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Preparation and Tungsten-183 NMR Characterization of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, $[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$, and $[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$

Judit Bartis, Yuliya Kunina, Michael Blumenstein, and Lynn C. Francesconi*

Department of Chemistry, Hunter College of the City University of New York,
New York City, New York 10021

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The preparation of the α-1 and α-2 isomers of the Wells−Dawson 17 tungsto derivatives by standard methods is accompanied by a significant proportion of the other isomer present as an impurity. In this study, the α-1 and α-2 isomers of $[Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ have been prepared in >98% purity by reacting isomerically pure $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ and $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$, respectively, with $ZnCl_2$, while rigorously controlling the pH at 4.7. The molecules were isolated as potassium salts. For ^{183}W NMR and ^{31}P NMR characterization, both molecules were ion exchanged by cation-exchange chromatography, maintaining the pH at 4.7, to obtain the lithium salts. Removal of water and isolation of a solid sample of $[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ was achieved by lyophilization at −40 °C. The chemical shift data from ^{31}P and ^{183}W NMR spectroscopy of the isolated $[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ and $[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ isomers are consistent with a mixture of the α-1 and α-2 isomers reported previously;[1] the molecules have the expected C_1 and C_s symmetry, respectively. The $[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ isomer is stable in the pH range of 4.6−6 at temperatures <35 °C. Using the same ion exchange and lyophilization techniques, the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer was isolated as the lithium salt; characterization by ^{183}W NMR spectroscopy confirms the C_1 symmetry.

Introduction

The octadecatungstodiphosphates $[P_2W_{18}O_{62}]^{6-}$ (α and *β* isomers) and the related lacunary compounds form a very stable family of polyoxotungstophosphates.[2] Removal of a WO unit from a cap WO_6 polyhedron of the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ (Wells−Dawson structure) results in the lacunary $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer which has C_s symmetry, and removal of a WO unit from a belt WO_6 polyhedron results in the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, which has C_1 symmetry.[3] Lacunary oxoanions are generally good ligands for transition metals, lanthanides and actinides.[2] The metal ion binds to the four (lanthanide and actinide) and five (transition metals) oxygen atoms of the defect oxoanion. Figure 1a,b shows the metal complexes of the α-2 and α-1 $[P_2W_{17}O_{61}]^{10-}$ isomers,[3,4] respectively, in polyhedral representations, where the vertices of the polyhedra represent oxygen atoms and the tungsten atoms are located within each polyhedron. Figure 1c,d shows the tungsten frameworks of the metal complexes of the α-2 and α-1 $[P_2W_{17}O_{61}]^{10-}$ isomers, respectively. In this representation, the heavy lines indicate edge shared polyhedra and the thin lines indicate corner-shared polyhedra.

In general, the preparation of lacunary α-1 and α-2 isomers of $[P_2W_{17}O_{61}]^{10-}$ or their metal complexes by standard methods is accompaned by a significant proportion of the other isomer present as an impurity. For example, Jorris reported the ^{183}W NMR spectrum of the $[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ species which contained the presence of ca. 17% of the α-1 isomer as an impurity.[1] This report was the first direct proof of the structure of the α-1 isomer. There have been few reports of metal complexes of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, probably due to the relative instability of the α-1 lacunary isomer,[3] and to our knowledge, there are no reports of structural characterization of pure (>98%) metal complexes of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ by X-ray crystallography or by ^{183}W NMR spectroscopy. ^{183}W NMR spectroscopy is a

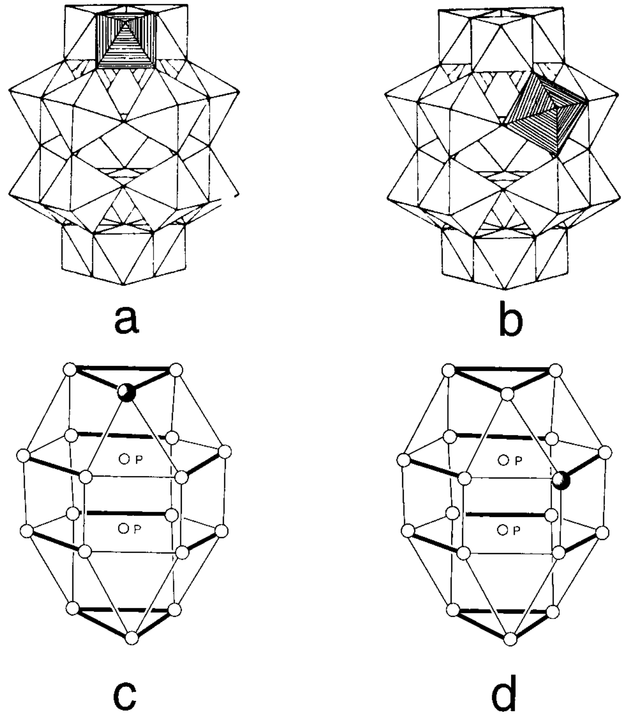

Figure 1. Representations of the two isomers formed upon substitution of a metal ion into the lacunary α-2 and α-1 $[P_2W_{17}O_{61}]^{8-}$ isomers. (a) and (b) represent the α-2 and α-1 $[P_2W_{17}O_{61}]^{8-}$ isomers, respectively, shown in polyhedral notation. The hatched octaheda contain the metal ion substituted into the $[P_2W_{17}O_{61}]^{8-}$ framework. (c) and (d) represent the α-2 and α-1 $[P_2W_{17}O_{61}]^{8-}$ isomers, respectively, showing the tungsten atom framework; see text.

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very sensitive method to assess the structure and stability of heteropolytungstates in solution.[5]

We report here 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 phosphorus-31 and tungsten-183 NMR spectroscopy. We chose the Zn complexes since the ^{183}W NMR spectrum and ^{31}P spectrum of the α-1/α-2 mixture had been reported,[1] offering an opportunity for a comparison of the ^{183}W and ^{31}P NMR chemical shift data for the isolated compounds. This is the first report of a ^{183}W NMR spectrum obtained for a pure (>98%) metal complex of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer. We also report for the first time the ^{183}W NMR spectrum of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, isolated as the lithium salt.

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. Dowex AG-50W-X2 cation exchange resin was used to convert the potassium salts to lithium salts. The molecule $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$[6] was prepared by following the method of Contant.[3,4] The α-2 lacunary isomer, $K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$, was prepared following the method of Finke.[7] Molecules $K_6[P_2W_{18}O_{62}]$ and $K_{12}[H_2P_2W_{12}O_{48}]$ were prepared according to literature methods.[4] Infrared spectra were recorded from KBr pellets on a Perkin-Elmer 1625 spectrophotometer. Elemental analyses were performed by E & R Microanalytical Laboratory, Inc., Corona, NY 11368.

To convert the potassium salts to lithium salts for preparation of concentrated aqueous solution for ^{183}W NMR spectroscopy, ion-exchange chromatography using Dowex AG50W-X2 in the Li^+ form was used. The resin, originally in the H^+ form, was converted to the Li^+ form using the following procedure. Two bed volumes of lithium acetate buffer, pH = 4.7, 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.

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 broad band probe. Typical acquisition parameters for ^{31}P spectra included the following: spectral width, 10 000Hz; acquisition time, 0.8 s; pulse delay, 1s; 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. For ^{183}W spectra in which $^{31}P-^{183}W$ couplings were to be resolved, the spectral width was decreased to 5000 Hz and the acquisition time increased to 3.2 s. Also, the data were zero-filled once before Fourier transformation for a final spectral resolution of 0.16 Hz. For all spectra, the temperature was controlled to ±0.2 °C. ^{31}P spectra were referenced 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 $Li_{10}\ [\alpha\text{-}1\ P_2W_{17}O_{61}]$. $K_9Li\ [\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$[3,4] (2.75 g, 0.6 mmol) was dissolved in approximately 80 mL of water to form a clear solution. This solution was loaded onto a Dowex AG-50W-X2 cation-exchange column in the lithium form (1 cm diameter, 11.7 mL volume) and eluted with water at a flow rate of 4 mL/min. The resulting clear, colorless solution was lyophilized at −40 °C. The resulting solid was dissolved in D_2O to prepare a 0.25 M solution for NMR spectroscopy.

Preparation of $K_8\ [\alpha\text{-}2\ \text{-}Zn(H_2O)P_2W_{17}O_{61}]$.[8] Method 1. This method generates the lacunary $[\alpha\text{-}2\text{-}P_2W_{17}\ O_{61}]^{8-}$ species in situ from the parent Wells−Dawson molecule. A 15 g (3 mmol) amount of $K_6[\alpha/\beta\text{-}P_2W_{18}O_{62}]$[4] was dissolved in 60 mL of water at 80 °C. $ZnCl_2$ (0.61 g, 4.5 mmol) was dissolved in a minimum amount of water. Potassium acetate (12.0 g, 0.12 mmol) was dissolved in 15 mL of water, and the pH was adjusted to 7 with acetic acid. The $ZnCl_2$ solution was added dropwise to the hot $K_6[\alpha/\beta\text{-}P_2W_{18}O_{62}]$ solution with stirring to give a light green solution. The potassium acetate solution was added dropwise to increase the pH of the solution to 5; the solution turned colorless. The resulting clear, colorless solution was cooled to 5 °C. In 2 h, crystals had formed and were collected and recrystallized three times from a minimum amount of hot water (70 °C) . IR data, KBr pellet: 1160 cm^{-1}, sh; 1085 cm^{-1}, s; 1063 cm^{-1}, m; 1017 cm^{-1}, m; 944 cm^{-1}, s, b; 917 cm^{-1}, s, b. Anal. Calcd for $K_8\ ZnH_2P_2W_{17}O_{62}\cdot 20H_2O$: K, 6.36%; P, 1.26%; W, 63.52%; Zn, 1.33%. Found: K, 6.35%; P, 1.13%; W, 63.29%; Zn, 1.14%.

Conversion of $K_8[\alpha\text{-}2\ \text{-}Zn(H_2O)P_2W_{17}O_{61}]$ to the Li Salt. The potassium salt obtained by method 1, above, 3 g (0.6 mmol), was dissolved in approximately 80 mL of water to obtain a clear solution. The solution was loaded onto a Dowex AG-50W-X2 cation-exchange column in the lithium form (11 mL, 1 cm diameter) and eluted with water at a flow rate of 4 mL/min. The resulting clear, colorless solution was rotary evaporated at ca. 50 °C to give a solid. For the NMR sample, the solid was dissolved in 2.5 mL of D_2O. ^{183}W NMR data showed a very pure product, but ^{31}P NMR showed less than 2% of the α-1 impurity.

Method 2. Isomerically pure $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}\ O_{61}]$[7] (5.0 g, 1 mmol) was suspended in 50 mL of lithium acetate buffer (1 M, pH = 4.7). To the stirred suspension, $ZnCl_2$ (1.5 mL, 1 M solution, 1.5 mmol) was added dropwise. Most of the $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ dissolved upon addition of the first few drops of $ZnCl_2$. The reaction mixture was filtered. The pH of the resulting solution was 4.5, and potassium chloride (5.0 g, 67 mmol) was added to the stirring solution to precipitate a white solid. The solid was collected by filtration and recrystallized by dissolving in a minimum amount of water (70 °C), filtering while hot, and cooling to 5 °C . Crystals were collected after 12 h. The ^{31}P NMR data showed very pure product with no detectable α-1 impurity.

Conversion of $K_8[\alpha\text{-}2\ \text{-}Zn(H_2O)P_2W_{17}O_{61}]$ to the Li salt. Conversion to the lithium salt was accomplished by a metathesis reaction wherein a stoichiometric amount of $LiClO_4$ was added to an aqueous solution of $K_8[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]$ to precipitate $KClO_4$.

Preparation of $K_8[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]$. (This preparation was briefly reported in ref 3.) $K_9Li\ [\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ (10 g, 2.2 mmol) was suspended in 100 mL of 1 M lithium acetate buffer, pH = 4.7, at room temperature. To the stirred suspension, 3 mL of a 1 M $ZnCl_2$ (3 mmol) solution was added dropwise. Most of the $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ dissolved upon addition of the first few drops of $ZnCl_2$. The suspension was filtered, and potassium chloride (10 g, 0.135 mol) was added to the stirred solution to precipitate a white solid. The solid was filtered out, washed with 35 mL of ethanol (10 min, stirring), and dried in vacuum. This solid was not recrystallized. Yield: 4.9 g, 70% yield. IR data, KBr pellet: 1140 cm^{-1}, sh; 1101 cm^{-1}, s; 1083 cm^{-1}, s; 1013 cm^{-1}, m; 947 cm^{-1}, s, b; 906 cm^{-1}, s, b. anal. Calcd for $K_8\ ZnH_2P_2W_{17}O_{62}\cdot 20H_2O$: K, 6.36%; P, 1.26%; W, 63.52%; Zn, 1.33%. Found: K, 6.37%; P, 1.11%; W, 63.17%; Zn, 1.18%.

Conversion of $K_8[\alpha\text{-}1\ \text{-}Zn(H_2O)P_2W_{17}O_{61}]$ to the Li Salt. $K_8[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]$ (3.0 g, 0.6 mmol) was converted to the lithium salt by the ion exchange procedure using a Dowex AG50W-X2 cation-exchange column in the lithium form as described above. The aqueous solution was then lyophilized at −40 °C. IR data, KBr pellet: 1120 cm^{-1}, m; 1101 cm^{-1}, s; 1085 cm^{-1}, s; 1014 cm^{-1}, m; 953 cm^{-1}, s, b; 907 cm^{-1}, s, b. The solid was dissolved in D_2O (2.5 mL) for collection of NMR data.

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(6) Although this lacunary species is reported as $K_9[\alpha\text{-}1\text{-}Li\text{-}P_2W_{17}O_{61}]$ in refs 3 and 4, a reviewer pointed out that there is little evidence that the lithium acts as other than a counterion. We will be referring to this lacunary species as $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ or $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ throughout the paper.

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Table 1. Phosphorus-31 NMR Data

compd	chem shift, δ, ppm[a] P2	P1	impurities (δ, ppm)
K$_9$[α-1-LiP$_2$W$_{17}$O$_{61}$][b]	−13.40	−9.50	
Li$_9$[α-1-LiP$_2$W$_{17}$O$_{61}$][c]	−13.48	−9.16	<5% [α-2-P$_2$W$_{17}$O$_{61}$] (−7.46, −14.29)
Li$_9$[α-1-LiP$_2$W$_{17}$O$_{61}$][d]	−13.14	−8.83	<5% [α-2-P$_2$W$_{17}$O$_{61}$] (−7.12, −13.95)
K$_{10}$[α-2-P$_2$W$_{17}$O$_{61}$][e]	−14.10	−7.28	
Li$_{10}$[α-2-P$_2$W$_{17}$O$_{61}$][d,e]	−13.95	−7.12	
Li$_{10}$[α-2-P$_2$W$_{17}$O$_{61}$][c,f]	−14.31	−7.48	<2% [α-1-P$_2$W$_{17}$O$_{61}$] (−8.15)
K$_8$[α-1-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$]	−13.45	−8.56	<1-2% [α-2-ZnP$_2$W$_{17}$O$_{61}$] (−14.61)
Li$_8$[α-1-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$][c]	−13.41	−8.42	<1-2% [α-2-ZnP$_2$W$_{17}$O$_{61}$] (−14.20)
Li8[α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$][d,e]	−13.90	−8.40	
K$_8$[α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$][f]	−14.15	−8.65	<2% [α-1-ZnP$_2$W$_{17}$O$_{61}$] (−13.43)
Li$_8$[α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$][f]	−14.11	−8.65	<2% [α-1-ZnP$_2$W$_{17}$O$_{61}$] (−8.55, −13.43)

[a] See text for data collection parameters. P1 is the phosphorus atom closest to the site of substitution; P2 represents the phosphorus atom remote to the substituent site. [b] 1 M LiCl, D$_2$O. [c] Li salt prepared by ion-exchange chromatography at pH = 5; see text. [d] LiClO$_4$ metathesis reaction. [e] Prepared by base degradation of pure [α-P$_2$W$_{18}$O$_{62}$]$^{6-}$ (method 2). [f] Prepared by method 1.

Results

Elemental analyses of the potassium salts are in agreement with the proposed formulae. Infrared spectroscopy data for K$_8$[α-1-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$] and Li$_8$[α-1-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$] show similarity to the lacunary K$_9$Li[α-1-P$_2$W$_{17}$O$_{61}$] species, consistent with the isostructural nature of the molecules. The K$_9$Li[α-1-P$_2$W$_{17}$O$_{61}$] species shows two strong bands at 1122 and 1081 cm^{-1}, representative of the P−O bonds. The Zn complexes show bands which are slightly shifted, 1101 and 1083 cm^{-1} (1085 cm^{-1}). The Li$_8$[α-1-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$] complex shows an additional medium band at 1120 cm^{-1}. All other bands are very similar in the three spectra. The IR data are consistent with the Zn complex retaining the structural integrity of the [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$ oxoanion cage. Similar observations apply to the K$_8$[α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$] case.

The ^{31}P NMR data are presented in Table 1. ^{31}P NMR is a very sensitive technique to assess the purity of the complexes. The presence of even small amounts (2−4%) of isomeric impurities can be easily determined by ^{31}P spectroscopy.[7] The ^{31}P spectra of K$_9$Li[α-1-P$_2$W$_{17}$O$_{61}$] and K$_{10}$[α-2-P$_2$W$_{17}$O$_{61}$] agree with published data.[4] The ^{31}P spectra for the isolated α-1 and α-2 [Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$] isomers also are consistent with the spectrum obtained for the mixture of α-1 and α-2 isomers.[1] For all four compounds, the data for the ion exchanged lithium salts vary only slightly from that for parent potassium salts.

In Table 1, P1 refers to the resonance attributed to the P atom closest to the site of substitution (or defect) and P2 refers to the P atom furthest from the site of substitution (or defect). The method of ion exchange appears to affect the chemical shifts of both the P1 and P2 resonances slightly. The variation of chemical shift is most noticeable for the P1 resonance of the lacunary [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$, perhaps reflecting the possibility of some K$^+$ ion or ClO$_4^-$ remaining in the ion-exchanged solution. The counterion may be quite important in the chemical shift of the P1 phosphorus atom close to the defect site in the [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$ isomer.

It is easily seen that, for both isomers, the chemical shift of the P2 (remote phosphorus) resonance does not vary greatly in going from the lacunary structure to the Zn complex. The chemical shift of the P1 (near phosphorus atom) resonance, however, experiences pronounced shifts (0.5−1 ppm) upon complexation with Zn(II) for both isomers.

We observed a small amount (<2%) of impurities in the ^{31}P NMR spectrum of [α-2-Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$, which was prepared from in situ degradation of K$_6$[α/β-P$_2$W$_{18}$O$_{62}$] (method 1). The ^{183}W NMR data, however, showed a highly pure product. The ^{31}P NMR and ^{183}W NMR data showed extremely pure product (>99%) when isomerically pure K$_{10}$[α-2-P$_2$W$_{17}$O$_{61}$] was used to prepare [α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$ (method 2). Figure 2a shows the ^{31}P spectrum of the K$^+$ salt of [α-2-Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$ prepared by method 2. The K$^+$ and Li$^+$ salts of [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$ show [α-2] impurities (<5%). The K$^+$ and Li$^+$ salts of the [α-1-Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$ molecule show <2% of the [α-2] impurity according to ^{31}P NMR data. Figure 3a shows the ^{31}P spectra of the potassium salt of the [α-1-Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$ complex.

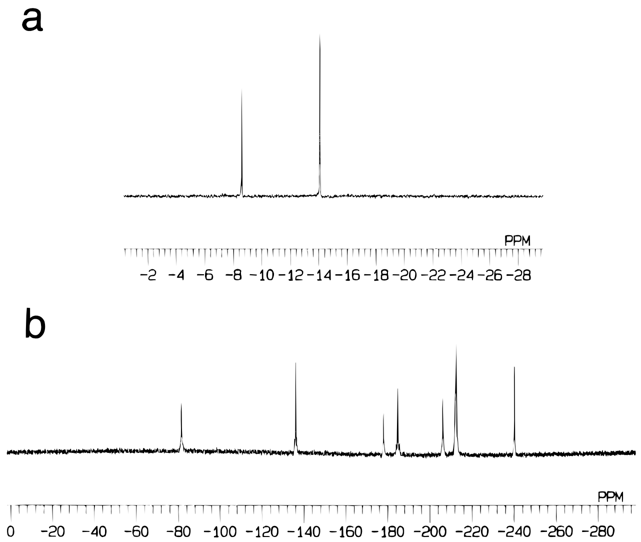

Figure 2. (a) ^{31}P NMR spectrum of [α-2-Zn(H$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$, 0.03 M in D$_2$O, 35 °C, 64 scans. (b) ^{183}W NMR spectrum of [α-2-Zn(H$_2$O)-P$_2$W$_{17}$O$_{61}$]$^{8-}$, 0.2 M in D$_2$O, 35 °C, pH = 3.8, 16 000 scans.

Table 2 shows the ^{183}W NMR chemical shift data for the lithium salts of [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$, [α-1-Zn(D$_2$O)-P$_2$W$_{17}$O$_{61}$]$^{8-}$, and [α-2-Zn(D$_2$O)-P$_2$W$_{17}$O$_{61}$]$^{8-}$. The ^{183}W NMR data for these molecules are shown in Figures 4a, 3b, and 2b, respectively. For both lithium salts of the lacunary [α-1-P$_2$W$_{17}$O$_{61}$]$^{10-}$ and [α-1-Zn(D$_2$O)-P$_2$W$_{17}$O$_{61}$]$^{8-}$, the expected 17 line pattern of chemical shifts is observed, where all of the peaks have equal integrated intensities, consistent with C_1 symmetry. Figures 3c and 4b show expansion of the upfield regions of each spectrum where the satellites due to W−O−W coupling and the coupling of each tungsten to phosphorus can be observed. The coupling constants are all 1−1.5 Hz. The chemical shifts of the isolated α-1 and α-2 [Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$]$^{8-}$ match those reported for the mixture[1] of the α-1 and α-2 isomers.

A seven-line pattern is observed in Figure 2b, for the Li$_8$[α-2-Zn(D$_2$O)P$_2$W$_{17}$O$_{61}$] complex. The integrated intensities reflect

Table 2. Tungsten-183 NMR Data[a]

compd	chem shift, δ, ppm
$Li_9[\alpha\text{-1-LiP}_2W_{17}O_{61}]$[b]	−104.24 (1), −115.23(2), −122.96 (1),−136.45 (1),−143.56 (1), −150.09 (1), −153.61 (1), −163.50 (1), −172.37(1), −174.02 (1), −177.06 (1), −200.77 (1), −203.52 (1), −217.74(1), −221.12 (1) −221.85 (1)
$Li_8[\alpha\text{-1-Zn}(H_2O)P_2W_{17}O_{61}]$[b]	−98.92 (1), −116.73 (1), −122.49 (1),−145.50 (1), −151.22 (1), −157.45(1), −167.11 (1), −173.03 (1),−175.56 (1), −176.57 (1), −193.15(1), −200.02 (1), −203.56 (1), −210.07 (1), −213.99 (1), −214.17 (1), −224.67 (1)
$Li_8[\alpha\text{-2-Zn}(H_2O)P_2W_{17}O_{61}]$[b]	−80.05 (2), −134.58 (2), −176.66(1),−183.40 (2), −204.70 (2),−210.63(2), −211.04 (4), −238.64 (2)

[a] See text for data collection parameters. Integrated intensities given in parentheses. [b] Li salt prepared by ion-exchange chromatography at pH = 5; see text.

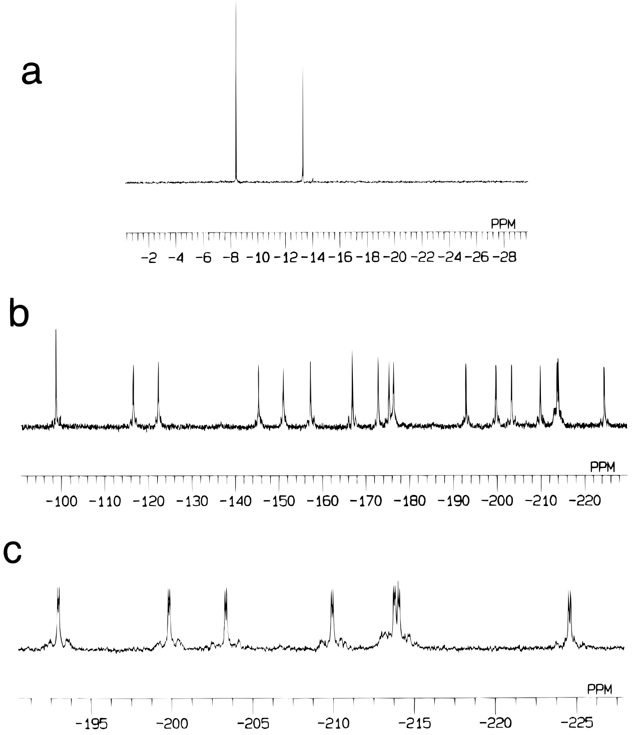

Figure 3. (a) ^{31}P NMR spectrum of $[\alpha\text{-1-Zn}(H_2O)P_2W_{17}O_{61}]^{8-}$, 0.03 M in D_2O, 35 °C, 64 scans. (b) ^{183}W NMR spectrum of α-1 $[Zn(H_2O)P_2W_{17}O_{61}]^{8-}$, 0.2 M in D_2O, pH = 5.3, 35 °C, 25 000 scans. (c) Expansion of the −190 ppm to 230 ppm region of (b).

the C_s symmetry of this molecule. Figure S1[9] shows the ^{183}W NMR spectrum for the lacunary species $Li_{10}[\alpha\text{-2-P}_2W_{17}O_{61}]$. The chemical shifts for this very well resolved spectrum are consistent with those reported in the literature.[5,7] Also, the satellites due to W−O−W coupling and the coupling of each tungsten to phosphorus (J_{W-P} =1−1.5 Hz) can be clearly observed (inset).

Figures S2−S4[9] show the expansions of the other regions of the spectra for molecules $[\alpha\text{-2-Zn}(D_2O)P_2W_{17}O_{61}]$, $Li_8[\alpha\text{-1-Zn-}(D_2O)P_2W_{17}O_{61}]$, and $Li_{10}[\alpha\text{-1-P}_2W_{17}O_{61}]$, respectively. We observe that, in the high-field region, coupling to P is not resolved, whereas, in the low-field region, the coupling is very well resolved.

Discussion

The $K_9Li[\alpha\text{-1-P}_2W_{17}O_{61}]$ compound was prepared as described by Contant[3,4] from the $K_{12}[H_2P_2W_{12}O_{48}]$ species. Maintaining the reaction pH between 4 and 5 is crucial for isolation of this species; the α-1 isomer easily isomerizes to the α-2 isomer under basic conditions. To convert to the lithium salt, the ion-exchange procedure was performed with control of the pH at 5.0. Removing the water was accomplished by lyophilization at −40 °C. Removing the water by freeze drying was important in this procedure as the lacunary $[\alpha\text{-1-P}_2W_{17}O_{61}]^{10-}$ isomer easily isomerizes to the α-2 species when heated. The pH of the metathesis reaction using $LiClO_4$ to exchange the K^+ to Li^+ was also rigorously controlled at pH 5.0. The pH of all solutions of this complex was always less than 6.4.

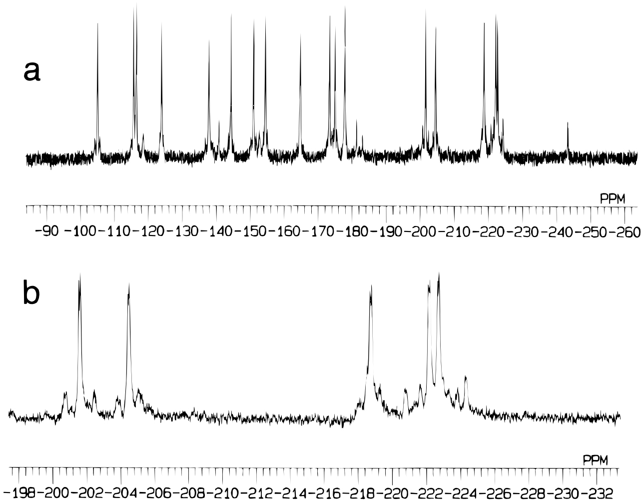

Figure 4. (a) ^{183}W NMR spectrum of $[\alpha\text{-1-Li P}_2W_{17}O_{61}]^{9-}$, 0.2 M in D_2O as the Li^+ salt, pH = 5.8, 35 °C, 16 000 scans. (b) Expansion of the −200 to −230 ppm region of (a).

The $[\alpha\text{-1-Zn}(H_2O)\text{-P}_2W_{17}O_{61}]^{8-}$ species was prepared from the reaction of $ZnCl_2$ with $K_9Li[\alpha\text{-1-P}_2W_{17}O_{61}]$. Maintaining the pH at 4.6 is again crucial to prevent isomerization to the α-2 species. Recrystallization of the $[\alpha\text{-1-Zn}(H_2O)P_2W_{17}O_{61}]^{8-}$ species from hot water results in mixtures of the α-1 and α-2 species. This is similar to the report by Pope[10] on the preparation of a $[\alpha\text{-1-OVP}_2W_{17}O_{61}]^{7-}$ species; upon recrystallization of the $[\alpha\text{-1-OVP}_2W_{17}O_{61}]^{7-}$ species from hot water, a mixture of the α-1 and α-2 isomers was obtained. Once the $[\alpha\text{-1-Zn}(H_2O)\text{-P}_2W_{17}O_{61}]^{8-}$ species is formed, it is stable for at least 1 week in aqueous solution at room temperature, pH = 6.0. Although we initially isolated the Li^+ salts of the $[\alpha\text{-1-Zn}(H_2O)P_2W_{17}O_{61}]^{8-}$ species by freeze drying, we subsequently found that the $[\alpha\text{-1-Zn}(H_2O)\text{ -P}_2W_{17}O_{61}]^{8-}$ species survives evaporation of the water at reduced pressures at temperatures less than 35 °C. It appears that the metal ion incorporated into the $[\alpha\text{-1-P}_2W_{17}O_{61}]^{10-}$ defect structure stabilizes the resulting $[\alpha\text{-1-P}_2W_{17}O_{61}]^{10-}$ metal complex. Furthermore the $[\alpha\text{-1-Zn-}(H_2O)P_2W_{17}O_{61}]$ species appears to be quite stable in the pH range 4.6−6.0 and temperatures less than 35 °C. It should be noted that the mixture of α-1 and α-2 isomers of $[OVP_2W_{17}O_{61}]^{7-}$

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(9) Supporting Information.

(10) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286.

could be successfully separated by chromatography on Sephadex,[10] also consistent with the retention of integrity of the [α-1-$OVP_2W_{17}O_{61}$] species during this chromatographic procedure.

As reported by Finke,[7] we found that the use of isomerically pure [α-2-$P_2W_{17}O_{61}]^{10-}$ starting reagent ensures isomerically pure [α-2-Zn(H_2O)$P_2W_{17}O_{61}]^{8-}$ complex, as determined by ^{31}P NMR spectroscopy. In situ formation of [α-2-$P_2W_{17}O_{61}]^{10-}$ from base degradation of [α/*β*-$P_2W_{18}O_{62}]^{6-}$ followed by reaction with $ZnCl_2$ resulted in a small amount (ca. 2%) of the α-1 species as an impurity. This impurity was observed in the ^{31}P NMR spectrum and not in the ^{183}W NMR spectrum.

In this study, we have isolated the [α-2-Zn(H_2O)$P_2W_{17}O_{61}]^{8-}$ and the [α-1-Zn(H_2O)$P_2W_{17}O_{61}$]]$^{8-}$ isomeric species in >98% purity according to ^{31}P NMR spectroscopy. The chemical shift values in ^{183}W NMR spectra for both of the [Zn(H_2O)$P_2W_{17}O_{61}]^{8-}$ isomers agrees well with the α-1/α-2 mixture isolated by Jorris[1].

The ^{183}W NMR spectrum of ion-exchanged lithium salt of the lacunary [α-1-$P_2W_{17}O_{61}]^{10-}$ showed 17 equally intense resonances, and the downfield resonances clearly showed W−O−W coupling as well as W−O−P coupling. This spectrum is consistent with C_1 symmetry of the molecule in which all 17 tungsten atoms are inequivalent and is, thus, consistent with removal of a $[WO]^{4+}$ group from the belt tungsten atoms. A small amount (<5%) of α-2 impurity was present in all preparations of lacunary [α-1-$P_2W_{17}O_{61}]^{10-}$.

Conclusion

The C_1 symmetry of the lacunary [α-1-$P_2W_{17}O_{61}]^{10-}$ species has been confirmed by ^{183}W NMR spectroscopy. As expected, 17 lines are observed, some exhibiting W−O−W coupling and W−O−P coupling, consistent with the defect occurring at one of the "belt" tungsten atoms. The [α-1-Zn^{II}(H_2O)$P_2W_{17}O_{61}]^{8-}$ species has been prepared in ≥98% purity by reaction of K_9Li[α-1-$P_2W_{17}O_{61}$] with $ZnCl_2$ at pH 4.6, with subsequent ion exchange, at pH 4.7, and lyophilization to form the Li^+ salt. The ^{183}W NMR spectral characterization of the isomer in aqueous solution matches the resonances reported previously for a mixture of the α-1 and α-2 isomers. The metal complex [α-1-Zn^{II}(H_2O)$P_2W_{17}O_{61}]^{8-}$ appears to be stable at room temperature, between pH values of 4.6 and 6.0. Preparation, purification, and isolation of other metal complexes of the [α-1-$P_2W_{17}O_{61}]^{10-}$ isomer should be possible, and we are pursuing that avenue.

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Supporting Information Available: Figure S1, showing the tungsten-183 NMR spectrum for the lacunary species [α-2-$P_2W_{17}O_{61}]^{8-}$, and Figures S2−S4, showing the expansions of regions of the ^{183}W NMR spectra for molecules [α-2-Zn(H_2O)$P_2W_{17}O_{61}]^{8-}$, [α-1-Zn(H_2O)-$P_2W_{17}O_{61}]^{8-}$, and [α-1-$P_2W_{17}O_{61}]^{10-}$ (5 pages). Ordering information is given on any current masthead page.

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