Aqueous Speciation Studies of Europium(III) Phosphotungstate

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The incorporation of lanthanide ions into polyoxometalates may be a unique approach to generate new luminescent, magnetic, and catalytic functional materials. To realize these new applications of lanthanide polyoxometalates, it is imperative to understand the solution speciation chemistry and its impact on solid-state materials. In this study we find that the aqueous speciation of europium(III) and the trivacant polyoxometalate, PW11O34\(^2-\), is a function of pH, counterion, and stoichiometry. For example, at low pH, the lacunary (PW11O34)\(^2-\) predominates and the 1:1 Eu(PW11O34)\(^{1-}\), 2, forms. As the pH is increased, the 1:2 complex, Eu(PW11O34)\(^{1-}\) species, 3, and (NH4)\(_2\){Eu(PW11O34)\(_4\)(W\(_6\)O\(_{20}\)\(_3\)(H\(_2\)O)\(_2\)(OH)\(_4\))\(_4\)H\(_2\)O, a Eu\(_3\) hydroxo/oxo cluster, 1, form. Counterions modulate this effect; large counterions, such as K\(^+\) and Cs\(^+\), promote the formation of species 3 and 1. Addition of Al\(^{III}\) as a counterion results in low pH and formation of (Eu\(_2\)(H\(_2\)O)\(_3\)(α-2-P\(_2\)W\(_7\)O\(_{28}\))\(_2\)\(_4\), 4, with Al\(^{III}\) counterions bound to terminal W–O bonds. The four species observed in these speciation studies have been isolated, crystallized, and characterized by X-ray crystallography, solution multinuclear NMR spectroscopy, and other appropriate techniques. These species are 1, (NH4)\(_2\){Eu(PW11O34)\(_4\)(W\(_6\)O\(_{20}\)\(_3\)(H\(_2\)O)\(_2\)(OH)\(_4\))\(_4\)H\(_2\)O (P\(_1\); a = 20.2000(0), b = 22.6951(6), c = 25.3200(7) Å; α = 65.6760(10), β = 88.5240(10), γ = 86.0369(10)°; V = 10550.0(5) Å\(^3\); Z = 2), 2, Al\(_2\)(H\(_2\)O)\(_3\){Eu(PW11O34)\(_4\)(W\(_6\)O\(_{20}\)\(_3\)(H\(_2\)O)\(_2\)(OH)\(_4\))\(_4\)H\(_2\)O (P\(_2\); a = 11.4280(23), b = 11.5930(23), c = 19.754(4) Å; α = 103.66(3), β = 95.29(3), γ = 102.31(3)°; V = 2456.4(9) Å\(^3\); Z = 2), 3, Cs\(_11\)Eu(PW11O34)\(_2\)28H\(_2\)O (P\(_3\); a = 12.8663(14), b = 19.8235(22), c = 21.7060(23) Å; α = 114.57(0), β = 91.86(0), γ = 102.91(0)°; V = 4858.3(9) Å\(^3\); Z = 2), 4, Al\(_2\)(H\(_2\)O)\(_3\){Eu(PW11O34)\(_4\)(α-2-P\(_2\)W\(_7\)O\(_{28}\))\(_2\)\(_4\)H\(_2\)O (P\(_4\); a = 12.649(6), b = 16.230(8), c = 21.518(9) Å; α = 111.223(16), β = 94.182(18), γ = 107.581(17)°; V = 3842(3) Å\(^3\); Z = 1).

Introduction

Polyoxometalates (POMs) containing Keggin and Wells–Dawson moieties are chemically robust, easily modified with respect to incorporation of transition metal ions, charge, size, and potential, and can be rendered soluble in water or organic solution. Due to these features, POMs have been developed as catalysts for oxidation and acid-dependent reactions.

Lanthanide (Ln) ions can offer unique functionality when combined with polyoxometalates. We envision that incorporation of Ln ions into POMs offers unique functionality, for example, in the creation of luminescent,\(^1\) magnetic, and Lewis acid catalytic centers.\(^2\) In the area of developing novel functional materials, lanthanide ions, by means of their multiple coordination numbers, can link polyoxometalates into solid-state oligomers\(^3,4\) and large wheel structures.\(^5–8\) POMs can serve as connectors and transfer agents for different monolacunary POMs.\(^9\)

While solid-state crystal structures show the numerous possibilities for use of lanthanide ions in forming new polyoxometalate families, understanding the solution speciation chemistry and its impact on the solid-state chemistry is critical to define new applications. Such an understanding of the complex solution speciation and dynamics for POMs, in general, and Ln POMs, specifically, is lacking. Polyoxometalate composition in aqueous solution is dynamic; multiequilibria exist depending on pH, counterion, concentration, and aging of the solution. Lanthanide ions also show complex dynamic behavior in aqueous solution.

We and others have studied the aqueous chemistry of lanthanide complexes of the monovacant lacunary polyoxometalates, specifically, (α-2-P\(_2\)W\(_7\)O\(_{28}\))\(_{10}^–\) and (α-1-P\(_2\)W\(_7\)O\(_{28}\))\(_{10}^–\) isomers, where the lanthanide ion is incorporated into the...
A number of species exist in solution and in the solid state, and focused solution speciation studies coupled with crystallography provide insight into the chemistry and stabilities of the solution species.

The trivanadic polyoxotungstate, \( \text{XW}_2\text{Os}_4\text{P}^{16-} \), has the potential to support lanthanide clusters. \( \text{XW}_2\text{Os}_4\text{P}^{16-} \) is derived from the Keggin structure (X = P, n = 9; X = Si, n = 10; X = As(V), n = 9), and this anion has six oxygen atoms available for bonding (in the A\( _\alpha \) form) and seven (in the B\( _\alpha \) form). We isolated a unique Ln\text{\textsubscript{2}} cluster tied together by PW\text{\textsubscript{2}}Os\text{\textsubscript{4}}\text{P}^{16-} under neutral to basic conditions.\textsuperscript{11} This species is very stable in water at pH 6.5–9. Examination of the solution chemistry of Eu(III) and PW\text{\textsubscript{2}}Os\text{\textsubscript{4}}\text{P}^{16-} revealed interesting and complex behavior of lanthanide phosphotungstates that is reported herein.

The objective of this work is to examine the speciation of lanthanide complexes of PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a function of solution conditions. To this end, we studied the variations of Eu(III) and PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} with respect to pH, counteration, and stoichiometry, parameters that are well-known to influence POM and Ln POM speciation. We employ Eu(III) in these studies because the shift properties allow convenient monitoring by \(^{31}\text{P} \text{NMR}.

To unambiguously assign the species, we optimized reaction conditions of Eu(III) and PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} to isolate the four compounds that are observed in the speciation studies. These compounds were characterized by appropriate solution and solid-state techniques, including multinuclear NMR and X-ray crystallography. The solid-state crystal structures not only are consistent with the solution species but also reveal the unique abilities of the countercations to influence speciation and structure.

**Experimental Section**

**General Methods.** All reagents were commercially available and used without further purification. Nanopure water was obtained from a Millipore Reverse Osmosis Direct-Q System. Elemental analyses were carried out by inductive coupled plasma atomic emission spectrometry (ICP-AES, SECTROFLAME M120E) as described below. IR spectra were recorded on a Perkin-Elmer 1625 FT-IR at room temperature from KBr pellets. Sodium 9-tungstophosphate \((\text{Na}_9\text{A-PW}_9\text{O}_{34}\text{)}\) was prepared according to a published method\textsuperscript{10} and identified by infrared spectroscopy.

**Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH.** Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O). Reaction Chemistry. Reaction of the Polyoxometalate A-\text{\textsuperscript{\textalpha}}-PW\text{\textsubscript{9}}Os\text{\textsubscript{3}}\text{~}^{9-} as a Function of Countercation and pH. Method i. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), KOAc (0.5 M), and CsOAc (0.5 M) were each prepared at pH 4.75 (30% D\( _2 \)O).
mmol) was added slowly to the above solutions with vigorous stirring, and the pH of resulting solutions were adjusted to 1, 3, 7, and 9 by adding diluted HCl or NaOH, followed by heating to 90 °C for 2 min. The solutions were cooled to room temperature and then placed into 10 mm NMR tubes. The 31P NMR spectrum was recorded and is shown in Figure 1. The pH did not change significantly during the NMR measurement.

A-PW₉O₄6 with Eu³⁺ (1:1 Stoichiometry) as a Function of Countercation and pH. Buffer solutions of LiOAc (0.5 M), NaOAc (0.5 M), and KOAc (0.5 M) were prepared at three pH values (4.5, 5.5, 6.5) (30% D₂O). Preparation of solutions: 0.056 mmol Eu³⁺ (50 µL of 1.12 M) was added into nine vials each containing 3 mL of buffer. A-PW⁹O₃₄⁻ (0.1527 g, 0.056 mmol) was added slowly with vigorous stirring to obtain slightly cloudy solutions that were heated at 90 °C for 2 min to form clear solutions. The solutions were cooled to room temperature and then placed into 10 mm NMR tubes. The 31P NMR spectra were recorded and are shown in Figures S1 and S2 (Supporting Information).

Expanded Study of A-PW₉O₄6 with Eu³⁺ (1:1 Stoichiometry) as a Function of Countercation, including Cs⁺ and Al(III). A 0.056 mmol amount of Eu³⁺ (50 µL of 1.12 M) was added into four vials containing 3 mL of H₂O (30% D₂O). A-PW₉O₄6⁻ (0.1527 g, 0.056 mmol) was added slowly to the above solutions with vigorous stirring; the resulting solutions were heated to 90 °C for 2 min. NaCl (0.990 g, 0.56 M), KCl (0.125 g, 0.56 M), CsCl (0.113 g, 0.22 M), and AlCl₃ (0.135 g, 0.19 M) were added to each of the vials during the heating stage. The vials were cooled to room temperature, and the pH of the solutions was measured and found in all cases except Al(III) to be ca. 7; for Al(III), the pH was 2–3. The solutions were placed into 10 mm NMR tubes. The 31P NMR spectra were recorded and are shown in Figures S1 and S2 (Supporting Information).

Reaction of A-PW₉O₄6 with Eu³⁺ as a Function of Organic Countercations, Tetrabutylammonium (TBA) Bromide and Tetraethylammonium (TEA) Bromide. (The following reaction performed in 1:1 or 2:1 Eu:A-PW₉O₄6⁻ stoichiometry yields the same product.) To EuCl₃·6H₂O (0.32 g, 0.87 mmol) dissolved in H₂O (25 mL) was added Na₉PW₉O₄₆·15H₂O (2.44 g, 0.87 mmol) to form a cloudy solution. After heating at 90 °C for 10 min, cooling and filtering off a small amount of insoluble material, tetrabutylammonium bromide (2.78 g, 8.7 mmol) was added to form a white precipitate. This crude precipitate can be collected by filtration. Further purification can be achieved by extracting three times with CH₂Cl₂ (50 mL). The organic layer was collected and the solvent evaporated and dried under vacuum.

Reaction of A-PW₉O₄6 with Eu³⁺ as a Function of Stoichiometry (Eu:A-PW₉O₄6⁻ = 0.5:1, 1:1, 2:1). The reaction of Eu³⁺ and A-PW₉O₄6⁻ in 2:1, 1:1, and 0.5:1 ratios was carried out in buffer solution NaOAc (0.5 M, pH 6.5). A 50 µL (0.056 mmol) volume of 1.12 M Eu³⁺ each was added into three vials containing 3 mL of NaOAc (0.5 M, pH 6.5) (30% D₂O). Amounts of 0.3054 g (0.112 mmol), 0.1527 g (0.056 mmol), and 0.07635 g (0.028 mmol) of A-PW₉ were added slowly to the above solutions with vigorous stirring. The resulting solutions were heated to 90 °C for 2 min, followed by cooling to room temperature. The 31P NMR

Figure 1. 31P NMR spectra for reactions of PW₉O₄6⁻ + Eu³⁺ (1:1 stoichiometry) as a function of pH. The numbers represent the species, see text, that give rise to the designated 31P NMR resonances.

Figure 2. 31P NMR spectra of reactions of PW₉O₄6⁻ + Eu³⁺ (1:1 stoichiometry) with different countercations (see text for concentrations of countercations, pH 7, except for Al(III), where the pH 2–3). The numbers represent the species, see text, that give rise to the designated 31P NMR resonances.
Figure 3. 31P NMR spectra of reactions of PW6O364− + Eu3+ as a function of stoichiometry. The boxed ratios represent the stoichiometric ratio of Eu: POM; therefore, the bottom spectrum represents the 1:2 Eu:PW6O364− stoichiometry, the middle spectrum represents the 1:1 Eu:PW6O364− stoichiometry, and the top spectrum represents 2:1 Eu:PW6O364− stoichiometry. The solution species are indicated by the numbers above the resonances; see text.

spectrum is shown in Figure 3. When the experiment was carried out in water, not NaOAc buffer, the same results are obtained with a few more unidentified peaks for the 1:2 Eu:PW6O364− combination (not shown).

Preparation and Crystallization of the Individual Species That Are Observed in Speciation Experiments. The syntheses of complexes 1–4 from Eu(III) and A-PW6O364− were optimized, and the complexes were isolated and characterized by X-ray crystallography, elemental analysis, infrared spectroscopy, and multinuclear NMR.

Preparation and Crystallization of (NH4)22[(Eu2PW9O34)4−(W2O7(H2O)(OH))4]4H2O, 1. 1 was prepared by a modification of the procedure reported previously.17 Solid Na9A-PW9O34·16H2O (4.90 g, 1.8 mmol) was added slowly to a solution of EuCl3·6H2O (0.66 g, 1.8 mmol) in 15 mL of H2O. The resulting cloudy solution was heated to about 80 °C and, within a few seconds, a clear solution formed. Solid NH4Cl (5.16 g, 54 mmol) was added to the hot solution, a white precipitate was formed immediately, and the solution was heated for an additional 5 min. After 1 h, the solution turned clear and then was cooled in an ice bath. The crystal- lized solid was collected by filtration and recrystallized from hot water. Yield: 2.78 g, 76%. X-ray-quality crystals were obtained at 4 °C by recrystallizing 1 g of the white crystalline solid from 8 mL of hot water. Anal. Calcd for (NH4)22[(Eu2PW9O34)4−(W2O7(H2O)(OH))4]4H2O: W, 60.11; Eu, 3.20; P, 1.31; Al, 0.57. Found: W, 64.71; Eu, 3.21; P, 1.10; Al, 0.67. IR (KBr, cm−1) (metal−oxygen stretching region): 1100 (m), 1046 (m), 954 (vs), 893 (m), 820 (s), 773 (vs), 722 (s).

Analytical Techniques. Elemental Analysis by ICP. (i) Standard Solution Preparation. The standard solution of P (0.2, 0.4, 0.6, 0.8, 1.2 ppm), Eu (1, 2, 4, 6 ppm), W (20, 40, 60, 80, 120 ppm), Al (0.5, 1, 1.5, 2.5 ppm), Na (1, 3, 5, 7 ppm), and K (1, 3, 5, 7 ppm) was prepared by diluting 1000 ppm ICP standard solution (GFS Chemicals, Inc.) with distilled water.

(ii) Sample Preparation. Crystals of complex 1–4 were collected by filtration, air-dried, and further dried in a desiccator over CaSO4, under vacuum for 1.5 h. The samples were left in the closed desiccator overnight. Afterward, 0.0508 g of 1, 0.0470 g of 2, 0.0526 g of 3, and 0.0510 g of 4 were each dissolved in 50 mL of distilled water. The 1 and 2 mL solutions from each stock solution were diluted to 25 mL with water and used for ICP measurements.

(iii) Measurement Method. The maximum wavelength for different element was selected (P, 213.618 nm; Eu, 381.970 nm; W, 239.709 nm; Al, 308.215 nm; Na, 589.592 nm; K, 766.496 nm). A calibration curve for each element was constructed. After the calibration curve of each element was completed, the concentrations (in ppm) were determined for the two solutions of each sample (40.64, 81.28 μg/mL of 1; 37.60, 75.20 μg/mL of 2; 42.08, 84.16 μg/mL of 3; 40.80, 81.60 μg/mL of 4). The concentrations, in ppm, were converted to weight percent of each element.

Collection of NMR Data. All NMR spectra were recorded on a JEOL GX-400 spectrometer with 5 or 10 mm tubes. Resonance frequencies were 161.8 MHz for 31P and 16.7 for 195W. Chemical shifts are given with respect to external 85% H3PO4 for 31P and 2.0 M Na2WO4 for 195W. Typical acquisition parameters for 31P spectra included the following: spectral width, 10 000 Hz; acquisition time, 0.8 s; pulse delay, 1 s; pulse width, 15 μs (5° tip angle). From 200 to 1000 scans were required. Generally, the 1 s pulse delay was sufficient for accurate integration of the 31P peaks and, thus, qualitative assessment of concentrations of species could be...
made. For $^{183}$W spectra, typical conditions included the following: spectral width, 10 000 Hz; acquisition time, 1.6 s; pulse delay, 0.5 s; pulse width, 50 μs (45° tip angle). From 1000 to 30 000 scans were acquired. For all spectra, the temperature was controlled to ±0.2 deg. For both $^{31}$P and $^{183}$W chemical shifts, the convention used is that the more negative chemical shifts denote more upfield resonances.

**Single-Crystal X-ray Structure Determination.** Crystals of 1–4 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 cold nitrogen on a Bruker SMART CCD diffractometer equipped with a sealed tube Mo anode (Ka radiation, $\lambda = 0.71073$ Å) and graphite monochromator or Nonius Kappa CCD diffractometer. The data were collected at around 100 K. Data collection, indexing, and initial cell refinements were all handled using SHELXTL software. The SHELX package of software was used to solve and refine the structures. The heaviest atoms were located by direct methods, and the remaining atoms were found in subsequent Fourier difference syntheses. For the ammonium salt 1, the data did not support discrimination between oxygen and nitrogen atoms. All refinements were full-squares on $F^2$. Crystal data and structure refinement parameters for 1–4 are listed in Table 1. Selected bond distances for 1–4 are given in Table 2. Final atomic coordinates and displacement parameters for 1–4 are given in the Supporting Information.

**Results**

**Solution Chemistry.** Solution Speciation of PW$_{11}$O$_{39}$$^{7-}$. A-PW$_6$O$_{34}^{9-}$ is formed from Na$_3$WO$_4$ and H$_2$PO$_4$ at pH 9.20,21 Hill and co-workers examined the fundamental stability of A- and B-PW$_6$O$_{34}^{9-}$ under buffered neutral (physiological pH 7.4) aqueous media by $^{31}$P NMR spectroscopy and found that, at equilibrium conditions, predominantly the monolacunary $\alpha$-PW$_{11}$O$_{39}$$^{7-}$ species formed in the presence of two buffers (sulfite and tris).$^{22}$ Also, unidentified phosphorus-containing products were formed that were buffer dependent. In this study, we examined the solution behavior of the A-PW$_6$O$_{34}^{9-}$, at equilibrium, under different pH (1–10) and countercation (Li$^+$, Na$^+$, K$^+$, Cs$^+$, Al$^{3+}$) conditions by $^{31}$P NMR (Supporting Information Table S1). In acidic solution the major species formed are H$_3$PO$_4$, the Keggin anion PW$_{11}$O$_{39}$$^{7-}$, and the monolacunary Keggin anion, PW$_{11}$O$_{39}$$^{7-}$. In buffer (0.5 M LiOAc, NaOAc, KOAc) at pH 4.75, only two species H$_3$PO$_4$ and PW$_{11}$O$_{39}$$^{7-}$ exist in the solution. Under neutral conditions, PW$_{11}$O$_{39}$$^{7-}$ along with PO$_4^{3-}$ and unidentified species were present, similar to the previous study.$^{22}$ In basic solutions, the major species formed are PO$_4^{3-}$ and WO$_4^{2-}$ (according to $^{183}$W NMR data), consistent with decomposition of the A-PW$_{11}$O$_{39}$$^{7-}$. The addition of the Al$^{3+}$ to the solution of A-PW$_{11}$O$_{39}$$^{7-}$ results in a lowering of the pH to about 2–3 and the observation of two equal-intensity peaks at −10.7 and −11.45 ppm that may indicate a Wells–Dawson anion, for example, the $\beta$-Wells–Dawson anion or an Al(III) adduct of the $\alpha$-P$_2$W$_{18}$O$_{62}$$^{6-}$ or possibly incorporation of the Al(III) into oxalate-P$_2$W$_{18}$O$_{62}$$^{6-}$. These two peaks were in small concentration (13%); the majority of


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**Table 1.** Crystal and Structure Refinement Data for Species 1–4

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<td>11 183/0/491</td>
<td>18 777/0/705</td>
<td>16 035/0/519</td>
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<td>R1 = 0.0572, wR2 = 0.1624</td>
<td>R1 = 0.0818, wR2 = 0.2135</td>
<td>R1 = 0.0946, wR2 = 0.2158</td>
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<td>R indices (all data)</td>
<td>R1 = 0.0624, wR2 = 0.1347</td>
<td>R1 = 0.0687, wR2 = 0.1770</td>
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<td>largest diff peak</td>
<td>5.373 and −4.87</td>
<td>11.94 and −3.807</td>
<td>8.071 and −7.938</td>
<td>9.386 and −8.749</td>
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</table>

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the species observed in the case of Al(III) addition are PW$_{11}$O$_{39}$$^{7-}$ and PW$_{15}$O$_{40}$$^{3-}$.

Solution Speciation of PW$_6$O$_{34}$$^{9-}$ with Eu$^{3+}$ After Mixing and Before Heating. The speciation reactions of PW$_6$O$_{34}$$^{9-}$ with Eu$^{3+}$ involve adding the polyoxometalate to a solution containing Eu(III) at the appropriate pH and counterion content. The solutions are heated for 2 min at 90 °C; after this heating step, the $^{31}$P NMR does not change over a period of days. Before the heating step, $^{31}$P NMR analysis shows that there are unidentified, broad $^{31}$P peaks that are likely due to chemical exchange processes of different species. For example, Figure S3 shows the $^{31}$P NMR spectra for a typical reaction of PW$_9$O$_{34}$$^{9-}$ and Eu(III), 1:1 stoichiometry, pH ca. 6−7, before heating and after heating at 90 °C. Before heating, the spectrum is broad and the peak positions do not correspond to any of the identified species. However, it is apparent that the broad peaks represent dynamic behavior of species that are in chemical exchange. For example, the peak at 25.89 ppm is clearly the largest peak and likely represents an average of the peaks of species 1, {Eu(PW$_{10}$O$_{38}$)$_3$(W$_2$O$_8$)(H$_2$O)$_2$(OH)$_4$}$^{22-}$ (28.97, 22.55 ppm), where the two chemically inequivalent (Eu,PW$_{10}$O$_{38}$) lobes of the molecule are engaged in a dynamic process. The other peaks at 13.82 and 2.80 ppm are also broad and may represent chemical exchange as well. The peak at 2.80 ppm appears to be an average between species 2 and 3 Eu(PW$_{11}$O$_{39}$)$^{7-}$ (5.28 ppm) and Eu(PW$_{11}$O$_{39}$)$_2$$^{11-}$ (0.57 ppm) reflecting an exchange process involving these species. The peak at 13.82 ppm possibly represents exchange between all three species. Heating this solution results in clear conversion to species 1 (28.97, 22.55 ppm) and species 2 and 3, Eu(PW$_{11}$O$_{39}$)$^{7-}$ (5.28 ppm) and Eu(PW$_{11}$O$_{39}$)$_2$$^{11-}$ (0.57 ppm), respectively.

Conversion of the broad peaks (Figure S3) to species 1−3 also occurs if the solution is allowed to age for 12 h at room temperature. Aging experiments of the heated solutions show that the spectra do not change during a period of days, suggesting that the system has reached equilibrium.

Table 2. Selected Bond Lengths (Å) for Species 1−4

<table>
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<tr>
<th>Compound</th>
<th>Eu(1−)−O(1)</th>
<th>Eu(1−)−O(6)</th>
<th>Eu(1−)−O(4)</th>
<th>Eu(1−)−O(1A)</th>
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<tr>
<td>1</td>
<td>2.436(10)</td>
<td>2.346(11)</td>
<td>2.391(13)</td>
<td>6.146(10)</td>
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<tr>
<td>2</td>
<td>2.346(11)</td>
<td>2.383(11)</td>
<td>2.557(11)</td>
<td>4.426(13)</td>
</tr>
<tr>
<td>3</td>
<td>5.907(13)</td>
<td>5.827(12)</td>
<td>6.146(13)</td>
<td>4.268(88)</td>
</tr>
<tr>
<td>4</td>
<td>6.288(88)</td>
<td>2.342(6)</td>
<td>2.362(23)</td>
<td>2.407(21)</td>
</tr>
</tbody>
</table>

Reaction of PW$_6$O$_{34}$$^{9-}$ with Eu$^{3+}$ (1:1 Stoichiometry) at Different pH Values. The $^{31}$P NMR spectra (Figure 1) for the reaction carried out at low pH (1−3) shows two peaks at 5.23 ppm and −11.93 ppm that correspond to species 2, Eu(PW$_{11}$O$_{39}$)$^{7-}$, and PW$_{11}$O$_{39}$$^{7-}$, respectively. Decomposition to PW$_{12}$O$_{39}$$^{9-}$ is also observed. Three species are observed at pH 7; these are 1, Eu(PW$_{10}$O$_{38}$)$_3$(W$_2$O$_8$)(H$_2$O)$_2$(OH)$_4$)$^{22-}$ (δ ppm: 28.55, 22.07), 2, Eu(PW$_{11}$O$_{39}$)$^{7-}$ (δ ppm: 5.25 ppm), and 3, Eu(PW$_{11}$O$_{39}$)$_2$$^{11-}$ (δ ppm: 0.5 ppm). The spectrum at pH 9 is dominated by species 1 and 3.

The reaction of PW$_6$O$_{34}$$^{9-}$ with Eu$^{3+}$ under varying pH values (4.5, 5.5, and 6.5) was examined in the presence of different cations (Li$^+$, Na$^+$, K$^+$) (Supporting Information, Figures S1 and S2). This experiment provides the opportunity to evaluate both the pH and counterion influence on speciation. With Li acetate or Na acetate buffer (0.5M) at pH 4.5 (Figure S1), the $^{31}$P NMR of PW$_6$O$_{34}$$^{9-}$ and Eu$^{3+}$ in a 1:1 mole ratio showed that 2 was the major solution species with the PW$_{11}$O$_{39}$$^{7-}$ ligand as a minor species. At pH 5.5, only species 2 was observed, while, at pH 6.5, two additional species 1 and 3 were present in the solution in low concentration.

Different behavior is observed with K$^+$ counterions (KOAc, 0.5 M). For example, at pH 4.5, the major species observed in solution are 2, Eu(PW$_{11}$O$_{39}$)$^{7-}$, and free PW$_{11}$O$_{39}$$^{7-}$, with 3, Eu(PW$_{11}$O$_{39}$)$_2$$^{11-}$, in significant concentration (Figure S2). Increasing the pH results in no observable free PW$_{11}$O$_{39}$$^{7-}$ and a significant increase in the concentration of species 3. In contrast to the Li$^+$ and Na$^+$ case, species 3 grows in significantly at the lower pH values with K$^+$ as the buffer, until it is the dominant species at pH 7.6. Species 1 begins to appear at a higher pH of 7.6 compared to 6.5 found for the Li$^+$ and Na$^+$ buffers.

Expanded Study of PW$_6$O$_{34}$$^{9-}$ with Eu$^{3+}$ (1:1 Stoichiometry) as a Function of Countercation. To further test the effect of countercations on speciation, a study of the speciation of PW$_6$O$_{34}$$^{9-}$ + Eu$^{3+}$ (1:1 stoichiometry, pH 7) with an expanded series of countercations was carried out.
Aqueous Speciation of Eu(III) Phosphotungstate

(Figure 2). With Na\(^+\) (not shown), K\(^+\), or NH\(_4\)\(^+\) (not shown), three species corresponding to 1 (28.8, 22.2 ppm), 2 (5.2 ppm), and 3 (0.5 ppm) can be identified, similar to studies reported above. Addition of Cs\(^+\) into the aqueous solution of PW\(_9\)O\(_{34}\)^9\(^-\) + Eu\(^{3+}\) (1:1 stoichiometry, pH 7) results in exclusively one species, 3, Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\).

Solutions containing the counterion Al(III) show the presence of species 4 that has been identified as Eu(α-2-P\(_2\)W\(_{17}\)O\(_{61}\))\(^{3-}\). As 31P NMR and crystallography; vide infra. This phenomenon was only seen in the presence of Al\(^{3+}\) and is possibly due to the acidity that Al\(^{3+}\) confers upon the solution; generally, the pH after treatment with AlCl\(_3\) was ca. 2−3. Also, the ability of Al(III) to bind to oxygen atoms of polyoxometalates may influence the formation of this species. Species 2 and 3, 1:1 Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\) and 1:2 Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\), respectively, are also found as the majority species in this solution (Figure 2).

The reaction of Eu(III) and A-PW\(_9\)O\(_{34}\)^9\(^-\) in H\(_2\)O, in both 1:1 or 2:1 Eu:A-PW\(_9\)O\(_{34}\)^9\(^-\) stoichiometry, with the addition of TBA\(^+\) or TEA\(^+\), resulted in isolation, by extraction into organic solution, of species 2, Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\), exclusively. The 31P NMR of the TBA salt (δ, ppm, 5.3, H\(_2\)O; δ, ppm, 9.6, CH\(_3\)CN) was identical with that for a genuine sample of TBA\(_2\)Eu(PW\(_{11}\)O\(_{39}\)) that was prepared directly by two methods (metathesis of the potassium salt of Eu(PW\(_{11}\)O\(_{39}\))\(^{4-}\), prepared by direct reaction of Eu(III) and PW\(_9\)O\(_{34}\)^9\(^-\) or by reaction of Eu(CIO\(_4\)) and TBA\(_2\)H(PW\(_{11}\)O\(_{39}\))\(^{2-}\) in CH\(_3\)CN). The samples of TBA\(_2\)H(EuPW\(_{11}\)O\(_{39}\)) prepared directly have been analyzed by elemental analysis, thus far.

Reaction of PW\(_9\)O\(_{34}\)^9\(^-\) with Eu\(^{3+}\) under Different Stoichiometries. The reaction of Eu\(^{3+}\) and A-PW\(_9\)O\(_{34}\)^9\(^-\) in 0.5:1, 1:1, and 2:1 Eu: POM stoichiometric ratios were studied in NaOAc buffered solution (0.5 M, pH 6.5), and 0.5:1, 1:1, and 2:1 Eu: POM stoichiometric ratios were observed in Solution Speciation Studies, and Description

Addition of AlCl\(_3\) to solutions of 1:1 Eu:PW\(_9\)O\(_{34}\)^9\(^-\), at 1.99 ppm, possibly due to decomposition of PW\(_9\)O\(_{34}\)^9\(^-\) 3. Also, the ability of Al(III) to bind to oxygen atoms of polyoxometalates may influence the formation of this species. Species 2 and 3, 1:1 Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\) and 1:2 Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\), respectively, are also found as the majority species in this solution (Figure 2).

The reaction of Eu(III) and A-PW\(_9\)O\(_{34}\)^9\(^-\) in H\(_2\)O, in both 1:1 or 2:1 Eu:A-PW\(_9\)O\(_{34}\)^9\(^-\) stoichiometry, with the addition of TBA\(^+\) or TEA\(^+\), resulted in isolation, by extraction into organic solution, of species 2, Eu(PW\(_{11}\)O\(_{39}\))\(^{2-}\), exclusively. The 31P NMR of the TBA salt (δ, ppm, 5.3, H\(_2\)O; δ, ppm, 9.6, CH\(_3\)CN) was identical with that for a genuine sample of TBA\(_2\)Eu(PW\(_{11}\)O\(_{39}\)) that was prepared directly by two methods (metathesis of the potassium salt of Eu(PW\(_{11}\)O\(_{39}\))\(^{4-}\), prepared by direct reaction of Eu(III) and PW\(_9\)O\(_{34}\)^9\(^-\) or by reaction of Eu(CIO\(_4\)) and TBA\(_2\)H(PW\(_{11}\)O\(_{39}\))\(^{2-}\) in CH\(_3\)CN). The samples of TBA\(_2\)H(EuPW\(_{11}\)O\(_{39}\)) prepared directly have been analyzed by elemental analysis, thus far.

Reaction of PW\(_9\)O\(_{34}\)^9\(^-\) with Eu\(^{3+}\) under Different Stoichiometries. The reaction of Eu\(^{3+}\) and A-PW\(_9\)O\(_{34}\)^9\(^-\) in 0.5:1, 1:1, and 2:1 Eu: POM stoichiometric ratios were studied in NaOAc buffered solution (0.5 M, pH 6.5), and the 31P NMR data are shown in Figure 3. The 31P NMR spectra show that at 0.5:1 Eu:_PW9O34^- stoichiometry, species 3, Eu(PW11O39)^2- dominates while 2, Eu(PW9O34)^2- is an unknown species at 1.99 ppm, possibly due to decomposition of PW9^- in solution. In smaller quantities, at 1:1 Eu:PW9O34^- stoichiometry, three distinct species coexist in solution; according to 31P NMR, these species are 1, [Eu(PW9O34)2(W9O4H2O)3(OH)3]22-, 2, and 3. At 2:1 Eu:PW9O34^-, one species, 2, is observed in the aqueous solution. The same speciation behavior is observed when the experiment is run in water, except that there are a few more small unidentified peaks in the 1:2 Eu:PW9O34^- sample, probably due to decomposition of PW9^- in solution.

Addition of AlCl3 to solutions of 1:1 Eu:PW9O34^- stoichiometry resulted in the small amount Eu(α-2-P2W17O61)31^- (Figure 2). In contrast, upon addition of Al to 2:1 Eu:PW9O34^- stoichiometry, the Eu(PW11O39)^2- species was isolated as crystals in 45% yield; vide infra.

Isolation, Characterization of the Four Complexes Observed in Solution Speciation Studies, and Description

(24) The peak at 1.99 ppm along with other small peaks were observed upon dissolving PW9O34^- alone in NaAc (0.5 M, pH 6.5, 30% D2O).

Scheme 1. Synthetic Strategy for Isolation of Species 1–4 from Eu(III) and Isolation of PW9O34^- of Crystal Structures. From careful analysis of the reactions reported above, we chose appropriate conditions to optimize the syntheses and isolate the four species 1–4 from reactions of PW9O34^- with Eu3+. This is important to confidently identify the species and understand their formation. The procedures are summarized in Scheme 1.

Species 1. The addition of NH4+ at pH 7–9 to a solution of PW9O34^- and Eu3+ results in the isolation of 1 as chunky colorless rectangular blocks. The 31P NMR chemical shifts (Table 3) for isolated crystalline samples of 1 are observed at 31.53 and 23.22 ppm and are dependent on solution conditions; in solution with different countercations present, the resonances are shifted upfield. We have reported the identical structure of the K+ salts of Y(III) and Eu(III) analogues of 1,17 and therefore, complete structural details

Table 3. Multinuclear NMR Data for 1–4

<table>
<thead>
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<th>Table 3. Multinuclear NMR Data for 1–4</th>
<th>31P NMR data (δ, ppm)</th>
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<tr>
<td>[Eu3(PW9O34)3(W9O4H2O)3(OH)3]22^-</td>
<td>31.53, 23.22</td>
</tr>
<tr>
<td>[Eu3(PW9O34)3(W9O4H2O)3(OH)3]22^-</td>
<td>31.53, 23.22</td>
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<td>[Eu3(PW9O34)3(W9O4H2O)3(OH)3]22^-</td>
<td>31.53, 23.22</td>
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<tr>
<td>[Eu3(PW9O34)3(W9O4H2O)3(OH)3]22^-</td>
<td>31.53, 23.22</td>
</tr>
</tbody>
</table>

* Chemical shifts for crystalline sample of 1 in water. The chemical shifts for samples with high concentrations of countercations and other species are found slightly upfield at 28.55 and 22.07 ppm. ** Howell, R. C.; Perez, F. G.; Jain, S.; Horrocks, W. D.; Rheingold, A. L.; Francesconi, L. C. Angew. Chem., Int. Ed. 2001, 40 (21), 4031–4034. These compounds were prepared directly from PW9O34^- for 13C NMR. The 31P NMR for these samples was identical with samples prepared via PW9O34^-.
of the NH₄⁺ salt are in the Supporting Information. Y(III) and Eu(III) also behave similarly with respect to solution speciation of PW₉O₃₄⁶⁻, and thus, the Y(III) analogues are useful for solution characterization using ¹⁸³W NMR because resonances corresponding to all W atoms can be observed. The resonances corresponding to W atoms close to the site of substitution are often not observed in the Eu(III) analogues.

Species 1 forms easily with PW₉O₃₄⁶⁻ at pH 6.5—9 in 76% yield and is uniquely stable in basic solution. From our previous work, multinuclear NMR and luminescence excitation spectra provide evidence that the cluster remains intact in aqueous solution, and the ³¹P NMR data, provided in this study, show that the cluster remains intact under basic conditions and different countercation content. Increasing the pH from 7 to 2.8. As the predominant polyoxotungstate species is the monovacant PW₁₁O₃⁹⁻ at lower pH (Table S1), it is very reasonable that addition of Eu(III) will form Eu(H₂O)₂PW₁₁O₃⁹⁻ especially in this case, with an excess of Eu(III). ³¹P NMR and elemental analysis are consistent with this formulation.

As shown in Figure 5, in the solid-state, 2 is an infinite one-dimensional polymer, similar to the Eu(H₂O)₂(SiW₁₁O₃⁹)⁵⁻ (K⁺ salt) species published by Mialane recently. The structure is similar also to Ce(H₂O)₃(α-SiW₁₁O₃⁹)⁵⁻ that also forms a one-dimensional polymer. Due to the smaller size of Eu³⁺ than Ce³⁺, it is reasonable that only two water molecules are coordinated to the Eu³⁺ rather than three water molecules that are found coordinated to Ce³⁺. The Eu³⁺ is coordinated to four oxygen atoms of the defect site of α-PW₁₁O₃⁹, to two water molecules, and to two neighboring oxygen atoms of PW₁₁O₃⁹ units through terminal oxygen atoms. As observed for most lanthanide complexes of monovacant polyoxometalates, the Eu(III) ion is in a distorted monocapped square antiprism environment. The Al(III) ion sits in the space between the α-PW₁₁O₃⁹ units and shows a weak connection (average Al−O: 2.87(3) Å) to a terminal oxygen atom of an adjacent polyoxometalate. The structure contains 35.3% solvent accessible space. Therefore, it is likely that water is located in this interstitial space as well.

The Eu(III)—O bond lengths to the four oxygen atoms in the Keggin defect are similar (average: 2.371 Å), and the average Eu(III)—O bond lengths to the two neighboring PW₁₁O₃⁹ moieties is longer at 2.453 Å. The Eu−O(H₂O) distance is 2.455 Å within the range of Eu−O(H₂O) bond distances. The interatomic distances between the europium centers are 6.288 Å. The bond lengths for the atoms in the tungsten–oxygen framework of Eu(H₂O)₂(PW₁₁O₃⁹)⁴⁺ compare favorably with other Keggin structures. Although 2 exists as an oligomer in the solid state, it is soluble in aqueous solution and the ³¹P NMR is identical with a sample of Eu(PW₁₁O₃⁹)⁴⁺, suggesting that the polymer dissociates into the monomeric form.

Species 3. Addition of Cs⁺ to PW₉O₃₄⁶⁻ and Eu³⁺ (1:1 stoichiometry) at pH 7 results in 3 as small colorless thick rectangular crystals. The crystal structure, Figure 6, shows that this species is a 1:2 Eu:PW₁₁O₃⁹⁻ complex, originally

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isolated by Peacock and Weakley.\textsuperscript{28} The \textsuperscript{31}P NMR shows one peak at 0.34 ppm that is identical with the 1:2 Eu(PW\textsubscript{11}O\textsubscript{39})\textsuperscript{2−} complex, prepared directly. The \textsuperscript{183}W NMR of 1:2 analogue Y(PW\textsubscript{11}O\textsubscript{39})\textsubscript{2} shows 11 peaks\textsuperscript{11,29} (Table 3), consistent with the C\textsubscript{2} structure revealed by X-ray crystallography. All 11 Cs\textsuperscript{+} ions were located and surround the Eu(PW\textsubscript{11}O\textsubscript{39})\textsubscript{2} species (Figure S7), with 1 Cs\textsuperscript{+} ion (C7) located in an interactive distance of 3.2 Å to both PW\textsubscript{11}O\textsubscript{39} lobes.

\textbf{Species 4.} Addition of Al\textsuperscript{3+} into the solution of PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9−} + Eu\textsuperscript{3+} (1:1 stoichiometry) results in colorless chunky prisms of 4 in 53% yield. X-ray crystallography reveals the dimeric structure \{Eu\textsubscript{2}H\textsubscript{2}O\textsubscript{3}(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\}\textsubscript{2}\textsuperscript{14−} (Figure 6) that we have observed before from the reaction of excess Eu(III) with α-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61}\textsuperscript{10−} in a KCl medium.\textsuperscript{14} However, in this case, the Al(III) serves as a counterion and forms weak connections with the terminal W−O bonds of adjacent \{Eu\textsubscript{2}H\textsubscript{2}O\textsubscript{3}(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\}\textsubscript{2}\textsuperscript{14−} units, seen in Figures 6 and 7.

The extended structure is composed of the anions of 4 linked together by surface bound Al\textsuperscript{3+} cations. The Al\textsuperscript{3+} ions, in a distorted trigonal prismatic coordination environment, bind to terminal oxygen atoms of two dimers (average Al−O distances: 2.77(5) Å) giving rise to chains along the crystallographic a axis (Figure 6), while, down the c axis, Al\textsuperscript{3+} links three \{Eu\textsubscript{2}H\textsubscript{2}O\textsubscript{3}(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\}\textsubscript{2}\textsuperscript{14−} units giving rise to the formation of discrete channels forming a porous 3D structure (pore size: 17 Å × 6 Å; Figure 7). This compound is less soluble in water than anions of similar size, probably due to the covalent bonding of the Eu\textsuperscript{3+} to a terminal oxygen of an adjacent polyoxoanion and to the surface bonding of the Al\textsuperscript{3+} cations. Both \textsuperscript{31}P and \textsuperscript{183}W NMR show good evidence to support the notion that the dimeric complex \{Eu\textsubscript{2}H\textsubscript{2}O\textsubscript{3}(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\}\textsubscript{2}\textsuperscript{14−} in the solid state dissociates in aqueous solution to form the monomeric form Eu(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\textsuperscript{7−} (Table 3).

\textbf{Discussion}

Three parameters, pH, countercation, and stoichiometry, have an important impact on the aqueous speciation of PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9−} and Eu\textsuperscript{3+}. The pH influences the speciation of the polyoxometalate PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9−}, alone, to form primarily PW\textsubscript{11}O\textsubscript{39}\textsuperscript{7−} ligand\textsuperscript{22} and decomposition products (Table S1) to which the Eu(III) can bind. The counterions modulate the reactivity and may be instrumental in anchoring polyoxometalate units together for assembling larger structures, such as the “sandwich” complex Eu(PW\textsubscript{11}O\textsubscript{39})\textsubscript{2}−, 3, and the hydroxido/oxo cluster, 1.\textsuperscript{30}

Under low pH conditions, the high acid content stabilizes the PW\textsubscript{11}O\textsubscript{39}\textsuperscript{7−} ligand as well as species 2, Eu(PW\textsubscript{11}O\textsubscript{39})\textsuperscript{14+}, the 1:1 species. As the base is increased, and proton competition with the PW\textsubscript{11}O\textsubscript{39}\textsuperscript{7−} ligand and Eu(PW\textsubscript{11}O\textsubscript{39})\textsuperscript{14+} (2) decreases, the concentration of the 1:2 complex, Eu(PW\textsubscript{11}O\textsubscript{39})\textsuperscript{3−} (3), is increased. Eventually at high pH, where PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9−} decomposes to PW\textsubscript{11}O\textsubscript{39}\textsuperscript{7−}, lower nuclearity phosphotungstates, as well as WO\textsubscript{2}− species 3 and 1, become major components of the solution, as seen in Figures 1, S1, and S2. Species 1 is comprised of the PW\textsubscript{11}O\textsubscript{39}\textsuperscript{11−} fragment and monotungstate units bound to Eu(III).

Cations have a significant effect on the speciation of PW\textsubscript{9}O\textsubscript{34}\textsuperscript{9−} and Eu(III). The hypothesis that large, less extensively hydrated alkali metal cations bind to the surfaces of the polyoxometalates and “anchor” the POM units in place for assembly into larger structures, such as the 1:2 sandwich structures, has been put forward.\textsuperscript{31,32} Ion pairing of large cations (Rb+) to POM surfaces was proposed by Kirby and Baker in a study to understand the solution “syn” structure of Th(α-2-P\textsubscript{2}W\textsubscript{17}O\textsubscript{61})\textsubscript{2}−.\textsuperscript{16−31} The formation of a 1:2 K+: SiW\textsubscript{10}O\textsubscript{39} species in a Cs\textsuperscript{+} environment has been reported recently by Laronze.\textsuperscript{32} In this latter study, similar to ours, treatment of the trivacant A-α-SiW\textsubscript{9}O\textsubscript{34}\textsuperscript{10−} with K\textsuperscript{+} and

\textsuperscript{(29)} Fedotov, M. A.; Pertsikov, B. Z.; Danovich, D. K. Polyhedron 1990, 9, 1249−1256.
\textsuperscript{(30)} We have also observed Eu(III) and Eu(III)−OH−Eu(III) dimeric units serving as countercations. These moieties bind to terminal W=O bonds of polyoxometalates: Zhang, C.; Howell, R. C.; Francesconi, L. C. Manuscript in preparation, 2004.
excess Cs⁺ results in isolation of Cs₁₅K(SiW₁₁O₃₉)₂, where K⁺ is bound in the cavity. This molecule is similar to 3, with cubic coordination about the K⁺ rather than square antiprismatic coordination geometry that is prevalent with the lanthanides. They propose, according to the solid-state crystal structure, that the Cs⁺ anchors the SiW₁₁O₃₉⁻ species in place for the formation of the 1:2 K⁺:POM complex. To substantiate this proposal, the solid-state structure of Cs₁₅K(SiW₁₁O₃₉)₂ shows that three Cs⁺ ions are bound to terminal oxygen atoms of each SiW₁₁O₃₉⁻ unit (with Cs−O distances of ca. 3.2 Å) perhaps stabilizing the K(SiW₁₁O₃₉)₁₅-solide state structure. The molecule dissociates in aqueous solution.

Similarly, we have observed that in aqueous solution K⁺ and Cs⁺ promote the formation of the 1:2 Eu(PW₁₁O₃₉)₁₁⁻ species. The formation of species 3, 1:2 Eu(PW₁₁O₃₉)₁₁⁻, is in significant concentration is observed at low pH (4.5) for solutions containing K⁺ buffer (Figure S2). In contrast 3 appears only at higher pH (6.5) with Li⁺- and Na⁺-containing buffers and in very low quantities (Figures 2 and S1). When Cs⁺ is employed as a counterion, 3 is the only species formed (Figure 2). These observations are consistent with ion pairing of K⁺ and Cs⁺ to the PW₁₁O₃₉ lobes, thus anchoring the PW₁₁O₃₉ lobes in position to form the 1:2 complex.

Considering the solid-state structure of Cs₁₁Eu(PW₁₁O₃₉)₂, one Cs⁺ (Cs7) is in close contact with the terminal W−O and bridging W−O oxygen atoms (3.2 Å) from both lobes and may be a prototype as to the role large cations have in stabilizing this structure. The remaining 10 Cs⁺ ions surround the sandwich complex. The Cs⁺ ions may insulate and stabilize the sandwich Eu(PW₁₁O₃₉)₂ ions in the crystal. Similar interaction of Cs⁺ ions with the metal oxygen surfaces may stabilize this structure in solution as well.

Ion pairing of alkali metal cations to polyoxometalates has been quantitated in recent studies. The larger and less extensively solvated alkali-metal cations form smaller (more neutral conditions and with Na⁺, K⁺, and NH₄⁺, PW₁₁O₃₉⁻ and lower nuclearity phosphotungstates (such as PW₁₀O₃₈⁻) can be trapped by the excess Eu(III) ions and monotungstate groups to form Eu₈ hydroxo/oxo cluster 1. The 2:1 Eu:PW₉O₃₄⁻ stoichiometry provides an excess of Eu(III) ions to promote formation of Eu(PW₁₁O₃₉)₁₁⁻, 3. With more Eu(III) present, as in 1:1 stoichiometry, under neutral conditions and with Na⁺, K⁺, and NH₄⁺, PW₁₁O₃₉⁻ and lower nuclearity phosphotungstates (such as PW₁₀O₃₈⁻) can be trapped by the excess Eu(III) ions and monotungstate groups to form Eu₈ hydroxo/oxo cluster 1. The 2:1 Eu:PW₉O₃₄⁻ stoichiometry provides an excess of Eu(III) ions to promote formation of Eu(PW₁₁O₃₉)₁₁⁻, 2.

The stoichiometry of Eu and PW₉O₃₄⁻ play an important role in the speciation of Eu polyoxometalates, as shown in Figure 3. In an excess of PW₉O₃₄⁻ at pH 7, decomposition to primarily PW₁₁O₃₉⁻ with some unidentified P-containing products and phosphate as well as tungstate (Table S1) results in formation of both Eu(PW₁₁O₃₉)₁₁⁻, 3, and Eu(PW₁₁O₃₉)₁₄⁻. 2. With more Eu(III) present, as in 1:1 stoichiometry, under neutral conditions and with Na⁺, K⁺, and NH₄⁺, PW₁₁O₃₉⁻ and lower nuclearity phosphotungstates (such as PW₁₀O₃₈⁻) can be trapped by the excess Eu(III) ions and monotungstate groups to form Eu₈ hydroxo/oxo cluster 1. The 2:1 Eu:PW₉O₃₄⁻ stoichiometry provides an excess of Eu(III) ions to promote formation of Eu(PW₁₁O₃₉)₁₁⁻, 2.

The crystal structures of species 2 and 4, shown in Figures 5−7, are instructive to examine the potential interaction of oxophilic Al(III) cations with polyoxometalate surfaces. Species 2 and 4 show weak interactions of the Al(III) ions with terminal oxygen atoms of the polyoxometalate. The interaction, although weak, allows connection of the polyoxometalates and buildup of a porous material, as seen in species 4.

We have investigated only the effects of pH and counterion in this study. However, other ions also can serve as templates or structure-directing groups. This was seen clearly in a recent report by Hill wherein the addition of carbonate to an aqueous solution of YIIICl₃ followed by addition of Na₈HA-α-PW₉O₃₄ and workup forms 33% of a new complex that consists of a Y₃(PW₉O₃₄)₁₀⁻ sandwich complex wherein CO₃²⁻ anchors the Y(III) ions and the two POM units. We find that species 1 forms without the addition of CO₃²⁻. In this case, carbonate appears to template
the formation of this sandwich complex. The structure is reminiscent of the Cu₃(PW₆O₁₉)₂ templated by nitrate anion.³⁷

We employ multinuclear NMR coupled with X-ray crystallography in these studies; these techniques allow us to understand the speciation unambiguously. We and others have also used luminescence of Eu(III) for the study of speciation of lanthanide polyoxometalates.⁴,¹²,¹⁴,¹⁷ Eu(III) luminescence is very informative to identify the number of species in solution, the coordination environment, and the number of bound water molecules. Luminescence studies (excitation, emission spectra, and luminescence lifetimes) of the 1:1 and 1:2 Eu:(PW₁₁O₃⁹)₇⁻ species have been reported.³⁸⁻⁴¹ These studies show that the 1:1 species has four bound water molecules, while the 1:2 species is not bound to water molecules. These are consistent with our structural and solution data, reported herein.

Conclusion

We have focused this study on understanding speciation chemistry of lanthanide complexes of the trivacant polyoxometalate PW₉O₃⁴⁻ in aqueous solution. The A-α-PW₉O₃⁴⁻ has 6 basic oxygen atoms that are available for bonding. The reaction products are highly dependent on the pH, countercation, and stoichiometry between Eu(III) and PW₉O₃⁴⁻. The four species that have been observed in solution speciation studies have been synthesized and thoroughly characterized in the solid state and in solution. The pH has a profound effect on the speciation; at low pH, (PW₁₁O₃⁹)₇⁻ predominates and the 1:1 Eu(PW₁₁O₃⁹)₁⁻, 2, forms. As the pH is increased, the 1:2 Weakley complex, Eu(PW₁₁O₃⁹)₁¹⁻ species, 3, and a Eu₈ hydroxo/oxo cluster, 1, forms. The countercations modulate this effect. Large countercations, such as K⁺ and Cs⁺, with low hydrodynamic radii (compared to Li⁺ and Na⁺) promote the formation of 1:2 Eu(PW₁₁O₃⁹)₄⁻ species, 3, and 1, at low pH values. We postulate that these large countercations can interact with the polyoxometalate surface and position one Eu(PW₁₁O₃⁹)₄⁻ unit for binding by a second (PW₁₁O₃⁹)₇⁻ moiety. The formation of {Eu(H₂O)₃-(α-2-P₂W₁₇O₆₁)}₂, 4, with Al(III) ions bound to terminal W=O bonds is observed when Al(III) is employed as a countercation.

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Supporting Information Available: Tables S1 and S2; ³¹P NMR chemical shifts for speciation of PW₉O₃⁴⁻ as a function of pH, buffer, and countercation and bond valence sum calculations; Figures S1–S7; and CIF files for the X-ray crystal structures of species 1–4. This material is available free of charge via the Internet at http://pubs.acs.org.

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