Polyoxometalates

DOI: 10.1002/ange.200502441

Step-by-Step Assembly of Trivacant Tungstosilicates: Synthesis and Characterization of Tetrameric Anions

*Nathalie Leclerc-Laronze, Mohamed Haouas, Jérôme Marrot, Francis Taulelle, and Gilbert Hervé**

Rational synthesis of large inorganic clusters from simple mononuclear or dinuclear metal complexes remains a challenge. Species with complex structures have been often obtained by a "one-pot" synthesis,[1] but their mechanism of formation is generally not known even if building units can be identified. Another approach, step-by-step control of the aggregation process, proved successful with reduced molybdenum compounds.[2] High-valent metal–oxo complexes are also especially suitable for such a strategy as the formation of highly reactive polyvacant intermediates is now well understood. For example, polyvacant polyoxotungstates have strongly basic oxygen atoms, which react with aquo-, oxo-, or thiometal complexes to give larger oligomeric species with new catalytic and magnetic properties.[3] However, we have recently shown with the trivacant ion A-α-$[SiW_9O_{34}]^{10-}$ (abbreviated as $\{SiW_9\}$; the A isomer results from the association of one tritungsten and three bitungsten groups) that protonation of oxygen atoms leads, in the first step and only in the presence of potassium cations, to a dimer by self-association of the two monomeric units.[4] Strongly basic oxygen atoms remain in the dimeric anion α-$[\{K(H_2O)_2\}Si_2W_{18}O_{66}]^{15-}$ (abbreviated as $\{Si_2W_{18}\}$), which can bind several transition-metal cations.[5] This anion can thus be the starting species for the construction of larger architectures through condensation reactions.

We report herein the synthesis and structural characterization of two polyanions: α-$[\{[K(H_2O)_2](\mu\text{-}H_2O)[Li(H_2O)_2]\}_2Si_4W_{36}O_{126}(H_2O)_4]^{16-}$ (**1**) and α-$[\{[K(H_2O)][K(H_2O)_4]\}_2Si_8W_{36}O_{136}]^{22-}$ (**2**). Anion **1** results from the direct association of two dimeric species, $[KSi_2W_{18}O_{66}]^{15-}$ and anion **2** through a $\{Si_4O_4\}$ cyclic assembling group. These two polyoxotungstate units can be considered as tetramers with respect to the initial A-α-$[SiW_9O_{34}]^{10-}$ ion.

The potassium salt of **1** was obtained by the addition of hydrochloric acid to an aqueous suspension of K_{15}α-$[KSi_2W_{18}O_{66}]$. Dissolution first occurs then precipitation of the hydrated potassium salt $K_{18}[K_2H_8Si_4W_{36}O_{130}]$. Crystals

[*] Dr. N. Leclerc-Laronze, Dr. M. Haouas, Dr. J. Marrot, Dr. F. Taulelle, Prof. G. Hervé
Institut Lavoisier, IREM UMR 8637
Université de Versailles Saint-Quentin-en-Yvelines
45 avenue des Etats-Unis
78035 Versailles Cedex (France)
Fax: (+33) 1-39-25-43-81
E-mail: herve@chimie.uvsq.fr

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

suitable for X-ray diffraction studies were obtained from a solution of this crude product in 2 M LiCl.[6] Crystal-structure analysis shows that anion **1** comprises the association of two dimeric subunits, $\{KLiSi_2W_{18}O_{64}(H_2O)_2\}$. The two $\{WO_6\}$ octahedra, which participate in the two W-O-W junctions, share a corner in each subunit (Figure 1). As for the parent

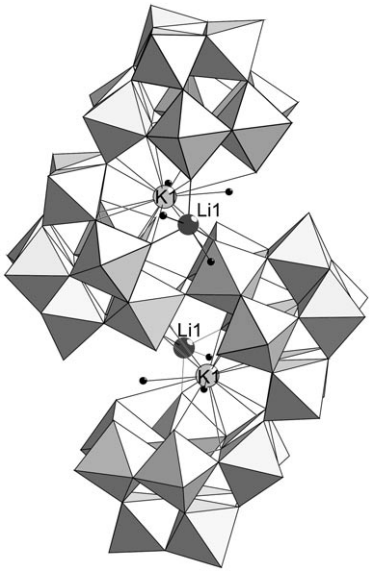

Figure 1. Combined polyhedra/ball-and-stick representation of **1**: $\{WO_6\}$ (gray polyhedra), potassium (gray ball), lithium (black ball), oxygen (small black ball).

dimeric anion,[4] there is a pocket in each subunit, which accommodates several cations: potassium, lithium, and protons. Two crystallographically non-equivalent subunits, **1a** and **1b**, have been found in the unit cell. In **1b**, there is no disorder on the positions of the potassium ion (K1), the lithium ion (Li1), and protons bound to the terminal oxygen atoms that surround the pocket. K1 and Li1 ions are arranged on each side of a $\{Si_2W_{18}\}$ subunit such that there is an inversion centre and the symmetry of the tetramer is *Ci*. In the external $\{SiW_9\}$ half of the $\{Si_2W_{18}\}$ subunit (Si3, W19–W27), three of the terminal oxygen atoms that surround the pocket are not bound to any metal cations. Bond lengths within the unit (W24–O90 = 2.12 Å, W25–O91 = 1.74 Å, W26–O97 = 2.05 Å; see Figure 2) show that the O atoms bound to W24 and W26 are protonated. Bond-valence calculations (see Supporting Information) reveal that O90 and O97 are biprotonated so that the pocket terminal ligands of W24 and W26 are water molecules.[7] Thus, there are eight protons bound to anion **1**, which is in good agreement with elemental analysis. The localization of the protons to only two of the three terminal oxygen atoms can be discussed by considering the lengths of the *trans*-W–O bonds between them (Figure 2). Starting from O85, which is bound to Li1 and K1 and must not be protonated (W23–O85 = 1.72 Å), the successive *trans*-W–O bonds are alternatively short (1.70 to 1.87 Å) and long (2.00 to 2.18 Å). This *trans*-influence explains why the last bond, W26–O97, is long as two protons are fixed on O97. The

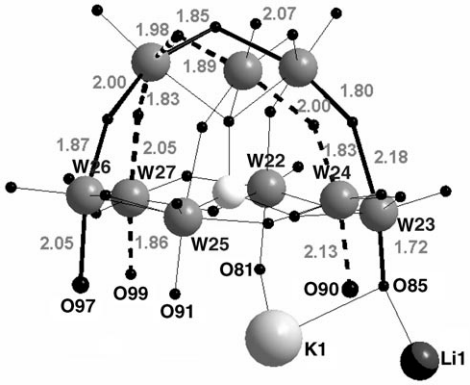

Figure 2. W–O bond lengths in the **1b** subunit; O90 and O97 correspond to water molecules.

neighboring terminal O91 atom associated with the same bitungsten group (with edge sharing tungsten octahedra) is not protonated, and in contrast to O90, which is associated with another bitungsten group, O91 is protonated. There are still alternate short (1.83 to 1.89 Å) and long (1.98 to 2.13 Å) *trans*-W–O bonds between the nonprotonated O99 and the protonated O90 atoms. Analogous coordination of water ligands in γ-$[SiW_{10}O_{34}(H_2O)_2]^{4-}$[8] to every second octahedron in the ring of six octahedra of the anion $[PMo_9O_{31}(H_2O)_3]^{3-}$ was reported previously.[9]

Inclusion of K1 in one side of the pocket results in a lateral distortion of the $\{Si_2W_{18}\}$ subunit. For example, the distance between O85 and O118 atoms is 3.23 Å on the side of K1 but the distance between the analogous O97 and O105 is 3.76 Å on the other side. For example, the O85-O118 distance is 3.23 Å on the side of K1, but the distance between the O97 and O105 is 3.76 Å on the other side. In the second $\{SiW_9\}$ half of the $\{Si_2W_{18}\}$ subunit, O118 and O105 correspond to O85 and O97, respectively. The O85–O118 distance is well adapted to the binding of a small cation such as Li^+, which thus bridges the two $\{SiW_9\}$ halves of $\{Si_2W_{18}\}$ on the same side as K1. This mode of binding of Li1 is analogous to the binding of one of the Co atoms in the $\{Co_2Si_2W_{18}\}$ complexes.[5] Spectrophotometric titration of **1** with Co^{2+} ions shows the formation of complexes with a Co/**1** ratio of about 2 and the corresponding complex has been synthesized. Unfortunately, the quality of the crystals was not sufficient to refine precisely the structure.

An interesting feature of the corner junction between the two $\{Si_2W_{18}\}$ subunits is the large value of the W30-O111-W31 angle (164°) in comparison with the corner junction between the two $\{SiW_9\}$ in $\{Si_2W_{18}\}$ (140°). Such a large angle is known in the association of the two $\{PW_9\}$ halves of the Dawson anion $[P_2W_{18}O_{62}]^{6-}$ and has important consequences in the localization of electrons in reduced derivatives.[10]

There is disorder in the positions of the potassium cation K2 and of the protonation sites for the independent unit **1a**; K2 occupies two positions, either in one side or the other of the pseudosymmetry plane comprising the Si1, Si2, W1, and W18 atoms (not shown). Due to the deformation of the anion resulting from the shift of the potassium atom out of this plane, all the atoms must be on two positions with occupation

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

factors of 1/2. In addition to K2, only the tungsten atoms W5 and W8 can be refined on two positions (A and B); these positions are about 0.48 Å apart for W5 and about 0.56 Å apart for W8. These findings are in agreement with the structure of the non-disordered anion, **1b**, wherein W23 and W26, which correspond to W5 and W8 in **1a**, are strongly displaced owing to the deformation described above.

Anion **1** is kinetically stable in acidic solutions as shown by polarography (see Supporting Information) and ^{183}W NMR spectroscopy. The NMR spectrum shows seven resonance signals between −126 and −171 ppm with relative intensities 2:5:2:2:4:2:1 (Figure 3; see the Supporting Information for complete NMR characteristics). Signals with intensities of 5 and 4 result from fortuitous degeneracy, and for the latter two very close signals ($\delta = -166.14$ and −166.22 ppm) of equal intensities can be seen with enhanced resolution (inset of Figure 3). A very sharp signal at $\delta = -103.8$ ppm, attributed to the Keggin anion α-$[SiW_{12}O_{40}]^{4-}$, corresponds to 10% of the W atoms present in solution after 5 h and 16% after 29 h and is due to a very slow evolution of the anion **1**.

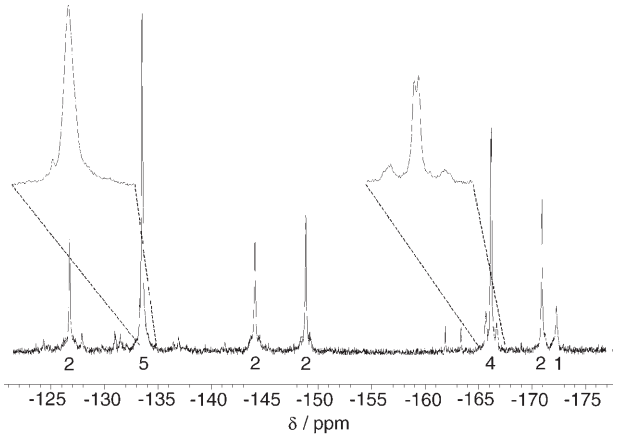

Figure 3. ^{183}W NMR spectrum of **1** (2×10^{-3} mol L^{-1} in H_2O/D_2O). The value underneath each signal indicates its relative intensity.

The apparent symmetry of **1** in solution is higher than that in the solid state as 18 resonance signals are expected from the structure of the non-disordered anion, **1b**. If we consider that the signal with a intensity of 5 is due to the superposition of three signals with intensities of 1, 2, and 2, then the ^{183}W NMR spectrum corresponds to ten non-equivalent tungsten atoms in **1**. Indeed, expansion of the spectrum around $\delta = 134$ ppm (see inset of Figure 3) shows a small signal for one W atom and a nonsymmetrical signal that could account for two equivalent plus another two equivalent W atoms. This observation can be explained by a rapid "jump" (compared with ^{183}W NMR time scale) of the potassium atom, K1, from left to right and right to left, that generates a pseudosymmetry plane. This dynamic behavior explains why only corner coupling (about 20 Hz) is observed but not the edge coupling (less than 10 Hz), thus preventing an assignment of the signals to tungsten atoms.

The potassium salt of **2** was obtained by adding hydrochloric acid to an aqueous suspension of the potassium salt $K_{15}\alpha$-$[KSi_2W_{18}O_{66}]$ in presence of potassium silicate. Anion **2** comprises the lateral association of two dimeric subunits, $\{KSi_2W_{18}O_{66}\}$, which are linked by a $\{Si_4O_4\}$ ring (Figure 4).[6] Since the cyclic species $[H_4Si_4O_{12}]^{4-}$ has been observed in aqueous silicate solution,[11] anion **2** can be considered as a condensation product of $[H_4Si_4O_{12}]^{4-}$ and two $\{Si_2W_{18}O_{66}\}$ units.

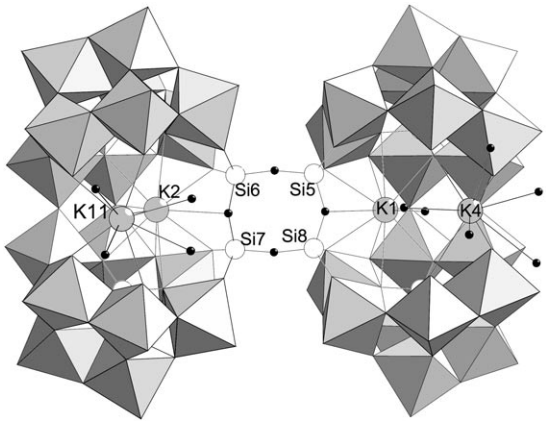

Figure 4. Combined polyhedra/ball-and-stick representation of **2:** labeling scheme as for Figure 1 except silicon (white ball).

The K1 potassium atom included in the pocket is on one side of the $\{Si_4O_4\}$ ring and another potassium atom, K4, is bound to the terminal oxygen atoms of the pocket on the other side. With M^{2+} transition-metal ions, anion **2** gives complexes in which M substitutes K4, but the quality of the crystals did not allow precise refinement of the structure.

In conclusion, condensation of $[SiW_9O_{34}]^{10-}$ anions in successive steps gives dimeric and tetrameric species. This strategy can be extended to other polyvacant polyoxotungsten structures. In **2**, the two subunits are linked by a tetraoxosilicate ring and we expect that new oligomeric anions can be obtained with other assembling groups such as polyphosphates and phosphonates.

Experimental Section

1: $K_{16}\alpha$-$[Si_2W_{18}O_{66}]\cdot25H_2O$[4] (12 g, 2.18 mmol) was suspended in water (65 mL). Dissolution of the solid occurred during addition of 1M HCl (12 mL; the pH was about 2.4). The solution was gently stirred and a white solid began to precipitate after 5 min. The reaction mixture was gently stirred for 12 h, then the solid was collected by filtration through a fine frit (yield: 5.4 g, 45%). This crude product was dissolved in 2M LiCl (5 g in 32 mL) and colorless crystals of **1** suitable for X-ray crystallography were obtained at room temperature within one day (yield: 30%). Elemental analysis (%) calcd for $K_{13}Li_3\alpha$-$[K_2Li_2H_8Si_4W_{36}O_{130}]\cdot74H_2O$: Li 0.32, K 5.44, W 61.44, Si 1.04; found: Li 0.39, K 5.40, W 61.18, Si 1.47. IR (KBr pellet): $\tilde{\nu} =$ 1004(w), 953(m), 877(s), 726(s), 637(m), 553(m), 528(sh), 374(w), 323(m) cm^{-1}.

Anion **1** can be characterized in solution by its polarogram. In formic acid/sodium formiate buffer (pH 3.4), it shows four successive

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

waves at −0.58, −0.69, −0.78, and about −0.95 V versus the saturated AgCl/Ag reference electrode (see Supporting Information).

The ^{183}W NMR spectrum of **1** was recorded with a solution obtained by cation exchange of the potassium salt through a H^+-saturated Prolabo IRN-77 resin. A time-averaged Fourier-transform ^{183}W NMR (20.8 MHz) spectrum was recorded on a Bruker Avance 500 spectrometer (26 °C, 10 mm sample tube; chemical shifts were referenced to the ^{183}W resonance of an external 2 M Na_2WO_4 solution in alkaline D_2O and to dodecatungstosilicic acid as secondary standard ($\delta = -103.8$ ppm)).

2: $K_{16}\alpha$-$[Si_2W_{18}O_{66}]\cdot 25\,H_2O$ (4.7 g, 0.86 mmol) was added to water (100 mL). A solution of K_2SiO_3 was prepared by dissolving SiO_2 (0.1 g, 1.7 mmol) with KOH (0.4 g, 7.1 mmol) in water (50 mL) at room temperature. The solution of K_2SiO_3 was slowly added to a suspension of the dimer and 1 M HCl (9.3 mL) was then added (the pH was about 3.5). The solution was filtered, and colorless crystals of **2** suitable for X-ray crystallography were obtained at room temperature within 10 days (yield: 20 %). Elemental analysis (%) calcd for $K_{22}[K_2Si_8W_{36}O_{136}]\cdot 54\,H_2O$: K 8.58, W 60.55, Si 2.06; found: K 8.14, W 60.41, Si 2.42. IR (KBr pellet): $\tilde{\nu} = 1173$(w), 1048(sh), 1002(m), 944(s), 885(s), 836(s), 738(s), 675(s), 646(s), 601(sh), 553(m), 524(sh), 474(m), 357(m), 324(m) cm^{-1}.

Received: July 13, 2005
Revised: September 13, 2005
Published online: November 22, 2005

Keywords: anions · cluster compounds · polyoxometalates · self-assembly · tungsten

[1] a) C. du Peloux, P. Mialane, A. Dolbecq, J. Marrot, F. Sécheresse, *Angew. Chem.* **2002**, *114*, 2932 – 2934; *Angew. Chem. Int. Ed.* **2002**, *41*, 2808 – 2810; b) A. Müller, A. M. Todea, J. van Slageren, M. Dressel, H. Bögge, M. Schmidtmann, M. Luban, L. Engelhardt, M. Rusu, *Angew. Chem.* **2005**, *117*, 3925 – 3929; *Angew. Chem. Int. Ed.* **2005**, *44*, 3857 – 3861.

[2] a) A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239 – 271; b) L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong, A. Müller, *Angew. Chem.* **2002**, *114*, 2929 – 2932; *Angew. Chem. Int. Ed.* **2002**, *41*, 2805 – 2808.

[3] Examples of recent work include: a) E. Cadot, M.-A. Pilette, J. Marrot, F. Sécheresse, *Angew. Chem.* **2003**, *115*, 2223 – 2226; *Angew. Chem. Int. Ed.* **2003**, *42*, 2173 – 2176; b) J. Marrot, M.-A. Pilette, F. Sécheresse, E. Cadot, *Inorg. Chem.* **2003**, *42*, 3609 – 3615; c) S. S. Mal, U. Kortz, *Angew. Chem.* **2005**, *117*, 3843 – 3846; *Angew. Chem. Int. Ed.* **2005**, *44*, 3777 – 3780; d) U. Kortz, F. Hussain, M. Reicke, *Angew. Chem.* **2005**, *117*, 3839 – 3843; *Angew. Chem. Int. Ed.* **2005**, *44*, 3773 – 3777.

[4] N. Laronze, J. Marrot, G. Hervé, *Chem. Commun.* **2003**, 2360 – 2361.

[5] a) N. Leclerc-Laronze, J. Marrot, G. Hervé, *Inorg. Chem.* **2005**, *44*, 1275 – 1281; b) L.-H. Bi, U. Kortz, *Inorg. Chem.* **2004**, *43*, 7961 – 7962.

[6] Crystals of **1** and **2** were mounted in a Lindemann tube. X-ray intensity data were collected on a Bruker X8-APEX2 CCD area-detector diffractometer by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Seven sets of narrow data frames (60 s per frame for **1** and 30 s for **2**) were collected at different values of θ (for 5 and 2 initial values of ϕ and ω, respectively for **1**; for 3 and 4 initial values of ϕ and ω, respectively for **2**) by using 0.5° increments of ϕ or ω. Crystal data and structure refinements: **1**: colorless crystal, $0.28 \times 0.26 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a =$ 18.7555(5), $b = 22.5419(5)$, $c = 23.7793(6)$ Å, $\alpha = 112.543(1)$, $\beta = 96.996(1)$, $\gamma = 104.136(1)$°, $V = 8739.8(4)$ Å^3, $Z = 2$, $\rho_{calcd} =$ 3.833 g cm^{-3}, $\mu(Mo_{K\alpha}) = 24.012$ mm^{-1}, $F(000) = 8782$, $T =$ 296(2) K. A total of 69677 independent reflections, 44418 observed with $I > 2\sigma(I)$, $R(\text{int}) = 0.057$, $R1 = 0.0492$, $wR2 =$ 0.1224, 2177 refined parameters. **2**: colorless crystal, $0.26 \times 0.14 \times 0.08$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a =$ 18.5206(7), $b = 20.9506(7)$, $c = 24.5669(9)$ Å, $\alpha = 91.972(2)$, $\beta =$ 104.569(2), $\gamma = 96.615(2)$°, $V = 9144.5(6)$ Å^3, $Z = 2$, $\rho_{calcd} =$ 3.836 g cm^{-3}, $\mu(Mo_{K\alpha}) = 23.141$ mm^{-1}, $F(000) = 9250$, $T =$ 296(2) K. A total of 100269 independent reflections, 48690 observed with $I > 2\sigma(I)$, $R(\text{int}) = 0.0841$, $R1 = 0.0547$, $wR2 =$ 0.1242, 2206 refined parameters. Data reduction was accomplished by using SAINT V7.03. The substantial redundancy in data allowed a semiempirical absorption correction (SADABS V2.10) to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data with SHELXTL V6.12. 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 number CSD 415593.

[7] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. A* **1991**, *47*, 192 – 197.

[8] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964 – 966.

[9] B. Hedman, *Acta Chem. Scand. Ser. A* **1978**, *32*, 439 – 446.

[10] a) G. M. Varga, E. Papaconstantinou, M. T. Pope, *Inorg. Chem.* **1970**, *9*, 662 – 667; b) X. Lopez, C. Bo, J. M. Poblet, *J. Am. Chem. Soc.* **2002**, *124*, 12574 – 12582.

[11] R. K. Harris, C. T. G. Knight, *J. Chem. Soc. Faraday Trans. 2* **1983**, *79*, 1539 – 1561.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim