# Inorganic Chemistry

# Cation-Directed Synthesis of Tungstosilicates. 2. Synthesis, Structure, and Characterization of the Open Wells–Dawson Anion α-[{K(H₂O)₂}(Si₂W₁₈O₆₆)]¹⁵⁻ and Its Transiton-Metal Derivatives [{M(H₂O)}(μ-H₂O)₂K(Si₂W₁₈O₆₆)]¹³⁻ and [{M(H₂O)}(μ-H₂O)₂K{M(H₂O)₄}(Si₂W₁₈O₆₆)]¹¹⁻

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The dimer α-[{K(H₂O)₂}(Si₂W₁₈O₆₆)]¹⁵⁻ (**1**), synthesized by reacting K₁₀A-α-[SiW₉O₃₄] with two equivalents of H⁺ in aqueous solution, has been characterized by polarography and ¹⁸³W NMR spectroscopy. Nine resonance signals have been observed with the tetrabutylammonium salt in dimethylformamide/acetonitrile solution, in agreement with the crystal structure of the anion which consists of two A-α-[SiW₉O₃₄]¹⁰⁻ associated through two W–O–W junctions. This anion derives from the Wells–Dawson structure by breaking four W–O–W junctions. The pocket between the two-half-anions can be filled by several metal cations. Reaction of transition-metal cations with **1** leads to the formation of [{M(H₂O)}(μ-H₂O)₂K(Si₂W₁₈O₆₆)]¹³⁻ (**1M**) (M = Co, Ni, Cu) and [{M(H₂O)}(μ-H₂O)₂K{M(H₂O)₄}(Si₂W₁₈O₆₆)]¹¹⁻ (**1M2**) (M = Mn, Co, Ni) complexes. One potassium is always included in the pocket with one or two transition metals. Because of the shift of the potassium cation to one side of the anion, the coordination modes of the two transition metals are different. Crystals of **1**, **1M**, and **1Co2** potassium salts are triclinic (*P*-1, *Z* = 2) and crystals of **1M2** potassium salts are monoclinic (*P*2(1)/*n*, *Z* = 4). The symmetry of **1M** and **1M2** complexes is *C*1 and they are present in the crystal as racemate inversion pairs.

## Introduction

The influence of the nature of the alkali cations on the formation, stability, and reactivity of molybdenum and tungsten polyoxometalates is now well documented.[1-4] In Part 1 of this study,[5] we have shown that the nature of the alkali cations influences the reactivity of the trivacant A-α-[SiW₉O₃₄]¹⁰⁻ species toward transition-metal cations. While the sodium salt leads at first to the metastable complex [{CoO(H₂O)}₃(SiW₉O₃₄)]¹⁰⁻, the potassium salt leads to the sandwich type complex [{Co(H₂O)}₃(SiW₉O₃₄)₂]¹⁴⁻. This behavior is analogous to that observed with phosphorus as the heteroatom. On the contrary, it has not been possible to obtain such sandwich-type complexes with tungsten groups although these compounds are well-known for phosphorus. In other respects, different multi-iron silicotungstates have been recently obtained from α-[SiW₉O₃₄]¹⁰⁻ depending on the nature of the precursor, sodium or potassium salt.[6]

The reactivity of polyoxotungstates is often under kinetic control, leading to a metastable species and, in a second step,

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(5) Laronze, N.; Marrot, J.; Hervé, G. *Inorg. Chem.* **2003**, *42*, 5857.
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to the thermodynamically stable species. In a preliminary study of the transformation of A-α-[SiW$_9$O$_{34}$]$^{10-}$ at pH of about 6 and to underline such a species, we observed that α-[SiW$_{11}$O$_{39}$]$^{8-}$ is obtained from the sodium salt (identified by its polarogram)[7] but that polarographic waves not attributable to any known species appeared before formation of α-[SiW$_{11}$O$_{39}$]$^{8-}$ if the potassium salt was used. In this paper, it will be shown that acidification of $K_{10}$A-α-[SiW$_9$O$_{34}$] in aqueous solution leads to the formation of a new tungstosilicate α-[Si$_2$W$_{18}$O$_{66}$]$^{16-}$ having an open structure related to the Wells−Dawson structure.[8] We investigated also the reaction of this anion with first-row transition-metal cations (Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$) and we determined the crystal structures of these complexes. A preliminary report of this work has been published.[9]

## Experimental Section

**Synthesis.** The number of water molecules of each complex was determined by thermogravimetry. Elemental analyses were performed by the Service Central d'Analyze of C.N.R.S. in Vernaison 69390, France.

**$K_{16}$α-[Si$_2$W$_{18}$O$_{66}$]·25H$_2$O (1-K).**[10] $K_{10}$A-α-[SiW$_9$O$_{34}$]·13H$_2$O (7.2 g, 2.5 mmol) was added in 100 mL of water. Dissolution of the solid occurred during addition of 1 M HCl (5 mL) (the pH was about 5.7) and reprecipitation occurred immediately. The precipitate was filtrated after gentle stirring for 30 min and was washed with a 2 M KCl solution. Yield: 4 g (55%). Anal. calcd (found) for K$_{16}$α-[Si$_2$W$_{18}$O$_{66}$]·25H$_2$O: K, 11.4 (10.0); W, 60.2 (58.9); Si, 1.02 (1.82). IR (KBr pellet, cm$^{-1}$): 1094 (w), 994 (m), 936 (m), 912 (sh), 865 (s), 823 (m), 730 (s), 663 (m), 552 (w), 523 (w), 372 (m), 350 (m), 321 (m).

Colorless crystals of K$_{16}$α-[Si$_2$W$_{18}$O$_{66}$]·25H$_2$O suitable for X-ray diffraction were obtained within 1 day by the same procedure but from solutions 10 times more dilute.

**(TBA)$_7$H$_8$α-[KSi$_2$W$_{18}$O$_{66}$]·7H$_2$O (1-TBA).** The potassium salt **1-K** (5 g) was added in 22 mL of water, 19 g of H$^+$ cationic resin (Prolabo IRN-77) was added, and 3.3 g of tetrabutylammonium bromide (TBABr) was immediately added to the clear solution after separation of the resin. A white precipitate appeared which was collected by filtration through a fine frit. Anal. calcd (found) for (TBA)$_7$H$_8$α-[KSi$_2$W$_{18}$O$_{66}$]·7H$_2$O: W, 53.21 (52.17); Si, 0.90 (1.28); C, 21.63 (20.61); N, 1.58 (1.54); H, 4.21 (4.13). IR (KBr pellet, cm$^{-1}$): 1484 (m), 1460 (m), 1381 (w), 1151 (w), 1107 (w), 1059 (w), 1008 (w), 961 (m), 912 (s), 825 (m), 780 (s), 685 (m), 565 (w), 459 (w), 374 (w), 335 (w).

**K$_{13}$[{M(H$_2$O)}($\mu$-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]·xH$_2$O (1M-K).** One molar HCl (8 mL) was added to K$_{10}$[SiW$_9$O$_{34}$]·13H$_2$O (11.5 g, 4 mmol) in suspension in 300 mL of water and 1 M MCl$_2$ (M = Co, Ni, Cu) aqueous solution (2 mL, 2 mmol) was added to the clear solution (the pH was about 5.9). Crystals of **1M-K** suitable for X-ray crystallography were obtained at room temperature within 1−2 days (yield: 30%).

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(9) Laronze, N.; Marrot, J.; Hervé, G. *Chem. Commun.* **2003**, 2360.
(10) The anion α-[[K(H$_2$O)$_2$](Si$_2$W$_{18}$O$_{66}$)]$^{15-}$ is abbreviated **1**, the potassium salt K$_{16}$α-[Si$_2$W$_{18}$O$_{66}$] **1-K**, and the tetrabutylammonium salt **1-TBA**. The transition-metal complexes [{M(H$_2$O)}($\mu$-H$_2$O)$_2$K-(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$ and [{M(H$_2$O)}($\mu$-H$_2$O)$_2$K{M(H$_2$O)$_4$}(Si$_2$W$_{18}$O$_{66}$)]$^{11-}$ are abbreviated **1M** and **1M2**, and their potassium salts **1M-K** and **1M2-K**, respectively.

Anal. calcd (found) for K$_{13}$[{Co(H$_2$O)}($\mu$-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]·40H$_2$O (**1Co-K**): Co, 1.03 (0.81); K, 9.52 (9.30); W, 57.57 (59.45); Si, 0.98 (1.46). IR (KBr pellet, cm$^{-1}$): 994 (m), 937 (m), 899 (sh), 869 (s), 805 (m), 737 (s), 636 (m), 551 (w), 524 (w), 353 (m), 330 (m).

Anal. calcd (found) for K$_{13}$[{Ni(H$_2$O)}($\mu$-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]·40H$_2$O (**1Ni-K**): Ni, 1.02 (0.46); K, 9.52 (8.95); W, 57.58 (59.81); Si, 0.98 (1.69). IR (KBr pellet, cm$^{-1}$): 997 (m), 941 (m), 897 (sh), 871 (s), 815 (m), 733 (s), 654 (m), 554 (w), 524 (w), 353 (m), 326 (m).

Anal. calcd (found) for K$_{13}$[{Cu(H$_2$O)}($\mu$-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]·40H$_2$O (**1Cu-K**): Cu, 1.10 (1.11); K, 9.51 (8.52); W, 57.53 (58.62); Si, 0.98 (1.66). IR (KBr pellet, cm$^{-1}$): 997 (m), 941 (m), 897 (sh), 871 (s), 808 (m), 733 (s), 654 (m), 554 (w), 524 (w), 353 (m), 326 (m).

**K$_{11}$[{M(H$_2$O)}($\mu$-H$_2$O)$_2$K{M(H$_2$O)$_4$}(Si$_2$W$_{18}$O$_{66}$)]·xH$_2$O (1M2-K).** One molar HCl (8 mL) was added to K$_{10}$[SiW$_9$O$_{34}$]·13H$_2$O (11.5 g, 4 mmol) in suspension in 300 mL of water and 1 M MCl$_2$ (M = Mn, Co, Ni) aqueous solution (4 mL, 4 mmol), was added to the clear solution. Crystals of **1M2-K** salts suitable for X-ray crystallography were obtained at room temperature (yield: 30%). Two types of crystals have been obtained for 1Co2-K. The first was triclinic (abbreviated 1Co2-K(A)), and the second was monoclinic (abbreviated 1Co2-K(B)) as the other 1M2-K salts.

Anal. calcd (found) for K$_{11}$[{Mn(H$_2$O)}($\mu$-H$_2$O)$_2$K{Mn(H$_2$O)$_4$}-(Si$_2$W$_{18}$O$_{66}$)]·39H$_2$O (**1Mn2-K**): Mn, 1.92 (1.6); K, 8.23 (7.88); W, 58.03 (59.64); Si, 0.99 (1.42). IR (KBr pellet, cm$^{-1}$): 995 (m), 942 (m), 886 (s), 861 (m), 808 (m), 734 (s), 656 (m), 548 (w), 525 (w), 355 (m), 324 (m).

Anal. calcd (found) for K$_{11}$[{Co(H$_2$O)}($\mu$-H$_2$O)$_2$K{Co(H$_2$O)$_4$}-(Si$_2$W$_{18}$O$_{66}$)]·25H$_2$O (**1Co2-K(A)**): Co, 2.15 (2.06); K, 8.59 (6.84); W, 60.63 (63.38); Si, 1.03 (1.52). IR (KBr pellet, cm$^{-1}$): 998 (m), 943 (m), 904 (sh), 882 (s), 858 (m), 806 (m), 734 (s), 651 (m), 550 (w), 528 (w), 353 (m), 322 (m).

Anal. calcd (found) for K$_{11}$[{Co(H$_2$O)}($\mu$-H$_2$O)$_2$K{Co(H$_2$O)$_4$}-(Si$_2$W$_{18}$O$_{66}$)]·36H$_2$O (**1Co2-K(B)**): Co, 2.08 (1.9); K, 8.29 (7.12); W, 58.5 (59.45); Si, 1.0 (1.45). IR (KBr pellet, cm$^{-1}$): 998 (m), 946 (m), 890 (s), 864 (m), 806 (m), 732 (s), 654 (m), 549 (w), 525 (w), 356 (m), 320 (m).

Anal. calcd (found) for K$_{11}$[{Ni(H$_2$O)}($\mu$-H$_2$O)$_2$K{Ni(H$_2$O)$_4$}-(Si$_2$W$_{18}$O$_{66}$)]·39H$_2$O (**1Ni2-K**): Ni, 2.05 (1.26); K, 8.21 (7.37); W, 57.95 (58.09); Si, 0.98 (1.37). IR (KBr pellet, cm$^{-1}$): 997 (m), 943 (m), 885 (s), 860 (m), 810 (m), 733 (s), 652 (m), 549 (w), 526 (w), 355 (m), 324 (m).

**Physical Techniques.** IR spectra (KBr pellets) were recorded on a Nicolet 550 apparatus. Thermogravimetry was carried out in air flow (60 mL min$^{-1}$) with a Perkin-Elmer electrobalance TGA-7 at a heating rate of 5 °C min$^{-1}$ up to 600 °C. UV−visible spectra were recorded on a Perkin-Elmer lambda 19 spectrometer. Time-average Fourier transform $^{183}$W (12.5 MHz) and $^{29}$Si (99.4 MHz) NMR spectra were recorded on a Bruker AC300 and Avance 500 spectrometers, respectively. The NMR spectra were recorded at ambient probe temperature (20−24 °C). Chemical shifts for $^{183}$W resonances were referred to the $^{183}$W resonance of external 2 M Na$_2$WO$_4$ solution in alkaline D$_2$O and to dodecatungstosilicic acid as secondary standard ($\delta = -103.8$ ppm). Chemical shifts for $^{29}$Si NMR were referenced to tetramethylsilane. Samples tubes were 10 mm for $^{183}$W and $^{29}$Si experiments.

Solid-state $^{29}$Si NMR spectra were acquired on a Bruker Avance 500 spectrometer with a 11.7 T field operating at 99.4 MHz, equipped with Bruker MAS 4 mm probe. Typically, $\pi/4$ pulse widths of 2.5 $\mu$s, repetition times of 25 s, and spectral widths of 68 kHz were used. The MAS speed employed was 10 kHz. All

**Table 1.** Crystal Data for **1Co-K**

| | |
|---|---|
| empirical formula | $K_{14}CoO_{95}Si_2W_{18}$ |
| formula weight | 5491.81 |
| space group | $P\bar{1}$ (No. 2) |
| $a$, Å | 12.9268(6) |
| $b$, Å | 18.9009(10) |
| $c$, Å | 20.9911(11) |
| $\alpha$, deg | 72.357(3) |
| $\beta$, deg | 77.377(2) |
| $\gamma$, deg | 75.640(2) |
| $V$, Å³ | 4677.3(4) |
| Z | 2 |
| $D_{calcd}$, g cm⁻³ | 3.899 |
| $\mu$, cm⁻¹ | 22.971 |
| $T$, °C | 20 |
| R1($F_o$)$^a$ | 0.0308 |
| wR2($F_o^2$)$^b$ | 0.0806 |

$^a$ R1 = $\sum|F_o| - |F_c|/\sum|F_c|$. $^b$ wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $1/w = \sigma^2 F_o^2 + (aP)^2 + bP$.

spectra were referenced relative to the standard tetramethylsilane. Decomposition of spectra was achieved using the dm2004 NMR simulation software.[11]

**X-ray Crystallography.** Single-crystal X-ray crystallographic analysis of **1Co-K** was performed on a Bruker X8-APEX2 CCD area-detector diffractometer and the other **1M-K** and **1M2-K** salts on a Siemens SMART diffractometer.

A crystal of **1Co-K** (0.26 × 0.08 × 0.04 mm³) was mounted in a Lindemann tube. X-ray intensity data were collected on a Bruker X8-APEX2 CCD area-detector diffractometer using Mo-$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Nine sets of narrow data frames (45 s per frame) were collected at different values of $\theta$, for 6 and 3 initial values of $\phi$ and $\omega$, respectively, using 0.5° increments of $\phi$ or $\omega$. Data reduction was accomplished using SAINT V7.03.[12] The substantial redundancy in data allowed a semiempirical absorption correction (SADABS V2.10)[12] 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 using SHELXTL V6.12.[13] Additional details are provided in Table 1.

Crystals of **1M-K** and **1M2-K** were mounted in Lindemann tubes. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector using Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Slightly more than one hemisphere of data was collected in 1271 frames with $\omega$ scans (width of 0.30° and exposure time of 30−60 s per frame depending of the crystals). Data reduction was performed with SAINT software. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction based on symmetry equivalent reflections was applied by using the SADABS program.[14] Lattice parameters were obtained from least-squares analysis of all reflections. The structure was solved by direct method and refined by full matrix least squares, on the basis of $F^2$, using the SHELX-TL software package.[15]
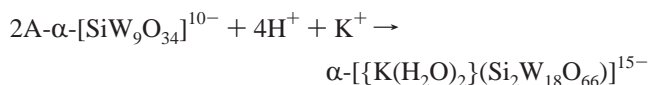
Crystallographic data are given in Supporting Information for **1M-K** (Table S1: **1Ni-K**, **1Cu-K**) and **1M2-K** (Table S2: **1Mn2-**

**K**, **1Co2-K(B)**, **1Ni2-K**) salts. See http://www.rsc.org/suppdata/cc/b3/b307276b/for crystallographic data in CIF format for **1-K** (CCDC 213848) and **1Co2-K(A)** (CCDC 213849).

As crystal structures for these complexes show disorder in the range of water molecules and some counterions, the exact formulas have been established considering elemental analysis, TG studies, and charge balance. The formula given in the tables correspond to the X-ray structure determination in agreement with CIF files.

## Results

**The Anion α-[{K(H₂O)₂}(Si₂W₁₈O₆₆)]¹⁵⁻ (1).** The anion **1** is formed by rapid addition of two equivalents of acid to the aqueous suspension of the potassium salt $K_{10}$A-α-$[SiW_9O_{34}]$ according to the reaction

$$2A\text{-}\alpha\text{-}[SiW_9O_{34}]^{10-} + 4H^+ + K^+ \rightarrow$$
$$\alpha\text{-}[\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{15-}$$

Protonation of A-α-$[SiW_9O_{34}]^{10-}$ led to a dissolution of the potassium salt and condensation of two units followed with immediate reprecipitation of the potassium salt **1-K**. The molecular structure of **1** (Figure 1a) consists of the association of two A-α-{SiW₉O₃₄} units through two oxygen atoms which were terminal ones in the parent A-α-$[SiW_9O_{34}]^{10-}$ anion. The two WO₆ octahedra which participate in the two W−O−W junctions share an edge in each half-anion. Thus, the two half-anions are associated in eclipsed fashion and the anion **1** has the conformation ααE as the Wells−Dawson anion α-$[P_2W_{18}O_{62}]^{6-}$.[16] The structure of **1** derives formally from the Wells−Dawson structure by the breaking of four of the six W−O−W junctions between the two subunits and a rotation of about 40° around the two remaining ones and can be referred to as an "open Wells−Dawson structure". The W7−O27−W11 and W9−O34−W10 angles of the junctions (147.7 and 148.2°, respectively) are similar to the W−O−W corner junction angles in each subunit (between 145 and 150°) and the bond lengths (between 1.91 and 2.03 Å) are in the normal range for corner W−O−W bridges. Considering only the oxo-tungstic framework, the anion $[Si_2W_{18}O_{66}]^{16-}$ has the ideal symmetry $C_{2v}$.

Terminal oxygen atoms of mono or polyvacant polyoxometalates are strongly basic and many transition-metal complexes have been obtained with mono-, di-, or trivacant silicotungstates.[17] In **1**, eight terminal oxygen atoms (four in each subunit) and the two oxygen atoms of the W−O−W junctions delimit a pocket which is a coordination site for metal cations. Actually, three potassium cations are bound to these oxygen atoms in the crystal structure of **1-K**. K1 is localized inside the pocket and bridges the two half-anions.

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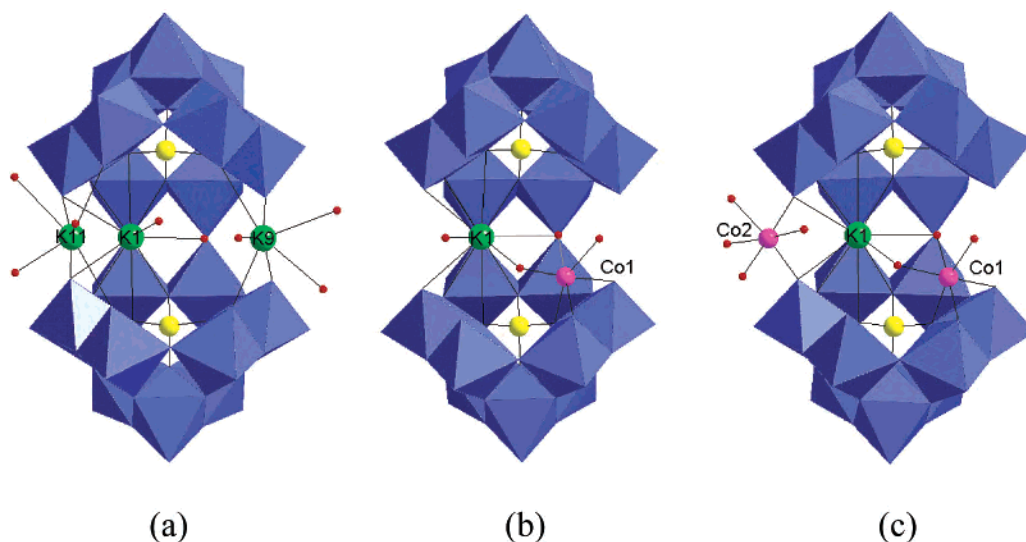
**Figure 1.** Combined polyhedral/ball-and-stick representation of the anions [{K(H$_2$O)$_3$}$_2${K(H$_2$O)$_2$}(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$ (a), [{Co(H$_2$O)}($\mu$-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$ (b), [{Co(H$_2$O)}($\mu$-H$_2$O)$_2$K{Co(H$_2$O)$_4$}(Si$_2$W$_{18}$O$_{66}$)]$^{11-}$ (c), showing tungsten (blue polyhedra), silicon (yellow), potassium (green), cobalt (pink), and oxygen (red) atoms. For **1Co** and **1Co2** only one enantiomer is represented.
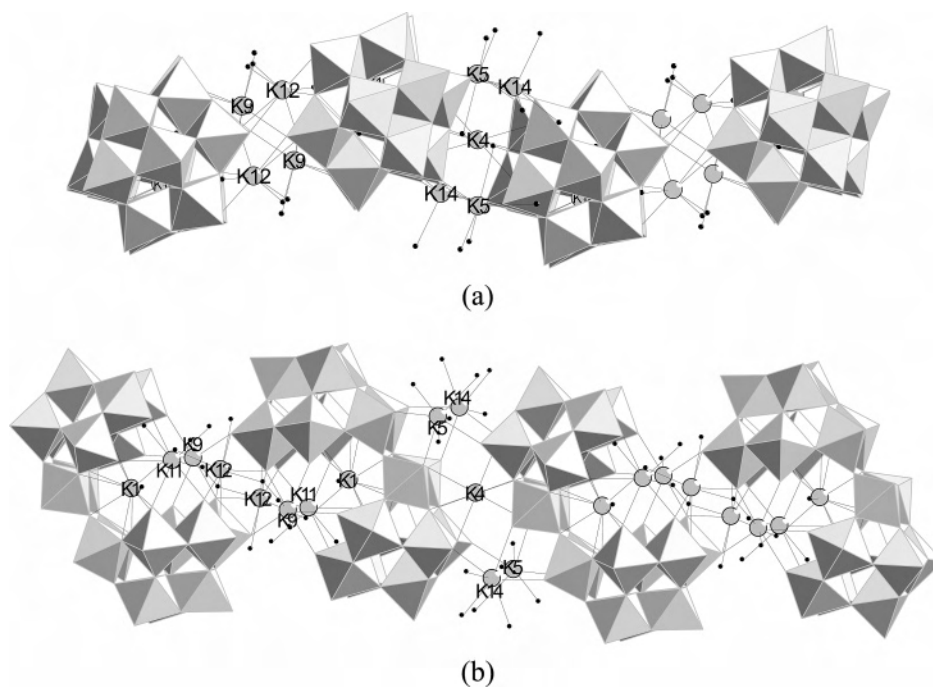


**Figure 2.** Combined polyhedral/ball-and-stick representation of K$_{16}\alpha$-[Si$_2$W$_{18}$O$_{66}$] **1-K** chains in the lattice; top view (a), side view (b), showing tungsten (light gray polyhedra), potassium (light gray ball), and oxygen (small black) atoms.

It is bound to nine oxygen atoms of [Si$_2$W$_{18}$O$_{66}$]$^{16-}$ and two terminal water ligands, with bond lengths in the range 2.76–3.22 Å. In each half-anion, two oxygens are shared with the SiO$_4$ tetrahedron, one is a terminal oxygen of the pocket and one is a bridging oxygen. The ninth oxygen atom (O34) belongs to the junction between the two half-anions. As a result, K1 is shifted to one side of the pocket and the ideal symmetry of [{K(H$_2$O)$_2$}(Si$_2$W$_{18}$O$_{66}$)]$^{15-}$ is only $C_s$. Two other potassium cations, K9 and K11, also bridge the two half-anions through terminal oxygen atoms (two in each subunit) and are thus localized at the periphery of the pocket. Their coordination sphere is completed by three water molecules. The K–O bond lengths are in the range 2.67–3.05 Å and 2.72–3.09 Å for K9 and K11, respectively.

Including these potassium atoms, the molecular structure can be written as [{K(H$_2$O)$_3$}$_2${K(H$_2$O)$_2$}(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$.

In the crystal, two [{K(H$_2$O)$_3$}$_2${K(H$_2$O)$_2$}(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$ anions are associated by their open faces through two potassium cations K12, each pocket near the other (Figure 2). K12 is bound to terminal oxygen atoms of the pocket and water molecules are shared with K1, K9, and K11. These two anions are related by an inversion center and these "inversion pairs" are linked in zigzag chains by potassium cations K4, K5, and K14 which are bound to oxygen atoms of the closed faces (opposite to the open faces) of the [Si$_2$W$_{18}$O$_{66}$]$^{16-}$ units of the pair. In the chains, the inversion pairs are related by another inversion center and the chains are linked in the crystal by other potassium cations.
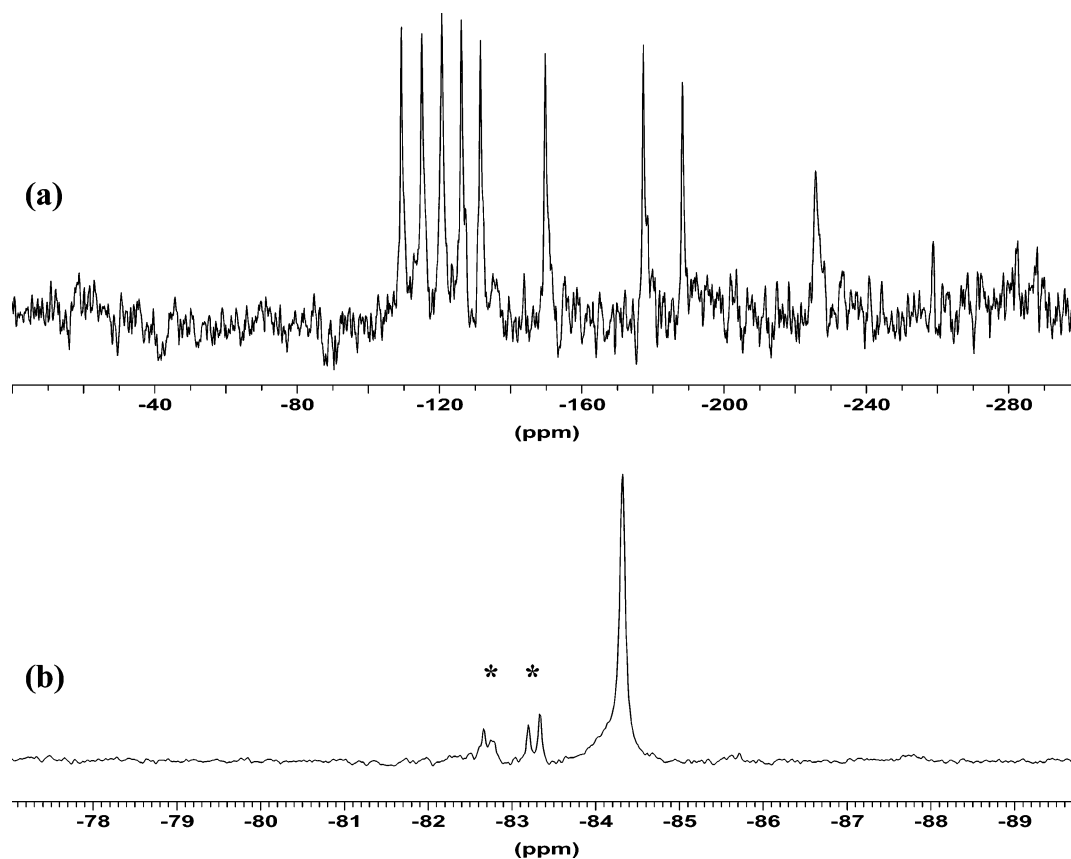
**Figure 3.** Liquid-state (a) $^{183}$W and (b) $^{29}$Si NMR spectra of **1-TBA** ($5 \times 10^{-2}$ mol L$^{-1}$ in DMF/CD$_3$CN). Asterisks indicate the signals of species due to partial transformation of the anion **1**.

Anion **1** can be characterized in solution by its polarogram. In acetic acid/sodium acetate buffer, pH 4.8, it shows three successive waves of 2, 4, and 2 electrons, at −0.67, −0.80, and −0.93 V, vs the saturated AgCl/Ag reference electrode (Figure S3) and is clearly distinct of the polarograms of α-[SiW$_9$O$_{34}$]$^{10-}$ (one wave of 4e at −0.79 V) and α-[SiW$_{11}$O$_{39}$]$^{8-}$ (two waves of 2e at −0.73 and −0.90 V) in the same medium.

The solubility of the potassium salt **1-K** in water is very low. To record the $^{183}$W and $^{29}$Si NMR solution spectra, a Li$^+$/K$^+$ cationic exchange was performed. Unfortunately, the anion **1** was not stable in these conditions and was transformed into the stable α-[SiW$_{11}$O$_{39}$]$^{8-}$ species, showing that the stability in solution strongly depends on the nature of the alkali metal cation. A rapid H$^+$/K$^+$ exchange using a resin followed by an immediate addition of tetrabutylammonium bromide led to the precipitation of an acid tetrabutylammonium salt of **1** (identified by its polarogram), which is soluble and stable in organic solvents. The $^{183}$W NMR spectrum of **1-TBA** in mixed dimethylformamide/acetonitrile solution shows nine signals of about the same intensity at −109.3, −115.0, −120.7, −126.2, −131.5, −149.8, −177.3, −188.3, and −225.8 ppm (Figure 3a) in the usual chemical shift range of polyoxotungstate based compounds.[18] One main signal at −84.3 ppm versus TMS is observed in the solution $^{29}$Si NMR spectrum, which accounts for 74% of total Si (Figure 3b). Four other weak

signals (each about 6.5% of total Si) are also observed. The solid-state $^{29}$Si NMR spectrum of **1-K** (Figure S4) shows a main signal at −84.4 ppm (70%) with a shoulder at −84.0 ppm (30%) in good agreement with the major signal obtained in liquid-state $^{29}$Si NMR spectrum. The splitting of the solid-state signal is likely due to the inequivalence of the two Si atoms in the crystal. The four weak signals probably result from partial transformation of **1** in aqueous acid medium before the precipitation of the tetrabutylammonium salt.

**Transiton-Metal Complexes Derived from Anion 1.** Reaction of transition-metal cations with **1** was studied by titration of a solution obtained by acidification of K$_{10}$A-α-[SiW$_9$O$_{34}$] with two protons and was monitored by visible spectroscopy (Figure S5). The curves obtained with Co$^{2+}$ and VO$^{2+}$ show the formation of complexes with metal/**1** ratio equal to about 2/1, without any evidence of intermediate 1/1 complexes. Nevertheless, the 1/1 and 2/1 metal complexes were isolated with M$^{2+}$ transition metals and crystals suitable for X-ray structure determinations were obtained.

1/1 complexes **1M** (M = Co, Ni, Cu) have the formulas [{M(H$_2$O)}(μ-H$_2$O)$_2$K(Si$_2$W$_{18}$O$_{66}$)]$^{13-}$ but a lack of metal was observed with nickel. The potassium cation K1 occupies the same position as in **1** and the cation M1 is coordinated to only one half-anion through a central oxygen atom shared with the SiO$_4$ tetrahedron and two terminal oxygen atoms (Figure 1b). Its coordination sphere is completed by three water molecules, two of them shared with K1. Since K1 is shifted to one side of the anion, M1 is on the other side and

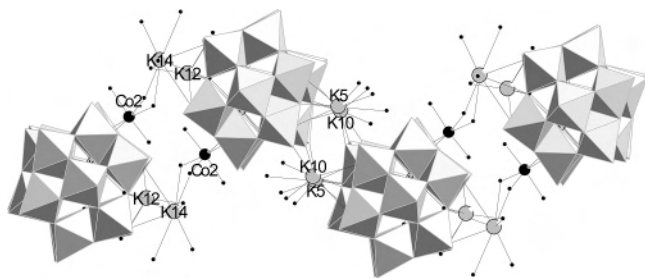(18) Chen, Y.-G.; Gong, J.; Qu, L.-Y. *Coord. Chem. Rev.* **2004**, *248*, 245.

**Figure 4.** Combined polyhedral/ball-and-stick representation of **1Co2** chains in the lattice of **1Co2−K(A)** showing tungsten (light gray polyhedra), potassium (light gray ball), cobalt (black), and oxygen (small black) atoms.

the symmetry of **1M** complexes is $C_1$. Two enantiomers must be considered which correspond to the binding of $M^{2+}$ to one or the other half-anion. The salts **1M-K** crystallize, as **1-K**, in a triclinic system (space group $P$-1) and **1M** complexes form in the crystal racemate inversion pairs in which they are associated through potassium cations by their open face. These pairs are associated in zigzag chains by potassium cations bound to the closed faces of the polyanions (Figure S6). Each inversion pair of the chain results from the previous one by a center of inversion. Actually, for **1Co-K**, there is a disorder of repartition of $Co^{2+}$ on the two positions corresponding to the two enantiomers, with occupation factors of 0.9 and 0.1. This means that the packing of the complexes in the crystal is mainly due to the oxotungstic framework and is compatible with the two enantiomers.
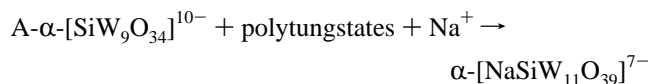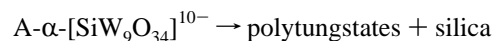
2/1 complexes **1M2** (M = Mn, Co, Ni) have the formulas $[\{M(H_2O)\}(\mu-H_2O)_2K\{M(H_2O)_4\}(Si_2W_{18}O_{66})]^{11-}$ and derive from **1M** complexes by coordination of a second metal cation (M2) which links the two subunits through two cis M−O bonds involving one terminal oxygen atom of each half-anion (Figure 1c). Its coordination sphere is completed by four water molecules. As **1M** complexes, the symmetry of **1M2** complexes is $C_1$ and two enantiomers have to be considered. In most cases, potassium salts **1M2-K** with 35–40 $H_2O$ were obtained and crystallize in a monoclinic system in which the inversion pairs are not directly bound (Figure S7). Moreover, there is in the crystal a disorder of repartition of the M1 cations on two positions corresponding to the two enantiomers; the best refinement was obtained with occupation factors of about 2/3 and 1/3. Fortunately, we were able to obtain triclinic crystals of **1Co2-K** with 25$H_2O$ (space group $P$-1) without such a disorder (salt abbreviated **1Co2-K(A)**). As for **1-K** and **1Co-K** salts, the two enantiomers are linked by their open face through potassium cations K14 which share water molecules with Co2 (Figure 4) which is involved in the racemate inversion pairs. These pairs are associated in zigzag chains by potassium cations bound to the closed faces of the polyanions and each inversion pair of the chain results from the previous one by a center of inversion.

**1M** and **1M2** complexes are metastable in aqueous solution. For example, the visible spectrum of an aqueous solution of **1Co2** evolved very slowly at room temperature (several days). The absorbance increased up to about 40 days without significant change of the absorption maxima.

## Discussion

The trivacant A-$[XW_9O_{34}]^{n-}$ anions (X being a tetrahedral atom) are the precursors of many polyoxotungstates. Depending on the experimental conditions, the structure can be closed to give Keggin-type polyanions (at least in two steps), two units can be directly associated to give Dawson-type polyanions, and two or more units can be associated through tungsten atoms or other heteroatoms (P, As, Sb, Bi, ...) to form more or less complex oligomeric structures. In general, small alkali metal cations ($Li^+$, $Na^+$) promote the closing of the structure and, on the contrary, bigger cations ($K^+$, $Rb^+$) promote the formation of oligomeric compounds.

For example, formation of the 11-tungstosilicate is observed when the sodium salt $Na_{10}A$-$\alpha$-$[SiW_9O_{34}]$ is acidified. This transformation results likely from the degradation of the metastable trivacant species and reaction with polytungstates:

$$A\text{-}\alpha\text{-}[SiW_9O_{34}]^{10-} \rightarrow \text{polytungstates} + \text{silica}$$

$$A\text{-}\alpha\text{-}[SiW_9O_{34}]^{10-} + \text{polytungstates} + Na^+ \rightarrow$$
$$\alpha\text{-}[NaSiW_{11}O_{39}]^{7-}$$

The monovacant $\alpha$-$[SiW_{11}O_{39}]^{8-}$ is stabilized more by coordination of a sodium cation than a potassium cation since the stability constants decrease in the order $Li^+ > Na^+ > K^+ > Rb^+$ as the ionic radius increases.[4a] Very likely, this does not mean that concurrent dimerization to $\alpha$-$[NaSi_2W_{18}O_{66}]^{15-}$ does not occur simultaneously, but first the sodium salt is more soluble than the potassium salt and second $Na^+$ seems to be less adapted than $K^+$ to take place in the pocket of the anion $\alpha$-$[Si_2W_{18}O_{66}]^{16-}$ since the angle between the two half-anions would be significantly less than 40° and the distance between some oxygen atoms would be too small. In conclusion, if $Na^+$ stabilizes more $\alpha$-$[SiW_{11}O_{39}]^{8-}$, $K^+$ very likely stabilizes more $\alpha$-$[Si_2W_{18}O_{66}]^{16-}$.

The nine resonance lines observed in the solution $^{183}$W NMR spectrum of **1-TBA** in nonaqueous solution are compatible with the symmetry $C_s$ of the polyanion $[\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{15-}$, not with $[Si_2W_{18}O_{66}]^{16-}$ which would have the symmetry $C_{2v}$ (five resonance lines). This means that, when the potassium salt **1-K** was treated by a resin under $H^+$ form in aqueous solution, the potassium cation K1 included in the pocket was not exchanged, underlying the strong affinity of this cation for the pocket. Nevertheless, this inclusion of $K^+$ is not sufficient to obtain a thermodynamically stable complex in aqueous solution but only increases the kinetic stability since a slow transformation to $[SiW_{11}O_{39}]^{8-}$ was observed.

The reactivity of the coordination site defined by the pocket between the two half-anions appears rather complicated. Several cations, potassium and one or two transition metals, can be bound to the oxygen atoms which surround the pocket. First of all, the presence of the potassium cation K1 in all the complexes underlines its strong coordination to the anion **1**, since it is not substituted by transition-metal

cations. It is shifted out the $C_2$ axis of the ideal anion $[Si_2W_{18}O_{66}]^{16-}$ (symmetry $C_{2v}$). If K1 was on the $C_2$ axis, the K−O bond lengths would be larger and the coordination number lower, decreasing the stability of the association. Because of the shift of K1, the two sides here and there of the pseudo-symmetry plane are not equivalent and the modes of coordination of the two-transition-metal cations M1 and M2 are different.

The first cation M1 in **1M** and **1M2** complexes is tricoordinated by only one half-anion as would be the 10th tungsten atom in the anion α-$[SiW_{10}O_{37}]^{10-}$, known only in complexes with transition-metal cations.[19] Actually, **1Co-K** and **1Cu-K** were obtained pure in the solid state, but, for **1Ni-K**, refinement of the occupancy of the Ni sites reveals a lack of nickel (0.63 instead of 1) in agreement with elemental analysis. This means that the constants of formation of **1Ni** complexes are probably not so large. Since **1-K** and **1M-K** salts crystallize in the same lattice (triclinic, *P*-1), salts with variable compositions between **1K** and **1M-K** can be obtained. Analogous compositional variations have been already observed with transition-metal complexes of polyoxotungstates.[20] Moreover, the M1 cations occupy several positions with fractional occupation factors revealing a disorder of repartition of the two enantiomers in the solid. It is not obvious to understand the factors which control this disorder since there is no disorder for **1Cu-K** and the occupation factors are 0.9/0.1 for **1Co-K** and 0.1/0.15/0.38 on three positions for the nickel deficient salt **1Ni-K**.

The second cation M2 has a different mode of coordination owing to steric hindrance and because K1 is bound to the oxygen atoms of the $SiO_4$ tetrahedra of the two half-anions. As for **1Ni-K**, the crystal structure and elemental analysis of **1Ni2-K** reveal a lack of Ni (1.5 instead of 2) underlying that nickel complexes are less stable than other metal complexes. In solution, the coordinated M2 cation has four water ligands and substitution by other ligands can be expected.

## Conclusion

Closed Wells−Dawson type polytungstates $[X_2W_{18}O_{62}]^{6-}$ (X = $P^V$, $As^V$) are prepared in acid solution (pH 1−2) and their formation needs lengthy boiling of the solution.[21] On the contrary, the open Wells−Dawson anion α-$[\{K(H_2O)_2\}$-$(Si_2W_{18}O_{66})]^{15-}$ is rapidly obtained at neutral pH and room temperature. The open anion can be considered as an intermediate in the formation of the closed framework. For that, it is necessary to remove the encrypted potassium cation without a rapid destruction of the anion which would lead to Keggin type species.

**Supporting Information Available:** One X-ray crystallographic file in CIF format, for **1M-K** (M = Co, Ni, Cu) and **1M2-K** (M = Mn, Co, Ni); two tables and five figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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