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# X-ray Study of $(NH_4)_7[H_2AsW_{18}O_{60}] \cdot 16H_2O$: First Example of a Heteropolyanion Containing Protons and Arsenic(III)

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The crystal structure of ammonium 18-tungstoarsenate(III), $(NH_4)_7[H_2AsW_{18}O_{60}] \cdot 16H_2O$, has been determined from three-dimensional X-ray data measured on a computer-controlled four-circle diffractometer at room temperature. The compound crystallizes in the monoclinic space group $C2/c$; lattice constants are $a = 21.937$ (5) Å, $b = 14.239$ (5) Å, $c = 22.177$ (9) Å, $\beta = 96.95$ (2)°, and $Z = 4$. The structure has been refined by a full-matrix least-squares method to a final $R$ factor of 0.066 for 6219 observed reflections. No correction could be applied for absorption. The $[H_2AsW_{18}O_{60}]^{7-}$ heteropolyanion is built up with two $XW_9O_{33}$ units sharing six oxygen atoms and joined in a $C_i$ fashion. Inside the first $XW_9O_{33}$ unit is As(III) with its lone pair directed toward the second unit. As revealed by NMR, this polyanion contains two protons inside, which cannot be titrated; thus the two $XW_9O_{33}$ units are different: one of them contains arsenic(III) and the other two protons.

## Introduction

In the last few years, several structures of tungsten or molybdenum heteropolyanions have been solved by X-ray, particularly those belonging to series with general formulas $[XM_{12}O_{40}]^{(8-n)-}$, $[XM_9O_{34}]^{(14-n)-}$, and $[X_2M_{18}O_{62}]^{(16-2n)-}$, where X is the heteroatom, $n$ its oxidation number, and M molybdenum or tungsten.[1-12] In this paper we shall use the shortened schematic notation $XM_{12}$, $XM_9$, $X_2M_{18}$.

All these compounds have structures of the "Keggin type"[13] or closely related to it. The heteroatom is either a fourth column element or a fifth column element with oxidation number 5.

However, heteropolyanions can also be prepared where the heteroelement still belongs to the fifth column but has oxidation number 3. Already published studies carried out in our laboratory showed that such a compound may be particularly highly condensed; for example, $[NaSb_9W_{21}O_{86}]^{18-}$ or $[NaAs_4W_{40}Co_2O_{140}]^{23-}$ can be prepared[14-16] and they are stable in neutral solutions. Working with acid solution (pH $\simeq 3$) we previously reported a condensed species of schematic formula $AsW_{18}$ which contains arsenic(III).[17]

The As/W ratio seems surprising with respect to the known structure of polyanions containing 18 tungsten atoms known as the "Dawson structure".[18] It is related to the Keggin structure [13] as follows: three adjacent corner-linked octahedra are removed from the Keggin anion, one from each of three edge-sharing $W_3O_{13}$ groups; it gives a $XW_9$ unit. Two such units are joined in $X_2W_{18}$ by sharing six oxygen atoms; thus they contain two heteroatoms.

Another interesting aspect of $As^{III}W_{18}$ is that arsenic(III) is not tetracoordinated in oxo compounds while the heteroatom is tetracoordinated in $X_2M_{18}$ polyanions having the Dawson structure.[18]

In order to throw light upon these points, we solved the structure of this compound by X-ray diffraction.

## Experimental Section

**Crystal Synthesis and Chemical Analysis.** A 330-g sample of sodium tungstate and 5.5 g of diarsenic trioxide were added into 350 cm$^3$ of water and boiled. After dissolution of the mixture, 140 cm$^3$ of a concentrated hydrochloric acid solution ($d$ 1.19) was added under stirring. The solution was kept boiling for 15 min. Yellow crystals appeared after 15 h. As shown by chemical analysis, the As/W ratio was equal to 1/18 and the cation was sodium.

In order to prepare crystals containing ammonium cations which are more suitable for crystallographic study, we dissolved 130 g of the sodium salt in 150 cm$^3$ of hot water, and 100 cm$^3$ of a 13% $NH_4Cl$ aqueous solution was then poured into the solution. Slow evaporation led to yellow crystals which were purified by several recrystallizations from water.

Chemical analysis was carried out as follows: the complex was destroyed by sodium hydroxide; ammonium cations were displaced and ammonia was titrated by acidimetry on a first part; on a second part, arsenic(III) was determined by iodometry after tungsten complexation by phosphate; on a third part, tungsten was precipitated by cinchonin and then ignited and weighed as tungsten trioxide.

Anal. Calcd for $(NH_4)_7[H_2AsW_{18}O_{60}] \cdot 16H_2O$: As, 1.57; W, 69.5; N, 2.06. Found (first sample): As, 1.59, 1.59; W, 69.7, 69.3; N, 1.97, 2.03; Cl, ≤0.2. Found (second sample): As, 1.57, 1.58; W, 69.7, 68.7; N, 2.00, 2.02; Cl, ≤0.2.

From these results it was inferred that the compound contains 18 tungsten atoms and 7 ammonium ions for 1 arsenic atom.

Potentiometric titration with sodium hydroxide showed that this salt has no proton which can be titrated. Charge balance led to the formula $(NH_4)_7AsW_{18}O_{59} \cdot nH_2O$.

We measured the amount of water by thermogravimetric analysis. The number of water molecules was between 16 and 18.

**Crystallographic Data.** Preliminary Laue and precession photographs showed a monoclinic unit cell.

Systematically absent reflections were $h + k = 2n + 1$ for $hkl$ and $l = 2n + 1$ for $h0l$. This is characteristic of $C2/c$ and $Cc$.

A crystal shaped approximately as a parallelepiped with approximate dimensions 0.12 × 0.12 × 0.07 mm was set up on a computer-controlled four-circle Philips PW 1100 diffractometer.

Lattice constants, determined by least squares from 25 reflections, are $a = 21.937$ (5) Å, $b = 14.239$ (5) Å, $c = 22.177$ (9) Å, $\beta = 96.95$ (2)°, and $V = 6876$ Å$^3$.

The density of crystals was measured by pycnometry in cyclohexane. The obtained value of 4.58 g/cm$^3$ led to 4 molecules per unit cell; the calculated value is then 4.57 if the formula is $(NH_4)_7AsW_{18}O_{59} \cdot 17H_2O$.

A total of 9588 independent reflections were collected at room temperature: radiation Mo K$\alpha$; graphite monochromator; scan type $\theta$–$2\theta$; scan speed 0.016° s$^{-1}$; scan length $(0.90 + 0.30 \tan \theta)$ degrees, if $\theta$ is Bragg angle; background measurements in fixed position before and after every scan during a time equal to half of the scan time; maximum recording angle $\theta_{Bragg} = 30°$; standard reflections $\bar{8}22$, $8\bar{2}\bar{2}$, and 040 measured every 2 h. No decrease of standards was observed.

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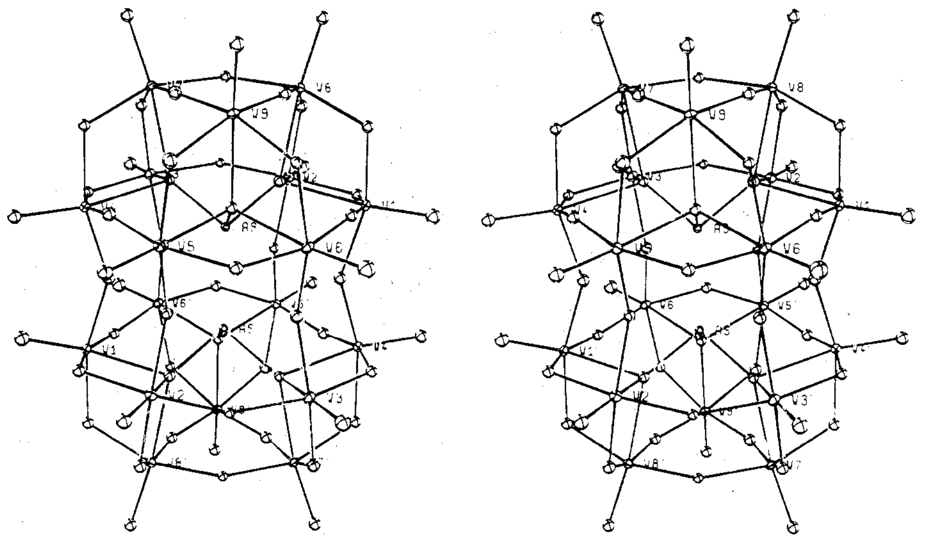

**Figure 1.** Stereoscopic ORTEP plotting of 18-tungstoarsenate(III) anion (with 20% probability ellipsoids).

**Table I.** Statistical Tests Based on $E$

| | exptl | calcd | |
|---|---|---|---|
| | | centrosym | noncentrosym |
| $E^2$ | 0.9999 | 1.0000 | 1.0000 |
| $\lvert E^2 - 1\rvert$ | 0.9615 | 0.9680 | 0.7360 |
| $\lvert E\rvert$ | 0.7964 | 0.7980 | 0.8860 |

Zero reflections were omitted from refinement. The final data set thus consisted of 6219 reflections. The intensities were corrected for Lorentz and polarization effects.

Since the crystal used for recording data had a poorly defined shape, no correction could be applied for absorption.

## Structure Determination and Refinement

Statistical tests[19] were used and applied to the whole 9588 collected reflections. They showed centrosymmetry (Table I).

In $C2/c$ there are eight general equivalent positions and the unit cell contains $As_4W_{72}$. Thus nine tungstens are in general eightfold positions and arsenic must be either in statistical distribution or in a special position.

A three-dimensional Patterson synthesis was calculated. Six peaks related to a planar hexagon of tungsten atoms were found. A first refinement led to $R = 0.42$ ($R = \sum|F_o - kF_c|/\sum F_o$, $k$ is the scale factor).

Refinements were made by least-squares methods minimizing $R = (\sum|F_o - kF_c|^2/\sum F_o^2)^{1/2}$.

A Fourier synthesis gave the positions of the three remaining tungsten atoms of the asymmetric unit. In a difference Fourier synthesis 30 oxygen atoms linked to the tungsten atoms could be located. $R$ dropped to 0.10.

Arsenic was found to be located on a general position with a statistical distribution. $R$ decreased to 0.09.

Eleven well-defined peaks, all in general positions, could be found in a last difference Fourier synthesis. They were attributed to the nitrogen atoms of the $NH_4^+$ cations and to the oxygen atoms of the water molecules but it is not clear which of them are, in fact, nitrogen or oxygen. Then $R$ dropped to 0.07.

A final $R$ value of 0.066 was obtained by using anisotropic temperature factors for tungsten and arsenic.

Atomic form factors were taken from Cromer and Waber.[20a] Account was taken of the real and imaginary part of the anomalous dispersion correction.[20b] Since it was not possible to distinguish the N atoms of the ammonium cations from the O atoms of the water molecules, we chose for these atoms a weighted atomic form factor. The weighing scheme took into account the numbers of water molecules and ammonium ions in the unit cell.

We must point out that 30 oxygen atoms linked to the 9 tungsten atoms could be located in the asymmetrical unit. Then the whole polyanion contains 60 oxygen atoms, while 59 only were expected from chemical analysis.

Moreover, the asymmetrical unit contains 8 to 9 water molecules and 3.5 ammonium cations. Therefore we should have found 12 peaks for the oxygen and nitrogen atoms, one of them being in a special position or in a general position with an occupancy factor of 0.5; however, we found only 11 peaks. These two points will be discussed later on.

No attempts were made to locate hydrogen atoms.

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

## Description of the Structure and Discussion

The cell contains four 18-tungstoarsenate anions.

The 18-tungstoarsenate anion (Figure 1) is built with two joined shells of nine $WO_6$ octahedra. Each of them contains three groups of three octahedra. In a group each octahedron is linked to its neighbors by sharing one edge and the three octahedra have a common vertex ($O_c$, Figure 2). These three groups are linked together by sharing vertices, building some kind of a basket. The same framework is found in the Keggin anion[13] in which a fourth group of three octahedra closes the basket. Such a $XW_9$ unit is usually said to be a B type.[21] Let us point out that $X_2M_{18}$ polyanions with Dawson structures[18]

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

| atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| W(1) | 0.214 14 (5) | 0.008 29 (8) | 0.913 40 (5) | 1.19 (4) | 1.39 (4) | 1.66 (4) | −0.32 (3) | 0.37 (3) | −0.15 (3) |
| W(2) | 0.351 61 (5) | 0.023 54 (8) | 0.992 02 (5) | 1.46 (4) | 1.57 (4) | 1.28 (4) | 0.12 (3) | 0.14 (3) | −0.02 (3) |
| W(3) | 0.434 94 (5) | 0.252 88 (9) | 1.011 85 (5) | 1.04 (4) | 1.94 (5) | 1.45 (4) | −0.17 (3) | 0.07 (3) | 0.04 (3) |
| W(4) | 0.361 72 (5) | 0.443 71 (8) | 0.952 77 (5) | 1.34 (4) | 1.37 (4) | 1.59 (4) | −0.29 (3) | 0.49 (3) | −0.13 (3) |
| W(5) | 0.205 94 (5) | 0.430 01 (8) | 0.863 00 (5) | 1.63 (4) | 1.37 (4) | 1.36 (4) | 0.21 (3) | 0.33 (3) | 0.11 (3) |
| W(6) | 0.134 90 (5) | 0.223 86 (9) | 0.846 15 (5) | 0.91 (4) | 1.92 (4) | 1.39 (4) | −0.11 (3) | 0.13 (3) | 0.07 (3) |
| W(7) | 0.413 30 (5) | 0.281 10 (9) | 0.860 69 (5) | 0.96 (4) | 1.81 (4) | 1.40 (4) | −0.36 (3) | 0.53 (3) | −0.13 (3) |
| W(8) | 0.334 37 (5) | 0.052 62 (8) | 0.841 43 (5) | 1.28 (4) | 1.40 (4) | 1.31 (4) | 0.04 (3) | 0.37 (3) | −0.24 (3) |
| W(9) | 0.258 15 (5) | 0.266 13 (8) | 0.773 20 (5) | 1.17 (4) | 1.72 (4) | 0.97 (3) | 0.07 (3) | 0.27 (3) | 0.11 (3) |
| As | 0.274 62 (23) | 0.235 80 (37) | 0.948 61 (22) | 0.98 (17) | 0.99 (18) | 0.97 (17) | −0.15 (15) | 0.24 (13) | −0.10 (14) |

[a] The anisotropic thermal parameters have units of Å$^2$. 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 N and O Atoms[a]

| atom | *x* | *y* | *z* | *B*, Å$^2$ | atom | *x* | *y* | *z* | *B*, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| O(1) | 0.1647 (11) | −0.0853 (17) | 0.9039 (10) | 2.5 (4) | O(4,5) | 0.2913 (9) | 0.4539 (15) | 0.8948 (9) | 1.9 (3) |
| O(2) | 0.3943 (10) | −0.0623 (16) | 1.0317 (10) | 2.3 (4) | O(4,7) | 0.4108 (9) | 0.4121 (14) | 0.8873 (8) | 1.5 (3) |
| O(3) | 0.5023 (11) | 0.2389 (18) | 1.0584 (11) | 2.7 (4) | O(5,6) | 0.1322 (9) | 0.3596 (14) | 0.8371 (9) | 1.7 (3) |
| O(4) | 0.3849 (10) | 0.5593 (16) | 0.9620 (10) | 2.2 (4) | O(5,9) | 0.2368 (10) | 0.3989 (16) | 0.7871 (10) | 2.2 (4) |
| O(5) | 0.1817 (10) | 0.5450 (17) | 0.8440 (10) | 2.4 (4) | O(6,1) | 0.1684 (9) | 0.1002 (14) | 0.8635 (9) | 1.7 (3) |
| O(6) | 0.0627 (12) | 0.1947 (19) | 0.8103 (11) | 3.0 (4) | O(6,9) | 0.1730 (8) | 0.2277 (14) | 0.7703 (8) | 1.4 (3) |
| O(7) | 0.4679 (9) | 0.2881 (15) | 0.8110 (9) | 1.9 (3) | O(7,8) | 0.3924 (8) | 0.1508 (13) | 0.8550 (8) | 1.3 (3) |
| O(8) | 0.3660 (9) | −0.0090 (15) | 0.7853 (9) | 1.8 (3) | O(8,9) | 0.2844 (9) | 0.1398 (14) | 0.7937 (9) | 1.6 (3) |
| O(9) | 0.2653 (9) | 0.2685 (15) | 0.6975 (9) | 1.8 (3) | O(9,7) | 0.3400 (10) | 0.3018 (16) | 0.8077 (10) | 2.0 (4) |
| O(1,4′) | 0.1865 (9) | 0.0684 (15) | 0.9828 (9) | 1.9 (3) | A | 0.6028 (17) | 0.2691 (28) | 0.9629 (17) | 4.7 (7) |
| O(2,5′) | 0.3116 (8) | 0.0757 (13) | 1.0560 (8) | 1.1 (3) | B | 0.6591 (12) | 0.4766 (20) | 0.2303 (12) | 2.5 (4) |
| O(3,6′) | 0.3797 (8) | 0.2644 (13) | 1.0727 (8) | 1.3 (3) | C | 0.4964 (18) | 0.0280 (29) | 0.1132 (18) | 5.2 (8) |
| O(As,1,2,8) | 0.2928 (9) | 0.1122 (14) | 0.9258 (9) | 1.6 (3) | D | 0.5821 (15) | 0.3378 (24) | 0.1646 (15) | 3.7 (6) |
| O(As,3,4,7) | 0.3536 (8) | 0.2853 (14) | 0.9408 (8) | 1.4 (3) | E | 0.5403 (15) | 0.1532 (23) | 0.2062 (14) | 3.6 (6) |
| O(As,5,6,9) | 0.2338 (8) | 0.2717 (13) | 0.8758 (8) | 1.2 (3) | F | 0.5599 (17) | 0.5557 (28) | 0.2882 (17) | 4.7 (7) |
| O(1,2) | 0.2767 (9) | −0.0545 (14) | 0.9685 (9) | 1.6 (3) | G | 0.4869 (14) | 0.4753 (22) | 0.1110 (14) | 3.2 (5) |
| O(1,8) | 0.2611 (9) | −0.0205 (15) | 0.8472 (9) | 1.7 (3) | H | 0.3453 (18) | 0.2248 (29) | 0.4077 (18) | 5.1 (8) |
| O(2,3) | 0.4092 (8) | 0.1229 (13) | 0.9998 (8) | 1.1 (3) | I | 0.7680 (18) | 0.3057 (28) | 0.0627 (17) | 4.8 (8) |
| O(2,8) | 0.3747 (9) | −0.0065 (15) | 0.9110 (9) | 1.7 (3) | J | 0.3964 (18) | 0.7357 (29) | 0.1742 (18) | 4.9 (8) |
| O(3,4) | 0.4299 (9) | 0.3853 (14) | 1.0068 (8) | 1.5 (3) | K | 0.4491 (19) | 0.9119 (30) | 0.2032 (18) | 5.1 (8) |
| O(3,7) | 0.4660 (8) | 0.2513 (14) | 0.9350 (8) | 1.4 (3) | | | | | |

[a] O atoms indexed (*i*,*j*) are bonded to the W atoms *i* and *j*. O atoms indexed (As,*i*,*j*,*k*) are bonded to As and to the W atoms *i*, *j*, and *k*. The W atoms symmetrical of W(*i*) with respect to the center of the anion are designed W(*i*′). The cation N atoms and the water O atoms which are not distinguished are noted A, B, C, ..., K.

**Table IV.** Some Distances to the Mean Plane of the Six Oxygen Atoms Joining the Two Shells

| atom | dist, Å | atom | dist, Å |
|---|---|---|---|
| O(1,4′) | 0.015 | W(3) | 1.88 |
| O(4,1′) | −0.015 | W(4) | 1.79 |
| O(2,5′) | −0.014 | W(5) | 1.81 |
| O(5,2′) | 0.014 | W(6) | 1.79 |
| O(3,6′) | 0.014 | W(7) | 4.57 |
| O(6,3′) | −0.014 | W(8) | 4.55 |
| W(1) | 1.84 | W(9) | 4.56 |
| W(2) | 1.83 | | |

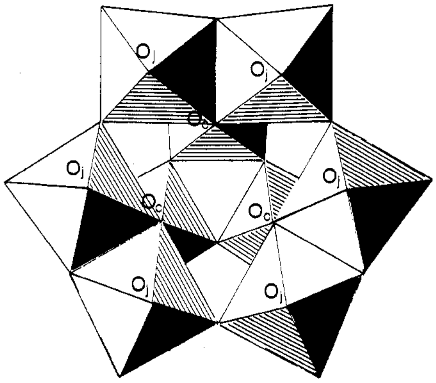

**Figure 2.** 18-Tungstoarsenate(III) anion with $WO_6$ octahedra framework in a $XW_9$ unit (ORTEP plotting).

**Table V.** Selected Distances and Angles between the Tungsten Atoms

| | Distances (Å) | | |
|---|---|---|---|
| W(1)–W(2) | 3.303 (2) | W(4)–W(5) | 3.746 (2) |
| W(1)–W(8) | 3.304 (2) | W(4)–W(7) | 3.372 (2) |
| W(1)–W(4′) | 3.639 (2) | W(5)–W(6) | 3.323 (2) |
| W(2)–W(3) | 3.742 (2) | W(5)–W(9) | 3.358 (2) |
| W(2)–W(8) | 3.341 (2) | W(6)–W(1) | 3.747 (2) |
| W(2)–W(5′) | 3.654 (2) | W(6)–W(9) | 3.369 (2) |
| W(3)–W(4) | 3.342 (2) | W(7)–W(8) | 3.686 (2) |
| W(3)–W(7) | 3.352 (2) | W(7)–W(9) | 3.714 (2) |
| W(3)–W(6′) | 3.680 (2) | W(8)–W(9) | 3.703 (2) |
| | Angles (deg) | | |
| W(1)W(2)W(3) | 121.41 (4) | W(6)W(1)W(2) | 120.41 (4) |
| W(2)W(3)W(4) | 117.30 (4) | W(7)W(8)W(9) | 60.35 (4) |
| W(3)W(4)W(5) | 122.02 (4) | W(8)W(9)W(7) | 59.59 (3) |
| W(4)W(5)W(6) | 119.40 (4) | W(9)W(7)W(8) | 60.06 (3) |
| W(5)W(6)W(1) | 119.35 (5) | | |

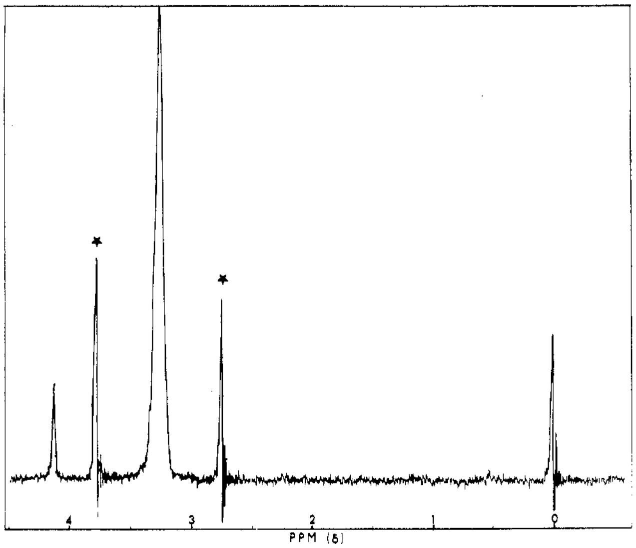

**Figure 3.** NMR spectrum in $D_2O$ of sodium 18-tungstoarsenate(III) with respect to pivalic acid.

are made of two joined units of A type.[21]

Whereas the two A type units of Dawson structure are related through a mirror plane, in 18-tungstoarsenate(III), the two shells are symmetrical with respect to an inversion center (at $^1/_4$, $^1/_4$, 0). These two shells are joined together by sharing six oxygen atoms ($O_j$, Figure 2) nearly as a plane hexagon. The nine tungsten atoms of the asymmetric unit are located in two parallel planes, themselves parallel to the plane of the six "$O_j$" oxygen atoms (Table IV).

The distances and the angles between the tungsten atoms, the W–O distances, and the angles within the $WO_6$ octahedra are given in Tables V and VI.

$WO_6$ octahedra are distorted as is usually found in heteropolyanions. The longer the W–O distance is, the larger is the coordination of the oxygen atom. We found an average value of 1.73 Å from W to an unshared oxygen, i.e., for a W–O double bond. The distance is 2.26 and 2.40 Å to an inner oxygen atom linked to three W atoms and one As atom.

In a given polyanion, arsenic is set up in one of the two cavities made by the tungsten atoms. It occupies the vertex

Table VI.[a] Selected Distances (Å) and Angles (deg) within Octahedra and Central Pyramid

| | O(1) | O(As,1,2,8) | O(1,4′) | O(1,6) | O(1,2) | O(1,8) |
|---|---|---|---|---|---|---|
| W(1)- | 1.72 (2) | 2.26 (2) | 1.92 (2) | 1.92 (2) | 1.94 (2) | 1.94 (2) |
| O(1)-W(1)- | | 169.7 (9) | 100.9 (10) | 100.4 (10) | 96.2 (10) | 97.4 (10) |
| O(As,1,2,8)-W(1)- | 169.7 (9) | | 85.5 (8) | 87.8 (8) | 75.8 (8) | 76.2 (8) |
| | O(2) | O(As,1,2,8) | O(2,5′) | O(2,3) | O(1,2) | O(2,8) |
| W(2)- | 1.72 (2) | 2.23 (2) | 1.91 (2) | 1.89 (2) | 2.00 (2) | 1.97 (2) |
| O(2)-W(2)- | | 168.2 (9) | 99.6 (9) | 99.7 (9) | 96.8 (9) | 97.4 (9) |
| O(As,1,2,8)-W(2)- | 168.2 (9) | | 89.3 (7) | 87.9 (7) | 75.6 (7) | 73.4 (7) |
| | O(3) | O(As,3,4,7) | O(3,6′) | O(2,3) | O(3,4) | O(3,7) |
| W(3)- | 1.71 (2) | 2.28 (2) | 1.93 (2) | 1.94 (2) | 1.89 (2) | 1.91 (2) |
| O(3)-W(3)- | | 171.2 (10) | 99.0 (9) | 100.8 (10) | 101.0 (10) | 99.3 (10) |
| O(As,3,4,7)-W(3)- | 171.2 (10) | | 87.7 (7) | 84.7 (7) | 73.9 (8) | 73.8 (7) |
| | O(4) | O(As,3,4,7) | O(4,1′) | O(4,5) | O(3,4) | O(4,7) |
| W(4)- | 1.73 (2) | 2.27 (2) | 1.88 (2) | 1.89 (2) | 1.98 (2) | 1.96 (2) |
| O(4)-W(4)- | | 167.4 (8) | 100.5 (10) | 102.2 (10) | 98.0 (9) | 97.2 (9) |
| O(As,3,4,7)-W(4)- | 167.4 (8) | | 87.4 (8) | 87.2 (8) | 72.4 (8) | 74.3 (8) |
| | O(5) | O(As,5,6,9) | O(5,2′) | O(4,5) | O(5,6) | O(5,9) |
| W(5)- | 1.76 (2) | 2.34 (2) | 1.88 (2) | 1.95 (2) | 1.93 (2) | 1.94 (2) |
| O(5)-W(5)- | | 172.9 (9) | 100.2 (9) | 100.0 (10) | 101.2 (10) | 97.6 (10) |
| O(As,5,6,9)-W(5)- | 172.9 (9) | | 85.6 (7) | 84.2 (8) | 74.5 (7) | 76.8 (8) |
| | O(6) | O(As,5,6,9) | O(6,1′) | O(1,6) | O(5,6) | O(6,9) |
| W(6)- | 1.73 (2) | 2.29 (2) | 1.87 (2) | 1.93 (2) | 1.94 (2) | 1.97 (2) |
| O(6)-W(6)- | | 169.3 (9) | 102.1 (10) | 100.2 (10) | 100.1 (10) | 94.3 (10) |
| O(As,5,6,9)-W(6)- | 169.3 (9) | | 87.9 (7) | 83.7 (7) | 75.5 (8) | 75.6 (7) |
| | O(7) | O(As,3,4,7) | O(7,8) | O(7,9) | O(3,7) | O(4,7) |
| W(7)- | 1.73 (2) | 2.33 (2) | 1.91 (2) | 1.90 (2) | 1.94 (2) | 1.96 (2) |
| O(7)-W(7)- | | 169.1 (8) | 101.2 (9) | 101.4 (9) | 99.5 (9) | 100.6 (9) |
| O(As,3,4,7)-W(7)- | 169.1 (8) | | 85.6 (7) | 87.5 (8) | 72.0 (7) | 73.0 (7) |
| | O(8) | O(As,1,2,8) | O(7,8) | O(8,9) | O(1,8) | O(2,8) |
| W(8)- | 1.73 (2) | 2.34 (2) | 1.89 (2) | 1.89 (2) | 1.93 (2) | 1.88 (2) |
| O(8)-W(8)- | | 170.6 (8) | 99.7 (9) | 100.7 (9) | 100.6 (9) | 99.9 (9) |
| O(As,1,2,8)-W(8)- | 170.6 (8) | | 85.7 (7) | 87.3 (7) | 74.6 (8) | 72.4 (8) |
| | O(9) | O(As,5,6,9) | O(7,9) | O(8,9) | O(5,9) | O(6,9) |
| W(9)- | 1.70 (2) | 2.40 (2) | 1.93 (2) | 1.93 (2) | 1.98 (2) | 1.94 (2) |
| O(9)-W(9)- | | 171.9 (8) | 101.1 (9) | 101.0 (9) | 100.8 (9) | 100.2 (9) |
| O(As,5,6,9)-W(9)- | 171.9 (8) | | 85.3 (7) | 84.3 (7) | 74.7 (8) | 73.5 (7) |

| | O(As,1,2,8) | O(As,3,4,7) | O(As,5,6,9) |
|---|---|---|---|
| As- | 1.89 (2) | 1.90 (2) | 1.82 (2) |
| O(As,1,2,8)-As- | | 95.6 (9) | 97.0 (9) |
| O(As,3,4,7)-As- | 95.6 (9) | | 99.8 (8) |

[a] The designation of the atoms is explained in Table III.

of a pyramid, the base of which is formed by the three "$O_c$" oxygen atoms (Figure 2). Thus arsenic is tricoordinated as could be expected from a chemical point of view. This is a typical difference with polytungstates having a Dawson structure[18] where the half-anion framework allows the heteroatom to be tetracoordinated. In the present case, the fourth direction corresponds to the As(III) lone pair and points toward the second shell. Therefore it is easy to understand why the second shell cannot contain any arsenic atom: two lone pairs of two arsenic atoms would point toward each other, preventing such an association $As^{III}{}_2W_{18}$.

The As–O distances and the angles of the pyramid are given in Table VI.

As pointed out earlier, the existence of seven $NH_4^+$ cations per $AsW_{18}$ polyanion, as revealed by chemical analysis, implies that either a nitrogen atom is located in general position with statistical distribution or a nitrogen atom is located in special position. We looked for the surrounding of any special position: there is not space enough for such a $NH_4^+$ cation in any of these special positions. This can be checked since no peak appears on any special position in a Fourier synthesis. Thus, the seventh $NH_4^+$ cation is in a general position with an occupancy factor of 0.5. Unfortunately, we did not find any peak in the Fourier synthesis with the corresponding height.

Various hypotheses can be made in order to explain this fact: (1) Such a peak, corresponding to a nitrogen atom with half-occupancy, cannot be seen in the difference Fourier synthesis because it is too low. (2) Among the 11 nitrogen and oxygen peaks, corresponding to $NH_4^+$ and $H_2O$, observed in the Fourier synthesis, one might be related to a site occupied either by an ammonium cation or by a water molecule.[22] This would restrain the number of water molecules to 15. (3) Finally, it could be assumed that the molecule contains only six cations. The chemical analysis could be wrong because crystals of heteropolyanion could have kept in some $NH_4Cl$. A relative $NH_4Cl$ overloading of 1% would change the number of $NH_4^+$ ions of the molecule from six to seven. Then there would be 6 $NH_4^+$ ions and 16 $H_2O$ molecules. This assumption was eliminated because chemical analysis revealed a very small amount of chlorine that indicates a $NH_4Cl$ overloading smaller than 0.3%; this value is not larger enough to change the adopted formula.

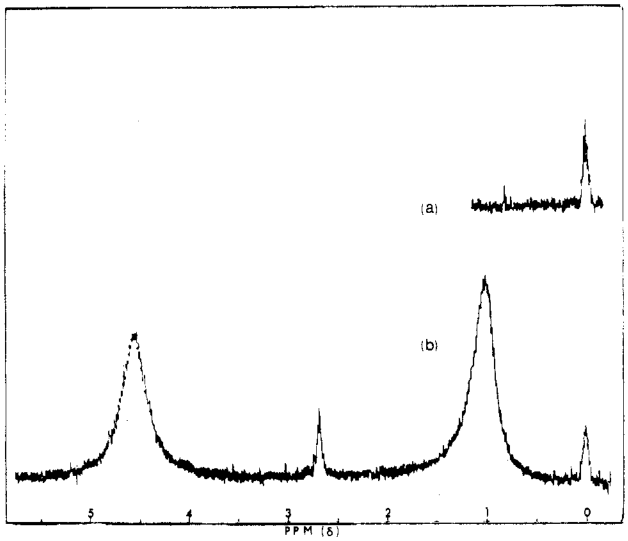

**Figure 4.** NMR spectrum in 99.95% deuterated dimethyl sulfoxide: (a) dimethyl sulfoxide alone, (b) ammonium 18-tungstoarsenate(III) in dimethyl sulfoxide.

This is a first problem. There is another one: the crystal structure determination led us to an anion formula of $[AsW_{18}O_{60}]^{9-}$ but we found only seven cations by chemical analysis. The uncertainty on analysis fails to explain such a discrepancy. Moreover we have to keep in mind that there is only 1 arsenic atom for 18 tungsten atoms made of two $W_9$ units. Let us point out that no species is known, with a Keggin structure,[13] which contains nothing inside. There is a heteroatom which can be silicon, germanium, arsenic, or phosphorus. If it is missing there are two protons: this is metatungstate[23] $[H_2W_{12}O_{40}]^{6-}$. In the case of the Dawson structure[18] all the known compounds have two heteroatoms. Thus, it could be assumed that our compound contains one arsenic in the first half-unit and two protons in the other. This would have the advantage to restore electroneutrality: $(NH_4)_7[H_2AsW_{18}O_{60}]$. In this respect let us point out that this heteropolyanion was prepared in acid solution with pH $\simeq 3$.

In order to check this last assumption, we carried out a NMR study by using $D_2O$ as solvent. The sodium salt of the 18-tungstoarsenate(III) was dissolved in $D_2O$ because the ammonium salt was not soluble enough to obtain the 0.1 M concentration required. The solution contained a known amount of pivalic acid ($(CH_3)_3CCO_2H$), which was used as an internal standard. The spectrum shown in Figure 3, recorded with a Varian A-60 at ordinary temperature, looks like the one obtained with metatungstate.[24] The large peak with a chemical shift of 3.2 ppm with respect to pivalic acid is given by the protons introduced by the hydration water of the polyanion. The acid proton of pivalic acid appears at the same place. A second peak at 4.1 ppm from pivalic acid is ascribed to nonexchangeable protons constitutive of the polyanion. Since the concentrations of polyanion and pivalic acid are known, the corresponding peak area ratio gave the number of nonexchangeable protons enclosed inside the polyanion. The result is 2 protons per 18 tungstens, experimental values being as follows: concentration of polyanion, 0.2 M; concentration of pivalic acid nonacid protons, 0.324 M; concentration of polyanion nonexchangeable protons, 0.376 M; number of exchangeable protons/polyanion ratio, 1.88.

The NMR technique was used once more to determine the $NH_4^+/H_2O$ ratio in $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot nH_2O$. The spectrum of the ammonium 18-tungstoarsenate(III), dissolved in 99.95% deuterated dimethyl sulfoxide, was recorded with a Varian XL 100 (Figure 4). Three different signals were observed with chemical shifts of 1.0, 2.7, and 4.5 ppm with respect to dimethyl sulfoxide. They are given by three different kinds of protons: the protons introduced by the crystallization water molecules, those which are inside the central cavity of the polyanion, and those belonging to the ammonium ions. We could easily estimate the third and first peak area ratio and thus the $NH_4^+/H_2O$ ratio. Results obtained and theoretical values expected in each of the two assumed hypotheses are given here: calculated, 1 ($7NH_4^+,16H_2O$), 0.875; 2 ($NH_4^+,15H_2O$), 0.933; found, 0.86 ± 0.02. Consequently the first hypothesis is retained, in agreement with the number of ammonium ions found by chemical analysis.

Therefore the true anionic species is $[H_2AsW_{18}O_{60}]^{7-}$ and the ammonium salt formula is $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot 16H_2O$.

## Conclusion

By its tungsten framework the title compound belongs to the $X_2M_{18}$ heteropolyanion family. However, it differs from the Dawson structure[18] by two features. It is built up of two joined $XW_9$ units of the B type instead of A type.[21] The two $XW_9$ units are not identical: the first one contains an arsenic(III) atom and the second one two protons. This is the first example of a heteropolyanion wiith two halves of a different kind.

Compounds with the same stoichiometric X/W ratio have been reported with heteroelements as Sb(III) and Te(IV).[25,26] These two atoms possess a lone pair as As(III) does. Though no structural determinations of these anions have been carried out, they can be expected to have similar structures from these work conclusions.

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**Registry No.** $(NH_4)_7[H_2AsW_{18}O_{60}]\cdot 16H_2O$, 71393-15-2; sodium tungstate, 11120-01-7; diarsenic trioxide, 1327-53-3.

**Supplementary Material Available:** A listing of structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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