Cation-Directed Structure Changes in Polyoxometalate Chemistry. Equilibria between Isomers of Bis(9-tungstophosphatodioxouranate(VI)) Complexes

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Abstract: The first examples of polyoxometalates incorporating uranyl hetero groups have been synthesized by reaction of $Na_9[A\text{-}PW_9O_{34}]$ with $UO_2(NO_3)_2$. Sodium, ammonium, and potassium salts of $[M_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ (M = Na, NH_4, K) were characterized by P and W NMR spectroscopy and single-crystal structural analysis. The sodium salt (**1**) contains an anion of C_i symmetry in which two PW_9O_{34} groups sandwich two UO_2^{2+} and two Na^+ cations. The uranium atoms have pentagonal-bipyramidal coordination, achieved by three equatorial bonds to one PW_9O_{34} and two bonds to the other. The sodium cations have approximate tetrahedral coordination geometry. Single-line P and five-line W NMR spectra confirm that the anion structure is maintained in solutions containing excess Na^+. The ammonium and potassium salts contain anions in which the UO_2^{2+} cations (pentagonal bipyramids) are unsymmetrically sandwiched between the PW_9O_{34} groups, as are two closely associated cations, one internal and one external. In solution both, salts give two-line P and nine-line W NMR spectra that are consistent with the solid-state structures. Solution equilibria are rapidly established between the two structure types and are dependent upon the concentrations and identities of the cations. Based on integrated P NMR spectra, the equilibrium constants for $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2M^+ \leftrightarrow [M_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2Na^+$ are 128 ± 12 ($M = K^+$) and 1.8 ± 0.8 ($M = NH_4^+$). The requirement of the second cation in order to satisfy the mass-action expression for K_{eq}, coupled with a W NMR spectrum that implies C_s symmetry, demonstrates that the external ion-paired cation undergoes rapid exchange between several surface sites of the heteropolyanion. Solutions of **1** are stable at pH 7 in the presence of excess sodium cations, and the anion is transferable into toluene by phase-transfer techniques. Addition of calcium ions to solutions of **1** generates a new one-line P NMR spectrum of a Ca derivative which is assumed to be isostructural with **1**.

Introduction

Much current research activity in polyoxometalate chemistry is driven by perceived and realized applications in many areas, especially catalysis, separations, imaging, and medicine.[1] The high thermal stability and radiation-resistant natures of polytungstates in particular attract attention to the use of these species for the separation and sequestration of radioactive wastes,[2] and we have recently been examining the formation and stabilities of heteropolytungstates incorporating lanthanide and actinide heteroatoms. Most of the known chemistry of such species centers around the type of complexes first reported by Weakley.[3] These can be described as 1:2 complexes of $Ln^{3+/4+}$ or An^{4+} with monovacant lacunary anion “ligands”, e.g., $[Ln^{III}(PW_{11}O_{39})_2]^{11-}$, with the metal cation occupying a square antiprismatic coordination site.[4]

However, although U^{IV} can be stabilized in such complexes,[3b,c] the aqueous solution chemistry of the early actinides is dominated by trans-dioxo cations of which uranyl, UO_2^{2+}, is the most well-known. We report here the first examples of heteropolytungstates that incorporate the sterically demanding linear $U^{VI}O_2$ group. Unexpectedly, these complexes are shown to form different isomeric structures that are determined by the identity of the countercation. This system provides the first unambiguous example of *reversible* cation control of heteropolyanion structure in solution.[5]

Experimental Section

Syntheses. Sodium 9-tungstophosphate ($Na_9[A\text{-}PW_9O_{34}]\cdot xH_2O$) was prepared according to the published method[6] and identified by infrared spectroscopy. Uranyl nitrate ($UO_2(NO_3)_2\cdot 6H_2O$) was purchased from Atomergic Chemetals Corp. and used without further purification. *CAUTION! Uranium compounds are radioactive and can cause cancers and skin and eye irritation.*

$Na_{12}[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]\cdot 42H_2O$ (1). Solid $Na_9[A\text{-}PW_9O_{34}]\cdot xH_2O$ (2.00 g, 0.082 mmol) was quickly added in small portions to a

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[1] Recent reviews include the following: *Polyoxometalates. From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; pp 1−411. Pope, M. T. In *Encyclopedia of Inorganic Chemistry*; King R. B., Ed.; John Wiley & Sons: Chichester, England, 1994; pp 3361−71. Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113. The following multiauthor special issues have also appeared: *Polyoxometalates*; Hill, C. L., Ed. *Chem. Rev.* **1998**, *98*, 1−387. *Polyoxometalates in Catalysis*; Hill, C. L., Ed. *J. Mol. Catal.* **1996**, *114*, 1−371.

[2] See, for example: Myasoedov, B. F.; et al. *Sov. Radiochem. (Engl. Transl.)* **1990**, *32*, 361; **1991**, *33*, 550.

[3] (a) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836. (b) Tourné, C. M.; Tourné, G. F. *Rev. Chim. Minér.* **1977**, *14*, 83. (c) Termes, S. C.; Pope, M. T. *Transition Met. Chem.* **1978**, *3*, 103.

[4] (a) Tourné, C. M,; Tourné, G. F.; Brianso, M. C. *Acta Crystallogr.* **1980**, *B36*, 2012. (b) Molchanov, V. N.; Kazanskii, L. P.; Torchenkova, E. A.; Simonov, V. I. *Sov. Phys. Crystallog. (Engl. Transl.)* **1979**, *24*, 96. (c) Bartis, J.; Sukal, S.; Dankova, M.; Kraft, E.; Kronzon, R.; Blumenstein, M.; Francesconi, L. *J. Chem. Soc., Dalton Trans.* **1997**, 1937.

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magnetically stirred solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.41 g, 0.082 mmol) in 100 mL of 0.2 M NaCl. Within a few seconds, the tungstophosphate had dissolved completely, and the solution turned yellow. Stirring continued for 20 min. Sodium chloride (22.2 g) was added, and traces of a precipitate were removed by filtration. The ^{31}P NMR spectrum of the filtrate gave a clean single peak at −9.7 ppm. The solution was stored in a refrigerator. After 10 days, crystals were collected on a glass frit, washed with cold deionized water, and air-dried. Yield: 1.8 g (72%). Anal. Found (calcd) for $Na_{14}U_2P_2W_{18}O_{114}H_{84}$: Na, 5.51 (5.30); U, 8.07 (7.83); P, 0.93 (1.02); W, 54.17 (54.45). NMR (δ/ppm): ^{31}P, −9.7 (2P); ^{183}W, −124.6 (4W), −141.1 (4W), −148.7 (4W), −182.2 (2W), −209.6 (4W).

$(NH_4)_{12}[(NH_4)_2(UO_2)_2(A\text{-}PW_9O_{34})_2]{\cdot}3H_2O$ (2). Complex **1** was prepared in solution as described above, and then ammonium chloride (21.3 g) instead of sodium chloride was added to the solution with stirring. A precipitate formed immediately, and the mixture was stirred for 1 h. The precipitate was collected on a medium-porosity glass frit. The crude product was added twice to 50 mL of ammonium chloride solution (4 M), and the mixed solution was stirred at ~40 °C for 1 h. The precipitate was collected on a glass frit and washed with cold deionized water. It was air-dried, giving a yield of 1.8 g (83%). The crystals were grown by dissolving a small amount of the product in deionized water, adding saturated ammonium chloride, and letting the water evaporate at room temperature. Anal. Found (calcd) for $N_{14}U_2P_2W_{18}O_{75}H_{62}$: N, 3.55 (3.70); U, 8.84 (8.97); P, 1.18 (1.17); W, 63.00 (62.37). NMR (δ/ppm): ^{31}P, −9.9 (1P), −11.3 (1P); ^{183}W, −118.5 (2W), −121.2 (1W), −148.6 (2W), −149.8 (4W), −165.2 (2W), −169.8 (2W), −179.0 (1W), −213.4 (2W), −218.6 (2W). Freshly isolated crystals suitable for X-ray analysis proved to be more highly hydrated (ca. $19H_2O$).

$K_{12}[K_2(UO_2)_2(A\text{-}PW_9O_{34})_2]{\cdot}xH_2O$ (3) was prepared according to a procedure similar to that for **2**. Instead of ammonium chloride, potassium chloride was added into the solution of **1**. The crude product was added twice into 2 M KCl solution. NMR (δ/ppm) ^{31}P, −9.9 (1P), −11.3 (1P); ^{183}W −114.2 (2W), −119.0 (1W), −146.9 (4W), −149 (2W), −163.0 (2W), −165.4 (2W), −178.5 (1W), −212.2 (2W), −221.0 (2W).

Crystallography. Crystals of **1**, **2**, and **3** were examined under a thin layer of mineral oil using a polarizing microscope. Selected crystals were mounted on a glass fiber and quickly placed in a stream of cold nitrogen on a Siemens SMART CCD diffractometer equipped with a sealed tube Mo anode (Kα radiation, $\lambda = 0.710\,73$ Å) and graphite monochromator. The data were collected at −100 °C. Procedures for matrix, data collection, and data reduction have been described.[7] The SHELX package of software was used to solve and refine the structures.[7] The heaviest atoms were located by direct methods, and the remaining atoms were found in subsequent Fourier difference syntheses. For the hydrated ammonium salt **2**, the data did not support discrimination between oxygen and nitrogen atoms. Therefore, ammonium ions were modeled as oxygen atoms, except in the case of N1 and N2, which are clearly distinguished by their coordination environments.

In the crystal structure of **2**, occupancy factors were varied in the early stage of refinement for the three chemically equivalent uranium sites. In the final refinement, these factors were rounded off and held fixed. All refinements were full-matrix least-squares on F^2. Crystal data and structure refinement parameters for **1** and **2** are listed in Table 1.

Table 1. Crystal Data for **1** and **2**

	1	**2**
formula	$Na_{14}U_2P_2W_{18}O_{72}{\cdot}38H_2O$	$(NH_4)_{14}U_2P_2W_{18}O_{72}{\cdot}19H_2O$
formula weight	6005.9	5593.9.
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
color	pale yellow	pale yellow
a (Å)	16.6797(8)	12.601(2)
b (Å)	14.6412(7)	20.175(3)
c (Å)	21.2925(10)	35.124(8)
β (deg)	112.2600(10)	99.06(2)
temperature (K)	173	173
Z	2	4
goodness-of-fit on F^2	1.157	1.069
weights (A, B)[a]	0.0591, 194	0.0620, 195
final R ($I > 2\sigma(I)$)	$R1 = 0.0549$ $wR2 = 0.1407$	$R1 = 0.0563$ $wR2 = 0.1343$
final R (all data)	$R1 = 0.0610$ $wR2 = 0.1458$	$R1 = 0.0839$ $wR2 = 0.1446$

[a] The weighting used is $w = 1/[\sigma^2(F_o^2) + (AP)^2 + (BP)]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**[a]

W4−O4d(U)	1.810(9)	U1−O2U	1.798(9)
W5−O5d(U)	1.836(8)	Na1−O2U	2.369(11)
W7−O7d(U)	1.822(9)	Na1−O2U no. 3	2.352(11)
W8−O8d(U)	1.841(9)	Na1−O6d no. 3	2.286(11)
W6−O6d(Na)	1.717(9)	Na1−O9d	2.299(11)
W9−O9d(Na)	1.743(9)	W4−O4d−U1	143.6(5)
U1−O4d	2.351(9)	W5−O5d−U1	145.4(5)
U1−O5d	2.304(8)	W7−O7d−U1 no. 3	112.9(4)
U1−O7d no. 3	2.333(9)	W8−O8d−U1 no. 3	112.1(4)
U1−O8d no. 3	2.327(9)	O4d−U1−O5d	75.5(3)
U1−O7*c* no. 3	2.488(8)	O7d no. 3−U1−O8d no. 3	121.3(3)
U1−O1U	1.807(9)		

[a] Symmetry transformations used to generate equivalent atoms: no. 3, $-x$, $-y$, $-z + 1$.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **2**

W4−O4d(U)	1.827(11)	U2−O1U2	1.805(10)
W5−O5d(U)	1.841(10)	U2−O2U2	1.782(11)
W8−O8d(U)	1.845(10)	N1−O2U1	2.83(2)
W9−O9d(U)	1.800(11)	N1−O2U2	2.82(2)
W15−O15d(U)	1.810(10)	N1−O6d	2.85(2)
W16−O16d(U)	1.837(11)	N1−O7d	2.88(2)
W17−O17d(U)	1.856(10)	N1−O14d	2.81(2)
W18−O18d(U)	1.815(11)	N1−O19d	2.85(2)
W6−O6d(NH_4)	1.761(12)	N2−O5d	3.26(2)
W7−O7d (NH_4)	1.724(12)	N2−O6d	3.00(2)
W14−O14d(NH_4)	1.758(12)	N2−O14d	2.85(2)
W19−O19d(NH_4)	1.756(11)	N2−O15d	2.81(2)
U1−O4d	2.315(12)	W4−O4d−U1	146.3(6)
U1−O5d	2.304(11)	W5−O5d−U1	145.9(6)
U2−O8d	2.304(10)	W8−O8d−U2	146.4(5)
U2−O9d	2.341(11)	W8−O9d−U2	147.3(6)
U1−O15d	2.359(11)	W15−O15d−U1	113.7(5)
U1−O16d	2.329(11)	W16−O16d−U1	113.1(5)
U2−O17d	2.323(11)	W17−O17d−U2	112.6(5)
U2−O18d	2.348(11)	W18−O18d−U2	114.1(5)
U1−O15c	2.552(11)	O4d−U1−O5d	77.6(4)
U2−O17c	2.563(11)	O8d−U2−O9d	76.8(4)
U1−O1U1	1.809(11)	O15d−U1−O16d	122.7(4)
U1−O2U1	1.760(11)	O17d−U2−O18d	123.2(4)

Final atomic coordinates and displacement parameters of **1** and **2** are given in the Supporting Information. Selected bond distances for **1** and **2** are given in Tables 2 and 3.

Physical Measurements. All NMR spectra were recorded on a Bruker AM-300WB spectrometer with 10-mm tubes. Resonance frequencies are 121.495 MHz for ^{31}P and 12.505 MHz for ^{183}W. Chemical shifts are given with respect to external 85% H_3PO_4 for ^{31}P and 2 M Na_2WO_4 for ^{183}W. All chemical shifts upfield of the references

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(5) It has, of course, long been evident that the countercations are not entirely innocent in polyoxometalate chemistry. The equilibria involved in the formation of isopolymolybdates are affected by the ionic strength of the supporting electrolyte; e.g., the formation of $[Mo_7O_{24}]^{6-}$ is enhanced at high $[Na^+]$ (Yagasaki, A.; Andersson, I.; Pettersson, L. *Inorg. Chem.* **1987**, *26*, 3926. Tytko, K. H.; Bäthe, G.; Cruywagen, J. J. *Inorg. Chem.* **1985**, *24*, 3132. Sasaki, Y.; Sillén, L. G. *Ark. Kemi* **1968**, *29*, 253). Certain polyoxotungstate structures, e.g., $[NaP_5W_{30}O_{110}]^{14-}$, incorporate internal, nonlabile sodium cations, and recently, Kirby and Baker (Kirby, J. F.; Baker, L. C. W. *Inorg. Chem.* **1998**, *37*, 5537) have postulated that the syn conformer of $[Th(P_2W_{17}O_{61})_2]^{16-}$ is stabilized by the binding of K^+ in the cleft.

(6) Domaille, P. J. *Inorg. Synth.* **1992**, *27*. 100.

(7) Sheldrick, G. M. *SHELXTL Structure Determination Software Programs*; Siemens Analytical X-ray Instruments: Madison, WI, 1993.

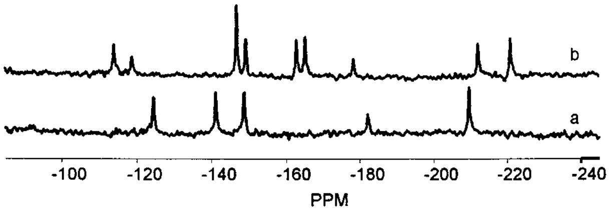

Figure 1. 12.50-MHz ^{183}W NMR spectra of solutions of **1** (a) and **3** (b).

are reported as negative. Crystals of **1** were dissolved in 0.2 M NaCl for NMR spectroscopy. Compounds **2** and **3** were dissolved in water for ^{31}P NMR, but in order to obtain sufficient concentrations for ^{183}W NMR, slurries of the salts were stirred with Li^+-form cation-exchange resin, and small amounts of ammonium or potassium chloride were added to the resulting solutions. Infrared spectra were recorded on a MIDAC FTIR instrument using KBr disks. UV−visible spectra were measured with a Hewlett-Packard 8451 A diode array spectrophotometer. All elemental analyses were performed by E & R Microanalytical Laboratory Inc. (Corona, NY). Water contents were determined by thermogravimetric analysis.

Equilibrium Constants. For the equilibrium constant measurements, **1** (60.95 mg, 0.01 mmol) was dissolved in a series of solutions composed of x mL of 50 mM NaCl, $(4 - x)$ mL of 50 mM KCl, and 2 mL of deuterium oxide: $x = 3.75, 3.50, 3.25, 3.00, 2.50, 2.00$. The solutions were stirred at room temperature for 30 min before ^{31}P NMR spectra were recorded. The ratios of $[Na_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ and $[K_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$ were calculated from the integrals of the ^{31}P NMR peaks. For the equlibrium between the sodium and ammonium derivatives, a similar titration experiment was performed using $(4 - x)$ mL of 50 mM NH_4Cl: $x = 3.00, 2.50, 2.00, 1.50, 1.00, 0.50$ mL of 50 mM NaCl.

Measurement of Stability. The sodium salt, **1** (0.1 g), was dissolved in 4 mL of 0.2 M NaCl (pH 6.95), and the pH was adjusted to 4.1, 4.8, and 5.7 with dilute HCl. For basic solutions, it was dissolved in 4 mL of 5% sodium borate solution, and the pH was adjusted to 8.1, 9.0, and 9.4 with dilute HCl. The stability at each pH was monitored by ^{31}P NMR.

Phase Transfer. The sodium salt (0.15 g) was dissolved in 30 mL of 0.2 M NaCl. The solution was transferred to a separatory funnel, and a solution of 0.35 g of tetra-*n*-heptylammonium bromide in 8 mL of toluene was added. The separatory funnel was vigorously shaken for a few minutes, and the two phases were allowed to separate. The toluene layer was yellow, and the aqueous layer was colorless. The ^{31}P NMR spectrum of the toluene solution showed a single resonance at $\delta = -12.3$ ppm.

Photolysis. The sodium salt was dissolved in sodium formate/formic acid buffer (pH 6). The solution was irradiated for 1 h using a 450-W Hanovia medium-pressure mercury lamp equipped with a Pyrex/water filter. The yellow solution turned dark brown. ^{31}P NMR and visible spectra were recorded on the photolyzed solution.

Results and Discussion

General. Once the reaction stoichiometry had been established from preliminary studies monitored by ^{31}P NMR, the synthesis of $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$ proved to be straightforward. Since $[PW_9O_{34}]^{9-}$ (PW_9) is not stable in aqueous solution, the reaction was carried out by addition of the solid sodium salt to a solution of $UO_2(NO_3)_2$. The ^{31}P NMR spectrum of the reaction solution showed a single peak at −9.7 ppm. The anion is stable only in the presence of excess sodium ion, and **1** crystallized in good yield from a solution kept at 5 °C for several days. The five-line ^{183}W NMR spectrum (intensity ratio 2:2:2:1:2, see Figure 1a) is consistent with the C_i structure subsequently revealed by X-ray crystallography (see below).

Addition of NH_4Cl into a solution of **1** immediately generated a pale yellow precipitate of the ammonium derivative, **2**. The ^{31}P NMR spectrum of an aqueous solution of the precipitate showed peaks at −9.9 and −11.3 ppm with an intensity ratio of 1:1. The ^{183}W NMR spectrum of **2** showed nine peaks with an approximate intensity ratio of 2:1:2:4:2:2:1:2:2. Elemental analysis and the NMR spectra of **2** are fully consistent with the C_s structure revealed by X-ray crystallography.

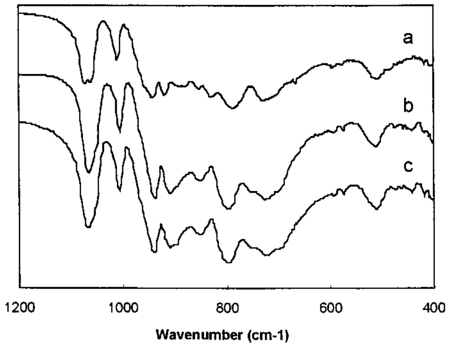

Figure 2. Infrared spectra of (a) the sodium salt of **1**, (b) the ammonium salt of **2**, and (c) the potassium salt of **3**.

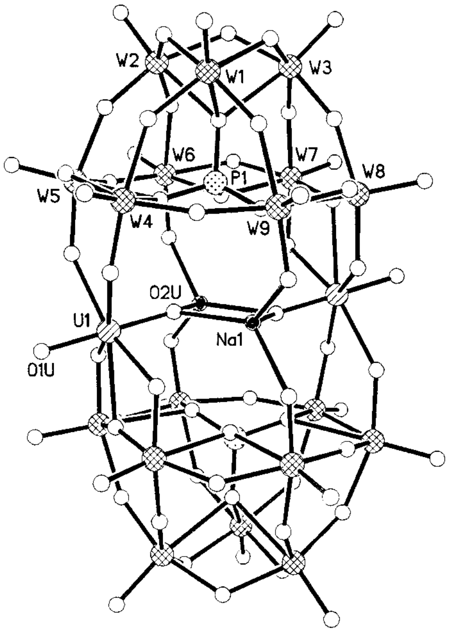

Figure 3. Ball-and-stick representation of the structure of **1** (C_i symmetry), showing labeling of tungsten (crosshatched), uranium (hatched), phosphorus (speckled), and sodium (black) atoms.

The potassium derivative, **3**, was obtained in a similar fashion by addition of KCl to a solution of the sodium salt. The solubility of **3** is much less than that of **2** in aqueous solutions. The ^{31}P NMR spectrum of **3** showed peaks at −9.9 and −11.3 ppm with an intensity ratio of 1:1. The ^{183}W NMR spectrum showed nine peaks with an approximate intensity ratio of 2:1:4:2:2:2:1:2:2 (Figure 1b). The NMR spectra of **3** are consistent with the partial structure revealed by X-ray crystallography.

The infrared spectra of **1**, **2**, and **3** are similar in the P−O stretching region, but the W- - -O stretching region of **1** is slightly different from those of **2** and **3** (Figure 2). The visible spectra of **1**, **2**, and **3** show identical charge-transfer bands (O → U) at 440 nm with $\epsilon = 450\ M^{-1}\ cm^{-1}$.

Structures. The structure of the anion of **1** (Figure 3) consists of two A-type α-PW_9 anions[8] that sandwich two uranyl and

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[8] The starting material, $Na_8HPW_9O_{34}\cdot nH_2O$, is believed to contain the β isomer, however (see arguments presented in Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881).

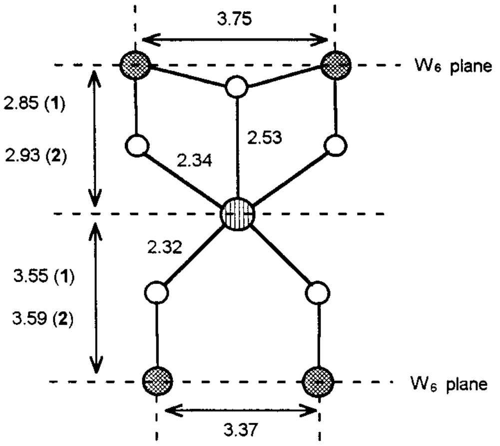

Figure 4. Equatorial coordination environment of UO_2^{2+} in the structures of **1**−**3**, showing the quasi pentagonal arrangement of oxygen atoms that is achieved by sandwiching the uranium atom between corner- and edge-shared WO_6 octahedra. Interatomic distances are given in angstrom units.

two sodium ions, leading to a structure of virtual C_i symmetry. In the filling of the sandwich, the UO_2^{2+} and Na^+ ions occupy opposite corners of a rectangular array. Each uranium atom adopts pentagonal-bipyramidal coordination, and each sodium atom has tetrahedral coordination. Each uranium atom forms two equatorial bonds to the "terminal" oxygens of an edge-shared pair of WO_6 octahedra of one PW_9 and three bonds to "terminal" and bridging oxygens of a corner-shared pair of octahedra of the other PW_9 (see Figure 4). This arrangement results in "long" and "short" U···W separations of 3.55 and 2.85 Å, respectively, as shown in the figure.

The structure of the anion of **2** (and of **3**[9]) maintains the relative orientations of the two PW_9 units observed in **1**, but the two uranyl cations now are unsymmetrically placed between the two PW_9 groups forming "short" (three-bond, U···W = 2.93 Å) junctions with one and "long" (two-bond, U···W = 3.59 Å) junctions with the other.[10] An ammonium (potassium) cation occupies a central site within the anion structure (Figure 5), and a second cation (designated as N2 in Figure 5) is attached to an external equatorial site. Mass-action considerations (see below) imply that the external cation is strongly ion-paired to the heteropolyanion in aqueous solution. The conversion from **1** to **2** (or **3**) lowers the overall anion symmetry from C_i to C_s if the "external" cation is ignored. The nine-line ^{183}W NMR spectra of **2** and **3** indicate that the anions have virtual C_s symmetry in solution. This implies that the external cation is labile and undergoes rapid exchange between, at least, two external sites.

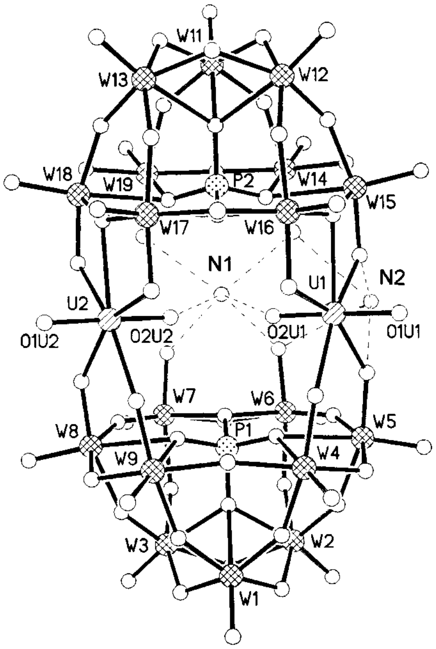

Figure 5. Ball-and-stick representation of the structure of **2** (and **3**) of virtual C_s symmetry if the external cation is ignored, and showing atom labeling. Broken lines indicate possible H-bonding interactions to internal and external NH_4^+ cations (N1 and N2, respectively).

Unless noted, the bond distances and angles in the PW_9 groups are not significantly different from those in structures previously reported.[11] Figures 3 and 5 illustrate the numbering of tungsten and phosphorus atoms. The oxygen atoms, with the exception of phosphate oxygens, oxo oxygens of uranyl cations and water, are given the lower number of the tungsten atoms to which they are bound (except where that would duplicate an existing number; in that case, the higher number is used). This is followed by a letter (a−d) designating the type of bridging in which the oxygen is involved. The letter a indicates a terminal oxo oxygen; b indicates oxygen-bridging edge-sharing tungstens; c indicates bridging corner-sharing tungstens; d indicates an oxo oxygen coordinating a uranium, sodium, or ammonium cation. The oxo oxygens of the uranyl cation are labeled O*n*U in **1** and O*n*U*m* in **2**, where $n = 1$ for the "external" and $n = 2$ for the "internal" oxygen, and *m* is the number of the uranium. The phosphate oxygens are numbered O*n*P in **1** and O*n*P*m* in **2**, where *m* is the number of the phosphorus. For a phosphate oxygen bridging three tungstens, $n = 1$. For phosphate oxygens bridging two tungstens, $n = 2-4$. Water and ammonium ions refined as oxygens are labeled O*n*W.

Except for $O(W_2)$, the oxygens of the pairs of corner-sharing tungstens have a mean U−O distance of 2.34(1) Å. These U−O bond distances are shorter (by ca. 0.15 Å) than those in $Na(UO_2)(OAc)_3$ [2.49(1) Å],[12] $(NH_4)_4\ (UO_2)(CO_3)_3$ [2.46(1) Å],[13] and $Rb(UO_2)(NO_3)_3$ [2.48(1) Å],[14] and this can be attributed to stronger electrostatic interactions to the highly negatively charged polyoxotungstate. The triply bridging $O(W_2U)$ oxygen has a mean U−O distance of 2.53(3) Å, which is significantly longer (ca. 0.2 Å) than the other U−O bond distances, as expected. The bonding interaction of the uranium to this bridging oxygen draws it farther away (by about 0.25 Å) from the least-squares plane of the six-tungsten belt than the other corner-sharing oxygens. The axial U−O bond distances in **1** and **2** are similar to those in complexes of carbonates

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(9) A crystallographic data set was collected for a crystal of **3**. The crystals are triclinic, space group $P\bar{1}$, with lattice constants $a = 12.0420(1)$ Å, $b = 17.7961(2)$ Å, $c = 20.2163(2)$ Å, $\alpha = 96.2680(10)°$, $\beta = 90.1500(10)°$, $\gamma = 103.2810(10)°$, $V = 4189.6(1)$ Å^3, and $Z = 2$. The crystals were extremely thin plates; a good crystal could not be found, and the diffraction was weak. The structure was partially solved with $R = 0.2644$ for 680 parameters and 8512 reflections with $F_o > 4\sigma(F_o)$ out of 19 221 independent reflections. The structure of the anion is identical to that of the ammonium derivative.

(10) There are three nominally equivalent sites for the uranium atoms between the PW_9 groups. Refinement demonstrated partial disorder to the extent of 5% occupancy of the third, "vacant" site.

(11) See, for example: Knoth, W. H.; Domaille, P. J.; Harlow, R. L. *Inorg. Chem.* **1986**, *25*, 1577. Xin, F.; Pope, M. T. *Organometallics* **1994**, *13*, 4881

(12) Zachariasen, W. H.; Plettiger, H. A. *Acta Crystallogr.* **1959**, *12*, 526.

(13) Graziani, R.; Bombieri, G.; Forsellini, E. *J. Chem. Soc., Dalton Trans.* **1972**, 2059.

(14) Hoard, J. L.; Stroupe, J. D. *Nat. Nucl. Energy Ser., Manhattan Proj. Technol. Sect., Div. 3* **1949**, *2*, 15.

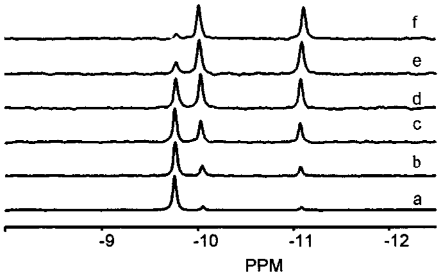

Figure 6. 121.5-MHz ^{31}P NMR spectra of solutions of the sodium salt of **1** in the presence of increasing concentrations of potassium. The molar ratios of (uncomplexed) K^+/Na^+ are (a) 0.03, (b) 0.06, (c) 0.09, (d) 0.13, (e) 0.22, and (f) 0.34. These values were computed from the quantities of NaCl, KCl, and $Na_{12}[Na_2(UO_2)_2(PW_9O_{34})_2]$ added, modified by the quantities of released and bound Na^+ and K^+ determined from the relative integrals of the Na and K derivatives.

[1.79(1) Å], nitrates[1.78(2) Å], and acetate [1.71(4) Å]. The internal U−O bond distances in **1** and **2** average 1.780(16) Å, and the external distances average 1.807(2) Å.

In **1**, the (internal) sodium cations have approximate tetrahedral coordination involving two oxygens from PW_9 units with a mean distance of 2.293(6) Å and two axial oxygens from the uranyl groups with a mean distance of 2.361(9) Å. Two other oxygens (O4P and O7d no. 3) might also be considered to have weak bonding interactions with the sodium cation, with distances of 2.852(10) and 2.935(12) Å, respectively. The least-squares plane of U_2Na_2 is tilted by 4.0(4)° from the parallel position with the least-squares planes of six-tungsten belts of the PW_9 groups.

In **2**, the internal ammonium cation (designated as N1 in Figure 5) is surrounded by six oxygens each within hydrogen-bonding distance: two axial uranyl oxygens and four uncoordinated oxygens of PW_9 units with a mean distance of 2.84(2) Å. The exact disposition of such internal H-bonds, and whether the cation is rotationally disordered, cannot be addressed. The external NH_4^+ (designated as N2 in Figure 5) has four oxygens of the anion within the H-bonding distance, 3.0(2) Å. The ammonium cation is located between one of the uranyl cations and the internal ammonium cation, and thus there are two equivalent positions on the anion. However, disorder of this ammonium over the two positions was not clearly observed in the structure of **2**, although the corresponding potassium cation in the partial structure[9] of **3** was found to be disordered over these two sites.

Solution Behavior. Aqueous solutions of the sodium salt slowly decompose unless prepared with excess sodium ions. Stability measurements were made on solutions prepared in 0.2 M NaCl. The anion appears to be indefinitely stable at pH ca. 7 but slowly decomposes in more acidic or basic solutions. At pH 8.1, decomposition was 30% after 7 days and was complete in 3 h at pH 9.4. At pH 6, solutions appeared stable for up to 4 days but had decomposed by about 10% after 23 days.

Although the ammonium and potassium salts **2** and **3** are less soluble than **1** and are isolated by precipitation, it is possible to observe the transformation from **1** to **2** or **3** in solution, and to evaluate the equilibrium constants for this process from P NMR spectra. Figure 6 shows the spectra of solutions of **1** titrated with KCl and illustrates the gradual conversion of a one-line spectrum for the sodium derivative to a two-line spectrum of the potassium derivative. Similar results were obtained for solutions in which NH_4Cl had been added to the sodium salt. Based on the integrated intensities of these spectra, the following equilibrium constants (at ca. 30 °C and $[Cl^-] = 33$ mM) were evaluated.

$$[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2NH_4^+ \rightleftharpoons [(NH_4)_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2Na^+ \qquad K = 1.8(8)$$

$$[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2K^+ \rightleftharpoons [K_2(UO_2)_2(PW_9O_{34})_2]^{12-} + 2Na^+ \qquad K = 128(12)$$

It is interesting to note that the equilibrium expression requires that *two* countercations are bound,[15] although the structure determinations and W NMR spectra of **2** and **3** show that one of these is external to the anion and undergoes rapid exchange over different surface sites. We attribute the greater stability of the potassium over the ammonium derivative to the stronger electrostatic attraction of K^+ to the anion surface.

Preliminary experiments were made with calcium, which has an ionic radius similar to that of sodium. Addition of the stoichiometric quantity, $2Ca^{2+}$/polyanion, to an aqueous solution of **1** yielded a solution with a single P NMR line at −11.1 ppm, suggesting the possible formation of an isostructural and very stable calcium derivative. This process could not be reversed in 4 M NaCl. Experiments with cesium cation were less conclusive and led to P NMR spectra with four major lines

Photochemistry. Solutions of **1** in sodium formate, acetate, and citrate buffers are unstable, presumably due to the formation of stable uranium carboxylate complexes. The color of the solution slowly darkened from yellow to brown over the course of a few days. The color change was most rapid in the formate buffer and was accelerated on exposure to light. Photochemical reduction of UO_2^{2+} to U^{IV} by carboxylates is well documented, e.g., in the case of formate.[16]

$$UO_2^{2+} + HCO_2^- \xrightarrow{h\nu} UO_2^+ + HCO_2$$

$$2HCO_2 \rightarrow CO_2 + HCO_2H$$

$$2UO_2^+ + 4H^+ \rightarrow UO_2^{2+} + U^{4+} + 2H_2O$$

When a solution of **1** in 0.2 M sodium formate (pH 6) was irradiated with a mercury lamp for 1 h, the resulting dark brown solution exhibited an absorption band at 440 nm that is attributed to U^{IV} to W^{VI} charge transfer. The P NMR spectrum of the photolyzed solution gave a major peak at +9.5 ppm, together with other minor peaks. The 9.5-ppm peak is coincident with that for an authentic example[3b] of the Weakley-type complex $[U^{IV}(PW_{11}O_{39})_2]^{10-}$. The same NMR spectrum was observed in a solution prepared by reaction of PW_9 with UCl_4. The U^{IV} heteropolyanion was isolated as a rubidium salt, and its structure was confirmed by X-ray analysis.[17]

Phase Transfer. When aqueous solutions of **1** were stirred with a solution of tetraheptylammonium bromide in toluene, the yellow color was completely transferred to the organic phase.[18] The toluene solution was stable for at least 1 week at room temperature and gave a single P NMR line at −12.3 ppm.

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(15) While the data strongly support the 1:2 stoichiometry for the sodium/potassium equilibrium (calculated values of "K_{eq}" assuming only that only one K^+ is bound to **3**, i.e., $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-} + K^+ = [K(UO_2)_2(PW_9O_{34})_2]^{13-} + 2Na^+$, are 246, 373, 463, 619, 1041, and 1737 M), the data for the sodium/ammonium equilibrium are less convincing and, if anything, marginally support a 1:1 stoichiometry ($K_{eq} = 15$, 38, 39, 38, 42, 34 M) in the concentration range of $[NH_4]^+$ studied.

(16) Roundhill, D. M. *Photochemistry and Photophysics of Metal Complexes*; Plenum Press: New York, 1994; p 313.

(17) $Rb_{10}[U(PW_{11}O_{39})_2]\cdot nH_2O$ is orthorhombic, space group *Pbcn*, $a = 37.0052(5)$ Å, $b = 14.2677(2)$ Å, $c = 71.7699(9)$ Å, $V = 37893.0(9)$ Å^3, and $Z = 12$. The structure was solved with $R = 0.1445$ for 1450 parameters and 33 560 reflections with $F_o > 4\sigma(F_o)$ out of 46 973 independent reflections. The anion structure is identical to that of $[U(GeW_{11}O_{39})_2]^{12-}$ (ref 4a).

(18) Katsoulis, D. E.; Pope, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2737.

Conclusions

The first examples of polyoxometalate complexes incorporating seven-coordinate (pentagonal-bipyramidal) heteroatoms have been prepared from the reaction of $Na_9[A\text{-}PW_9O_{34}]$ with $UO_2(NO_3)_2$. In behavior unprecedented for polyoxometalate chemistry, the resulting anion structures are controlled by the identities and relative concentrations of the countercations. Isomerization equilibria are established in aqueous solution, and equilibrium constants can be evaluated from P NMR measurements. The sodium derivative, $[Na_2(UO_2)_2(PW_9O_{34})_2]^{12-}$, is formed rapidly in solutions containing excess Na^+ and is easily and efficiently transferred into nonaqueous solvents such as toluene, suggesting a process for sequestration and heavy-metal binding of uranyl and other actinyl cations.

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Supporting Information Available: Tables of crystal data and positional and thermal parameters for **1** and **2**, along with thermal ellipsoid figures for anions **1** and **2** (PDF). X-ray crystallographic files for **1** and **2**, in CIF format, are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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