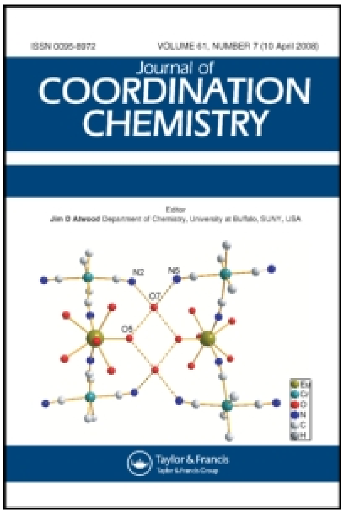

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PREPARATION AND STRUCTURE OF TETRAMETHYLAMMONIUM HYDROGEN TRIPEROXOTRIMOLYBDODISULFATE TRIHYDRATE, $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$

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A novel peroxopolyoxomolybdate compound, $[N(CH_3)_4]_3$ $[H(SO_4)_2$ $(MoO_2(O_2))_3]\cdot 3H_2O$, has been obtained from a strongly acidic aqueous solution of a molybdate-sulfate system as the monoclinic crystal of $P2_1/n$, a = 13.497(3), b = 15.231(4), c = 32.603(2) Å, β = 103.113(9)°, and V = 6577(2) Å^3. The final R-value was 0.0986 for 395 parameters using 7162 reflections. Each of the two crystallographically independent polyanions contains three molybdenum atoms with five O^{2-}, one O_2^{2-}, and two sulfate groups, one of which is a tripod ligand apical to the molybdenum plane, and the other is a bipod ligand equatorial to the Mo plane.

KEYWORDS: structure, preparation, molybdosulfate, peroxomolybdate

INTRODUCTION

The chemistry of polyoxometalates, isopolyoxometalates and heteropolyoxometalates, has been well established in fundamental and applied fields.[1] On the contrary, the chemistry of peroxopolyoxometalates, polyoxometalates having peroxo group(s) O_2^{2-}, appears to be less explored although some applications in catalysis[2] and material sciences[3] have been examined. Hence, it is worthwhile to study the formation and structural chemistry of peroxopolyoxometalates, for the polyoxometalate chemistry and for understanding of its chemistry in such applications.

In the course of our studies on the preparation and structural analysis of peroxopolyoxometalates, a novel compound $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$ has been isolated from the molybdate-sulfate system as single crystals and its

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structure has been determined by a single crystal X-ray diffraction study. This peroxopolyanion was prepared under analogous conditions to the preparation of dihydrogentetraperoxohexatungstodisulfate salt, $[N(CH_3)_4]_4[\{H(SO_4)W_3O_7(O_2)_2\}_2O]$, which has been reported.[4] Although the tungstate compound has a condensate structure of two trinuclear tungstosulfate units which has one sulfate group as a tripodal ligand, the present molybdosulfate has two crystallographically independent trinuclear moieties which involve two sulfate groups as bipodal and tripodal ligands.

A systematic study by Stomberg *et al.*[5] on peroxoisopolyoxomolybdates showed several kinds of nuclearity and structures peculiar to the peroxopolyoxomolybdates. Other than this work, only one structure as a peroxopolyoxomolybdate has been reported – octaperoxotetramolybdophosphate, $[(PO_4)(MoO(O_2)_2)_4]^{3-}$, which can behave as an oxidation catalyst.[6] The present compound offers an example of peroxoheteropolymolybdates, and the first example having sulfur as hetero atoms.

EXPERIMENTAL

Preparation

The present compound $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$ is formed from a strongly acidic aqueous solution of molybdate and sulfate under conditions analogous to tetraperoxohexatungstodisulfate previously reported.[4] To a 10 mL aqueous solution of 3.4 g $Na_2MoO_4\cdot 2H_2O$, 1.5 mL of 30% H_2O_2 aqueous solution was added, and the pH was promptly adjusted to about 0.5 by 60% nitric acid. Then 4.8 g of $N(CH_3)_4HSO_4$ in 8 mL of H_2O was added; the molar ratio of Mo/S was about 0.5. The orange-colored microcrystalline product formed after 24 h at room temperature was removed by suction filtration, and the filtrate was kept at room temperature. Orange-colored tabular crystals appeared in a few days. Anal. Calcd. for $C_{12}H_{43}N_3O_{23}S_2Mo_3$(%): C 15.18; H 4.56; N 4.43. Found: C 15.10; H 4.53; N 4.47. The solution after the filtration was rather stable at room temperature and decomposition occurred after several weeks with orange-colored precipitation. The crystals obtained were also stable at room temperature and no obvious decay could be observed in several weeks. The formation of this compound was tested in the range of pH 0 to 3 and Mo/S molar ratio 0.25 to 3.

For the pH adjustment 60% H_2SO_4 may be used in place of 60% HNO_3. Hydrochloric acid or perchloric acid cannot be recommended. Addition of hydrochloric acid causes generation of Cl_2 and decomposition of hydrogen peroxide; perchloric acid precipitates $N(CH_3)_4ClO_4$. The use of tetramethylammonium halide is also not recommended, because of formation of halo-compounds and decomposition of H_2O_2. As for the source of tetramethylammonium, $N(CH_3)_4HSO_4$ was most appropriate to prevent decomposition of hydrogen peroxide and for keeping the pH lower.

X-ray Diffraction Measurements and Structure Determination

A single crystal with dimensions 0.2 × 0.2 × 0.2 mm^3 was mounted on RIGAKU AFC-5R automated four-circle diffractometer at the Department of Chemistry, Faculty of Science, The University of Tokyo with a graphite monochromated Mo

Kα radiation (λ = 0.71069 Å, 50 kV, 180 mA) at 298 K. Intensity measurements were carried out under the following conditions: ω-scan with scanning speed = 8° min^{-1}; $4° \leq 2\theta \leq 55°$ ($0 \leq h \leq 19$, $0 \leq k \leq 21$, $-46 \leq l \leq 46$); three standard reflections were monitored every 200; psi-scen on three reflections. Crystallographic data are:

$C_{23}H_{43}N_3Mo_3O_{23}S_2$, Fw = 949.43, monoclinic, $P2_1/n$, a = 13.497(3), b = 15.231(4), c = 32.603(2) Å, β = 101.113(9)°, V = 6577(2) Å^3, Dm = 1.92, Dc = 1.92 g cm^{-3}, Z = 8, μ(Mo Kα) = 13.07 cm^{-1}, and F(000) = 3824.

Calculations for structure determination and refinements were carried out on a HITAC M680 computer at the Computer Center, Institute for Molecular Science. An absorption correction based on the psi-scans was applied using a program in UNICS III.[7] Patterson vectors were calculated by SHELXS86,[8] and full-matrix least-squares refinement and Fourier syntheses were carried out by SHELX76.[9] Atomic scattering factors and anomalous dispersion factors were cited from International Tables for X-ray Crystallography.[10] Of the total 16421 reflections, 7162 unique ones with $Fo \leq 3.0\sigma(Fo)$ and $4° \leq 2\theta \leq 50°$ were used for calculations; those with 2θ higher than 50° were discarded because of the low intensities and accuracy. All molybdenum and sulfur atoms were located from Patterson vectors; all other non-H atoms were found from successive difference Fourier syntheses. Anisotropic thermal parameters were applied to Mo and S; C, N and O atoms were refined isotropically. Refinement of 395 parameters gave a final R-value 0.0986.

The rather high R-value seems to be caused by disorder in the structure and the long c-dimension of 32.603(2) Å. The value is the best among those for a number of crystals subjected for intensity measurements. Although disorder is suggested from the very weak intensities and low accuracy for the reflections in the higher 2θ range, nothing was found in the refinement process.

RESULTS AND DISCUSSION

Preparation of the Compound

Formation of the tetramethylammonium salt of the complex was surveyed in the pH range of 0 to 3 and Mo/S molar ratio range of 0.25 to 3. The result is shown in Figure 1a. The compound could be obtained in the lower pH range 0 to 1 and the lower Mo/S molar ratio 0.25 to 1.5. In the higher pH range the product was peroxodimolybdate. If the Mo/S molar ratio range becomes higher, the color of the solution is weak orange but no products were obtained. In comparison with the formation range for tetraperoxohexatungstodisulfate, shown in Figure 1b, the pH ranges were similar, whereas the allowed W/S molar ratio range for the tungstate is rather small.

The rather low pH range seems not to be necessary for formation of the metal peroxide moiety itself, because, for example, the structure of tetraperoxohexatungstodiphosphate prepared at pH 5 involves the same peroxotungstate moiety. However, the corresponding peroxomolybdate moiety is not known. Stomberg *et al.*[5c] reported the structure of tetraperoxotrimolybdate prepared at pH 8.3–9.2, but the molybdate moiety of tetraperoxotrimolybdate is not identical with that in

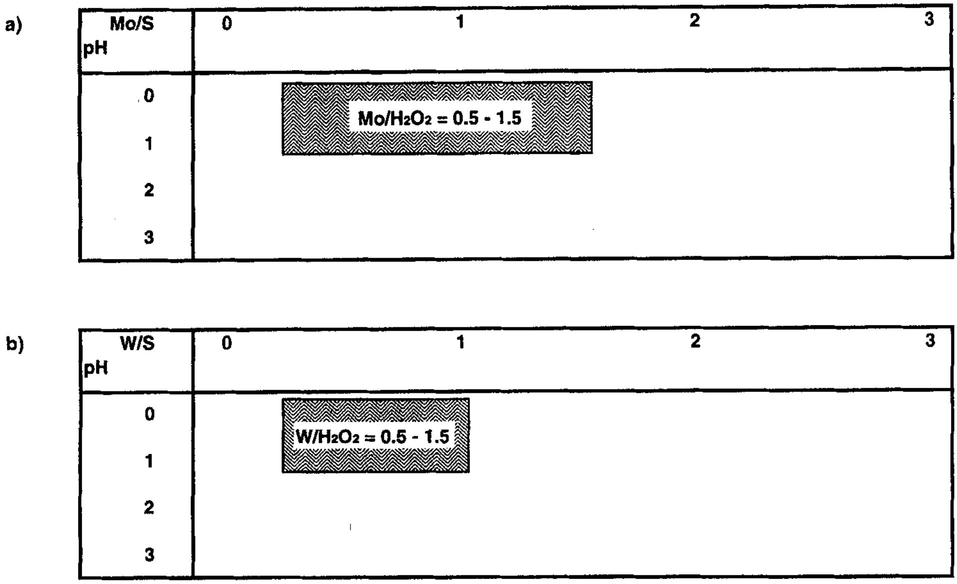


Figure 1 Formation range of a) $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$ and b) $[N(CH_3)_4]_4[\{H(SO_4)W_3O_7(O_2)_2\}_2O]$.

the present triperoxotrimolybdodisulfate. The lower pH for the present compound may be due to the strong acidity of sulfuric acid.

The tungstate needed a rather small value of metal/S ratio compared to molybdate in spite of the fact that the ratio in the polyanion is 2.0 for the tungstate and 1.5 for the molybdate. This is an unsolved problem.

As for the counter cations, only tetramethylammonium has given a well-developed crystal so far among the counter cations we have examined. Some other tetraalkylammoniums such as tetra-*n*-butylammonium or tetraethylammonium gave poor crystalline products.

Structure Description

The refined atomic coordinates and equivalent/isotropic thermal parameters are listed in Table 1. There are two crystallographically independent polyanions in the asymmetric unit, though the structures are essentially the same. The ORTEP[11] views of both polyanions with atomic notations and their polyhedra are shown in Figure 2. The polyanion involves three molybdenum atoms forming a triangle. Each Mo atom is coordinated by four bridging oxygen atoms (Ob) one of which, O123 or O456, is shared by three Mo atoms, one terminal oxygen (Ot) and one peroxo group O_2^{2-}. Thus the Mo atom takes a pentagonal bipyramid coordination sphere. Mo2 and Mo5 share two equatorial edges of their coordination polyhedra with another two Mo atoms, Mo1 and Mo3 or Mo4 and Mo6, respectively. The peroxo groups are approximately in the Mo plane, at the *trans* positions of three-coordinated O123 or O456. Two sulfate groups are involved in each polyanion; one behaves as a tripodal ligand to three Mo atoms, and the other as a bipodal ligand

Table 1 Atomic coordinates and equivalent isotropic thermal parameters with Esd's in parentheses

Atom	*x/a*	*y/b*	*z/c*	*U*eq/*U*iso
Mo1	0.3033(1)	0.1247(1)	0.51191(5)	0.0381(9)
Mo2	0.2435(1)	0.24998(9)	0.43516(4)	0.0307(8)
Mo3	0.3002(1)	0.3824(1)	0.51454(5)	0.0390(9)
Mo4	0.4254(1)	0.40321(9)	0.24163(4)	0.0264(8)
Mo5	0.4948(1)	0.27479(9)	0.31699(4)	0.0263(8)
Mo6	0.4441(1)	0.14826(9)	0.23454(4)	0.0259(8)
S1	0.0966(3)	0.2537(4)	0.5064(2)	0.051(3)
S2	0.4081(4)	0.2523(3)	0.5881(2)	0.047(3)
S3	0.6386(3)	0.2880(3)	0.2445(1)	0.030(2)
S4	0.3282(3)	0.2782(3)	0.1618(1)	0.034(2)
O123	0.3044(8)	0.2558(6)	0.4971(3)	0.027(2)
O456	0.4301(7)	0.2712(6)	0.2540(3)	0.025(2)
O1T	0.422(1)	0.1021(9)	0.5071(4)	0.059(4)
O2T	0.351(1)	0.2566(8)	0.4197(4)	0.053(4)
O3T	0.416(1)	0.4105(9)	0.5080(4)	0.060(4)
O4T	0.3046(9)	0.4164(8)	0.2452(4)	0.041(3)
O5T	0.3859(8)	0.2592(7)	0.3335(4)	0.035(3)
O6T	0.3315(9)	0.1145(8)	0.2410(4)	0.042(3)
O12	0.2445(10)	0.1298(8)	0.4541(4)	0.049(3)
O23	0.2394(8)	0.3800(7)	0.4529(3)	0.034(3)
O45	0.4863(8)	0.3949(7)	0.3008(3)	0.031(3)
O56	0.5063(8)	0.1480(7)	0.2970(3)	0.029(2)
O1S1	0.1509(10)	0.1738(9)	0.5245(4)	0.052(3)
O1S2	0.3483(9)	0.1776(8)	0.5717(4)	0.048(3)
O2S1	0.0978(9)	0.2535(8)	0.4616(4)	0.044(3)
O3S1	0.147(1)	0.3309(9)	0.5246(4)	0.056(4)
O3S2	0.3458(9)	0.3336(8)	0.5733(4)	0.047(3)
O4S3	0.5799(8)	0.3659(7)	0.2285(3)	0.028(2)
O4S4	0.3858(8)	0.3591(7)	0.1792(3)	0.032(3)
O5S3	0.6413(9)	0.2820(7)	0.2906(4)	0.039(3)
O6S3	0.5893(8)	0.2073(7)	0.2248(3)	0.032(3)
O6S4	0.3942(9)	0.1985(7)	0.1765(4)	0.037(3)
O1P1	0.243(1)	0.012(1)	0.5041(5)	0.071(4)
O1P2	0.275(1)	0.031(1)	0.5464(5)	0.074(4)
O2P1	0.1521(10)	0.2961(9)	0.3862(4)	0.053(4)
O2P2	0.156(1)	0.1989(9)	0.3862(4)	0.061(4)
O3P1	0.271(1)	0.477(1)	0.5491(5)	0.076(5)
O3P2	0.233(1)	0.493(1)	0.5065(5)	0.071(4)
O4P1	0.478(1)	0.5207(9)	0.2523(4)	0.055(4)
O4P2	0.444(1)	0.5056(9)	0.2082(4)	0.056(4)
O5P1	0.5878(9)	0.2298(8)	0.3639(4)	0.042(3)
O5P2	0.5797(9)	0.3231(8)	0.3660(4)	0.049(3)
O6P1	0.5170(9)	0.0385(8)	0.2403(4)	0.047(3)
O6P2	0.4757(9)	0.0593(8)	0.1975(4)	0.041(3)
O7T	-0.002(1)	0.254(1)	0.5125(5)	0.076(5)
O8T1	0.497(1)	0.2533(9)	0.5722(5)	0.069(4)
O8T2	0.420(1)	0.2533(9)	0.6333(4)	0.057(4)
O9T	0.7395(10)	0.2950(8)	0.2371(4)	0.049(3)
OXT1	0.237(1)	0.2707(9)	0.1767(5)	0.062(4)
OXT2	0.3173(10)	0.2815(8)	0.1181(4)	0.053(3)
OW1	0.320(1)	0.114(1)	0.6779(5)	0.071(4)
OW2	0.428(2)	0.201(2)	-0.1025(7)	0.133(8)
OW3	0.581(1)	0.031(1)	-0.0780(5)	0.086(5)
OW4	0.657(1)	0.0600(10)	0.3306(5)	0.067(4)

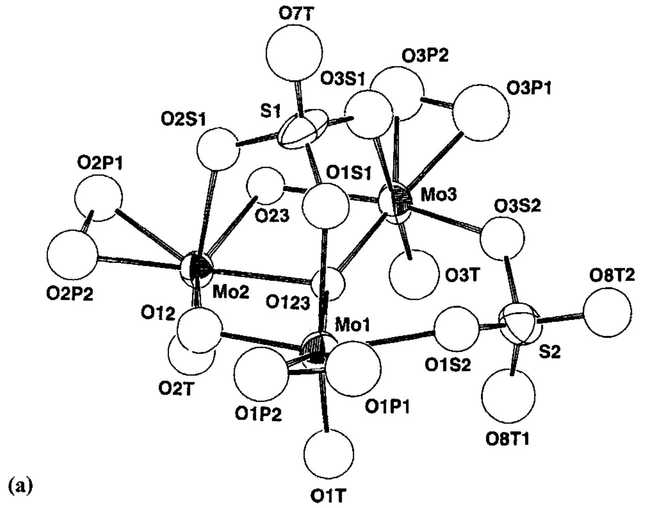
Table 1 *Continued*

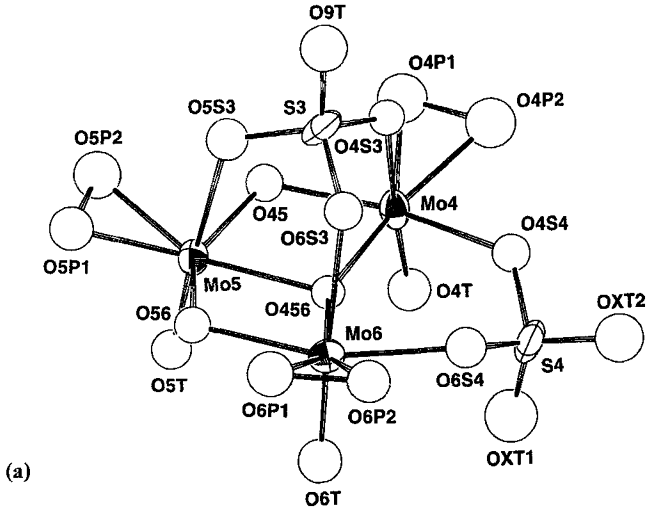
Atom	*x/a*	*y/b*	*z/c*	*U*eq/*U*iso
OW5	0.436(1)	0.148(1)	0.0821(6)	0.093(5)
OW6	0.805(1)	0.189(1)	0.3390(5)	0.079(5)
N1	0.0640(9)	0.2608(8)	0.2685(4)	0.025(3)
N2	0.674(1)	0.2470(10)	0.4826(5)	0.044(4)
N3	0.741(1)	0.038(1)	0.1702(5)	0.044(4)
N4	0.1430(10)	0.0270(9)	0.1257(4)	0.033(3)
N5	0.609(1)	0.0065(9)	0.6241(4)	0.033(3)
N6	0.023(1)	0.019(1)	0.5939(6)	0.057(5)
C1	-0.013(2)	0.227(1)	0.2929(6)	0.050(5)
C2	0.031(2)	0.242(1)	0.2234(6)	0.052(5)
C3	0.073(2)	0.359(2)	0.2756(7)	0.066(6)
C4	0.161(2)	0.219(1)	0.2841(7)	0.064(6)
C5	0.748(4)	0.243(3)	0.455(2)	0.17(2)
C6	0.618(3)	0.326(3)	0.4776(1)	0.17(2)
C7	0.712(3)	0.231(2)	0.525(1)	0.13(1)
C8	0.605(4)	0.176(3)	0.472(2)	0.20(2)
C9	0.681(2)	0.111(2)	0.148(1)	0.11(1)
C10	0.838(3)	0.024(2)	0.157(1)	0.13(1)
C11	0.708(4)	-0.043(4)	0.165(2)	0.21(2)
C12	0.762(3)	0.052(2)	0.215(1)	0.14(1)
C13	0.190(2)	0.082(2)	0.0974(7)	0.068(6)
C14	0.102(1)	0.081(1)	0.1559(6)	0.045(5)
C15	0.217(2)	-0.0377(2)	0.1490(7)	0.066(6)
C16	0.064(2)	-0.024(2)	0.1003(7)	0.068(6)
C17	0.570(2)	0.066(2)	0.6536(8)	0.086(8)
C18	0.535(2)	-0.061(2)	0.6037(8)	0.086(8)
C19	0.691(2)	-0.044(2)	0.6499(9)	0.088(8)
C20	0.640(2)	0.059(2)	0.5913(8)	0.077(7)
C21	-0.051(4)	0.066(3)	0.566(2)	0.20(2)
C22	0.079(3)	0.089(3)	0.615(1)	0.16(2)
C23	0.060(4)	-0.032(3)	0.565(1)	0.19(2)
C24	-0.023(4)	-0.033(4)	0.621(2)	0.24(2)

*U*eq for Mo and S; *U*iso for O, N and C.
$U\text{eq} = (1/3)\ \Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

to two Mo atoms. The tripodal one coordinates to Mo atoms from one side of the triangle, and three Ot atoms from another side. The bipodal sulfate bridges two Mo atoms at the end corners of the triangle, and the Ob atoms are approximately in the Mo plane mentioned above. One of the coordination-free terminal oxygen atoms of the bipodal sulfate group, O8T2 or OXT2, is also coplanar to the plane. As this bipodal group is supported by two Ob atoms, it is seen nodding in the ORTEP view.

Selected interatomic distances and bond angles are listed in Tables 2 and 3, respectively. The Mo-O distances are within the normal values. A strong *trans* effect of the terminal oxygen is found in Mo1-O1S1, Mo2-O2S1, Mo3-O3S1, Mo4-O4S3, Mo5-O5S3 and Mo6-O6S3 (2.23(1)–2.31(1) Å). The O-O distances and O-Mo-O angles in the peroxomolybdenum moieties are also normal. In the tripodal sulfate groups, the S1-O7T distance of 1.38(2) Å is reasonable for S = O bonding; the considerably longer S3-O9T distance of 1.43(1) Å is from hydrogen bonding with a water molecule OW1. The SO_4 polyhedra are slightly distorted with the O-S-O angles in the range of 107.2(8) to 111.0(9)°. The S-Ob distances in the bipodal SO_4





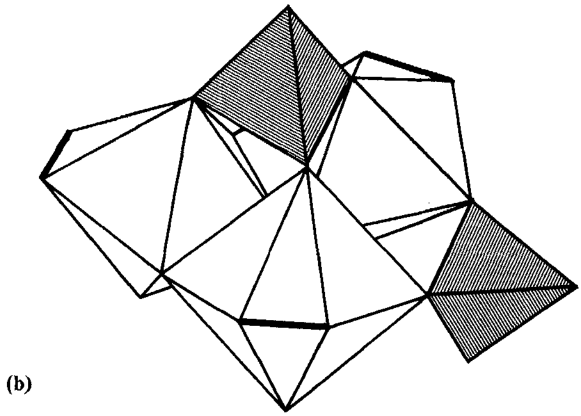


Figure 2 The anion structure of $[H(SO_4)_2(MoO_2(O_2))_3]^{3-}$. a) ORTEP views of two crystallographically independent polyanions with atomic notations. b) A polyhedra model of the polyanion, sulfate groups are *shaded* and peroxo groups are bolded.

Table 2 Selected interatomic distances in $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$

Atom	Distance (Å)	Atom	Distance (Å)
Mo1-O1T	1.68(1)	Mo5-O5T	1.68(1)
Mo1-O123	2.06(1)	Mo5-O456	2.07(1)
Mo1-O12	1.90(3)	Mo5-O45	1.90(1)
Mo1-O1S1	2.30(1)	Mo5-O56	2.05(1)
Mo1-O1S2	2.09(1)	Mo5-O5S3	2.31(1)
Mo1-O1P1	1.90(2)	Mo5-O5P1	1.91(1)
Mo1-O1P2	1.91(2)	Mo5-O5P2	1.92(1)
O1P1-O1P2	1.40(2)	O5P1-O5P2	1.43(2)
Mo2-O2T	1.63(1)	Mo6-O6T	1.66(1)
Mo2-O123	2.03(1)	Mo6-O456	2.00(1)
Mo2-O12	1.93(1)	Mo6-O6S3	2.23(1)
Mo2-O23	2.07(1)	Mo6-O6S4	2.03(1)
Mo2-O2S1	2.29(1)	Mo6-O6P1	1.93(1)
Mo2-O2P1	1.95(1)	Mo6-O6P2	1.92(1)
Mo2-O2P2	1.95(1)	O6P1-O6P2	1.44(2)
O2P1-O2P2	1.48(2)	S1-O7T	1.38(2)
Mo3-O3T	1.67(1)	S1-O1S1	1.48(1)
Mo3-O123	2.01(1)	S1-O2S1	1.47(1)
Mo3-O23	2.02(1)	S1-O3S1	1.43(1)
Mo3-O3S1	2.29(1)	S2-O8T1	1.40(1)
Mo3-O3S2	2.04(1)	S2-O8T2	1.45(1)
Mo3-O3P1	1.92(2)	S2-O1S2	1.44(1)
Mo3-O3P2	1.91(2)	S2-O3S2	1.52(1)
O3P1-O3P2	1.40(2)	S3-O9T	1.43(1)
Mo4-O4T	1.67(1)	S3-O4S3	1.47(1)
Mo4-O456	2.05(1)	S3-O5S3	1.50(1)
Mo4-O45	1.95(1)	S3-O6S3	1.49(1)
Mo4-O4S3	2.28(1)	S4-OXT1	1.41(1)
Mo4-O4S4	2.11(1)	S4-OXT2	1.41(1)
Mo4-O4P1	1.93(1)	S4-O4S4	1.51(1)
Mo4-O4P2	1.95(1)	S4-O6S4	1.53(1)
O4P1-O4P2	1.44(2)	OW1-OW4[a]	2.69(3)
OW1-O9T[b]	2.76(2)	OW4-O56	2.50(2)
OW2-OW6[c]	2.83(3)	OW4-OW6	2.77(3)
OW3-OW5[d]	2.74(3)	OW6-O5S3	2.83(2)
OW3-O23[e]	2.56(2)		

Symmetry operations: a; 1 − x, − y, 1 − z, b; − 0.5 + x, 0.5 − y, 0.5 + z, c; − 0.5 + x, 0.5 − y, − 0.5 + z, d; 1 − x, − y, − z, e; 0.5 + x, 0.5 − y, − 0.5 + z

of S2 are slightly different, the S2-O1S2 of 1.44(1) Å is shorter than the S2-O3S2 of 1.52(1) Å, as well as the Ot; 1.40(2) Å of S2-O8T1 and 1.45(1) Å of S2-O8T2. The O-S-O angles are in the range of 105.0(8) to 109.6(8)° except O8T1-S2-O8T2 of 116.2(9)°. In the S4 bipod, the S-Ob distances (1.51(1) and 1.53(1) Å) are approximately 0.1 Å longer than the S-Ot ones (1.41(1) Å). The O-S-O angles are in 106.7(7) to 110.9(8)°, but for the OXT1-S4-OXT2 of 115.2(8)°. Thus the bipodal sulfate groups show larger distortions than the tripodal ones. The network of hydrogen bonding appears to be formed among waters of crystallization or between water and the polyanions, as the relevant distances listed in Table 2 suggest.

In order to determine the position of protonation of the polyanion, bond valences of each Mo-O or S-O bond were calculated based on the literature;[12] effects of hydrogen bonding with water molecules were taken into account. The low values of

Table 3 Selected bond angles in $[N(CH_3)_4]_3[H(SO_4)_2(MoO_2(O_2))_3]\cdot 3H_2O$

Atom	Angle (°)	Atom	Angle (°)
O1P1-Mo1-O1P2	43.0(6)	O8T2-S2-O1S2	109.3(8)
O2P1-Mo2-O2P2	44.6(6)	O8T2-S2-O3S2	105.0(8)
O3P1-Mo3-O3P2	43.1(6)	O8T1-S2-O8T2	116.2(9)
O4P1-Mo4-O4P2	43.6(5)	O4S3-S3-O5S3	108.3(6)
O5P1-Mo5-O5P2	43.7(5)	O4S3-S3-O6S3	110.4(6)
O6P1-Mo6-O6P2	43.8(5)	O5S3-S3-O6S3	107.8(6)
O1S1-S1-O2S1	107.2(8)	O9T-S3-O4S3	110.3(7)
O1S1-S1-O3S1	110.4(8)	O9T-S3-O5S3	109.4(7)
O2S1-S1-O3S1	108.7(8)	O9T-S3-O6S3	110.5(7)
O7T-S1-O1S1	111.0(9)	O4S4-S4-O6S4	107.6(6)
O7T-S1-O2S1	109.8(9)	OXT1-S4-O4S4	110.9(8)
O7T-S1-O3S1	109.7(9)	OXT1-S4-O6S4	108.7(8)
O1S2-S2-O3S2	106.9(8)	OXT2-S4-O4S4	107.5(7)
O8T1-S2-O1S2	109.3(8)	OXT2-X4-O6S4	106.7(7)
O8T1-S2-O3S2	109.6(8)	OXT1-S4-OXT2	115.2(8)

1.65 for O23 and 1.68 for O56 support that these two Ob atoms are protonated; the rather short hydrogen bonding distances of 2.57 Å for O23-OW3 and 2.50 Å for O56-OW4 also support this concluson. Although O8T2 gave a value of 1.59 lower than O23 and O56, no other evidence such as hydrogen bonding with water was observed for O8T2. Hence, the authors conclude that O23 and O56 are protonated rather than O8T2.

The interatomic distances are illustrated in Figure 3 for each triad of Ob atoms in the tripodal sulfate groups, molybdenum atoms on the equatorial plane, and Ot

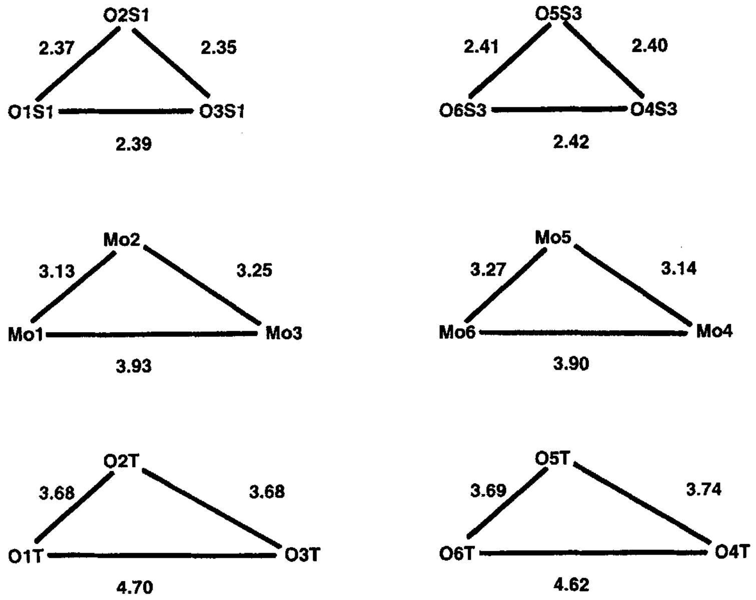


Figure 3 Interatomic distances among Ob in tripod sulfate, Mo on the equatorial plane and Ot protruding from the respective Mo atoms (from upper) in each polyanion.

atoms protruding from the respective Mo atoms. Owing to the structural integrity of the SO_4 tetrahedron, the triangle becomes greater in the order from the tripod 3Ob to the 3Ot. Thus the coordination polyhedra of Mo are axially inclined to gather their tops to the tripodal center and to open their Ot bottoms. The interatomic distances of O1S2-O3S2 (2.38 Å) and O4S4-O6S4 (2.45 Å) are shortened enough for bipodal coordination of sulfate owing to the inclination mentioned above and the pentagonal coordination around the Mo atom on the equatorial plane.

A structure related to the present one was reported by Fuchs *et al.*[13] for $Rb_2SMo_3O_{13}$ crystallized from a strongly sulfate-acidic ($2<H^+/MoO_4^{2-}$) aqueous solution of Na_2MoO_4 and Rb_2SO_4 with a Mo/S ratio lower than 0.5, or from a 1:3 melt of MoO_3 and Rb_2SO_4. The $SMo_3O_{13}^{2-}$ unit in this rubidium salt has a tripodal SO_4 spanning three MoO_6 octahedra sharing equatorial edges similar to the present compound but without bipodal SO_4. The units are connected by sharing two other edges to extend a one-dimensional infinite chain (see Figure 4), different from the present structure, in which the corresponding edges are blocked by the peroxo groups at the corners to accomplish the pentagonal bipyramidal coordination. The interatomic distances between Ob and the bipodal sulfate in the present compound (2.38 and 2.45 Å) are much shorter than the corresponding one in the rubidium salt (3.65 Å). The angles of Mo1-Mo2-Mo3 (75.9 (1)°) and Mo4-Mo5-Mo6 (74.9(1)°) in the present compound are smaller than the corresponding angle (90°) in the rubidium salt, due to the equatorial pentagonal coordination in the present one.

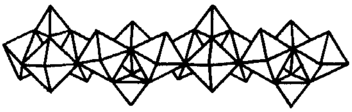


Figure 4 The anion structure of $SMo_3O_{13}^{2-}$ from Ref. 13.

Another related structure, $[\{H(SO_4)W_3O_7(O_2)_2\}_2O]^{4-}$, is shown in Figure 5.[4] The present polyanion has essentially the same structure with one half of the tungstate but a bipodal sulfate group. One of the terminal atoms in tungstate (O4) is substituted by O_2^{2-} in the molybdate complex; one of the Ob (O11) in the tungstate by Ot. The two Ob atoms coupling the W3 moieties in the tungstate (O11′ and O12)

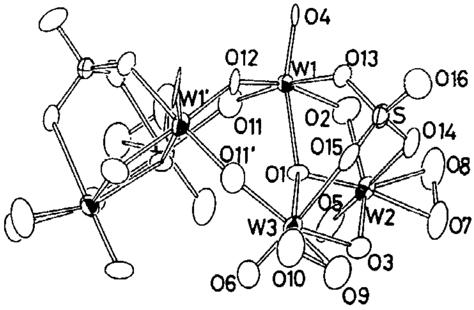


Figure 5 The anion structure of $[\{H(SO_4)W_3O_7(O_2)_2\}_2O]^{4-}$ from Ref. 4.

are Ob atoms to the bipodal sulfate group in the present compound. The protonation to the polyanion was found at O2 in the tungstate, the corresponding position to O23 and O56 in molybdate. Thus the two crystallographically independent polyanions in the present compound can be regarded as both halves of the tungstate complex. Considering the similarity of the preparation conditions for these two compounds as mentioned above, this similarity of their structures is quite reasonable.

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