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Articles

Lanthanide Complexes of the α-1 Isomer of the $[P_2W_{17}O_{61}]^{10-}$ Heteropolytungstate: Preparation, Stoichiometry, and Structural Characterization by ^{183}W and ^{31}P NMR Spectroscopy and Europium(III) Luminescence Spectroscopy

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The α-1 and α-2 $[P_2W_{17}O_{61}]^{10-}$ isomers, derivatives of the Wells−Dawson molecule, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, may be useful ligands for stabilizing high-valent metal ions and lanthanides and actinides. However, the potential utility of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand has not been realized. Specifically, for the lanthanides, the stoichiometry, structure, and purity of the lanthanide complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer are ambiguous. We have prepared lanthanide (Ln) complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer in ≥98% isomeric purity, according to ^{31}P NMR data. ^{183}W NMR data clearly showed, for the first time, that the C_1 symmetry of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ lanthanide complexes was maintained in solution. We determined the stoichiometry of the lanthanide complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer in solution by two different methods: a complexometric titration method and excited state lifetime measurements and luminescence titrations for the europium(III) analogue. All experiments show a 1:1 Ln:$[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ ratio. The ^{31}P NMR data showed that the lanthanides with smaller ionic radii (higher charge-size ratio) form stable complexes, even surviving crystallization from hot water. On the other hand, the lanthanum analogues were not stable in solutions of high lithium content. The tetrabutylammonium salt of the $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ complex showed ≥98% isomeric purity and the C_1 symmetry required for a derivative of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$. Also the tetrabutylammonium cation stabilized the $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ complex; a mixed tetrabutylammonium, lithium salt was stable in water for weeks according to ^{31}P NMR spectroscopy.

Introduction

The α-1 and α-2 $[P_2W_{17}O_{61}]^{10-}$ isomers, derivatives of the Wells−Dawson molecule, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ (Figure 1), may be useful ligands for stabilizing high-valent metal ions and lanthanides (Ln) and actinides. Well-characterized, stable, water soluble complexants may find a number of applications in biochemistry and medicine, catalysis, separation of lanthanides and high-valent actinide ions from nuclear waste streams, and stabilization of radioactive lanthanides for radiotherapy. In the medicinal area, for example, a number of families of polyoxoanions have been shown to interact with enzymes specifically, suggesting that these compounds may be valuable for study of the structure and function of enzymes and proteins.[1,2] Polyoxoanions, including derivatives of the $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, have also been noted for antiviral activity.[3] In the area of catalysis, while there are few reports of derivatives of the Wells−Dawson molecule, the "Keggin" derivatives are well-known thermal catalysts and, recently, photocatalysts, for oxidative transformation of various organic molecules in solution.[4a−f] Transition metal derivatives of isomerically pure $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand are probably among the best characterized polyoxoanion species to be subjected to oxidation catalysis studies.[4g] The $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer is chiral, and metal

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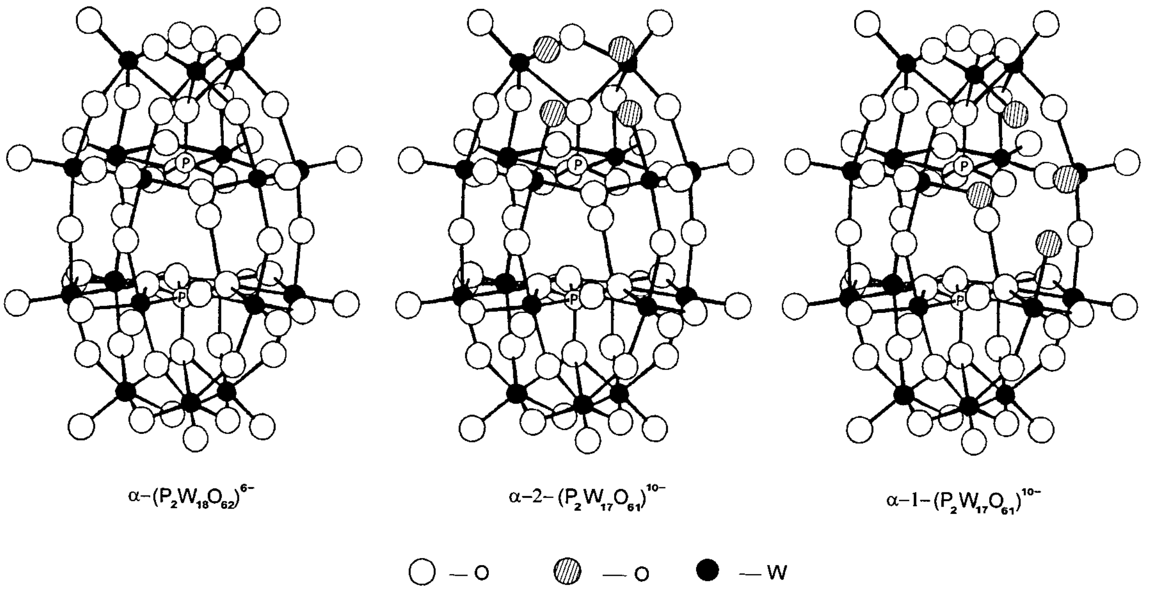

Figure 1. The parent [α-$P_2W_{18}O_{62}$]$^{6-}$ Wells−Dawson structure and the lacunary [α2-$P_2W_{17}O_{61}$]$^{10-}$ isomer and [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomers. The filled circles represent tungsten atoms, the open circles represent oxygen atoms, and the hatched circles represent oxygen atoms available for bonding to lanthanide ions.

complexes of this ligand could possibly offer opportunities for development of chiral catalysts.

Another potential use of the α-1 and α-2 [$P_2W_{17}O_{61}$]$^{10-}$ isomers may be found in nuclear waste processing. The trivalent lanthanides as well as Am(III) and Cm(III) bind to the monovacant α-2 Wells−Dawson anion.[5,6] The [α2-$P_2W_{17}O_{61}$]$^{10-}$ anion appears to provide an oxophilic chemical environment and show preference for small tetravalent lanthanide and actinide ions. Oxidation of Ce(III) and the difficult one-electron oxidations of trivalent Pr, Tb, Am, Cm, Bk, and Cf in aqueous solution appear to be facilitated by complexation with the lacunary heteropolyanion [α2-$P_2W_{17}O_{61}$]$^{10-}$.[6−10] A method was developed to separate U(IV) from Pu using complexation to [α2-$P_2W_{17}O_{61}$]$^{10-}$.[11]

Polyoxometalates and similar ligands, such as condensed phosphates, aluminates, and silicates, may play a role in development of new ligands for complexation of radiolanthanides for radiotherapy. A number of isotopes of the lanthanides provide suitable radionuclides for therapy. For example, ^{153}Sm has excellent physical properties for radiotherapeutic applications, and the phosphonate complexes of ^{153}Sm are being utilized in the radiopharmaceutical ^{153}Sm-ethylenediaminetetramethylenephosphonic acid (EDTMP) for palliation of pain from metastatic bone cancer.[12] ^{153}Sm and ^{90}Y, conjugated to antibodies via derivatized aminocarboxylate ligands, are presently being tested in animal models.[13] Aminosilicates containing the β-emitter ^{166}Ho have been tested for tumor cell killing effectiveness with the BT-20 human mammary carcinoma cell line.[14] Recently, in a phase I/II trial, antitumor effects were noted against chemotherapy-resistant ovarian cancer and resulted in prolonged disease-free survival of patients with a ^{177}Lu-labeled monoclonal antibody.[15] It appears that the entire lanthanide series may provide useful isotopes for a variety of radiotherapeutic applications, and new ligand development is warranted.

Stability constant measurements of Ce(III) and Ce(IV)[16] complexes of both the α-1 and α-2 [$P_2W_{17}O_{61}$]$^{10-}$ isomers show that the ligands form Ce(IV) complexes with thermodynamic stability constants (log β_2) in the range of the well-known amino carboxylate chelating agents, for example EDTA and DTPA. The stability constants (log β_2) for the Ce(III) complexes of both the α-1 and α-2 [$P_2W_{17}O_{61}$]$^{10-}$ isomers are about 1 order of magnitude less, suggesting that these polyoxoanions may be excellent ligands for complexing high charge/size transition metals, lanthanides, and actinides. However, in the case of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ ligand, the potential utility of this ligand has not been realized. Specifically, for the lanthanides, the stoichiometry of the Ln complexes of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer is ambiguous.[16,17] To evaluate this ligand as a complexant for rare

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earth and transuranic ions, it is necessary to understand the stoichiometry and stabilities of the lanthanide and actinide complexes. It is also necessary to verify their structures as derivatives of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer and to validate the purities of the complexes.

In this report, we unambiguously prove the stoichiometry of lanthanide (III) complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer using two approaches. We developed a method employing standardized buffered polyoxoanion solutions and competitive titrations with EDTA, monitored by ^{31}P NMR spectroscopy for determination of the stoichiometry of the Lu^{3+} analogue. We used luminescence excitation spectroscopy to determine stoichiometry of the Eu^{3+} complex. We also prove the structure, examine the purity, and assess the stability of a variety of lanthanide complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer in solution as the potassium, lithium, sodium, and tetrabutylammonium salts with the use of multinuclear, specifically ^{183}W and ^{31}P, NMR spectroscopy.

Key Prior Knowledge

Lanthanide (Ln) complexes of the lacunary $[P_2W_{17}O_{61}]^{10-}$ heteropolytungstate were first reported in 1971 by Peacock and Weakley.[18] In that report the 1:2 Ln:tungstates, $K_{17}[Ln(P_2W_{17}O_{61})_2]$ complexes, prepared by in situ degradation of the parent $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ under neutral to basic aqueous conditions and reaction with Ln(III) salts, were characterized by elemental analysis and UV (and visible for Ce(III)) spectroscopy. Subsequent work showed that the lanthanide complexes prepared in such a fashion contained the $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer.[19] The $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, Figure 1, is obtained by base degradation of the parent Wells–Dawson molecule; effectively, removal of a $[WO]^{4+}$ unit from a "cap" WO_6 polyhedron of the parent $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ results in the defect or lacunary structure of C_s symmetry. The lanthanide ion binds to the four oxygen atoms of two defect oxoanions to form the 1:2 sandwich complex. The 1:1 Ln:$[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ complexes were observed by absorbance spectroscopy using Ce(III) in that first report and subsequently observed by electrochemical[9] and NMR techniques,[19b,c] but have not been isolated.

In contrast, there have been very few reports of metal complexes of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$, probably due to the instability of the α-1 lacunary isomer. The lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, C_1 symmetry, shown in Figure 1, can be viewed as removal of a WO unit from a "belt" WO_6 polyhedron of the parent $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$.[20,21] The $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ species is formed concurrently with $[H_2P_2W_{12}O_{48}]^{12-}$ upon the degradation of $[P_2W_{18}O_{62}]^{6-}$. In aqueous solution at $pH > 5$, isomerization to $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ occurs, and under acidic conditions ($<$pH $= 4.3$), decomposition to the parent $[P_2W_{18}O_{62}]^{6-}$ occurs.[20,22] Treatment at high temperatures induces isomerization also. The stabilization of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer under conditions of high lithium content has been reported.[20,21] Although the lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ species has been isolated by precipitation, as a species with the formulation $K_9Li[\alpha1\text{-}P_2W_{17}O_{61}]$, the location and function of the lithium ion have not been demonstrated by crystallography or by spectroscopic techniques. The lacunary $K_9Li[\alpha1\text{-}P_2W_{17}O_{61}]$ species has been characterized by ^{31}P NMR spectroscopy, elemental analysis of the precipitated but not crystallized solid, and polarographic techniques.[20,21] We also reported the first structural characterization of the lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, isolated as the lithium salt by ^{183}W NMR spectroscopy.[23]

Crystallographic data are often difficult to obtain for large oxoanion species, and probably due to rapid isomerization and instability of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, only two X-ray structures of metal complexes of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ have been reported in a very recent review article.[24] These two structures are $U(\alpha2\text{-}P_2W_{17}O_{61})(\alpha1\text{-}P_2W_{17}O_{61})^{16-}$, where the ligands are in a cis conformation, and $U(\alpha1\text{-}P_2W_{17}O_{61})_2{}^{16-}$, where the ligands are disposed in a trans conformation. There has been limited solution multinuclear NMR spectroscopic data for $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes.[23,25,26] The first direct proof of the structure of a transition metal complex of the α-1 isomer was provided by Jorris et al. in the report of the ^{183}W NMR spectrum of the $[\alpha2\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ species, containing ca. 17% of the α-1 isomer as an impurity.[25] We have reported recently the preparation, isolation, and stability of α-1 and α-2 isomers of $[Zn(H_2O)P_2W_{17}O_{61}]^{8-}$, each in ≥98% purity, and characterization by both ^{31}P and ^{183}W NMR spectroscopy.[23] Harmalker reported the preparation and characterization by ^{31}P, ^{51}V NMR and EPR spectroscopy, of both the α-1 and α-2 isomers of $[VO(P_2W_{17}O_{61})]^{7-}$.[26a] While the ESR data were similar for both the α-1 and α-2 isomers, the ^{31}P, ^{51}V NMR data demonstrated incorporation into the appropriate sites. Massart et al. report the ^{31}P NMR data for Mo^{VI} incorporation into the α-1 site.[26b]

The stoichiometry of lanthanide (Ln) complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer is ambiguous. The data and interpretations are inconsistent between the studies of two groups,[16,17] and certain preparations are irreproducible in our hands.[17a] Qu et al.[17] reported the preparation and elemental analysis for a series of lanthanide ions complexed to $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$. Elemental analysis of both the recrystallized tetrabutylammonium salts and unrecrystallized potassium salts are consistent with the 1:2 formulation, $[Ln(\alpha1\text{-}P_2W_{17}O_{61})_2]^{17-}$, for all of the lanthanides. They report cyclic voltammetry data for selected lanthanide ions and ^{31}P NMR data for the lanthanum analogue. Their spectrophotometric titration studies with Ce^{3+} (buffer conditions not reported) show the formation of the 1:2 sandwich complex only. On the other hand, spectrophotometric studies with Ce^{3+} and $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ in sodium acetate buffer, conducted by Ciabrini and Contant,[16] detect the formation of both the 1:1 complex and the 1:2 sandwich complex. For Ce^{3+}, the conditional stability constants, determined by spectrophotometric techniques in 1 M $LiNO_3$, are slightly higher for the 1:2 complexes ($\log \beta_1 = 6.5$ and $\log \beta_2 = 8.1$). The 1:1 Ce(III):$[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ species was isolated by precipitation, not recrystallization, and characterized by visible spectroscopy,

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infrared spectroscopy, and elemental analysis. It is not clear that the 1:2 Ce(III):$[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ was isolated cleanly. The authors state that the 1:2 complex does not form quantitatively unless a high concentration of sodium ions and excess ligand are present, and this species may be unstable, due to steric considerations. The difference between the 1:1 and 1:2 complexes, shown by their IR and absorption data, is very subtle. The conditional stability constants, determined from polarographic studies in 1 M $LiNO_3$, for the 1:1 and 1:2 Ce(IV) $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes ($\log \beta_1 = 21$ and $\log \beta_2 = 27$) indicate that both Ce(IV) species are 1 order of magnitude more stable than the Ce(III) complexes, suggesting a high charge: size ratio requirement for the most stable complexes. The techniques used in both of these studies do not provide direct structural proof for the isolation of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer and do not unambiguously prove the stoichiometry and isomeric purity of the compounds.

The goals of our study were to prepare high-purity lanthanide complexes of the unusual $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, to completely understand the stoichiometry and stabilities of lanthanide(III) complexes, encompassing the entire lanthanide series, and also to verify their structure as derivatives of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, since this ligand may be quite useful for some of the applications mentioned.

Experimental Section

General Comments. All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Distilled, deionized water was used throughout. The molecule $K_9Li[\alpha1\text{-}P_2W_{17}O_{61}]$ was prepared following the method of Contant.[20,21] The molecules $K_6[P_2W_{18}O_{62}]$ and $K_{12}[H_2P_2W_{12}O_{48}]$ ("Wells–Dawson" ion) were prepared according to literature methods.[27] Infrared spectra were recorded from KBr pellets on a Perkin-Elmer 1625 spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory at the University of Illinois, Urbana, IL, and E & R Microanalytical Laboratory, Inc., Corona, NY. A standard solution of EDTA (0.0993 M) was purchased from Fisher. The aqueous solutions of the lanthanide metals, used for NMR titrations, were standardized by complexometric titration with EDTA using xylenol orange as an indicator. An aqueous solution of $CoCl_2$, buffered at pH = 5 with sodium acetate, was standardized with EDTA.[28] Preparation and standardization of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer for titrations is described below.

Collection of NMR Data. NMR spectra were obtained on a JEOL GX-400 spectrometer. ^{31}P spectra at 161.8 MHz were acquired using either a 10 mm broad band probe or the broad band decoupler coil of a 5 mm reverse detection probe. ^{183}W spectra at 16.7 MHz were recorded utilizing a 10 mm low-frequency broadband probe. Typical acquisition parameters for ^{31}P spectra included the following: spectral width, 10 000 Hz; acquisition time, 0.8 s; pulse delay, 1 s; pulse width, 15 μs (50° tip angle). From 50 to 500 scans were required. 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. The temperature was controlled to ± 0.2 deg. ^{31}P spectra were referenced to a H_3PO_4 standard in D_2O which has a 0.67 ppm upfield chemical shift relative to 85% H_3PO_4, and ^{183}W spectra were referenced to 2.0 M Na_2WO_4. For both ^{31}P and ^{183}W chemical shifts, the convention used is that the more negative chemical shifts denote upfield resonances.

Preparation of Lanthanide Complexes of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ Isomer. Although isolation of solid samples of lanthanide derivatives of "cage" polyoxoanions by other workers involve 1:2 Ln:oxoanion stoichiometry, we reacted the Ln:$K_9Li[\alpha1\text{-}P_2W_{17}O_{61}]$ reagents in 1:1 as well as 1:2 ratios. The solids isolated were checked by ^{31}P NMR spectroscopy to assess the isomeric purity of the samples. The solids were then recrystallized from hot water, and the ^{31}P NMR was checked after recrystallization. The general method for the preparation of the potassium salts of lanthanide $[\alpha1\text{-}(P_2W_{17}O_{61})]^{10-}$ compounds is given below.

To 10 g of $K_9Li[\alpha1\text{-}P_2W_{17}O_{61}]$, suspended in 100 mL of lithium acetate buffer at pH = 4.7, was added dropwise 3 mL (3 mmol) (1.5 mL (1.5 mmol) for the 1:2 compounds) of an aqueous 1 M $LnCl_3$ solution dropwise; the solution was then stirred for a few minutes. The pH of the resulting solution was 4.4–4.5. Potassium chloride (7 g) was added to precipitate a solid. The resulting suspension was cooled in the freezer for 2 h and then filtered. Recrystallization was accomplished by dissolving the solid in the minimum amount of hot water at 60–70 °C. (For example, 8.6 g of the 1:1 Lu:$[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complex was suspended in ca. 15 mL of hot water; 10 mL of hot water was added dropwise until the solution cleared.) The solution was gravity filtered while hot, and the clear, gray colored solution was placed into the freezer for 30 min. The resulting white solid was filtered and air-dried in the hood. The La, Yb, Eu, Lu, and Y analogues were prepared in this fashion. Selected analytical data is given in Table 1.

Ion Exchange of the Lanthanide Complexes of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$. To convert the potassium salts to lithium or sodium salts for preparation of concentrated aqueous solutions for ^{183}W NMR spectroscopy, ion-exchange chromatography using Biorad AG50W-X2 in the Li^+ or Na^+ form was used. The resin, originally in the H^+ form, was converted to the Li^+ or Na^+ form using the following procedure. Two bed volumes of lithium acetate or sodium acetate buffer, 0.5 M, pH = 5, were loaded onto the resin with a flow rate of 2 mL/min. The resin was soaked in a third bed volume for 10 h, followed by washing with 2 bed volumes of water.

About 0.6 mmol of the complexes formulated as the 1:1 $[Ln(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ or 1:2 $[Ln(\alpha1\text{-}P_2W_{17}O_{61})_2]^{17-}$ was dissolved in ca. 1000 mL of water to obtain a clear solution. The solution was loaded onto a Biorad AG-50W-X2 cation-exchange column in the Li^+ or Na^+ form and eluted with water at a flow rate of 4 mL/min. The resulting clear solution was rotary evaporated at ca. 50 °C to give a solid. For the NMR, the solid was dissolved in 2.5 mL of D_2O. The ^{31}P NMR of the lithium salts matched that of the potassium salts, verifying that the species had not isomerized or decomposed during the ion-exchange procedure.

Conversion of potassium salts to lithium salts was also achieved by metathesis using $LiClO_4$. A typical example of the ion-exchange procedure is described for $K_7[La(\alpha1\text{-}P_2W_{17}O_{61})]$ as follows. $K_7[La(\alpha1\text{-}P_2W_{17}O_{61})]$ (2.9 g, 0.6 mmol) was added as a solid to $LiClO_4$ (0.64 g, 6 mmol), dissolved in 2.5 mL of D_2O. The mixture was stirred for a few minutes and centrifuged and filtered to remove $KClO_4$.

Preparation of the Tetrabutylammonium Salt of $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$. This procedure follows the method developed by Finke et al. for substituted $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ complexes.[29] It is very important to maintain the pH in the range 4.5–5.2 to preserve the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer; therefore the procedure was carried out with constant monitoring of the pH using a pH meter. A sample (5 g, 1.01 mmol)) of the potassium salt of $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ was dissolved in 150 mL of water. A solution of 0.18 M H_2SO_4 was used to adjust and maintain the pH in the range 4.5–5.2. To this clear, colorless solution was added tetrabutylammonium chloride (2.29 g, 7.09 mmol) with stirring, while the pH was maintained in the range 4.5–5.2 with 0.18 M H_2SO_4. The solution was treated with 34 mL of acetonitrile and 67 mL of methylene chloride. Upon shaking, two layers separated. The organic (bottom) layer was collected and rotary evaporated at 40 °C. Methylene chloride, 5 mL, was added to dissolve the solid. Diethyl ether (25 mL) was added to precipitate a solid, which was then triturated with ether and dried under vacuum. The compound was recrystallized from acetonitrile–ether. ^{31}P NMR data of the nonrecrystallized compound, taken in D_2O to compare the chemical shifts for the other $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ derivatives, confirm the >98% isomeric purity. The recrystallized $[N(C_4H_9)_4]_6H[Lu(\alpha1\text{-}P_2W_{17}O_{61})]$ was not soluble in water. To obtain ^{31}P NMR data in water and ^{183}W NMR data, the sample was

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Table 1. Elemental Analysis and Mass Spectrometry Data for Selected Lanthanide (α1-$P_2W_{17}O_{61}$] Polyoxoanions

	obsd	calcd	mass spectrometry
$K_7[Lu(\alpha 1\text{-}P_2W_{17}O_{61})]\cdot 22H_2O$[a]			
K	4.96	5.47	FAB^-:
P	1.24	1.24	4170.6 $\{K_2H_2Lu[\alpha\text{-}P_2W_{17}O_{61}]\}(-O,-WO_3)$
W	60.70	62.41	
H	0.89	0.88	
Lu	2.94	3.49	
O (by difference)	29.27	26.52	
% H_2O	8.1	7.9	
$K_7[Yb(\alpha 1\text{-}P_2W_{17}O_{61})]\cdot 19H_2O$[a]			
K	5.11	5.53	
P	1.22	1.25	
W	62.63	63.11	
H	0.74	0.77	
Yb	3.37	3.49	
O (by difference)	26.93	25.85	
% H_2O	6.48	6.92	
$K_7[La(\alpha 1\text{-}P_2W_{17}O_{61})]\cdot 13H_2O$[a]			
K	5.22	5.69	
P	1.29	1.29	
W	64.91	64.98	
H	0.56	0.54	
La	2.37	2.89	
O (by difference)	25.65	24.61	
% H_2O	4.87	4.59	
$K_7[La(\alpha 1\text{-}P_2W_{17}O_{61})]\cdot 22H_2O$ (Separate Preparation)[b]			
K	5.45	5.49	
P	1.14	1.24	
W	63.15	62.86	
La	2.57	2.79	
% H_2O	7.31	7.96	
$(N(C_4H_9)_4)_6H[Lu(\alpha\text{-}P_2W_{17}O_{61})]\cdot 5H_2O$			
C	20.44[a](21.78)[b]	19.36	5292.6 $(N(C_4H_9)_4)_4H_2[Lu(\alpha\text{-}P_2W_{17}O_{60})]^-$
H	4.01 (4.24)	3.82	5050.3 $(N(C_4H_9)_4)_3H_2[Lu(\alpha\text{-}P_2W_{17}O_{60})]^-$
N	1.49 (1.60)	1.41	4973.3 $(N(C_4H_9)_4)_2H_3[Lu(\alpha\text{-}P_2W_{17}O_{59})]^-$
W	53.08 (50.04)	52.29	
P	0.94 (1.01)	1.04	electrospray:
Lu	3.99 (2.74)	2.92	2654.7 $\{[Lu(P_2W_{17}O_{61})]TBA_4H\}^{2-}$
O	16.05 (18.59)	19.16	1689.0 $\{[Lu(P_2W_{17}O_{61})]TBA_3H\}^{3-}$
(by difference)			1206.2 $\{[Lu(P_2W_{17}O_{61})]TBA_2H\}^{4-}$
% H_2O	1.37	1.51	916.4 $\{[Lu(P_2W_{17}O_{61})]TBAH\}^{5-}$

[a] Analysis by University of Illinois, microanalytical lab. [b] Analysis by E & R, Inc., Corona, NY.

converted to the water soluble lithium salt by metathesis with $LiClO_4$. Analytical data is collected in Table 1.

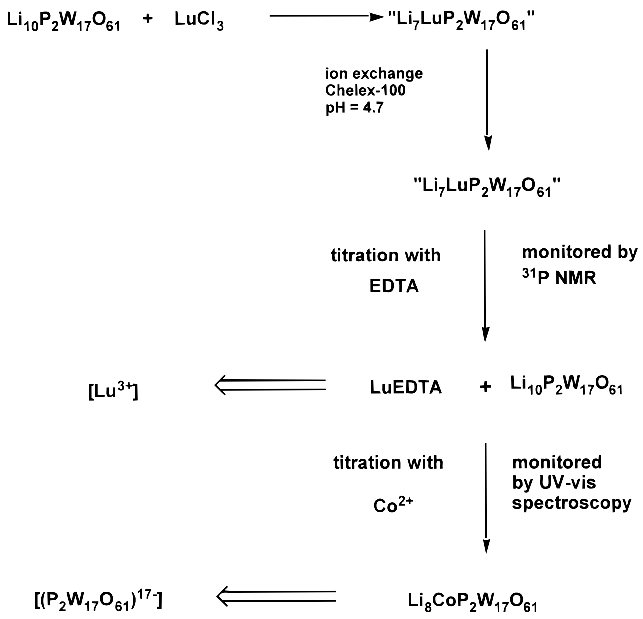
NMR Titrations To Determine Stoichiometry. Preliminary Procedures. Preparation of the Chelex-100 Resin. The resin was transformed to the H^+ form using 2 bed volumes of 1 M HCl with a 2 mL flow rate and washed with 5 bed volumes of H_2O followed by 3 bed volumes of LiOAc buffer at pH 4.7. The resin was soaked in the third volume of LiOAc buffer for at least 5 h. The use of fresh resin is important in order to make sure that the extra Ln is removed efficiently.

Standardization of $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ Solutions. The general procedure to obtain 20 mL of 0.022−0.025 M solution of the $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand follows. $K_9Li[\alpha 1\text{-}P_2W_{17}O_{61}]$ (2.46 g) was ion exchanged to the lithium salt at pH = 4.7 using the Biorad AG50W-X2, following the procedure described above; 1 bed volume of water was used to ensure that all of the compound eluted. The effluent was lyophilized to a solid. The solid was dissolved in D_2O (7 mL) and LiOAc buffer (ca. 0.5 M, pH = 4.7) to prepare 20 mL of solution; 0.5 mL of the $Li_{10}[\alpha 1\text{-}P_2W_{17}O_{61}]$ solution was placed in a UV−vis cuvette with 2 mL of the lithium acetate buffer. To this solution was added $CoCl_2$ (0.2979 M) in 5 or 10 μL increments, and the absorbance was recorded at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gave a sharp breakpoint when all the $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in a 1:1 stoichiometric ratio. Three titrations were run for each standardization; the agreement was within 1%. A typical titration for one standardization is shown in Figure S1 (Supporting Information). The solution was stored in the freezer to prevent isomerization to the $[\alpha 2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer.

Titration of $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ Monitored by ^{31}P NMR Spectroscopy. Generally, 0.5 mL of the standardized buffered $Li_{10}[\alpha 1\text{-}P_2W_{17}O_{61}]$ solution was placed into a 5 mm NMR tube. (The concentrations were in the range 0.015−0.022 M, buffered with Li acetate at pH 4.7, and the solutions contain 30% D_2O.) The ^{31}P NMR spectrum was recorded. An aliquot of 25−30 μL of the standardized $LnCl_3$ solution (concentration was always ca. 0.1 M) was added to achieve 4:1, 4:2, 4:3, 4:4, and 4:6 $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$:Ln ratios. The resulting solution was shaken well in the NMR tube, and the ^{31}P NMR spectrum was recorded immediately upon mixing.

Procedures for Determining the Ln:$[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ Stoichiometry of the Complex. Lutetium Complex of $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$. The general procedure, illustrated in Scheme 1, consists of three steps. The first step involved the preparation of the Lu^{3+} complex of $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$, followed by ion-exchange chromatography in order to remove any extra Lu^{3+}. The sample was checked by ^{31}P NMR to ensure that Chelex resin did not decompose the $Lu^{3+}-[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ complex. The second step involved the titration with EDTA followed by ^{31}P NMR, giving the Lu^{3+} content of the sample. The last step of this procedure allowed the determination of the amount of [α1-

Scheme 1. Determination of the [Lu^{3+}]:[α1-$P_2W_{17}O_{61}$]$^{10-}$ Ratio of the Complex



$P_2W_{17}O_{61}$]$^{10-}$ in the sample by titration with Co^{2+}, monitored by absorption spectroscopy.

1. Preparation of the Sample. The standardized Li_{10}[α1-$P_2W_{17}O_{61}$]$^{10-}$ (6 mL, 0.122 mmol) (0.02032 M) was measured into a vial, and 1.8 mL (0.1828 mmol) of $LuCl_3$ (0.1015 M) was added. The solution was stirred and loaded on the Chelex-100 ion-exchange resin, prepared as described above. The volume of the resin used for this particular experiment was 1 mL, and the sample was eluted with water at a flow rate of 3 mL/min, calculated for a buret with 1 cm diameter. (This volume of the resin used was calculated for the total amount of Lu^{3+} on the basis of the resin capacity of 0.4 mequiv/mL with additional 100% excess.) The sample was eluted with 1 bed volume of distilled water, concentrated by rotary evaporation at less than 50 °C, and stored in the freezer.

2. Determination of the Lu Content in the Sample. The sample prepared above (0.5 mL) was measured into the 5 mm NMR tube, and 80 μL of a 0.0993 M EDTA solution was added; the solution was shaken, and after 2 h the ^{31}P NMR spectrum of the sample was recorded. Depending on the results of the NMR, more EDTA was added in 10, 5, or 3 μL increments. After each addition of EDTA the sample was left to stand at least for 2 h before the ^{31}P NMR spectrum was recorded. The EDTA addition was stopped when all the Lu ion was removed from the Lu complex of [α1-$P_2W_{17}O_{61}$]$^{10-}$ according to the ^{31}P NMR. This titration was repeated two more times, and the Lu content of the complex is calculated on the basis of the amount of EDTA added.

3. Determination of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ concentration. The sample (0.5 mL), prepared in step 1, was measured into a glass UV−vis cuvette. EDTA was added in the amount determined in step 2, followed by the addition of 2 mL of LiOAc buffer, pH = 4.7, 0.5 M. The solution was shaken and left for 2 h. To this solution was added $CoCl_2$ (0.2979 M) in 5 or 10 μL increments, and the absorbance was recorded at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gave a sharp breakpoint when all the [α1-$P_2W_{17}O_{61}$]$^{10-}$ reacted with the Co^{2+} in a 1:1 stoichiometric ratio. Three titrations were performed for each determination; the agreement was within 1−5%.

Europium Complex of [α1-$P_2W_{17}O_{61}$]$^{10-}$. Laser Excitation Luminescence Spectroscopy. A Continuum YG581 pulsed Nd:YAG laser pumped TDL50 tunable dye laser was used to obtain the excitation spectra, lifetime, and intensity data of the Eu complexes of [α1-$P_2W_{17}O_{61}$]$^{10-}$.[30] The $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ion (579−581 nm) was excited.[31] The $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm was monitored in each case. All measurements were carried out at 25.0 ± 0.1 °C. The commercially available Peakfit program, which employs a nonlinear regression method, was used in the data analysis. The concentration of the samples used for the measurements was in the 40−50 μM range. K_7[Eu(α1-$P_2W_{17}O_{61}$)] was prepared and recrystallized, following the method described in the synthesis section. For lifetime measurements of the Eu excited state in D_2O, the complex was recrystallized once and lyophilized two times from 99.99% D_2O.

For titration experiments, standardized 0.0179 M Li_{10}[α1-$P_2W_{17}O_{61}$]$^{10-}$ in 0.5 M LiOAc buffer was used; this solution was diluted to 40 μM Li_{10}[α1-$P_2W_{17}O_{61}$]$^{10-}$ with distilled H_2O. A 2 mM $EuCl_3$ stock solution was added in 10 μL increments, and the excitation spectra were recorded.

Results and Discussion

Standardization of [α1-$P_2W_{17}O_{61}$]$^{10-}$. To obtain accurate solution titration data for polyoxoanions to determine stoichiometry, an accurate determination of the concentration of the polyoxoanion is critical. While the synthesis of K_9Li [α1-$P_2W_{17}O_{61}$]·20H_2O has been reported and elemental analysis data of the precipitated, not recrystallized, salt have been reported along with infrared data, electrochemical data, and ^{31}P NMR data,[20,21] weighing small amounts of the sample may not provide the convenience or accuracy required for solution experiments. This species is very sensitive to isomerization, and in our hands, upon synthesis of the lacunary species, we obtained a variable amount of water and sometimes salts used in the synthesis remained in the precipitated product. It is often inconvenient and expensive to perform elemental analyses on all samples used for solution studies. Furthermore, storage conditions may alter the formulation of the K_9Li(α1-$P_2W_{17}O_{61}$)·20H_2O.

To utilize this material for titration experiments, especially sensitive fluorescence titration experiments, where exact concentrations and high isomeric purity are necessary, we developed a simple method for standardization of the polyanion. In this study, we standardized solutions of our polyoxoanion species by complexometric titration with cobalt(II). It has been reported that cobalt(II) forms stable complexes with both the [α2-$P_2W_{17}O_{61}$]$^{10-}$ and [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomeric lacunary species (stability constants: $\log \beta = 5.57$ and 7.66, respectively).[32] Titrating the lacunary species with cobalt(II) and monitoring the visible absorption, at λ =544 nm, resulted in a clean breakpoint when 1:1 stoichiometry is attained.

Structure, Purity, and Stability. 1:1 Stoichiometry. When reacted in 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric ratios in water and isolated by precipitation as the K^+ salts, the rare earth ions Eu^{3+},Yb^{3+}, and Lu^{3+} (and Y^{3+}, often considered an analogue for the lanthanide ions) formed stable complexes with the [α1-$P_2W_{17}O_{61}$]$^{10-}$ ligand. Infrared spectroscopic data of the lanthanide [α1-$P_2W_{17}O_{61}$]$^{10-}$ complexes were nearly identical to the lacunary K_9Li[α1-$P_2W_{17}O_{61}$] species, consistent with the isostructural nature of the molecules (Figure S2, Supporting Information). Elemental analysis and mass spectrometry data of *recrystallized* samples were consistent with the 1:1 formulation. However, other techniques, such as multinuclear NMR spectroscopy, should be used concomitantly to ascertain purity and structure of the complexes. In this case, it is also important to note that elemental analysis may not distinguish between a 1:1 complex, K_7[Ln(α1-$P_2W_{17}O_{61}$)] and the 1:2 complex with Ln as a counterion, for example, K_{14}Ln[Ln(α1-$P_2W_{17}O_{61}$)$_2$].

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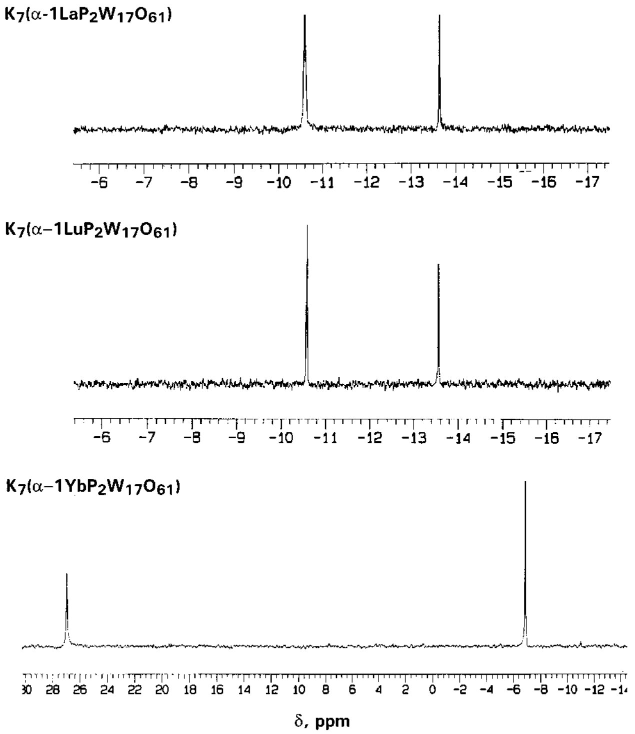

Figure 2. ^{31}P NMR spectra of $K_7[Ln(\alpha1\text{-}P_2W_{17}O_{61})]$ complexes, ca. 10 mM, taken in D_2O.

Table 2. ^{31}P NMR Data for Ln(III) Complexes of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ [a]

compound	chem shift,[a] δ, ppm P1	P2	solvent
$Li_9[\alpha1\text{-}LiP_2W_{17}O_{61}]$	−9.16,	−13.48	D_2O
$TBA_7[\alpha1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	−7.38,	−11.97	DMSO
$TBA_xLi_y[\alpha1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$[b]	−9.97,	−13.16	D_2O
$K_7[\alpha1\text{-}La(H_2O)_4P_2W_{17}O_{61}]$	−10.58,	−13.64	D_2O
$K_7[\alpha1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	−10.57,	−13.55	D_2O
$K_7[\alpha1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$	27.00,	−6.84	D_2O
$K_7[\alpha1\text{-}Y(H_2O)_4P_2W_{17}O_{61}]$	−10.58,	−13.61	D_2O

[a] See text for data collection parameters. P1 is the phosphorus atom closest to the site of substitution; P2 represents the phosphorus atom remote from the substitution site. [b] The tetrabutylammonium salt was ion exchanged by metathesis with $LiClO_4$ to form the aqueous soluble mixed TBA^+, Li^+ salt.

The ^{31}P NMR spectroscopy of the lanthanide complexes of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ showed two peaks confirming >98% α-1-isomeric purity. The data are shown in Figure 2 for the La, Lu, and Yb analogues and Figure S3 (Supporting Information) for Eu and Y. The chemical shifts are given in Table 2. The chemical shifts are in the range found for $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes. The line widths at half-height (Table 2) range from 3.4 to 23.4 Hz. The $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer[20,21,23] and its transition metal[25] and lanthanide complexes[17a,33] can be distinguished from the α-2 isomer easily: the lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ and its metal complexes with strong ionic character generally show chemical shifts of ca. δ −9.5 to −10.5 ppm for P(1) and −13 to −14 ppm for P(2) in water. (The α-2 isomers show the resonance for P(1) between δ 7 and 8 ppm and the resonance for P(2) at ca. δ 14 ppm in water.) The chemical shift value for P(1) for the V^V and Mo^{VI} analogues of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ are found at −12.3 and −12.2 ppm, respectively, reflecting the covalent nature of the bonding to the polyanion with these early transition metal ions.[26a,b] The 1:1 lanthanide $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ compounds can be recrystallized from hot water without significant decomposition as determined by ^{31}P NMR data. Often a small amount of isomerization to the α2 isomer[34] occurred during the crystallization process.

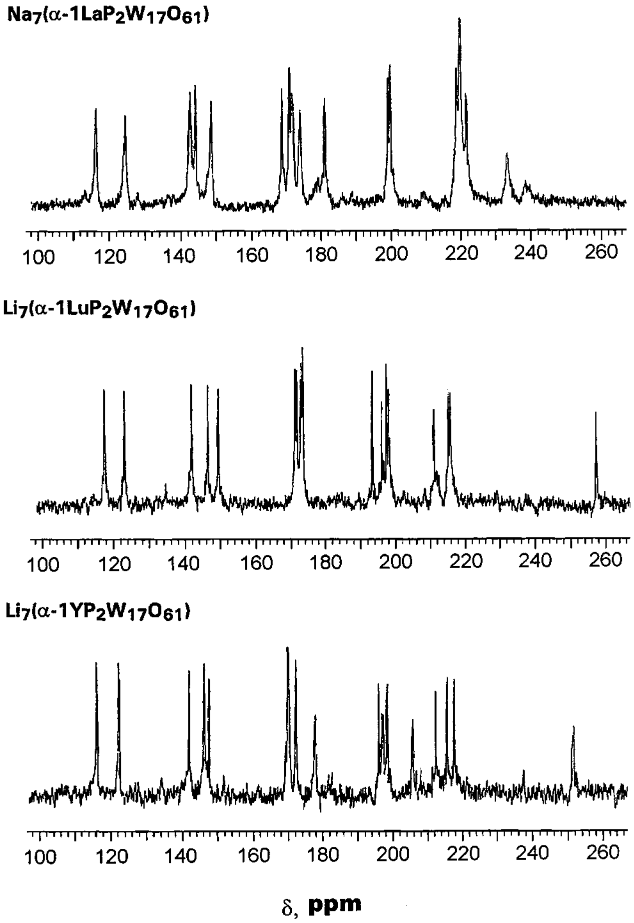

Figure 3. ^{183}W NMR spectra of $[Ln(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ complexes ion exchanged to either Na^+ or Li^+ salts, see text.

The lanthanum analogue, however, was not stable in the presence of a high concentration of Li^+ ions. When a pure sample of the potassium salt of the 1:1 $[La(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ species was ion exchanged to the lithium salt, the ^{31}P NMR spectrum showed significant amounts of the lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer (Figure S4, Supporting Information). After addition of $LaCl_3$ to the solution, the peaks due to the lacunary $[\alpha1\text{-}(P_2W_{17}O_{61})]^{10-}$ species disappeared and only the $[La(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ complex with a small amount of the α-2 impurity could be observed. This phenomenon was not observed when the complex was ion exchanged to the Na^+ salt. Therefore, the ^{183}W NMR spectrum shown in Figure 3 for the La analogue was taken as a sodium salt.

The ^{183}W NMR data, shown in Figure 3 and Table 3, confirmed that the molecules possess the expected C_1 symmetry. Fifteen to seventeen resonances were observed in the ^{183}W NMR spectra for the sodium salt of the lanthanum analogue, and the

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(33) Some of these results were reported at the Rare Earth Research Conference, 1996, Duluth, MN. Conference proceedings: Bartis, J.; Dankova, M.; Blumenstein, M.; Francesconi, L. C. *J. Alloys Compd.*, **1997**, *249*, 56.

(34) We have observed both 1:1 and 1:2 complexes of lanthanides and the α-2 isomer (ref 19c). The chemical shifts of both species are very close to those found for species D in Figures 4 and S3. Therefore we cannot say which α-2-isomeric species are formed as impurities in the recrystallization process.

Table 3. ^{183}W NMR Data for Lanthanide [α1-$P_2W_{17}O_{61}$]$^{10-}$ Complexes[a]

compound	chemical shift, *δ*, ppm
Li_9[α1-Li$P_2W_{17}O_{61}$][b]	−104.24, −115.23 (2), −122.96, −136.45, −143.56, −150.09, −153.61, −163.50, −172.37, −174.02, −177.06, −200.77, −203.52, −217.74, −221.12, −221.85
Na_7[α1-La$(H_2O)_4P_2W_{17}O_{61}$][b]	−116.12, −124.37, −142.41, −143.91, −148.31, −168.47, −170.59, −171.29, −173.60, −180.78, −198.82, −199.49, −218.61, −219.64, −220.52, −221.43, −233.02
Li_7[α1-Lu$(H_2O)_4P_2W_{17}O_{61}$][b]	−118.02, −123.59, −142.39, −147.01, −149.94, −171.64, −172.08, −173.40, −173.87, −193.71, −196.45, −197.84, −198.50, −211.51, −215.66, −216.21, −257.84
Li_7[α1-Y$(H_2O)_4P_2W_{17}O_{61}$][b]	−116.44, −122.60, −142.28, −146.57, −147.92, −170.21, −170.46, −172.55, −177.96, −196.30, −197.38, −198.80, −206.16, −212.80, −216.13, −218.18, −252.31
TBA_xLi_y[α1-Lu$(H_2O)_4P_2W_{17}O_{61}$][c]	−116.60, −127.34, −138.74, −142.63, −142.29, −161.70, −168.80, −169.53, −171.50, −190.64, −193.10, −195.30, −208.61, −210.77, −213.74

[a] Spectra taken in D_2O, see text for details. [b] Ion exchanged to Li^+ or Na^+ salt over Dowex AG50W-X2, see text. [c] Counterion exchanged by metathesis using $LiClO_4$.

lithium salts of the Lu and Y analogues showed the number of resonances required for a C_1 symmetry complex of [α1-$P_2W_{17}O_{61}$]$^{10-}$.

At this stage, our data allow us to unambiguously state that the lanthanide complexes are 98% isomerically pure as the [α1-$P_2W_{17}O_{61}$]$^{10-}$ complexes (^{31}P NMR data). The ^{183}W NMR data clearly showed, for the first time, that the C_1 symmetry of the Ln complexes of [α1-$P_2W_{17}O_{61}$]$^{10-}$ was maintained in solution. The ^{31}P NMR data showed clearly that the later lanthanide ions with smaller ionic radii (higher charge:size ratio) form stable [α1-$P_2W_{17}O_{61}$]$^{10-}$ complexes under conditions of high lithium content, consistent with Contant's data.[16,20,21] It appears that the basic vacant site in the [α1-$P_2W_{17}O_{61}$]$^{10-}$ defect structure requires a metal ion with high charge:size ratio for stabilization.

It appears, from Contant's data[16] for Ce(III) and from our data for the remainder of the lanthanide series, that the lanthanide complexes of [α1-$P_2W_{17}O_{61}$]$^{10-}$ have the stoichiometry 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$. The other scenario could be that the species obtained is the 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ complex and an extra one (or more) surface-bound Ln^{3+} ion(s) may be required to stabilize the 1:2 "sandwich" conformation. This type of surface-bound lanthanide ion has been observed before: surface supported actinide, Th(IV), and lanthanide, Er(III), complexed to a triad of surface oxygen atoms of the $UMo_{12}O_{40}{}^{8-}$ anion form oligomeric species.[35] The stoichiometry of the lanthanide complexes of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer was an issue that we needed to address.

Stoichiometry Determination. NMR Titrations: Eu, La, Lu. To examine the stoichiometry of the Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ complexes, the ^{31}P NMR spectrum of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ ligand was monitored with Ln^{3+} added at different ligand:Ln molar ratios. The ^{31}P NMR titration data wherein the $LnCl_3$ is added to the ligand is shown in Figure 4 and Figure S5 (Supporting Information), for Eu, La, and Lu, respectively. Table S1 presents the actual conditions for each experiment. At the start, the pure lacunary species was present. As $LnCl_3$ was added to the [α1-$P_2W_{17}O_{61}$]$^{10-}$ solution, the lacunary species decreased and the formation of one complex was observed. The intensity of these peaks increased as the Ln concentration was increased and was maximized when the ratio of Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ was 1−1.25. The set of peaks corresponding to [α1-$P_2W_{17}O_{61}$]$^{10-}$ complex decreased concomitantly. The chemical shifts of this complex correspond to those of the previously isolated and characterized complex. Increasing the [α1-$P_2W_{17}O_{61}$]$^{10-}$:Ln ratio to 4:6 or larger amounts of Ln does not change the spectrum. Performing the titration in the reverse order yields a similar result, only the 1:1 species is observed. Using 0.5 M NaOAc, to mimic the conditions of Contant,[16] also resulted in the observation of the formation of a 1:1 species only.

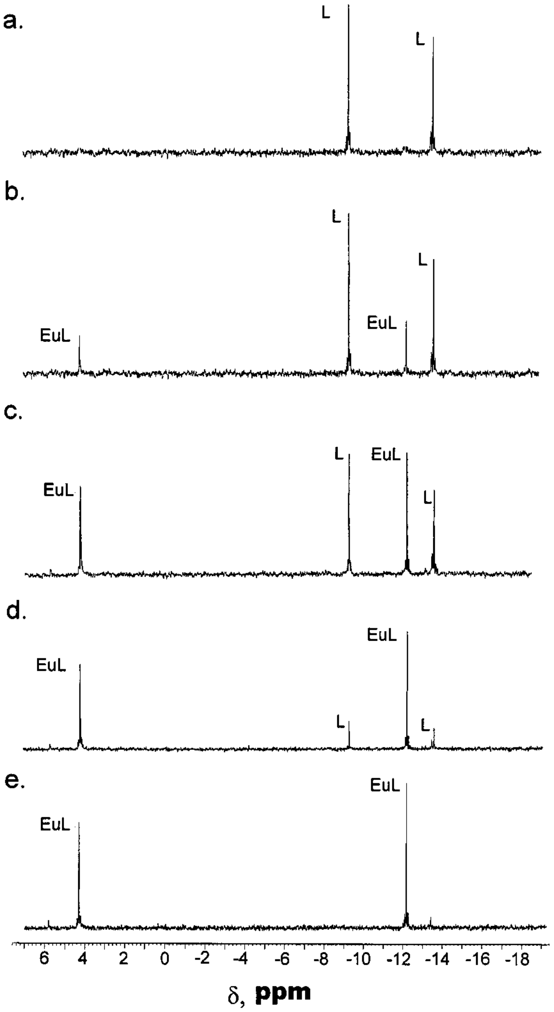

Figure 4. ^{31}P NMR titration of [α1-$P_2W_{17}O_{61}$]$^{10-}$ (L) with $EuCl_3$ at pH = 4.7. Ratio of Eu^{3+}:L: (a) 0; (b) 1:4; (c) 1:2; (d) 3:4; (e) 1:1.

It appears that, for the lanthanide ions and conditions employed in this study, only one species is formed in 0.5 M acetate (lithium or sodium) buffer at pH 4.7, with a stoichiometric ratio of 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$. While this experiment suggested a 1:1 complex formed, it is not clear if all the lanthanide ion added was incorporated into the polyoxoanion forming the 1:1 complex or half of it acted as a counterion and the other half formed a sandwich complex with two of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ polyoxoanion units. Thus, the stoichiometry of the complex needed to be analyzed after removal of all the lanthanide possibly acting as a counterion.

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(35) Molchanov, V. N.; Tatjanina, I. V.; Torchenkova, E. A. *J. Chem. Soc. Chem. Commun.* **1981**, 93.

Complexometric Titration Monitored by ^{31}P NMR Spectroscopy for Lutetium. Chelex-100, a strong chelating ion-exchange resin, was used to remove the Ln ions not incorporated into the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complex, as described in the Experimental Section. Elemental analysis of the evaporated effluent from the Chelex column failed in determining the Lu, W, P content of the ion-exchanged complex; therefore a series of titration experiments described in the Experimental Section and outlined in Scheme 1 were performed to determine both the Lu and $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ concentrations in a pure sample of the $Lu[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complex (determined from ^{31}P NMR).

The method developed for determination of lutetium content was based on the observation that EDTA removes Lu from the lutetium $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complex quantitatively, in a 1:1 molar ratio, according to the following equation. This reaction can be monitored conveniently by ^{31}P NMR spectroscopy.

$$Li_7[Lu(\alpha1\text{-}P_2W_{17}O_{61})] + \text{EDTA} \rightarrow Li_{10}[\alpha1\text{-}P_2W_{17}O_{61}] + \text{Lu}-\text{EDTA}$$

Titrating the ion-exchanged sample of lutetium $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ complex with EDTA and monitoring the end point by ^{31}P NMR gave the concentration of the Lu incorporated into the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ polyoxoanion. Figure 5 shows the results of titration with EDTA. The top spectrum in Figure 5 shows the ^{31}P NMR spectrum of the pure Lu complex of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$. As the EDTA was added, new sets of resonances characteristic of the lacunary $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ appeared. As the amount of EDTA added to the solution was increased, the peaks of the Lu complex decreased until they disappeared when the Lu:EDTA molar ratio reached 1. Because the amount of standard EDTA solution added was known, the Lu^{3+} content of the sample could be calculated.

The solution containing free $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand and Lu−EDTA complex was titrated with Co^{2+} following the absorption spectra at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gave a sharp breakpoint when all the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in a 1:1 stoichiometric ratio, as shown in Figure 6. This determination allowed calculation of the $(\alpha1\text{-}P_2W_{17}O_{61})^{10-}$ ligand content.

Table 4 presents the results of three separate experiments where the $Lu:[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ ratio was consistently close to 1. The results agree within 3−5%. For each experiment, the ratio of $Lu:[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ was 1.5 at the start of the reaction, showing that Chelex-100 ion-exchange resin removes the extra Lu^{3+} countercations efficiently. When the Biorad AG50W-X2 was used, the titration experiments consistently gave the result as 1.5 $Lu^{3+}:[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometry indicating that the resin did not remove counterion Lu^{3+}. Freshly prepared Chelex-100 resin is required; regenerated resin does not efficiently remove the Lu^{3+} countercation.

The mixture of Lu−EDTA and $[Co(\alpha1\text{-}P_2W_{17}O_{61})]^{8-}$ was monitored also by ^{31}P and ^{1}H NMR spectroscopy to ensure that, during the titration experiments, Co^{2+} reacted with $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ and did not replace the Lu from the Lu−EDTA complex. ^{31}P NMR showed the formation of $[Co(\alpha1\text{-}P_2W_{17}O_{61})]^{8-}$, and ^{1}H NMR indicates that Lu−EDTA was not affected by the addition of Co^{2+}; the reaction proceeded according to the equation below. These results are expected on the basis of the magnitudes of the critical stability constants[36] of Lu^{3+}−EDTA ($\log K = 19.80$) and Co−EDTA ($\log K = 16.26$) The stability constant of $[Co(\alpha1\text{-}P_2W_{17}O_{61})]^{8-}$ is reported to be $\log K = 7.66$.[32]

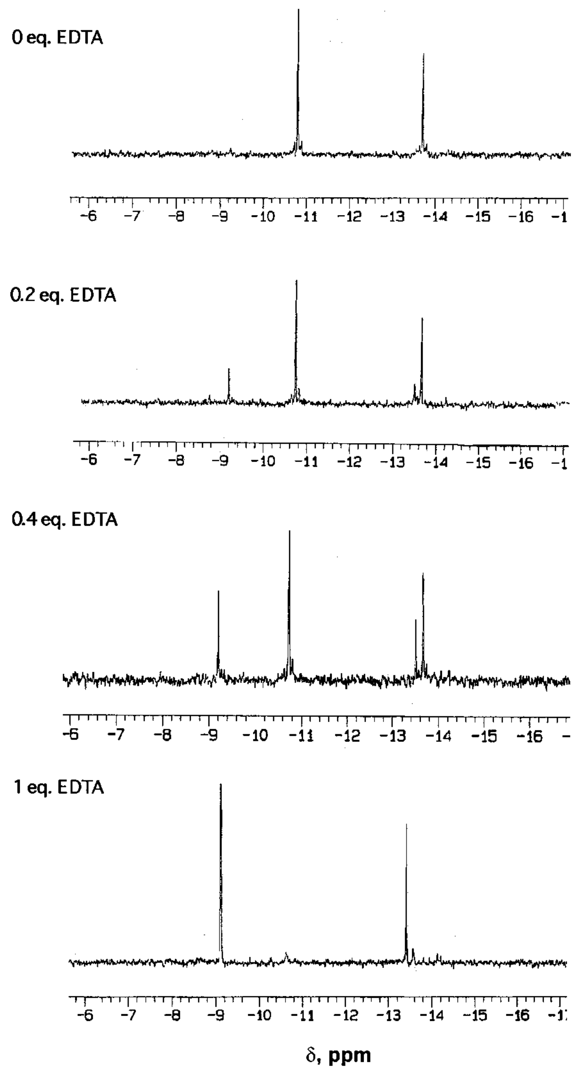

Figure 5. ^{31}P NMR titration of the lithium salt of $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$. The top spectrum shows the complex with no EDTA added. Other spectra show successive additions of a standard solution of EDTA. This experiment allows determination of the number of moles of Lu in the complex. See text.

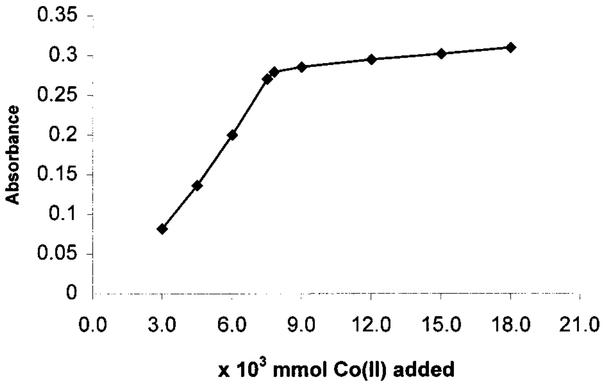

Figure 6. Plot of absorbance of the solution when Co(II) is titrated into a $Li_{10}(\alpha1\text{-}P_2W_{17}O_{61})$ + Lu−EDTA mixture. This experiment gives the number of moles of $(\alpha1\text{-}P_2W_{17}O_{61})^{10-}$ in the complex. See text.

$$Li_7[\alpha1\text{-}P_2W_{17}O_{61}] + Co^{2+} + \text{Lu}-\text{EDTA} \rightarrow Li_8[Co(\alpha1\text{-}P_2W_{17}O_{61})] + \text{Lu}-\text{EDTA}$$

Attempts to remove the La^{3+} ion with EDTA from the La complex of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$, quantitatively, failed, due to the

Table 4. Summary of Titration Results

expt no.	Lu, $\times 10^6$ mol	$[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ $\times 10^6$ mol	$Lu:(\alpha1\text{-}P_2W_{17}O_{61})^{10-}$
1	8.14	7.45	1.09
2	6.65	5.99	1.12
3	7.94	7.67	1.04

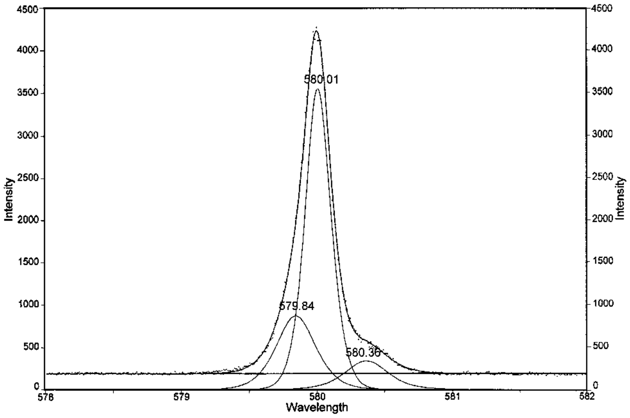

Figure 7. $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of a 40 mM $K_7[Eu(\alpha1\text{-}P_2W_{17}O_{61})]$ solution in H_2O. The experimental spectrum is shown resoved into its components. The major peak at 580.01 nm is assigned to the $K_7[Eu(\alpha1\text{-}P_2W_{17}O_{61})]$ species. The peak at 579.84 nm is assigned to $K_7[Eu(\alpha2\text{-}P_2W_{17}O_{61})]$, and the peak at 580.36 nm is assigned to $K_{17}[Eu(\alpha2\text{-}P_2W_{17}O_{61})_2]$. See text and footnote 39.

lower stability constant of La−EDTA. The use of stronger chelating ligands (higher La−ligand stability constants) for La^{3+} such as DTPA or DOTA, in a similar method, were not possible because of the low solubility of these ligands in water.

Luminescence Spectroscopy Data. Laser-excited Eu^{3+} luminescence spectroscopy is a powerful tool for monitoring the binding of this ion to ligands in solution.[39] The $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ion in the range 577−581 nm is excited[30,31,37,38] by a tunable dye laser while the $^5D_0 \rightarrow {}^7F_2$ emission band at 614 nm is monitored. The excited lifetimes are relatively long; durations in the millisecond region are not uncommon under certain circumstances. Since the $^7F_0 \rightarrow {}^5D_0$ transition occurs between nondegenerate energy levels, neither of which can be split by a ligand field, a single environment gives rise to only a single transition. If more than one Eu^{3+} environment is present, each will have its characteristic transition energy.[37]

The excitation spectrum of the europium complex of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$, dissolved in H_2O, showed three components, the major narrow band at 580.01 nm and two others with lower intensities at 579.84 and 580.36 nm, shown in Figure 7. The low-intensity peaks can be attributed to the α-2-isomeric impurities contained in the sample.[39] The lifetime of the Eu excited state measured at 580.01 nm was 0.254 ms in H_2O and 2.83 ms in D_2O. The exponential decay of the lifetime in D_2O is shown in Figure S6 (Supporting Information).

The excited state lifetime of the Eu^{3+} is very sensitive to the number of water molecules coordinated to the ion, because a weak vibronic coupling between the excited electronic state and the O−H vibrational manifold of coordinated water provides an efficient radiationless deexcitation pathway. Replacement of H_2O with D_2O eliminates the efficient deexcitation pathway and causes lifetimes to increase dramatically.[30,37] On the basis of this observation Horrocks and Sudnick developed a method for determining the number of water molecules coordinated to the Eu^{3+}. The experimentally determined decay constant, or reciprocal lifetime, of Eu^{3+} has been shown to be linear with the number of water molecules bound in the first coordination sphere of Eu^{3+}. Therefore, from measurements of lifetimes separately in H_2O and D_2O solution it is possible to determine the number of coordinated molecules, q, from

$$q = 1.05[\tau^{-1}(H_2O) - \tau^{-1}(D_2O)] \qquad (\tau = \text{lifetime})$$

Using this equation and the lifetimes of the Eu^{3+} complex of $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$, measured in H_2O and D_2O, $q = 3.8 \pm 0.5$. These data are consistent with four water molecules coordinated to the Eu^{3+}. This result is in agreement with the 1:1 formulation of the $K_7[Eu(\alpha1\text{-}P_2W_{17}O_{61})]$ complex where the Eu^{3+} binds to four oxygens of the polyoxoanion and the other four coordination sites are occupied by water molecules. One other study using lifetime measurements to determine stoichiometry has been reported.[40] In this study, lifetime measurements of Cm^{3+}, Eu^{3+}, Dy^{3+}, Sm^{3+}, and Tb^{3+} complexes of $SiW_{11}O_{39}{}^{8-}$ and $PW_{11}O_{39}{}^{7-}$ were measured in H_2O and D_2O. The complexes with a metal:ligand molar ratio of 1:1 showed the number of coordinated water molecules to be equal to 4−6, consistent with a 1:1 complex. For complexes with a metal:ligand ratio of 1:2, the number of coordinated water molecules was found to be 0.1−0.5.

The stoichiometry of the complex was also determined by titrating 40 μM solutions of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand with Eu^{3+} while monitoring the intensity of the excitation maximum at 580.07 nm. The plot of the intensities versus the $Eu:[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ molar ratio gave a sharp breakpoint when the ratio reached 1, as shown in Figure 8. These results are consistent with the 1:1 $[Eu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ formulation.

Tetrabutylammonium Salt of $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$. The analytical data (elemental analysis and mass spectrometry) for the recrystallized tetrabutylammonium salt of $[Lu(\alpha1\text{-}P_2W_{17}O_{61})]^{7-}$ is consistent with the 1:1 formulation. The electrospray mass spectrum suggests that the major species is $TBA_6H[Lu(\alpha1\text{-}P_2W_{17}O_{61})]$. The main series of ions corresponds to the TBA_4 to TBA_1 series with charge states 2− to 5−. One

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(36) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1974; Vol. 1.

(37) Horrocks, W. DeW., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.

(38) Horrocks, W. DeW., Jr.; Wu, S. R. *Inorg. Chem.* **1995**, *34*, 3724.

(39) The excitation spectra of the 1:1 $K_7[Eu(\alpha2\text{-}P_2W_{17}O_{61})]$ and the 1:2 $K_{17}[Eu(\alpha2\text{-}P_2W_{17}O_{61})_2]$ were obtained to identify the low-intensity peaks in the $Eu(\alpha1\text{-}P_2W_{17}O_{61})^{10-}$ complex. The 1:1 $K_7[Eu(\alpha2\text{-}P_2W_{17}O_{61})]$ complex shows one narrow band at 579.79 nm, and the excited state lifetime of Eu^{3+} in this complex is 0.241 ms, similar to the lifetime of the α-1 isomer, indicating that there are a few water molecules coordinated to the Eu^{3+} ion, expected for a 1:1 complex, where the polyoxoanion ligand occupies only four of the coordination sites of the Eu^{3+}. The 1:2 $K_{17}[Eu(\alpha2\text{-}P_2W_{17}O_{61})_2]$ sandwich complex shows two absorption bands at 579.8 and 580.4 nm revealing two different Eu^{3+} environments. While the ^{31}P NMR spectrum of this complex shows a very clean compound with only two resonances, it is likely that, under high dilution (40 mM) of the fluorescence spectroscopy, $[Eu(\alpha2\text{-}P_2W_{17}O_{61})_2]^{17-}$ dissociates into the 1:1 $[Eu(\alpha2\text{-}P_2W_{17}O_{61})]^{7-}$ complex; the peak at 580.4 nm corresponds to the sandwich $[Eu(\alpha2\text{-}P_2W_{17}O_{61})_2]^{17-}$ molecule. The lifetime measured at 580.4 nm is 3 ms, indicating that there are no water molecules coordinated to the Eu^{3+} (Luo, Q.-H.; Bartis, J.; Horrocks, W. DeW.; Francesconi, L. C.) Speciation of polyoxoanions may be concentration dependent; dilution may induce degradation of polyoxoanions. (Fourier, M.; Thouvenot, R.; Rocchiccioli-Deltcheff, C. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 349.) The excitation spectrum is recorded at much lower concentration, 40 μM, compared to 10−20 mM used for ^{31}P NMR measurements. A diluted solution of 1:1 $[Eu(\alpha2\text{-}P_2W_{17}O_{61})]^{7-}$ (<40 μM) can be concentrated to 10−20 mM to give the appropriate NMR spectrum, suggesting that the 1:1 $[Eu(\alpha2\text{-}P_2W_{17}O_{61})]^{7-}$ complex is intact throughout the concentration range (μM−mM) used in this study.

(40) Yusov, A. B.; Fedoseev, A. M. *Zh. Prikl. Spektrosk.* **1988**, *49*, 929.

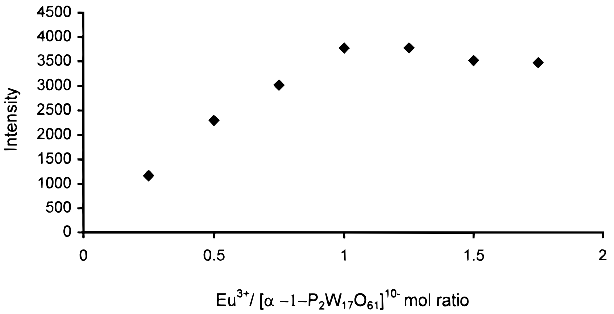

Figure 8. Plot of intensities for ${}^7F_0 \rightarrow {}^5D_0$ excitation spectra of 40 μM (α1-$P_2W_{17}O_{61}$)$^{10-}$ ligand titrated with Eu^{3+}, $\lambda_{ex} = 580.07$ nm. The decrease in luminescence intensity as the free Eu(III) concentration is increased after the breakpoint is a result of an energy transfer process between bound and free Eu(III). (S. Wu and W. DeW. Horrocks, manuscript in preparation.)

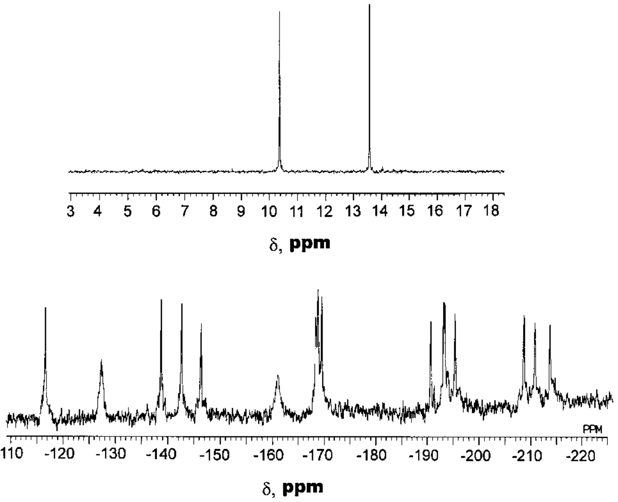

Figure 9. Tetrabutylammonium salt of [Lu(α1-$P_2W_{17}O_{61}$)]$^{7-}$ taken as a mixed TBA, Li salt. (a) ^{31}P NMR spectrum taken in D_2O. (b) ^{183}W NMR spectrum taken in D_2O at 50 °C.

other electrospray ionization mass spectral analysis conducted on molybdenum and tungsten “cage” compounds of the Lindquist, Keggin, octamolybdate, decatungstate, and Dawson structures showed the polyoxoanions as base peaks with a minimal degree of fragmentation.[41] We also observed minimal fragmentation utilizing this technique on rhenium(V) and -(VI) substituted polyoxoanions.[42] Polyoxoanions are highly negatively charged molecules, and the parent ions form adducts with cations, such as tetrabutylammonium, in this case.

^{31}P NMR spectroscopy data, taken in DMSO as well as in water (mixed TBA, Li$^+$ salt) show two resonances indicating ≥98% isomeric purity. The chemical shifts in water, given in Table 2 and Figure 9, compare well to the chemical shift range for the lacunary [α1-$P_2W_{17}O_{61}$] isomer and transition metal and lanthanide complexes. The ^{183}W NMR experiments, taken in D_2O at 50 °C, on the mixed tetrabutylammonium plus Li$^+$ salt, prepared by metathesis from $LiClO_4$, confirm the C_1 symmetry required for the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer; the data are shown in Figure 9. The tetrabutylammonium salt of [Lu(α1-$P_2W_{17}O_{61}$)]$^{7-}$ is stable for weeks in water as the mixed TBA$^+$, Li$^+$ salt and as the TBA salt in acetonitrile, according to ^{31}P NMR data. The TBA cation apparently stabilizes the lanthanide ion complexes of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer; to contrast this stability, the potassium and lithium salts isomerize to the [α2-$P_2W_{17}O_{61}$]$^{10-}$ complex under the same conditions.

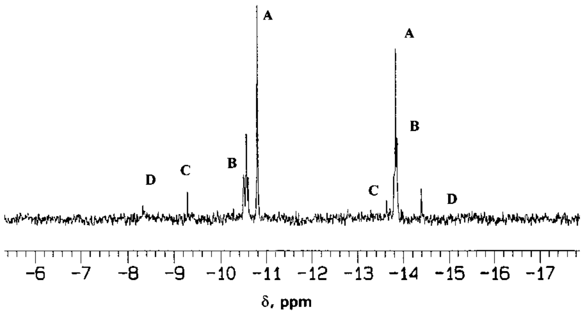

Figure 10. ^{31}P NMR spectra of the La^{3+} complex of [α1-$P_2W_{17}O_{61}$]$^{10-}$ prepared in a 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric ratio: A = major peaks observed with a 1:1 La^{3+}:[α1-$P_2W_{17}O_{61}$]$^{10-}$ ratio; B = unidentified species, presumably a La^{3+} complex of [α1-$P_2W_{17}O_{61}$]$^{10-}$, C = [α1-$P_2W_{17}O_{61}$]$^{10-}$; D = α-2 impurity. For details, see text.

Reactions Performed with 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ Stoichiometry. The early lanthanide ions, La and Sm, upon reaction in a 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric ratio at room temperature in lithium acetate buffer, isolated as a potassium salt and before crystallization, showed primarily the same two peaks (labeled A on Figure 10) in the ^{31}P NMR data as observed in the 1:1 Ln^{3+}:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric reactions; however, these early lanthanide ions also showed significant amounts of a second species (labeled B in Figure 10), with chemical shift values close to those of the first species. Upon recrystallization from hot water, the second species remained. Unfortunately, we have not yet been able to adjust conditions to maximize and, thus, isolate this secondary species.

When reactions were performed in a 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric ratio, precipitated as a K$^+$ salt, and before crystallization, the ^{31}P NMR chemical shift data for the later rare earth ions, Eu, Yb, Lu (and Y), showed only two resonances, identical to the chemical shifts obtained for the species from reactions with 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometry. Upon recrystallization from hot water, however, the ^{31}P NMR spectra showed the same two major resonances (labeled A in Figure S7, Supporting Information) but also showed a small amount of the lacunary [α1-$P_2W_{17}O_{61}$]$^{10-}$ species (labeled C in Figure S7) and a small amount of the unknown species (labeled B) as well as the resonances, labeled D, due to an α-2 impurity (either the [Ln(α2-$P_2W_{17}O_{61}$)$_2$]$^{17-}$ or the [Ln(α2-$P_2W_{17}O_{61}$)]$^{7-}$ species).[34] The chemical shifts of the species formed upon reaction in 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometry are summarized in Table S2 (Supporting Information).

It appears, therefore, for all Ln(III) ions, that the major species, A, isolated and crystallized from reactions performed with both 1:1 and 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometries is the same since their ^{31}P NMR are identical. The experiments described above for Lu(III) and Eu(III) allow us to conclude that this major species (A) is the 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ species. Our data and interpretations are consistent with the conclusions of Ciabrini and Contant[16] for the early lanthanide ion, Ce(III). They observed formation of both the 1:1 and 1:2 Ce(III):[α1-$P_2W_{17}O_{61}$]$^{10-}$ complexes. While the apparent stability constant data showed a slightly higher log *K* for the 1:2 complex, the 1:1 complex appeared to be easier to isolate, perhaps, as they suggest, due to steric encumbrance of the two [α1-$P_2W_{17}O_{61}$]$^{10-}$ ligands. We have attempted to grow X-ray crystals of a number of analogues of [Ln(α1-$P_2W_{17}O_{61}$)]$^{7-}$;

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(42) Venturelli, A.; Smirnoff, A.; Nilges, M.; Belford, R. L.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans.* **1999**, 301.

however, to date, the crystals did not diffract well enough to collect a high-quality data set. We are continuing crystallization attempts. It is likely that the secondary species, B (Figure 10 and Figure S7), are the 1:2 complexes. We hope to cleanly isolate and identify these species in the future.

Conclusion

We have prepared lanthanide complexes of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer in ≥98% isomeric purity, and we have proven this according to ^{31}P NMR data, one of the most sensitive probes for determination of isomeric purity of heteropolytungstates containing phosphorus.[43] Samples prepared in 1:1 and 1:2 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ stoichiometric ratios gave the same major species, according to ^{31}P NMR spectroscopy. Our ^{183}W NMR data clearly showed, for the first time, for the major species, that the C_1 symmetry of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ lanthanide complexes was maintained in solution. Our ^{31}P NMR data showed, consistent with Contant's data, that the lanthanides with smaller ionic radii (higher charge:size ratio) formed stable complexes, even surviving crystallization from hot water. On the other hand, the lanthanum analogues were not stable in solutions of high lithium content. Finally, the tetrabutylammonium salt of the [Lu(α1-$P_2W_{17}O_{61}$)]$^{7-}$ complex showed ≥98% isomeric purity and maintained the C_1 symmetry of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ species in solution. Also the tetrabutylammonium cation stabilized the [Lu(α1-$P_2W_{17}O_{61}$)]$^{7-}$ complex; a mixed tetrabutylammonium, lithium salt was stable in hot water for weeks according to ^{31}P NMR spectroscopy.

The stoichiometry of the lanthanide complexes of the [α1-$P_2W_{17}O_{61}$]$^{10-}$ isomer (major species) has been determined in solution by two different methods: a complexometric titration method for Lu^{3+}, once all of the Lu^{3+} serving as a counterion was removed by using freshly prepared Chelex resin, and excited state lifetime measurements and luminescence titrations for the Eu(III) analogue. Both the NMR titration and luminescence spectroscopic methods consistently prove the 1:1 formulation of Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$. When lanthanides were reacted with the [α1-$P_2W_{17}O_{61}$]$^{10-}$ species in a 1:2 ratio, we observed a major species, identified as the 1:1 Ln:[α1-$P_2W_{17}O_{61}$]$^{10-}$ complex by ^{31}P NMR spectroscopy, and a minor species. We have not at this time been able to isolate the minor species.

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Supporting Information Available: Figures S1−S7 and Tables S1 and S2 showing titration data and ^{31}P NMR data for preparations with 1:2 Ln:[α-1$P_2W_{17}O_{61}$]$^{10-}$ stoichiometry. This material is available free of charge via the Internet at http://pubs.acs.org.

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