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Synthesis and Structure of Potassium Octatungstodiarsenate(III)

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The formation of polyoxo complexes between tungsten(VI) and arsenic, antimony, or bismuth(III) heteroatoms has been the object of only a few reports.[1-6] Their structures have been determined by X-ray diffraction[7-10] in a few cases or only proposed[11] in others. In all cases, the structure emphasizes the stereochemical role of the lone pair of the X(III) heteroelement, which is at the center of the polyoxotungstate framework.

In the 21-tungsto-9-antimonate structure,[12] in addition to the three central Sb heteroatoms, six Sb atoms are linked to W atoms through terminal oxygens and are, therefore, external with regard to the polyoxotungstic frame. We report here the synthesis and the structure of the 8-tungsto-2-arsenate(III) with such nonequivalent heteroatoms: one arsenic is central while the second one is external.

Experimental Section

Preparation of the Compound $K_7(AsW_8O_{30}AsOH)\cdot 12H_2O$. A 36-g sample of potassium arsenate(III) was added to 500 mL of a solution of 1 M potassium tungstate obtained by attack of tungstic oxide by potassium hydroxide. The lukewarm solution was acidified by hydrochloric acid (120–130 mL of HCl (6 M)) until pH 8. The potassium salt crystallized from the solution. An excellent yield is obtained, close to 90 per 100 vs. tungsten.

Crystal Structure. The unit cell dimensions and space group were determined from preliminary oscillations and Weissenberg photographs. The symmetry was monoclinic, and the systematic absences ($0k0$, $k = 2n + 1$) led either to centrosymmetric $P2_1/m$ or to noncentrosymmetric $P2_1$ space group. The measured density agreed with the calculated one ($d_{\text{calcd}} = 4.41$, $d_{\text{measd}} = 4.15$ g cm^{-3}) for $Z = 2$. Statistics on normalized structure factors led to centrosymmetric $P2_1/m$ and implied that the asymmetric unit is half of the polyanion.

A crystal shaped approximately as a parallelepiped with dimensions $0.065 \times 0.10 \times 0.29$ mm^3 was set up on a computer-controlled four-circle Philips PW1100 diffractometer. Lattice constants determined from 25 reflections were $a = 9.756$ (3) Å, $b = 20.979$ (5) Å, $c = 9.789$ (3) Å, $\beta = 101.67$ (3)°, and $V = 1920$ Å^3. Intensities were collected at room temperature in a θ–2θ scan mode with Mo Kα radiation, graphite monochromator up to $\theta_{\max} = 25°$. The scan length was ($1.20 + 0.30 \tan \theta$) with background measurements in fixed positions before and after every scan during a time equal to half the scan time; the scan speed was 0.02°/s.

Three standard reflections measured every 50 remained constant. A total of 3429 independent reflections were collected, among them 2784 with $F_o > 7\sigma(F)$ were the final data set. Their intensities were corrected for Lorentz and polarization factors. Absorption corrections were performed ($\mu = 248.6$ cm^{-1}).

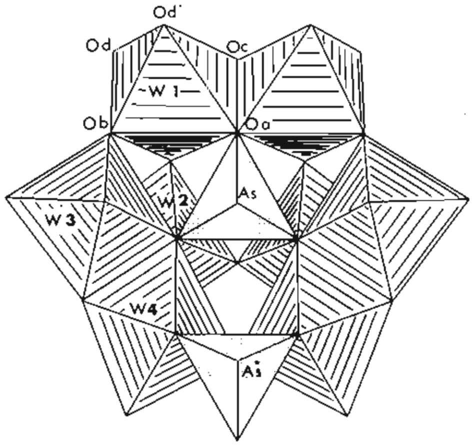

Figure 1. Polyedral model with tungsten numbering and designation of oxygen atoms in the polyanionic structure. Oa bridge WO_6 octahedra and the central As atom. Ob and Oc oxygen link WO_6 octahedra respectively by vertex and by edges. Od are bounded to one W atom; if two Od are linked to the same W, the prime is added to the O atom cis to Oa. Numbers refer to the W atom to which O atoms are linked; As* is bounded to Od'$_4$ and to a third oxygen OAs*.

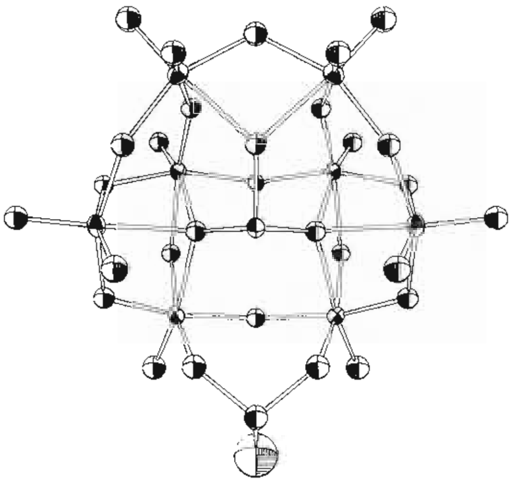

Figure 2. ORTEP plot of the 8-tungsto-2-arsenate(III) anion (with 50% probability ellipsoids).

The structure was solved by direct methods (MULTAN[13]). The five highest peaks were introduced as W atoms ($R = 0.23$). The value of U of one atom is about 5 times those of the four other ones and evidences an As atom. Alternative Fourier synthesis and full-matrix least-squares refinements show all the other atoms. Due to the relative weak density, eight water molecules were found, while thermogravimetric determination led to a number of 12. In the last least-squares cycles a weighted scheme of the form $w = 2.0535/\sigma^2(F)$ was introduced. The final R values are $R = \sum(||F_o| - |F_c||)/\sum F_o = 0.0381$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^{\,2})^{1/2} = 0.0375$.

All calculations were carried out on the IRIS 80 computer of the University with SHELX programs.[14]

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given Table I.

Results and Discussion

The cell contains two 8-tungsto-2-arsenate ions. The tungstic structure (Figure 1 and 2) of the anion is composed of two edge-sharing groups of three WO_6 octahedra and one of two WO_6 octahedra. These groups are linked together by sharing vertices. This tungstic structure can be described according to designation rules we proposed[15] as a B-type β-enneatungstic anion that has lost a WO_6 octahedron of the rotated tritungstic group.

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Table I. Fractional Atomic Coordinates and Thermal Parameters[a]

atom	x/a	y/b	z/c	B_{iso}, Å^2	B_{eq}, Å^2
W(1)	0.03466 (8)	0.17099 (3)	0.03060 (7)		1.54 (2)
W(2)	0.11774 (7)	0.16183 (3)	0.42340 (7)		1.20 (2)
W(3)	0.33391 (8)	0.08406 (3)	0.24883 (8)		1.56 (2)
W(4)	0.47113 (7)	0.16078 (3)	0.54490 (8)		1.50 (2)
As	0.3482 (2)	0.2500	0.2213 (3)		1.29 (6)
As*	0.7428 (3)	0.2500	0.4716 (3)		2.64 (8)
K(1)	0.8387 (4)	0.0989 (2)	0.7121 (5)		2.8 (1)
K(2)	0.7567 (5)	0.1174 (2)	0.2539 (5)		3.1 (1)
K(3)	0.2466 (6)	0.0734 (2)	0.7907 (6)		4.4 (2)
K(4)	0.2537 (6)	0.2500	0.7705 (7)		2.6 (2)
Od(1)	−0.105 (1)	0.1181 (6)	0.011 (1)	2.4 (2)	
Oc(11)	−0.068 (2)	0.2500	0.017 (2)	2.1 (3)	
Oa(11)	0.184 (2)	0.2500	0.104 (2)	1.5 (3)	
Ob(13)	0.185 (1)	0.1147 (5)	0.106 (1)	1.0 (2)	
Od′(3)	0.469 (1)	0.1101 (6)	0.166 (1)	2.5 (2)	
Od(3)	0.325 (1)	0.0025 (5)	0.219 (1)	2.0 (2)	
Ob(12)	0.018 (1)	0.1788 (5)	0.252 (1)	1.6 (2)	
Oa(234)	0.318 (1)	0.1859 (5)	0.332 (1)	1.7 (2)	
Oc(23)	0.180 (1)	0.0819 (5)	0.368 (1)	1.6 (2)	
Oc(34)	0.457 (1)	0.0858 (5)	0.437 (1)	1.8 (2)	
Od′(4)	0.626 (1)	0.1849 (6)	0.451 (1)	2.3 (2)	
Ob(22)	0.129 (2)	0.2500	0.478 (2)	1.4 (3)	
Od(2)	−0.006 (1)	0.1352 (5)	0.514 (1)	1.8 (2)	
Oc(24)	0.290 (1)	0.1517 (5)	0.580 (1)	1.6 (2)	
Ob(44)	0.466 (2)	0.2500	0.584 (2)	1.6 (3)	
OAs*	0.799 (3)	0.2500	0.665 (4)	8.1 (8)	
Od(4)	0.569 (1)	0.1332 (6)	0.698 (1)	2.5 (2)	
Od′(1)	0.070 (1)	0.1714 (5)	−0.137 (1)	1.0 (2)	
Ow(1)	0.976 (1)	0.0076 (7)	0.204 (2)	3.7 (3)	
Ow(2)	0.717 (1)	0.0185 (6)	0.442 (2)	3.5 (3)	
Ow(3)	0.643 (2)	0.0278 (7)	0.050 (2)	4.3 (3)	
Ow(4)	0.439 (2)	0.1658 (8)	0.915 (2)	4.0 (4)	

[a] Esd's in parentheses refer to the last decimal place.

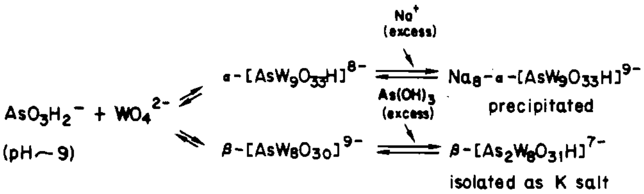
Table II. Selected Interatomic Distances (Å)

W(1)-Oa(11)	2.228 (10)	K(1)-Od(4)	2.702 (13)
W(2)-Oa(234)	2.361 (11)	K(1)-Od(2)	2.800 (12)
W(3)-Oa(234)	2.301 (11)	K(1)-Od(3)	2.820 (12)
W(4)-Oa(234)	2.370 (11)	K(1)-Od′(1)	2.873 (12)
W(1)-Ob(12)	2.208 (11)	K(1)-Ow(1)	2.887 (16)
W(2)-Ob(12)	1.801 (11)	K(1)-Od(1)	2.896 (14)
W(1)-Ob(13)	1.910 (11)	K(1)-Ow(2)	3.157 (15)
W(3)-Ob(13)	1.913 (12)	K(2)-Od(1)	2.963 (13)
W(2)-Ob(22)	1.922 (4)	K(2)-Od′(3)	2.769 (13)
W(4)-Ob(44)	1.914 (3)	K(2)-Ob(12)	2.859 (12)
W(1)-Oc(11)	1.925 (8)	K(2)-Od′(4)	2.893 (13)
W(2)-Oc(23)	1.902 (11)	K(2)-Od(2)	3.096 (12)
W(3)-Oc(23)	2.075 (11)	K(2)-Ow(2)	2.852 (15)
W(2)-Oc(24)	2.044 (11)	K(2)-Ow(3)	2.803 (16)
W(4)-Oc(24)	1.875 (11)	K(3)-Oc(24)	2.737 (12)
W(3)-Oc(34)	1.982 (11)	K(3)-Od′(1)	2.863 (12)
W(4)-Oc(34)	1.885 (11)	K(3)-Ow(4)	2.801 (17)
W(1)-Od(1)	1.734 (12)	K(3)-Ow(1)	2.763 (16)
W(2)-Od(2)	1.727 (11)	K(3)-Ow(2)	3.059 (15)
W(3)-Od(3)	1.734 (11)	K(3)-Ow(3)	2.724 (12)
W(4)-Od(4)	1.705 (12)	K(4)-Ob(22)	2.879 (17)
W(1)-Od′(1)	1.740 (12)	K(4)-Oc(24)	2.852 (12)
W(3)-Od′(3)	1.766 (12)	K(4)-Ob(44)	3.024 (17)
W(4)-Od′(4)	1.982 (12)	K(4)-Od′(1)	2.723 (12)
As-Oa(11)	1.772 (16)	K(4)-Ow(4)	2.713 (17)
As-Oa(234)	1.787 (11)		
As*-Od′(4)	1.766 (12)		
As*-OAs*	1.861 (35)		

One arsenic atom is the central atom of the heteropolyanion and is bonded to three Oa oxygens, the second one is linked to two Od′ atoms, the tricoordination of As is completed by an O-H group.

As in all heteropolyanions, the WO_6 octahedra are distorted (Table II). The more an oxygen atom is shared, the longer is the related W-O distance. For example, Oa_{11}-W_1 is shorter than Oa_{234}-W_2 (or 3 or 4), which are in the range of those found in other tungstic structures.[4,7,11] W-Od distances do not depend on the kind of Od atom except in the case of Od'_4 linked to As*. In this case, the length (1.98 Å) is similar to the W-Oc or Ob length

Scheme I



(Table II). The As heteroatom occupies the vertex of a regular pyramid, the base of which is formed by three Oa atoms. The distance of the As* atom to OAs* is slightly longer. The lone pairs of both As atoms have the same direction as it is shown by the parallelism of the planes defined by the Oa atoms on the one hand and by Od'_4 and OAs* on the other hand.

A network of K^+ cations links the polyanions in the cell. K-O distances are reported Table II. They are in the range 2.7-3.1 Å. K_1 bound four anions and other K atoms only two. Water molecules set bridges between cations.

The various tungstoarsenate structures known up to now[7-10] always contained α-AsW_9O_{33} subunits. The 8-tungsto-2-arsenate is the first example of a β-type structure in this As^{III}-W family. This can be rationalized by reference to Lipscomb[16,17] who noted that no heteropoly- or isopolyanion structure contained MO_6 octahedra with more than two unshared oxygen atoms.

It can be assumed that in tungstate-arsenite mixtures involving many species in equilibrium, compounds that do not agree with Lipscomb's rule such as β-$[AsW_9O_{33}H]^{8-}$ or α-$[AsW_8O_{30}]^{9-}$ are in small amount and, conversely, corresponding geometric isomers α-$[AsW_9O_{33}H]^{8-}$ or β-$[AsW_8O_{30}]^{9-}$ are in larger amount. Species isolated from tungstate-arsenite solutions with a W/As ratio of 9 at pH ∼9 support this assumption: (1) Addition of an alkaline salt (i.e., NaCl) to such solutions precipitates the corresponding salt of α-$[AsW_9O_{33}H]^{8-}$. (2) Addition of arsenite favors β-

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$[AsW_8O_{30}As(OH)]^{7-}$. Polarography showed that it was the only one heteropolyanion in solution when W/As = 2[18] (Scheme I).

In conclusion, the structure of the title compound confirms the prominent role of As^{III} stereochemistry (pyramidal structure and lone pair) in the polycondensation of coordinated tungsten(VI) atoms in polyoxoanions. A type-B environment involving the three bonds of As(III) is always obtained. The stereochemistry and nature of possible α or β species in solution are consistent with Lipscomb's rule, and individual compounds can be isolated upon addition of suitable reagents.

Registry No. $K_7(AsW_8O_{30}AsOH)\cdot 12H_2O$, 95406-35-2; potassium arsenate(III), 95344-35-7; potassium tungstate, 37349-36-3.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic temperature factors of W, As, and K atoms (13 pages). Ordering information is given on any current masthead page.

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(18) The polarograms of $As_2W_8O_{31}H^{7-}$ and $AsW_9O_{33}H^{9-}$, recorded in 1 M sodium acetate/1 M acetic acid buffer, have well-defined first waves of two electrons. Half-wave potentials vs. the saturated calomel electrode are, respectively, −0.67 and −0.78 V.

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Synthesis and Characterization of Osmium Porphyrins

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During the course of our work on osmium-substituted myoglobin (osmoglobin),[2] we found that we could use $Os_3(CO)_{12}$ instead of the hazardous OsO_4[3] as a starting material for the preparation of osmium porphyrins. Here, we illustrate this method by reporting the synthesis of [Os(MIX-DME)(CO)L], where MIX-DME is mesoporphyrin IX dimethyl ester and L is either ethanol or pyridine.[4] Good yields of pure $[Os(MIX\text{-}DME)O_2]$ may be obtained from the oxidation of [Os(MIX-DME)(CO)L] complexes by *tert*-butyl hydroperoxide (TBHP). TBHP also has been used successfully as an oxidant for ruthenium porphyrins.[5]

Experimental Section

Materials. $Os_3(CO)_{12}$ and octaethylporphyrin (OEP) were purchased from Strem Co., Ltd., whereas mesoporphyrin IX dimethyl ester (MIX-DME) was obtained from Sigma Co., Ltd. All solvents used were of analytical grade. *tert*-Butyl hydroperoxide (TBHP) was supplied by Aldrich. Triphenylphosphine (Merck) was twice recrystallized from absolute ethanol before use.

Procedure for the Synthesis of [OsP(CO)L] (PH_2 = OEP, MIX-DME; L = EtOH, py). A mixture of $Os_3(CO)_{12}$ (0.1 g) and PH_2 (0.1 g) in diethylene glycol monomethyl ether (~80 mL) was refluxed under an argon atmosphere with vigorous stirring for about 8 h. The solution was cooled to room temperature. Upon addition of a saturated aqueous solution of NaCl, crude [OsP(CO)] precipitated. The product was filtered, air-dried, and then purified by chromatography using either a silica gel or an alumina column and a CH_2Cl_2/acetone mixture (3:1) as the eluent. Pure [OsP(CO)] was obtained by further chromatography using CH_2Cl_2 as the eluent (overall yeild ~70%). Dissolution of [OsP(CO)] in a donor solvent L followed by the addition of excess *n*-hexane led to the precipitation of [OsP(CO)L] in nearly quantitative yield.

[Os(MIX-DME)(CO)EtOH] was prepared as a brick red solid from $Os_3(CO)_{12}$ (0.1 g), MIX-DME (0.1 g), and EtOH (1 mL). Anal. Calcd for $OsC_{39}H_{46}N_4O_6$: C, 54.9; H, 5.16; N, 6.56. Found: C, 55.0; H, 5.20; N, 6.40. ^1H NMR: Table I. IR (Nujol mull): $\nu(C{\equiv}O)$ 1902 cm^{-1}.

[Os(MIX-DME)(CO)py] was prepared as a brick red solid from $Os_3(CO)_{12}$ (0.1 g), MIX-DME (0.1 g), and py (0.5 mL). Anal. Calcd for $OsC_{42}H_{45}N_5O_5$: C, 56.7; N, 5.10; N, 7.87. Found: C, 56.6; H, 5.20; N, 7.40. ^1H NMR: Table I. IR (Nujol mull): $\nu(C{\equiv}O)$ 1902 cm^{-1}. UV-Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 392 (5.2), 508 (4.0), 538 (4.2).

[Os(OEP)(CO)L] (L = EtOH, py). These complexes were characterized as described previously.[3]

Procedure for the Synthesis of *trans*-[$OsPO_2$]. [OsP(CO)] (0.1 g) was stirred with TBHP (2 mL) in CH_2Cl_2/EtOH solution (1:1, ~50 mL) at room temperature for 1–2 h. After evaporation of ca. two-thirds of the solvent, a violet-black crystalline solid gradually deposited. This was then purified by chromatography using either a silica gel or an alumina column and with a CH_2Cl_2/acetone mixture (10:1) as the eluent. Overall yield varied between 60% and 80%.

[Os(MIX-DME)O_2] was prepared as a black solid from [Os(MIX-DME)(CO)] (0.1 g) and TBHP (1 mL). Anal. Calcd for $OsC_{36}H_{40}N_4O_6$: C, 53.2; H, 4.67; N, 6.9. Found: C, 53.5; H, 4.38; N, 6.60. UV-Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 376 (4.87), 431(sh) (4.04), 577 (3.76). IR (Nujol mull): $\nu_{as}(OsO_2)$ 839 cm^{-1}.

[Os(OEP)O_2]. This complex was characterized as described previously.[6]

[Os(OEP)(OEt)$_2$]. [Os(OEP)O_2] (50 mg) and PPh_3 (50 mg) were stirred in a CH_2Cl_2/EtOH mixture (1:1) at room temperature. The course of the reaction was monitored by following the UV-vis spectral changes. When the 577-nm band had completely disappeared, the solution was evaporated to dryness. IR analysis of the solid product showed that Ph_3PO formed (peaks at 712 and 1175 cm^{-1}). The osmium product was purified by chromatography using either a silica gel or an alumina column and CH_2Cl_2 as the eluent. An orange-red solid separated that was identified as *trans*-[Os(OEP)(OEt)$_2$].[7] UV-Vis spectrum in CH_2Cl_2, λ_{max}/nm (log ϵ): 370 (4.72), 495 (3.74), 527 (3.70).

Physical Measurements. Elemental analyses were performed by the Australian National Laboratory. IR spectra of Nujol mulls were measured on a Perkin-Elmer 577 spectrometer (4000–200 cm^{-1}). Electronic absorption spectra of freshly prepared solutions were measured with a Beckman Acta CIII spectrophotometer. ^1H NMR spectra were measured with a JEOL FX90Q Fourier transform NMR spectrometer, using tetramethylsilane as an internal reference.

Results and Discussion

The preparative method developed with $Os_3(CO)_{12}$ as a starting material is applicable to many different porphyrins, including protoporphyrin IX dimethyl ester and substituted *meso*-tetraphenylporphyrins.[8] Similar metal insertions also have been observed in ethoxyethanol (boiling point ~135 °C), although longer reaction times (~24 h) are usually required. The relatively low value of the CO stretching frequency in [Os(MIX-DME)(CO)py] (1902 cm^{-1}) indicates that $d\pi\ (M^{II}) \rightarrow \pi^*$ (CO) back-bonding is more extensive than in [Ru(MIX-DME)(CO)Im] ($\nu(C{\equiv}O)$ 1940 cm^{-1}).[9] Additional evidence for the strong $d\pi$ donor character of Os^{II} comes from electronic absorption spectral data: The α and β bands of [Os(MIX-DME)(CO)py] (538 and 508 nm) fall at shorter wavelengths than those of a Ru^{II} analogue (554 and 522 nm),[9] thereby indicating that $d\pi\ (M^{II}) \rightarrow \pi^*$ (porphyrin) interactions are greater in the case of the 5d central atom. These $d\pi \rightarrow \pi^*$ (ligand) effects on the electronic and vibrational spectra of ruthenium and osmium porphyrins are reasonably well understood.[10]

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