Cation-Directed Synthesis of Tungstosilicates. 1. Syntheses and Structures of $K_{10}A$-α-$[SiW_9O_{34}]$·$24H_2O$, of the Sandwich-Type Complex $K_{10.75}[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}A$-α-$[K_2\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]$·$32H_2O$ and of $Cs_{15}[K(SiW_{11}O_{39})_2]$·$39H_2O$

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The influence of the nature of alkali metal cations on the structure of the species obtained from the trivacant precursor A-α-$[SiW_9O_{34}]^{10-}$ has been studied. Starting from the potassium salt **1**, $K_{10}A$-α-$[SiW_9O_{34}]$·$24H_2O$, the sandwich-type complex **2**, $K_{10.75}[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}A$-α-$[K_2\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]$·$32H_2O$, has been obtained. The crystal structures of these two compounds consist of two A-α-$[SiW_9O_{34}]^{10-}$ anions linked by a set of potassium (**1**) or cobalt plus potassium cations (**2**), and the relative orientation of the two half-anions is the same. Attempts to link two A-α-$[SiW_9O_{34}]^{10-}$ anions by tungsten atoms instead of cobalt failed whatever the alkali metal cation. Moreover, the nondisordered structure of $Cs_{15}[K(SiW_{11}O_{39})_2]$·$39H_2O$ is described. Two $[SiW_{11}O_{39}]^{8-}$ anions are linked through a potassium cation with a "trans-oid" conformation, and the potassium occupies a cubic coordination site.

Introduction

It is now well-established that polycondensation reactions of oxoanions leading to polyoxoanions are strongly dependent on the nature and the concentration of cations in solution. This is especially true for polysilicates[1] but also for polyoxometalates obtained from $[MO_4]^{n-}$ anions (mainly M = V, Mo, W) for which the nature of the alkali metal cations (Li^+, Na^+, K^+, ...) influences both the kinetic and thermodynamic stabilities of numerous species.[2] In some cases, selective interactions of alkali or alkaline-earth metal cations with polyoxometalates have been studied in solution[3] but often only the conditions required for the synthesis and/or analysis of X-ray structural data give information about these interactions.[4]

Heteropolyoxotungstates obtained with phosphorus constitute the richest family. Three main types can be considered: Keggin anions related to $[PW_{12}O_{40}]^{3-}$; Wells−Dawson anions related to $[P_2W_{18}O_{62}]^{6-}$; the species related to $[P_2W_{21}O_{71}(H_2O)_3]$.[6−] Each type includes isomers and vacant species obtained by formal elimination of 1, 2, 3, ..., tungsten atoms.[5] The common intermediate in the synthesis of these three types of tungstophosphates is A-$[PW_9O_{34}]^{9-}$, which is obtained at pH 9−10: Keggin anions are formed by closing the framework in two steps, Wells−Dawson anions by direct fusion of two A-$[PW_9O_{34}]^{9-}$, and $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ by association of two A-$[PW_9O_{34}]^{9-}$ through three trans O═W−H_2O fragments in three successive steps.[4] Formation of Keggin type tungstophosphates is favored by lithium or sodium cations, but on the contrary, obtention of the compounds related to $[P_2W_{21}O_{71}(H_2O)_3]^{6-}$ requires the more or less exclusive presence of potassium or rubidium. On the other hand, the mechanism of formation of the Wells−Dawson anion is not clearly understood.

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All the known tungstosilicates are of the Keggin type, but nothing at all excludes a priori the formation of the two other types of compounds since A-$[SiW_9O_{34}]^{10-}$ is well-known.[6] Actually, only synthesis of the sodium salt $Na_{10}A$-$[SiW_9O_{34}]$ has been described (α and β isomers) and these salts were always utilized as precursors for synthesis of other tungstosilicates or complexes with first-row transition metals, lanthanides, etc. To find out if the nature of the alkaline counterion influences the type of tungstosilicates formed from A-$[SiW_9O_{34}]^{10-}$, we prepared the potassium salt and determined its crystal structure and we investigated the reaction with tungstate and first-row transition metal cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}). In the first part, we present also the crystal structure of a potassium−cesium salt of α-$[SiW_{11}O_{39}]^{8-}$ without disorder as previously reported[7] and which shows the strong selectivity of the interaction of vacant heteropolytungstates with alkaline cations, depending on their size. In a second part, we will present the formation of new tungstosilicates having an open Wells−Dawson type structure.

Experimental Section

Synthesis. The total number of water molecules of each complex has been determined by thermogravimetry. Elemental analyses were performed by the Service Central d'Analyse of CNRS in Vernaison 69390, France.

$K_{10}A$-α-$[SiW_9O_{34}]\cdot24H_2O$ (1). K_8-α-$[SiW_{11}O_{39}]\cdot13H_2O$[8] (10 g, 3.12 mmol) was dissolved in 100 mL of water at 50 °C upon stirring. The solution was cooled to room temperature (solution A). A second solution was prepared by dissolving K_2CO_3 (2.58 g, 18.72 mmol) in 22 mL of water at room temperature. The solution of potassium carbonate was slowly added to the solution A. Then, the pH was ∼9.4. After being stirred for 20 min, the solution was filtered if it was not completely clear (solution B).

After 2 days, colorless crystals of $K_{10}A$-α-$[SiW_9O_{34}]\cdot24H_2O$ suitable for X-ray diffraction were obtained. To obtain a better yield, K_2CO_3 (8 g, 0.058 mol) was added to the solution B. The mixture was gently stirred for 2 h, and a white precipitate appeared slowly. The solid was collected by filtration through a fine frit, washed with a saturated KCl solution (6 mL), and dried in air. Yield: 6.6 g (73%). IR spectra and polarograms in acetic buffer pH = 4.75 (one wave of $4e^-$ at −0.79 V/SCE) of crystals and powder are identical. Anal. Calcd (found) for $K_{10}A$-α-$[SiW_9O_{34}]\cdot24H_2O$: K, 12.82 (13.71); W, 54.25 (53.7); Si, 0.92 (1.07). IR. (KBr pellet, cm^{-1}): 1089 (w), 988 (m), 921 (m), 853 (s), 799 (s), 719 (s), 659 (w), 549 (m), 527 (m), 435 (w).

$K_{10.75}[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}A$-$\alpha$-$[K_2\{Co(H_2O)_2\}_3$-$(SiW_9O_{34})_2]\cdot32H_2O$ (2). A 6 mmol (0.78 g) amount of $CoCl_2$ was dissolved in 20 mL of water, and **1** (11.52 g, 4.00 mmol) was added with gentle stirring. The purple powder was collected by filtration on a fine frit, washed with cold water, and dissolved in 30 mL of water at 40−50 °C. Purple crystals of **2** suitable for X-ray crystallography were obtained at room temperature (yield: 30%). Anal. Calcd (found) for $K_{10.75}[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}A$-$\alpha$-$[K_2\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]\cdot32H_2O$: Co, 3.72 (3.24); K, 8.40 (8.55); W, 55.73 (55.47); Si, 0.95 (1.22). IR (KBr pellet, cm^{-1}): 990 (m), 929 (m), 877 (s), 795 (s), 695 (m), 526 (m).

$Cs_{15}[K(SiW_{11}O_{39})_2]\cdot39H_2O$ (3). The potassium salt **1** (11.5 g, 4.0 mmol) was added in 50 mL of water. To solubilize the powder, the mixture was heated at 80 °C and 1 M HCl (9.7 mL) was added (the pH was about 6.3). A CsCl solution (13.5 g dissolved in 8.3 mL, 0.08 mol) was added, and a white precipitate appeared, which was collected by filtration through a fine frit. The crude product was dissolved in water (2 g in 50 mL), and colorless crystals of **3** suitable for X-ray diffraction were obtained after a few days. Anal. Calcd (found) for $Cs_{15}[K(SiW_{11}O_{39})_2]\cdot39H_2O$: Cs, 24.66 (23.19); K, 0.48 (0.58); W, 50.03 (49.9); Si, 0.69 (1.11). IR (KBr pellet, cm^{-1}): 1006 (sh), 989 (m), 941 (m), 901 (sh), 871 (s), 810 (m), 781 (m), 741 (s), 558 (m), 524 (m), 478 (w).

Physical Techniques. IR spectra (KBr pellets) were recorded on a Fourier transformed 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.

X-ray Crystallography. Crystals of dimensions $0.14 \times 0.10 \times 0.10$ (**1**), $0.18 \times 0.04 \times 0.02$ (**2**), and $0.16 \times 0.10 \times 0.06$ mm^3 (**3**) were glued to a glass fiber. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector using Mo Kα radiation (λ = 0.710 73 Å). Slightly more than one hemisphere of data was collected in 1271 frames with ω scans (width of 0.30° and exposure time of 30 s per frame for **1** and **3** and 60 s for **2**). Data reduction was performed with SAINT software. Data were corrected for Lorentz and polarization effects, and an semiempirical absorption correction based on symmetry-equivalent reflections was applied by using the SADABS program.[9] 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, based on F^2, using the SHELX-TL software package.[10] Crystallographic data are given in Table 1.

1: crystal structure analysis, monoclinic, space group $C2/m$; total reflections collected, 33 152; independent reflections, 12 712 (9185 $F_o > 4\sigma(F_o)$); a hemisphere of data collected up to a $2\theta_{max}$ value of 60.09°; number of variables, 664; $R_1 = 0.0457$, $wR_2 = 0.0937$, and $S = 1.072$; highest residual electron density, 2.657 e $Å^{-3}$.

2: crystal structure analysis, triclinic, space group $P\bar{1}$; total reflections collected, 64 451; independent reflections, 45 407 (19 962 $F_o > 4\sigma(F_o)$); a hemisphere of data collected up to a $2\theta_{max}$ value of 60.69°; number of variables, 1456; $R_1 = 0.0697$, $wR_2 = 0.1122$, and $S = 0.927$; highest residual electron density, 3.422 e $Å^{-3}$.

3: crystal structure analysis, triclinic, space group $P\bar{1}$; total reflections collected, 17 585; independent reflections, 12 386 (6702 $F_o > 4\sigma(F_o)$); a hemisphere of data collected up to a $2\theta_{max}$ value of 59.53°; number of variables, 597; $R_1 = 0.0735$, $wR_2 = 0.1625$, and $S = 0.949$; highest residual electron density, 4.903 e $Å^{-3}$.

As crystal structures for these complexes show disorder in the range of water molecules and some counterions, the exact formulas have been established by considering elemental analysis, TG studies, and charge balance. The formula given in the Table 1 correspond to the X-ray structure determination in agreement with CIF files.

Results

Syntheses. Preparation of the potassium salt of A-α-$[SiW_9O_{34}]^{10-}$ was performed by hydrolysis of α-$[SiW_{11}O_{39}]^{8-}$,

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Table 1. Crystal Data for **1**−**3**

	1	**2**	**3**
empirical formula	$K_{10}O_{45.75}SiW_9$	$Cl_{0.25}Co_{3.75}K_{12.50}O_{94.75}Si_2W_{18}$	$Cs_{14}KO_{96}Si_2W_{22}$
fw	2805.74	5600.08	7536.72
space group	$C2/m$ (No. 12)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	33.7316(13)	18.0876(3)	12.0793(1)
b, Å	16.5324(6)	23.7446(3)	12.7145(2)
c, Å	17.2177(6)	24.4063(1)	19.3029(3)
α, deg	90	117.684(1)	96.633(1)
β, deg	103.479(1)	102.326(1)	101.626(1)
γ, deg	90	97.079(1)	117.731(1)
V, Å³	9337.2(6)	8763.34(19)	2494.23(6)
Z	8	4	1
D_{calcd}, g cm⁻³	3.992	4.245	5.018
μ, cm⁻¹	231.07	249.60	304.59
T, °C	23	23	23
R1(F_o)^a	0.0457	0.0697	0.0735
wR2(F_o^2)^b	0.0937	0.1122	0.1625

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

as previously reported for the sodium salt.[8] The one single difficulty is that the potassium salt K_8-α-[SiW₁₁O₃₉] is not much soluble in water and can crystallize again when K_2-CO₃ is added. So aqueous potassium carbonate was first added (stoichiometric amount) and then as a solid and in excess to increase the yield of **1**. The solubility of **1** in water is very low.

Since A-α-[SiW₉O₃₄]¹⁰⁻ is only metastable in solution, the cobalt complex was obtained by addition of solid K₁₀A-α-[SiW₉O₃₄] in an aqueous solution of a cobalt salt. Heating the mixture to 40−50 °C led to a purple solution, very different from the pink solution obtained when the sodium salt Na₁₀A-α-[SiW₉O₃₄] was used. It is now well-known that A-α-[{(M(H₂O)}₃(SiW₉O₃₇)]¹⁰⁻ complexes can be obtained from the sodium precursor[11] (M^{n+} can be a divalent or trivalent first-row transition metal). The X-ray structure of the purple complex **2** has shown that it is a "sandwich" type complex [{Co(H₂O)₂}₃(SiW₉O₃₄)₂]¹⁴⁻ analogous to the complexes obtained with numerous transition metals from K₉A-α-[PW₉O₃₄].[12]

The complex **2** belongs to the same type that [P₂W₂₁O₇₁-(H₂O)₃]⁶⁻ with three cobalt atoms bound to two A-α-[XW₉O₃₄]$^{n-}$ subunits (X = P or Si) instead of three tungsten atoms. So we tried to prepare the corresponding compounds with silicium, [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻, [Si₂W₂₀O₇₀(H₂O)₂]¹²⁻, and [Si₂W₂₁O₇₁(H₂O)₃]⁸⁻ (the stability of these species depending on the pH), from K₁₀A-α-[SiW₉O₃₄]. Unfortunately, even in the presence of a bigger cation such as cesium, all attempts failed. The cause may be the high charge of the first member of the series [Si₂W₁₉O₆₉(H₂O)]¹⁶⁻ which could destabilize this anion. An other cause could be a competition with the direct association of the two subunits leading to an open Dawson-type structure as it will be reported elsewhere. This direct association has not been reported up to now with phosphorus compounds.
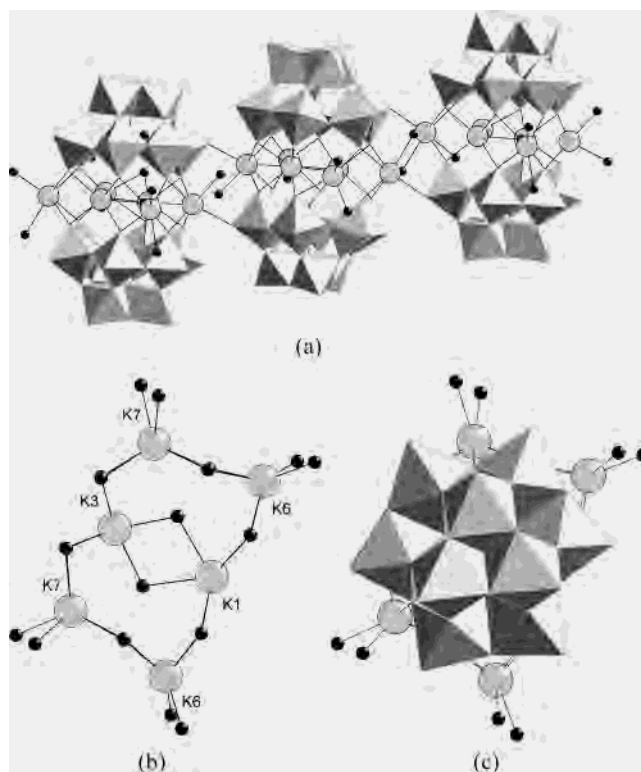
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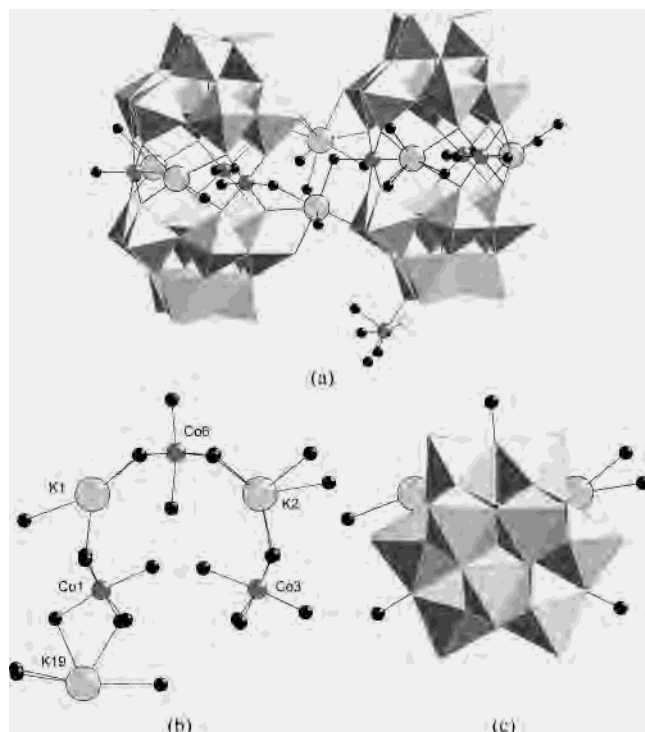
Figure 1. Combined polyhedral/ball-and-stick representation of K₁₀A-α-[SiW₉O₃₄] (**1**) (a), the ring of potassium cations between the two half-anions (b), and on top view (c), showing tungsten (light gray polyhedra), potassium (light gray ball), and oxygen (black) atoms.

In the course of these assays, crystals of the potassium−cesium salt **3** of α-[SiW₁₁O₃₉]⁸⁻ have been obtained showing that, even if the transformation of aqueous K₁₀A-α-[SiW₉O₃₄] in α-[SiW₁₁O₃₉]⁸⁻ is slower than in the presence of small Li⁺ and Na⁺ cations, it can compete with other reactions.

Structures. The solid-state structure of **1** (Figure 1a) consists of the association of two A-α-[SiW₉O₃₄]¹⁰⁻ anions with six potassium cations, leading to a dimer of C_s symmetry. The arrangement of the WO₆ octahedra around the SiO₄ tetrahedron (association of one {W₃O₁₀} and three {W₂O₈} fragments) in each anion is identical with that found for similar compounds containing Si^{IV} or P^{V} as a central atom. Two potassium atoms (K₁ and K₃), on the symmetry

Figure 2. Combined polyhedral/ball-and-stick representation of $K_{10.75}$-$[Co(H_2O)_6]_{0.5}[Co(H_2O)_4Cl]_{0.25}$A-$\alpha$-$[K_2\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]$ (**2**) (a), the ring of cobalt and potassium cations between the two half-anions (b), and on top view (c), showing tungsten (light gray polyhedra), potassium (light gray ball), cobalt (medium gray), and oxygen (black) atoms.

plane, are inside the cage between the two anions and linked together by two water molecules, forming a $\{K_2(H_2O)_2\}$ central group (Figure 1b). The four other ones (K_6 and K_7) are outside the cage (Figure 1c) and participate to the link between the dimers in the lattice (K_7 in Figure 1a). All these potassium atoms form two bonds with two "terminal" oxygen atoms of pairs of WO_6 octahedra of each α-$[SiW_9O_{34}]^{10-}$ anion of the dimer, these pairs being edge-shared (K_3 and K_6) or corner-shared (K_1 and K_7), alternately.

The solid-state structure of **2** (Figure 2a) consists of the association of two A-α-$[SiW_9O_{34}]^{10-}$ anions with three cobalt and two potassium cations (K_1 and K_2), leading to a dimer. The arrangement of the WO_6 octahedra around the SiO_4 tetrahedron in each anion and the relative orientation of the two associated anions are the same as in **1**. Due to the unexpected absence of a third potassium cation between the two subunits, there is not any symmetry element in the solid state (symmetry C_1). The three cobalt cations are bound to two "terminal" oxygen atoms of pairs of edge-shared WO_6 octahedra of each A-α-$[SiW_9O_{34}]^{10-}$ anion of the dimer and to two trans water molecules, one inside and the other one outside the cage between the two anions (Figure 2b). The two potassium cations K_1 and K_2 are bound to two terminal oxygen atoms of pairs of corner-shared WO_6 octahedra and are outside the cage (Figure 2c). Two other potassium cations (K_{19}) link the dimer complexes in the lattice. In addition, two other cobalt cations are cationic counterions, [Co-$(H_2O)_6]^{2+}$ and $[Co(H_2O)_4Cl]^+$.

The solid-state structure of **3** (Figure 3a) consists of the association of two α-$[SiW_{11}O_{39}]^{8-}$ anions with a potassium

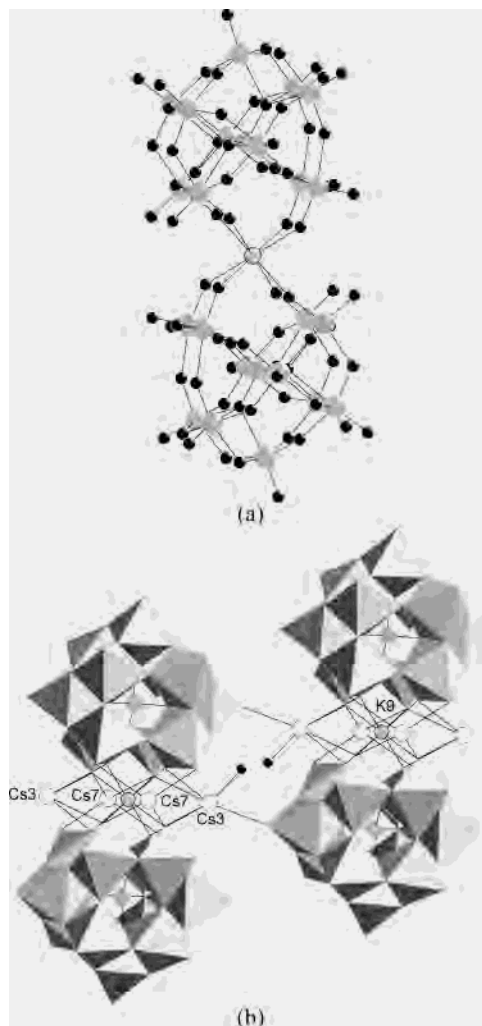**Figure 3.** Ball-and-stick representation of $[K(SiW_{11}O_{39})_2]^{15-}$ (a) and combined polyhedral/ball-and-stick representation of $Cs_{15}[K(SiW_{11}O_{39})_2]$ (**3**) (b), showing tungsten (light gray polyhedra), potassium (light gray ball), cesium (white), and oxygen (black) atoms.

cation (K_9) and corresponds to the complex $[K(SiW_{11}O_{39})_2]^{15-}$. The coordination site of K_9 is defined by four "terminal" oxygen atoms such as a square in each subunit, with a side of 2.90 ± 0.07 Å, and the coordination number of K^+ is 8. The eight oxygen atoms form an quasi perfect cube. The potassium cation is on the center of symmetry of the complex which belongs to the C_i group. It results that one α-$[SiW_{11}O_{39}]^{8-}$ unit is turned with regard to the second, a pair of corner-shared WO_6 octahedra in one subunit facing a pair of edge-shared WO_6 octahedra of the other one. In the solid state, four additional cesium cations (Cs_3 and Cs_7) are bound to four terminal oxygen atoms of the central coordination site, two of them belonging to each subunit. They participate to the links between the dimer complexes in the lattice (see Cs_3 in Figure 3b) in two perpendicular directions.

Stability of 2 in Aqueous Solution. Aqueous solutions of **2** are not stable, but the evolution is very slow at room temperature (several days). It was monitored by visible spectroscopy and at 50 °C to increase the rate (Figure 4). The purple solution of **2** shows a maximum at 506 nm. The absorbance increased up to about 5 h without significant
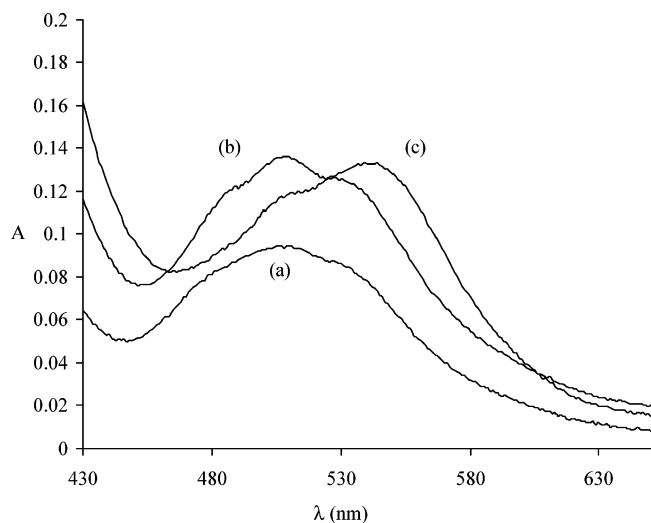
Figure 4. Evolution with time of the visible spectra of a purple aqueous solution of **2** heated at 50 °C: initial (a); after 5 h (b); after 68 h (c).

change of the maxima. A shift to higher wavelengths (maximum at 540 nm) was observed after. So, two complexes, unidentified up to now, are formed successively. Several intermediates have been described during evolution of the similar complex A-α-$[\{Co(H_2O)_2\}_3(PW_9O_{34})_2]^{12-}$. The first intermediate has been written as $[Co_2PW_9O_{34}]^{7-}$, and the final species is B-α-$[\{Co(H_2O)_2\}_2Co_2(PW_9O_{34})_2]^{10-}$. Maybe the same transformation of A-α to B-α sandwich-type complexes occurs with tungstosilicates.

Discussion

Three types of transition metal complexes related to the $[XW_9O_{34}]^{n-}$ trivacant species are known up to now (X is the heteroatom, P, Si, or As): A-$[\{M_3O_3(H_2O)_3\}(XW_9O_{34})]^{m-}$ (α and β isomers); A-α-$[\{M(H_2O)_2\}_3(XW_9O_{34})_2]^{m-}$; B-$\alpha$-$[\{M(H_2O)_2\}_2M_2(XW_9O_{34})_2]^{m-}$ (M is the transition metal). The first is a Keggin-type complex in which three WO^{4+} groups are substituted by three $M(H_2O)^{2+}$ groups and the two others are sandwich-type complexes. With X = P, all these complexes are known, but with X = Si, if Keggin trinuclear complexes have been described many years ago, the B-type sandwich complexes have been obtained only recently[13] and the mechanism of formation is still unknown. From our best knowledge, complex **2** is the first report of an A-type sandwich complex with silicon. As it has been already shown for phosphorus compounds, its formation needs potassium as alkaline cation in solution. If, as usual, some potassium cations are bound to terminal oxygen atoms of A-α-$[SiW_9O_{34}]^{10-}$ in the solid-state structure of **2**, it is not obvious to understand, from the difference in size, why sodium cations could not play the same role. Indeed, a rapid exchange occurs in solution between K^+ and Na^+ cations bound to the analogous $[P_2W_{20}O_{70}(H_2O)_2]^{10-}$ anion.[3] Moreover, it is not certain that K^+ cations are bound to A-α-$[\{Co(H_2O)_2\}_3(SiW_9O_{34})_2]^{14-}$ in solution and favor its formation. On the contrary, small alkaline cations such as Li^+

and Na^+ interact strongly with monovacant $[XW_{11}O_{39}]^{n-}$ species to form very stable complexes in solution. Maybe, in the same way, these small cations could stabilize intermediate species between A-α-$[SiW_9O_{34}]^{10-}$ and A-α-$[\{Co_3O_3(H_2O)_3\}(SiW_9O_{34})]^{6-}$, for example the hypothetical monovacant complex A-α-$[\{Co_2O(H_2O)_n(SiW_9O_{34})\}]^{8-}$. Such a complex has been proposed as an intermediate with phosphorus.[4c] On this assumption, the role of potassium would be not to stabilize A-type sandwich complexes in solution but to not stabilize monovacant Keggin-type intermediates, because it has a larger size than Na^+.

The strong selectivity of the interaction of monovacant Keggin-type species with alkali metal cations is well demonstrated by the solid-state structure of **3**. This is the first example of a non-disordered structure of α-$[SiW_{11}O_{39}]^{8-}$ with alkali metal cations.[14] The concentration of Cs^+ in solution was twice as much K^+, but K^+ has been selectively complexed by the heteropolyanion in agreement with previous solutions studies which have shown that stability of metal/α-$[SiW_{11}O_{39}]^{8-}$ complexes decreases with size beyond a radius 0.7−0.8 Å.[3a] Of course, $[K(SiW_{11}O_{39})_2]^{15-}$ is probably not very stable in solution and the 1:1 complex $[K(SiW_{11}O_{39})]^{7-}$ would be predominant. Each α-$[SiW_{11}O_{39}]^{8-}$ anion of **3** is a tetradentate ligand, binding the potassium cation through the four oxygen atoms of the vacancy. The two subunits adopt a "trans-oid" conformation (Figure 3a) as it has been observed with 1:2 lanthanide complexes.[15] However, the relative orientation of the two anions is not the same since the coordination sphere of potassium is a cube instead of a square-antiprism for lanthanide cations.[16]

The solid-state arrangements of the two A-α-$[SiW_9O_{34}]^{10-}$ anions in **1** and **2** are similar, indicating that the interaction of the six oxygen atoms of the vacancy with cations does not strongly depend on the nature and the size of the cations (except of course for lanthanide cations which have larger coordination numbers).[17] The main difference is due to the presence of three water molecules bound to the three hexacoordinated cobalt atoms, in the cage between the two half-anions. A priori, two relative orientations can be expected when two A-$[SiW_9O_{34}]^{10-}$ anions are associated opposite each other. The first corresponds to the association of the two anions in eclipsed fashion, as observed in **1** and **2**. In the second the two anions are combined in staggered fashion. This conformation had been observed in Na_9HA-β-$[SiW_9O_{34}]\cdot23H_2O$.[18] The difference is likely due to the strong distortion of the hexagon formed by the six oxygen atoms of the vacancy for the α isomer (alternately long, 4.32 Å, and short O−O distances, 3.11 Å, Figure 5). This distortion is not so important for the β isomer (3.96 and 3.35

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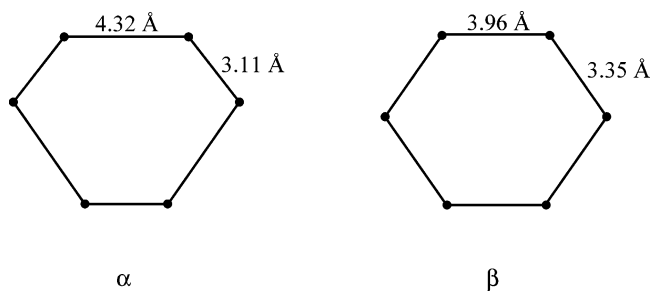(18) Robert, F.; Tézé, A. *Acta Crystallogr.* **1981**, *B37*, 318.

Figure 5. Distortion of the hexagon formed by the six oxygen atoms of the coordination site of the α and β isomers of A-$[SiW_9O_{34}]^{10-}$. Distances between oxygen atoms are mean values.

Å, respectively), and in this case, corner-shared octahedra of one anion and edge-shared octahedra of the other one can be connected together by cations.

Comparison with the solid-state structure of $Na_7H_3[A$-α-$[SiW_9O_{34}]\cdot H_2O^{19}$ shows also that the interaction of the trivacant species with alkali metal cations is dependent on the protonation state. In this salt, the A-α-$[H_3SiW_9O_{34}]^{7-}$ anions are not associated to form dimers in the solid state. The protons are likely bound to oxygen atoms of the vacancy which, in consequence, cannot interact with alkali metal cations. We can think that such a behavior may play also a role in solution and must be taken into account to control the formation of either Keggin, sandwich, or Wells−Dawson type derivatives from the trivacant precursor.

Supporting Information Available: Three X-ray crystallographic files in CIF format for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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