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SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE COMPLEXES OF THE LACUNARY WELLS-DAWSON HETEROPOLYANIONS

by

Judit Bartis

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1997

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

Sept 2, 1997
Date

Lynn C. Francesconi
Chair of Examining Committee

Sept. 2, 1997
Date

Executive Officer

Supervisory Committee

The City University of New York

Abstract

SYNTHESIS AND CHARACTERIZATION OF LANTHANIDE COMPLEXES OF THE LACUNARY WELLS-DAWSON HETEROPOLYANIONS

by

Judit Bartis

Adviser: Professor Lynn C. Francesconi

The preparation of the α–1 and α-2 isomers of the lacunary Wells-Dawson heteropolyanions 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 $[ZnP_2W_{17}O_{61}]^{8-}$ and lanthanide complexes of the $[P_2W_{17}O_{61}]^{10-}$ heteropolyoxotungstate have been prepared in > 98% purity, and characterized by multinuclear NMR spectroscopy among the other techniques. The first direct proof of the C_1 symmetry of the α–1 isomer has been obtained by ^{183}W NMR spectroscopy.

Solution titration data monitored by ^{31}P NMR spectroscopy show that both the 1:1 and 1:2 Ln: $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ exist in aqueous solution at pH=4.7 for a variety of Ln ions proceeding across the lanthanide series. The $[Ln(\alpha\text{-}2\ P_2W_{17}O_{61})_2]^{17-}$ family of complexes show a nine line pattern in the ^{183}W NMR spectrum at room temperature for the lanthanum derivative, consistent with a

symmetrical structure (C_{2h} or C_{2v} symmetry), and seventeen, line pattern for the lutetium analog, suggesting a lower symmetry (C_2). High temperature ^{183}W NMR experiments on the $[Lu(\alpha\text{-}2\ P_2W_{17}O_{61})_2]^{17-}$ compound showed reversible broadening and coalescence of the resonances, due to a dynamic effect, possibly rotation of the oxoanion ligand.

The crystal structure of the $K_{17}[Lu(\alpha\text{-}2\ P_2W_{17}O_{61})_2]$ shows the lutetium ion bound to four oxygen atoms of the $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ in a square antiprismatic coordination environment. ^{183}W NMR data for the isolated $[Ln(\alpha\text{-}2\ P_2W_{17}O_{61})_2]^{17-}$ complexes in aqueous solution are consistent with the crystal structure data.

The solution stoichiometry of the lanthanide complexes of the $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ has been determined using complexometric titration experiments combined with ^{31}P NMR spectroscopy. The results show that α-1 $[P_2W_{17}O_{61}]^{10-}$ complexes with lanthanides in 1:1 stoichiometric ratio only.

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TO MY SON

AND

TO MY GRANDMOTHER

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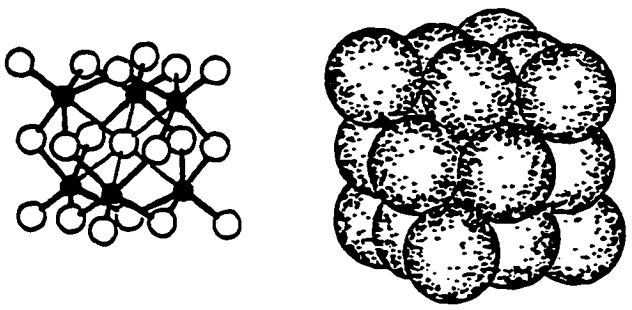
Introduction

Polyoxoanions are polyanionic aggregates of transition metals like V^{v}, Nb^{v}, Ta^{V}, Mo^{VI} or W^{VI}. They are prepared by the protonation and condensation of the simple metal-oxygen anion WO_4^{2-} at low pH [1]. The formation of these polynuclear oxoanions was discovered in the mid -19th century and during the past two decades there has been a renewed interest in their chemistry due to the development of analytical instrumentation, expansion of synthetic methodology, and the industrial application of polyoxoanions as catalysts.

Since the metal is in its highest oxidation state, there are no electrons available for metal-metal bonding and the polyoxoanions are held together only by metal-oxygen bonds. The formation of these metal-oxygen clusters is the result of a favorable combination of ionic radii and charge and of accessibility of empty d orbitals for metal – oxygen π bonding [1].

Polyoxoanions incorporating heteroatoms are called heteropolyoxoanions. The most common heteroatoms are Si, P, Ge and As, which are tetrahedrally-coordinated in the central cavity of the heteropolyanion. They form various structures depending on their size.

One of the simplest structural types of the polyoxotungstates is the octahedral $W_6O_{19}^{2-}$ anion, so called Lindquist structure [2] shown in Figure 1.



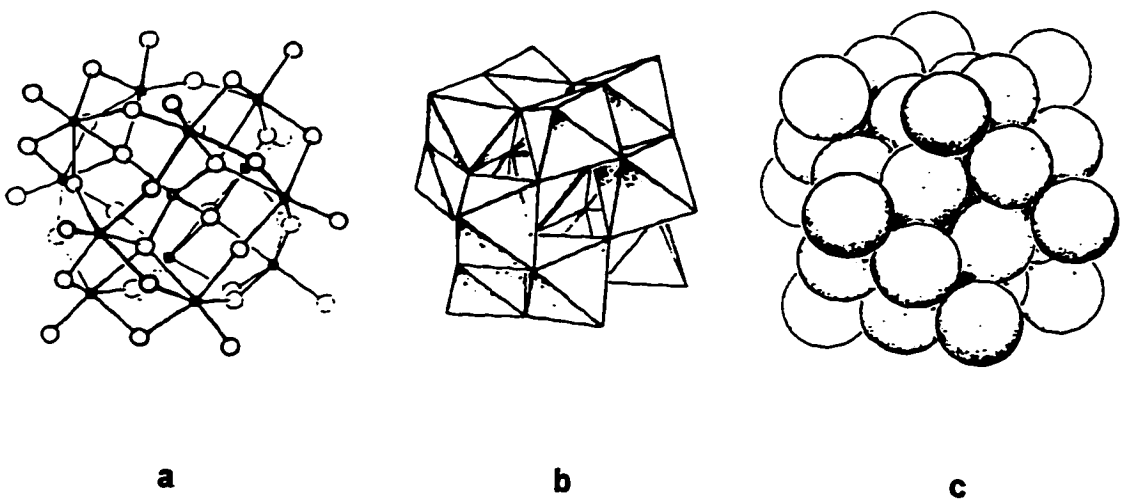
a. b.

Figure 1. a) Stick and ball model of $W_6O_{19}^{2-}$ where filled circles represent tungsten centers, open circles represent oxygen centers. b) space filling representation of the $W_6O_{19}^{2-}$.

Three different type of metal-oxygen bonds can be distinguished at each tungsten center: one very short (1.69 A) terminal WO bond which corresponds to a double bond, four somewhat longer (1.92 A) bonds to doubly bridging OW_2 oxygens which correspond to single bonds, and a very long weak bond (2.33 A) to the central sixfold bridging OW_6. This structure can be viewed as a neutral W_6O_{18} cage encapsulating an O^{2-} anion.

The terminal and bridging oxygen atoms are quite non-basic and nonreactive. These molecules can be activated, or made more basic, by replacing one or more of the hexavalent metal sites with lower valent metal atoms, and the oxygens adjacent to the substitution site bear negative surface charge density.

The α-$XW_{12}O_{40}$ (X= Si, P, Ge, etc.) Keggin ion shown in Figure 2. is an important representative of heteropolytungstates [3]. This structure has T_d symmetry and is based on a central XO_4 tetrahedron surrounded by twelve WO_6 octahedra, arranged in four groups of three edge shared W_3O_{13} units [1].



a b c

Figure 2. The Keggin ion [1] ($XW_{12}O_{40}$)

a) ball and stick representation. Filled circles represent tungsten centers, open circles represent oxygen centers.

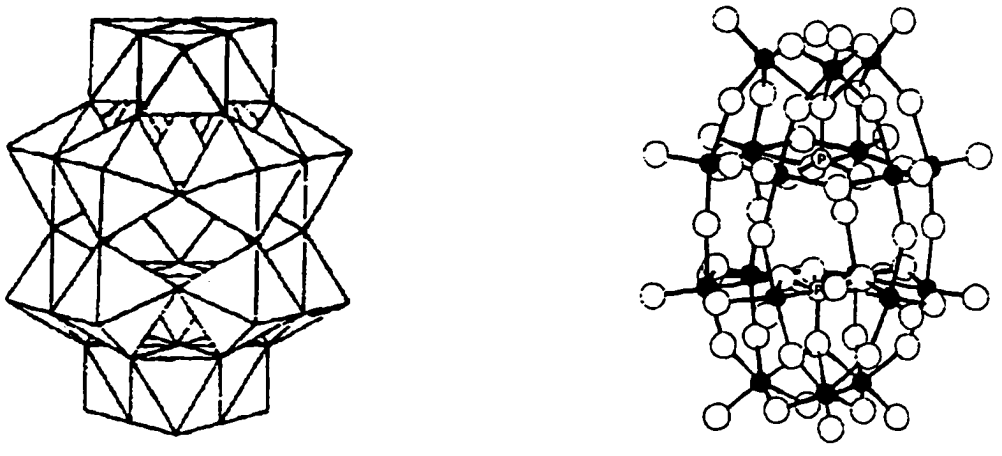
b) polyhedral representation [4]. Each octahedron represents a WO_6 unit where the W is within the octahedron and oxygens are at the vertices of the octahedron. The heteroatom X is in the central cavity of the molecule as XO_4 tetrahedron

c) space filling representation.

Several topologically inequivalent geometries are possible for the for the parent $M_{12}O_{36}$ cage structure, based on the arrangement of four groups of edge shared M_3O_{13} octahedron around a central XO_4^{n-} tetrahedron. All of the M atoms are equivalent in the α isomer (T_d symmetry). Rotation of one triad relative to the other three results in the β isomer [1].

When solutions of $[XW_{12}O_{40}]^{n-}$ (X = Si, n=4, X = P, n=3) are treated with base (pH=5), a complex series of hydrolysis reactions occur leading to a variety of "lacunary" anions or "defect" structures by removal of one, two three tungsten-oxygens units from the Keggin structure. These defect structures can act as ligands to mono, di, trinuclear complexes according to the number of vacant sites. These defect strucures can form very stable complexes with transition metal or lanthanide/actinide complexes.

The Wells-Dawson $X_2W_{18}O_{62}$ (X=P,As, etc.) consists of 18 octahedra and it contains two heteroatoms in its central cavity [5]. The molecule has two types of tungsten atoms, six cap and twelve belt. It forms two isomers, an α isomer with D_{3h} symmetry and a β isomer which has a D_{3d} symmetry. The difference between the two isomers is the rotation of the three cap WO_6 octahedra by $\pi/3$. The existence of a third γ isomer for the $(As_2W_{18}O_{62})^{6-}$ has been confirmed by ^{183}W NMR [6].



a b

Figure 3. The $(\alpha-P_2W_{18}O_{62})^{6-}$ Wells-Dawson molecule in a) polyhedral[4] and b) ball and stick representation.

Removal of one or more W atoms with their terminal oxygens at high pH generates the so called "lacunary" or "defect" structures which are very good ligands for transition metals, lanthanides and actinides [1]. Genarally one transition metal binds in the cavity. Recently Randall and Finke isolated a Ru(IV) dimer where a $O=Ru^{IV}-O-Ru^{IV}=O$ unit is trapped within two $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ moieties [7].

The lanthanide compounds isolated in the solid state thus far have been the 1:2 Ln: $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ "sandwich complexes, originally discovered by Peacock and Weakley [8] in 1971. In many cases reports of lanthanide complexes of monovacant Keggin or Wells – Dawson oxoanions have been limited to synthesis, elemental analysis and spectroscopic titrations using Ce(III).

Heteropolyoxoanions have wide applications in catalysis, biochemistry and material science due to their high ionic charges, acid-base properties and ionic weights. Various types of polyoxoanions are used as homogeneous and heterogeneous catalysts [9] in the hydration of propene, n-butene, and isobutene, and in the oxygenation of alkenes or alkanes.

Polyoxoanions have also been noted for anti-viral activity [10-15]. In the work cited, polyoxoanions show significant activity against HIV in a variety of cell lines with virtually no toxicity.

The chemistry of polyoxoanion complexes in aqueous solution is associated with many difficulties. There are multiple equilibria occurring, and polyoxoanion structure and stability are very dependent on the environment (pH, counterion and concentration). It is very difficult to obtain crystals, or they are highly disordered. Elemental analysis is often inaccurate. They tend to condense or decompose in the conditions used in mass spectrometric analysis, therefore the interpretation of data can be misleading.

This dissertation describes in detail our extensive structural studies of lanthanide complexes of Wells-Dawson heteropolyoxotungstates.

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Chapter 1

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

INTRODUCTION

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 [α-2-$P_2W_{17}O_{61}]^{10-}$ isomer which has C_s symmetry, and removal of a WO unit from a belt WO_6 polyhedron results in the lacunary [α-1-$P_2W_{17}O_{61}]^{10-}$ isomer which has C_1 symmetry.[1] Lacunary oxoanions are generally good ligands for transition metals, lanthanides and actinides.[2] The metal ion binds to the four (lanthanide and actinide) and four (transition metals) oxygen atoms of the defect oxoanion. Figure 1.1, a and b, show the metal complexes of the α-2 and α-1 $[P_2W_{17}O_{61}]^{10-}$ isomers[1,3], respectively, in polyhedral representation, where the vertices of the polyhedra represent oxygen atoms and the tungsten atoms are located within each polyhedron. Figure 1.1, c and d, show the tungsten framework 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. Figure 1. 2, a and b, shows the two isomers in ball and stick representation, where the hatched circles represent the oxygens available for complexation with metals.

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 accompanied by a significant proportion of the other isomer present as an impurity. For example, Jorris reported the ^{183}W NMR spectrum of the [α-2-

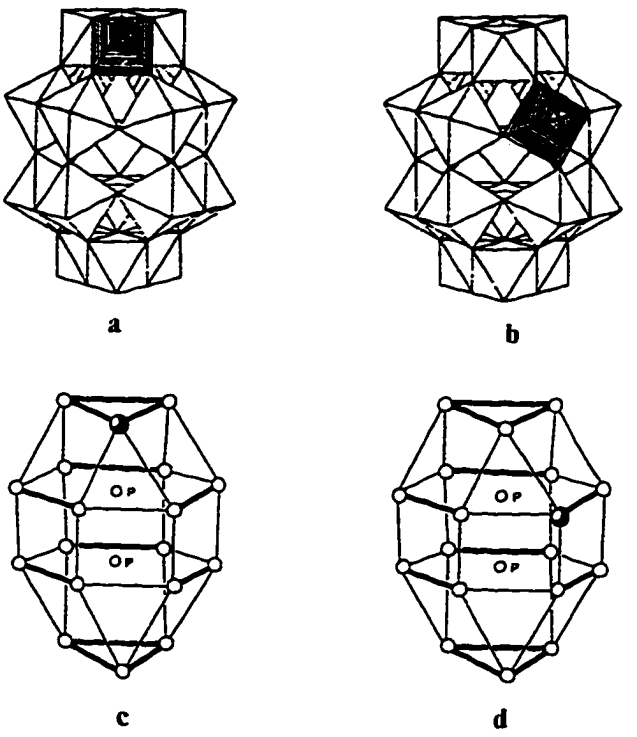


Figure 1.1. a) α-2 and b) α–1 $[P_2W_{17}O_{61}]^{10-}$ isomers in polyhedral notation. The hatched octahedra represent the site of substitution.

c) and d) represent the α–2 and α-1 $[P_2W_{17}O_{61}]^{10-}$ isomers respectively, showing the tungsten atom framework.

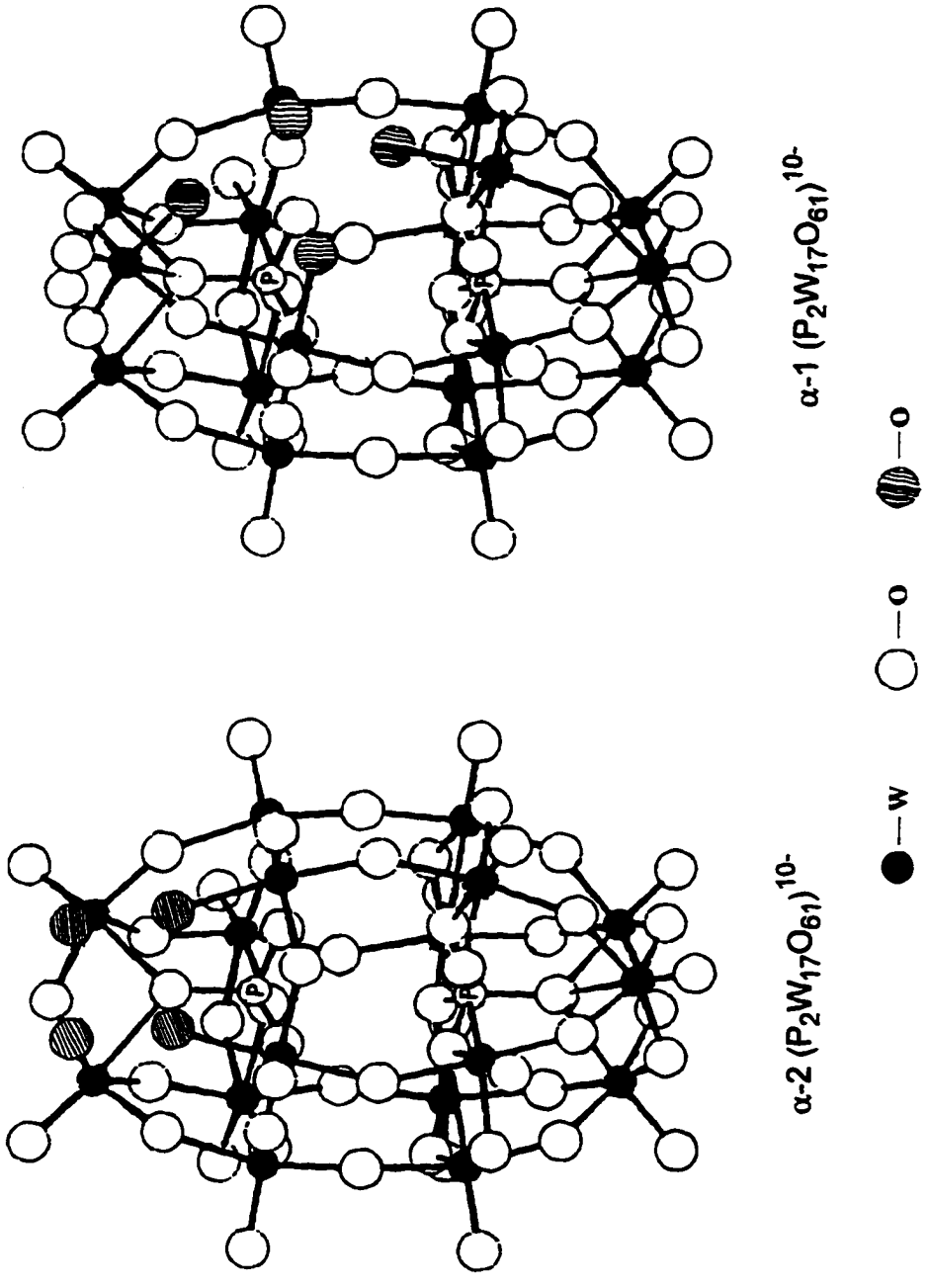


Figure 1.2. Ball and stick representation of the α-2 and α-1 $(P_2W_{17}O_{61})^{10-}$.

$Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ species which contained the presence of ca. 17% of the α-1 isomer as an impurity [4]. 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 very sensitive method to assess the structure and stability of heteropolytungstates in solution. [5]

This chapter discusses 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 and ^{31}P NMR spectra of the α-1 /α-2 mixture had been reported[4] 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

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 $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ was prepared following the method of Contant.[1,3] The α-2 lacunary isomer, $K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$, was prepared following the method of Finke[6]. Molecules $K_6[P_2W_{18}O_{62}]$ and $K_{12}[H_2P_2W_{12}O_{48}]$ were prepared according to literature methods.[3] 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 hours, 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 broadband probe. Typical acquisition parameters for ^{31}P spectra included: spectral width: 10,000Hz; acquisition time: 0.8 s; pulse delay: 1s; pulse width : 15μsec (50 degree tip angle). From 50 to 500 scans were required. For ^{183}W spectra, typical conditions included: spectral width: 10,000Hz; acquisition time: 1.6 s; pulse delay: 0.5s; pulse width: 50 μsec (45 degree tip angle). From 1,000 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 5,000Hz and

the acquisition time increased to 3.2s. Also, the data were zero-filled once before Fourier transformation for a final spectral resolution of 0.16Hz. For all spectra, the temperature was controlled to ±0.2 degree. ^{31}P spectra were referenced to a H_3PO_4 standard in D_2O, which has 0.67 ppm upfield chemical shift relative to 85% H_3PO_4. ^{183}W spectra were referenced to 2.0 M Na_2WO_4. For both ^{31}P and ^{183}W NMR, the convention used is that the more negative chemical shifts denote upfield resonances.

Preparation of Li_{10} [α-1 $P_2W_{17}O_{61}$]. K_9Li [α-1-$P_2W_{17}O_{61}$][3,4] (2.75 g, 0.6 mmoles) 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), pH = 4.7, and eluted with water at a flow rate of 4 mL/ min. The resulting clear, colorless solution with a pH=5 was lyophilized at -40°C. The resulting solid was dissolved in D_2O to prepare a 0.25M solution for NMR spectroscopy.

Preparation of K_8 [α-2 -$Zn(H_2O)P_2W_{17}O_{61}$].

Method 1. This method generates the lacunary [α-2-P_2W_{17} O_{61}]$^{8-}$ species in situ from the parent Wells-Dawson molecule. 15 g (3 mmoles) of K_6[α/β-$P_2W_{18}O_{62}$][3] was dissolved in 60 mL water at 80°C. $ZnCl_2$ (0.61g, 4.5 mmol) was dissolved in a minimum amount of water. Potassium acetate (12.0 g, 0.12 mmol) was dissolved in 15 mL water and the pH was adjusted to 7 with acetic acid. The $ZnCl_2$ solution was added dropwise to the hot K_6[α/β-$P_2W_{18}O_{62}$] 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 two hours, 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. Elem. anal., calc. for $K_8 ZnH_2P_2W_{17}O_{62} \cdot 20 H_2O$: 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 [α-2 -$Zn(H_2O)P_2W_{17}O_{61}$] to 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), pH=4.7, 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, and ^{31}P NMR showed less than 2% of the α-1 impurity.

Method 2. Isomerically pure $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^6$ (5.0g, 1 mmol) was suspended in 50 mL of lithium acetate buffer (1M, pH=4.7). To the stirred suspension, $ZnCl_2$ (1.5 mL, 1M 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. 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 hours. The ^{31}P NMR data showed very pure product with no detectable α-1 impurity.

Conversion of α-1 or α-2 $K_8[Zn(H_2O)P_2W_{17}O_{61}]$ to Li salt by metathesis with $LiClO_4$. Conversion to the lithium salt was accomplished by a metathesis reaction with excess $LiClO_4$. In order to prepare 3mL of an approximately 0.2 M solution, 1g, 9.6 mmol of $LiClO_4$ was dissolved in 2 mL of D_2O. 2.9g, 0.6 mmol of the $K_8[Zn(H_2O)P_2W_{17}O_{61}]$ is added as a solid to this solution and stirred for a

few minutes. The solution is centrifuged and the precipitate which contains the $KClO_4$ decanted.

Preparation of K_8 [α-1-$Zn(H_2O)P_2W_{17}O_{61}$]. K_9Li [α-1-$P_2W_{17}O_{61}$] 10g, 2.2 mmol was suspended in 100 mL of 1M lithium acetate buffer, pH=4.7, at room temperature. To the stirred suspension, 3 mL of a 1M $ZnCl_2$ (3 mmol) solution was added dropwise. Most of the K_9Li [α-1-$P_2W_{17}O_{61}$] 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, washed with 35 mL of ethanol (10 minutes, 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; 1013cm^{-1}, m; 947 cm^{-1}, s,b; 906 cm^{-1}, s,b. Elem. anal., calc. for $K_8 ZnH_2P_2W_{17}O_{62} \cdot 20 H_2O$: 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 [α-1-$Zn(H_2O)P_2W_{17}O_{61}$] to Li salt. K_8[α-1-$Zn(H_2O)P_2W_{17}O_{61}$] (3.0 g, 0.6 mmol) was converted to the lithium salt by the ion exchange procedure using 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_20 (2.5 mL) for collection of NMR data.

RESULTS

Elemental analyses of the potassium salts are in agreement with the proposed formulae. Infrared spectroscopy data for the K_8[α-1-$Zn(H_2O)P_2W_{17}O_{61}$] and Li_8 [α-1-$Zn(H_2O)P_2W_{17}O_{61}$] show similarity to the lacunary K_9Li [α-1-$P_2W_{17}O_{61}$] species, consistent with the isostructural nature

of the molecules. The $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ species shows two strong bands at 1122 and 1081 cm^{-1}, representative of the terminal W=O bonds. The Zn complexes show bands which are slightly shifted, 1101 cm^{-1} and 1083 cm^{-1} (1085 cm^{-1}). The Li_8 $[\alpha\text{-}1\text{-}Zn(H_2O)P_2W_{17}O_{61}]$ 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 $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ oxoanion cage. Similar observations apply to the K_8 $[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]$ case.

The ^{31}P NMR data are presented in Table 1.1. ^{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.[6] The ^{31}P spectra of K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ and $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ agree with published data.[3] The ^{31}P spectra for the isolated α-1 and α-2 $[\text{-}Zn(D_2O)P_2W_{17}O_{61}]$ isomers also are consistent with the spectrum obtained for the mixture of α-1 and α-2 isomers.[4] For all four compounds, the data for the ion exchanged lithium salts vary only slightly from the parent potassium salts.

In Table 1.1, P1 refers to the resonance attributed to the P atom closer to the site of substitution (or defect) and P2 refers to the P atom further 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 $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, 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 $[\alpha\text{-}1\text{ -}P_2W_{17}O_{61}]^{10-}$ isomer.

Table 1.1. Phosphorus-31 NMR Data.

Compound	Chemical Shift, δ,ppm[a]		
	P2	P1	
$K_9[\alpha\text{-}1Li\ P_2W_{17}O_{61}]$[b]	-13.40	-9.50	
$Li_9[\alpha\text{-}1Li\ P_2W_{17}O_{61}]$[c]	-13.48	-9.16	(<5% [α-2 $P_2W_{17}O_{61}$, -7.46, -14.29)
$Li_9[\alpha\text{-}1Li\ P_2W_{17}O_{61}]$[d]	-13.14	-8.83	(<5% [α-2 $P_2W_{17}O_{61}$, -7.12, -13.95)
$K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$[e]	-14.10	-7.28	
$Li_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$[d,e]	-13.95	-7.12	
$Li_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$[c,f]	-14.31	-7.48	(<2% [α-1 $P_2W_{17}O_{61}$, -8.15)
$K_8[\alpha\text{-}1\ Zn(H_2O)P_2W_{17}O_{61}]$	-13.45	-8.56	(<1-2% [α-2 $ZnP_2W_{17}O_{61}$],, -14.16)
$Li_8[\alpha\text{-}1\ Zn(H_2O)P_2W_{17}O_{61}]$[c]	-13.41	-8.52	(<1-2% [α-2 $ZnP_2W_{17}O_{61}$], -14.20)
$Li_8[\alpha\text{-}2\ Zn(H_2O)P_2W_{17}O_{61}]$[d,e]	-13.90	-8.40	
$K_8[\alpha\text{-}2\ Zn(H_2O)P_2W_{17}O_{61}]$[f]	-14.15	-8.65	(<2% [α-1 $ZnP_2W_{17}O_{61}$], -13.43)
$Li_8[\alpha\text{-}2\ Zn(H_2O)P_2W_{17}O_{61}]$[f]	-14.11	-8.65	(<2% [α-1 $ZnP_2W_{17}O_{61}$]-8.55,.-13.43)

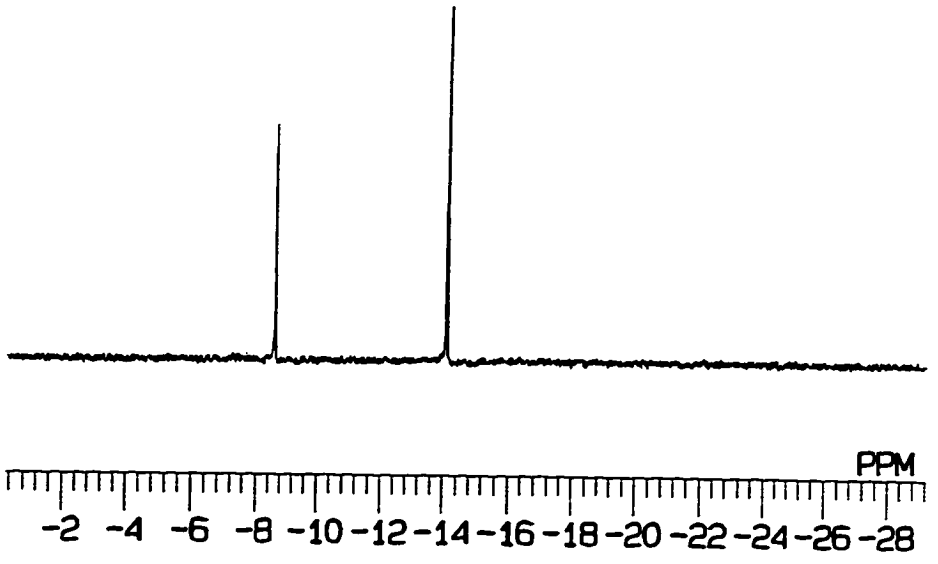
a. See text for data collection parameters. P1 is the phosphorus atom closer to the site of substitution, P2 represents the phosphorus atom remote to the substitution site. b. 1M LiCl, D_2O c. Li salt prepared by ion exchange chromatography at pH=5, see text. d. $LiClO_4$ metathesis reaction e. prepared by base degradation of pure $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ (method 2). f. prepared by method 1.

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 $[\alpha\text{-}2\text{-}Zn(D_2O)P_2W_{17}O_{61}]^{8-}$, which was prepared from in situ degradation of $K_6[\alpha/\beta\text{-}P_2W_{18}O_{62}]$ (Method 1). The W-183 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 $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ was used to prepare $[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]^{8-}$ (Method 2). Figure 1.3 a shows the ^{31}P spectrum of the K^+ salt of $[\alpha\text{-}2\text{-}Zn(D_2O)P_2W_{17}O_{61}]^{8-}$ prepared by method 2. The K^+ and Li^+ salts of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ show [α-2] impurities (<5%). The K^+ and Li^+ salts of the $[\alpha\text{-}1\text{-}Zn(D_2O)P_2W_{17}O_{61}]^{8-}$ molecule show <2% of the [α-2] impurity according to ^{31}P NMR data. Figure 1.4 a shows the ^{31}P spectra of the potassium salt of the $[\alpha\text{-}1\text{-}Zn(D_2O)P_2W_{17}O_{61}]^{8-}$ complex.

Table 1.2. shows the ^{183}W NMR chemical shift data for the lithium salts of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, $[\alpha\text{-}1\text{-}Zn(D_2O)\text{-}P_2W_{17}O_{61}]^{8-}$ and $[\alpha\text{-}2\text{-}Zn(D_2O)\text{-}P_2W_{17}O_{61}]^{8-}$. The ^{183}W NMR data for these molecules are shown in Figures 1.5a, 1.4b and 1.3b, respectively. For both lithium salts of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ and $[\alpha\text{-}1\text{-}Zn(D_2O)\text{-}P_2W_{17}O_{61}]^{8-}$, the expected seventeen line pattern of chemical shifts is observed, where all of the peaks have equal integrated intensities, consistent with C_1 symmetry. Figures 1.4c and 1.5b show expansion of the upfield regions of each spectrum where the satellites due to

a.



b.

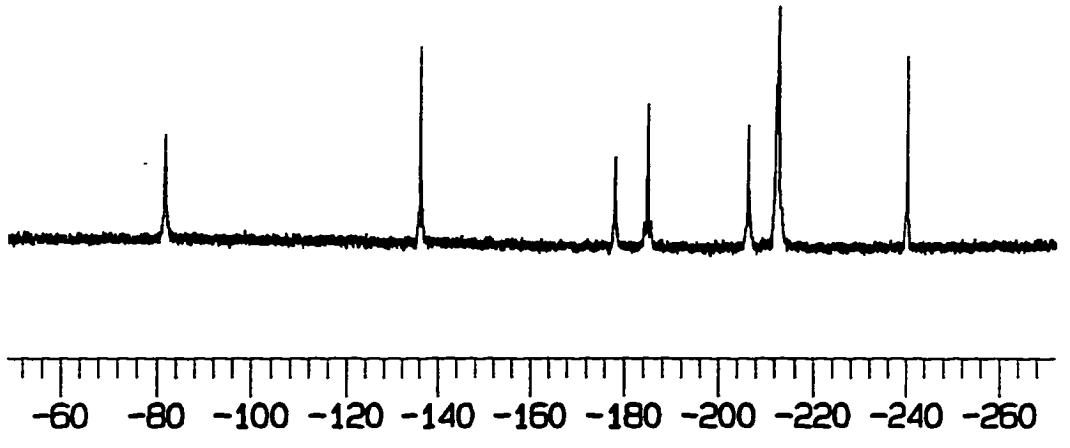


Figure 1.3. a) ^{31}P NMR spectrum of the α-2 $K_8[Zn(H_2O)P_2W_{17}O_{61}]$, 0.03 M in D_2O, 35 °C, 64 scans. b) ^{183}W NMR spectrum of α-2 $Li_8[Zn(H_2O)P_2W_{17}O_{61}]$, 0.2 M in D2O, 35 °C, 16 000 scans, pH=3.8.

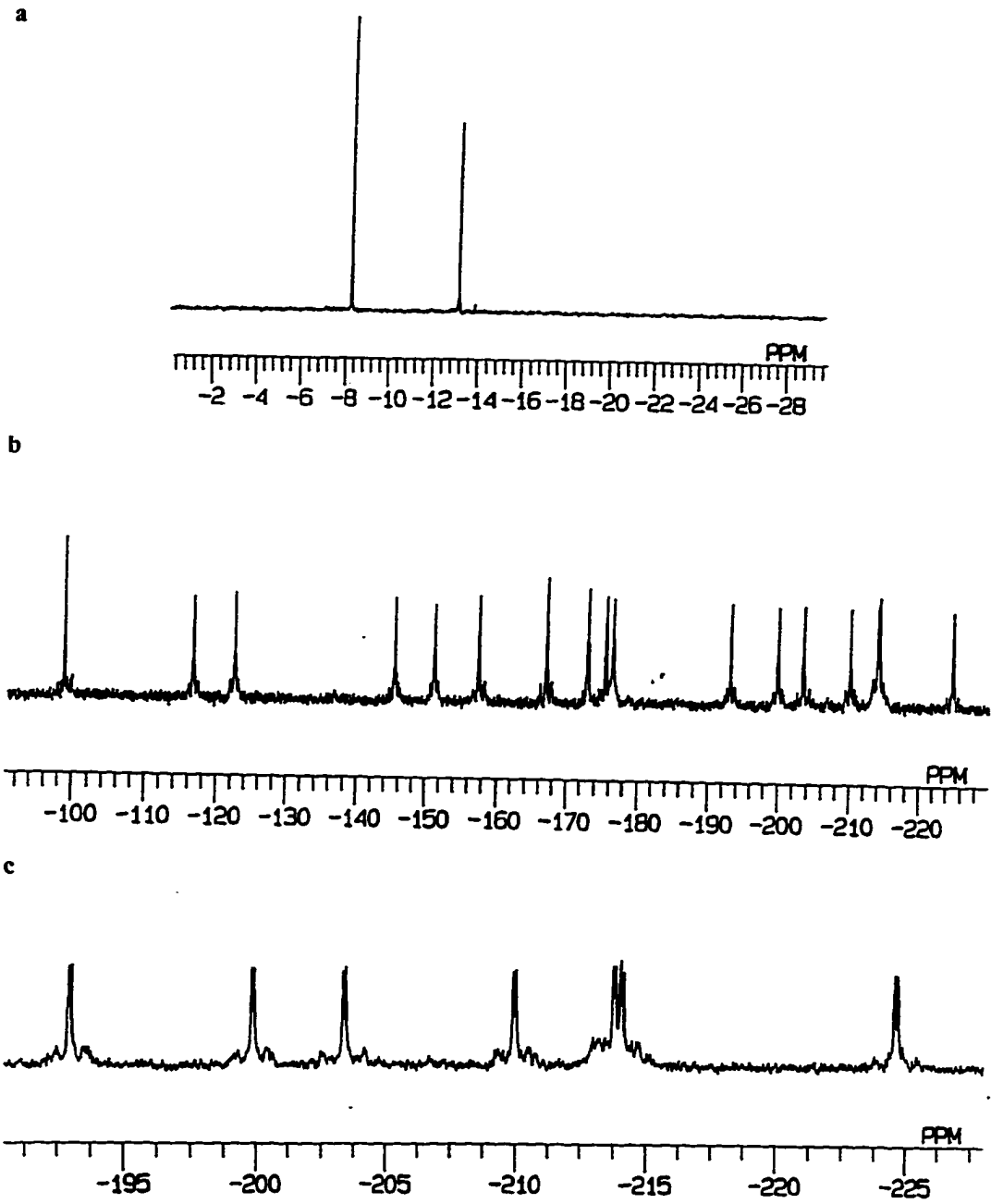
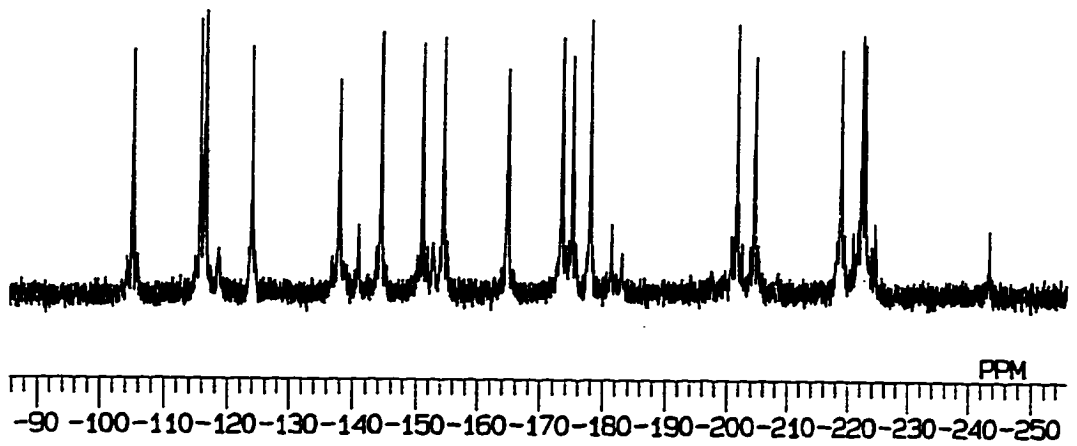


Fig. 1.4. a) ^{31}P NMR of $K_8[\alpha\text{-}1Zn(H_2O)P_2W_{17}O_{61}]$, 0.03M in D_2O, 35°C, 64 scans. b) ^{183}W NMR spectra of $Li_8[\alpha\text{-}1Zn(H_2O)P_2W_{17}O_{61}]$, 0.2 M in D2O, pH = 5.3, 35°C, 25 000 scans. c) Expansion of the –190 ppm to –230 ppm region of b).

a



b

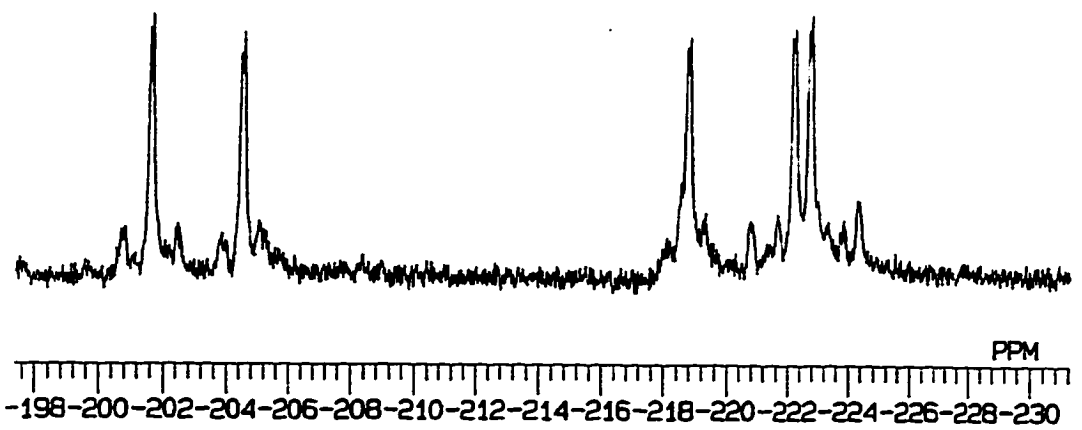


Fig. 1.5. a) ^{183}W NMR of $Li_9[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$, 0.2 M in D2O, pH= 5.8, 35°C, 16,000 scans. b) expansion of the –200 to –230 ppm region of a).

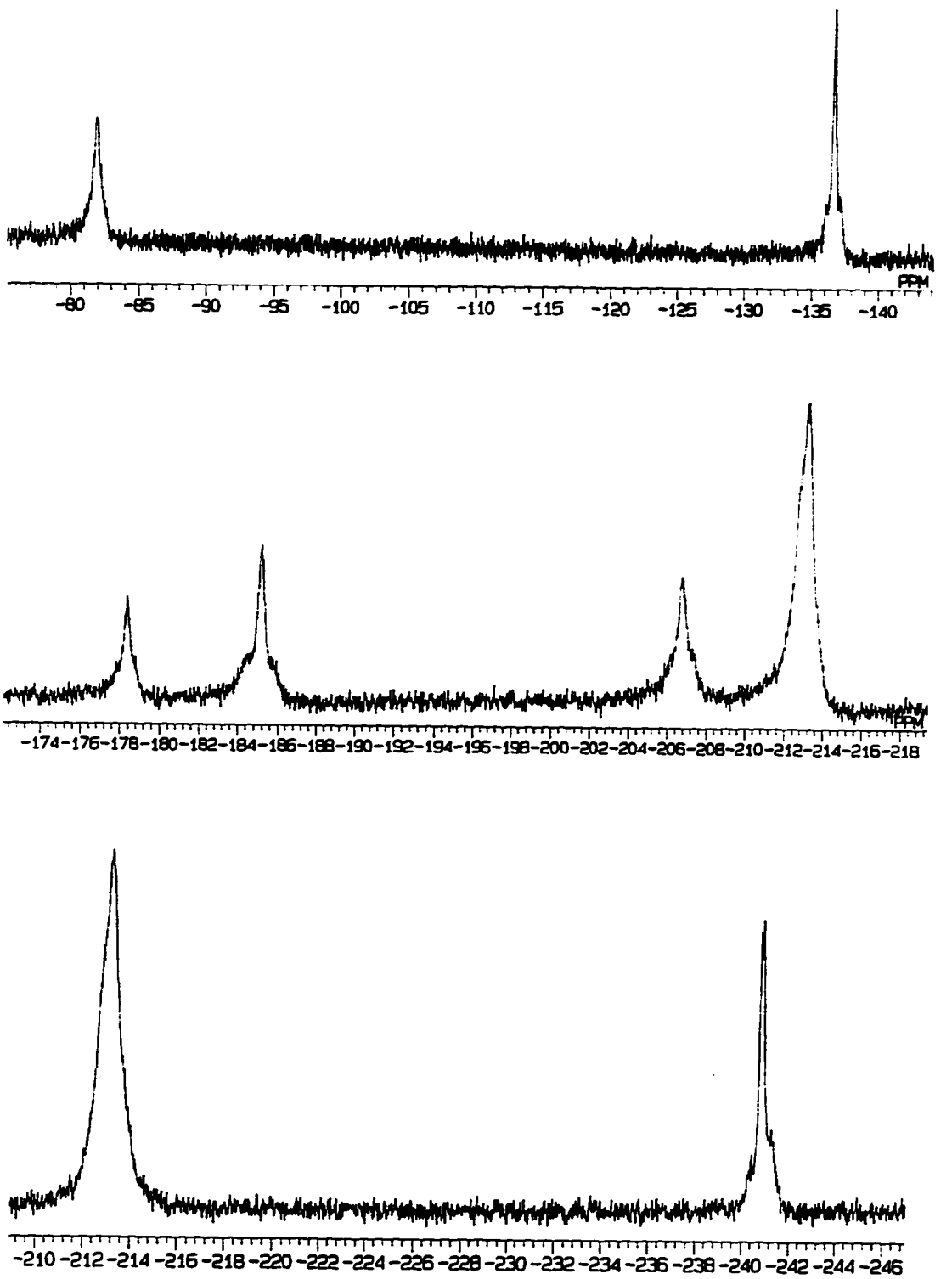


Fig. 1.6. Expansions of the ^{183}W NMR spectrum of the $Li_8[\alpha\text{-}2\text{-}Zn(H_2O)P_2W_{17}O_{61}]$.

Table 1.2. Tungsten-183 NMR Data.[a]

Compound	Chemical Shift, δ,ppm
Li_9 [α-1Li $P_2W_{17}O_{61}$][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 [α-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 [α-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.

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 $[Zn(D_2O)\text{-}P_2W_{17}O_{61}]^{8-}$ match those reported for the mixture[4] of the α-1 and α-2 isomers.

A seven line pattern is observed in Figure 1.3b, for the $Li_8[\alpha\text{-}2\text{-}Zn(D_2O)P_2W_{17}O_{61}]$ complex. The integrated intensities reflect the C_s symmetry of this molecule. Also, the satellites due to W-O-W coupling and the coupling of each tungsten to phosphorus ($J_{W\text{-}P}$ =1-1.5 Hz) can be clearly observed (Fig.1.6).

DISCUSSION.

The K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ compound was prepared as described by Contant[1,3] 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 $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer easily isomerizes to the α-2 species when heated.

The $[\alpha\text{-}1\text{-}Zn(H_2O)\text{-}P_2W_{17}O_{61}]^{8-}$ species was prepared from the reaction of $ZnCl_2$ with K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$. Maintaining the pH at 4.6-4.7 is again crucial to prevent isomerization to the α-2 species or decomposition. Recrystallization of the $[\alpha\text{-}1\text{-}Zn(H_2O)\text{-}P_2W_{17}O_{61}]^{8-}$ species from hot water results in mixtures of the α-1and α-2 species. This is similar to the report by Pope[7] on the preparation of a $[\alpha\text{-}1\text{-}OVP_2W_{17}O_{61}]^{7-}$ species; upon recrystallization of the $[\alpha\text{-}1\text{-}OVP_2W_{17}O_{61}]^{7-}$ species from hot water, a mixture of the α-1 and α-2 isomers was obtained. Once the $[\alpha\text{-}1\text{-}Zn(H_2O)\text{-}P_2W_{17}O_{61}]^{8-}$

species is formed, it is stable for at least one week in aqueous solution at room temperature, pH=6.0. Although we initially isolated the Li^+ salts of the [α-1-$Zn(H_2O)$ -$P_2W_{17}O_{61}]^{8-}$ species by freeze drying, we subsequently found that the [α-1-$Zn(H_2O)$ -$P_2W_{17}O_{61}]^{8-}$ species survives evaporation of the water at reduced pressures at temperatures less than 35°C. It appears that the metal ion incorporated into the [α-1-$P_2W_{17}O_{61}]^{10-}$ defect structure stabilizes the resulting [α-1- $P_2W_{17}O_{61}]^{10-}$ metal complex. Furthermore the [α-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-1and α-2 isomers of $[OVP_2W_{17}O_{61}]^{7-}$ could be successfully separated by chromatography on Sephadex[7], 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[6], we found that the use of isomerically pure [α-2-$P_2W_{17}O_{61}]^{10-}$ starting reagent insures 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[4].

The ^{183}W NMR spectrum of ion exchanged lithium salt of the lacunary [α-1-$P_2W_{17}O_{61}]^{10-}$ showed seventeen equally intense resonances, 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 seventeen 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 $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$.

CONCLUSION

The C_1 symmetry of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species has been confirmed by ^{183}W NMR spectroscopy. As expected, seventeen 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 $[\alpha\text{-}1\text{-}Zn(II)(H_2O)P_2W_{17}O_{61}]^{8-}$ species has been prepared in ≥ 98% purity by reaction of K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ with $ZnCl_2$ at pH 4.6, with subsequent ion exchange, at pH 5, 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, $[\alpha\text{-}1\text{-}Zn(II)(H_2O)P_2W_{17}O_{61}]^{8-}$, 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 $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer should be possible.

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Chapter 2

Preparation and Characterization of Lanthanide Complexes of the α-1 $(P_2W_{17}O_{61})^{10-}$ Heteropolyoxotungstate.

INTRODUCTION

We have used the lacunary [α–1 $P_2W_{17}O_{61}]^{10-}$ to prepare Lanthanide complexes. Using multinuclear NMR spectroscopy we prove the structure and isomeric purity of the [α–1Ln $P_2W_{17}O_{61}]^{7-}$ complexes.

Studies of lanthanide complexes of the [α-1- $P_2W_{17}O_{61}]^{10-}$ isomer have been conducted recently by two groups [1,2]. The data and interpretations are inconsistent between the two studies and certain preparations are irreproducible in our hands[1a]. Qu et al. [1] recently reported the preparation and elemental analysis for a series of lanthanide sandwich $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})_2]^{10-}$complexes. They also report cyclic voltammetry data for selected samples and ^{31}P NMR data for the lanthanum complex only, although from the spectrum the presence of the lacunary species or an isomeric impurity cannot be determined. The solids have been isolated by precipitation and not recrystallized. Their preparations were not reproducible in our hands [1a]. The isomeric purity of the starting [α -1- $P_2W_{17}O_{61}]^{10-}$ reagent (prepared by base degradation of the parent $[\beta\text{-}P_2W_{18}O_{62}]^{6-}$) for some of the preparations is not well documented [1b]. Ciabrini et al. [2] showed the formation of [α–1Ce$P_2W_{17}O_{61}]^{7-}$ and $[Ce(\alpha\text{-}1\text{-}P_2W_{17}O_{61})_2]^{10-}$

complexes by polarographic and spectrophotometric titrations. According to their findings the sandwich complex is less stable than the 1:1 complex, however they don't have convincing evidence about the isolation of either of them. The polarographic and spectrophotometric techniques used in these studies do not provide direct structural proof for the isolation of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer.

Crystallographic data are often difficult to obtain for large oxoanion species and, probably due to the rapid isomerization and instability of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, no X-ray structure of a metal complex of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ has yet been solved. To unambiguously prove the structure and purity of the lanthanide complexes of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, we use multinuclear NMR spectroscopy, specifically ^{183}W and ^{31}P NMR spectroscopy.

EXPERIMENTAL

Preparation of Lanthanide Complexes of the $[\alpha\text{-}1\text{-}(P_2W_{17}O_{61})]^{10-}$ Isomer.

The Ln:K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ reagents were reacted in 1:1 as well as 1:2 ratios. The general method for the preparation of the potassium salts of lanthanide $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ compounds is given. To ten grams of K_9Li $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$, suspended in 100 mL of lithium acetate buffer at pH=4.7, was added 3 mL (1.5 mL for the 1:2 compounds) of an aqueous 1M $LnCl_3$ solution dropwise; the solution was 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 two hours and filtered or decanted depending on the texture of the compound. In order to

recrystallize the compounds, the solid is dissolved in the minimum amount of hot water at 60-70 °C. (For example: 8.6 g of the complex in ca. 15 mL of water and than 10 more is added droppwise until the solution clears out.) It is gravity filtered and the clear, gray colored solution is placed into the freezer for 30 min, and the resulting white solid is separated by decanting the water. It is air dried in the hood. Selected analytical data are given in Table 2.1.

Ion exchange of Lanthanide Complexes of the $[\alpha\text{-}1\text{-}(P_2W_{17}O_{61})]^{10-}$

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^+ or Na^+ form was used. The resin, originally in the H^+ form, was converted to the Li^+ or Na^+ form using a previously described procedure. (Two bed volumes of lithium acetate buffer, 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 hours, followed by washing with 2 bed volumes of water. The amount of resin used is calculated based on its capacity given.) About 0.6 mmol of the $K_7[\alpha\text{-}1Ln\ P_2W_{17}O_{61}]$ or $K_{17}[\alpha\text{-}1Ln(P_2W_{17}O_{61})_2]$ was dissolved in ca.1000 mL of water to obtain a clear solution. The solution was loaded onto a Dowex Ag-50W-X2 cation exchange column in the Li^+ or Na^+ form and eluted with water at a flow rate 4mL/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.

Conversion of potassium salts to lithium salts or sodium salts was also achieved by metathesis using $LiClO_4$. A typical example of the ion-exchange procedure is described for the $K_7[\alpha\text{-}1La\ P_2W_{17}O_{61}]$ as follows:

6 mmol (0.64 g) $LiClO_4$ is dissolved in 2.5 mL D_2O, 0.6 mmol (2.9 g) of the $K_7[\alpha\text{-}1La\ P_2W_{17}O_{61}]$ is added as a solid and stirred for a few minutes. The solution is centrifuged to remove $KClO_4$ and filtered.

Preparation of tetrabutylammonium salt of [α-1 Lu ($P_2W_{17}O_{61}$)]

This procedure follows the method developed by the Finke group for substituted $[\alpha\text{-}2\text{-}\ P_2W_{17}O_{61}]^{10-}$ complexes [3]. It is very important to maintain the pH in the range of 4.5-5.2 to preserve the α-1 $P_2W_{17}O_{61}$ isomer, therefore the procedure is carried out while constantly monitoring the pH using a pH meter. A sample (5g, 1.01 mmol)) of the potassium salt of [α-1 Lu($P_2W_{17}O_{61}$)] (1:1 complex) was dissolved in 150 mL water. A solution of 0.18M H_2SO_4 was used to adjust and maintain the pH in the range of 4.5- 5.2. To this clear, colorless solution, tetrabutylammonium chloride (2.29g, 7.09 mmol) was added to the stirring solution while the pH was maintained in the range of 4.5-5.2 with 0.18M H_2SO_4. The solution is treated with 34 mL of acetonitrile and 67 mL of methylene chloride. Upon shaking the two layers separate. The organic (bottom) layer is collected and rotary evaporated at 40°C. Methylene chloride, 5 mL, is 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

Table 2.1. Elemental Analysis and Mass Spectrometry Data for Selected Lanthanide [α-1-$P_2W_{17}O_{61}$] Polyoxoanions.

	Obsd.	Calcd.	Mass Spectrometry
K_7 [Lu[α–1-$P_2W_{17}O_{61}$]] . 22 H_2O[a]			
K	4.96	5.47	FAB⁻:
P	1.24	1.24	4170.6{$K_2H_2Lu[P_2W_{17}O_{61}]$}(-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[α-1-$P_2W_{17}O_{61}$]] . 19 H_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[α-1-$P_2W_{17}O_{61}$]] . 13 H_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[α-1-$P_2W_{17}O_{61}$]] . 22 H_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	

Table 2.1.(cont.) Elemental Analysis and Mass Spectrometry Data for Selected Lanthanide [α-1-$P_2W_{17}O_{61}$] Polyoxoanions.

	Obsd.		Calcd.	Mass Spectrometry
$(N(C_4H_9)_4)_7[Lu[\alpha 1\text{-}P_2W_{17}O_{61}]]\cdot 5H_2O$.				
				FAB⁻
C	20.44[a](21.78)[b]		21.96	5292.4
				$(N(C_4H_9)_4)_4H_2[Lu[P_2W_{17}O_{60}]]^-$
H	4.01	(4.24)	4.31	5050.4
				$(N(C_4H_9)_4)_3H_2[Lu[P_2W_{17}O_{60}]]^-$
N	1.49	(1.60)	1.60	4793.3
				$(N(C_4H_9)_4)_2H_3[Lu[P_2W_{17}O_{59}]]^-$
W	53.08	(50.04)	51.02	
P	0.94	(1.01)	1.01	Electrospray:
Lu	3.99	(2.74)	2.86	2653.7 $\{[Lu(P_2W_{17}O_{61})]TBA_4H\}^{2-}$
O (by difference)	16.05	(18.59)	17.24	
$\%H_2O$	1.37		1.47	

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

compound, taken in D_2O, to compare the chemical shifts for other α-1 compounds, confirm the >98% α-1-$P_2W_{17}O_{61}$ isomeric purity.

The recrystallized $[N(C_4H_9)]_7[\alpha\text{-}1\ LuP_2W_{17}O_{61}]$ is not soluble in water. In order to obtain ^{31}P and ^{183}W NMR data, the sample was transformed to the water soluble Li salt by metathesis with $LiClO_4$ described in the previous chapter.

Selected analytical data is collected in Table 2.1.

RESULTS AND DISCUSSION.

IR spectroscopy

Infrared spectroscopy data of the lanthanide $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ derivatives show similarity to the lacunary $K_{10}[\alpha 1\text{-}P_2W_{17}O_{61}]$ species consistent with the isostructural nature of the molecules (Fig.2.1) The different lanthanide species have nearly identical IR spectra. The data are summarized in Table 2.2.

Multinuclear NMR

When reacted in 1:1 Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometry , the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer forms rather stable complexes with the lanthanide ions Yb, Eu and Lu (and Y, often considered an analog for the lanthanide ions). Elemental analysis and preliminary mass spectrometry data are consistent with the 1:1 formulation.

The ^{31}P NMR spectroscopy of the nonrecrystallized samples, shown in Figures 2.2 and 2.3, confirms >98% α-1-isomeric purity. These compounds can be recrystallized from hot water and the ^{31}P NMR data after recrystallization shows very small amount of isomerization to the α -2-isomer. Chemical shifts

data are summarized in Table 2.3. The ^{183}W NMR spectra of the ion exchanged complexes (Figure 2.4) show seventeen resonances, consistent with the expected C1 symmetry of the molecule. Chemical shifts are summarized in Table 2.4.

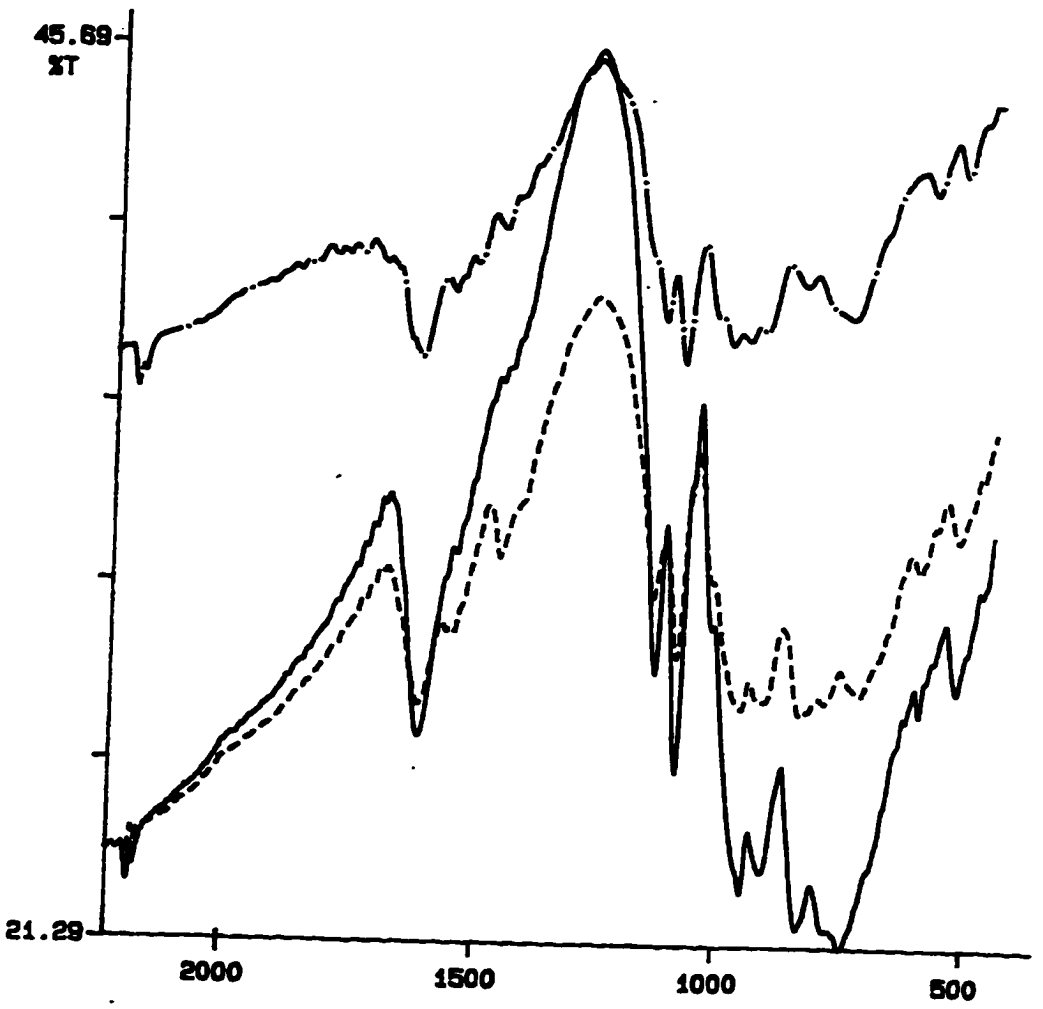
The lanthanum analog, however, is not stable in the presence of Li^+ ions. Figure 2.5 shows the ^{31}P NMR spectrum of the lanthanum complex of $[\alpha\text{-}1\text{-}(P_2W_{17}O_{61})]^{10-}$ isomer (peaks labeled as (a)) as a lithium salt. The complex contains significant amounts of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer (peaks labeled as (b)). After adding $LaCl_3$ to the solution the peak of the lacunary $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ species disappear and two resonances for the $[La\ \alpha\text{-}1\text{-}(P_2W_{17}O_{61})]^{7-}$ complex can be observed with a small amount of the α-2 impurity (peaks labeled as (c).[1]

This phenomenon is not observed when the complex is ion exchanged to the Na^+ salt. Therefore the ^{183}W NMR spectrum of the $[La\ \alpha 1\text{-}(P_2W_{17}O_{61})]^{7-}$ complex was taken as a sodium salt (Figure 2.4). When reacted in 1:2 Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ ratio, the ^{31}P NMR chemical shift data for Yb, Lu and Y show two resonances which are identical to the 1:1 species. These data lead us to believe that the two reaction conditions, the two reaction conditions,

---

[1] The impurity at -12.55 ppm is unknown. It could be the parent Wells-Dawson molecule which formed in the conditions of the ion-exchange (pH, higher concentration), or another species with higher nuclearity and symmetry.

Figure 2.1 IR spectra of selected $K_7[\alpha\text{-}1\ LnP_2W_{17}O_{61}]$ and the lacunary $K_7[\alpha\text{-}1\ LnP_2W_{17}O_{61}]$



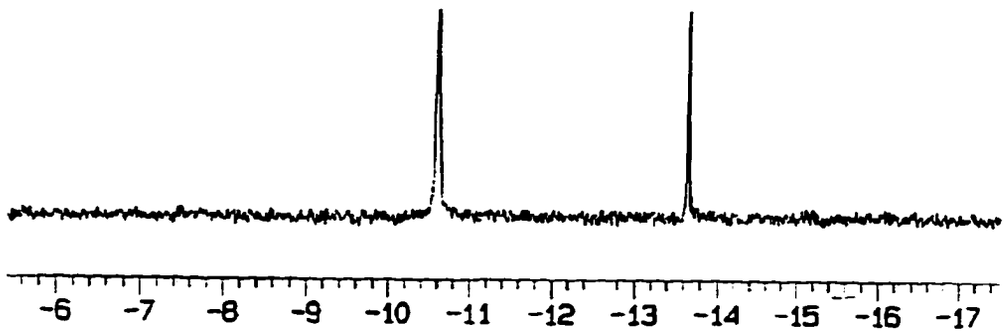
$K_7[\alpha\text{–}1\text{-}La(H_2O)_4P_2W_{17}O_{61}]$ (_____)
$K_9[\alpha\text{–}1\text{-}LiP_2W_{17}O_{61}]$ (-·-·-·-)
$K_7[\alpha\text{–}1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$ (--------)

Table 2.2. Infrared Spectroscopy Data.

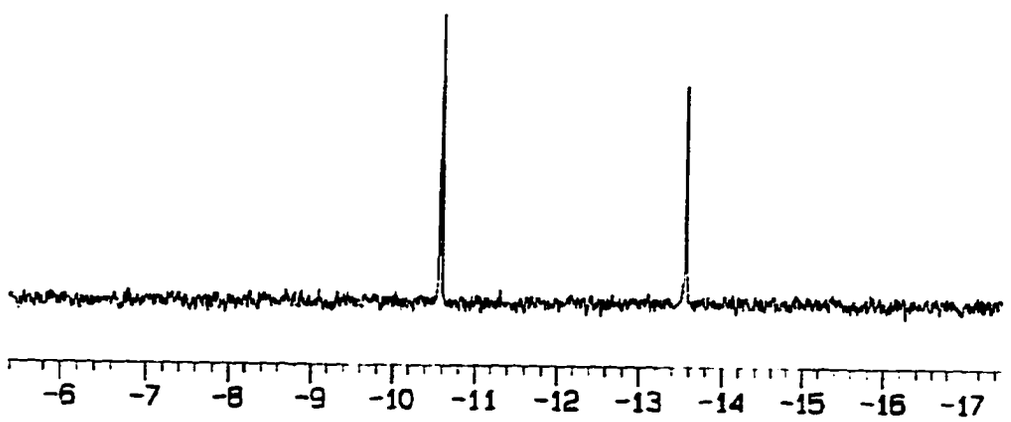
Compound	ν P-O	ν W-O
$KgLi[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$	1119.9 (s), 1078.8 (s), 1008.2 (sh)	984.7(m), 955.4 (m)
$K_7[\alpha\text{-}1\text{-}La(H_2O)_4P_2W_{17}O_{61}]$	1131.6 (s), 1084.6 (s)	955.3 (m) 908.3 (m)
$K_7[\alpha\text{-}1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$	1131.6 (s), 1084.6 (s), 1014.1 (sh)	949.5 (s) 902.5 (s)
$K_7[\alpha\text{-}1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	1126.3 (s), 1079.3 (s)	950.0 (m) 897.1 (m)
$TBA_7[\alpha\text{-}1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	1155.3 (sh), 1090.6 (s), 1014.2 (sh)	949.6 (s), 902.6 (s)
$K_7[\alpha\text{-}1\text{-}Y(H_2O)_4P_2W_{17}O_{61}]$	1131.6 (s), 1084.6 (s), 1020.0 (sh)	955.3 (m), 908.3 (m)

Figure 2.2. ^{31}P NMR spectra of the $K_7(\alpha\text{-}1LnP_2W_{17}O_{61})$ complexes.

$K_7(\alpha\text{-}1LaP_2W_{17}O_{61})$



$K_7(\alpha\text{-}1LuP_2W_{17}O_{61})$



$K_7(\alpha\text{-}1YP_2W_{17}O_{61})$

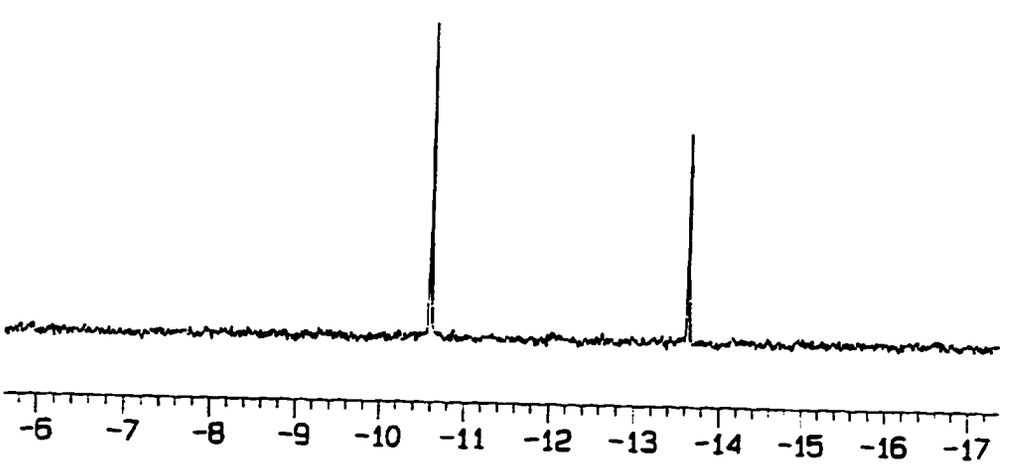


Figure 2.3. ^{31}P NMR spectra of a) $K_7(\alpha\text{-}1\text{-}EuP_2W_{17}O_{61})$ and b) K_7 (α-1-$YbP_2W_{17}O_{61}$).

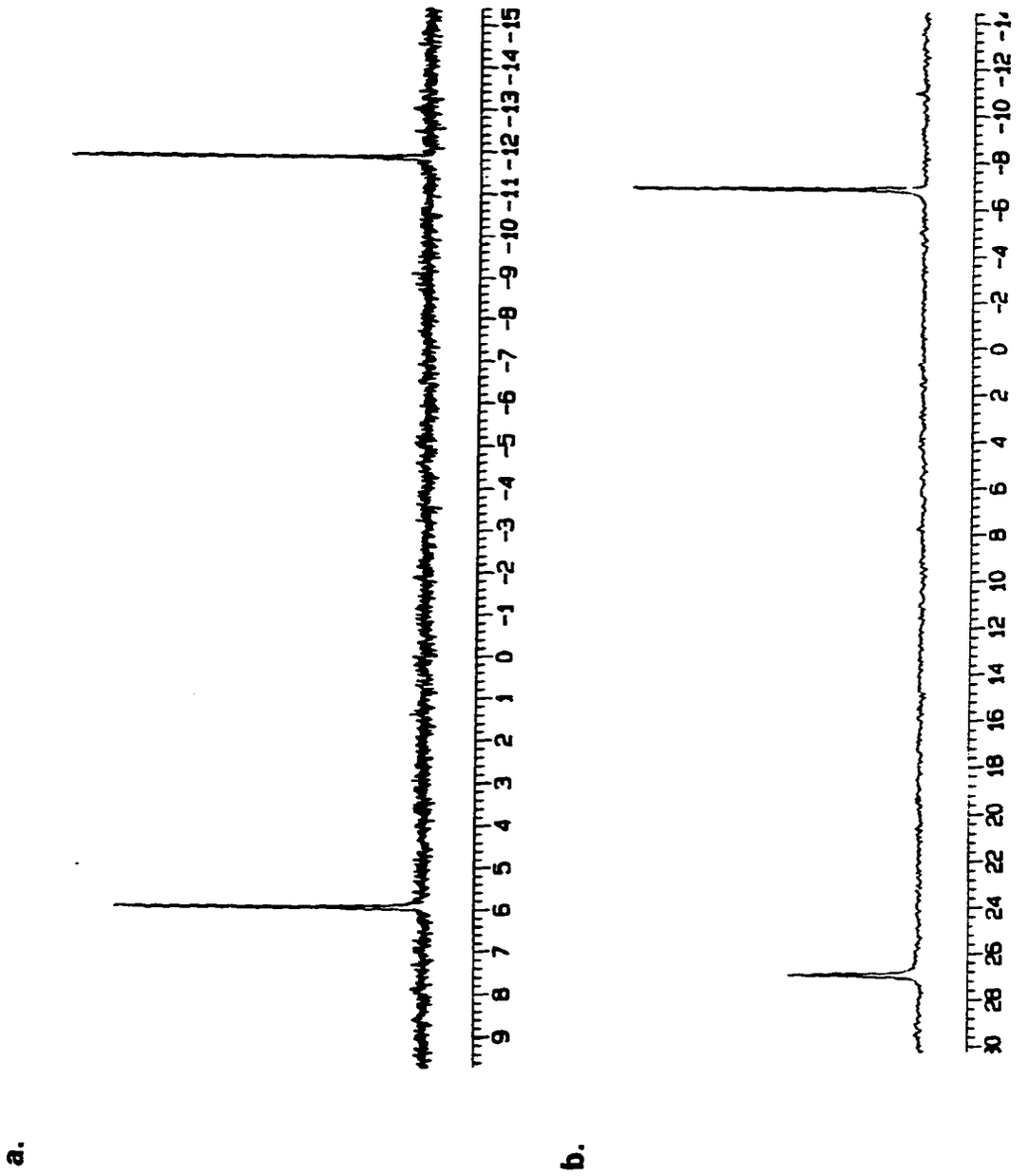
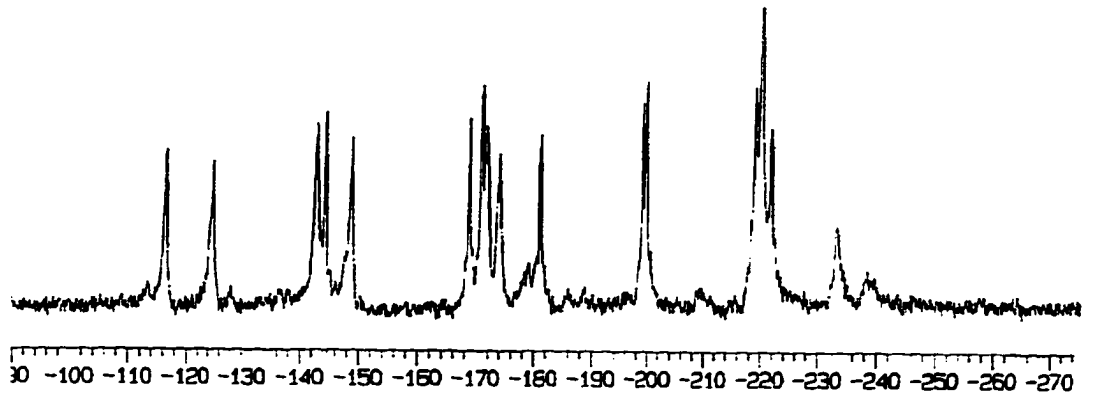


Table 2.3. ^{31}P NMR Data

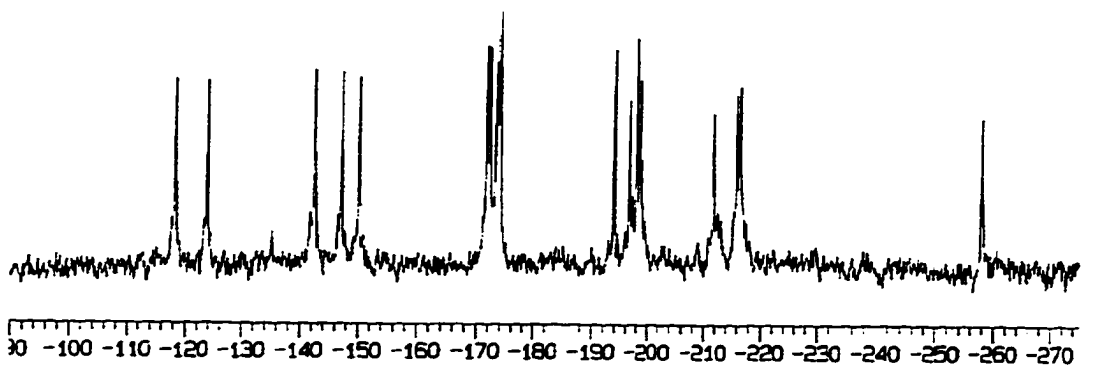
Compound	Chemical Shift, δ, ppm	Solvent
Lig[α-1-$LiP_2W_{17}O_{61}$]	-9.16, -13.48	D_2O
TBA_7[α-1-$Lu(H_2O)_4P_2W_{17}O_{61}$]	-7.38, -11.97	DMSO
TBAxLiy[α-1-$Lu(H_2O)_4P_2W_{17}O_{61}$]	-9.97, -13.16	D_2O
K_7[α-1-$La(H_2O)_4P_2W_{17}O_{61}$]	-10.58, -13.64	D_2O
K_7[α-1-$Lu(H_2O)_4P_2W_{17}O_{61}$]	-10.57, -13.55	D_2O
K_7[α-1-$Yb(H_2O)_4P_2W_{17}O_{61}$]	27.00, -6.84	D_2O
K_7[α-1-$Y(H_2O)_4P_2W_{17}O_{61}$]	-10.58, -13.61	D_2O

Figure 2.4. ^{183}W NMR spectrum of the $[\alpha\text{-}1LnP_2W_{17}O_{61}]^{7-}$ complexes.

$Na_7(a\text{-}1LaP_2W_{17}O_{61})$



$Li_7(a\text{-}1LuP_2W_{17}O_{61})$



$Li_7(a\text{-}1YP_2W_{17}O_{61})$

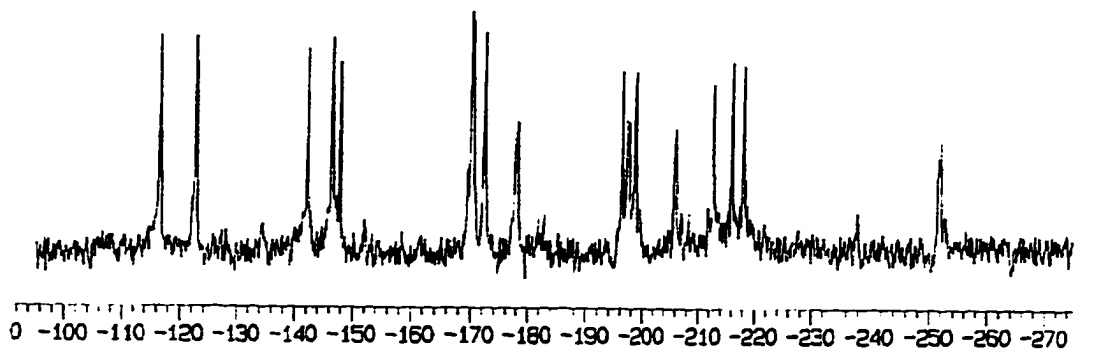
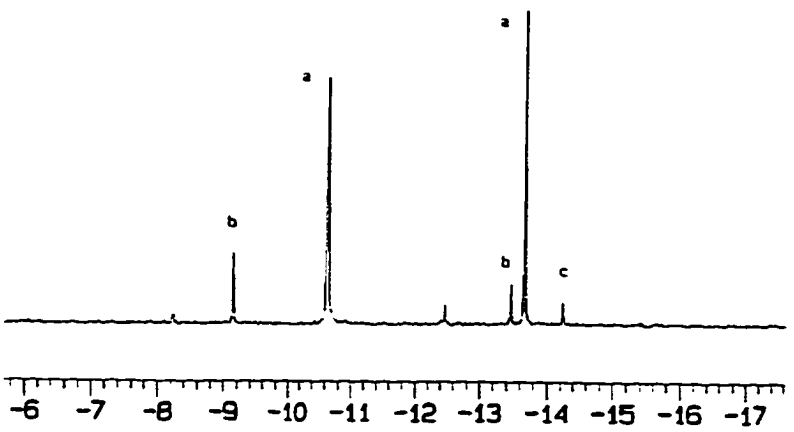


Table 2.4. ^{183}W NMR Data.

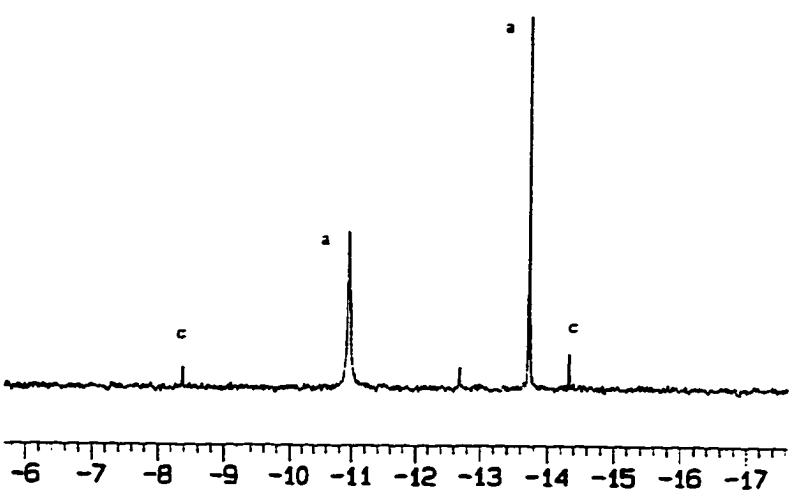
Compound	Chemical Shift, δ, ppm
$Na_7[\alpha\text{-}1\text{-}La(H_2O)_4P_2W_{17}O_{61}]$	-116.124, -124.371, -142.406, -143.908, -148.307, -168.467, -170.593, -171.290, -173.599, -180.784, -198.818, -199.478, -218.612, -219.638, -220.518, -221.434, -233.017
$Li_7[\alpha\text{-}1\text{-}Y(H_2O)_4P_2W_{17}O_{61}]$	-116.440, -122.598, -142.279, -146.568, -147.924, -170.208, -170.464, -172.553, -177.959, -196.303, -197.384, -198.795, -206.162, -212.796, -216.131, -218.184, -252.306
$Li_7[\alpha\text{-}1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	-118.016, -123.587, -142.389, -147.007, -149.939, -171.637, -172.077, -173.396, -173.873, -193.701, -196.450, -197.842, -198.502, -211.513, -215.655, -216.205, -257.840
$Li_9[\alpha\text{-}1\text{-}LiP_2W_{17}O_{61}]$	-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
$TBA_xLi_y[\alpha\text{-}1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]$	-116.600, -127.340, -138.740, -142.625, -146.291, 161.700, -168.797, -169.530, -171.500, -190.644, 193.100, 195.299, -208.605, -210.768, -213.737

Figure 2.5. ^{31}P NMR of the $Li_7(\alpha\text{–}1LaP_2W_{17}O_{61})$

$Li_7(\alpha\text{–}1LaP_2W_{17}O_{61})$ in D_2O



with $LaCl_3$ added



1:1 and 1:2 Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, lead to identical species. However, for all lanthanide:$[\alpha\text{ -}1\text{-}P_2W_{17}O_{61}]^{10-}$ reactions performed with 1:2 stoichiometry, upon crystallization from hot water, the ^{31}P NMR data show decomposition (Figures 2.6-8) to the lacunary $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ labeled as peak C and a small amount of another unknown species, labeled as peak B. Peaks A have same chemical shifts of the complex prepared in 1:1 Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometric ratio. The resonances labeled as D are due to α-2 isomerization. Chemical shifts of the ^{31}P NMR data of the recrystallized complexes are summarized in Table 2.5

It is conceivable that 1:2 species are forming in these high temperature conditions represented by peaks B, but they are not stable enough to be isolated. This observation is in agreement with the observation made by Ciabrini [2] who found that the Ce (III) and Ce (IV) react with the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ in both 1:1 and 1:2 stoichiometry but the sandwich complex is less stable. (The formation of these complexes was followed by spectrophotometric titrations, and their stability constants were measured by competition method and potentiometric titration. They report the isolation of both 1:1 and 1:2 Ce : $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complex, which are characterized by IR, polarography and absorbtion spectroscopy . Elemental analysis is reported for the nonrecrystallized 1:1 complex only. These techniques do not prove the isomeric purity of these compounds. Furthermore the difference between the 1:1 and 1:2

complex shown in the IR and absorbtion spectroscopy data is very subtle to prove the existence of a clean product.)

Another explanation could be that the 1:2 species are forming only and extra one (or more) surface bound Ln^{3+} ion(s) is/are required to stabilize a "sandwich" conformation. The chemical shift of the La complex prepared in a 1:1 ratio matches the chemical shifts reported by Qu et al.[1] who claimed the $K_{17}[La(\alpha\text{-}1P_2W_{17}O_{61})_2]$ as a sandwich complex.

The analytical data for the tetrabutylammonium salt of Lu $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$. shown in Table 2.1, is consistent with the 1:1 formulation. ^{31}P NMR spectroscopy in water and DMSO shows two resonances indicating >98% isomeric purity. (Fig. 2.9). The molecule appears to be stable in solution for weeks at room temperature and for a few days at 50 °C, according to ^{31}P NMR data. In contrast the lithium and potassium salts isomerize under the same conditions. The complex was ion exchanged to the lithium salt by metathesis with $LiClO_4$ to measure the ^{183}W NMR spectrum; the spectrum confirms the C1 symmetry (Fig.2.10).

Figure 2.6 ^{31}P NMR spectrum of the recrystallized La complex of the [α-1 $P_2W_{17}O_{61}]^{10-}$ prepared in 1:2 stoichiometric ratio.

A= [α-1 $LaP_2W_{17}O_{61}]^{7-}$ B= unknown C= [α-1 $P_2W_{17}O_{61}]^{10-}$ D =α-2 impurity

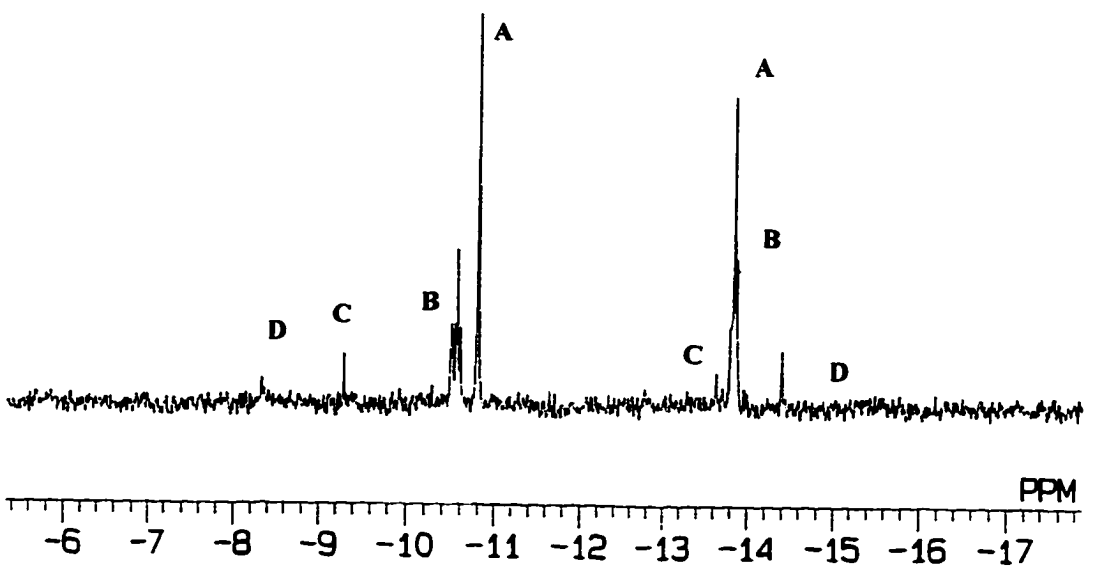


Figure 2.7. ^{31}P NMR spectrum of the recrystallized Lu complex of the [α-1 $P_2W_{17}O_{61}]^{10-}$ prepared in 1:2 stoichiometric ratio.

A= [α-1 $LuP_2W_{17}O_{61}]^{7-}$ B= unknown C= [α-1 $P_2W_{17}O_{61}]^{10-}$ D =α-2 impurity

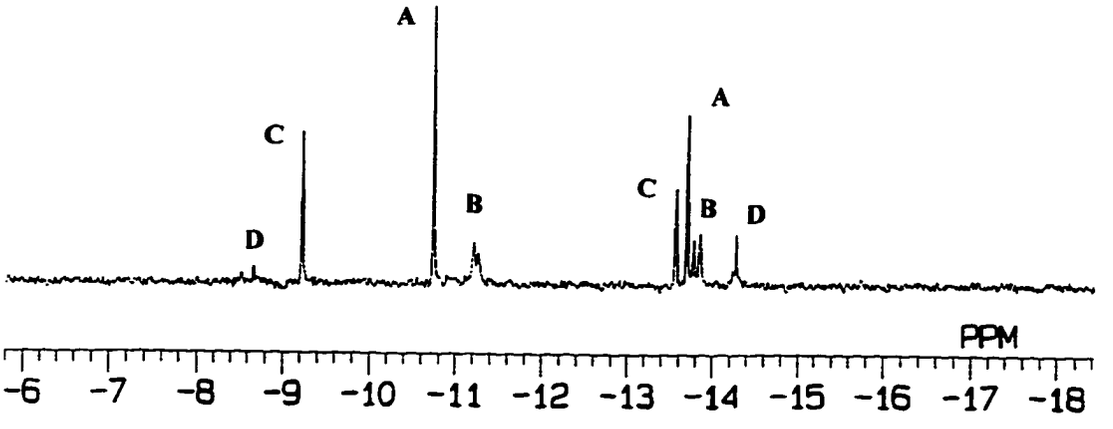


Figure 2.8. ^{31}P NMR spectrum of the recrystallized Y complex of the [α-1 $P_2W_{17}O_{61}]^{10-}$ prepared in 1:2 stoichiometric ratio.

A= [α-1 $YP_2W_{17}O_{61}]^{7-}$ B= unknown C= [α-1 $P_2W_{17}O_{61}]^{10-}$ D =α-2 impurity

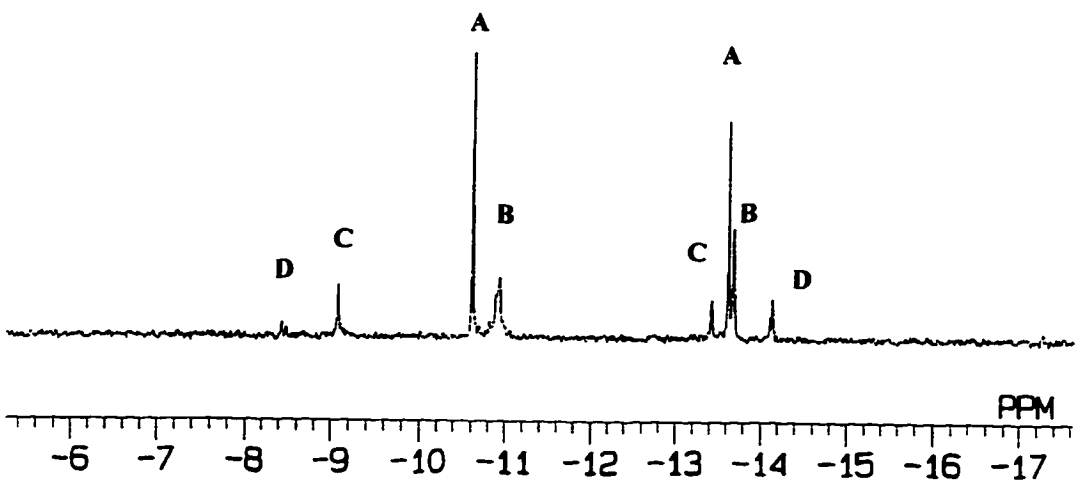
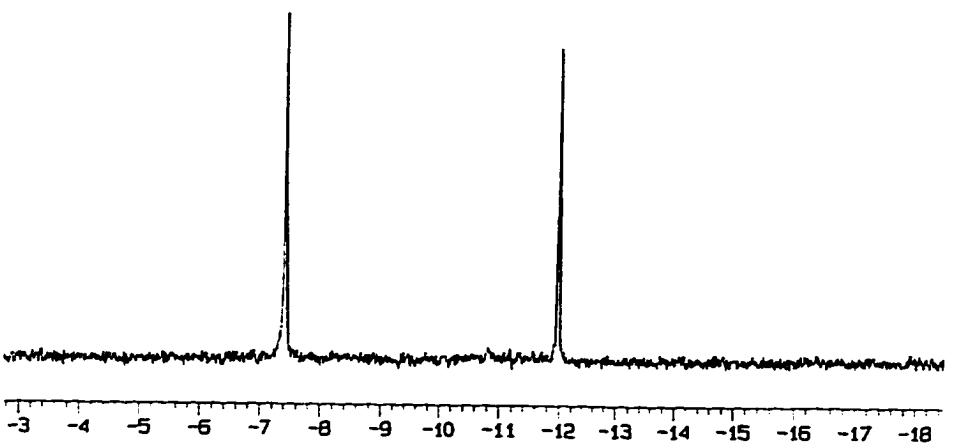


Table 2.5. ^{31}P NMR chemical shifts of the recrystallized Ln complexes of the [α-1 $P_2W_{17}O_{61}$] prepared in 1:2 stoichiometric ratio.

Ln	Peaks (ppm)			
	A	B	C	D
La	-10.61	-10.37	- 9.11	-14.21
	-13.65	-13.65	-13.47	- 8.20
Lu	-10.66	-11.14	- 9.14	-14.20
	-13.63	-13.78	-13.49	- 8.51
Y	-10.65	-10.97	- 9.11	-14.18
	-13.66	-13.68	-13.46	- 8.46

Figure 2.9 ^{31}P NMR spectrum of the a) α-1 $TBA_xH_y[LuP_2W_{17}O_{61}]$ in DMSO and b) $TBA_xLi_y[LuP_2W_{17}O_{61}]$ in H_2O.

a.



b.

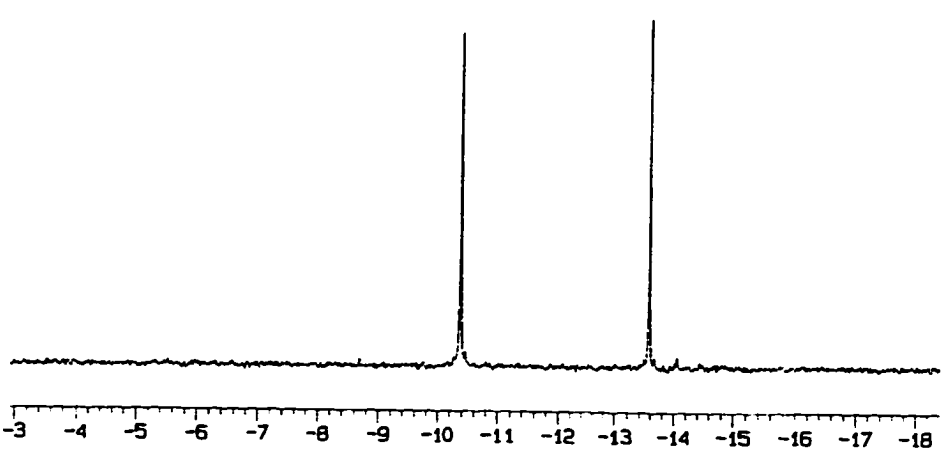
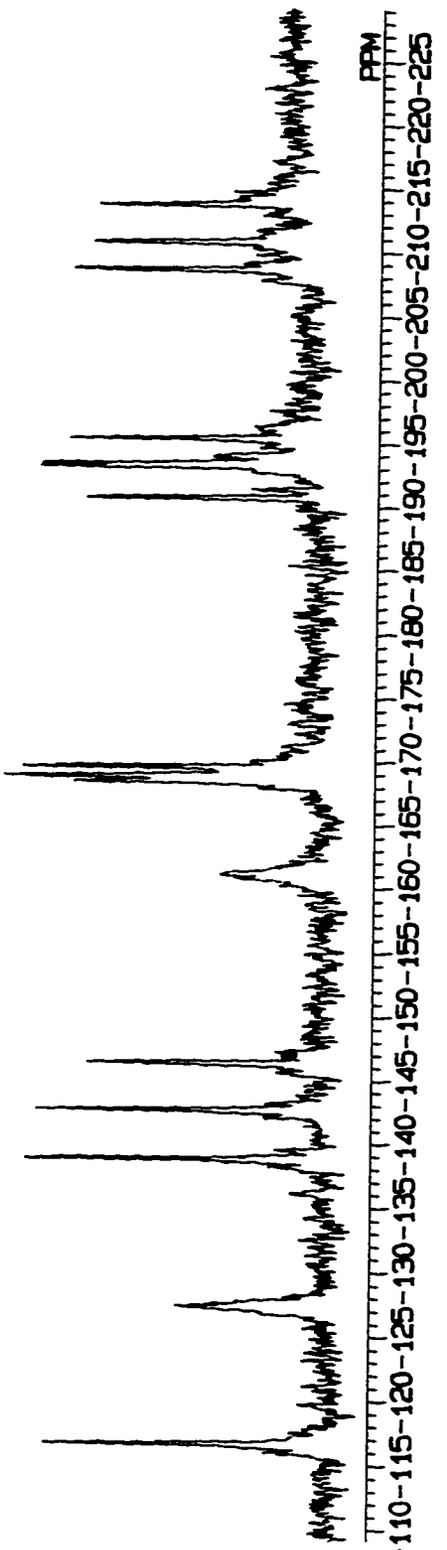


Figure 2.10. ^{183}W NMR spectrum of $TBA_xLi_y[LuP_2W_{17}O_{61}]$ in D_2O.



SUMMARY AND CONCLUSIONS

We can state, from our ^{31}P NMR data, that the lanthanide complexes are 98% isomerically pure as the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes. Our ^{183}W NMR data clearly shows, for the first time, that the C_1 symmetry of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ lanthanide complexes is maintained in solution. Our ^{31}P NMR data show that the lanthanides with smaller ionic radii (higher charge/size ratio) form stable complexes, with the α -1 isomer, consistent with the Contant data. The later lanthanides form fairly stable complexes with the the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, even surviving crystallization from hot water. It appears that the basic vacant site in the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ defect structure requires high valent metal ion (high charge/size ratio) for stabilization. . Finally, the tetrabutylammonium salt of the Lu $(\alpha\text{-}1\text{-}P_2W_{17}O_{61})^{7-}$ complex shows $\geq$ 98% isomeric purity and maintains the C_1 symmetry of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species in solution. Also tetrabutylammonium counterions have a stabilizing effect on the α -1 strucure, which is mainained in solution for days even at high temperature.

Spectroscopic and complexometric titration experiments have been designed in order to elucidate the stoichiometry of these complexes. These are discussed in the next chapter.

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Chapter 3.

Stoichiometric Studies of Lanthanide Complexes of $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$.

INTRODUCTION

The stoichiometry of the Ln^{3+} $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes has been a considerable confusion in the literature as well as in our previous work. Qu et al.[1] reported the preparation and elemental analyses for a series of lanthanide ions complexed to $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$. Elemental analysis of both the recrystallized tetrabutylammonium salts and unrecrystallized potassium salts suggest the 1:2 formulation, $[Ln\ (\alpha\text{-}1\text{-}P_2W_{17}O_{61})_2]^{17-}$, for all of the lanthanides. Their spectrophotometric titration studies with Ce^{3+} shows the formation of the sandwich complex only.

In contrast polarographic and spectrophotometric studies with Ce^{3+}:$[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ conducted by Ciabrini and Contant [2] detect the formation of both the 1:1 and the 1:2 sandwich complexes. They have concluded that the 1:1 complex is more stable than the sandwich molecule.

We isolated complexes of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ with lanthanides in 1:1 and 1:2 Ln: $(\alpha\text{-}1\text{-}P_2W_{17}O_{61})$ stoichiometric ratio, however ^{31}P and ^{183}W NMR spectra are identical for both species. Elemental analysis is inconclusive, since we don't know if all the lanthanide is incorporated into the polyoxoanion and forms $K_7[\alpha\text{-}1\text{-}LnP_2W_{17}O_{61}]$, or half of it acts as countercations, perhaps surface bound to stabilize a sandwich complex forming $K_{14}Ln[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})_2]$. The elemental analysis gives the same results for both cases. In order to determine

the solution stoichiometry we used ion exchange and titration experiments as well as luminescence excitation spectroscopy of the Eu^{3+} complexes.

EXPERIMENTAL

General Comments. All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Distilled, deionized water was used throughout. A standard solution of EDTA (0. 0993M) was purchased from Fisher. The aqueous solutions of the lanthanide metals were standardized by complexometric titration with EDTA using xylenol orange as an indicator. An aqueous solution of $CoCl_2$, was standardized with EDTA, buffered at pH=5 with sodium acetate buffer, by absorption spectroscopy [3]. To convert the potassium salts to lithium salts for increased solubility of the $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ species in aqueous solution for monitoring by ^{31}P NMR spectroscopy, ion exchange chromatography using Dowex AG50W-X2 in the Li^+ form was used, as described previously. The concentrations of aqueous solutions of the lithium salts of $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ were determined by titration with $CoCl_2$ as described below. In order to remove any excess Ln ion before determining the stoichiometry of the Ln : $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ complex, Bio-Rad Chelex 100 Chelating Ion Exchange Resin in Na form, (100-200) mesh was used.

Preparation of the Chelex-100 resin

The resin was transformed to H+ form using two bed volumes of 1M HCl with 2mL flow rate, washed with 5 bed volumes of H_2O followed with 3 bed volumes of lithium acetate buffer at pH 4.7. The resin was soaked in the third volume of

lithium acetate buffer for at least 5 hours. We found that the use of fresh resin is necessary in order to make sure that the extra Ln is removed efficiently.

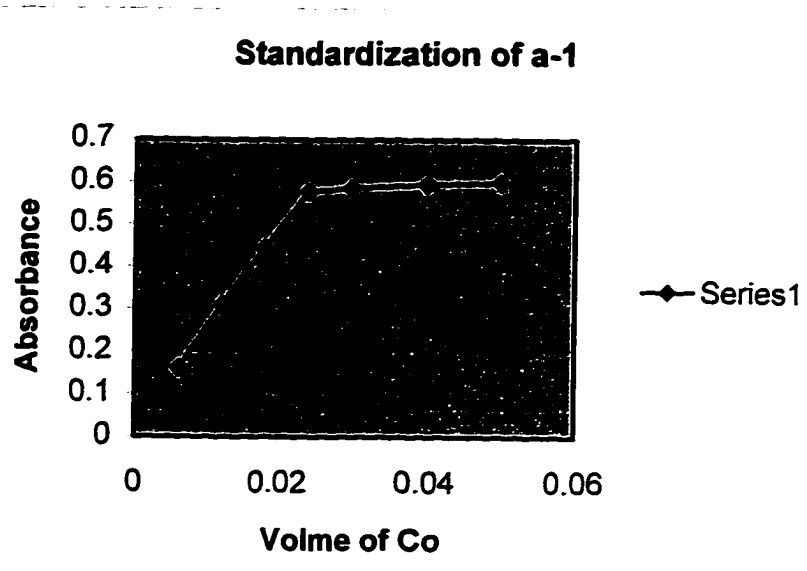
Standardization of $[\alpha\text{-1-}P_2W_{17}O_{61}]^{10-}$ solutions. The general procedure to obtain 20 mL of 0.022-0.025M solution of the $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ ligand follows. K_{10} $[\alpha\text{-1 }P_2W_{17}O_{61}]$ (2.46g) was ion exchanged to the lithium salt at pH =4.7 using the Dowex AG50W-X2, following the procedure described in the previous chapters, one 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 (7mL) and enough lithium acetate buffer (ca. 0.5M, pH=4.7) to prepare 20 mL of solution. 0.5 mL of the $Li_{10}[\alpha\text{-1 }P_2W_{17}O_{61}]$ solution was placed in a UV-vis cuvette with 2 mL of the lithium acetate buffer. To this solution $CoCl_2$ (0.2979 M) was added in 5 or 10 μL increments and the absorbance was recorded at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gives a sharp breakpoint when all the $[\alpha\text{-1-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in 1:1 stoichiometric ratio. Three titrations were run for each standardization; the agreement was within 1%. Figure 3.1 shows a typical titration for one standardization. The solution is stored in the freezer to prevent isomerization to the $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ isomer.

Procedure for titration of $[\alpha\text{-1-}P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ monitored by ^{31}P NMR Spectroscopy.

Generally, 0.5 mL of the standardized buffered $Li_{10}[\alpha\text{-1-}P_2W_{17}O_{61}]$ solution is placed into a 5 mm NMR tube, using volumetric pipette. (The concentrations are in the range of 0.015-0.022 M buffered with lithium acetate at pH 4.7, the solutions contain 30% D_2O) The ^{31}P NMR spectrum is recorded. An aliquot of 25-30 μL of the standardized $LnCl_3$ solution (concentration is always ca. 0.1M)

Fig. 3.1. Titration plot of $Li_{10}[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ with Co^{2+}.

Co (mL)	Asorbance
0.006	0.1612
0.012	0.3098
0.018	0.4427
0.024	0.5775
0.03	0.5853
0.04	0.5947
0.05	0.5987



is added to achieve 4:1, 4:2, 4:3, 4:4 and 4:6 [α-1-$P_2W_{17}O_{61}$]: Ln ratios. The resulting solution is shaken well in the NMR tube and the ^{31}P NMR spectrum is recorded immediately upon mixing. The titration data for La, Eu, and Lu are shown in Figures 3.2, 3.3, and 3.4, respectively. The data including concentrations of ligand, lanthanide salt, relative molar ratios and integrations are tabulated in Tables 3.1 and 3.2.

Procedure for determining the Ln : [α-1 $P_2W_{17}O_{61}]^{10-}$stoichiometry of the complex.

The general procedure summarized in Scheme 3.1. consists of three steps. The first step involves the preparation of the Lu polyoxoanion complex, followed by ion exchange chromatography in order to remove any extra $Lu3^+$. The sample is checked by ^{31}P NMR in order to make sure that Chelex resin does not decompose the Lu heteropolyanion complex. The second step involves the titration with EDTA followed by ^{31}P NMR, which gives the Lu^{3+} content of the sample. The last step of this procedure allows determination of the amount of [α-1-$P_2W_{17}O_{61}]^{10-}$ in the sample by titration with Co^{2+} followed by absorption spectroscopy.

1. Preparation of the sample: 6 mL (0.122 mmol) of the standardized Li_{10}[α-1 $P_2W_{17}O_{61}$] (conc.0.02032 M) is measured into a vial. 1.8 mL (0.1828 mmol) $LuCl_3$ is added. The solution is stirred for 2 minutes and it is run through the chelating Chelex 100 ion exchange resin prepared as described above. Volume of the resin used for this particular experiment was 1 mL and the flow rate is 3 mL/min, calculated for a burette with 1 cm diameter. (This volume of the resin used was calculated for the total amount of Lu^{3+} based on the resin capacity of 0.4 meq/ml, with additional 100% excess). The sample is eluted with

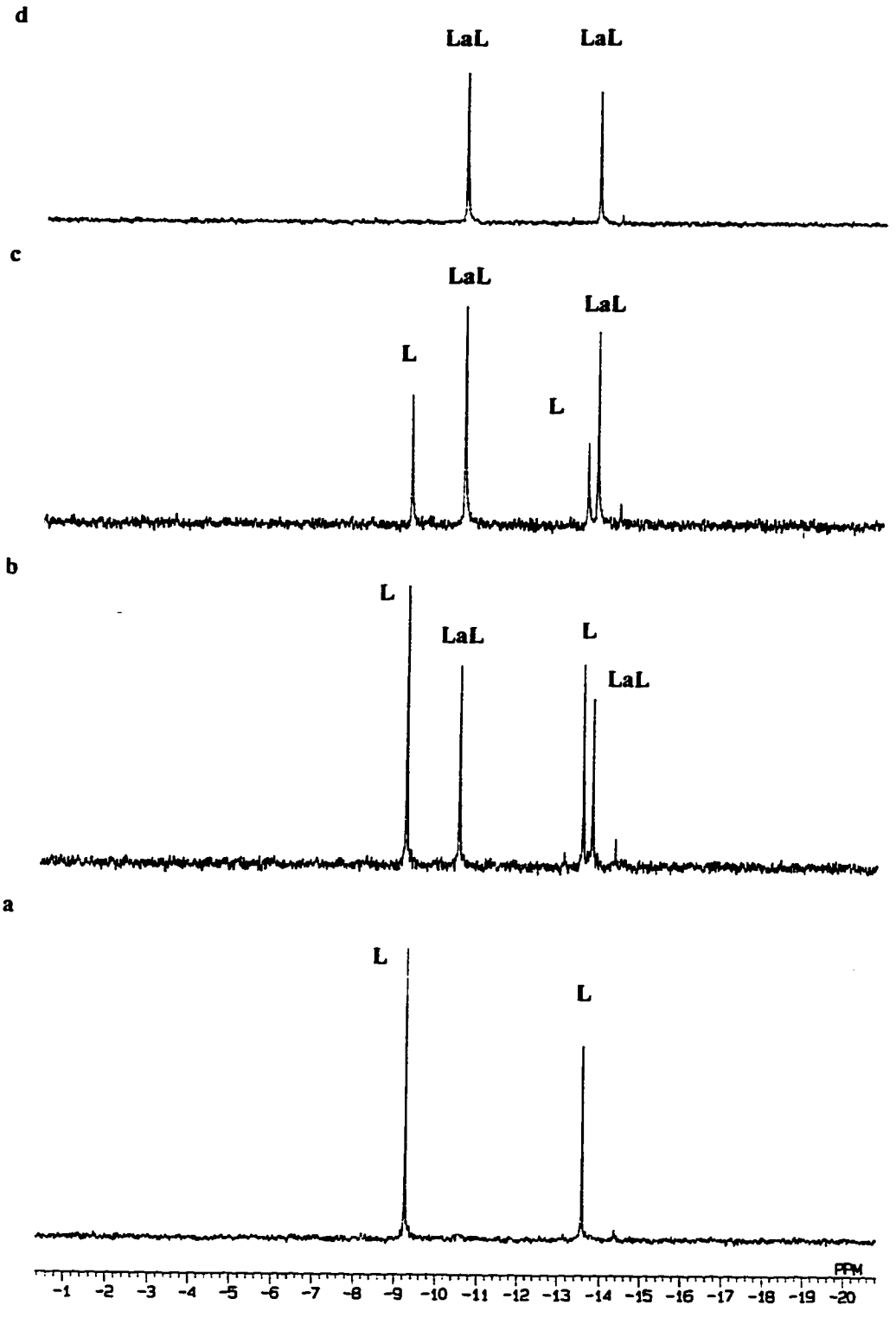


Fig. 3.2. ^{31}P NMR titration of α-1 $Li_{10}P_2W_{17}O_{61}$ (L) with $LaCl_3$ at pH 4.7. Ratio of La:L a) 0, b)1:2, c) 3:4, d) 1:1.

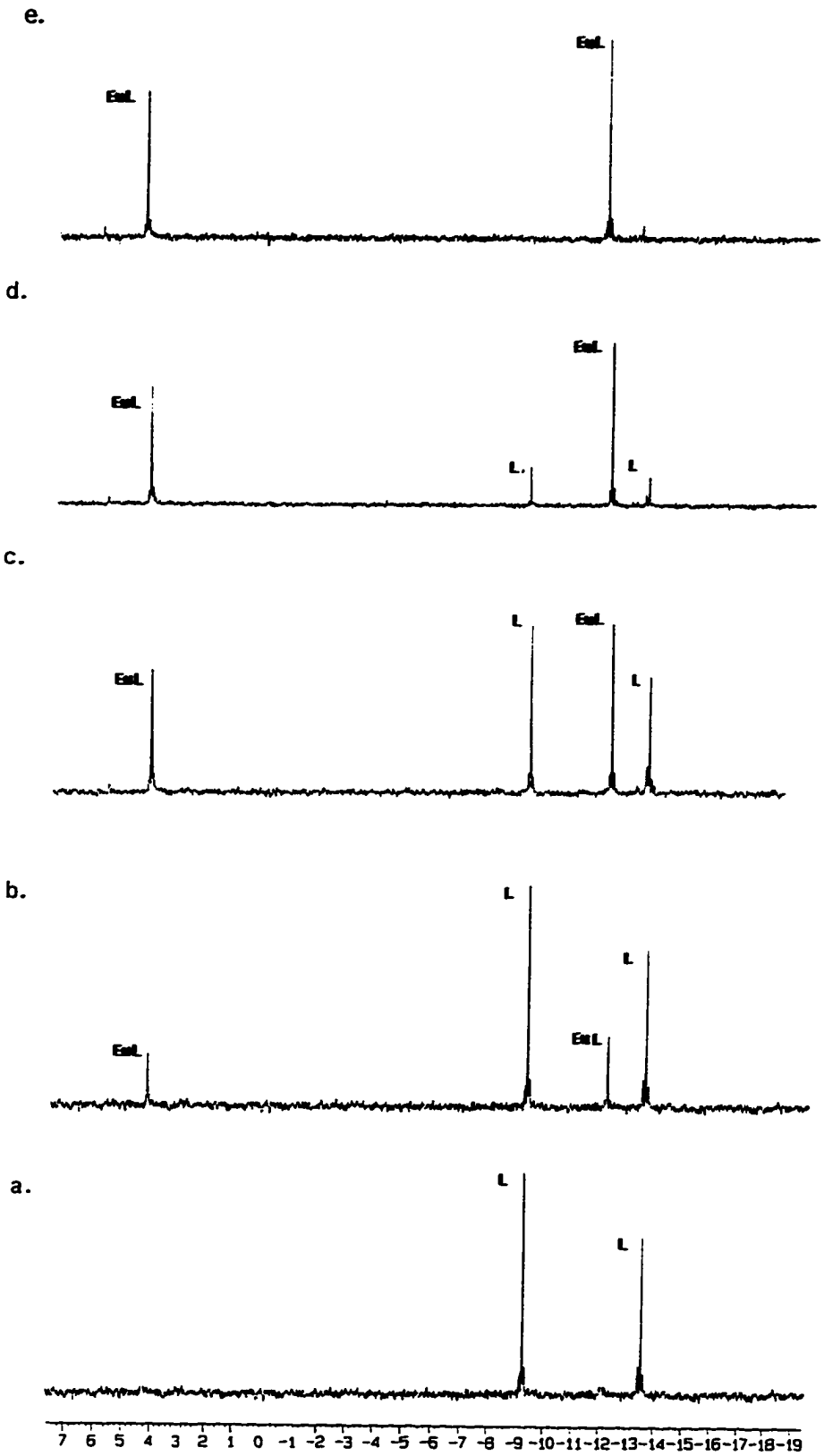


Fig.3.3. ^{31}P NMR titration of α-1 $Li_{10}P_2W_{17}O_{61}$ (L) with $EuCl_3$ at pH 4.7. Ratio of Eu:L a) 0, b)1:4, c) 1:2, d) 3:4, e) 1:1.

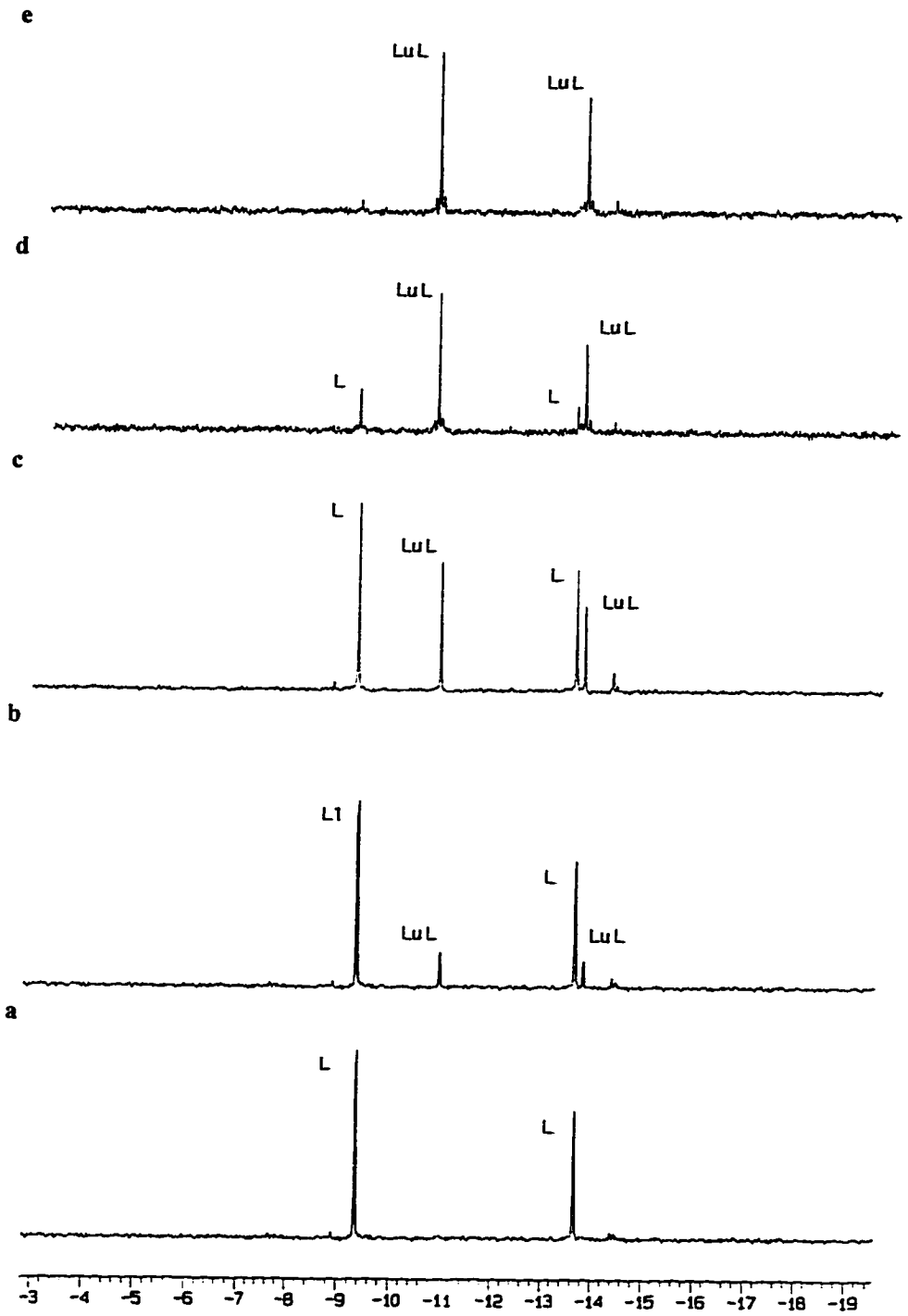


Fig. 3.4. ^{31}P NMR titration of α-1 $Li_{10}P_2W_{17}O_{61}$ (L) with $LuCl_3$ at pH 4.7. Ratio of Lu:L a) 0, b)1:4, c) 1:2, d) 3:4, e) 1:1.

Table 3.1. Titration conditions of $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ solution.

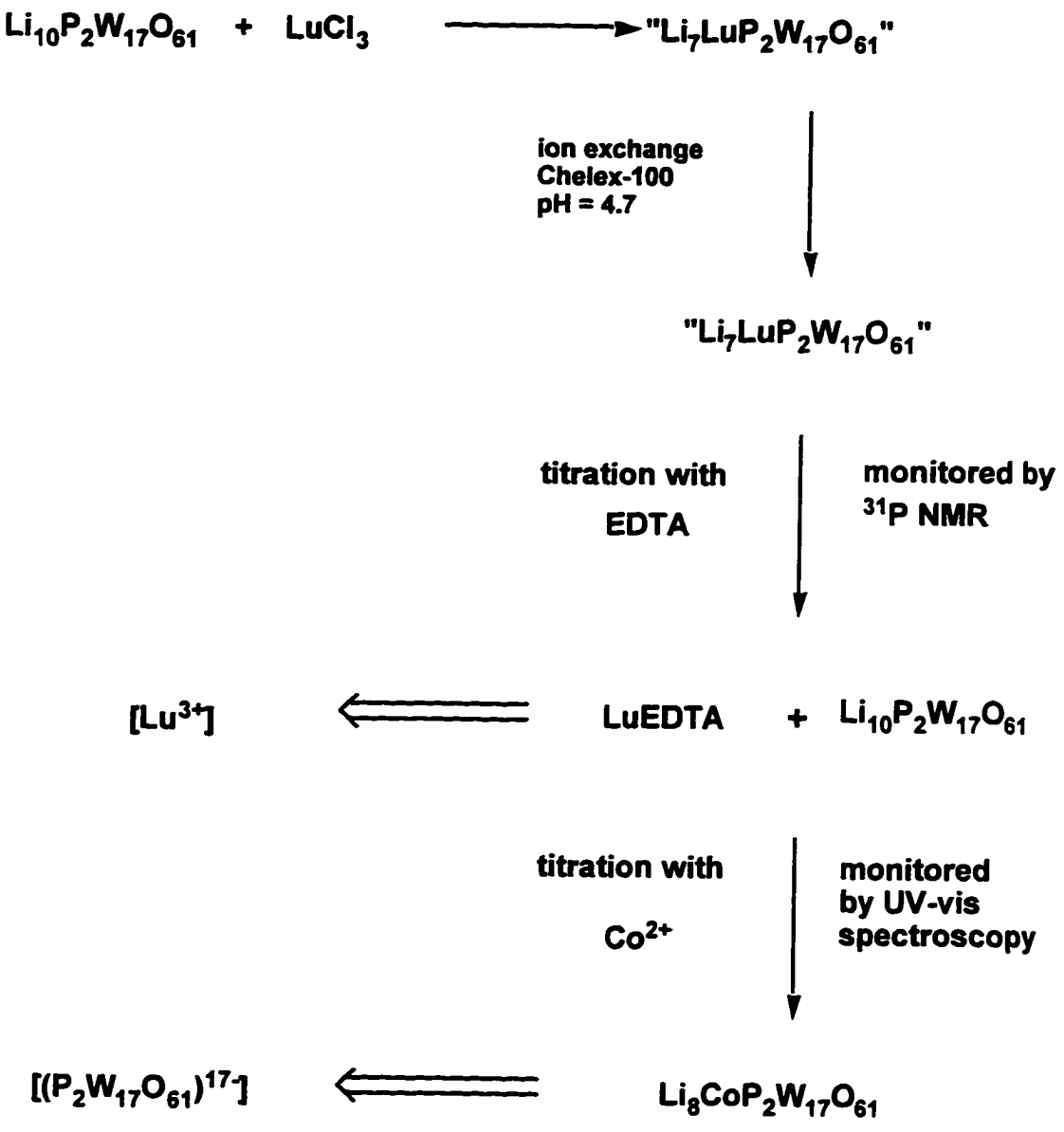
Ln	conc. $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$	conc. Ln^{3+}
Lu	0.01541 M	0.10212M
La	0.01847 M	0.09118M
Eu	0.02110 M	0.10025M

Table 3.2. Integration for P 1(low field) resonance of the $(\alpha\text{–}1\ P_2W_{17}O_{61})^{10-}$ and Ln complexes. L= $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ Ln=Lanthanide , Pα-2 = α-2 isomeric impurity.

Ln	$[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$: Ln	$P1_L$	$P1_{LnL}$	Pα-2
La^{3+}	4:1	1.00	0.25	0.05
	4:2	1.00	0.83	0.09
	4:3	0.55	1.00	0.06
	4:4	0.07	1.00	0.04
Lu^{3+}	4:1	1.00	0.21	0.05
	4:2	1.00	0.74	0.12
	4:3	0.33	1.00	
	4:4	0.15	1.00	0.07

Scheme 3.1.

Determination of the $[Lu^{3+}]$: $[\alpha\text{-}1P_2W_{17}O_{61}]^{10-}$ ratio of the complex



one bed volume of distilled water and concentrated by rotary evaporation at less than 50°C, and stored in freezer.

2. Determination of the Lu content in the sample: 0.5 mL of the sample prepared above is measured into the 5 mm NMR tube and 80 μL 0.0993 M EDTA is added, the solution is shaken and after two hours the ^{31}P NMR of the sample is recorded. Depending on the results of the NMR more EDTA is added in 10, 5, or 3 μL increments. After each addition of EDTA the sample is left to stand at least for two hours before taking its ^{31}P NMR spectrum. The EDTA addition is stopped when all the Lu ion is removed from the LuHPA according to the ^{31}P NMR. This titration is repeated two more times, and the Lu content of the complex is calculated based on the amount of EDTA added. One set of titration data with EDTA is shown in Fig. 3.5

3. Determination of the $[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-}$ HPA concentration.

0.5 mL of the sample prepared in step 1 is measured into a glass UV-vis cuvette. EDTA is added in the amount determined in step 2, followed by the addition of 2 mL lithium acetate buffer pH 4.7, 0.5 mL. The solution is shaken and left for two hours. To this solution $CoCl_2$ (0.3M or 0.5M) was added in 5 or 10 μL increments and the absorbance was recorded at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gives a sharp breakpoint when all the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in 1:1 stoichiometric ratio. Three titrations were run for each standardization; the agreement was within 1-5%. Figure 3.6 shows a typical titration for one experiment. Results for three different experiments are summarized in Table 3.3

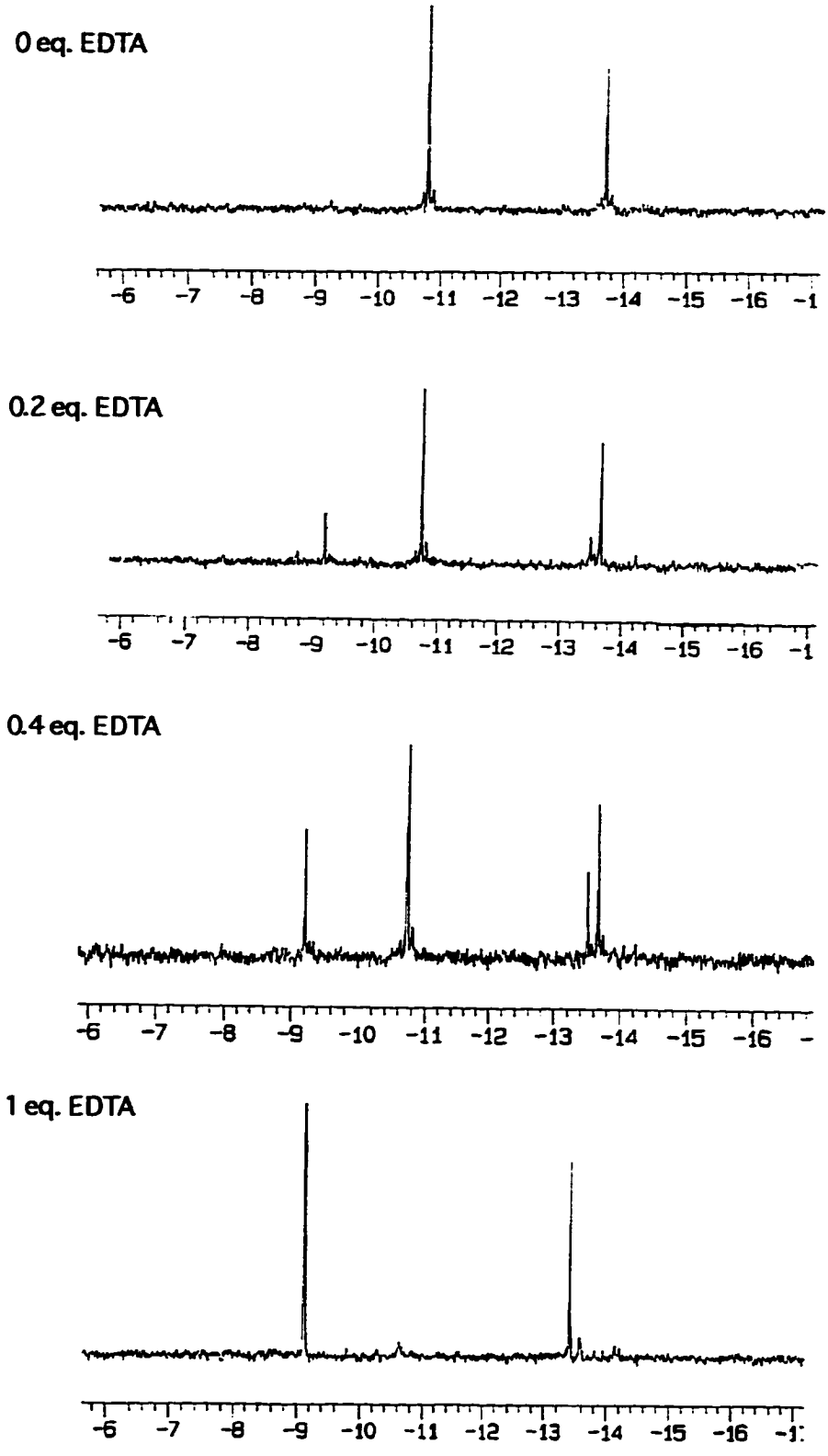


Fig.3.5. ^{31}P NMR titration of the $Li_7[\alpha\text{-}1\ LuP_2W_{17}O_{61}]$ with EDTA.

Fig. 3.6. Plot of absorbance of Co(II) titrated into $Li_{10}[\alpha\text{-}1\ P_2W_{17}O_{61}]$ + Lu-EDTA mixture.

Vol.Co(II)mL	Absorbance
0.01	0.0817
0.015	0.1364
0.02	0.2004
0.025	0.2706
0.026	0.2796
0.03	0.2858
0.04	0.2953
0.05	0.3024
0.06	0.3102

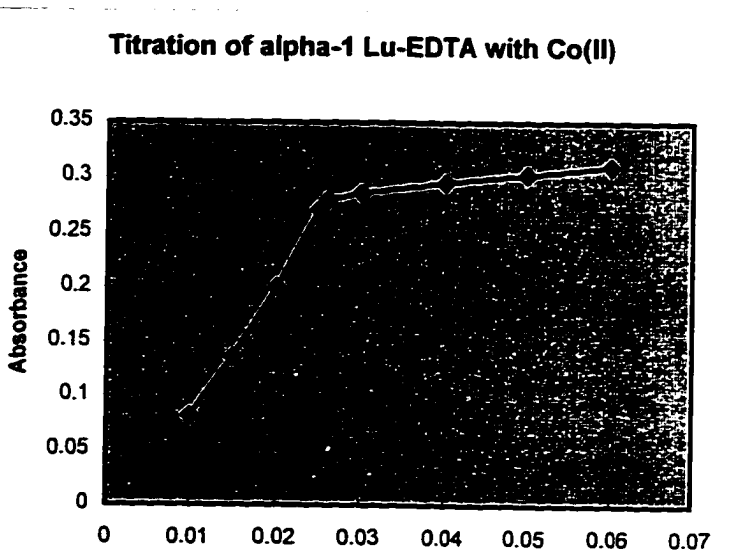


Table 3.3. Summary of the titration results

Experiment	Lu # mol	$(P_2W_{17}O_{61})^{10-}$ # mol	Lu:$(P_2W_{17}O_{61})^{10-}$ ratio
1	8.1426×10^{-6}	7.4475×10^{-6}	1.0933
2	6.6531×10^{-6}	5.958×10^{-6}	1.1167
3	7.9440×10^{-6}	7.6709×10^{-6}	1.0356

Laser Excitation Luminescence Spectroscopy of the Eu complexes. (Experiments were done in collaboration with Prof. W.DeW. Horrocks Jr. at Pennsylvania State University.)

A continuum YG581 pulsed Nd:YAG laser pumped tunable laser dye laser was used to obtain the excitation spectra, lifetime and intensity data of the Eu HPA complexes. [4] The $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+} ion (579-581 nm) was excited.[5] The $^5D_0 \rightarrow {}^7F_0$ 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. $K_7[\alpha\text{-}1\ EuP_2W_{17}O_{61}]$ was prepared and recrystallized, following the method described in the previous chapter. 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} $[\alpha\text{-}1\ P_2W_{17}O_{61}]$ in 0.5M lithium acetate buffer was used diluted to 40 μM with distilled H_2O. 2 mM $EuCl_3$ stock solution was added in 10 μL increments and the excitation spectra were recorded.

Collection of NMR data. NMR spectra were obtained on a Jeol GX-400 spectrometer. ^{31}P spectra at 161.8 MHz were acquired using the broad band decoupler coil of a 5 mm reverse detection probe. Typical acquisition parameters for ^{31}P spectra included: spectral width: 10,000Hz; acquisition time: 0.8 s; pulse delay: 1s; pulse width : 15μsec (50 degree tip angle). From 200 to 500 scans

were required. For all spectra, the temperature was controlled to ±0.2 degree. ^{31}P spectra were referenced to a H_3PO_4 standard in D_2O, which has 0.67 ppm upfield chemical shift relative to 85% H_3PO_4. The convention used is that the more negative chemical shifts denote upfield resonances.

RESULTS AND DISCUSSION

Titration Data. The isolation and characterization of the Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ molecules by elemental analysis, TGA, as well as multinuclear NMR spectroscopy was discussed in the previous chapter [6]. In order to examine the stoichiometry of the L n: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complexes the ^{31}P NMR spectra of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand were monitored with Ln^{3+} added at different ligand:Ln molar ratios.

Figures 3.2, 3.3, and 3.4 show ^{31}P NMR titration data wherein the $LnCl_3$ is added to the ligand. Table 3.1 presents the actual conditions for each experiment. At the start , the pure lacunary species is present. As $LnCl_3$ is added to the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ solution, the lacunary species decreases and the formation of one complex is observed. The intensity of this peak increases as the Ln concentration is increased and it is complete when the ratio of Ln: $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ is 1-1.25. The set of peaks corresponding to [Ln (α-1-$P_2W_{17}O_{61}$)2] complex decreases concomitantly. The chemical shifts of this complex correspond to those of the previously isolated and characterized Ln [α-1-$P_2W_{17}O_{61}$] complexes. Increasing the [α-1-$P_2W_{17}O_{61}$]:Ln ratio to 4:6 or larger amounts of Ln does not change the spectrum.

These results don't change when the titration is performed in reverse order, titrating the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species into a $LnCl_3$ solution, changing counterions or raising the temperature. We observed the formation of the 1:1 species only.

It appears that for all lanthanide ions and conditions employed in this study, one species is formed in acetate buffer at pH 4.7 at ratios of 1:1 Ln : $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, but we were not sure at this point if all the lanthanum added is incorporated into the polyoxoanion forming the 1:1 complex or half of it acts as a counter ion and the other half forms a sandwich complex with two of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ unit. Thus the stoichiometry of the complex needs to be analyzed after all the lanthanide acting as a counterion is removed. Chelex 100 a strong chelating ion exchange resin, was used to remove the Ln^{3+} ions which are not incorporated into the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complex. Elemental analysis failed in determining the Lu, W, P content of the ion exchanged complex, therefore we performed a series of titration experiments in order to determine the Lu and $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ concentrations in the sample as described below. This method is based on the observation that EDTA removes Lu From the Lu $[P_2W_{17}O_{61}]$ complex quantitatively, in 1:1 molar ratio, according to the following equation:

$$[\alpha\text{-}1\text{-}LuP_2W_{17}O_{61}]^{7-} + [EDTA]^{4-} \rightarrow [\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-} + [Lu\text{-}EDTA]^{-}$$

The reaction can be monitored by ^{31}P NMR spectroscopy.

Titrating the ion exchanged $Li_7[\alpha\text{-}1\text{-}LuP_2W_{17}O_{61}]$ complex with EDTA and monitoring the end point by ^{31}P NMR gives us the concentration of the Lu incorporated into the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ unit. Fig 3.5 shows the results of

titration with EDTA. It starts out with the spectrum of the complex with no EDTA added. As the EDTA is added a new set of resonances characteristic of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ appear. As the amount of EDTA in solution increases the peaks of the LuHPA decrease until disappear when the Lu:EDTA molar ratio reaches 1. Knowing the exact concentration and the amount of EDTA added, the Lu^{3+} content of the sample can be calculated. This solution containing the free $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand, and the Lu-EDTA complex is titrated with Co^{2+} following the absorption spectrum at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gives a sharp breakpoint when all the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in 1:1 stoichiometric ratio, as shown in Figure 3.6.

Table 3.3 presents the results of three different experiments where the Lu : $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ ratio is consistently close to 1, even though the ratio of Lu : $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ was 1.5 at the start of the reaction. This shows that the Chelex-100 ion exchange resin removes the extra Lu efficiently. When the Biorad AG50W-X2 was used the titration experiments consistently gave the result as 1.5 Lu : $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometry. The same is true if the Chelex 100 resin was used as being regenerated after one usage. Therefore it is necessary to use freshly prepared Chelex-100 resin.

We performed many controlled experiments in order to check the accuracy of these series of titrations. The results always agreed with the theoretical values within 3-5 %.

The mixture of LuEDTA and $Co[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{8-}$ was monitored by ^{31}P and ^{1}H NMR in order to make sure that during the titration experiments the Co^{2+}

does react with the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ and does not replace the Lu from the LuEDTA complex. ^{31}P NMR shows the formation of the $[\alpha\text{-}1\text{-}CoP_2W_{17}O_{61}]^{8-}$ and ^{1}H NMR indicates that the LuEDTA is not affected by the addition of the Co^{2+}, following the equation below:

$$[\alpha\text{-}1\ P_2W_{17}O_{61}]^{10-} + Co^{2+} + [Lu\text{-}\ EDTA]^{-} \rightarrow [\alpha\text{-}1\ CoP_2W_{17}O_{61}]^{8-} + [Lu\text{-}\ EDTA]^{-}$$

These results were expected based on the magnitudes of the critical stability costants [7] of the Lu with EDTA, which is higher (19.80) than the Co-EDTA (16.26). The stability constant of the $[\alpha\text{-}1\ CoP_2W_{17}O_{61}]^{8-}$ is reported as 7.66 [2].

Attempts to remove the La^{3+} ion with EDTA from the La $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ complex quantitatively, failed, due to the lower stability constant of LaEDTA, (reported as 15.46 [7]) compared to the Lu-EDTA. The use of stronger chelating ligands to La^{3+} like DTPA or DOTA is not possible because of the low solubility of these complexes in water.

Preliminary Luminescence Spectroscopy Data

Lanthanide ions are distinguished among metallic cations in their ability to luminesce in solution at room temperature. Eu(III) and Tb(III) are the most strongly emitting members of the Ln series [8]. Laser excited Eu^{3+} luminescence spectroscopy is a powerful tool for monitoring the binding of this ion to ligands in solution. The $^{7}F_0 \rightarrow {}^{5}D_0$ transition of Eu^{3+} ion in the range 577-581 nm is excited [8-10] by a tunable dye laser while the $^{5}D_0 \rightarrow {}^{7}F_0$ emission band at 614 nm is monitored. The excited lifetimes are relatively long; duration in the millisecond region are not uncommon under certain circumstances. Since the

Fig.3.7. $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of 40 μM $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ solution in H_2O.The experimental spectrum is shown resolved into its components. $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ at 580.01 nm, $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ at 580.36 nm, $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ at 579.84 nm.

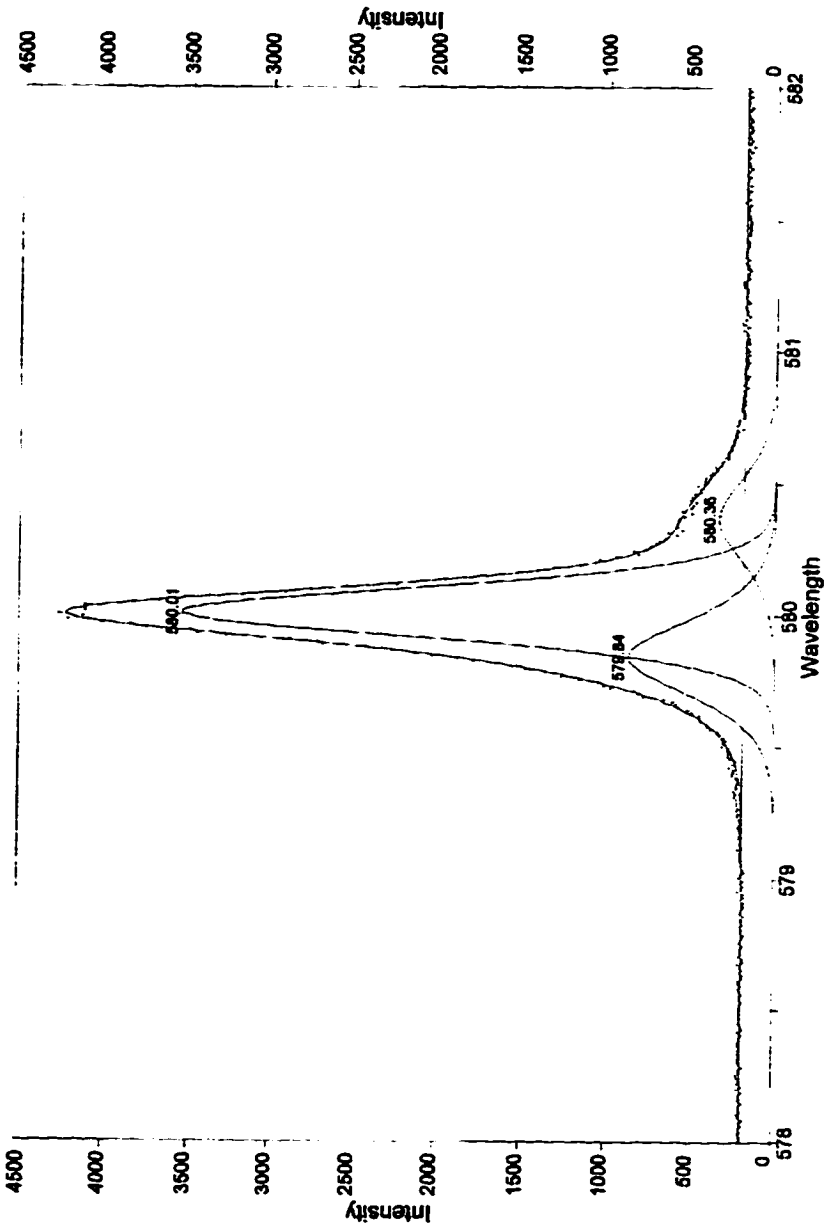
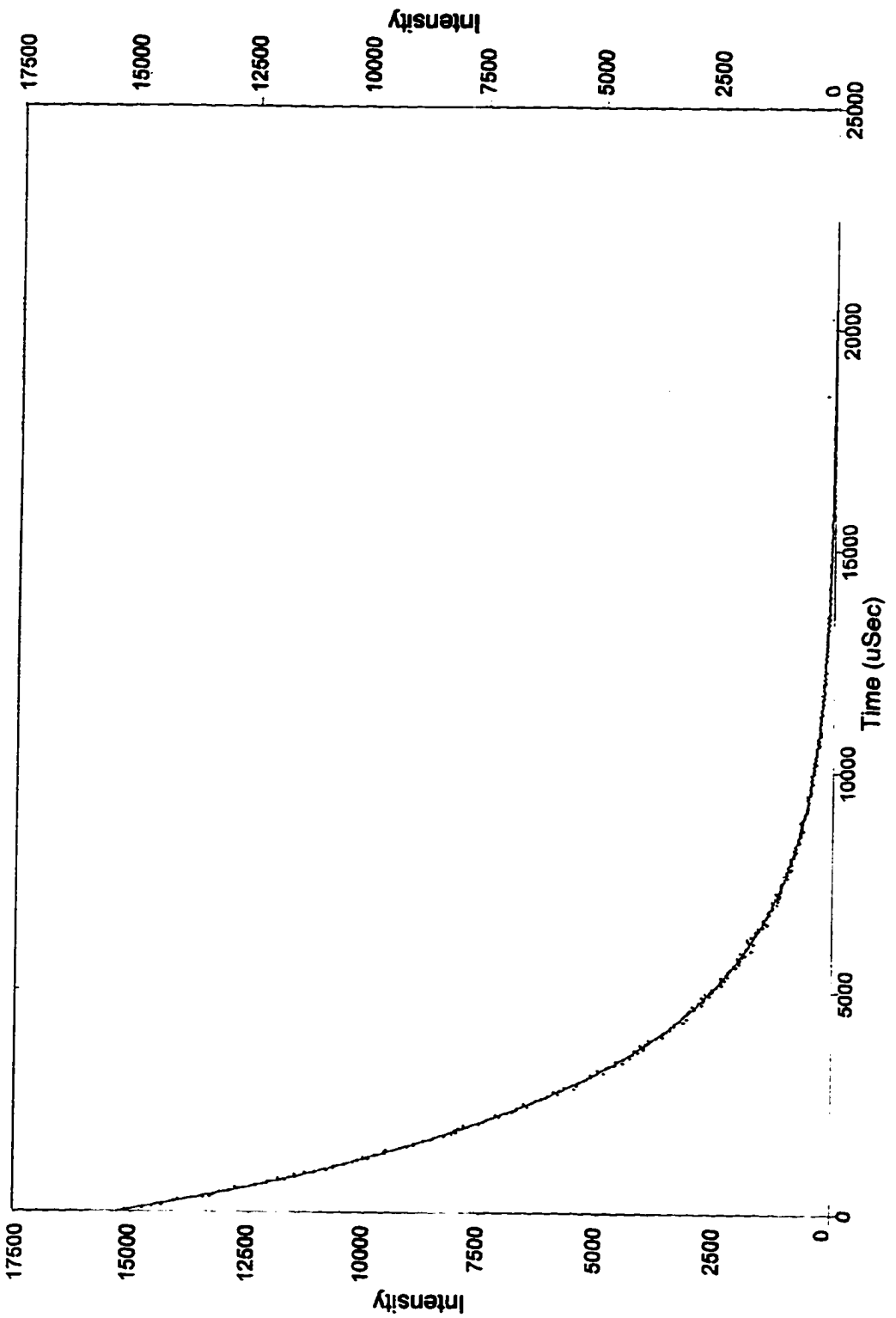


Fig. 3.8. Excited state luminescence decay of the $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ in D_2O.



$^7F_0 \rightarrow {}^5D_0$ 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 [10].

The excitation spectrum of the $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ dissolved in H_2O, shows one narrow band at 580.01 nm, which is resolved into three components: one major peak and two others with lower intensities as shown in Fig. 3.7. The low intensity peaks can be attributed to the alpha-2 isomeric impurities contained in the sample. After recrystallization of the complex, the ^{31}P NMR shows the presence of a small amount of alpha-2 isomer. The lifetime of the Eu excited state measured at 580.01 nm is 0.254 ms in H_2O and 2.826 ms in D_2O, The exponential decay of the lifetime in D_2O is shown in Fig. 3.8.

The excitation spectra of the 1:1 $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ and the 1:2 $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ were obtained for comparison. The 1:1 $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ complex show one narrow band at 579.79 nm (Fig. 3.9) , the excited state lifetime of the Eu^{3+} in this complex is 0.241 ms, similar to the lifetime of the α -1 isomer. However the 1:2 $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ sandwich complex has two absorption bands at 579.8 and 580.4 nm with approximately equal intensities, revealing two different Eu^{3+} environments presumably interconverting to each other (Fig.3.10.). The ^{31}P NMR spectrum of this complex shows a very clean compound with only two resonances. One possible explanation for this phenomenon could be that in the excitation spectrum of the

Fig. 3.9. $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of 40 μM $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ solution in H_2O.The experimental spectrum is shown resolved into its components. $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ at 579.79 nm

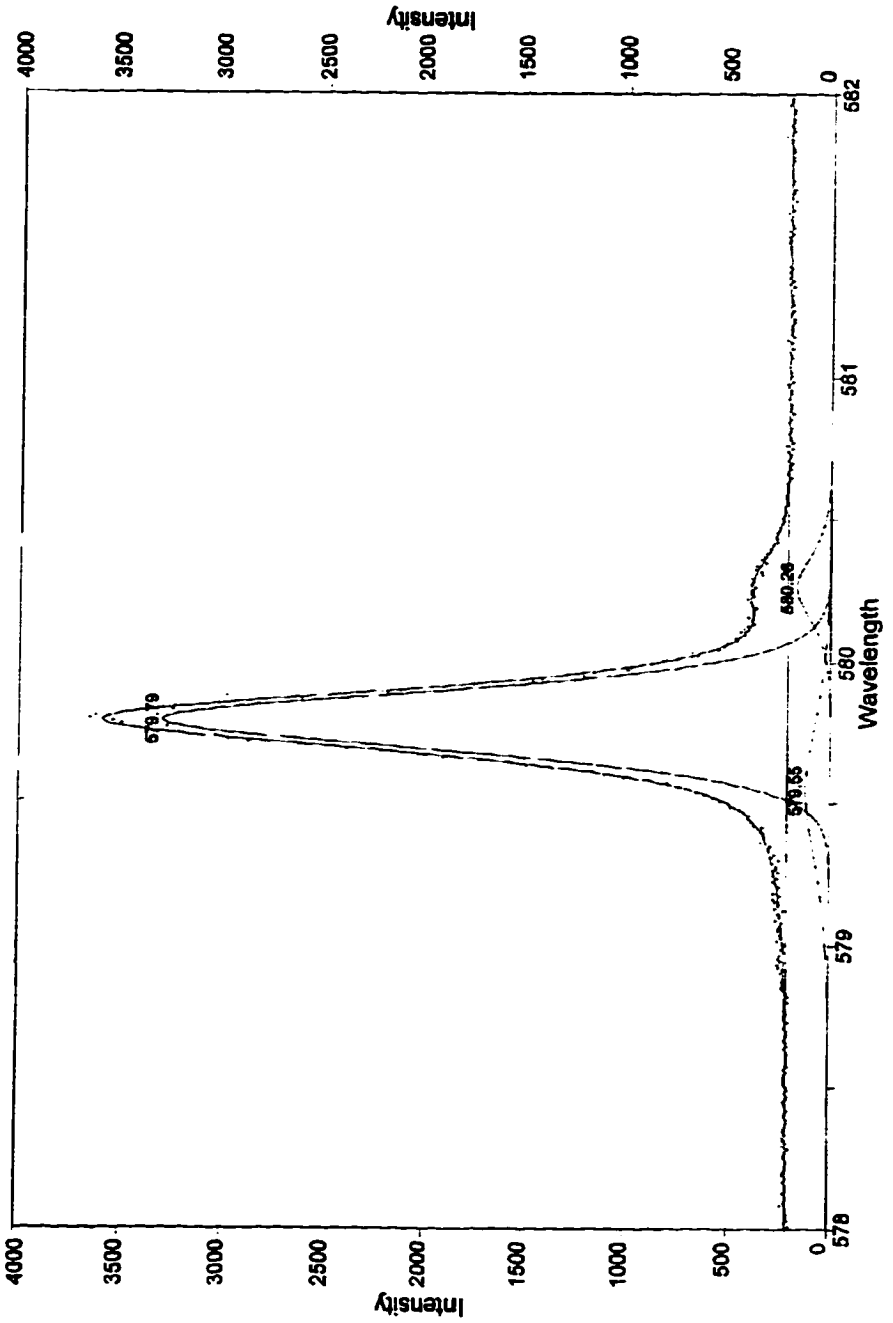
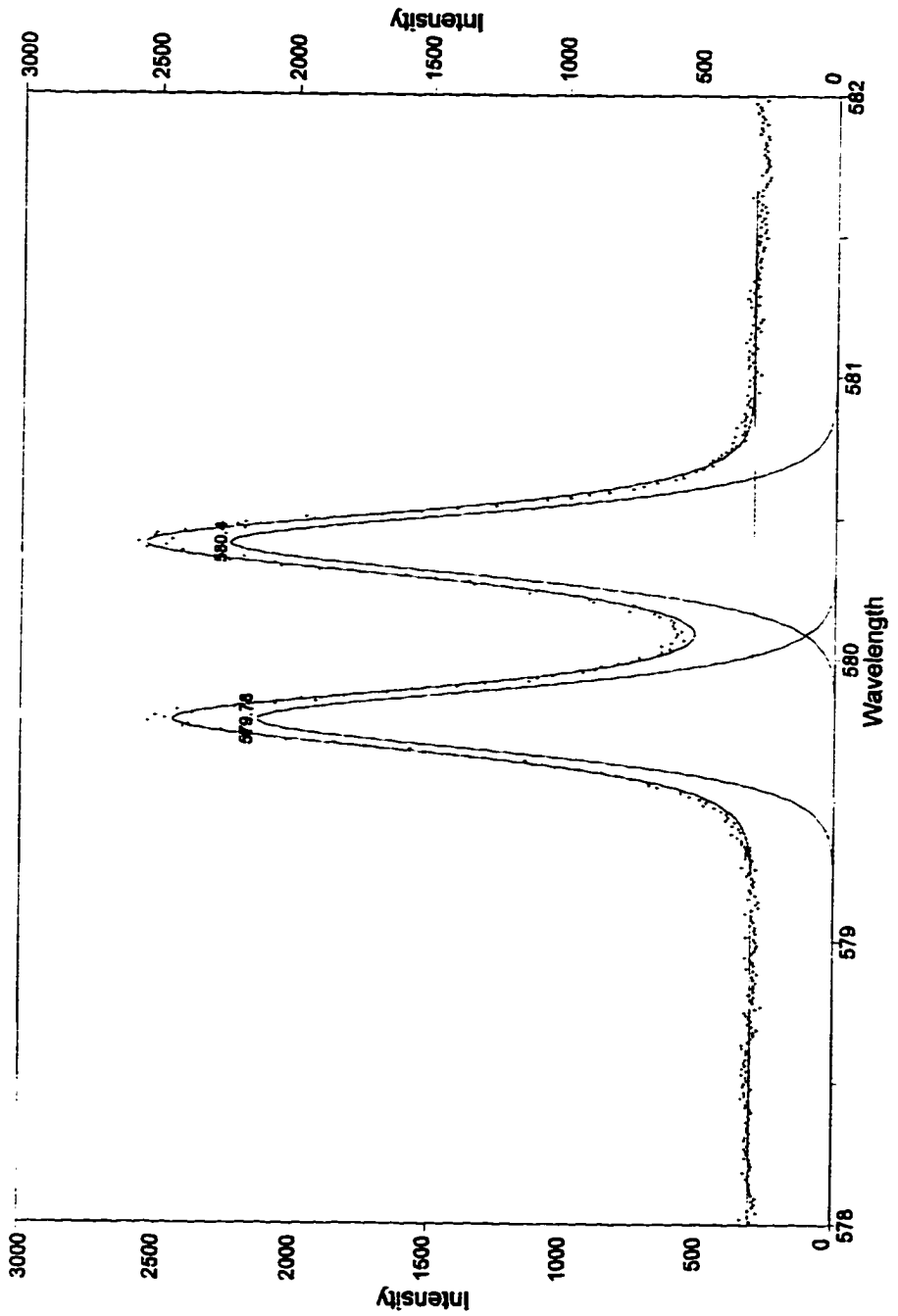


Fig.3.10. $^7F_0 \rightarrow {}^5D_0$ excitation spectrum of 40 μM $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ solution in H_2O.The experimental spectrum is shown resolved into its components.



1:2 $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ we see the sandwich complex decomposing into the 1:1 $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ complex, with one peak at 579.78 nm corresponding to the 1:1 $K_7[\alpha\text{-}2\text{-}EuP_2W_{17}O_{61}]$ and the other peak at 580.4 nm corresponds to the sandwich $K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$ molecule. Lifetime measurement data for the two peaks, confirm this hypothesis. The lifetime at 579.78 nm is 0.250 ms, indicating that there are a few water molecules coordinated to the Eu^{3+} ion, which expected for a 1:1 complex, where the polyoxoanion ligand occupies only four of the coordination sites of the Eu^{3+}. The lifetime measured at 580.4 nm is much higher, 3 ms, indicating that there is no water molecule coordinated to the Eu^{3+}. This result is consistent with the presence of a 1:2 sandwich complex, where the two polyoxoanion ligands occupy eight of the coordination sites of the Eu^{3+}. The reason for not observing this in the ^{31}P NMR spectrum, could be that polyoxoanions are concentration dependent [11], dilution induces their degradation in less condensed species. The excitation spectrum is recorded at much lower concentration, 40μM compared to 10 mM used for the ^{31}P NMR measurenent .

The excited state lifetime of the Eu^{3+} is very sensitive to the number of water molecules coordinated to the ion, because the 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 [10]. Based on this observation Horrocks and Sudnick developed a method for determining the number of water molecules coordinated to the Eu. The experimentally determined decay constant, or lifetime, of Eu has been shown to be linear with the number of waters in the

first coordination sphere of Eu. Therefore, from measurements of lifetimes separately

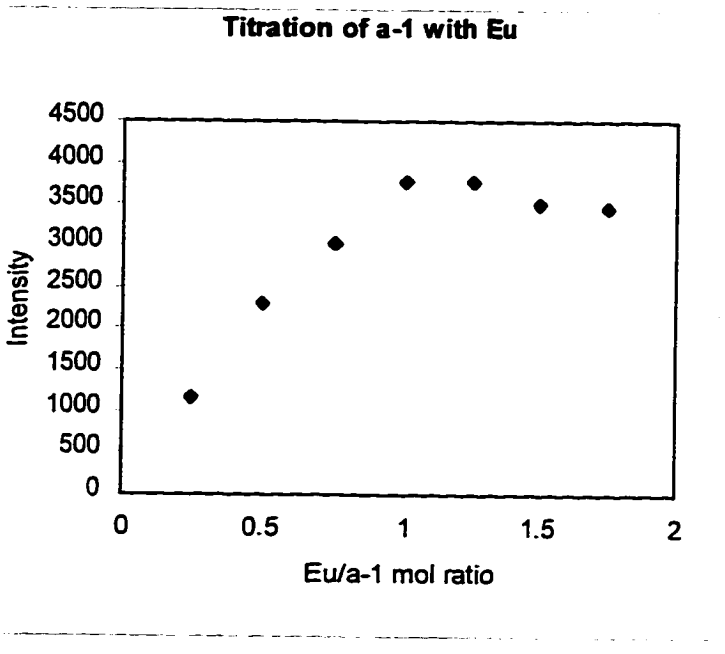
in H_2O and D_2O solution, it is possible to determine the number of coordinated molecules, *q*, from :

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

Using this equation and the lifetimes of the $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ measured in H_2O and D_2O, q = 3.8. Therefore it is clear that there are four water molecules coordinated to the Eu. This result is in agreement with the 1:1 formulation of the $K_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ complex where the Eu^{3+} binds to four oxygens of the polyoxoanion and the other four coordination site is taken by water molecules. The possible error of these measurement is ± 0.5 water molecule.

The stoichiometry of the complex was also determined by titrating 40 μM solutions of the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ with Eu^{3+} while monitoring the intensity of the excitation maximum at 580.07 nm. The plot of the intensities versus the molar ratio of Eu:$[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ gives a sharp break point when the ratio reaches 1 as shown in Figure 3.11.

Fig. 3.11. Plot of intensities for $^7F_0 \rightarrow {}^5D_0$ excitation spectra of 40 μM $Li_7[\alpha\text{-}1\text{-}EuP_2W_{17}O_{61}]$ solution in H_2O, as a function of Eu^{3+}/ $Li_{10}[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ molar ratio. λ_{ex} = 580.07 nm.



CONCLUSION:

The stoichiometry of the $[\alpha\text{-1-LnP}_2W_{17}O_{61}]^{7-}$ complexes has been determined by two different method: by complexometric titrations for Lu and luminescence spectroscopy measurements of Eu. Both method consistently prove the 1:1 formulation of the $[\alpha\text{-1-LnP}_2W_{17}O_{61}]^{7-}$.

^{31}P NMR shows formation of only one complex in solution at pH 4.7 for Lu, La and Eu, which is complete when the molar ratio of Ln:$[\alpha\text{-1-P}_2W_{17}O_{61}]^{10-}$ is one or higher. Luminescence lifetime measurements determined that there are four water molecules coordinated to the Eu^{3+} ion in the $K_7[\alpha\text{-1-EuP}_2W_{17}O_{61}]$ complex, consistent with the 1:1 formulation. Luminescence titration experiments further confirm this stoichiometry.

The excitation spectrum of the 1:1 complexes of α-1 and α-2 $[Eu P_2W_{17}O_{61}]^{7-}$ complexes is very similar containing one absorption band at 580.07 and 579.79 nm respectively, which is consistent with one single Eu environment in solution.The excitation spectrum of the 1:2 K_{17} $[\alpha\text{-2-Eu}(P_2W_{17}O_{61})_2]$ complex contains two different Eu^{3+} sites, however the ^{31}P NMR spectrum shows the existence of only one complex in solution. These results confirm the usefulness of luminescence excitation spectroscopy in characterizing lanthanide polyoxoanion complexes.

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Chapter 4.

Preparation and Characterization of Lanthanide Complexes of the α-2-$(P_2W_{17}O_{61})^{10-}$ Heteropolyoxotungstate.

INTRODUCTION

The α-2-$(P_2W_{17}O_{61})$ isomer, discussed in this chapter, is distinguished from the α-1 isomer by removal of a $[W{=}O]^{4+}$ group from the "capping" triad of tungsten polyhedra (Figure 1.1a). Complexation of this "ligand" with lanthanide ions result in the "sandwich" complexes. The lanthanide ion binds to the four oxygen atoms of each of two defect oxoanions. (Figure 4.1 and 4.2)

Lanthanide (Ln) complexes of heteropolytungstates were reported in 1971 by Peacock and Weakley [1] . In that report the 1:2 Ln: tungstates $K_{17}[\alpha\text{-2-Ln}(P_2W_{17}O_{61})_2]$, were isolated and characterized by elemental analysis, UV, and visible for (Ce(III)) spectroscopy.

The crystal structure of the $[\alpha\text{-2-Ce}(P_2W_{17}O_{61})_2]^{16-}$ (heavy metal framework reported only) shows the 1:2 Ce(IV): α-2- heteropolyanion formulation.[2] Tourne reported the preparation and characterization of the $[U(IV)(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{16-}$ species by elemental analysis, polarography, and spectroscopy. [3] Recently, spectrophotometric titrations and electrochemical data confirm the existence of $[\alpha\text{-2-Ce}(P_2W_{17}O_{61})]^{7-}$ and the 1:2 complex, $[\alpha\text{-2-Ce}(P_2W_{17}O_{61})_2]^{17-}$.[4,5]

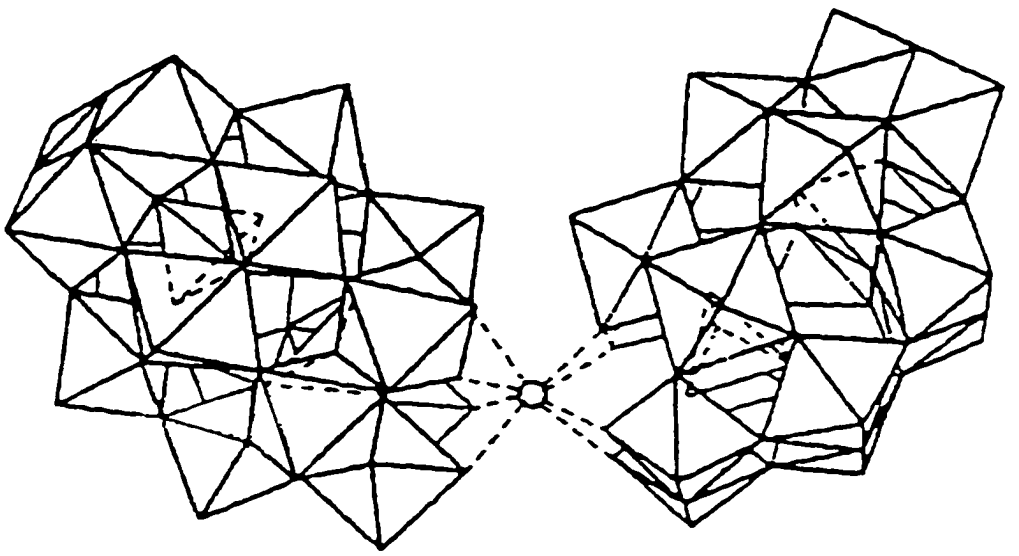
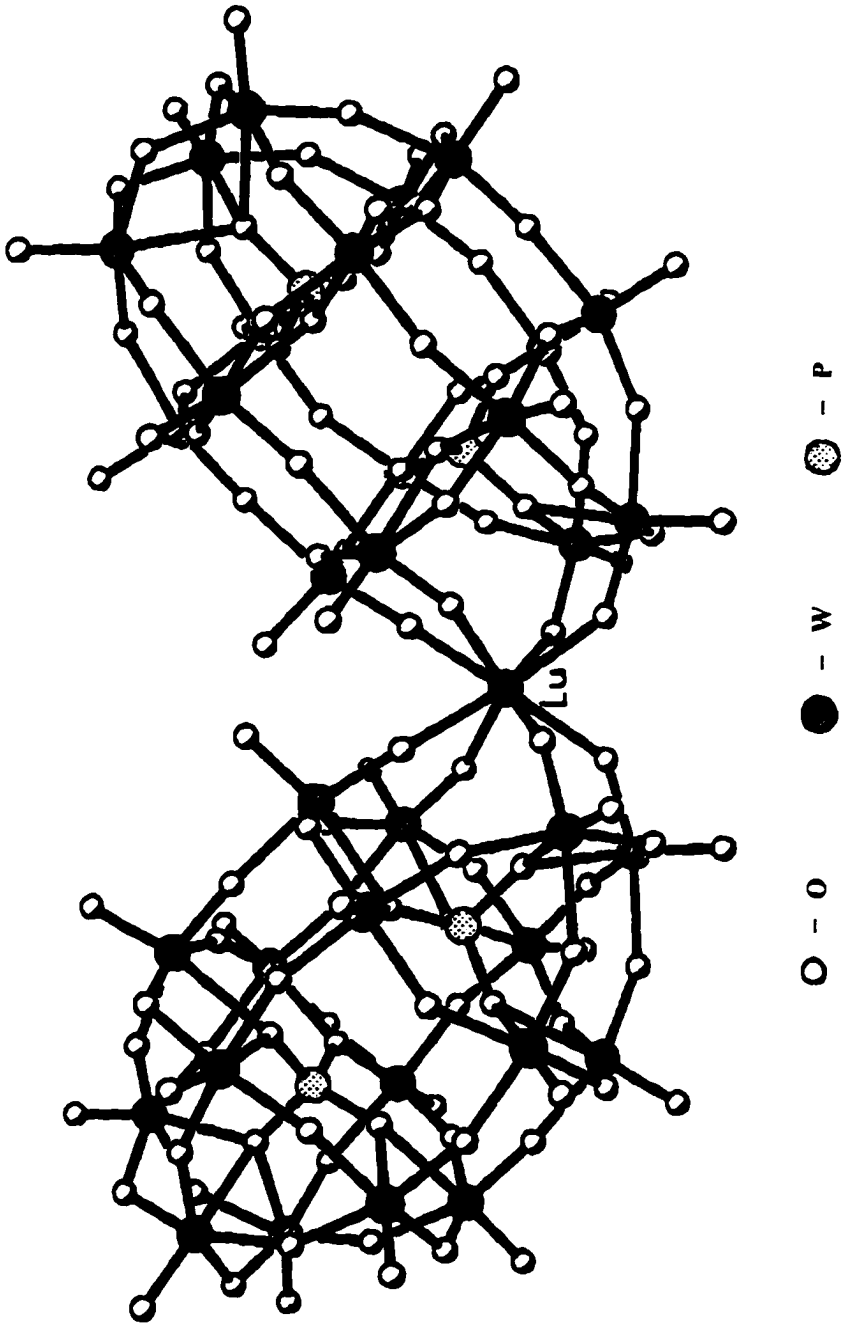


Figure 4.1. Polyhedral representation of the $[Ln(P_2W_{17}O_{61})_2]^{17-}$ sandwich complex. Each octahedron represents a WO_6 unit, where the W is within the octahedron, oxygens at the vertices of the octahedron.

Figure 4.2. The structure of $K_{17}[\alpha\text{-}2\ Lu(P_2W_{17}O_{61})_2]$ in stick and ball representation.



We have prepared and studied a series of lanthanide complexes of the α-2-($P_2W_{17}O_{61}$) heteropolyoxotungstate by multinuclear (^{183}W and ^{31}P) NMR spectroscopy among the other techniques. The tetrabutylammonium salt of the lacunary α-2-($P_2W_{17}O_{61}$) has been prepared by metathesis of the potassium salt.

EXPERIMENTAL

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 "Wells-Dawson" ion, $(P_2W_{18}O_{62})^{6-}$ as the potassium salt, was prepared using literature methods.[6] The α-2 lacunary isomer, $K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$, was prepared following the method of Finke.[7] 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. TGA data were kindly provided by TA Instruments, Newcastle, Delaware. FAB- Mass Spectra were run on a VG ZAB- SE. Samples were dissolved in water and the matrix 3:1 dithiothreitol: dithioerythritol or glycerol.

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 preparation of the resin has been described in the previous chapters.

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: spectral width: 10,000Hz; acquisition time: 0.8 s; pulse delay: 20s; pulse width : 15μsec (50 degree tip angle). From 50 to 500 scans were required. For ^{183}W spectra, typical conditions included: spectral width: 10,000Hz; acquisition time: 1.6 s; pulse delay: 0.5s; pulse width: 50 μsec (45 degree tip angle). From 1,000 to 30,000 scans were acquired. ^{31}P spectra were referenced to a H_3PO_4 standard in D_2O, which has 0.67 ppm upfield chemical shift relative to 85% H_3PO_4. ^{183}W spectra were referenced to 2.0 M Na_2WO_4. For both ^{31}P and ^{183}W NMR, the convention used is that the more negative chemical shifts denote upfield resonances.

Preparation of Complexes.

The $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ family of compounds was prepared using the slightly modified method of Peacock and Weakley[1a], involving base degradation of the parent compound, $[P_2W_{18}O_{62}]^{6-}$. When the potassium acetate is added to the solution it is very important to stop when the solution clears and to keep the pH below 5. Otherwise the lanthanides hydrolyze and form an insoluble precipitate. Isomerically pure $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$, used for the preparation of the tetrabutylammonium salt of the lacunary compound, was prepared by the method of Finke.[7]

Crystallization of $K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$. $K_{17}[Lu(P_2W_{17}O_{61})_2]$ (1g) was dissolved in ca 10 mL of water in a 25 mL vial at 80C to obtain a clear solution. KCl (400 μL) was added dropwise. The solution remained clear. The vial was placed into a beaker with sodium acetate buffer at pH=4.7 and covered and left at room temperature. Within 24 hours, very small crystals formed ; the mother liquor was placed into a new vial and replaced into the beaker with the buffer. Small needle crystals formed after two weeks. The mother liquor was placed into a vial and replaced into the buffer solution. After three days, crystals formed.

The X-ray crystal structure has been solved by Prof. R. Rogers of the Chemistry Dept., University of Alabama and Prof. V. Young of the Chemistry Dept., University of Minnesota.

Solution of Crystal Structure.

Data Collection

A crystal of the compound was attached to a glass fiber and mounted on the Siemens SMART system for data collection at 173(2)K. An initial set of cell constants was calculated from reflections harvested from three sets of 30 frames. These initial sets of frames are oriented such that orthogonal wedges of reciprocal space were surveyed. This produces orientation matrices determined from an unknown number reflections. Final cell constants were calculated from a set of 8192 strong reflections from the actual data collection. Final cell constants reported in this manner usually are about one order of magnitude better in

precision than reported from four-circle diffractometers. Table 1 contains additional crystal and refinement information.

In this data collection technique, known as a hemisphere collection, randomly oriented region of reciprocal space is surveyed to the extent of 1.3 hemispheres to a resolution of 0.84Å. Three major swaths of frames are collected with 0.30° steps in ω. In the event the lattice is triclinic some additional sets of frames are collected to better model the absorption correction.

Structure Solution and Refinement

All calculations were performed using SGI INDY R4400-SC or Pentium computers using the SHELXTL V5.0 suite of programs. The space group P$\bar{1}$ was determined based on systematic absences and intensity statistics [ref]. A successful direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Several full-matrix least squares/difference Fourier cycles were performed which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual (or group if appropriate) isotropic displacement parameters.

This structure is based on data originally collected at the University of Northern Illinois and the structural solution was partially completed there. The structural solution was completed at the University of Minnesota. The solution suffers from what appears to be a bad absorption correction. Many atoms refine to negative values even though all are isotropic. An attempt was made at refining

only the tungsten atoms as anisotropic, but many of these have unrealistically small values. A full isotropic refinement was completed with the exception of twelve oxygen atoms that had to be fixed at positive isotropic values. In addition to the $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ complex are found 16 potassium cations and an additional 42 oxygen atoms associated with water. The overall charge on the complex is 17- so it is assumed that one hydronium ion is incorporated in the structure. This structure is very similar to that published by Molchanov[ref], on the cerium analog. The quality of the structure is suitable to determine connectivity and the gross structural features of the molecule.

Metathesis of $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ to form $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$. The following method is a modification of the metathesis method developed by Finke. [7] $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (5 g,1.02 mmol) was dissolved in H_2O (500 mL) to form a clear solution, pH=6.2. The pH was gradually adjusted to 5.65 with sulfuric acid (0.18M). Tetrabutylammonium bromide (3.29g, 10.2 mmol) was added slowly while the pH of the solution was maintained in the range of 5.5-7.5 with 0.18M sulfuric acid. The resulting white cloudy solution was extracted with 34 mL CH_3CN and 67 mL CH_2Cl_2. The mixture was shaken for 5 minutes. The clear organic layer was collected and rotary evaporated at 50°C. Methylene Chloride (5 mL) was added to dissolve the resulting solid to give a clear faint yellow-green solution. Addition of diethylether (25 mL) resulted in the precipitation of a white solid. The solid was filtered and dried in vacuo. The compound was recrystallized from acetonitrile.

To collect ^{31}P NMR data in D_2O, a metathesis procedure was used.[8] Solid $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (64 mg) was stirred into a solution of $LiClO_4$ (10 mg) in 0.5 mL D_2O. The resulting solution was cooled to 2-3°C. A solid, presumably $TBAClO_4$, was separated from the solution by centrifugation.

Elemental analysis, TGA and Mass Spectral data are given in Table 4.1. ^{31}P and ^{183}W NMR data are given in Tables 4.2 and 4.3, respectively.

Table 4.1. Analytical Data for $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ Complexes

		calcd.	obsd.	TGA	Mass Spectometry (FAB^-)[a]
$K_{17}[\alpha\text{-}2\text{-}La(P_2W_{17}O_{61})_2]\cdot 30\ H_2O$					
	W	64.64	64.47	5.561	
	P	1.28	1.27		
	K	6.87	6.70		
	La	1.44	1.35		
$K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]\cdot 27\ H_2O$					
	W	64.76	64.51	5.080	FAB^- 8606 $KLiLu(P_2W_{17}O_{61})_2(-O, -WO_3)$
	P	1.28	1.32		4391 $KLi_2Lu(P_2W_{17}O_{61})$
	K	6.88	6.64		4388 $KLi\ H_4Lu(P_2W_{17}O_{61})$
	Lu	1.81	1.63		4152 $KLiLu(P_2W_{17}O_{61})(-WO_3)$
					ES- 4420$[Li_3H_{12}Lu(P_2W_{17}O_{61})_2]^{2-}$
					4326 $[Li_3H_3Lu(P_2W_{17}O_{61})]^-$
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}(P_2W_{17}O_{61})]\cdot 4.5\ H_2O$					
	W	48.65	50.82		FAB^- 4202 $[Li_2H_7\ (P_2W_{17}O_{61})]^-$
					4178 $[Li\ H_8\ (P_2W_{17}O_{61})]^-$
	P	0.96	0.88		
	C	26.92	24.70		
	H	5.20	4.94		
	N	1.96	1.85		

a. see text

Table 4.2. Phosphorus-31 NMR Data.

Compound	Chemical Shift, δ,ppm[a]		Solvent[b] (peaks due to protonation)	
	P2	P1		
$K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$[c]	-14.10	-7.28	D_2O	
$K_{17}[\alpha\text{-}2\ Lu(P_2W_{17}O_{61})_2]$	-14.15	-8.17	D_2O	
$K_{17}[\alpha\text{-}2\ La(P_2W_{17}O_{61})_2]$	-14.15	-8.17	D_2O	
$K_{17}[\alpha\text{-}2\ Yb(P_2W_{17}O_{61})_2]$	-22.76	-8.70	D_2O	
$K_{17}[\alpha\text{-}2\ Eu(P_2W_{17}O_{61})_2]$	-13.23	+3.14	D_2O	
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\ P_2W_{17}O_{61}]$	-13.60	-9.10	$DMSO/H_2O$	
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\ P_2W_{17}O_{61}]$	-11.56	-7.26	DMSO,	11.17
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\ P_2W_{17}O_{61}]$	-11.95	-6.55	CH_3CN,	-10.47
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\ P_2W_{17}O_{61}]$	-13.63	-7.77	D_2O,$LiClO_4$	

a. See text for data collection parameters. P1 is the phosphorus atom closer to the site of substitution, P2 represents the phosphorus atom remote to the substitution site. b. In organic solvents, protonation of the oxoanions results in multiple peaks, see text. c. chemical shifts from ref 19.

Table 4.3. ^{183}W NMR Data.[a]

Compound	Chemical Shift, δ,ppm
$K_{10}[\alpha\text{–}2\ P_2W_{17}O_{61}]$[c]	-242.3 (2), -225.0 (2), -222.7 (2),-218.9 (2), -179.6 (1), -175.8 (2),-159.6 (2), -140.8(2), -127.9 (2)
$Li_{17}\ [La(\alpha\text{–}2\ P_2W_{17}O_{61})_2]$[d]	-137.55 (2),-146.75 (2),-178.97 (2),-180.51 (1), -193.81(2), -194.10 (2),-213.71 (2),- 218.52 (2), -219.61 (2),-239.95 (2)
$Li_{17}\ [Yb(\alpha\text{–}2\text{-}P_2W_{17}O_{61})_2]$[d]	-134.36 (1), -135.50 (1) ,-144.96 (1), -153.84 (1) -173.14(1), -180.76 (1), -183.22 (1), -184.50 (1), -207.04 (1) ,-208.87 (1), -210.85 (1) , -212.21 (1), -215.55 (2), -229.11 (1), -239.30 (1), -240.32
$Li_{17}\ [Lu(\alpha\text{–}2\text{-}P_2W_{17}O_{61})_2]$[d]	-134.66 (1), -135.46 (1) ,-154.26 (1), -155.10 (1) -181.75(1), -183.44 (2), -211.18 (1), -212.43 (1), -212.87 (1), -217.74 (2), -218.51 (1), -220.16 (1), -235.30 (1), -242.37 (1), -245.86 (1)
$[N(C_4H_9)_4]_9H(\alpha\text{–}2\text{-}P_2W_{17}O_{61})$[e]	-93.61 (2), -112.19 (1), -123.73 (2), -156.43 (2), -174.86 (2), -177.76 (2), -180.87 (2), -183.40 (2), -189.34 (2)

a. See text for data collection parameters. Integrated intensities given in parentheses. Spectra measured in D_2O.b.measured as a Na^+ salt, (resonances similar to reference 13d). c. from reference 13 c, we obtained a similar spectrum. d.Li salt prepared by ion exchange chromatography at pH=5, see text. e. measured in DMSO/D_2O.

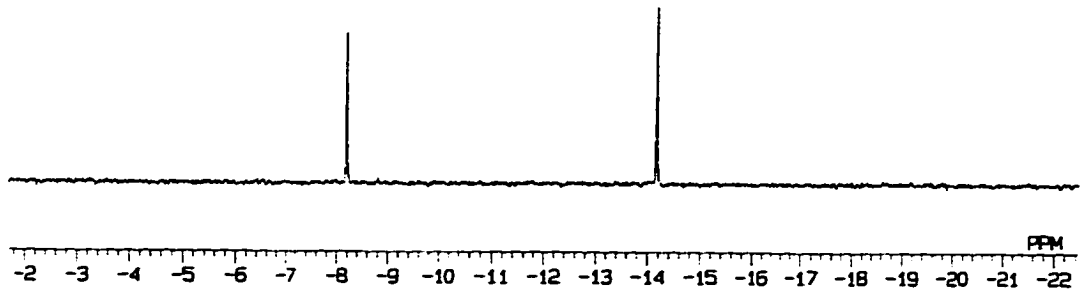
RESULTS AND DISCUSSION.

The elemental analysis, TGA data, mass spectrometry and ^{31}P and ^{183}W NMR data are consistent with the the $K_{17}[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ formulation. The crystal structure of the $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ shows that the Lu ion binds to the four oxygen of the two polyoxoanion unit in a square antiprismatic fashion. (Figure 4.2)

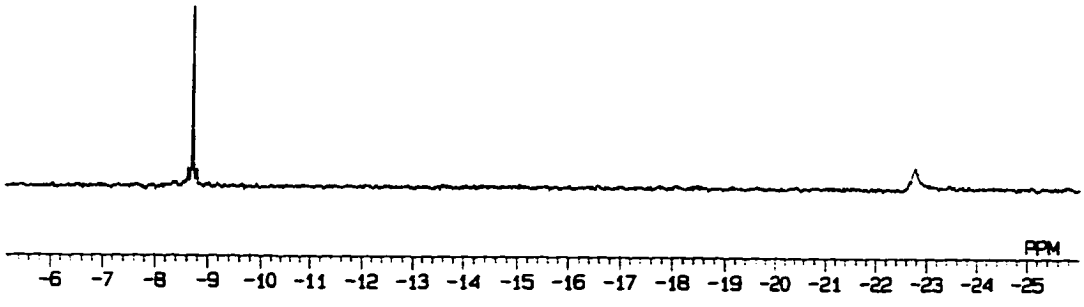
^{31}P NMR Spectroscopy

The ^{31}P NMR data (Figure 4.3, Table 4.2) show that the $K_{17}[\ \alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2\ ]$ family of compounds differ from the lacunary $(\alpha\text{-}2\text{-}P_2W_{17}O_{61})^{10-}$ starting material and, further, the complexes are > 99% isomerically pure. In general, preparations of metal complexes of lacunary α-1 and α-2 isomers of $[P_2W_{17}O_{61}]^{10-}$ by standard methods (base degradation of $(P_2W_{18}O_{62})^{6-}$) are accompanied by a significant proportion of the other isomer present as an impurity.[7] ^{31}P NMR is an extremely sensitive technique to determine isomeric purity of the α-1 and α-2 isomers as well as to ascertain any other phosphorus containing impurities.[7] (The α-1-isomer of the lacunary $[P_2W_{17}O_{61}]^{10-}$ [37] and transition metal[9,10] and lanthanide complexes[11,12] of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$, generally show chemical shifts of ca 9.5-10.5 ppm for P1 and 13-14 ppm for P2 in water. The α-2-isomers show the resonance for P1 between 7-8 ppm and the resonance for P2 at ca 14 ppm in water.) ^{31}P NMR

$K_{17}[\alpha\text{-}2\text{-}La(P_2W_{17}O_{61})_2]$



$K_{17}[\alpha\text{-}2\text{-}Yb(P_2W_{17}O_{61})_2]$



$K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$

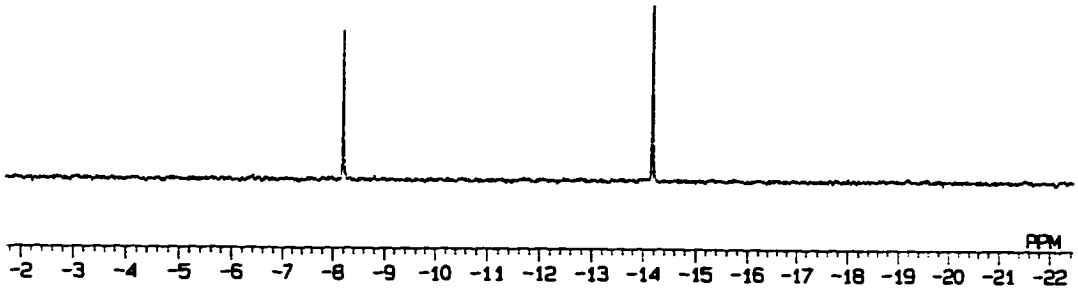


Fig. 4.3. ^{31}P NMR spectra of $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ complexes in D_2O.

data show that the potassium salts form the α-2 isomers with remarkably no evidence of isomerization. The ^{183}W NMR spectra, discussed below, corroborate these results.

NMR titration experiments performed under acidic conditions using ^{31}P NMR spectroscopy[13] have identified the 1:1 and 1:2 Ln: $[P_2W_{17}O_{61}]^{10-}$ complexes for the paramagnetic lanthanide ions, Eu,Tb,Dy and Tm. The titration experiments indicated that only the 1:2 La:$[P_2W_{17}O_{61}]^{10-}$ and the 1:1 Lu:$[P_2W_{17}O_{61}]^{10-}$ complexes were formed. The latter is in contrast to our work where we isolate the 1:2 Lutetium: [α-2 $P_2W_{17}O_{61}]^{10-}$ complex as a potassium salt (elemental analysis, TGA, mass spectrometry). In addition, crystallographic work confirms the 1:2 formulation for $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ (Figure 4.2.) Further, in titration experiments buffered in the pH range of 4-5, we observe the formation of both the 1:1 and 1:2 Ln: $[P_2W_{17}O_{61}]^{10-}$ (Ln=La, Eu, Lu) complexes by ^{31}P NMR spectroscopy as discussed in the following chapter.

Infrared spectroscopy data[13] (Table 4.4 and Figure 4.4) for the lanthanide $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ derivatives and the tetrabutylammonium salt of the lacunary species show similarity to the lacunary $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ species, consistent with the isostructural nature of the molecules. The lanthanide derivatives (potassium salts) and the tetrabutylammonium salt of the lacunary species show strong bands at ca 1084 cm^{-1} and ca 950 cm^{-1}, characteristic of the P-O and terminal W-O stretches.

Table 4.4. Infrared Spectroscopy Data, υ_{max}/cm^{-1}[a]

$K_{10}[\alpha\text{–}2\text{-}P_2W_{17}O_{61}]$[b]	1084 (s), 1022, 985 (s),940, 905, 880, 805, 740
$K_{17}[La(\alpha\text{–}2\text{-}P_2W_{17}O_{61})_2]$	1084.6 (s), 1025.9 (w), 943.6 (s), 890.7 (sh), 831.9 (s), 767.3 (s), 591.0 (w), 526.4 (w)
$K_{17}[Lu(\alpha\text{–}2\text{-}P_2W_{17}O_{61})_2]$	1084.6 (m), 1020.0 (w), 943.6 (s), 908.3 (sh), 831.9 (s), 773.2 (s), 732.1 (sh) , 591.0(w), 532.3 (w)
$[N(C_4H_9)_4]_9H(\alpha\text{–}2\text{-}P_2W_{17}O_{61})$	1084.6 (m), 949.5 (s), 914.2 (m), 814.3 (s), 779.0 (s), 732.0 (sh), 591.0 (w), 526.4 (w)

a. measured from KBr pellets. b. from reference 19.

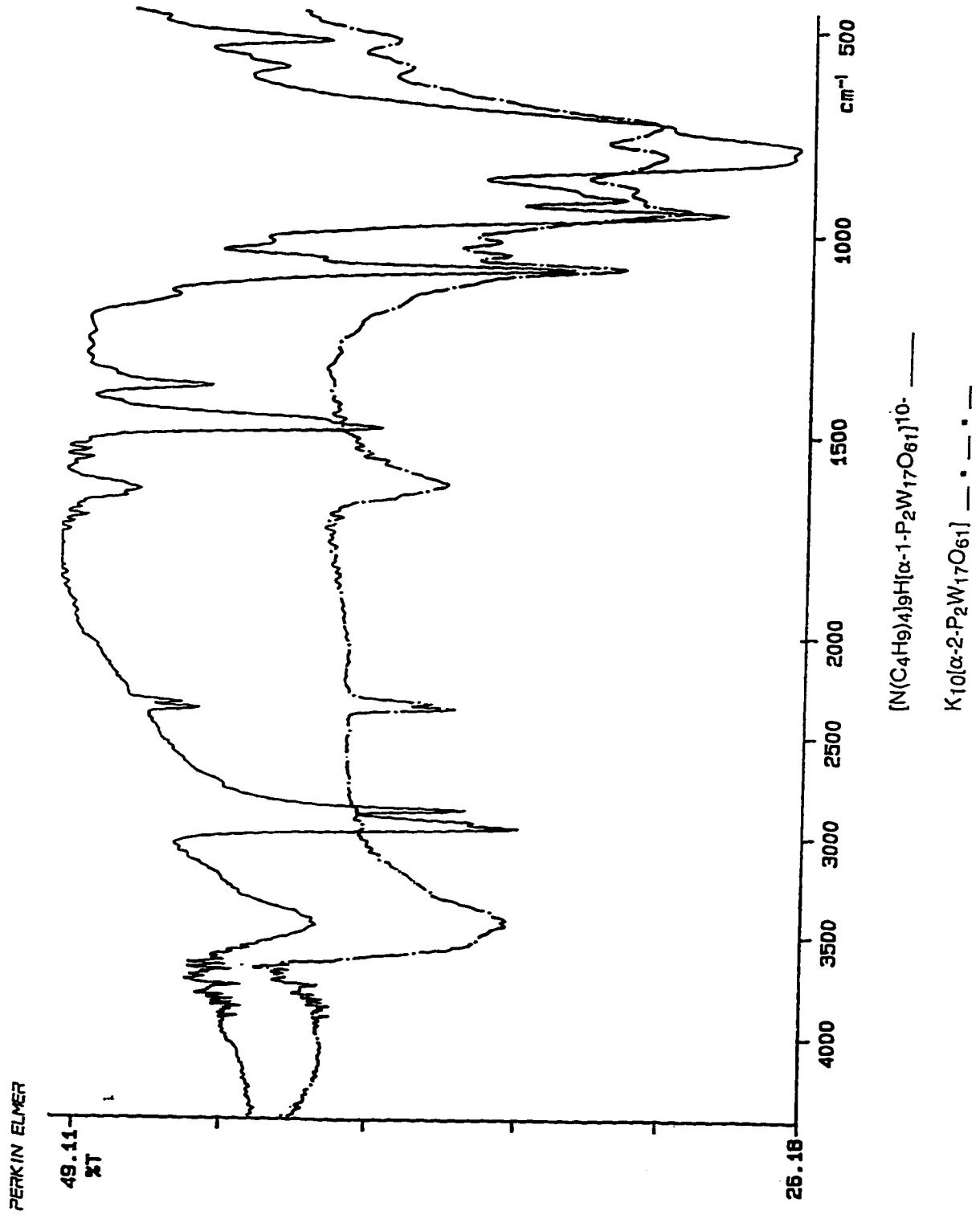


Fig. 4.4. IR spectra of the $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ and $K_{10}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})$.

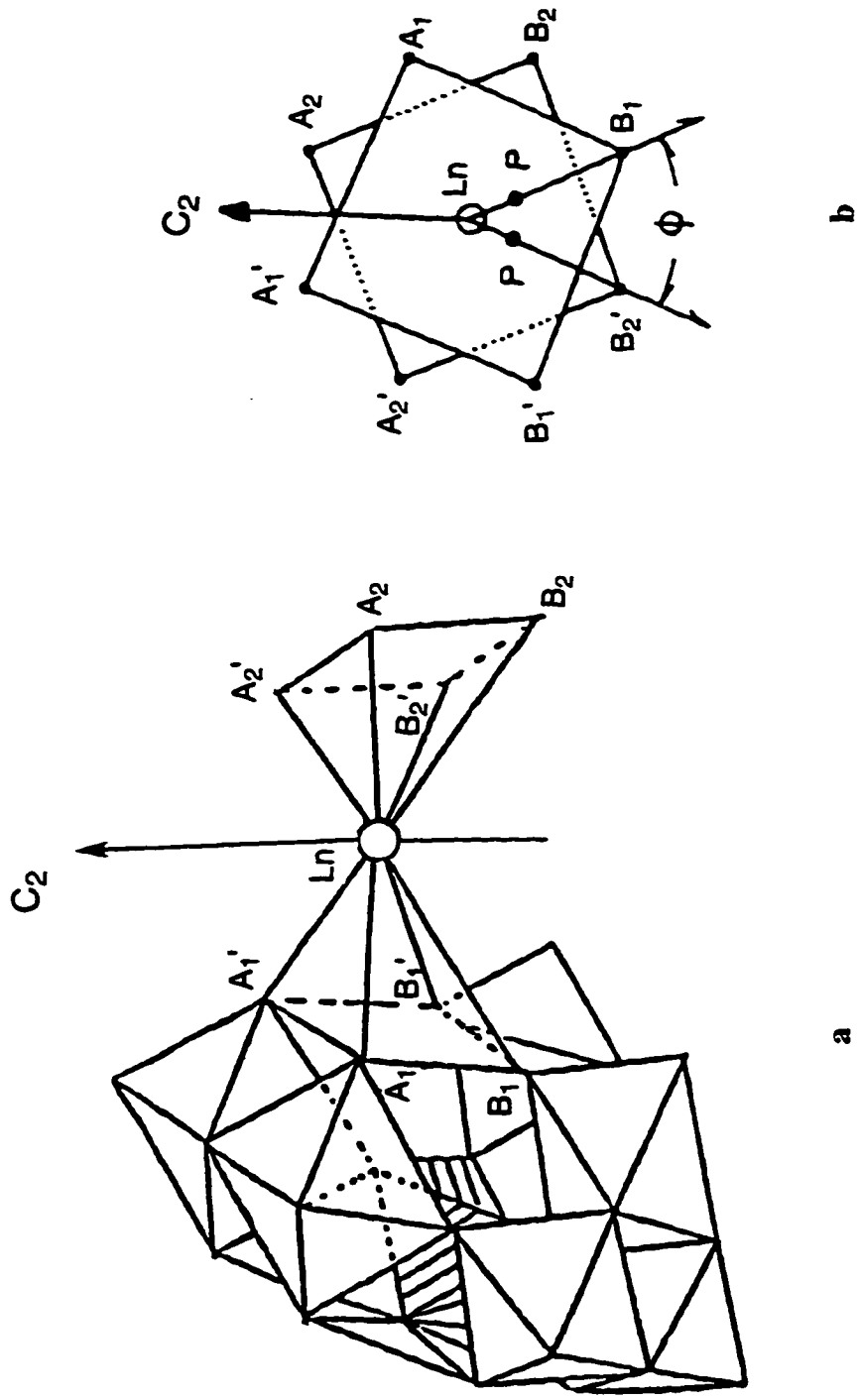
^{183}W NMR Spectroscopy

^{183}W NMR spectroscopy allows characterization of the solution structure of the molecules. ^{183}W NMR chemical shifts are given in Table 4.3.

In order to obtain a concentrated 0.2 M solution necessary for the 183W NMR measurement the K+ counterions need to be exchanged to Li^+, using ion exchange chromatography. For the $K_{17}[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ complex the use of buffered resin is very important. Otherwise the complex partially decomposes to the $(P_2W_{18}O_{62})^{6-}$ parent molecule. Figure 4.5 shows the ^{183}W NMR spectrum taken at 23°C for the $K_{17}[Ln(P_2W_{17}O_{61})_2]$ complexes . The spectrum of the lanthanum complex shows nine resonances (integration: 2:2:2:1:2:2:2:2:2). The lutetium analog, $[Lu(P_2W_{17}O_{61})_2]^{17-}$, as well as the ytterbium analog, at room temperature show 16 (integration:1:1:1:1:1:1:1:1:1:1:1:1:2:1:1:1), and 15 resonances (integration:1:1:1:1:1:2:1:1:1:2:1:1:1:1:1), respectively, representing 17 unique W atoms. The chemical shifts for these species are different from the lacunary $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species or the lanthanide derivatives of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ which also have 17 inequivalent tungsten atoms. [9,11] The ^{31}P NMR spectra show only two resonances for the two phosphorus atoms of each oxoanion unit, consistent with the equivalence of the two oxoanion halves of the molecule. The resonances each integrate for 1 tungsten. Scheme 4.1a represents $[Ln(P_2W_{17}O_{61})_2]^{17-}$, shown in Figure 4.1. The corners of the squares represent oxygen atoms forming the defect site in the lacunary (α-2-

$P_2W_{17}O_{61})^{10-}$ oxoanions 1 and 2. Oxygen atoms A and A' belong to polyhedra which are edge shared and oxygen atoms B and B' belong to polyhedra which are corner shared. Scheme 1a represents the molecule where the oxygen atoms are eclipsed, $\phi=0^o$, the molecule has C_{2v} symmetry, the two oxoanion lobes are in a "syn" position. The molecule has C_{2h} symmetry when $\phi=180^o$; this situation corresponds to the conformer where the two oxoanion lobes are disposed in an "anti" position. A recent crystal structure of $[O\{Ru^{IV}Cl(\alpha\text{-}2P_2W_{17}O_{61})\}_2]^{16-}$ shows the two $(\alpha\text{-}2P_2W_{17}O_{61})^{10-}$ lacunary polyoxoanions in the "anti" eclipsed conformation.[14] In both of these limiting cases, a nine line spectrum is observed. For La, nine resonances are observed in the ratio 2:2:2:1:2:2:2:2:2, consistent with C_{2v} or C_{2h} symmetry. When $0<\phi<180^o$, (Scheme 4.1b) the resulting structures have a two fold rotation axes, but no symmetry planes, therefore the 17 tungsten atoms in each oxoanion half are nonequivalent , and

Scheme 4.1. **a)** part of $[Lu(P_2W_{17}O_{61})_2]^{17-}$ **b)** side view of the complex upon rotation by ϕ.



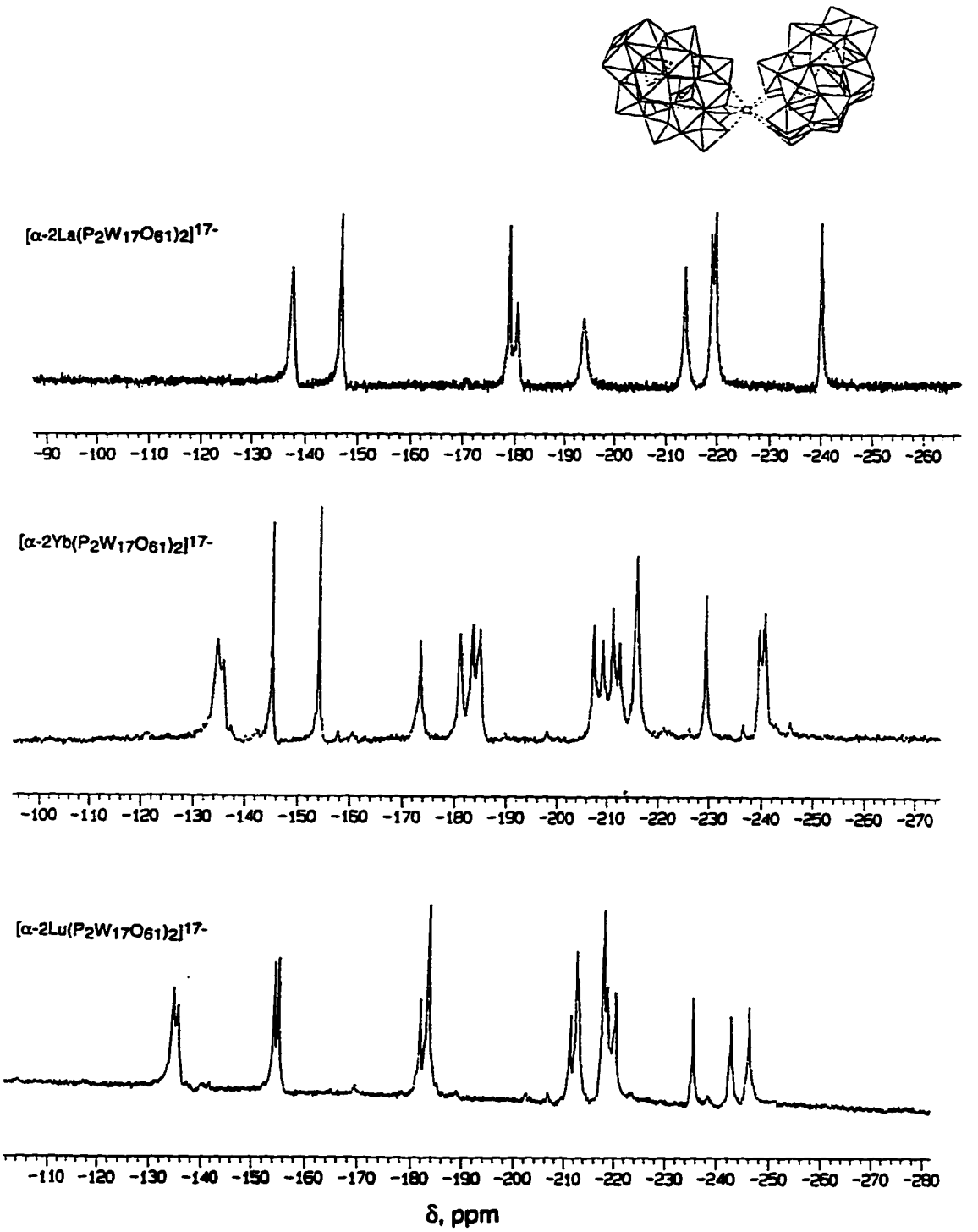


Figure 4.5. ^{183}W NMR spectra of $Li_{17}[Ln(P_2W_{17}O_{61})_2]$complexes.

each lacunary $(\alpha\text{-}2P_2W_{17}O_{61})^{10-}$ half is related to the other by a two fold rotation. Therefore seventeen resonances are expected in the ^{183}W NMR spectrum. The lanthanide ion is in square antiprismatic coordination geometry as confirmed by X-ray crystallography.

Figure 4.6 shows the effect of increasing the temperature of the $[Lu(P2W_{17}O_{61})_2\ ]^{17-}$ solution. At elevated temperatures, a broadening and coalescence of peaks is observed. Reducing the temperature to 25°C results in the original sixteen line pattern. The tungsten NMR data clearly show that as the ionic radius decreases, from lanthanum to lutetium, the solution structures become less symmetrical at room temperature. A dynamic effect may be occurring wherein the lacunary $(\alpha\text{-}2P_2W_{17}O_{61})^{10-}$ oxoanion halves are rotating; the nine line pattern represents a fast rotation on the NMR timescale and the seventeen line pattern represents freezing out the structure where the lanthanide ion is in square antiprismatic coordination geometry. The ^{31}P NMR remains the same at high temperature, there is no evidence of decomposition to the lacunary $[(\alpha\text{-}2P_2W_{17}O_{61})]^{10-}$ and 1:1 $Lu:[(\alpha\text{-}2P_2W_{17}O_{61})]^{10-}$ species formation. We also noticed that, for $[Lu(\alpha\text{-}2P_2W_{17}O_{61})_2]^{17-}$, as the pH is lowered from pH=3 to 0.3, the ^{183}W NMR peaks broaden and coalesce until, at pH=0.3, the ^{183}W NMR spectrum (Figure 4.7) looks similar to the spectrum for $[Lu(\alpha\text{-}2P_2W_{17}O_{61})_2]^{17-}$ obtained under neutral pH at 94°C. The ^{31}P spectrum broadens slightly but does not shift significantly at the lower pH values. No

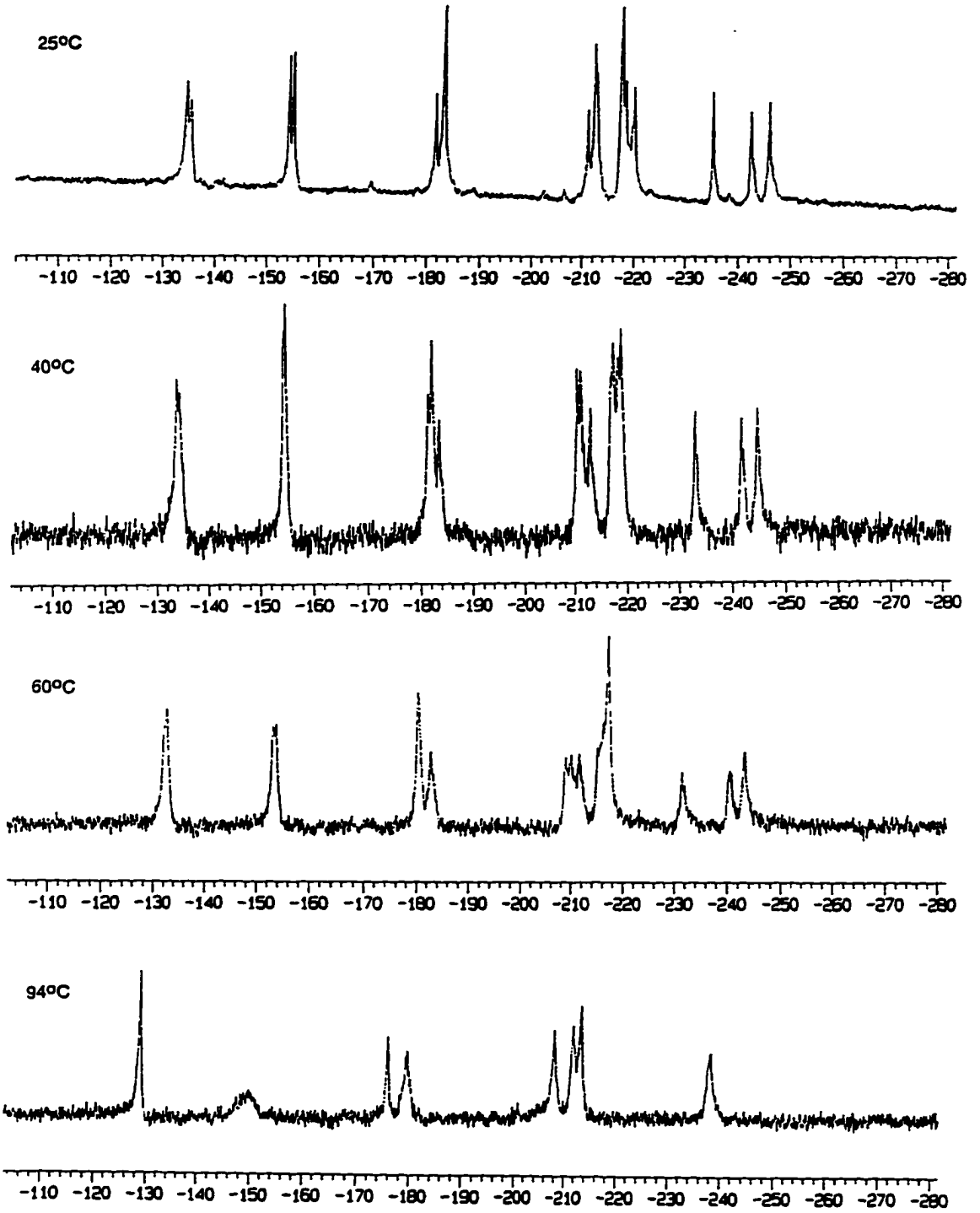


Fig. 4.6. Variable temperature ^{183}W NMR spectra of $Li_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$.

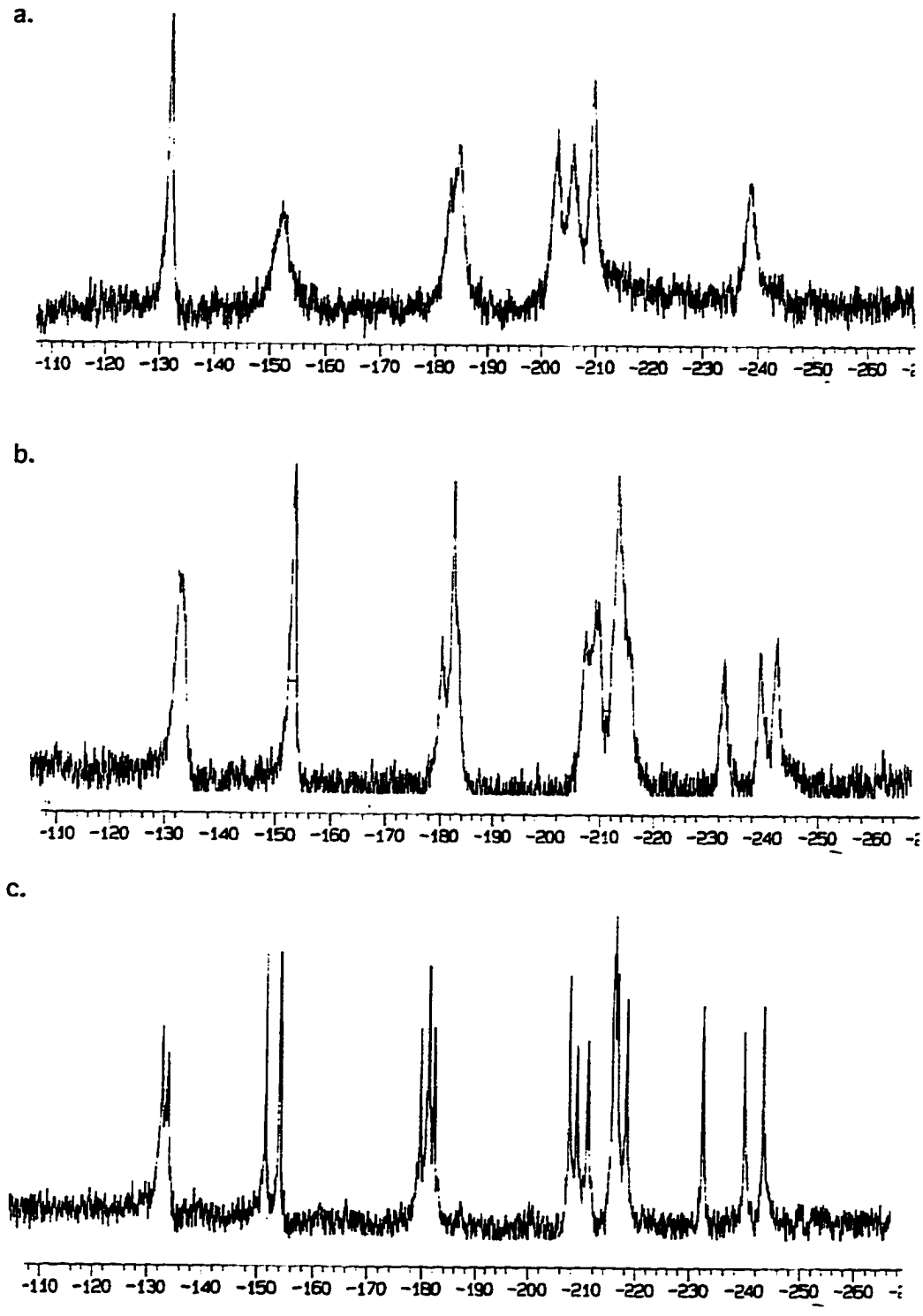


Figure 4.7. Low pH study of the $Li_{17}[Lu(P_2W_{17}O_{61})_2]$

a) pH=0.3, b)pH=2.4, c)pH=3.8

evidence of decomposition and formation of $(P_2W_{18}O_{62})^{6-}$ is observed in ^{183}W or ^{31}P NMR spectroscopy. It appears that at low pH, a similar dynamic process to that at high temperature under neutral conditions may be occurring in the $[Lu(\alpha\text{-}2P_2W_{17}O_{61})_2]^{17-}$ species. It is very likely at low pH, that the most basicoxygen atoms bonded to the Lu^{3+} ion,[δ,15] will be protonated and the Lu-O bonds weakened, facilitating a dynamic process. The mechanism of the dynamic process is difficult to ascertain without further experimentation. The effects observed may be due to rotation or twisting of the lacunary oxoanion halves or Ln-O bond breaking and recombination in different orientations, a fast process on the NMR timescale when facilitated by protonation of the basic oxygen atoms or high temperature.[16]

Characterization of the $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$.

The ^{183}W NMR data and ^{31}P NMR data as well as infrared spectroscopy indicate the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ structural integrity is maintained in the tetrabutylammonium salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$. Infrared spectroscopy data[8] (Table 4.4 and Figure 4.4) confirm the lacunary α-2-$[P_2W_{17}O_{61}]$ structure. Elemental analysis is often unreliable for polyoxoanions and, in this case, we observe high W% and low C%. ^{31}P and ^{183}W NMR spectroscopy are better

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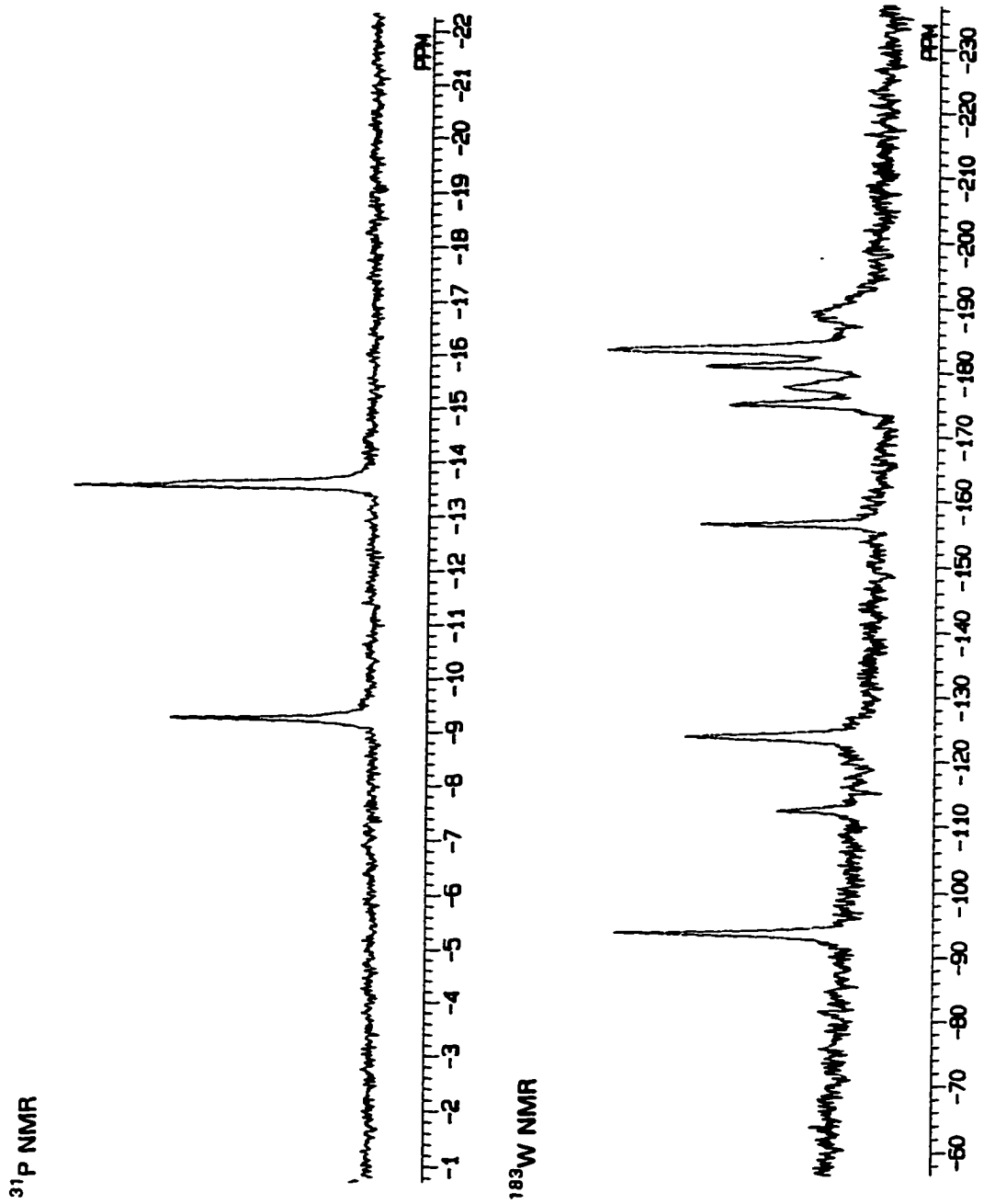
δ Replacement of the W^{6+} in the parent $[\alpha\text{-}2P_2W_{17}O_{62}]^{6-}$ with a lower-valent metal ion increases the basicity of the bridging oxygen atoms adjacent to the lower-valent metal ion. For a discussion of this phenomenon see ref. 15.

Fig. 4.8. The ^{31}P NMR and ^{183}W NMR spectra of $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$



indicators of the purity of molecules.[7] Using these techniques, we observe no evidence of $(\alpha\text{-}P_2W_{18}O_{61})^{6-}$. Figure 4.8 shows the ^{31}P and ^{183}W NMR spectra, taken in DMSO/D_2O (1.5:1), for the tetrabutylammonium salt, $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}(P_2W_{17}O_{61})]$ (insoluble in D_2O). The ^{183}W NMR spectrum taken in DMSO/H_2O mixture shows nine resonances in the ratio 2:1:2:2:2:2:2:2:2, consistent with C_s symmetry and thus, the α-2 isomer. Two resonances are observed in the ^{31}P NMR spectrum in 1.5:1 DMSO: D_2O and two resonances are observed in D_2O containing a stoichiometric amount of $LiClO_4$ to increase the solubility of the anion. The tetrabutylammonium cations

are partially replaced with Li^+ in this metathesis reaction.[8] ^{31}P NMR spectra, taken in pure organic solvents result in additional small peaks due to small amounts of protonated species. This phenomenon has been observed previously.[17] For example, a small peak at ca 11 ppm is observed for the tetrabutylammonium salt of $[\alpha\text{–}2\ P_2W_{17}O_{61}]^{10-}$ taken in pure organic solvents (Table 2). Addition of water and $[N(C_4H_9)_4]OH$ to the solvent allows exchange of the protons and the observation of only two resonances.[17] The tetrabutylammonium salt of $[\alpha\text{–}2\ P_2W_{17}O_{61}]^{10-}$ is in >98% isomeric purity; there is no evidence for the α1- isomer. We did not observe the formation of the tetrabutylammonium salt of $(\alpha\text{-}P_2W_{18}O_{61})^{6-}$ in this reaction by either ^{31}P or ^{183}W NMR spectroscopy. To avoid formation of $(\alpha\text{-}P_2W_{18}O_{61})^{6-}$, the pH must be maintained at 5-7 during the metathesis reaction. Reported attempts at the

preparation of the tetrabutylammonium salt of $[\alpha\text{–}2\ P_2W_{17}O_{61}]^{10-}$ resulted in no precipitation in the metathesis reaction or formation of $(\alpha\text{-}P_2W_{18}O_{61})^{6-}$, upon acidification[18]. We find that following a modification of a metathesis method developed by Finke and coworkers[7,8a], maintaining the pH in the range 5.5-7 is important in avoiding $(\alpha\text{-}P_2W_{18}O_{61})^{6-}$. Also, extraction with CH_2Cl_2 is neccessary as a precipitate does not form upon addition of tetrabutylammonium bromide to $[\alpha\text{–}2\ P_2W_{17}O_{61}]^{10-}$.

CONCLUSION.

Lanthanide complexes of polyoxoanions have been prepared and characterized in aqueous solution by multinuclear NMR spectroscopy. The tetrabutylammonium salt of the lacunary $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ has been prepared and characterized by ^{31}P and ^{183}W NMR spectroscopy.

The $[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]^{17-}$ family of complexes shows nine line patterns in the ^{183}W NMR spectroscopy at room temperature for the lanthanum derivative, consistent with a symmetrical structure (C_{2v} or C_{2h} symmetry), and seventeen line patterns for ytterbium and lutetium analogs, suggesting that the heavier lanthanide ions, with smaller ionic radii, have a lower symmetry in solution. High temperature ^{183}W NMR experiments on the $[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]^{17-}$ compounds show reversible broadening and coalescence of the resonances, presumably due to a dynamic effect, possibly rotation of the

oxoanion ligands. Broadening and coalescence is observed at low pH for the [α-2-Lu($P_2W_{17}O_{61}$)2]$^{17-}$ compound, indicating that protonation of basic oxygen atoms may facilitate the dynamic effect.

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Chapter 5

Stoichiometric Studies of Lanthanide Complexes of $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$.

INTRODUCTION

The 1:2 lanthanide : oxoanion stoichiometry has been presumed for most studies involving lanthanide (Ln) or actinide (An) complexes of the monovacant Wells-Dawson anions. The crystal structure of the lanthanide Wells-Dawson derivative, $[\alpha\text{-}2\text{-}Ce(P_2W_{17}O_{61})_2]^{16-}$ (tungsten framework found only) [1]. and the $[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]^{17-}$ discussed in the previous chapter show the 1:2 Ln : α-2- heteropolyanion formulation. Other studies of the lanthanide or actinide $[P_2W_{17}O_{61}]^{10-}$ complexes are consistent with 1:2 formulation as well. For example, the preparation and characterization of the $[U(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ species by elemental analysis, polarography, and spectroscopy has been reported [2]. (In competition studies, Th(IV) replaces the Ln(III) from the $[Ln(SiW_{11}O_{39})_2]^{4-}$ and $[Ln(P_2W_{17}O_{61})_2]^{17-}$ (the isomeric purity not determined) structures, leading to the conclusion that the An(IV) species are more stable than the Ln (III) species.) The 1:1 complexes were observed by spectrophotometric titration but not isolated. Recently, spectrophotometric titrations and electrochemical data suggest the existence of $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ and the 1:2 complex, $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ [3,4]. In a recent study, the 1:1 and 1:2 Ln: $(\alpha\text{-}2\text{-}P_2W_{17}O_{61})$ species have been observed in ^{31}P NMR titration experiments for a variety of lanthanide ions[5]. From the solution titration data, it appears that the early lanthanide ions form exclusively 1:2 complexes, the

middle lanthanide ions form both 1:1 and 1:2 complexes and the later lanthanides form exclusively 1:1 complexes in aqueous solution.

In contrast to the study described above [5], we isolated and characterized by elemental analysis, TGA, mass spectrometry, X-ray crystallography (Lu complex), and multinuclear NMR spectroscopy the 1:2 Ln: $[\alpha\text{-}2\text{-}\ P_2W_{17}O_{61}]^{10-}$ species [6]. Since we observed conflicts between work reported in literature[5] and our own work [6], we investigated the potential for forming both 1:1 and 1:2 Ln: $[\alpha\text{-}2\text{-}\ (P_2W_{17}O_{61})\ ]$ complexes for representative lanthanides under the conditions generally used for the preparation of metal complexes of this isomer. The formation and stability properties of 1:1 Ln: $[\alpha\text{-}2\text{-}(P_2W_{17}O_{61})\ ]$ may augur well for the preparation of 1:1 complexes as synthetic targets for catalysis, medicine and environmental applications. This chapter presents the solution titration data in pH range of 5-6 using ^{31}P NMR spectroscopy to monitor speciation of the Ln: $[\alpha\text{-}2\text{-}\ (P_2W_{17}O_{61})\ ]$ complexes to confirm the stoichiometries. Also presented are our observations on the unusual and unexpected isomerization of the $[\alpha\text{-}2\text{-}\ (P_2W_{17}O_{61})\ ]^{10-}$ lacunary species to the $[\alpha\text{-}1\text{-}\ (P_2W_{17}O_{61})\ ]^{10-}$ isomer in the presence of Li^+ ion at pH=4.7.

EXPERIMENTAL

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 "Wells-Dawson" ion, $(P_2W_{18}O_{62})^{6-}$ as the potassium salt, was prepared using literature methods[8]. The α-2 lacunary isomer, $K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$, was prepared following the method of Finke [9]. A standard solution of 0.0993 M EDTA was purchased from Fisher. The aqueous solutions of the lanthanide metals were standardized by complexometric titration with EDTA using xylenol orange as an indicator [10]. An aqueous solution of $CoCl_2$ was standardized with EDTA, buffered at pH=5 with sodium acetate buffer, and monitored by absorption spectroscopy [10]. The potassium salt of $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ was ion exchanged to the more soluble Li^+ salt or Na^+ salt using ion exchange at pH=4.7 or 5.5, respectively, as described previously. The concentration of aqueous solutions of the sodium or lithium salts of $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ were determined by titration with $CoCl_2$, as described below. To convert the potassium salts to lithium or sodium salts for increased solubility of the $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ species in aqueous solution for monitoring by ^{31}P NMR spectroscopy, ion exchange chromatography using Dowex AG50W-X2 in the Li^+ or Na^+ form was used. The resin, originally in the H^+ form, was converted to the Li^+ or Na^+ forms 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 hours, followed by washing with 2 bed volumes of water. The same procedure was used to convert the resin to the sodium form, with the exception that sodium acetate at pH=5.5 was used.

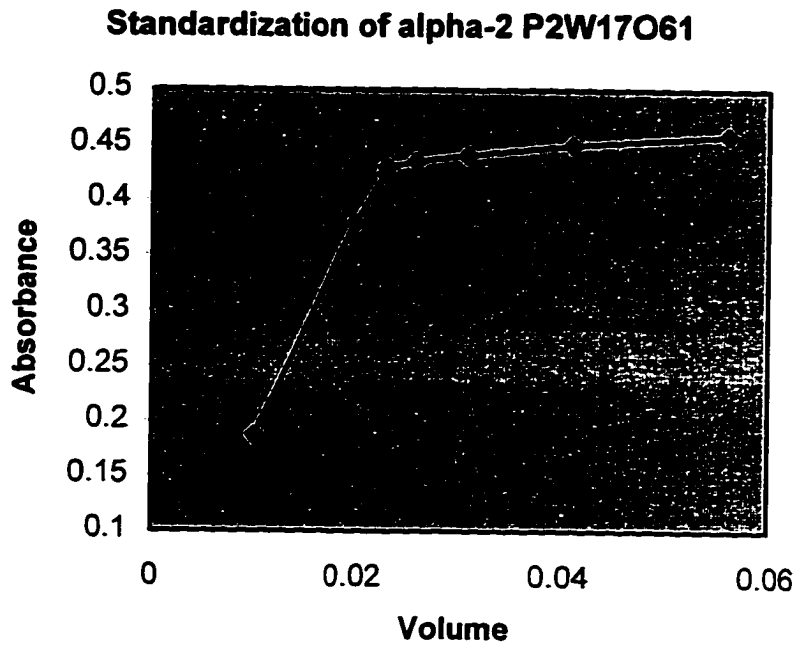
Standardization of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ solutions. The general procedure to obtain 20 mL of 0.022-0.025M solution of the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand follows. $K_{10}[\alpha\text{-}2\ P_2W_{17}O_{61}]$ (2.46g) was ion exchanged to the lithium or sodium salts at pH =4.7 and 5.5, respectively using the procedure above. One bed volume of water was used to ensure that all of the compound eluted. The effluent was rotary evaporated to a solid. The solid was dissolved in D_2O (7mL) and enough buffer to prepare 20 mL of solution. The buffers were lithium acetate buffer (ca. 0.5M, pH=4.7) for europium and sodium acetate buffer (ca. 0.5M, pH=5.5) for lutetium, lanthanum and yttrium. To an aliquot of 1 mL of this solution $CoCl_2$ (0.2979M) was added in 5 or 10 μL increments and the absorbance was recorded at 544 nm. The absorbance plotted against the volume of $CoCl_2$ added gives a sharp breakpoint when all the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ reacted with the Co^{2+} in 1:1 stoichiometric ratio. At least three titrations were run for each standardization; the agreement was within 1%. Figure 5.1 shows typical titration for one standardization. The solution is stored in the freezer to prevent isomerization to the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer.

Procedure for titration of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ monitored by ^{31}P NMR Spectroscopy. Titration of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$.

Generally, 0.5 mL of the standardized buffered $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ solution (measured with volumetric pipet) is placed into a 5 mm NMR tube. (The concentrations are in the range of 0.022-0.025 M buffered with lithium acetate for Eu and sodium acetate for La, Y, Lu; the solutions contain 30% D_2O) The ^{31}P NMR spectrum is recorded. An aliquot of 25-30 μL of the standardized $LnCl_3$ solution (concentration is always ca. 0.1M, Table 5.1) is added to achieve

Fig. 5.1. Standardization of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ with $CoCl_2$ at pH = 5.

mL of Co	absorbance
0.01	0.1877
0.02	0.3787
0.023	0.423
0.0231	0.4295
0.026	0.4347
0.031	0.4405
0.041	0.4496
0.056	0.459



4:1, 4:2, 4:3, 4:4 and 4:6 [α-2-$P_2W_{17}O_{61}$]: Ln ratios. The resulting solution is shaken well in the NMR tube and the ^{31}P NMR spectrum is recorded immediately upon mixing. The titration data for La, Eu, Y and Lu are shown in Figures 5.2, 5.3, 5.4 and 5.5, respectively. The data including concentrations of ligand, lanthanide salt, relative molar ratios and integrations are tabulated in Tables 5.1 and 5.2.

Preparation of K_7[α-2-$LuP_2W_{17}O_{61}$]

5g (1.017 mmol) of α-2 $K_{10}[P_2W_{17}O_{61}]$ is dissolved in 50 mL 0.5 M sodium acetate buffer at pH 5.5, at 70°C, to form a clear solution. 1.2g (3.08 mmol) $LuCl_3$ is dissolved in a minimum amount of water and added it dropwise to the K_{10}[α-2-$P_2W_{17}O_{61}$] solution while stirring. 5g of KCl is added to the reaction mixture while solution stays clear. The resulting solution is cooled in the refrigerator. After a few hours a white precipitate forms, which usually contains the impurity of the 1:2 sandwich complex. The precipitate is dissolved in 50 mL sodium acetate buffer at pH 5.5 at 70°C, and 1.5 mL 1M $LuCl_3$ is added, followed by the addition of 3g of KCl. The clear solution is placed into the refrigerator. The resulting white precipitate is collected and recrystallized twice from hot water at 70 °C.

Preparation of K_7[α-2-$EuP_2W_{17}O_{61}$]

10g (2.035 mmol) of α-2 $K_{10}[P_2W_{17}O_{61}]$ is dissolved in 70 mL 0.5 M lithium acetate buffer at pH 4.7, at 70°C, to form a clear solution. 2.24g (6.1 mmol) $EuCl_3$ is dissolved in a minimum amount of water and added it dropwise to the α-2 $K_{10}[P_2W_{17}O_{61}]$ solution while stirring. The resulting gray, cloudy solution is

cooled in the refrigerator. After a few hours a white precipitate formed. ^{31}P NMR shows a clean product, which is recrystallized from hot water twice.

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: spectral width: 10,000Hz; acquisition time: 0.8 s; pulse delay: 1s; pulse width : 15μsec (50 degree tip angle). From 200 to 500 scans were required. For ^{183}W spectra, typical conditions included: spectral width: 10,000Hz; acquisition time: 1.6 s; pulse delay: 0.5s; pulse width: 50 μsec (45 degree tip angle). From 1,000 to 30,000 scans were acquired. For all spectra, the temperature was controlled to ±0.2 degree. ^{31}P spectra were referenced to a H_3PO_4 standard in D_2O, which has 0.67 ppm upfield chemical shift relative to 85% H_3PO_4. ^{183}W spectra were referenced to 2.0 M Na_2WO_4. For ^{31}P and ^{183}W chemical shifts, the convention used is that the more negative chemical shifts denote upfield resonances.

Fig. 5.2. ^{31}P NMR titration of α-2 $Na_{10}P_2W_{17}O_{61}$ (L) with La^{3+} in sodium acetate buffer at pH =5.5. ratio of La:L a) 0, b)1:4, c) 1:2, d) 3:4, e) 5:4.

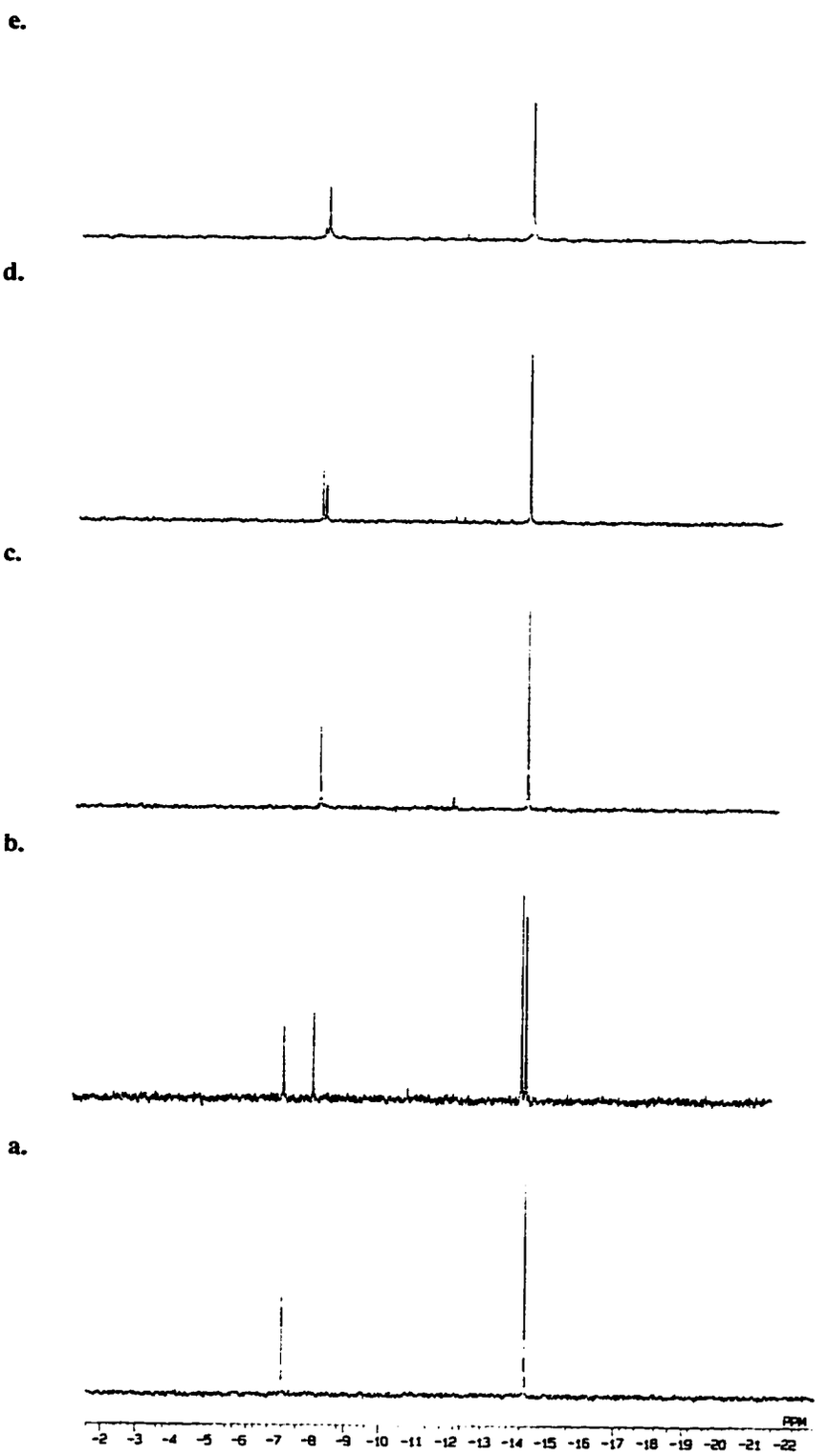


Fig. 5.3. ^{31}P NMR titration of α–2 $Li_{10}P_2W_{17}O_{61}$ (L) with $EuCl_3$ at pH 4.7, ratic of Eu:L a) 0, b)1:2, c) 3:4, d) 1:1, e) 6:4

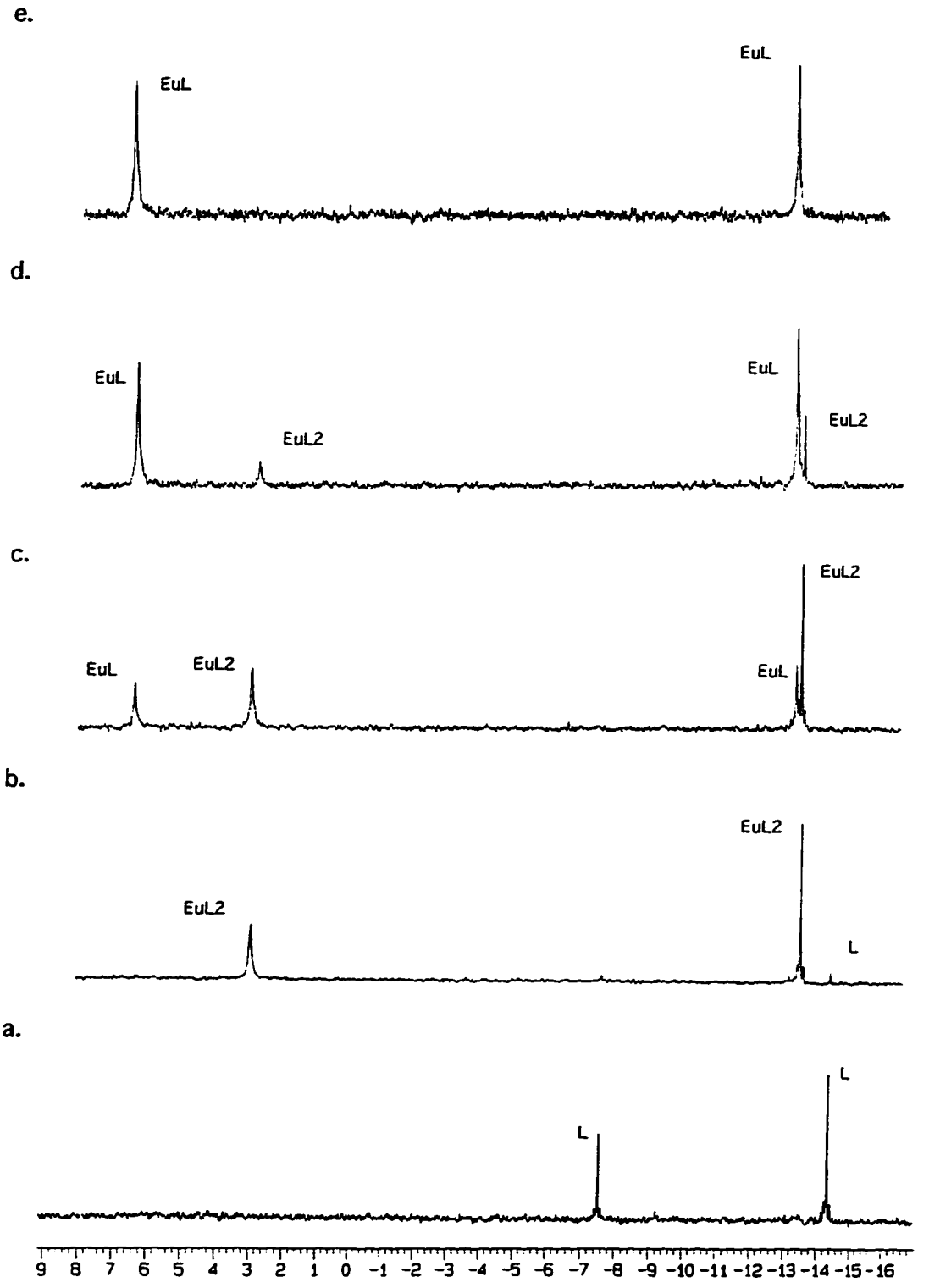


Fig. 5.4. ^{31}P NMR Titration of α-2 $Na_{10}P_2W_{17}O_{61}$ (L) with YCl_3 at pH 5.5. Ratio of Y:L a) 0, b)1:2, c) 3:4, d) 1:1, e) 6:4.

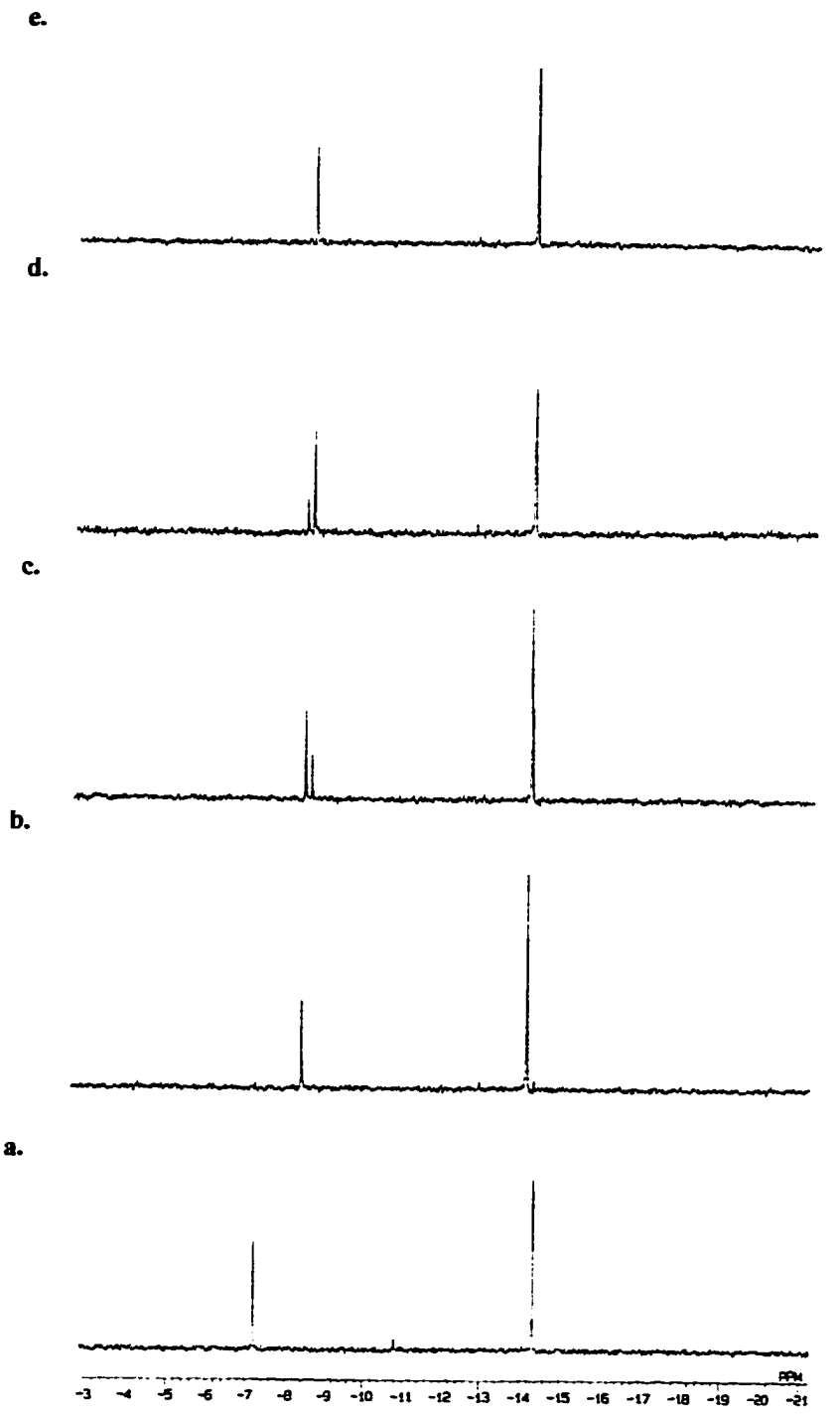


Fig. 5.5. ^{31}P NMR titration of α-2 $Na_{10}(P_2W_{17}O_{61})$ with $LuCl_3$ at pH 5.5. ratio of Eu:L a) 0, b)1:4, c) 1:2, d) 3:4, e) 1:1.

L= $(P_2W_{17}O_{61})^{10-}$

Lu 1:1 = $[LuP_2W_{17}O_{61}]^{7-}$

Lu 1:2 = $[Lu(P_2W_{17}O_{61})_2]^{17-}$

Fig. 5.5.

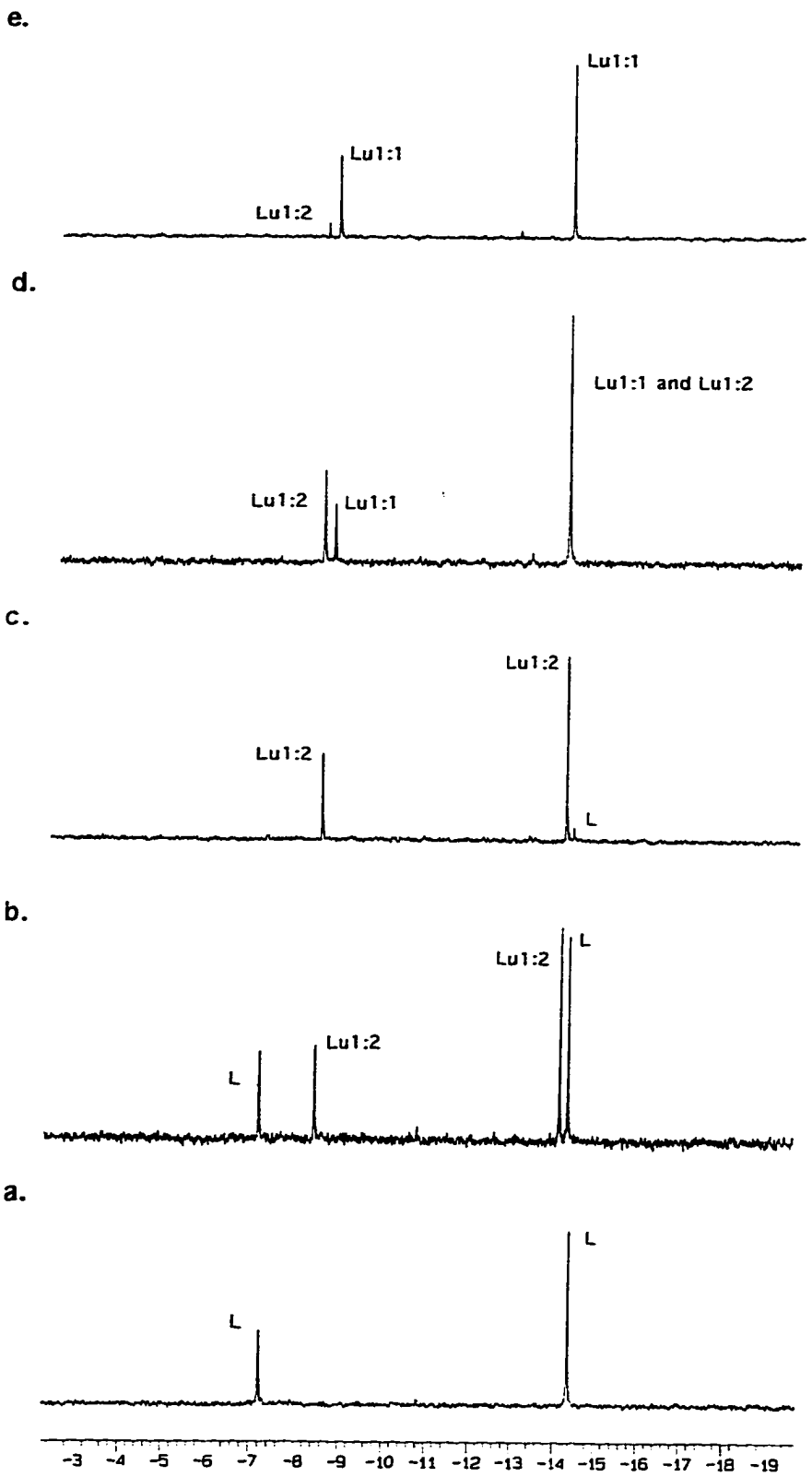


Table 5.1. Titration conditions of $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ solution.

Ln	conc. $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10}$	Counter ion	pH	conc. Ln^{3+}
Lu	0.02384M	Na^+	5.5	0.10212M
La	0.02384M	Na^+	5.5	0.09118M
Eu	0.022919M	Li^+	4.7	0.10025M
Y	0.02384M	Na^+	5.5	0.10114M

Table 5.2. Integration for P 1(low field) resonance of the $(\alpha\text{–}2\ P_2W_{17}O_{61})^{10-}$ and Ln complexes. L= $[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$ Ln=Lanthanide

Ln	$[\alpha\text{-}2\ P_2W_{17}O_{61}]^{10-}$: Ln	$P1_L$	$P1_{LnL2}$	$P1_{LnL}$
La^{3+}	4:1	1	1.05	0.00
	4:2	0	1.00	0.00
	4:3	0	1.00	0.65
	4:4	0	0.11	1.00
Eu^{3+}	4:1	0.53	1.00	0.00
	4:2	0.00	1.00	0.00
	4:3	0.00	1.41	1.00
	4:4	0.00	0.21	1.00
Lu^{3+}	4:1	1	1.03	0.00
	4:2	0	1.00	0.00
	4:3	0	1.00	0.54
	4:4	0	0.16	1.00
Y^{3+}	4:1	1	0.92	0.00
	4:2	0	1.00	0.00
	4:3	0	1.00	0.38
	4:4	0	0.30	1.00

RESULTS AND DISCUSSION

Titration Data. The isolation and characterization of the 1:2 Ln: [α-2-$P_2W_{17}O_{61}]^{10-}$ molecules by elemental analysis, TGA, as well as multinuclear NMR spectroscopy was discussed in the previous chapter[6]. Also the crystal structure of the $K_{17}[\alpha$–2-Lu$(P_2W_{17}O_{61})_2]$ discussed in Chapter 4 shows the 1:2 Ln: [α-2-$P_2W_{17}O_{61}]^{10-}$ stoichiometry. From that work, we established the ^{31}P chemical shifts of the 1:2 Ln: [α-2-$P_2W_{17}O_{61}]^{10-}$ complexes.[6] These are given in Table 5.3 for comparison with chemical shifts for the new species. P1 refers to the resonance attributed to the P atom closer to the site of substitution (or defect) and P2 refers to the P atom furthest from the site of substitution (or defect). The α-2-isomers generally show the resonance for P1 between 7-8 ppm and the resonance for P2 at ca 14 ppm in water. (The resonances for the α-1-isomers are generally quite different, for example P1 is found between 9-10 ppm and P2 at ca 13-14 ppm in water[8]).

Figures 5.2, 5.3, 5.4 and 5.5 show ^{31}P NMR titration data wherein the $LnCl_3$ is added to the ligand. Table 5.1 presents the actual conditions for each experiment. At the start , the pure lacunary species is present. As $LnCl_3$ is added to the [α-2-$P_2W_{17}O_{61}]^{10-}$ solution, the lacunary species decreases and one complex is observed at 4:2 ratio of [α-2-$P_2W_{17}O_{61}]^{10-}$: Ln. The chemical shifts of this complex correspond to those of the previously characterized "sandwich " complex [Ln (α-2-$P_2W_{17}O_{61})_2]^{17-}$. As the concentration of Ln is increased to [α-2-$P_2W_{17}O_{61}]^{10-}$:Ln 4:3, another set of peaks grows in the ^{31}P

Table 5.3. ^{31}P NMR chemical shifts (ppm) for 1:1 and 2:1 Ligand:Ln complexes:

Ln	[L]:[Ln]=1		[L]:[Ln]=2	
	P_1	P_2	P_1	P_2
Lu	-8.70	-14.09	-8.39	-14.19
La	-8.09	-14.25	-8.19	-14.23
Y	-8.35	-14.16	-8.50	-14.18
Eu	3.06	-13.40	6.65	-13.10

L= Li_{10} [α-2 $P_2W_{17}O_{61}$] in 0.5 lithium acetate buffer at pH 4.7 for Eu
L=$Na_{10}(P_2W_{17}O_{61})$ in 0.5 M sodium acetate buffer at pH=5.5, for La, Lu, Y.
Ln=lanthanide

NMR spectrum and the intensity of this set of peaks increases as the Ln concentration is increased. The set of peaks corresponding to [Ln (α-2-$P_2W_{17}O_{61}$)$_2$]$^{17-}$ complex decreases concomitantly. The peaks corresponding to the [Ln (α-2-$P_2W_{17}O_{61}$)$_2$]$^{17-}$ complex disappear when the [α-2-$P_2W_{17}O_{61}$]:Ln ratio is approximately 1-1.25. Increasing the [α-2-$P_2W_{17}O_{61}$]:Ln ratio to 4:6 or larger amounts of Ln does not change the spectrum. The observation of the second set of peaks as the Ln concentration is increased to approach a 1:1 [α-2-$P_2W_{17}O_{61}$]:Ln ratio is consistent with the formation of the 1:1 [α-2-$P_2W_{17}O_{61}$]:Ln complex.

For Lutetium, we performed the reverse titration, titrating the [α-2-$P_2W_{17}O_{61}$] species into a $LuCl_3$ solution. We observed immediate formation of the 1:1 species. When the [α-2-$P_2W_{17}O_{61}$]:Ln ratio was 2:1, we observed formation of the [Ln (α-2-$P_2W_{17}O_{61}$)$_2$]$^{17-}$ complex. Upon addition of excess [α-2-$P_2W_{17}O_{61}$] so that the [α-2-$P_2W_{17}O_{61}$]:Ln ratio was greater than 2:1, a set of peaks corresponding to the lacunary species grew in along with the peaks corresponding to the [Ln(α-2-$P_2W_{17}O_{61}$)$_2$] species. The chemical shifts are identical to the species seen in the first titration.

It appears that for the lanthanide ions employed in this study, two species are formed in acetate buffer in the pH range of 4.7-5.5. One set of peaks in the ^{31}P NMR data corresponds to the 1:2 Ln: [α2-$P_2W_{17}O_{61}$]$^{10-}$ species, which we and others have characterized in solid state and in solution [5,6]. The other species forms at ratios of 1:1 Ln : [α–2-$P_2W_{17}O_{61}$]$^{10-}$ in both titrations where the $LnCl_3$ salt is titrated into the ligand or in the case where the ligand is added to the $LnCl_3$ salt. To further characterize the 1:1 Ln : [α2-$P_2W_{17}O_{61}$]$^{10-}$ species, a ^{183}W NMR spectrum was recorded on a sample of pure 1:1 Lu : [α2-

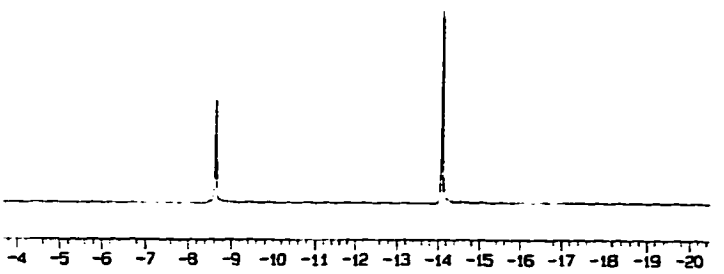
$P_2W_{17}O_{61}]^{10-}$ according to ^{31}P NMR spectroscopy (Fig. 5.6.a. and 5.6.b.). Fig. 5.6.c contains the ^{183}W NMR spectrum of the sandwich $Li_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$ for comparison. As opposed to the sandwich complex, the ^{183}W NMR spectrum of the complex prepared in 1:1 Lu:$[\alpha 2\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometry shows 9 resonances (integration ratio: 2 : 2: 1: 2 : 2 : 2 :3: 3 :2), expected for the molecule with C_s symmetry. The chemical shifts of the 183 W NMR resonances are different from the chemical shifts from the lacunary species and they are summarized in Table 5.4.

Observations on the Isomerization of the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ Isomer to the $[\alpha 1\text{-}P_2W_{17}O_{61}]^{10-}$ Isomer.

In the titration experiments described above, we used isomerically pure $[\alpha 2\text{-}P_2W_{17}O_{61}]^{10-}$ prepared by the method of Finke [9], verified by ^{31}P NMR spectroscopy prior to standardization and use for titration. At the outset of our work, we used lithium acetate buffer at pH=4.7. In the first experiment, with $EuCl_3$, the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand was prepared fresh and used within one day. However, when the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ ligand was allowed to stand at room temperature in a closed vial for two weeks, we observed that we could not standardize the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ solution: the break point was not clean. ^{31}P NMR spectroscopy revealed that the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ solution was impure, the impurity peaks appeared to be the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species and a small amount of the Wells-Dawson ion, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. In fact, upon heating the sample to 90°C for one hour, the peaks assigned to the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species appeared to increase according to ^{31}P NMR spectroscopy (Fig.5.7).

Fig. 5.6. a) ^{31}P NMR spectrum of $Li_7[\alpha\text{–}2\ LuP_2W_{17}O_{61}]$ in D_2O at room temperature,
b) ^{183}W NMR spectrum of $Li_7[\alpha\text{–}2\ LuP_2W_{17}O_{61}]$ at 50°C, in D_2O.
c) ^{183}W NMR spectrum of $Li_{17}[\alpha\text{–}2\ Lu(P_2W_{17}O_{61})_2]$ in D_2O.

a.



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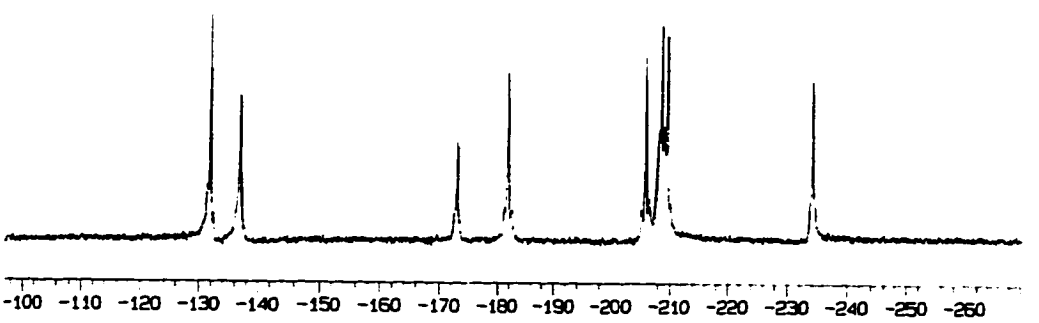

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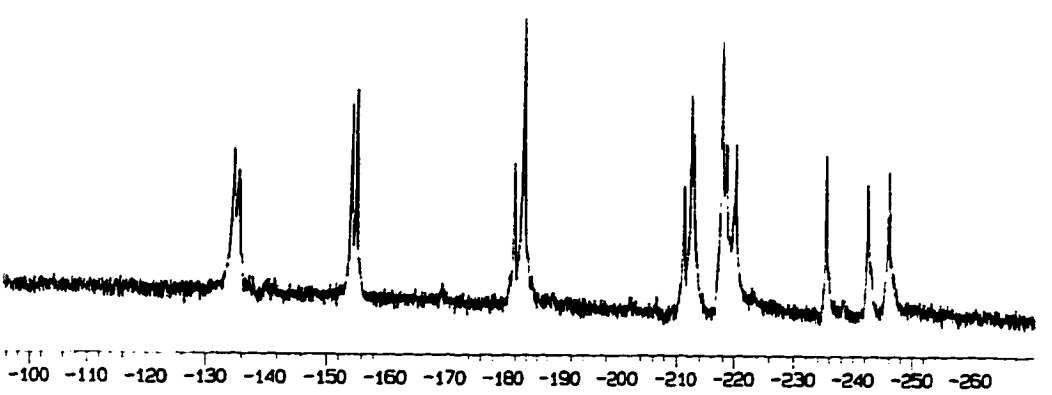
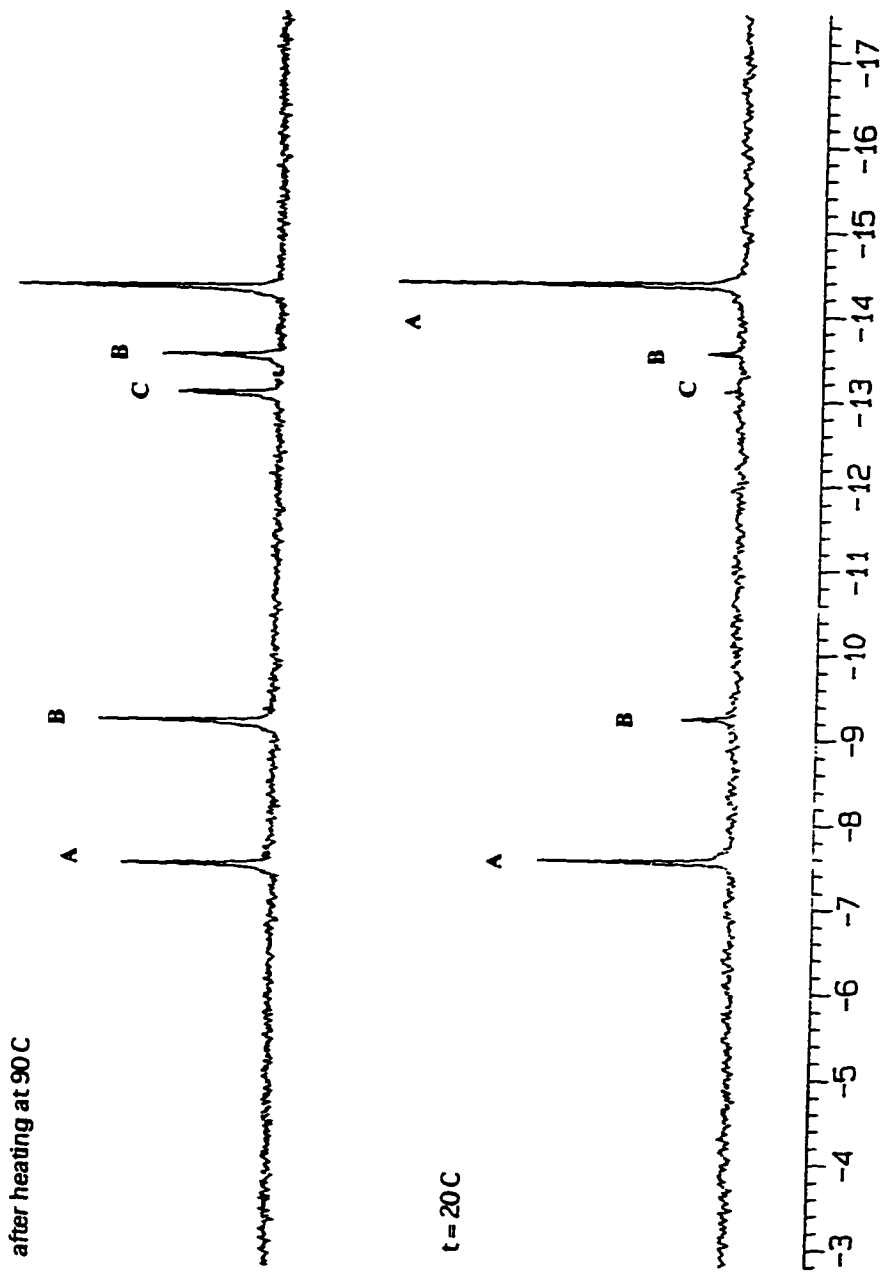


Table 5.4. ^{183}W NMR data

Compound	δ (ppm)
$Li_7LuP_2W_{17}O_{61}$	-131.81 (2), -136.83 (2), -172.94(1), -181.74 (2), -205.82 (2), -208.46 (2), -208.83 (2), -209.41 (2), -234.08 (2)
$[(\alpha\text{–}2\text{-}P_2W_{17}O_{61})^{10-}]^a$	-242.3 (2), -225.0 (2), -222.7 (2), -218.9 (2),-179.6 (1), -175.8 (2),-159.6 (2), -140.8(2), -127.9 (2)

a. From reference 12, we obtained a similar spectrum.

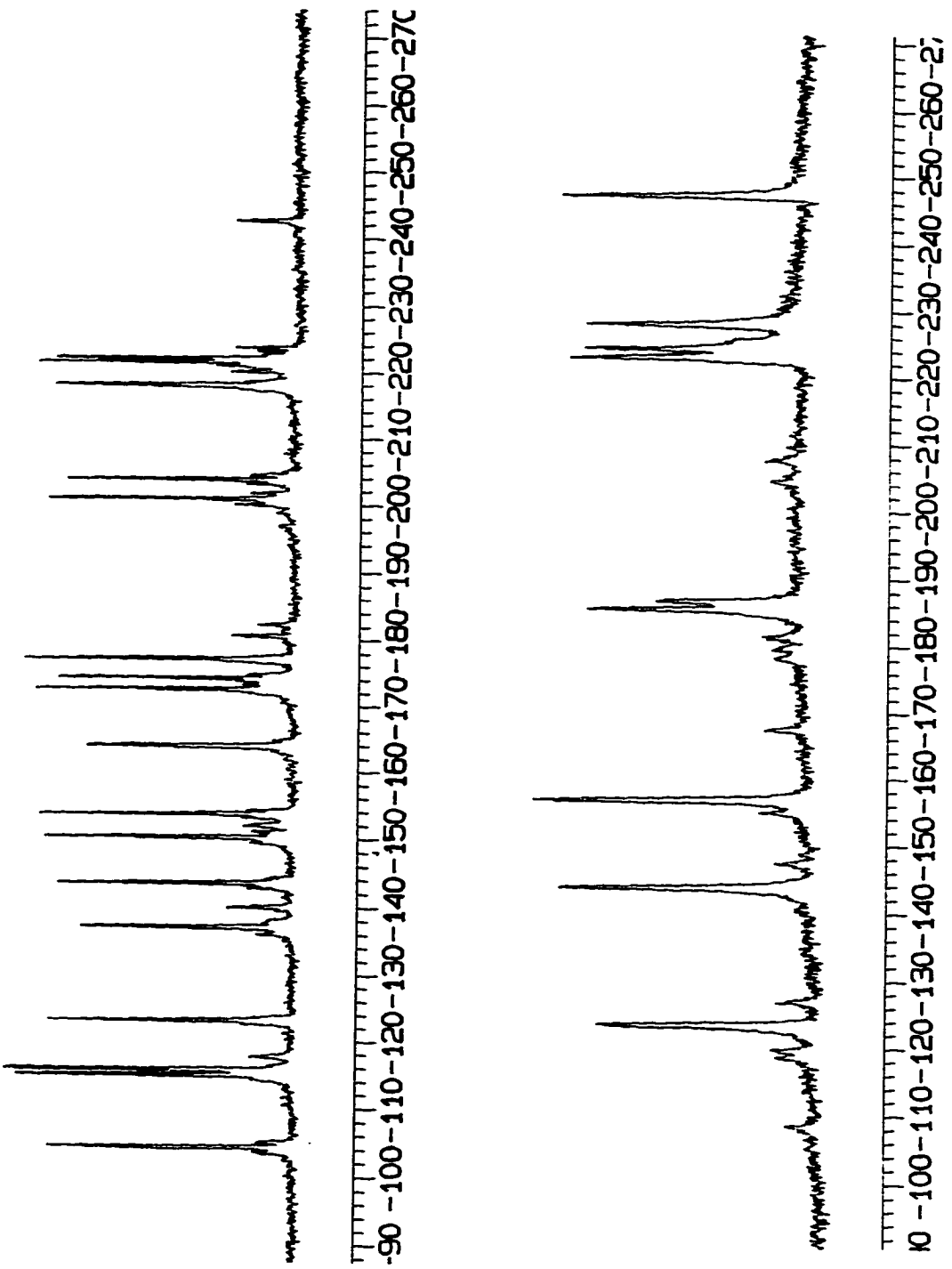
Fig. 5.7. ^{31}P NMR spectra of $Li_{10}[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ at room temperature, and after heating at 90°. Peaks labeled A= $Li_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$, B = $Li_{10}[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$, C = $Li_6(P_2W_{18}O_{62})$.



^{183}W NMR spectroscopy on the solution of the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ containing the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ impurity indeed shows small peaks corresponding to the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species. The ^{183}W NMR data are shown in Figure 5.8. This figure compares the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ (top) containing the α-2 isomer as impurity and the $[\alpha\text{–}2\text{-}P_2W_{17}O_{61}]^{10-}$ (bottom) containing the α-1 as impurity. ^{31}P NMR data for the solution of the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ containing the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ impurity in (Figure 5.7.) indicates that the content of isomeric impurities increases upon heating. This is a surprising result considering the fact that the α -1 isomer is usually unstable at high temperature.

The use of sodium acetate buffer at pH=4.7 suppressed the formation of the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ species, however a small amount of the Wells-Dawson ion, $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ species formed at this pH. Increasing the pH to 5.5 suppressed formation of the Wells-Dawson ion. The stabilizing effect of the Li^+ ions on the α–1 isomer of $[P_2W_{17}O_{61}]^{10-}$ lacunary species has been observed by Contant and coworkers[11]. From our work, we observe that a high concentration of lithium ions and a pH of $\leq$5 (4.7) appears to stabilize the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer. We observe that the conditions initially used for our titration experiments (0.5M Lithium ion buffer, pH$\leq$5.0) can, in fact, result in formation of the $[\alpha1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer from the $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer. Changing the buffer to sodium acetate resulted in stabilization of the $[\alpha2\text{-}P_2W_{17}O_{61}]^{10-}$ species and increasing the pH to 5.5, suppressed formation of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$.

Fig. 5.8. ^{183}W NMR spectra of the (top) α-1 $Li_{10}(P_2W_{17}O_{61})$ containing α-2 impurities, and (bottom) α–2 $Li_{10}(P_2W_{17}O_{61})$ containing α-1 impurities.



CONCLUSION

The $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ forms two type of complexes with lanthanides depending on the Ln: $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ stoichiometry, at pH 4.7 - 5.5, in lithium or sodium acetate buffer. The 1:1 Lu: $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ complex has been isolated in order to characterize it by ^{183}W NMR spectroscopy. The ^{183}W NMR spectrum of this complex show a molecule with Cs symmetry which is expected for the K_7 [α-2- $LuP_2W_{17}O_{61}$] complex.

The considerable effect of counter ions and pH on the $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ lacunary species is observed. The lacunary $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ isomerizes to the α –1 isomer when high concentrations of Li^+ ions are present at pH = 4.7 and the extent of isomerization increases with increasing temperature. The presence of Na^+ ions in solution at pH 4.7 favors the formation of $(P_2W_{18}O_{62})^{6-}$ which can be suppressed by raising the pH to 5.5.

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