it relies on polarization measurements. Snyder[15] gives quantitative measurements for $\gamma_{A_{1g}}{}^2$ and $\gamma_{E_g}{}^2$ which are 0.018 and 2.264 Å^4 amu^{-1}, respectively, from which one calculates (with eq 11) two values of τ: 2.69 and 1.40. These values of τ yield, using eq 6, the ratios 0.64 and 0.57 for I^+/I^-. By comparing these ratios with the experimental ones measured on the four terpenes (cf. Table I), we conclude that the lower frequency corresponds to the asymmetric vibration Q^-. These values of τ also yield values of Δ_z^- for (+)-α-pinene of $+1.40 \times 10^{-4}$ and $+0.90 \times 10^{-4}$, respectively, values that straddle the experimentally determined value of $(+1.1 \times 10^{-4})\gamma^2$ values of highly polarized bands are generally too high, however, as a result of errors introduced by collisional effects and by the finite angle over which the scattered light is gathered. As $\gamma_{A_{1g}}{}^2$ decreases, the two values of τ which eq 11 produces approach one another until, in the limit of $\gamma_{A_{1g}}{}^2 = 0$, τ has only a single value of 1.90. With this value one calculates Δ_z^- for (+)α-pinene to be $+1.15 \times 10^{-4}$, close to the experimental value. These data are summarized in Table I.

As is evident from the table, the equations derived above for the two-group model reproduce acceptably the magnitude and signs of the Δ_z's associated with what was assigned as the in-phase and out-of-phase coupled methylene scissoring vibrations in the four terpenes shown in Table I. As such, this constitutes a determination by Raman optical activity of the absolute configuration of those molecules.

Generalizing the model to include more than two groups would enable one to calculate the Raman and Raman CD intensities of any normal vibration of a molecule, and we are currently engaged in its solution. One looks forward to the day when the entire stereochemistry of a molecule with a given configuration may be solved by ROA, provided of course that equal advances are made in the field of vibrational assignments.

Acknowledgment. The authors are indebted to the Natural Sciences and Engineering Council of Canada, the Atkinson Foundation, and the University of Toronto for financial support. We also wish to thank Dr. L. D. Barron for transmitting to us several manuscripts before their publication.

Appendix

We wish to demonstrate that Barron's modified two-group model[4] may be written in terms of a single angle and a single distance and is therefore not physically different from the model proposed by the authors in ref 5.

Define $\mathbf{u}_1$ and $\mathbf{u}_2$ as unit vectors along the main axes of the two groups of ref 5. If $\mathbf{R}_{12}$ is a vector of magnitude R_{12} directed along a line joining the origins of the two groups, one can show that the quantities $\cos\theta$ and $R_{12}\sin\theta$, in terms of which all the pertinent quantities Δ_x^+, Δ_x^-, Δ_z^+, and Δ_z^- of ref 5 are defined, may be written as

$$\cos\theta = \mathbf{u}_1\cdot\mathbf{u}_2$$

$$R_{12}\sin\theta = \mathbf{u}_1 \times \mathbf{u}_2\cdot\mathbf{R}_{12}$$

If one now tilts group 1 through δ_1 and group 2 through δ_2 out of the x–z plane, then $\mathbf{u}_1$ and $\mathbf{u}_2$ become

$$\mathbf{u}_1 = (0, \sin\delta_1, \cos\delta_1)$$

$$\mathbf{u}_2 = (-\sin\theta\cos\delta_2, -\sin\delta_2, \cos\theta\cos\delta_2)$$

(assuming $\mathbf{u}_1$ was originally along the x axis). $\mathbf{R}_{12} = (0, -R_{12}, 0)$. The inner and vector-triple products now become

$$\mathbf{u}_1\cdot\mathbf{u}_2 = \cos\theta\cos\delta_1\cos\delta_2 - \sin\delta_1\sin\delta_2$$

$$(\mathbf{u}_1 \times \mathbf{u}_2\cdot\mathbf{R}_{12}) = R_{12}\sin\theta\cos\delta_1\cos\delta_2$$

When these quantities are now used in place of $\cos\theta$ and $R_{12}\sin\theta$ in the equations of ref 5, one obtains the new equations of reference 4. In other words, one may define a new angle θ' and a new distance R'_{12} such that

$$\cos\theta\cos\delta_1\cos\delta_2 - \sin\delta_1\sin\delta_2 = \cos\theta'$$

and

$$R_{12}\sin\theta\cos\delta_1\cos\delta_2 = R'_{12}\sin\theta'$$

in terms of which all the ROA of the modified, two-group model of reference 4 may be written.

Tungsten-183 NMR and X-ray Study of a Heteropolyanion $[As_2W_{21}O_{69}(H_2O)]^{6-}$ Exhibiting a Rare Square-Pyramidal Environment for Some Tungsten(VI)

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Abstract: The compound $H_2Rb_4[As_2W_{21}O_{69}(H_2O)]\cdot 34H_2O$ was synthesized and its crystal structure determined. It crystallizes in the hexagonal space group $P6_3/mmc$; the lattice constants are as follows: $a = b = 16.926$ (7) Å, $c = 18.767$ (8) Å; $Z = 2$. The structure has been refined by full-matrix least squares to a final R factor of 0.059 for 1572 reflections collected at room temperature. As confirmed by the ^{183}W NMR study, the $[As_2W_{21}O_{69}(H_2O)]^{6-}$ heteropolyanion is made of two AsW_9O_{33} units, joined together in an asymmetrical way by three tungsten atoms among which one is octahedrally surrounded and two are in a square-pyramidal environment.

Some structures of heteropolyanions with As(III) as a heteroatom have been recently published: $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot 16H_2O$[1] and $(NH_4)_{23}[NH_4As_4W_{40}O_{140}Co_2(H_2O)_2]\cdot nH_2O$.[2]

These two structures contain the AsW_9O_{33} unit derived from the Keggin structure[3] by removing a W_3O_{13} group. The lone pair of arsenic(III) points toward the outside of the shell made by the nine-linked WO_6 octahedra. It prevents this unit from catching a fourth W_3O_{13} group to give a Keggin heteropolyanion or to

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(1) Y. Jeannin and J. Martin-Frère *Inorg. Chem.*, **18**, 3010 (1979).

(2) M. Leyrie, G. Hervé, A. Tézé, F. Robert, and Y. Jeannin, *Inorg. Chem.*, **19**, 1746 (1979).

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condense with an other AsW_9O_{33} group to form $As_2W_{18}O_{60}$ with two groups directly linked by six oxygen atoms as in the Dawson structure.[4] However, there are other ways of condensation than the Keggin or Dawson structure formation, leading to the species previously noted[1,2] containing several AsW_9O_{33} units: in $[H_2AsW_{18}O_{60}]^{7-}$, AsW_9O_{33} is joined with a $H_2W_9O_{33}$ unit which does not contain As(III); in $[As_4W_{40}O_{140}]^{28-}$, four AsW_9O_{33} units are joined together by four other octahedra and the molecule appears as a complex crown.

The 21-tungstodiarsenate(III)[5] is a new example of a heteropolyanion containing As(III). The question is: how is the structure made to give enough space for the two lone pairs?

Experimental Section

Crystal Synthesis and Chemical Analysis. The 21-tungstodiarsenic(III) acid easily crystallizes, but the crystals are not suitable for a X-ray diffraction study, because they lose water as soon as they are taken out of their solution. The rubidium salt was chosen because single crystals are much more stable.

In order to prepare the 21-tungstodiarsenic(III) acid, we dissolved 1 mol of sodium tungstate and 1/21 mol of diarsenic trioxide into 350 mL of boiling water. A 2-mol sample of concentrated hydrochloric acid was added under stirring. By evaporation, yellow crystals appeared after 24 h together with a white precipitate. They were purified by several recrystallizations in 3 M hydrochloric acid. Finally the heteropolyacid was extracted from the hydrochloric solution with diethyl oxide according to Drechsel method.[6] The heavy layer was treated by water and diethyl oxide evaporated. Crystals of the acid were slowly formed. As shown by chemical analysis the W/As ratio was 21/2.

The rubidium salt was precipitated from the acid solution by adding rubidium chloride. After several recrystallizations in 1 M HCl, thin yellow needles appeared.

Chemical analysis was carried out as follows: rubidium was weighed as tetraphenylborate. Some complex was destroyed by sodium hydroxide: first, arsenic(III) amount was titrated by iodometry after tungsten complexation by phosphate; second, tungsten was precipitated by cinchonin and weighed as tunsten trioxide. The water content was measured by thermogravimetry.

Anal. Cald for $H_2Rb_4[As_2W_{21}O_{69}]\cdot 35H_2O$: As, 2.46; Rb, 5.62; W, 63.4. Found: As, 2.48; Rb, 5.26; W, 64.1.

If ammonium or potassium salt is prepared, chemical analysis showed that they contain six cations per mole of polyanion (experimental result: K/As = 2.85; NH_4/As = 2.95). Thus, the formula appears to be $H_2Rb_4[As_2W_{21}O_{69}]\cdot 35H_2O$.

Crystallographic Data. Preliminary Laue and precession photographs showed an hexagonal unit cell. Possible space groups are $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. A crystal shaped approximately as a hexagonal prism (length ca. 0.3 mm and thickness ca. 0.08 mm) was put into a capillary Lindemann glass along its c axis (parallel to the length of the crystal) and set on a laboratory-made automatic diffractometer. Lattice constants, determined by least squares from nine reflections, are as follows: $a = b = 16.926$ (7) Å and $c = 18.767$ (8) Å. The density of the crystals was measured in cyclohexane, by pycnometry. The obtained value, 4.40 g/cm^3, led to two molecules per unit cell; the calculated value is 4.34 g/cm^3 if the formula is as above.

A total of 1572 independent reflections were collected at room temperature: radiation, Mo Kα; crystal-focus distance, 230 mm; crystal-counter distance, 230 mm; scan type, θ-2θ; scan speed, 0.54°/min; asymmetrical scan taking into account the Kα_1-Kα_2 dispersion; background measurements in fixed position before and after every scan during 28 s; maximum Bragg angle 25°; scintillation counter connected to a pulse-height analyser set on Mo Kα energy so that 90% of the intensity was counted; graphite monochromator in front of the counter window; standard reflections 4 0 3 and $\bar{5}$ 10 6 measured every 50 reflections; no decrease of standards was observed.

Lorentz and polarization corrections were applied. Only 636 reflections with an observed structure factor greater than 10.0 were kept for refinement. For every observed structure factor F_o, a standard deviation was computed as $\sigma = F_o\Delta I/2I$, where I is the integrated intensity and ΔI its statistical error.

Structure Determination and Refinement. Statistical tests[7] were computed with the 1572 collected reflections (Table I). They led to the centrosymmetric $P6_3/mmc$ space group. It has 24 general equivalent positions, and the unit cell contains four arsenics and 42 tungstens. Thus, the arsenic and some tungsten atoms are in a special position.

Table I. Statistical Tests Based on E

		calcd	
	exptl	centrosym	noncentrosym
$\lvert E\rvert$	0.831	0.798	0.886
E^3	1.503	1.596	1.329
$\lvert E^2 - 1\rvert$	0.874	0.968	0.736
$(E^2 - 1)^2$	1.678	2.000	1.000

A three-dimensional Patterson synthesis was calculated. Two peaks corresponding respectively to 12 and 24 tungsten atoms were found. A first refinement of their coordinates gave $R = 0.27$ ($R = \sum|F_o - kF_c|/\sum F_o$; k is the scale factor and F_o and F_c are the observed and calculated structure factors).

Refinements were made by least squares, minimizing $R_w = [\sum(w_i|F_o - kF_c|)^2/\sum(w_iF_o)^2]^{0.5}$ and inverting the full matrix; w_i is the weight attributed to each reflection: $w_i = 1.0$ was first taken; $w_i = 2F_o/\Delta I$ was introduced in the final refinement.

A subsequent Fourier synthesis gave positions of the six remaining tungsten atoms, six rubidiums, the four arsenic atoms, and all the oxygen atoms belonging to the heteropolyanion. R dropped to 0.097.

An unresolved weak electron density, then, was left inside the anion (about 0.5 Å from tungsten W(3) and in the mirror plane). Weakley noticed the same phenomenon in $[P_2W_{21}O_{71}]^{6-}$ structure.[8] It has been understood as a possible statistical distribution of W(3) between two positions W(3) and W(3′). Indeed, R improvement is 1% if respective occupation factors of $^2/_3$ and $^1/_3$ are applied. Four peaks were found in the last Fourier difference synthesis that were attributed to oxygen of water molecules. Thus, 32 peaks among 70 were located.

Since the crystal used for the recording of data was set in a Lindemann glass capillary, its faces were not easily seen. Then, only an empirical correction was applied for absorption.[9] Structure factors were multiplied by $\exp[10^{-4}(ah^2 + bk^2 + cl^2 + dhk + ehl + fkl)]$; a, b, ..., and f coefficients were determined from refinement. R dropped to 0.070 with $a = 2.81$, $b = 6.24$, $c = -4.60$, $d = 4.68$, $e = 3.69$, $f = -0.82$.

A final R value of 0.059 was obtained by using anisotropic temperature factors for W, As, and Rb and introducing the weighting scheme. Corresponding R_w is 0.062.

Atomic form factors were taken from ref 10. The real and imaginary part of the anomalous dispersion was taken into account for W, As, and Rb.

It has to be pointed that 38 water molecules could not be located. Also, six rubidium atoms were found (three per molecule) whereas chemical analysis gave a value nearer to four rubidiums per molecule. It was not possible to find the last one in a special position corresponding to the two missing atoms. Then, as far as chemical analysis is correct, if there are two more rubidiums, they might be statistically distributed at a site of a higher multiplicity giving a too low electron density to be seen. Such difficulties to locate intermolecular materials have been already encountered in structures of this type.[11]

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given in Tables II and III.

Description of the Structure and Discussion

The unit cell contains two 21-tungstodiarsenate(III) anions.

The anion (Figure 1) is made of two AsW_9O_{33} units identical with those found in other heteropolyanions containing As(III) as a central atom.[1-2] Arsenic is on the apex of a AsO_3 pyramid. Each of these oxygens is the common vertex of three octahedra making a W_3O_{13} group. Each WO_6 octahedron of W_3O_{13} is linked to its neighbors in this group by sharing one edge in such a way that the three octahedra have a common vertex. These W_3O_{13} groups are bound to each other by sharing an octahedron corner. The two AsW_9O_{33} units are linked by three tungsten atoms lying in a mirror plane (Figure 1b). Each of these tungstens is bound to four oxygen atoms belonging to four different W_3O_{13} groups. A fifth oxygen atom makes complete a square-pyramidal environment. The anion has a threefold symmetry axis perpendicular to the mirror plane.

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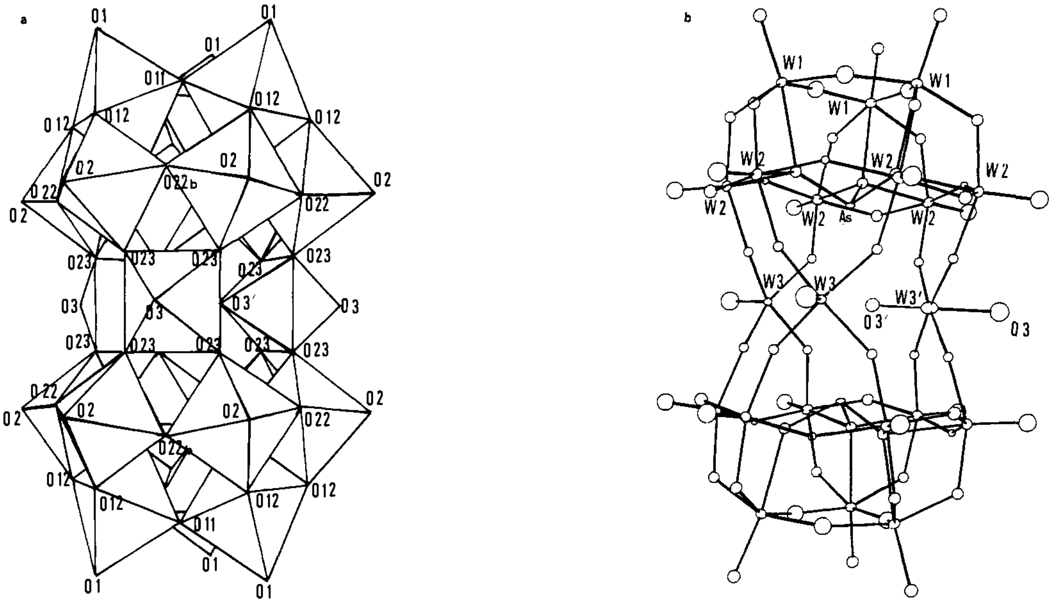

Figure 1. ORTEP of the $[As_2W_{21}O_{69}(H_2O)]^{6-}$ heteropolyanion.

Table II. Atomic Coordinates and Anisotropic Thermal Parameters of W, As, and Rb Atoms[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.4059 (1)	−0.4059 (1)	−0.0627 (1)	1.92 (9)	1.92 (9)	1.34 (9)	1.09 (12)	0.09 (5)	−0.09 (5)
W(2)	0.1213 (1)	−0.5382 (1)	0.0830 (1)	1.36 (8)	1.67 (8)	1.74 (6)	0.53 (8)	−0.11 (8)	0.22 (8)
W(3)	0.2300 (3)	−0.2300 (3)	0.2500	1.20 (25)	1.20 (25)	0.98 (25)	0.88 (26)		
W(3')	0.2489 (10)	−0.2489 (10)	0.2500	2.51 (62)	2.51 (62)	2.36 (72)	0.18 (90)		
As	0.3333	−0.3333	0.1064 (5)	1.38 (33)	1.38 (33)	0.40 (34)	0.69 (17)		
Rb	0.4970 (5)	−0.4970 (5)	0.2500	4.74 (56)	4.74 (56)	2.41 (42)	3.64 (62)		

[a] The anisotropic temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Atomic Coordinates and Isotropic Thermal Parameters of Oxygen Atoms[a]

Atom	x	y	z	B, Å^2
O(As122)	0.387 (2)	−0.387 (2)	0.064 (2)	1.9 (9)
O(11)	0.281 (2)	−0.281 (2)	−0.070 (3)	3.9 (14)
O(12)	0.115 (2)	−0.364 (2)	0.017 (1)	1.8 (6)
O(22)	0.468 (2)	−0.468 (2)	0.102 (2)	2.3 (8)
O(22b)	0.219 (1)	−0.219 (1)	0.063 (2)	0.8 (6)
O(23)	0.168 (2)	−0.322 (2)	0.178 (1)	1.3 (5)
O(1)	0.429 (2)	−0.429 (2)	−0.154 (2)	2.3 (9)
O(2)	0.034 (3)	−0.324 (3)	0.090 (2)	4.3 (9)
O(3)	0.176 (5)	−0.176 (5)	0.250	5.8 (27)
O(3')	0.304 (8)	−0.304 (8)	0.250	2.7
A	0.247 (5)	−0.247 (5)	−0.250	6.8 (29)
B	0.052 (10)	−0.312 (11)	−0.250	12.6 (39)
C	0.173 (5)	−0.173 (5)	−0.091 (6)	10.6 (34)
D	0.333	−0.333	−0.250	6.6 (56)

[a] O atoms indexed (ij) are bonded to W(i) and W(j). O atoms indexed (Asijk) are bonded to As and to the W atoms i, j, and k. Two structurally equivalent tungsten atoms are referred to as W(i) and W(i). O(22) is an O atom bonded to W(2) atoms of the same W_3O_{13} unit and O(22b) is an O atom bonded to W(2) atoms of two different W_3O_{13} units. O atoms of water molecules are noted A, B, C, and D.

This description does not take into account the disorder previously found for W(3). From the $^2/_3$:$^1/_3$ ratio, it appears that one tungsten over the three is in the W(3') site (Figure 2). The statistical occupation results from an equal distribution of the polyanion around the threefold axis.

Six rubidium atoms were located in the unit cell. Each anion is surrounded by three of them. They are in the mirror plane. Each of them has ten nearest neighbors: two oxygen atoms of the water molecules, two oxygens (O(22)) and four oxygens (O(23) of one anion (Figure 1a), and two terminal oxygen atoms (O(1)) of two other anions.

Eighteen H_2O molecules were found in the mirror plane between two polyanions. Twelve other water molecules surround the anions above the holes created between two linked W_3O_{13} groups (O(11),O(12),O(22b),O(12), Figure 1a).

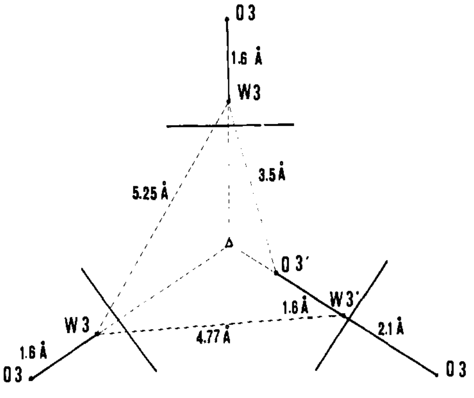

Figure 2. W and O atoms arrangement in the mirror plane.

It seems presumptuous to attempt to locate H_3O^+ ions. However, a difference Fourier synthesis shows up a peak in the position $^2/_3,^1/_3,^1/_4$, the height of which is consistent with an oxygen atom. The refinement of its temperature factor leads to a stable value of B equal to 6. It is interesting to note that three of the 18 H_2O molecules previously found are located at equivalent positions at about 2.52 Å from this oxygen. Thus, this set might be a $H_9O_4^+$ ion. Lundgren[12] expects such an ion to be planar in its minimum energy configuration. The four oxygens are in a same plane. Moreover the O–O distance is in good agreement with that one observed in other compounds such as 2.56 Å in $HBr{\cdot}4H_2O$, 2.59 Å in $HClO_4{\cdot}^5/_2H_2O$, and 2.58 Å in $HClO_4{\cdot}^7/_2H_2O$.[12]

When all these atoms are located, large channels are found along the 0,0 z axis with a radius of ca. 4 Å. The 38 water molecules that have not been found are likely to be situated in

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[12] J. Olof Lundgren, *Acta Univ. Ups., Abstr. Uppsla Diss Fac. Sci.*, **82**, (1974).

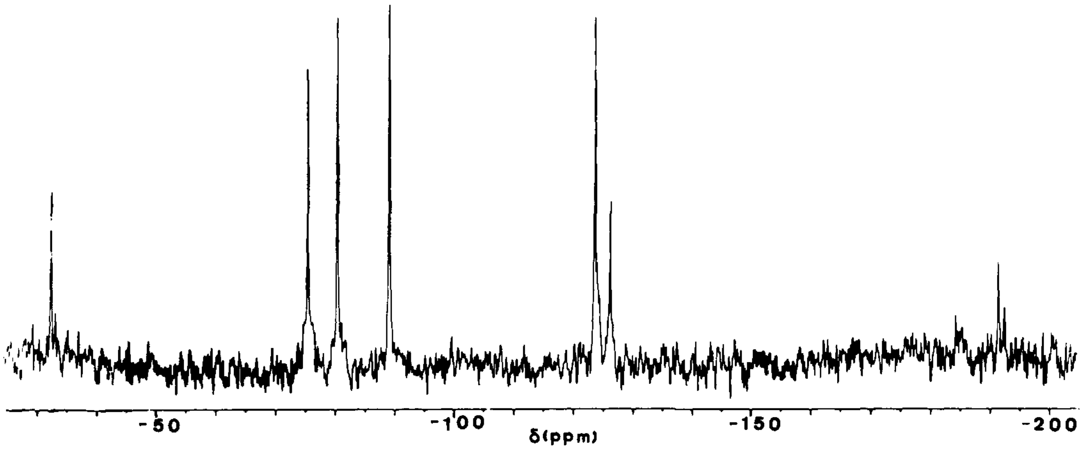

Figure 3. ^{183}W NMR spectrum of $[As_2W_{21}O_{69}(H_2O)]^{6-}$ in deuterated dimethyl sulfoxide.

Table IV. Some Selected Interatomic Distances (Å)

W(1)-W(1)	3.686 (5)	W(1)-O(1)	1.86 (4)
W(1)-W(2)	3.351 (3)	W(1)-O(As122)	2.44 (5)
W(2)-W(2)	3.347 (6)	W(1)-O(11)	1.91 (3)
W(2)-W(3)	3.642 (3)	W(1)-O(12)	1.90 (4)
W(2)-O(2)	1.63 (6)	W(3)-O(3)	1.59 (10)
W(2)-O(As122)	2.29 (3)	W(3)-O(23)	1.92 (3)
W(2)-O(12)	1.91 (3)		
W(2)-O(22)	1.90 (3)		
W(2)-O(22b)	1.92 (2)		
W(2)-O(23)	1.92 (2)		
W(3')-O(3')	1.62 (17)	Rb-O(1)	2.81 (4)
W(3')-O(3)	2.15 (10)	Rb-B	2.86 (19)
W(3')-O(23)	1.88 (3)	Rb-O(22)	2.91 (4)
As-O(As122)	1.77 (4)	Rb-O(23)	3.16 (3)

these channels. Evans[13] has studied a series of Keggin compounds. He found an increase of the unit cell volume of 29 Å^3/H_2O. From the volume of the channel divided by 38, the number of nonlocated water molecules, we find a volume of 25 Å^3. This seems sound.

The main W—W, W—O, As—O, and Rb—O distances are given in Table IV. They do not suggest any particular remarks. However it is worth pointing out the distances observed around W(3) tungsten. To our knowledge, examples of tungsten with a square-pyramidal environment are rare. One was found by Zikmund[14] who have solved the structure of $Ca_3WO_5Cl_2$. The WO_5^{4-} ion exhibits a W═O distance of 1.725 Å besides two distances of 1.888 Å and two distances of 1.911 Å to four coplanar O atoms; W is 0.553 Å above the plane. In our compound the W(3)═O(3) distance is 1.6 Å, the four W(3)—O(23) bonds are 1.92 Å; W(3) is displaced toward the outside of the polyanion, 0.44 Å from the plane of the four O(23) oxygen atoms.

The W(3′) environment is different: W(3′)—O(23) distances are equal to 1.88 Å; W(3′) is only 0.11 Å distant from the plane of the four O(23) atoms and it is displaced toward the inside of the polyanion (Figure 2).

The following interpretation can be proposed. A long W—O distance between W and a terminal oxygen atom is currently attributed to oxygen protonation.[15] Thus W(3′) is considered to be coordinated to a water molecule. However, to our knowledge, there is no example of a W(VI) in an oxygen environment without, at least, one particularly short W═O bond. This suggests that an oxygen atom could exist inside the polyanion that would "pull" W(3′) inside. Such an oxygen atom statistically distributed around the threefold axis seems elusive. However, it is worth noting that some faint residual electron density appears in the mirror plane but not on the threefold axis, and a position related to a third of an oxygen atom can be refined although *R* does not decrease significantly. The corresponding W(3′)═O(3′) distance is 1.6 Å. Thus this W(3′) tungsten would be displaced because the doubly bonded oxygen is the one inside the polyanion.

In heteropolyanions, terminal doubly bonded oxygen atoms is always found outside of the polyanion but, in our compound, W(3) and W(3′) do not belong to the AsW_9 subunits; they are atoms linking the two shells of the polyanion. The W(3)—O(3′) distance is 3.5 Å, excluding any interaction of W(3) with O(3′).

This discussion is supported by results which really are at the border line of the method accuracy. It appeared then wise to check this result by another different method. A ^{183}W NMR study was carried out thanks to the Bruker Company on a WP 250 spectrometer. The spectrum (Figure 3) has been recorded at room temperature: number of scans, 20 000; pulse width, 50 μs (with a 90-μs pulse for 90°); acquisition time, 1.35 s; delay, 0.5 s; spectrum width, 6000 Hz; exponential multiplication, 1. The rubidium salt of the heteropolyanion was dissolved in fully deuterated dimethylsulfoxide (2.5 g in 6 mL). Chemical shifts are given with respect to a molar solution of Na_2WO_4 in D_2O. Seven peaks are observed with area ratios close to 1:2:4:4:4:4:2.

In the presently established structure, there are seven structurally different kinds of tungsten atoms: W(3′); the two W(3) atoms; three groups of four W(2) atoms according to their distance to W(3′); the four W(1) atoms farthest from W(3′) and the two W(1) atoms nearest to W(3′). If the W(3) and W(3′) atoms were equivalent, three peaks would only occur, with area ratios of 3:12:6.

Then, the crystallographic discussion is fully confirmed.

Conclusion

A new heteropolyanion of As(III) has been studied and its structure solved.

As observed in previously described structures, As(III) is in the middle of an AsW_9O_{33} unit of the so-called B type.[16] Two AsW_9O_{33} units are linked by three tungsten atoms that keep the units distant from one another.

It is worth pointing out the unusual square-pyramidal environment of two of these tungstens and the asymmetrical way the two units are linked. This asymmetry has been checked by using ^{183}W nuclear magnetic resonance.

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Supplementary Material Available: A listing of structure factors amplitudes (5 pages). Ordering information is given on any current masthead page.

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