3)	7604(3)	-10(2)	17(1)
O(3)	8911(3)	8242(3)	1531(2)	17(1)
O(4)	10000	10000	0	14(1)
N(1)	3333	6667	-1185(4)	16(1)
C(2)	1747(4)	6176(4)	-1538(3)	25(1)
C(1)	3333	6667	-123(5)	29(1)

## 4 Discussion

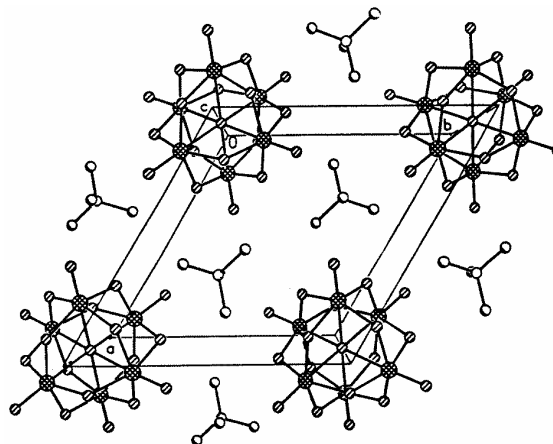
Each Mo atom is coordinated by six O atoms in a distorted octahedral arrangement, consisting of a displacement of Mo towards the terminal O atoms. The six  $\text{MoO}_6$  coordination octahedra in each anion share a common vertex at the central O atom. Each octahedron shares four edges with adjacent octahedra, but no faces are shared. The overall symmetry of the anion is roughly  $m\bar{3}m$  ( $O_h$ ). The geometry of the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  anion in this structure is in close agreement with those previously determined. As in the Bis (tetraphenylarsonium), (18-crown-6) $\text{K}^+$  and  $\text{Mo}(\text{S}_2\text{CNET}_2)_4^+$  complexes and in contrast to the  $\text{HN}_3\text{P}_3(\text{NMe}_2)_6^+$  complex. No significant asymmetry is observed in the Mo-O-Mo bridges [6, 7, 8].

The marked asymmetry in the one single case has been attributed to interionic C-H.....O hydrogen bonding [9, 10]. The crystal structure consists of layers perpendicular to the  $c$ -axis. One of these layers is depicted in fig. 2. This may be because of the inter-layer interactions.

This compound can be considered as a  $d^0$  non-VSEPR multinuclear system and it had been shown that multinuclear complexes may be considered as intermediate states of aggregation between molecule and extended solid. This complex confirms that if all other things being equal, an increase in coordination number increases ligand repulsion and thus tends to decrease the tendency towards nonclassical structures. Tendency to decrease of  $\pi$  bonding contribution and maximize  $\sigma$  bonding contribution is the reason of these distorted structures.



**Fig. 1** The ORTEP diagram of the only one independent  $[\text{Mo}_6\text{O}_{19}]^{2-}$  anion in the structure and the numbering system.



**Fig. 2** Crystal packing (view along 3-fold symmetry axis).

**Table 3** Selected bond lengths (Å).

Bond	Length	Bond	Length
Mo(1)-O(1)	1.688(2)	O(4)-Mo(1)#1	2.3206(3)
Mo(1)-O(3)	1.892(2)	O(4)-Mo(1)#2	2.3206(3)
Mo(1)-O(2)	1.901(2)	O(4)-Mo(1)#4	2.3206(3)
Mo(1)-O(3)#1	1.951(2)	O(4)-Mo(1)#5	2.3206(3)
Mo(1)-O(2)#2	1.969(2)	N(1)-C(2)	1.495(4)
Mo(1)-O(4)	2.3206(3)	N(1)-C(2)#6	1.495(4)
O(2)-Mo(1)#3	1.969(2)	N(1)-C(2)#7	1.495(4)
O(3)-Mo(1)#4	1.951(2)	N(1)-C(1)	1.497(8)
O(4)-Mo(1)#3	2.3206(3)		

Symmetry transformations used to generate equivalent atoms

#1:  $-x + y + 1, -x + 2, z$ ; #2:  $y, -x + y + 1, -z$ ; #3:  $x - y + 1, x, -z$

#4:  $-y + 2, x - y + 1, z$ ; #5:  $-x + 2, -y + 2, -z$ ; #6:  $-x + y, -x + 1, z$

#7:  $-y + 1, x - y + 1, z$

**Table 4** Selected bond angles (°).

Bond	Angle	Bond	Angle
O(1)-Mo(1)-O(3)	105.52(11)	Mo(1)#1-O(4)-Mo(1)#5	90.241(12)
O(1)-Mo(1)-O(2)	102.38(11)	Mo(1)#3-O(4)-Mo(1)#2	89.759(12)
O(3)-Mo(1)-O(2)	89.26(10)	Mo(1)#1-O(4)-Mo(1)#2	90.241(12)
O(1)-Mo(1)-O(3)#1	104.02(11)	Mo(1)#5-O(4)-Mo(1)#2	89.759(12)
O(3)-Mo(1)-O(3)#1	87.85(15)	Mo(1)#3-O(4)-Mo(1)	90.241(12)
O(2)-Mo(1)-O(3)#1	153.24(10)	Mo(1)#1-O(4)-Mo(1)	89.759(12)
O(1)-Mo(1)-O(2)#2	101.24(11)	Mo(1)#5-O(4)-Mo(1)	180.000(16)
O(3)-Mo(1)-O(2)#2	153.19(10)	Mo(1)#2-O(4)-Mo(1)	90.241(12)
O(2)-Mo(1)-O(2)#2	86.65(3)	Mo(1)#3-O(4)-Mo(1)#4	90.241(12)
O(3)#1-Mo(1)-O(2)#2	84.06(10)	Mo(1)#1-O(4)-Mo(1)#4	89.759(12)
O(1)-Mo(1)-O(4)	177.25(9)	Mo(1)#5-O(4)-Mo(1)#4	90.241(12)
O(3)-Mo(1)-O(4)	77.22(7)	Mo(1)#2-O(4)-Mo(1)#4	180.000(10)
O(2)-Mo(1)-O(4)	77.27(7)	Mo(1)-O(4)-Mo(1)#4	89.759(12)
O(3)#1-Mo(1)-O(4)	76.14(7)	C(2)-N(1)-C(2)#6	109.5(2)
O(2)#2-Mo(1)-O(4)	76.02(7)	C(2)-N(1)-C(2)#7	109.5(2)
Mo(1)-O(2)-Mo(1)#3	116.33(12)	C(2)#6-N(1)-C(2)#7	109.5(2)
Mo(1)-O(3)-Mo(1)#4	116.86(11)	C(2)-N(1)-C(1)	109.4(2)
Mo(1)#3-O(4)-	180.000(10)	C(2)#6-N(1)-C(1)	109.4(2)
Mo(1)#1			
Mo(1)#3-O(4)-	89.759(12)	C(2)#7-N(1)-C(1)	109.4(2)
Mo(1)#5			

**Table 5** Selected torsion angles (°).

O(1)-Mo(1)-O(2)-Mo(1)#3	-179.49(13)	O(1)-Mo(1)-O(4)-Mo(1)#1	94.4(19)
O(3)-Mo(1)-O(2)-Mo(1)#3	-73.76(13)	O(3)-Mo(1)-O(4)-Mo(1)#1	-90.35(7)
O(3)#1-Mo(1)-O(2)-Mo(1)#3	10.0(3)	O(2)-Mo(1)-O(4)-Mo(1)#1	177.49(7)
O(2)#2-Mo(1)-O(2)-Mo(1)#3	79.73(11)	O(3)#1-Mo(1)-O(4)-Mo(1)#1	0.58(7)
O(4)-Mo(1)-O(2)-Mo(1)#3	3.31(10)	O(2)#2-Mo(1)-O(4)-Mo(1)#1	87.80(7)
O(1)-Mo(1)-O(3)-Mo(1)#4	-179.45(13)	O(1)-Mo(1)-O(4)-Mo(1)#2	4.2(19)
O(2)-Mo(1)-O(3)-Mo(1)#4	77.90(14)	O(3)-Mo(1)-O(4)-Mo(1)#2	179.41(8)
O(3)#1-Mo(1)-O(3)-Mo(1)#4	-75.49(14)	O(2)-Mo(1)-O(4)-Mo(1)#2	87.25(7)
O(2)#2-Mo(1)-O(3)-Mo(1)#4	-3.2(3)	O(3)#1-Mo(1)-O(4)-Mo(1)#2	-89.66(7)

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O(4)-Mo(1)-O(3)-Mo(1)#4	0.79(10)	O(2)#2-Mo(1)-O(4)-Mo(1)#2	-2.44(7)
O(1)-Mo(1)-O(4)-Mo(1)#3	-85.6(19)	O(1)-Mo(1)-O(4)-Mo(1)#4	-175.8(19)
O(3)-Mo(1)-O(4)-Mo(1)#3	89.65(7)	O(3)-Mo(1)-O(4)-Mo(1)#4	-0.59(8)
O(2)-Mo(1)-O(4)-Mo(1)#3	-2.51(7)	O(2)-Mo(1)-O(4)-Mo(1)#4	-92.75(7)
O(3)#1-Mo(1)-O(4)-Mo(1)#3	-179.42(7)	O(3)#1-Mo(1)-O(4)-Mo(1)#4	90.34(7)
O(2)#2-Mo(1)-O(4)-Mo(1)#3	-92.20(7)	O(2)#2-Mo(1)-O(4)-Mo(1)#4	177.56(7)

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