

Crystal Structure and Thermal Stability Study on Tetrabutylammonium Hexamolybdate $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}](\text{TBAM})$

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(2003. 8. 5 접수)

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(Received August 5, 2003)

요 약. $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}](\text{TBAM})$ 의 결정구조는 X-ray 분석기로 결정되었다. 그 결정은 monoclinic 계이며 $a=16.314(5)$, $b=17.288(5)$, $c=17.776(4)$ Å, $\beta=101.47(3)$ 그리고 $z=4$ 의 결정파라미터를 갖는 space group 이 $C2/c$ 인 결정이다. $[\text{Mo}_6\text{O}_{19}]^{2-}$ 음이온에서, Mo 원자는 팔면체의 여섯 개 모서리를 차지하며 각 Mo 원자는 여섯개의 산소원자에 배위되어 찌그러진 팔면체 배위 기하학을 지닌다. Mo-O_t(말단기), Mo-O_b(연결된), 그리고 Mo-O_c(중앙)의 평균거리는 각각 1.680 Å, 1.931 Å 및 2.325 Å이다. $[n\text{-Bu}_4\text{N}]^+$ 양이온에서 N 원자는 약간 찌그러진 사면체 모형을 갖는다. 격자안에서 폭 넓은 C-H...O 수소결합이 있으며, 그것에 의하여 분자들을 연결하고 결정구조를 안정화 한다. 열분석에 의하여 제목의 열적분해는 두개의 전이가 일어나며 356.0와 803.5 °C에서 각각 무게를 잃는다. 그리고 분해된 생성물은 Mo₂O₇로 추정된다. 따라서, 제목의 화합물은 높은 열적 안정성을 갖는다.

주제어: 이이소플리옥소테이트, 결정구조, 열적 안정성

ABSTRACT. The crystal structure of $[n\text{-Bu}_4\text{N}]_2[\text{Mo}_6\text{O}_{19}](\text{TBAM})$ ($n\text{-Bu}_4\text{N}$ =tetrabutylammonium) has been determined by X-ray crystallography. It crystallizes in the monoclinic system, space group $C2/c$, with lattice parameters $a=16.314(5)$, $b=17.288(5)$, $c=17.776(4)$ Å, $\beta=101.47(3)$, and $Z=4$. In $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion, Mo atoms occupy six vertices of octahedron and each Mo atom is coordinated by six oxygen atoms to adopt distorted octahedral coordination geometry. The average bond distance of Mo-O_t (terminal), Mo-O_b (bridged) and Mo-O_c (central) are 1.680 Å, 1.931 Å, and 2.325 Å, respectively. In $[n\text{-Bu}_4\text{N}]^+$ cation, the N atom possesses a slightly distorted tetrahedral geometry. There are some potential extensive C-H...O hydrogen bonds in the lattice, by which connecte molecules and stabilize the crystal structure. Thermogravimetric analysis suggests that thermal decomposition of the title compound includes two transitions and it loses weight at 356.0 and 803.5 °C, respectively, and the residue presumable be Mo₂O₇. Accordingly, the title compound has high thermal stability.

Keywords: Isopolyoxomolybdate, Tetrabutylammonium, Crystal Structure, Thermalstability

INTRODUCTION

It is well known that polyoxoanions conjugated with organic molecules have the ability for photochromism, and that photochromism involving these compounds is truly reversible.¹⁻⁷ In order to prepare reversible photochromism materials, photosensitive organic molecules as donor and Type I polyoxometalate anions having easily reduced properties⁸ as acceptor have been adopted. Such anions are still of interest because of their high electron acceptor capability.⁹ Xu *et al* has reported reversible photochromism charge-transfer salt using photosensitive tetrabutylammonium (TBA) as donor and the hexamolybdate dianion ($\text{Mo}_6\text{O}_{19}^{2-}$) as acceptor under ultraviolet irradiation.¹⁰ However, the crystal structure of tetrabutylammonium hexamolybdate [*n*-Bu₄N]₂[Mo₆O₁₉] (TBAM) has never been reported. In this paper, we report the crystal structure of TBAM, and the thermal stability of it.

EXPERIMENT SECTION

Hydrothermal synthesis of TBAM. An acetonitrile solution of the tetrabutylammonium bromide (TBABr) and isopolyoxomolybdate Mo₆O₁₉²⁻ are mixed with stirring and its pH value was adjusted to 6 with dilution HCl, then the mixture was sealed in a 25 mL stainless-steel reactor with Teflon liner at 100 °C for 72 h, resulting in the formation of the light blue crystals of the title complex. Yield: 85%. Calc. for C₃₂H₇₂Mo₆N₂O₁₉: C, 28.16%; H, 5.31%; N, 2.05%. Anal. Found: C, 28.01%; H, 4.98%; N, 1.97%.

X-ray structure determination. The selected crystal of [*n*-Bu₄N]₂[Mo₆O₁₉] was mounted on an Rigaku Raxis-IV diffractometer. Reflection data were measured at 293 K, using graphite monochromated Mo-K_α (λ=0.71073 Å) radiation ω scan mode. Intensities were corrected for Lorentz and polarization effects and empirical absorption, and the data reduction using SADABS program.¹¹ The structure were solved by direct methods using SHELX-97.¹² All the nonhydrogen atoms were refined on F² anisotropically by full-matrix least squares method. The hydrogen atom positions were fixed geometri-

Table 1. Summary of Crystallographic Results for [*n*-Bu₄N]₂[Mo₆O₁₉]

Color/shape	light blue/prism
Empirical formula	C ₃₂ H ₇₂ Mo ₆ N ₂ O ₁₉
Formula weight	1364.56
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a, Å	16.314(5)
b, Å	17.288(5)
c, Å	17.776(4)
β, °	101.47(3)
Cell volume, Å ³	4913(2)
Z	4
D (calcd.) Mg/m ³	1.845
Abs coeff. mm ⁻¹	1.552
F(000)	2728
Radiation	Mo K _α (λ=0.71073 Å)
Temp. K	293(2)
θ range, °	1.73 to 27.48
Limiting indices	-15 ≤ h ≤ 20, -14 ≤ k ≤ 22, -22 ≤ l ≤ 20
Reflections collected	6760
Independent reflections	4144 [R _{int} =0.0299]
R [I > 2σ(I)]	R1=0.0334, wR2=0.0563
R (all data)	R1=0.1010, wR2=0.0641
Goodness-of-fit on F ²	0.898
Largest diff. peak and hole	0.490 and -0.420 eÅ ⁻³

cally at calculated distances and allowed to ride on the parent carbon atoms. The contributions of these hydrogen atoms were included in structure-factor calculations. The final least-square cycle gave R=0.0334, R_w=0.0563 for 2572 reflections with I > 2σ(I); the weighting scheme, w=1/[σ²(F_o²)+(0.0259P)²+0.0000P], where P=(F_o²+2F_c²)/3. Atomic scattering factors and anomalous dispersion corrections were taken from *International Table for X-Ray Crystallography*.¹³ A summary of the key crystallographic information is given in Table 1. The final position parameters of nonhydrogen atoms are given in Table 2. Selected bond lengths (Å), possible hydrogen bonds (Å) and bond angles (°) are presented in Table 3, respectively.

RESULT AND DISCUSSION

Structure. The crystal structure of the complex [*n*-Bu₄N]₂[Mo₆O₁₉] consists of a symmetry [Mo₆O₁₉]²⁻

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq}
Mo(1)	3689(1)	2892(1)	1705(1)	51(1)
Mo(2)	5000	1544(1)	2500	46(1)
Mo(3)	5000	4243(1)	2500	59(1)
Mo(4)	5620(1)	2896(1)	1431(1)	51(1)
O(1)	2747(2)	2870(2)	1122(2)	73(1)
O(2)	3935(2)	3985(2)	1843(2)	60(1)
O(3)	4453(2)	2901(2)	992(2)	55(1)
O(4)	3944(2)	1799(2)	1848(2)	50(1)
O(5)	5000	2900(3)	2500	37(1)
O(6)	3441(2)	2896(2)	2711(2)	53(1)
O(7)	5000	566(3)	2500	70(2)
O(8)	5512(2)	1808(2)	1644(2)	50(1)
O(9)	5507(2)	3988(2)	1646(2)	58(1)
O(10)	5000	5215(3)	2500	85(2)
O(11)	6084(2)	2918(2)	672(2)	71(1)
N(1)	2470(2)	141(2)	516(2)	49(1)
C(1)	3812(5)	-1269(6)	2430(5)	115(3)
C(2)	3178(4)	-705(4)	2571(3)	74(2)
C(3)	2540(4)	-492(4)	1853(3)	65(2)
C(4)	2930(3)	57(3)	-1353(2)	50(1)
C(5)	5033(3)	1215(4)	-345(3)	68(2)
C(6)	4132(3)	1361(3)	-267(3)	53(1)
C(7)	3787(3)	672(3)	85(3)	57(2)
C(8)	2877(3)	795(3)	156(3)	49(1)
C(9)	2115(5)	-1428(6)	-1946(4)	110(3)
C(10)	2380(5)	-1404(4)	-1098(4)	84(2)
C(11)	2211(4)	-629(4)	-768(3)	72(2)
C(12)	2535(3)	-623(3)	104(3)	59(2)
C(13)	180(5)	1784(4)	1268(5)	97(2)
C(14)	413(4)	1113(4)	826(4)	77(2)
C(15)	1346(3)	1033(4)	882(3)	67(2)
C(16)	1550(3)	323(3)	463(3)	57(2)

anion and two $[n\text{-Bu}_4\text{N}]^+$ cations. Fig. 1 shows a perspective view of the title compound with atomic numbering scheme, and Fig. 2 shows a perspective view of the crystal packing in the unit cell.

In $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion, six Mo atoms locate at the six vertexes of slightly distorted octahedron and nineteen oxygen atoms are divided into three categories, with one oxygen atom lying in the central of above octahedron (O_c), six oxygen atoms occupying the terminal positions of above octahedron (O_t) and twelve oxygen as bridged atoms (O_b) bridging six Mo atoms, respectively. All the angles of Mo-O_c-Mo

are nearly 90° or 180° . Each Mo atom possesses a distorted octahedral coordination geometry, which is coordinated by six oxygen atoms with the central atom and one terminal oxygen atom in axial position, and four bridged oxygen atoms occupying equatorial position. As seen from the Table 3, the *trans* bond angles forming by terminal oxygen atom, Mo atom and central oxygen atom are close to 180° , and the *cis* angles of O-Mo-O are nearly to 90° . Because of the existence of bridged oxygen atoms, the angles of opposite O_b -Mo- O_b are all smaller than 180° with average O_b -Mo- O_b about 153° . The average bond distance of Mo-O_t 1.680 Å equates to that in TPPM [TPPM=bis(2,4,6-triphenylpyryllium) hexamolybdate], the distance Mo-O_b 1.931 Å and Mo-O_c 2.325 Å are longer than those in TPPM [Mo-O_b 1.917 Å and Mo-O_c 2.312 Å]¹⁰. But all these values are in the range of with those reported previously.¹⁴⁻¹⁵

In the slight distorted octahedral geometry of $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion, three σ_h symmetrical planes were occupied by three molecular planes, each of which contained thirteen atoms (four Mo atoms, four O_b atoms, four O_t atoms and one O_c atom) and the largest deviations of which are 0.012, 0.045 and 0.016 Å, respectively. The above three molecular planes are almost vertical each other, with the dihedral 89.82 , 89.90 and 89.92° , respectively.

In the $[n\text{-Bu}_4\text{N}]^+$ cation, the N atom adopts a slightly distorted tetrahedral geometry with the C-N-C bond angles ranging from 108.1° to 111.5° . The C-N and C-C bond lengths fall within the normal rang.

There are some potentially weak (C-H...Y hydrogen bonds, Y=O) interactions in the lattice.¹⁶⁻¹⁷ The O(3) atom with C(6) atom in $[n\text{-Bu}_4\text{N}]^+$ cation forms potentially weak C-H...O intramolecular interactions, the donor and acceptor distance is 3.4435 Å for C(6)-H(6A)...O(3). The O(1) atom with C(8) atom forms C-H...O intermolecular interactions, the donor and acceptor distance being 3.2600 Å for C(8)-H(8B)...O(1) (symmetry code: $1/2-x, 1/2-y, -z$). The bond angles of C(6)-H(6A)...O(3) and C(8)-H(8B)...O(1) are 164.86° and 131.18° , respectively. In the solid state, these interactions together with electrostatic forces connected molecules and stabilize the crystal structures.

Table 3. Selected bond lengths (Å) and bond angles (°) of the title compound

Mo(1)-O(1)	1.674(3)	Mo(1)-O(6)	1.910(3)
Mo(1)-O(2)	1.937(3)	Mo(1)-O(4)	1.942(3)
Mo(1)-O(3)	1.945(3)	Mo(1)-O(5)	2.3177(10)
Mo(2)-O(7)	1.690(5)	Mo(2)-O(4)#1	1.926(3)
Mo(2)-O(4)	1.927(3)	Mo(2)-O(8)#1	1.929(3)
Mo(2)-O(8)	1.932(3)	Mo(2)-O(5)	2.345(5)
Mo(3)-O(10)	1.680(5)	Mo(3)-O(9)	1.918(3)
Mo(3)-O(9)#1	1.921(3)	Mo(3)-O(2)	1.942(3)
Mo(3)-O(2)#1	1.943(3)	Mo(3)-O(5)	2.321(5)
Mo(4)-O(11)	1.675(3)	Mo(4)-O(3)	1.909(3)
Mo(4)-O(8)	1.935(3)	Mo(4)-O(6)#1	1.936(3)
Mo(4)-O(9)	1.939(3)	Mo(4)-O(5)	2.3228(7)
O(5)-Mo(1)#1	2.3177(10)	O(5)-Mo(4)#1	2.3229(7)
O(6)-Mo(4)#1	1.936(3)		
O(1)-Mo(1)-O(6)	103.90(15)	O(1)-Mo(1)-O(2)	103.94(17)
O(6)-Mo(1)-O(2)	87.60(14)	O(1)-Mo(1)-O(4)	101.96(17)
O(6)-Mo(1)-O(4)	87.55(14)	O(2)-Mo(1)-O(4)	154.06(12)
O(1)-Mo(1)-O(3)	102.99(15)	O(6)-Mo(1)-O(3)	153.10(11)
O(2)-Mo(1)-O(3)	85.92(15)	O(4)-Mo(1)-O(3)	86.98(14)
O(1)-Mo(1)-O(5)	178.85(17)	O(6)-Mo(1)-O(5)	76.75(9)
O(2)-Mo(1)-O(5)	76.99(15)	O(4)-Mo(1)-O(5)	77.09(15)
O(3)-Mo(1)-O(5)	76.35(8)	O(7)-Mo(2)-O(4)#1	103.15(10)
O(7)-Mo(2)-O(4)	103.30(10)	O(4)#1-Mo(2)-O(4)	153.54(19)
O(7)-Mo(2)-O(8)#1	103.52(10)	O(4)#1-Mo(2)-O(8)#1	87.02(14)
O(4)-Mo(2)-O(8)#1	86.85(13)	O(7)-Mo(2)-O(8)	103.87(10)
O(4)#1-Mo(2)-O(8)	86.80(13)	O(4)-Mo(2)-O(8)	86.91(14)
O(8)#1-Mo(2)-O(8)	152.61(19)	O(7)-Mo(2)-O(5)	180.0
O(4)#1-Mo(2)-O(5)	76.85(10)	O(4)-Mo(2)-O(5)	76.70(10)
O(8)#1-Mo(2)-O(5)	76.48(10)	O(8)-Mo(2)-O(5)	76.13(10)
O(10)-Mo(3)-O(9)	103.12(10)	O(10)-Mo(3)-O(9)#1	103.46(10)
O(9)-Mo(3)-O(9)#1	153.4(2)	O(10)-Mo(3)-O(2)	103.19(10)
O(9)-Mo(3)-O(2)	86.96(14)	O(9)#1-Mo(3)-O(2)	87.03(14)
O(10)-Mo(3)-O(2)#1	103.35(10)	O(9)-Mo(3)-O(2)#1	87.07(14)
O(9)#1-Mo(3)-O(2)#1	86.84(14)	O(2)-Mo(3)-O(2)#1	153.46(19)
O(10)-Mo(3)-O(5)	180.000(1)	O(9)-Mo(3)-O(5)	76.88(10)
O(9)#1-Mo(3)-O(5)	76.54(10)	O(2)-Mo(3)-O(5)	76.81(10)
O(2)#1-Mo(3)-O(5)	76.65(10)	O(11)-Mo(4)-O(3)	104.18(15)
O(11)-Mo(4)-O(8)	104.82(17)	O(3)-Mo(4)-O(8)	87.83(15)
O(11)-Mo(4)-O(6)#1	102.77(15)	O(3)-Mo(4)-O(6)#1	153.04(12)
O(8)-Mo(4)-O(6)#1	86.13(14)	O(11)-Mo(4)-O(9)	102.08(17)
O(3)-Mo(4)-O(9)	87.13(15)	O(8)-Mo(4)-O(9)	153.05(12)
O(6)#1-Mo(4)-O(9)	86.47(15)	O(11)-Mo(4)-O(5)	178.19(17)
O(3)-Mo(4)-O(5)	76.89(9)	O(8)-Mo(4)-O(5)	76.62(14)
O(6)#1-Mo(4)-O(5)	76.16(9)	O(9)-Mo(4)-O(5)	76.45(15)
Mo(1)-O(2)-Mo(3)	115.93(16)	Mo(4)-O(3)-Mo(1)	116.74(13)
Mo(2)-O(4)-Mo(1)	116.48(15)	Mo(1)-O(5)-Mo(1)#1	179.3(2)
Mo(1)-O(5)-Mo(3)	90.27(12)	Mo(1)#1-O(5)-Mo(3)	90.43(12)
Mo(1)-O(5)-Mo(4)	90.01(3)	Mo(1)#1-O(5)-Mo(4)	89.99(3)

Table 3. continued

Mo(3)-O(5)-Mo(4)	89.98(12)	Mo(1)-O(5)-Mo(4)#1	89.99(3)
Mo(1)#1-O(5)-Mo(4)#1	90.01(3)	Mo(3)-O(5)-Mo(4)#1	90.35(12)
Mo(4)-O(5)-Mo(4)#1	179.7(2)	Mo(1)-O(5)-Mo(2)	89.73(12)
Mo(1)#1-O(5)-Mo(2)	89.57(12)	Mo(3)-O(5)-Mo(2)	180.0
Mo(4)-O(5)-Mo(2)	90.02(12)	Mo(4)#1-O(5)-Mo(2)	89.65(12)
Mo(1)-O(6)-Mo(4)#1	117.10(14)	Mo(2)-O(8)-Mo(4)	117.22(15)
Mo(3)-O(9)-Mo(4)	116.68(16)	C(16)-N(1)-C(8)	109.2(4)
C(16)-N(1)-C(12)	108.2(4)	C(8)-N(1)-C(12)	111.5(4)
C(16)-N(1)-C(4)	111.5(4)	C(8)-N(1)-C(4)	108.1(4)
C(12)-N(1)-C(4)	108.3(4)		

Symmetry transformations used to generate

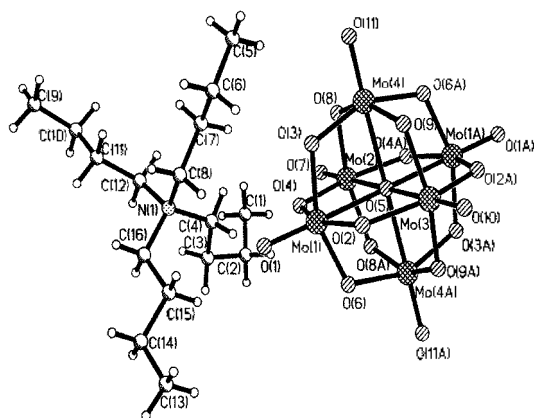


Fig. 1. Molecular structure for [*n*-Bu₄N]₂[Mo₆O₁₉] with the atomic numbering scheme.

Thermogravimetric analysis. The curves of the thermogravimetric (TG) analysis and differential thermal gravimetric (DTG) analysis for the title com-

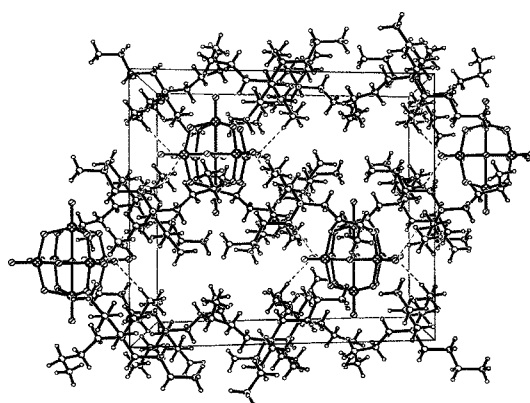


Fig. 2. A view of the crystal packing down the *a* axis for [*n*-Bu₄N]₂[Mo₆O₁₉].

pound are shown in the Fig. 3. It can be seen that the thermal decomposition of the compound includes two transitions. There are two endothermic peaks,

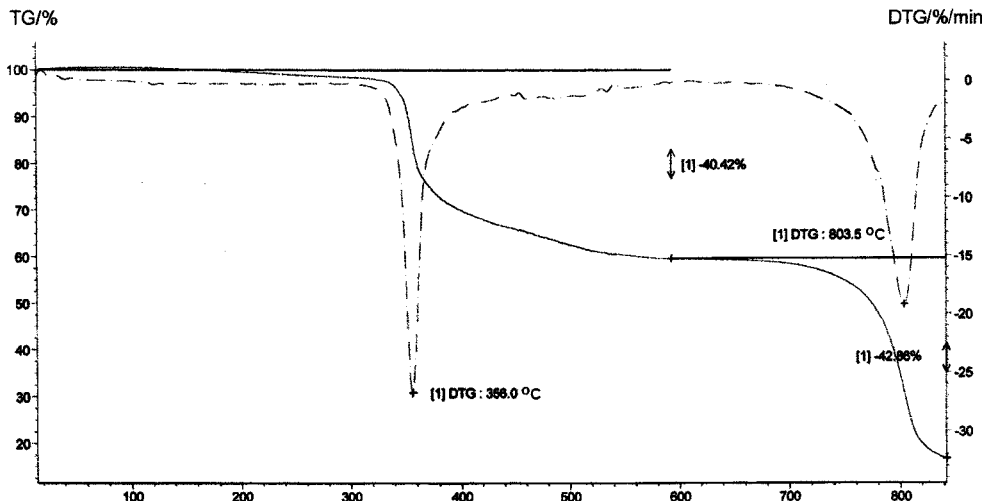


Fig. 3. TG/DTG curves of [*n*-Bu₄N]₂[Mo₆O₁₉].

one intense heat-absorbing peak at 356.0 °C and the other at 803.5 °C. It shows no decomposition before 356.0 °C; but at 356.0 °C, decomposition occurs. On the base of weight changes in the TG curve, the first process of the weight loss (40.42%) corresponds to the loss of two $[n\text{-Bu}_4\text{N}]^+$ groups and four oxygen atoms of $[\text{Mo}_6\text{O}_{19}]^{2-}$ anions (found 40.42%, calc. 40.16%) (356.0-600.0 °C), with an intense endothermic phenomenon; the second process of the weight loss (42.86%) is attributed to the further decomposition of the $[\text{Mo}_6\text{O}_{15}]$ group and the residue may be Mo_2O_2 (found 16.41%, calc. 16.72%) (600.0-803.5 °C). The title compound also has high thermal stability.

Acknowledgments. This work was supported by Natural Science Foundation of Shandong Province (No. Y2002B06), China.

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