A Large, Novel Polyoxotungstate: $[As^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$**

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Polyoxoanions comprise a unique family of metal–oxygen cluster species considering the variety of structures and interesting properties in catalysis, materials science, and medicine.[1–4] Polyoxometalates were first reported more than 100 years ago, but the structures of many species were only discovered recently by using single-crystal X-ray diffraction. The availability of this analytical tool has led to the structural characterization of a large number of novel polyoxoanions with different shapes and sizes.

It is apparent that during the last couple of years not only the number but also the size of many novel structures has been increasing dramatically. Until recently the isopolyanion $[Mo_{36}O_{112}(H_2O)_{18}]^{8-}$[5] as well as the heteropolyanions $[As_4W_{40}O_{140}]^{28-}$[6] and $[H_7P_8W_{48}O_{148}]^{33-}$[7] were examples of the largest polyoxometalates reported. However, very recently Müller et al. reported a class of gigantic polyoxomolybdate spheres, baskets, and rings containing up to 248 molybdenum atoms,[8] and Pope et al. reported on a polyoxotungstate with 148 tungsten atoms, $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$.[9]

At this point it is important to realize that the mechanism of formation of polyoxometalates is still not well understood and commonly described as self-assembly. Therefore, it is usually not possible to design a multistep sequence for the synthesis of a novel polyoxometalate. As a result, the design of novel polyoxometalates remains a challenge.

Herein we report the synthesis and structural characterization of the largest tungstoarsenate(III) known to date, $[As^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$ (**1**). This novel polyoxoanion is isolated in an acidic medium (pH 2) with good yield (71%). We have also synthesized the antimony(III) analogue, $[Sb^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$ (**2**), in very good yield (90%). This compound was characterized by FTIR spectroscopy and elemental analysis.

The compact structure of **1** with idealized C_{2h} symmetry (Figures 1 and 2) consists of four inner (β-AsW_9O_{33}) and two outer (α-AsW_9O_{33}) fragments, which are linked together by a total of eleven corner-sharing WO_6 octahedra, so that **1** may be formulated as $[(\beta\text{-}AsW_9O_{33})_4(\alpha\text{-}AsW_9O_{33})_2(WO_2)_4(WO(H_2O))_6WO_5(H_2O)]^{26-}$. The arrangement of the six (AsW_9O_{33}) subunits resembles a chair conformation of cyclohexane.

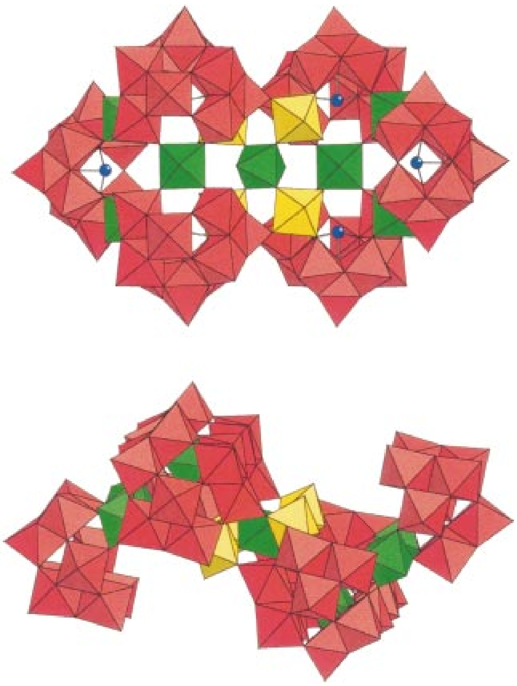

Figure 1. Polyhedral representation of $[As^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$ (**1**); top view (upper) and side view (lower). Arsenic atoms are blue and all WO_6 octahedra composing (AsW_9O_{33}) fragments are red. The remaining WO_6 octahedra are either *cis*-$O_2W(\mu_2\text{-}O)_4$ (yellow) or *trans*-$O(H_2O)W(\mu_2\text{-}O)_4$ (green).

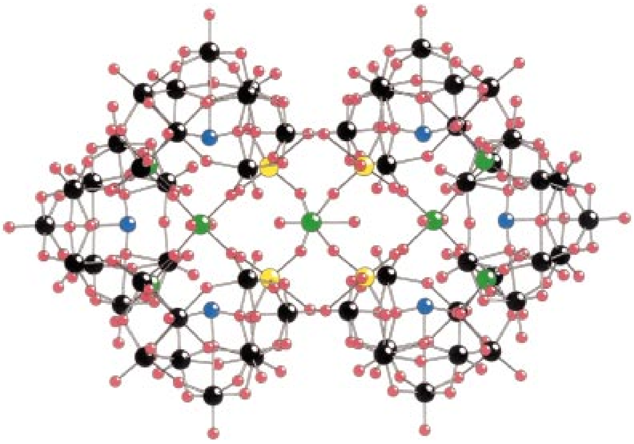

Figure 2. Ball-and-stick representation of $[As^{III}_6W_{65}O_{217}(H_2O)_7]^{26-}$ (**1**). The color code is as follows: O: red, As: blue, W atoms of (AsW_9O_{33}) fragments: black, remaining W atoms of *cis*-$O_2W(\mu_2\text{-}O)_4$ or *trans*-$O(H_2O)W(\mu_2\text{-}O)_4$: yellow or green, respectively..

There are also alternative possibilities of rationalizing the structure of **1**. The dimeric nature of **1** could be emphasized by the formula $[WO(H_2O)\{As_3W_{32}O_{108}(H_2O)_3\}_2]^{26-}$. On the other hand, it should be remembered that **1** was synthesized from $[As_2W_{19}O_{67}(H_2O)]^{14-}$ and such fragments can easily be identified in the structure of **1** (Figures 2 and 3). However, it must be realized that the dilacunary polyanion $[As_2W_{19}O_{67}(H_2O)]^{14-}$ consists of two (α-AsW_9O_{33}) subunits linked by a $WO(H_2O)$ center. This is best represented by the formula $[WO(H_2O)(\alpha\text{-}AsW_9O_{33})_2]^{14-}$ (Figure 4). In the

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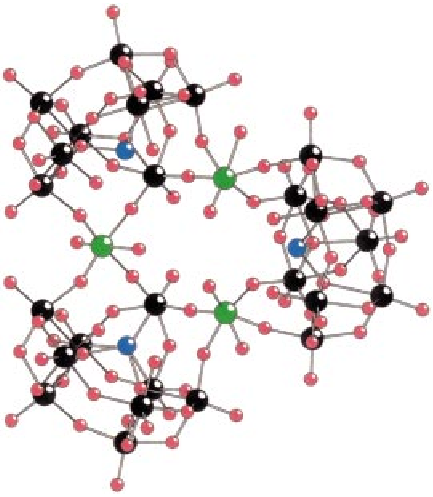

Figure 3. Ball-and-stick representation showing a trimeric cyclic subunit of **1**. The $(\alpha\text{-AsW}_9\text{O}_{33})$ unit (right) and the two $(\beta\text{-AsW}_9\text{O}_{33})$ units (left) are linked to each other by three *trans*-$\text{O(H}_2\text{O)W}(\mu_2\text{-O})_4$ groups. The color code is the same as in Figure 2.

structure of **1**, two types of $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ fragments can be identified, $[\text{WO(H}_2\text{O)}(\alpha\text{-AsW}_9\text{O}_{33})(\beta\text{-AsW}_9\text{O}_{33})]^{14-}$ and $[\text{WO(H}_2\text{O)}(\beta\text{-AsW}_9\text{O}_{33})_2]^{14-}$. This means that the mechanism of formation of **1** can be described as a condensation of $[\text{WO(H}_2\text{O)}(\alpha\text{-AsW}_9\text{O}_{33})_2]^{14-}$ polyanions accompanied by 60° rotation of groups of edge-shared WO_6 octahedra. It might also be useful to represent the synthesis of **1** by Equation (1).

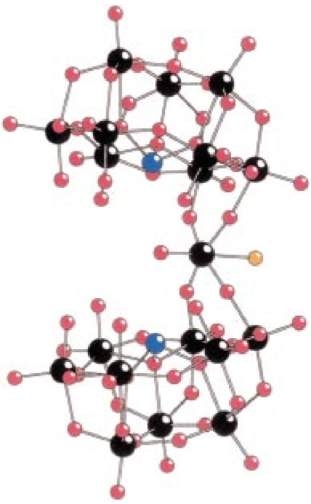

Figure 4. Ball-and-stick representation of $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ as a result of a single crystal X-ray analysis for $\text{K}_{6.25}\text{NaNi}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 31.5\,\text{H}_2\text{O}$. W: black, As: blue, O: red. The single water molecule (O: orange) is bound to the tungsten atom bridging the two $(\alpha\text{-AsW}_9\text{O}_{33})$ fragments.

$$3\,[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-} + 8\,\text{WO}_4^{2-} + 32\,\text{H}^+ \longrightarrow [\text{As}_6\text{W}_{65}\text{O}_{216}(\text{OH})_2(\text{H}_2\text{O})_6]^{26-} + 12\,\text{H}_2\text{O} \quad (1)$$

This shows clearly that some extra tungsten atoms are needed, which must become available during the course of the reaction, most likely as a result of $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$ rearrangement. This polyanion is synthesized at pH 6–6.5, and it is known that upon acidification the two lacunary sites are consecutively filled by tungsten atoms. The monolacunary polyanion $[\text{As}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})]^{10-}$ is stable at pH 2–4 and in very acidic medium (around pH 0) the polyanion $[\text{As}_2\text{W}_{21}\text{O}_{69}(\text{H}_2\text{O})]^{6-}$ is dominant. Apparently neither of the two polyanions is stable between pH 0–2. Interestingly we discovered that **1** can only be synthesized in the pH range 1.5–2.0.

The structure of **1** may be considered as the larger relative of the crown polyanion $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ reported by Hervé et al. some time ago.[6] This species is composed of four $(\alpha\text{-AsW}_9\text{O}_{33})$ fragments linked by four WO_6 octahedra. However, the synthesis of $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ involved stoichiometric interaction of tungstate and metaarsenite at pH 4. Another difference is that **1**, as opposed to $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$, is a rather closed structure. Furthermore for $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ there is only one type of tungsten atom linking the $(\alpha\text{-AsW}_9\text{O}_{33})$ units, *cis*-$\text{O}_2\text{W}(\mu_2\text{-O})_4$, whereas in **1** there are two types, four *cis*-$\text{O}_2\text{W}(\mu_2\text{-O})_4$ and seven *trans*-$\text{O(H}_2\text{O)W}(\mu_2\text{-O})_4$ (see Figure 1).

Pope et al. recently reported the very large polyoxotungstate $[\text{As}_{12}\text{Ce}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ with a compact structure based on twelve $[\text{AsW}_9\text{O}_{33}]^{9-}$ and four $[\text{W}_5\text{O}_{18}]^{6-}$ units.[9] These are held together by an extra 30 WO_6 octahedra and 16 Ce^{3+} (or La^{3+}) ions. It is amazing that just like $[\text{As}_4\text{W}_{40}\text{O}_{140}]^{28-}$ this compound is synthesized from the composing elements rather than from a preformed polyoxoanion.

The protonation sites of **1** were identified by bond valence sum calculations.[10] As a result, seven of the 65 tungsten atoms in **1** are bound to a terminal water molecule, which is *trans* to a terminal oxo group (green octahedra in Figure 1). The central W atom (W33) belongs to this group, because crystallographic refinement indicated that it is disordered over two symmetry-related positions slightly off the crystallographic inversion center. Therefore the coordination of W33 is better described as *trans*-$\text{O(H}_2\text{O)W}(\mu_2\text{-O})_4$ instead of *trans*-$(\text{HO})_2\text{W}(\mu_2\text{-O})_4$. The result of an elemental analysis indicated that the remaining 26 negative charges of **1** are balanced by potassium cations. However, single crystal X-ray diffraction allowed identification of only half of the potassium ions, probably as a result of disorder. Four of these cations (K1, K1′, K4, K4′) are located inside the two pockets of **1** apparently stabilizing the chair structure of the polyanion. The other nine potassium ions occupy external positions and they are bound to oxo groups of neighboring polyoxoanions as well as to terminal water molecules.

Since **1** is diamagnetic, we decided to study its solution properties by ^{183}W NMR. Solid LiClO_4 was added to an aqueous solution of the potassium salt of **1** in order to increase its solubility. If the solid-state structure of **1** is retained in solution, 18 peaks with intensity ratios 4:4:4:4:4:4:4:4:4:4:4:4:4:4:4:2:2:1 are expected. The ^{183}W NMR spectrum (12.5 MHz, Bruker AM-300WB spectrometer) resulted in the expected number of peaks between $\delta = -80$ and -230. However, the spectrum is quite congested and peak overlap does not allow a more detailed interpretation. Interestingly Pope et al. encountered the same problem for $[\text{As}_{12}\text{La}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$ with at least 15 of the 21 expected ^{183}W NMR signals in a very similar chemical shift range between $\delta = -60$ and -260.[9]

A detailed investigation of the chemical and physical properties of **1** and **2** is currently underway.

Experimental Section

The potassium salt of **1** was synthesized by using $K_{14}[As_2W_{19}O_{67}(H_2O)]$ as a precursor. The existence of the dilacunary polyanion $[As_2W_{19}O_{67}]^{14-}$ was proposed by Tourné et al. many years ago, but the synthetic conditions were only qualitatively described and no structural characterization by single-crystal X-ray diffraction has been reported.[11] We synthesized $K_{14}[As_2W_{19}O_{67}(H_2O)]$ by addition of As_2O_3 (0.89 g, 4.5 mmol), $Na_2WO_4 \cdot 2H_2O$ (18.8 g, 57 mmol), and KCl (0.67 g, 9.0 mmol) to 50 mL H_2O at 80 °C with stirring. After dissolution the pH was adjusted to 6.3 by adding 12 M HCl dropwise. The solution was kept at 80 °C for 10 min and then filtered. Finally 15 g KCl was added and the solution stirred for 15 minutes. The white precipitate formed was isolated by filtration and dried at 80 °C resulting in 15.4 g product (yield 95 %). Purity of this material was verified by FTIR spectroscopy. IR (KBr disk): $\tilde{\nu} = 941, 892, 803, 742, 629, 504, 462, 442\ cm^{-1}$. We were also able to crystallize $[As_2W_{19}O_{67}(H_2O)]^{14-}$ from a sodium acetate buffer (0.5 M, pH 5.5) as a mixed potassium-sodium-nickel salt, $K_{6.25}NaNi[As_2W_{19}O_{67}(H_2O)] \cdot 31.5H_2O$. Single-crystal X-ray diffraction showed the expected dilacunary polyanion (see Figure 4).[12] It becomes apparent that in the solid state (and most likely also in solution) the structure is stabilized by potassium ions. X-ray analysis suggested that a potassium ion was disordered over the two lacunary sites (occupancy 0.5 for each). Probably for steric reasons, each polyanion can accommodate only one potassium ion. The nickel ion was disordered over three positions (occupancy 0.33 for each) external from the lacunary sites.

The synthesis of the title anion **1** was accomplished by dissolving 3.0 g (0.57 mmol) of $K_{14}[As_2W_{19}O_{67}H_2O]$ (synthesized as described above) in 40 mL H_2O. The pH was adjusted to 1.9 by addition of 4 M HCl, then the solution was heated and boiled for 15 min. The hot solution was filtered and allowed to stand in a closed container at room temperature. At this point the pH was 2.1. The following day colorless crystals started to form, and after 2 weeks 1.8 g (yield 71 %) of crystalline product was isolated. The synthetic procedure for **1** is very similar to that of Hervé et al. for $K_{10}[As_2W_{20}O_{68}(H_2O)]$ and the only, but important, difference is the pH after acidification. If the pH is less than 1.5 before heating, then $[As_2W_{20}O_{68}(H_2O)]^{10-}$ is formed; if the pH is between 1.5–2.0 then **1** is formed. $K_{26}[As_6W_{65}O_{217}(H_2O)_7] \cdot 15H_2O$: elemental analysis (%): calcd (found): K 5.9 (6.7), As 2.6 (2.8), W 69.1 (69.0); IR (KBr disk): $\tilde{\nu} = 969, 914, 887, 824, 769, 714, 670, 630, 485, 442\ cm^{-1}$. Crystal structure analysis for $K_{26}[As_6W_{65}O_{217}(H_2O)_7] \cdot 76H_2O$: crystal dimensions $0.28 \times 0.22 \times 0.22$ mm, mounted on a glass fiber; $T = 171(2)$ K; Siemens SMART CCD single-crystal diffractometer equipped with a Mo anode and a graphite monochromator ($\lambda = 0.71073$ Å). An approximate sphere of data was collected out to a $2\theta_{max}$ value of 56.9°; ω scans; Lorentzian and polarization correction; semi-empirical (SADABS) absorption correction ($\mu = 27.183\ mm^{-1}$; min/max transmission 0.0138/0.0480); total reflections collected: 58950; independent reflections: 32038; $R(int) = 0.091$; $R(sig) = 0.129$. Space group $P\bar{1}$; $a = 18.272(3)$, $b = 19.141(4)$, $c = 24.156(5)$ Å, $\alpha = 100.034(3)$, $\beta = 106.969(3)$, $\gamma = 111.885(3)°$, $V = 7107(2)$ Å^3, $Z = 1$; $\rho_{calcd} = 4.180\ Mg\,m^{-3}$; structure solution by direct methods, refinement against $|F^2|$ over all reflections, $R_1 = 0.076$ for 20200 independent reflections with $I > 2\sigma(I)$ and 988 parameters, $Rw_2 = 0.184$ for all reflections; highest residual electron density 6.74 e Å^{-3}. Software used: Siemens SMART, SAINT, SHELXTL.[13] No hydrogen atoms were included.[12b]

The synthesis of **2** was accomplished by dissolving $Na_9[\alpha\text{-}SbW_9O_{33}] \cdot 19.5H_2O$[14] (6.5 g, 2.3 mmol), $Na_2WO_4 \cdot 2H_2O$ (0.76 g, 2.3 mmol), and KCl (1.5 g, 20.7 mmol) in 40 mL H_2O. The pH was adjusted to 1.0 by addition of 4 M HCl and the solution was boiled for 15 min. The hot solution was then filtered and 3.0 g CsCl were added. After stirring for 15 min the light-yellow precipitate was isolated by filtration and air dried resulting in 6.5 g (yield 90 %) of product. $Cs_{26}[Sb_6W_{65}O_{217}(H_2O)_7] \cdot 50H_2O$: elemental analysis (%): calcd (found): Cs 16.7 (17.0), Sb 3.5 (3.9), W 57.9 (56.0); IR (KBr disk): $\tilde{\nu} = 965, 894, 814, 746, 716, 677, 628, 533, 437\ cm^{-1}$.

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[1] "Polyoxometalates": *Chem. Rev.* **1998**, *98*, 1–390.

[2] *Polyoxometalates: From Platonic Solids to Anti Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**.

[3] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56–70; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48.

[4] M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.

[5] B. Krebs, I. Paulat-Böschen, *Acta Crystallogr. Sect. B* **1982**, *38*, 1710–1718.

[6] M. Leyrie, G. Hervé, *Nouv. J. Chim.* **1978**, *2*, 233.

[7] R. Contant, A. Tézé, *Inorg. Chem.* **1985**, *24*, 4610–4614; R. Contant, *Inorg. Synth.* **1990**, *27*, 104–111.

[8] A. Müller, S. Q. N. Shah, H. Bögge, M. Schmidtmann, *Nature* **1999**, *397*, 48–50, and references therein.

[9] K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem.* **1997**, *109*, 1513–1516; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445–1448.

[10] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *41*, 244–247.

[11] a) C. Tourné, A. Revel, G. Tourné, M. Vendrell, *C. R. Acad. Sci. Ser. III* **1973**, *277*, 643–645; b) C. Tourné, G. Tourné, *C. R. Acad. Sci. Ser. III* **1975**, *281*, 933–936.

[12] Crystal structure analysis for $K_{6.25}NaNi[As_2W_{19}O_{67}(H_2O)] \cdot 31.5H_2O$: crystal dimensions $0.24 \times 0.16 \times 0.06$ mm, mounted on a glass fiber; $T = 167(2)$ K; Siemens SMART CCD single-crystal diffractometer equipped with a Mo anode and graphite monochromator ($\lambda = 0.71073$ Å). An approximate sphere of data was collected out to a $2\theta_{max}$ value of 56.6°; ω scans; Lorentzian and polarization correction; semi-empirical (SADABS) absorption correction ($\mu = 25.212\ mm^{-1}$; min/max transmission 0.147910/0.355847); total reflections collected: 52531; independent reflections: 21837; $R(int) = 0.079$; $R(sig) = 0.096$. Space group $P\bar{1}$; $a = 11.7468(7)$, $b = 17.4175(11)$, $c = 24.1241(14)$ Å, $\alpha = 71.2420(10)$, $\beta = 77.1150(10)$, $\gamma = 85.7750(10)°$, $V = 4555.9(5)$ Å^3, $Z = 2$; $\rho_{calcd} = 4.054\ Mg\,m^{-3}$; structure solution by direct methods, refinement against $|F^2|$ over all reflections, $R_1 = 0.059$ for 16121 independent reflections with $I > 2\sigma(I)$ and 748 parameters, $Rw_2 = 0.136$ for all reflections; highest residual electron density 4.73 e Å^{-3}. Software used: Siemens SMART, SAINT, SHELXTL.[13] No hydrogen atoms were included. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-411888 ($K_{26}[As_6W_{65}O_{217}(H_2O)_7] \cdot 76H_2O$) and -411889 ($K_{6.25}NaNi[As_2W_{19}O_{67}(H_2O)] \cdot 31.5H_2O$).

[13] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473; SHELXTL Structure Determination Software Programs, Siemens Analytical X-ray instruments, Madison, WI, **1990**; SAINT Users Manual, Version 4.050, Siemens Analytical X-ray instruments, Madison, WI, **1996**.

[14] M. Bösing, I. Loose, H. Pohlmann, B. Krebs, *Chem. Eur. J.* **1997**, *3*, 1232–1237.