© 1997 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, ***70***, *2101—2105 (1997)* 2101

Structures of Tetrakis(*t*-butylammonium) Diperoxotetramolybdate(4−) and -tungstate(4−)

Tomoji Ozeki* and Toshihiro Yamase*,†

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152

†Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received January 14, 1997)

Hydrogen-bonded columnar structures have been observed in tetrakis(*t*-butylammonium) diperoxotetramolybdate-(4−) (**1**) and -tungstate(4−) (**2**). **1**, $[(CH_3)_3CNH_3]_4[Mo_4O_{12}(O_2)_2]$, crystallizes in the tetragonal space group $I\,4$ with $a=16.312(2)$, $c=6.352(1)$ Å, $V=1690.2(5)$ Å^3, $Z=2$. **2**, $[(CH_3)_3CNH_3]_4[W_4O_{12}(O_2)_2]$, crystallizes in the tetragonal form, $I\bar{4}$, with $a=16.488(3)$, $c=6.349(2)$ Å, $V=1725.9(9)$ Å^3, $Z=2$. In each crystal, four *t*-butylammonium cations bridge two $[M_4O_{12}(O_2)_2]^{4-}$ (M = Mo, W) anions through hydrogen bonds to terminal and bridging oxo-ligands to make a columnar structure along the *c* axis.

Peroxide ligands show various modes of coordination in the polyoxoperoxometalate anions.1) Examples include non-bridging with the η^2 configuration,2) μ_2-bridging with the $\eta^1:\eta^2$ configuration,3,4) μ_3-bridging with the $1:2\kappa^2O;2:3\kappa^2O'$ configuration3) and μ_4-bridging with the $1:2\kappa^2O;3:4\kappa^2O'$ configuration.2) To the best of our knowledge, X-ray structure determinations on polyoxoperoxomolybdates and -tungstates have only been carried out with alkali metal,2) ammonium,3) and tetraalkylammonium4) cations as counter cations, all of which show isotropic features in the ionic interactions between the cations and anions. In order to investigate how the cations showing anisotropic interactions with anions affect the formation of the polyoxoperoxometalates and their crystal packing, we initiated structural studies on polyoxoperoxomolybdate and -tungstate salts containing amphiphilic cations as counter cations. As our first attempt, we employed the *t*-butylammonium cation and obtained two compounds: tetrakis(*t*-butylammonium) diperoxotetramolybdate(4−) (**1**) and -tungstate(4−) (**2**). Here, we report on the crystal structures of **1** and **2**.

Experimental

Single crystals of **1** and **2** were prepared as follows: 1 mL of $(CH_3)_3CNH_2$ (9.5 mmol) was added to a suspension of 8.63 mmol of MoO_3 (1.24 g) or WO_3 (2.0 g) in 20 mL distilled water and refluxed for 80—120 min until the solution became almost clear. After cooling the solution to room temperature, the residue was filtered off and 1.0 mL of a 30% H_2O_2 aqueous solution was added to the filtrate. At this point, the pH of the solution was around 8. After keeping the solution at room temperature for a few weeks, tetragonal pillar crystals were obtained. The yield for **1** was 32—34% based on Mo; for **2** it was 45—50% based on W. Found for compound **1**: C, 20.51; N, 5.98 H, 5.17%. Calcd for $Mo_4O_{16}C_{16}N_4H_{48}$: C, 20.38; N, 5.94; H, 5.28. Found for compound **2**: C, 14.92; N, 4.35; H, 3.76%. Calcd for $W_4O_{16}C_{16}N_4H_{48}$: C, 14.81; N, 4.29; H, 3.74%. D_m were measured by a flotation method in $C_2H_4Br_2/CCl_4$ for **1** and $CH_2I_2/C_2H_4Br_2$ for **2**.

Single crystals of the title compounds were mounted on a Rigaku AFC5S four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation. Crystal data and the experimental conditions are summarized in Table 1. Three control reflections, measured every 100 reflections, showed no significant changes. Lorentz-polarization and absorption5) corrections were applied. The W atom was located by analyzing the three-dimensional Patterson synthesis for **2**. Succeeding least-squares and difference Fourier calculations located the O, C, and N atoms. All of the non-hydrogen atoms were refined with the anisotropic mode by the full-matrix least-squares program. The initial fractional coordinates for Mo, O, C, and N in **1** were taken from their counterparts in **2**. The H-atom positions were calculated based on the staggered conformation and treated with the riding model. Neutral-atom scattering factors were taken from Maslen, Fox and O'Keefe;6) anomalous dispersion parameters from Creagh and McAuley;7) and mass attenuation coefficients from Creagh and Hubbell.8) All of the calculations were done using the teXsan program suite9) and SHELXL93 program.10) The final atomic parameters are listed in Tables 2 and 3 for **1** and **2**, respectively.11)

The ^{183}W NMR spectrum of **2** was recorded for its 0.6 mol dm^{-3} solution in D_2O using a 10 mm diameter NMR tube on a JEOL GX500 spectrometer at 20.7 MHz. Twenty-microsecond pulses were applied with a repetition time of 1.0 s; 4000 scans were accumulated. The ^{183}W chemical shift was referenced to the external 2.0 mol dm^{-3} Na_2WO_4 in D_2O.

Results and Discussions

An X-ray structure analysis revealed that single crystals of **1** comprise *t*-butylammonium cations and $[Mo_4O_{12}(O_2)_2]^{4-}$ anions. Figure 1 shows an ORTEP12) drawing of the $[Mo_4O_{12}(O_2)_2]^{4-}$ anion in **1**. The basic metal–oxygen framework in this structure is identical with that of the $[Mo_4O_{12}(O_2)_2]^{4-}$ anion in $K_4[Mo_4O_{12}(O_2)_2]$.2) An X-ray structure analysis of **2** showed that crystals of **2** consist of *t*-butylammonium cations and $[W_4O_{12}(O_2)_2]^{4-}$ anions,

Table 1. Crystal Data and Experimental Conditions

	1	**2**
Formula	$[(CH_3)_3CNH_3]_4[Mo_4O_{12}(O_2)_2]$	$[(CH_3)_3CNH_3]_4[W_4O_{12}(O_2)_2]$
Formula weight	936.3	1288.0
Space group	$I\bar{4}$	$I\bar{4}$
a/Å	16.312(2)	16.488(3)
c/Å	6.352(1)	6.349(2)
V/Å^3	1690.2(5)	1725.9(9)
Z	2	2
D_m/g cm^{-3}	1.83	2.48
D_x/g cm^{-3}	1.84	2.48
Crystal shape	Tetragonal pillar	Tetragonal pillar
Crystal size/mm	$0.20 \times 0.20 \times 0.50$	$0.125 \times 0.125 \times 0.40$
Crystal color	Yellow	Colorless
Temperature/K	298	298
Radiation	Mo $K\alpha$ (λ =0.71069 Å)	Mo $K\alpha$ (λ =0.71069 Å)
μ(Mo $K\alpha$)/mm^{-1}	1.52	13.35
A	0.727—0.760	0.192—0.256
Number of reflections for cell parameters	25	23
2θ range for cell parameters	20°—25°	20°—25°
Number of measured reflections	1412	2791
Number of independent reflections (Friedel pairs were not averaged)	1401	2498
R_{int}	0.023	0.019
Number of observed reflections	1198	1993
Criterion for observed	$I > 2\sigma(I)$	$I > 2\sigma(I)$
2θ range	5°—60°	5°—60°
$(\sin\theta/\lambda)_{\max}$/Å^{-1}	0.704	0.704
	$0 \le h \le 22$	$-23 \le h \le 23$
Range of indices	$0 \le k \le 22$	$0 \le k \le 23$
	$0 \le l \le 8$	$0 \le l \le 8$
Scan mode	2θ–ω	2θ–ω
Scan speed (ω)/° min^{-1}	4.0	4.0
Number of parameters	91	91
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
w	$[\sigma^2(F_o^2)+(0.025P)^2]^{-1}$ where $P=(F_o^2+2F_c^2)/3$	$[\sigma^2(F_o^2)+(0.04P)^2]^{-1}$ where $P=(F_o^2+2F_c^2)/3$
R	0.023	0.032
wR	0.048	0.067
S	1.16	1.09
$(\Delta/\sigma)_{\max}$	0.005	0.003
$(\Delta\rho)_{\max}$/eÅ^{-3}	0.33	0.50
$(\Delta\rho)_{\min}$/eÅ^{-3}	−0.37	−0.86

which have the same metal–oxygen framework as those of the $[Mo_4O_{12}(O_2)_2]^{4-}$ anions in **1** and in $K_4[Mo_4O_{12}(O_2)_2]$.[2)] In both crystals **1** and **2**, the $[M_4O_{12}(O_2)_2]^{4-}$ anions (M=Mo, W) are located at the crystallographic $\bar{4}$ site, resulting in that all the M atoms are equivalent. The anions show approximate D_{2d} symmetry, the twofold axes of which are shown in Fig. 1. The interatomic distances in **1** and **2** are listed in Table 4. Each metal atom is surrounded by six oxygen atoms to form a distorted MO_6 octahedron of approximately C_{2v} symmetry: two terminal O atoms, O1 and O2; two bridging O atoms, O3 and its symmetry equivalent; and two peroxide O atoms O4 and its symmetry equivalent. The four MO_6 octahedra are linked to each other by sharing edges with one another. The metal–oxygen distances are 1.714 to 1.765 Å for the terminal O atoms, 1.925 to 1.943 Å for the bridging O atoms and 2.222 to 2.243 Å for the peroxide O atoms. This bonding pattern provides us with an alternative description of the $[M_4O_{12}(O_2)_2]^{4-}$ structure: two $O_2{}^{2-}$ groups weakly linked to a nominally neutral M_4O_{12} group consisting of four distorted MO_4 tetrahedra sharing corners. A neutral ring structure consisting of corner-shared MO_4 tetrahedra was first proposed for the Mo_6O_{18} ring in $[\alpha\text{-}Mo_8O_{26}]^{4-}$ by Fuchs and Hartl,[13)] and similar ring structures can be found in several polyoxomolybdates, among which are the Mo_4O_{12} ring in $[(CH_3)_2AsMo_4O_{15}H]^{4-}$[14)] and Mo_5O_{15} in $[P_2Mo_5O_{23}]^{6-}$.[15)]

The ^{183}W NMR spectra of **2** showed a single peak at −0.59 ppm with $\Delta\nu_{1/2} = 3.2$ Hz, which designates that all of the W atoms in the anion are also equivalent in solution. This is the first measurement of the ^{183}W NMR chemical shift

Table 2. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for **1**

Atom	x	y	z	U_{eq} [a]
Mo	0.06714(1)	0.12451(1)	0.00156(9)	0.0237(1)
O1	0.1141(2)	0.1691(2)	0.2171(5)	0.0341(7)
O2	0.0799(2)	0.1923(2)	−0.2019(5)	0.0350(7)
O3	0.1486(2)	0.0452(2)	−0.0799(4)	0.0273(6)
O4	0.0434(1)	0.0126(2)	0.1916(4)	0.0241(5)
N	0.1951(2)	0.0553(2)	0.4960(10)	0.0311(6)
C1	0.2833(3)	0.0842(2)	0.4992(15)	0.0378(7)
C2	0.2844(5)	0.1662(3)	0.6110(10)	0.063(2)
C3	0.3116(3)	0.0922(4)	0.2715(8)	0.061(1)
C4	0.3322(3)	0.0190(3)	0.6190(10)	0.063(2)

a) $U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 3. Fractional Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for **2**

Atom	x	y	z	U_{eq}
W	0.06586(1)	0.12414(1)	0.00213(10)	0.0281(1)
O1	0.1138(4)	0.1690(4)	0.2216(12)	0.044(2)
O2	0.0779(4)	0.1922(4)	−0.2064(11)	0.043(2)
O3	0.1467(3)	0.0457(3)	−0.0810(8)	0.032(1)
O4	0.0426(3)	0.0133(4)	0.1921(8)	0.030(1)
N	0.1978(3)	0.0569(3)	0.496(2)	0.037(1)
C1	0.2851(5)	0.0868(5)	0.498(3)	0.047(2)
C2	0.2869(8)	0.1664(7)	0.614(2)	0.074(4)
C3	0.3148(8)	0.0965(9)	0.273(2)	0.077(4)
C4	0.3330(7)	0.0225(8)	0.619(2)	0.074(4)

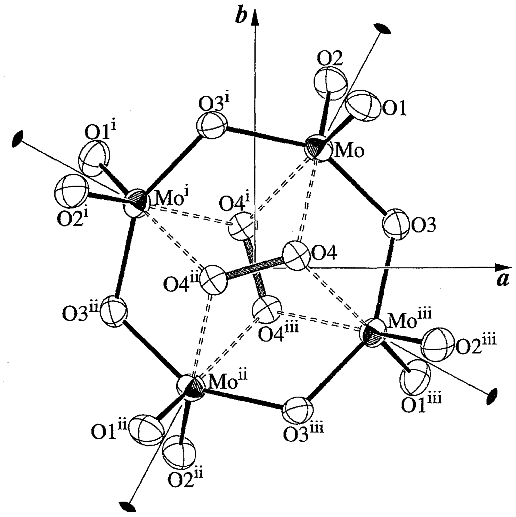

Fig. 1. ORTEP drawing of the $[Mo_4O_{12}(O_2)_2]^{4-}$ anion viewed down the c axis. Non-crystallographic twofold axes are shown. Displacement ellipsoids are scaled to enclose 50% probability levels. See Table 4 for the notation of the symmetry codes.

Table 4. Interatomic Distances (Å) in **1** and **2**

	1	**2**
M–O1	1.729(3)	1.765(7)
M–O2	1.714(3)	1.747(7)
M–O3	1.925(2)	1.931(5)
M–O3^{i}	1.939(2)	1.943(5)
M–O4	2.222(2)	2.222(5)
M–O4^{i}	2.225(3)	2.243(6)
O4–O4^{ii}	1.473(4)	1.473(10)
M–M^{i}	3.2633(5)	3.2769(8)
C1–N	1.514(4)	1.522(9)
C1–C2	1.515(7)	1.51(2)
C1–C3	1.524(10)	1.52(2)
C1–C4	1.532(7)	1.53(2)
N···O1	2.886(5)	2.894(11)
N···O2^{iii}	2.891(5)	2.887(13)
N···O3^{iv}	2.804(7)	2.819(15)

Symmetry codes are as follows: i) $-y,x,-z$; ii) $-x,-y,z$; iii) $y,-x,-z$; iv) $x,y,1+z$.

for W atoms coordinated by the peroxide ligands of μ_4-bridging with the $1:2\kappa^2O;3:4\kappa^2O'$ configuration. The only reported ^{183}W NMR chemical shifts for the peroxotungstate are those for $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $[PW_xO_y]^{\omega-}$ ($x=$ 1—4) anions, which showed highly upfield shifts, as much as −620—−700 ppm.[4] On the other hand, the ^{183}W chemical shift for **2** showed only a slight shift from WO_4^{2-}. The difference in the ^{183}W NMR chemical shifts between these compounds may be ascribed to a difference in the geometry between the W nuclei and the peroxide ligands. The W atoms in the $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ and $[PW_xO_y]^{\omega-}$ anions are coordinated by at least one peroxide ligand of the η^2-terminal configuration with the W–O distances of 1.66—1.97 Å.[4] On the other hand, each W atom in $[W_4O_{12}(O_2)_2]^{4-}$ is separated from the O atoms of the peroxide ligands by 2.222—2.243 Å. As discussed above, its coordination sphere approximates a distorted tetrahedron disregarding the weak bonds to the peroxide ligands, resulting in its chemical shift being only slightly deviated from $WO_4{}^{2-}$.

Figure 2 shows the columnar structure built up by the hydrogen bonds. Unlike $[(CH_3)_3CNH_3]_4[V_4O_{12}]$,[16] where the N atoms in *t*-butylammonium cations have contacts only to the terminal O atoms of the $[V_4O_{12}]^{4-}$ anion, N atoms in the *t*-butylammonium cations in **1** and **2** are hydrogen-bonded to both the terminal and bridging O atoms of the $[M_4O_{12}(O_2)_2]^{4-}$ anions. The N···O distances to the bridging O atoms are shorter than those to the terminal O atoms, suggesting that the bridging O atoms are stronger hydrogen-bond acceptor than the terminal O atoms. An MP2/STO-3G level ab initio molecular-orbital calculation using the Gaussian94 program[17] showed that the bridging O atoms are slightly more negatively charged than the terminal O atoms; the Mulliken charge of the bridging O atom is −0.40 and that of the terminal O atom is −0.35.

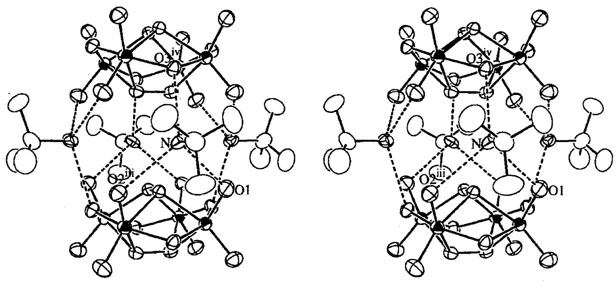

Fig. 2. Hydrogen bonded columnar structure of $[(CH_3)_3CNH_3]_4[W_4O_{12}(O_2)_2]$ viewed down the *b* axis. Symmetry codes are the same as those defined in Table 4.

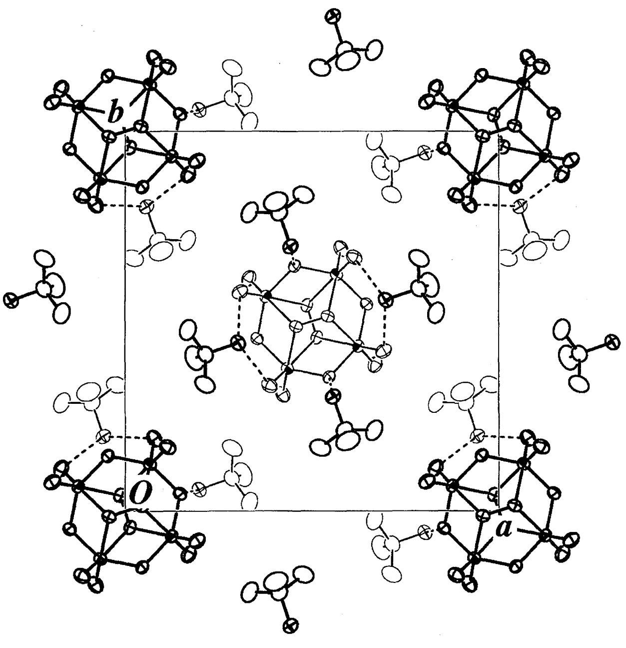

Fig. 3. Packing diagram of $[(CH_3)_3CNH_3]_4[W_4O_{12}(O_2)_2]$ viewed down the *c* axis. Hydrogen bonds are shown in broken lines. Atoms with the fractional coordinates of $z \approx 1$ are shown in solid lines and those with $z \approx 0.5$ in thin lines.

The two crystals, **1** and **2**, are isomorphous. Figure 3 shows a packing diagram of the crystal **2** viewed down the *c* axis. The $[M_4O_{12}(O_2)_2]^{4-}$ anions occupy the $\bar{4}$ site of the crystal at $x=y=z=0$ and $x=y=z=1/2$. The $[M_4O_{12}(O_2)_2]^{4-}$ anions and the NH_3 groups of the *t*-butylammonium cations form hydrophilic channels around $x \approx 0.0$, $y \approx 0.0$, and $x \approx 0.5$, $y \approx 0.5$ along the crystallographic *c* axis. The region around $x \approx 0.5$, $y \approx 0.0$ is a hydrophobic channel along the crystallographic *c* axis surrounded by the *t*-butyl groups of the *t*-butylammonium cations. It was shown that introducing amphiphilic alkylammonium cations to the polyoxoperoxometalate crystals resulted in a columnar structure constructed by alternating hydrophilic and hydrophobic channels.

The authors thank Dr. Y. Nakamura for the measurement of ^{183}W NMR spectrum.

References

1) See, for example: M. H. Dickman, and M. T. Pope, *Chem. Rev.*, **94**, 569 (1994), and references therein.

2) R. Stomberg, L. Trysberg, and I. Larking, *Acta Chem. Scand.*, **24**, 2678 (1970).

3) I. Persdotter, L. Trysberg, and R. Stomberg, *Acta Chem. Scand.*, **A40**, 83 (1986).

4) L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, and J.-M. Brégeault, *Inorg. Chem.*, **33**, 871 (1994).

5) J. De Meulenaer and H. Tompa, *Acta Crystallogr.*, **19**, 1014 (1965).

6) E. N. Maslen, A. G. Fox, and M. A. O'Keefe, "International Tables for Crystallography," ed by A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht (1992), Vol. C, pp. 500—502.

7) D. C. Creagh and W. J. McAuley, "International Tables for Crystallography," ed by A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht (1992), Vol. C, pp. 219—222.

8) D. C. Creagh and J. H. Hubbell, "International Tables for Crystallography," ed by A. J. C. Wilson, Kluwere Academic Publishers, Dordrecht (1992), Vol. C, pp. 200—206.

9) Molecular Structure Corporation, "teXsan, Single Crystal Structure Analysis Software, Version 1.6," Molecular Structure Corporation, The Woodlands, TX 77381, U. S. A. (1993).

10) G. M. Sheldrick, "SHELXL93, Program for the Refinement of Crystal Structures," University of Göttingen, Germany (1993).

11) The anisotropic displacement tensors, hydrogen atom coordinates, complete lists of the geometry, and the struture factor tables are deposited as Document No. 70030 at the Office of the Editor of Bull. Chem. Soc. Jpn.

12) M. N. Burnett and C. K. Johnson, "ORTEP-III, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S. A. (1996).

13) J. Fuchs and H. Hartl, *Angew. Chem.*, **88**, 385 (1976).

14) K. M. Barkigia, L. M. Rajković, M. T. Pope, and C. O. Quicksall, *J. Am. Chem. Soc.*, **97**, 4146 (1975).

15) R. Strandberg, *Acta Chem. Scand.*, **27**, 1004 (1973).

16) P. Román, A. S. José, A. Luque, and J. M. Gutiérrez-Zorrilla, *Inorg. Chem.*, **32**, 775 (1993).

17) M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, "Gaussian 94," Gaussian Inc., Pittsburgh, PA (1995).