X-Ray Structure of Keggin-type Peroxo Polyoxometalate A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$

Gyu-Shik Kim,[*] **Huadong Zeng,**[†] **and Craig L. Hill**[†]

Department of Science Education, Kangwon National University, Chunchon 200-701, Korea
[†]*Department of Chemistry, 1515 Pierce Drive, Emory University, Atlanta, GA 30322, USA*
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The title polyoxometalate (POM), A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$ (A-α-**1**)[1] was shown to have potent *anti*-HIV-1 activity (median effective antiviral concentration against HIV-1 in human peripheral blood mononuclear cells (PBMC), EC$_{50}$, ~1 μM) while being minimally cytotoxic (median inhibitory concentration, IC$_{50}$, >100 μM also in PBMC) in 1994.[2,3] Unfortunately this POM isn't stable in aqueous solution and decomposes into other POMs with the corresponding Keggin complex, A-α-[SiNb$_3$W$_9$O$_{40}$]$^{7-}$, depending on conditions, generally being the dominant product. Very recently this POM, often generated *in situ* given its instability, has proven to be an effective starting material for the preparation of a range of new or larger supramolecular POMs containing the SiNb$_3$W$_9$ unit.[4-6] The instability of peroxoniobium POMs, in which the (Nb^{V}O$_2$)$^{3+}$ unit has been substituted for a (W^{VI}O)$^{4+}$ type I "octahedral" unit has rendered difficult the purification and structural characterization of such POMs in the past.[7] Given the growing importance of A-α-**1**, this study sought the specific goal associated with this unstable POM, *i.e.*, to obtain a good quality single crystal X-ray diffraction study to determine the nature, and in particular, the orientation of the peroxo groups. This goal has been met as described in this note. Furthermore, the possibility of using this peroxoniobium POM anion as a synthon in both aqueous and organic solvents is of interest and could lead to other supramolecular POM species based on the SiNb$_3$W$_9$ unit.

Experimental Section

Materials and Methods. Na$_2$WO$_4$·2H$_2$O (AESAR) was obtained from a commercial source and used as received. All solvents were at least reagent grade and were used without further purification. Both α-Na$_{10}$SiW$_9$O$_{34}$·23H$_2$O[8] and K$_7$HNb$_6$O$_{19}$·13H$_2$O[9] were prepared using literature methods. Infrared spectra were recorded on a Nicolet 510 M FTIR spectrometer using 3-5 wt.% of sample in KBr pellets. Tungsten-183 NMR (ref = 2.0 M Na$_2$WO$_4$ in D$_2$O) spectra were acquired at ambient temperature using an INOVA 400 FT NMR spectrometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, U. S. A.

Synthesis of A-α-Cs$_6$H[Si(NbO$_2$)$_3$W$_9$O$_{37}$]·9H$_2$O (A-α-Cs$_6$H1). K$_7$HNb$_6$O$_{19}$·13H$_2$O (1.91 g, 1.39 mmol) was dissolved in 250 mL of 0.5 M aqueous H$_2$O$_2$. To this stirred solution, 20 mL of 1.0 M aqueous HCl was added dropwise, to give a bright yellow solution, followed by addition of 7.82 g (2.72 mmol) of solid α-Na$_{10}$SiW$_9$O$_{34}$·23H$_2$O. After the solid Na$_{10}$SiW$_9$O$_{34}$ had fully dissolved, 25.0 g (46.5 mmol) of solid CsCl was added to precipitate the Cs salt of A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$ and the resulting orange yellow mixture stirred for 15 min. The precipitate was filtered on a medium glass frit and washed with two 20-mL portions of diethyl ether. Drying in air gave 9.11 g of yellow powder (86.9% yield based on the hexaniobate precursor). Anal. Calcd. (found) for Cs$_6$H$_{19}$SiNb$_3$W$_9$O$_{52}$: H, 0.48 (0.53); Si, 0.78 (0.78); Cs, 22.2 (22.1); Nb, 7.76 (7.72); W, 46.1 (45.8). FTIR (KBr, 1100-400 cm^{-1}): 994 (w), 957 (m), 903 (vs), 868 (sh), 789 (vs), 673 (vw), 592 (w), 534 (w). 482 (vw) cm^{-1}. The TGA data suggest the presence of ~9 H$_2$O molecules of hydration per POM, so this many were used in the elemental analysis above. This is within experimental error of the number of H$_2$O moloucules per POM in the X-ray structure.

X-ray Structure of A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$ (A-α-1). X-ray quality crystals of the cesium salt were grown from aqueous solution by slow evaporation at ambient temperature. A colorless block crystal with dimensions of 0.20 × 0.20 × 0.17 mm was mounted on a glass fiber and X-ray diffraction data were collected at room temperature using a Siemens SMART® platform diffractometer equipped with a CCD area detector and a normal focus molybdenum-target X-ray tube (λ = 0.71073 Å).[10] Data frames were collected using a narrow frame method with scan width 0.30° in ω and an exposure time of 10-30 s/frame (2θ_{max} = 56.78°). The data were integrated using the Siemens SAINT program.[11] Crystal was face-indexed for absorption corrections. An empirical absorption correction based on the entire data set was applied using SADABS.[12] Redundant reflections were averaged. The corrected data were used in subsequent structure solutions and refinements. The structure was solved by direct methods using SHELXTL-PC v. 5.03 and refined by full-matrix-least-squares-on-F^2 techniques (with F^2 > 2σ(F$_o$^{2})) using SHELXL-97, incorporated in SHELXTL-PC v. 5.03.[13] Direct methods located the heavy atoms (W, Cs and Nb); other non-hydrogen atoms were located by successive Fourier difference synthesis. Anisotropic temperature factors were applied to all atoms, except O8 and Ow5, Ow6, Ow8 and Ow9. Disorder of Cs8 and some hydrated water (Ow5, Ow6, Ow8 and Ow9) were observed as indicated by high temperature factors, which is not uncommon in the crystal structures of POM compounds. The occupancy of

Table 1. Summary of X-ray crystallographic data for **1**

	$Cs_{6.66}H_{0.34}[Si(NbO_2)_3W_9O_{37}]$ $\cdot 7H_2O$ (A-α-**1**)
empirical formula	$Cs_{6.66}H_{13.34}O_{50}SiNb_3W_9$
f.w.	3660.9
crystal color/shape	colorless/block
crystal size, mm	$0.20 \times 0.20 \times 0.17$
crystal system	monoclinic
space group	$C2/c$ (No. 15)
T, K	298
a, Å	18.4852 (8)
b, Å	21.1362 (9)
c, Å	26.1679 (11)
α, deg	90
β, deg	92.98 (0)
γ, deg	90
V, Å^3	10210.2 (8)
Z	8
ρ_{calcd}, g cm^{-3}	4.76
F(000)	12452
μ, mm^{-1}	25.53
θ range, deg	1.46-28.39
no. measd reflcns	25781
no. indep reflcns	11938
no. parameters	634
Goodness of fit	0.978
final R_1 [I > 2σ(I)]	0.0586
final wR_2 [I > 2σ(I)]	0.1319
Largest diff. peak and hole (e.Å^{-3})	3.542 and -4.193

$^a R_1 = \Sigma \, || F_o | - | F_c || / \Sigma | F_o |$. $^b wR_2 = [\Sigma \, w(F_o^2 - F_c^2)^2 / \Sigma \, w(F_o^2)^2]^{1/2}$.

Cs8 was refined using a program-supplied free variable to be 32%, therefore the total amount of Cs$^+$ was determined to be 6.66 in the asymmetric unit. To balance the total negative charge of seven in the POM anion 0.34 equivalent of proton is assumed in the empirical formula. Occupancy of 50% was given to the O atoms in the above-mentioned disordered water molecules without further refining their occupancies. The X-ray data collection, structure solution and refinement parameters are summarized in Table 1. Crystallographic data for the structure reported here have been deposited with FIZ (Deposition # 413046). These data can be obtained free of charge *via* FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, e-mail: *crysdata@fiz-karlsruhe.de*.

Results and Discussion

X-ray crystallography and ^{183}W NMR (of the lithiated cesium salt, A-α-Cs$_6$H**1**) provided definitive evidence that the same isomer exists in both the solid state and in aqueous solution, and that A-α isomerism is maintained in both circumstances. ORTEP and polyhedral illustrations of the polyanion portion, A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$ (A-α-**1**) are provided in Figure 1. Selected bond distances and angles are given in Table 2.

The X-ray structure analysis reveals that the title compound
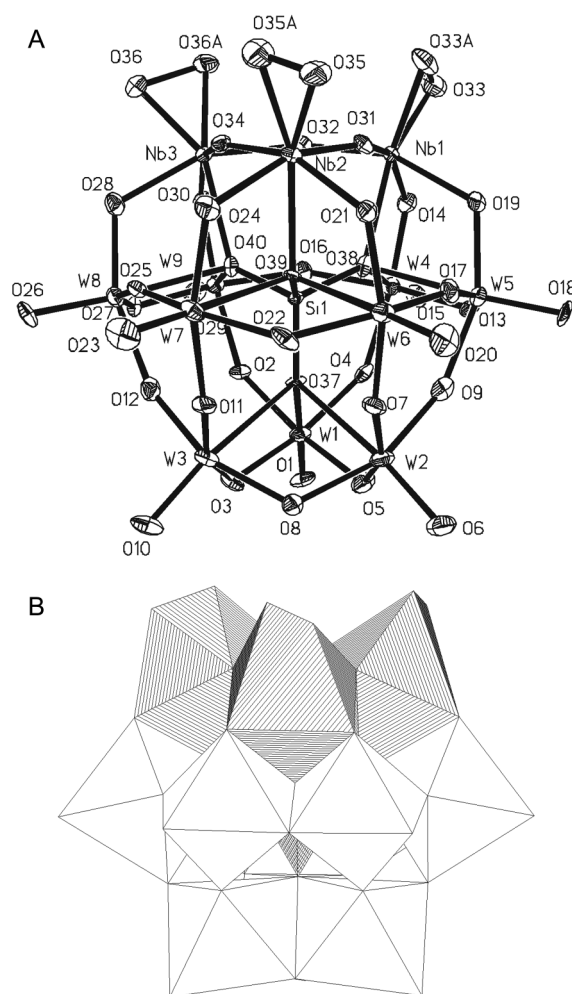
Figure 1. Structure of the polyanion unit A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$] in A-α-**1**. A: ORTEP drawing with 30%-probability thermal ellipsoids; B: polyhedral drawing. The Nb^V(O$_2$)O$_5$ heptahedra, the internal SiO$_4$ tetrahedron, and the WO$_6$ pseudo-octahedra are depicted in dark, intermediate and light shading, respectively.

contains Cs$^+$/H$^+$ cations, A-α-[Si(NbO$_2$)$_3$W$_9$O$_{37}$]$^{7-}$ (A-α-**1**) anions, and water molecules. Each of the three Nb atoms in the anion is coordinated by four doubly-bridging O atoms, one quadruply-bridging O atom, and one terminal η^2-coordinated peroxo group to form a distorted pentagonal bipyramidal polyhedron. Such coordination polyhedra containing η^2-coordinated peroxo units are seen in three other structurally determined high nuclearity[14] polyoxoanions, β_3-[(Co^{II}O$_4$)W$_{11}$O$_{31}$(O$_2$)$_4$]$^{10-}$ [15-17] A-β-[P(NbO$_2$)$_3$W$_9$O$_{37}$]$^{6-}$ [18] [P$_2$(NbO$_2$)$_6$W$_{12}$O$_{56}$]$^{12-}$.[7] The average peroxide (Op-Op) bond length in the polyanion (1.46(1) Å) is between those reported for α-[P$_2$(NbO$_2$)$_6$W$_{12}$O$_{56}$]$^{12-}$ (1.43 Å),[7] non-coordinated O$_2^{2-}$ (1.49 Å)[19] and A-β-[P(NbO$_2$)$_3$W$_9$O$_{37}$]$^{6-}$ (1.51 Å).[18] The average Op-Nb-Op (44.1°) is similar to those in α-[P$_2$(NbO$_2$)$_6$W$_{12}$O$_{56}$]$^{12-}$ (43.7°)[7] and [Nb(O$_2$)$_4$]$^{3-}$ (43.3°),[20,21] but is smaller than those of A-β-[P(NbO$_2$)$_3$W$_9$O$_{37}$]^6 (45.2°).[18] The peroxo groups largely eclipse the trans O-Nb-O units in the semi-equatorial plane (actually a C$_{4v}$ pyramidal cone resulting from the overall structural distortion of the NbO$_7$ units). The nine W atoms in the POM anion exhibit the

**Table 2**. Selected bond distances [Å] and angles [°] for **1**

Distances							
Nb(1)-O(32)	1.839(12)	Nb(2)-O(31)	1.859(12)	Nb(3)-O(34)	1.852(13)	W-O$_t$	1.712(13)
Nb(1)-O(33)	1.945(15)	Nb(2)-O(35A)	1.930(16)	Nb(3)-O(36A)	1.957(14)	W-O$_b$	1.910(13)
Nb(1)-O(33A)	1.959(14)	Nb(2)-O(35)	1.948(13)	Nb(3)-O(36)	1.958(14)	W-O$_c$	2.381(11)
Nb(1)-O(19)	2.035(11)	Nb(2)-O(34)	2.034(12)	Nb(3)-O(30)	2.039(12)	O(33)-O(33A)	1.44(2)
Nb(1)-O(31)	2.042(13)	Nb(2)-O(24)	2.057(13)	Nb(3)-O(32)	2.045(12)	O(35)-O(35A)	1.43(2)
Nb(1)-O(14)	2.080(13)	Nb(2)-O(21)	2.062(13)	Nb(3)-O(28)	2.059(12)	O(36)-O(36A)	1.51(2)
Nb(1)-O(38)	2.298(12)	Nb(2)-O(39)	2.341(11)	Nb(3)-O(40)	2.314(12)		
Angles							
Nb(2)-O(31)-Nb(1)	148.4(6)	O(39)-Si(1)-O(38)	108.0(6)		O(39)-Si(1)-O(40)	110.1(6)	
Nb(1)-O(32)-Nb(3)	149.2(7)	O(39)-Si(1)-O(37)	109.4(6)		O(38)-Si(1)-O(40)	108.6(6)	
Nb(3)-O(34)-Nb(2)	148.7(7)	O(38)-Si(1)-O(37)	110.8(7)		O(37)-Si(1)-O(40)	110.0(6)	

O$_t$: terminal oxygen, O$_b$: doubly-bridged O atoms, O$_c$: quadruply-bridged O atoms.

conventional distorted octahedra (*ca.* C$_{4v}$ local symmetry) typical of the "type I" octahedral geometry in Keggin polyanions.

The three peroxo groups of A-α-**1** as a grouping or unit are not equivalent in the solid state. That is, they are not related by a C$_3$ axis of symmetry trisecting the three NbO$_7$ units. Given this point, there are 3 possible general descriptions of the orientation of these three terminal peroxo groups to one another. First, they could be related by an approximate (but non-crystallographically imposed) C$_3$ axis. This would lead to the highest symmetry arrangement, *ca.* C$_3$ (or C$_{3v}$). They could be related by a mirror plane (2 of the 3 peroxo groups have similar orientations, but the third peroxo group has a different orientation). This would lead to *ca.* C$_s$ symmetry of the grouping. Finally, they could be best described as having no apparent symmetry relationship with respect to one another (C$_1$ symmetry). The structure of A-α-**1** indicates that while the three peroxo groups appear to approach a C$_3$ orientation with respect to one another, they are rigorously C$_1$.

The two-line ^{183}W NMR (0.1 M lithiated A-α-Cs$_6$H**1** in D$_2$O; δ (intensity): −111.4 (6) and −138.4 (3)) spectrum shown in Figure 2 clearly indicates that A-α-Cs$_6$H**1** possesses apparent C$_{3v}$ symmetry in solution. Yet, it is clear from the somewhat different orientations of the peroxo groups relative to one another in the crystal structure of A-α-Cs$_6$H**1** that the polyanion unit as a whole has lower symmetry than C$_{3v}$, and that the ^{183}W NMR spectrum should have more than two lines if the solid state symmetry is maintained in solution. There are two possible explanations for this. The first is that the peroxo groups are fluxional and equilibrating on the ^{183}W NMR time scale so that all are equivalent, and thus the proximal or "belt" tungsten atoms are all equivalent. This would lead to the observed two-line spectrum. The second is that the orientations of the three peroxo groups are, in fact, different as they are in the solid state, but that this difference represents such a small perturbation on the tungsten nuclei that they are effectively magnetically equivalent (*i.e.* the I = 1/2 ^{183}W nuclei "see" effectively the same magnetic environment). The first explanation is extremely unlikely because fluxionality of this type hasn't been seen in
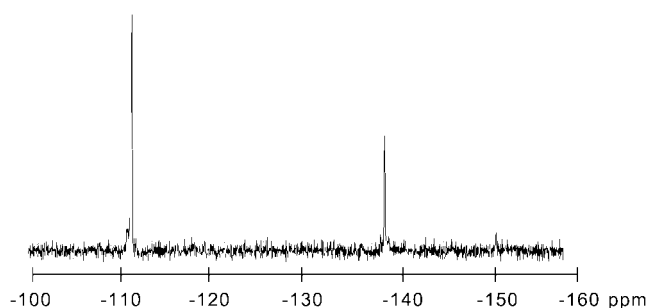
Figure 2. ^{183}W NMR spectrum of lithiated A-α-Cs$_6$H[Si(NbO$_2$)$_3$-W$_9$O$_{37}$] (A-α-Cs$_6$H**1**) (0.1 M) in D$_2$O with 3 equivalents of aqueous H$_2$O$_2$.

any other peroxo-containing polyoxometalate complexes nor the polyperoxometalates[14,15] nor is a facile chemistry involving peroxo group equilibration by detachment or re-attachment on such a rapid time scale reasonable. Furthermore, if such dynamic processes were operable, one would expect to see significantly larger thermal ellipsoids than those exhibited by A-α-**1** (see Figure 1) or by those exhibited in many other X-ray structures of d^0 polyperoxometalate species. Therefore, we are left to conclude that apparent C$_{3v}$ symmetry of A-α-**1** derives from the fact that the orientation of the peroxo groups has too little effect on the tungsten nuclei to significantly impact the chemical shifts of these atoms.

POM anions are linked together through Cs$^+$ cations and crystalline water molecules. All the surface O atoms of the POM anion, including the terminal oxo and peroxo, the bridging μ_2-O atoms between Nb and W atoms, and the bridging μ_2-O atoms between W and W atoms except O4, O5, O7, O13 and O25, are involved in forming coordination with Cs$^+$ cations of different asymmetric units. The Cs$^+$ cations are surrounded by 9 to 12 oxygen atoms from POMs and crystalline water molecules, with Cs-O bond ranging from 2.92 to 3.79 Å. For example, Cs8 is surrounded by two POM anions with the (NbO$_2$)$_3$ unit head-on to each other and coordinated to three μ_2-O-Nb$_2$ atoms (O31, O32, and O34) and three terminal η^2-coordinated peroxo oxygens (O33A, O35A and O36A) that come from one POM anion to give a

total coordination number of 12.

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