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Lanthanide complexes of polyoxometalates: characterization by tungsten-183 and phosphorus-31 nuclear magnetic resonance spectroscopy †

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Lanthanide complexes of three classes of polyoxoanions have been characterized by multinuclear (^{183}W and ^{31}P) NMR spectroscopy among other techniques. The tetrabutylammonium salt of the lacunary $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$, prepared by metathesis of the potassium salt, was isomerically pure according to ^{183}W and ^{31}P NMR spectroscopy. The $K_{13}[Ln(SiW_{11}O_{39})_2]$ family of complexes show a six-line pattern in the ^{183}W NMR spectrum at 40 °C for the lanthanum derivative, consistent with a symmetrical structure (C_{2h} or C_{2v} symmetry), and eleven-line patterns for the ytterbium and lutetium analogues at 23 °C, suggesting a lower symmetry (C_2) for complexes of the heavier lanthanide ions. The same phenomenon was observed for the $[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]^{17-}$ family of compounds. High-temperature ^{183}W NMR experiments on the $[Lu(SiW_{11}O_{39})_2]^{13-}$ and the $[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]^{17-}$ compounds showed a reversible broadening and coalescence of the resonances, due to a dynamic effect, possibly rotation of the oxoanion ligands.

We have been interested in applications of lanthanide polyoxoanions to biological systems. Polyoxoanions[1] are mineral-like compounds with regular arrays of early transition-metal ions and oxygen atoms. They have found use as agents to aid in crystallization of proteins.[2] A number of families of polyoxoanions have been shown to interact with enzymes specifically, suggesting that these compounds may be valuable for study of the structure and function of enzymes and proteins.[3,4] The basic sites of polyoxoanions likely experience non-covalent interactions with amino acids in proteins and enzymes. A recent crystal structure presents a model for the hydrogen bonding of most basic sites of the oxoanion decavanadate with residues of a dipeptide.[5]

Polyoxoanions have also been noted for antiviral activity.[6–13] In the work cited, they show significant activity against human immunodeficiency virus (HIV) in a variety of cell lines with virtually no toxicity. The mechanism of the anti-HIV activity may be due to activity against HIV reverse transcriptase and protease as well as potent inhibition of the binding between CD4, a membrane glycoprotein on T-cell lymphocytes, and gp120 the envelope glycoprotein on HIV. The interaction of CD4 with gp120 facilitates the entrance of HIV into T-lymphocytes.

Lanthanide complexes of polyoxoanions appear to show consistently high activity against HIV. A recent broad screen of polyoxometalates[9] showed that $K_{13}[Ce(SiW_{11}O_{39})_2]$ was one of the most potent oxoanions in inhibition of HIV-1 and simian immunodeficiency virus. Time-of-addition experiments indicated that the mechanism of the anti-HIV action could be attributed to inhibition of virus-cell binding. Further, in flow cytometric studies, the compounds did not interfere with the binding of OKT4A/Leu-3a monoclonal antibody to the CD4 receptor of uninfected cells, but they inhibited binding of anti-gp120 monoclonal antibody to HIV-1 infected cells. Thus, the binding of the polyoxoanions to the viral envelope protein gp120 appeared to be responsible for their anti-HIV activity. Recently a europium heteropolytungstate, $[NH_4]_{12}H_2[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 13H_2O$, displayed potent anti-HIV-1 activity.[10] This heteropolytungstate interferes with virus infection at a very early step such as adsorption and/or penetration into cells.

Heteropolyanions present challenging problems when considered for biological work or when testing for activity as drugs. Exact formulae need to be established for these biological studies. The use of a combination of elemental analysis, TGA and mass spectral studies may allow exact formulations for biological tests. Elemental analysis by itself is often unreliable for polyoxoanions. Also, it is crucial that one understand the speciation of the potential drug molecule in investigations of polyoxoanions for antiviral applications. Polyoxoanions tend to dissociate into clusters of lower nuclearity depending on the pH and composition of the solution. A study by Hill *et al.*[6] of the speciation of the isomers A- and B-$[PW_9O_{34}]^{9-}$ in aqueous solution, buffered at pH 7 using three unrelated buffers, underscores the potential for rearrangement and degradation of polyoxoanions under conditions found in biological systems. In that seminal study the two isomers were prepared and characterized in the solid state. Monitoring the speciation in aqueous solution by ^{31}P NMR spectroscopy showed that both isomers formed identical distributions of phosphorus-containing products in the buffered solutions. Further, the distribution of these products was different among the three buffered solutions. Following this example, it is crucial to understand the structure, stabilities and potential speciation of oxometalates under the assay conditions, generally aqueous solution, in order to obtain meaningful results in biological assays. Herein we report studies of the solution structure of a series of lanthanide oxometalates in aqueous solution using multinuclear NMR spectroscopy. Biological and solution studies of the stability of the molecules under a variety of buffer conditions will be reported subsequently.

Lanthanide (Ln) complexes of heteropolytungstates were reported in 1971 by Peacock and Weakley.[14] In that report the 1:2 lanthanide tungstates $K_9[Ln(W_5O_{18})_2]$, $K_{13}[Ln(SiW_{11}O_{39})_2]$ and $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ were isolated and characterized by elemental analysis, UV and (visible for Ce^{III}) spectroscopy. These

† *Supplementary data available* (No. SUP 57232, 10 pp.): IR, mass and NMR spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1.

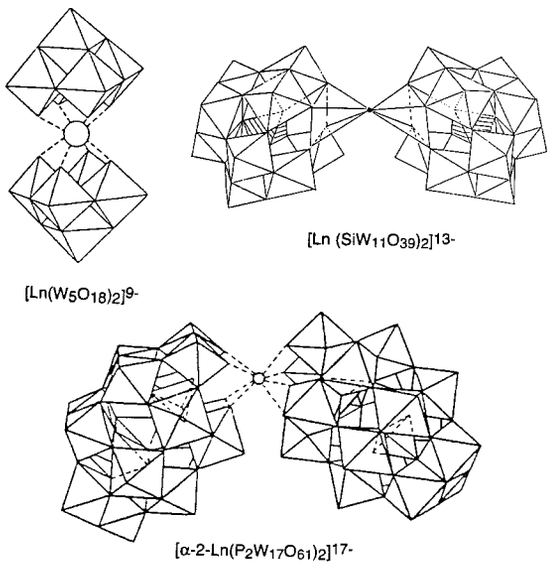


Fig. 1 Structures of lanthanide polyoxoanions in polyhedral representation. The tungsten atoms are contained within the octahedral. The vertices represent oxygen atoms

complexes can be considered as derivatives of the well known 'cage' polyoxotungstate $[W_6O_{19}]^{2-}$ (Lindquist structure) and heteropolytungstates α-$[SiW_{12}O_{40}]^{4-}$ (Keggin structure) and α-$[P_2W_{18}O_{62}]^{6-}$ (Wells–Dawson structure). Replacement of a $[WO]^{4+}$ unit from two tungstates and complexation of the resulting 'ligand' with lanthanide ions result in the 'sandwich' complexes. The lanthanide ion binds to the four oxygen atoms of each of two defect oxoanions. Fig. 1 shows structures of the three families of compounds in polyhedral representation, where the vertices of the polyhedra represent oxygen atoms and the tungsten atoms are located within each polyhedron.

Key Prior Literature

The crystal structure of $[Ln(W_5O_{18})_2]^{9-}$ shows the lanthanide ions in square-antiprismatic co-ordination geometry bound to two W_5O_{18} units.[15] The uranium(IV) and cerium(IV) analogues show isomorphous geometry.[16] Recent multinuclear NMR studies (^{17}O, ^{183}W) on lanthanide (La–Yb) and actinide (Th or U) analogues confirm the symmetry in solution.[17,18]

Many studies involve lanthanide or actinide (An) complexes of the monovacant Keggin and Dawson anions. Crystal structure analysis of $[Ce(SiW_{11}O_{39})_2]^{12-}$ and $[U(GeW_{11}O_{39})_2]^{12-}$ shows that the M^{IV} is co-ordinated to four oxygen atoms of each of two monovacant Keggin anions in square-antiprismatic co-ordination.[19] Recently, a number of crystallographic studies where lanthanide ions are incorporated into the monovacant Keggin structures $[Ln(XMo_{11}O_{39})_2]^{13-}$ (Ln = Nd or Pr, X = Ge or Si) have been reported.[20] Electrochemical data provide convincing evidence for formation of both the 1:1 and the 1:2 Ce^{III}: $[XW_{11}O_{39}]^{n-}$ complexes (X = P, n = 7; Si, 8; Ge, 8),[21] consistent with spectrophotometric titrations conducted in the early study by Peacock and Weakley.[14]

The crystal structure of the $[\alpha\text{-}2\text{-}Ce(P_2W_{17}O_{61})_2]^{16-}$ (heavy-metal framework reported only) shows the 1:2 Ce^{IV}: α-2-heteropolyanion formulation.[22] Tourne and Tourne[23] reported the preparation and characterization of the $[U^{IV}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ species by elemental analysis, polarography and spectroscopy. Recently, spectrophotometric titrations and electrochemical data confirmed the existence of $[\alpha\text{-}2\text{-}Ce(P_2W_{17}O_{61})]^{7-}$ and the 1:2 complex $[\alpha\text{-}2\text{-}Ce(P_2W_{17}O_{61})_2]^{17-}$.[21,24] The α-2-$P_2W_{17}O_{61}$ isomer, discussed in this report, is distinguished from the α-1 isomer by removal of a $[W{=}O]^{4+}$ group from the 'capping' triad of tungsten polyhedra; the α-1 isomer results when a $[W{=}O]^{4+}$ group is removed from the 'belt' tungstate polyhedra. The α-1 isomer is relatively unstable, isomerizing to the α-2 isomers. We have recently reported complexes of the α-1 isomer in >98% purity as determined by ^{31}P and ^{183}W NMR spectroscopy, with Zn,[25] and find that lanthanide ions form stable complexes with the α-1 isomer in >98% purity.[26]

Multinuclear NMR studies, especially ^{183}W and ^{31}P NMR spectroscopy, are very sensitive methods to assess the structure and stability of heteropolytungstates in solution.[27,28] The ^{183}W NMR data for the $[Ln(PW_{11}O_{39})_2]^{12-}$ family of compounds (prepared *in situ*) show symmetrical spectra for the early lanthanides and after gadolinium the data are consistent with rotation of one $PW_{11}O_{39}$ half relative to the other and inequivalence of the tungsten atoms of each heteropolytungstate.[29] The ^{31}P chemical shifts for the $[Ln(An)(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (Ln = Ce^{IV}, An = Th^{IV} or U^{IV}) and their assignments have been reported.[30] The 1:1 and 1:2 Ln: α-2-$P_2W_{17}O_{61}$ species have been observed in ^{31}P NMR titration experiments for a variety of lanthanide ions.[31] From these 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.

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 'Keggin' ion, $[SiW_{12}O_{40}]^{4-}$, as the acid and the 'Wells–Dawson' ion, $[P_2W_{18}O_{62}]^{6-}$, as the potassium salt, were prepared using literature methods.[32] The α-2 lacunary isomer $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ was prepared following the method of Finke and co-workers.[28] Infrared spectra were recorded from KBr pellets on a Perkin-Elmer 1625 spectrophotometer. Elemental analyses were performed by E & R Microanalytical Laboratory, Inc., Corona, New York. The TGA data were kindly provided by TA Instruments, Newcastle, Delaware. FAB Mass spectra were run on a VG ZAB-SE instrument. Samples were dissolved in water and the matrix dithiothreitol–dithioerythritol (3:1) or glycerol.

To convert the potassium salts into lithium salts for preparation of concentrated aqueous solutions 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 using the following procedure. Two bed volumes of lithium acetate buffer, pH 5 were loaded onto the resin with a flow rate of 2 cm^3 min^{-1}. The resin was soaked in a third bed volume for 10 h followed by washing with two bed volumes of water.

Collection of NMR data

The NMR spectra were obtained on a JEOL GX-400 spectrometer: ^{31}P spectra at 161.8 MHz were acquired using either a 10 mm broad-band probe or the broad-band decoupler coil of a 5 mm reverse detection probe; ^{183}W spectra at 16.7 MHz were recorded utilizing a 10 mm low-frequency broad-band probe. Typical acquisition parameters for ^{31}P spectra included: spectral width, 10 000 Hz; acquisition time, 0.8 s; pulse delay, 20 s; pulse width, 15 μs (50° tip angle). From 50 to 500 scans were required. For ^{183}W spectra, typical conditions included: spectral width, 10 000 Hz; acquisition time, 1.6 s; pulse delay, 0.5 s; pulse width, 50 μs (45° tip angle). From 1000 to 30 000 scans were acquired. The ^{29}Si spectra at 79.3 MHz were recorded utilizing a 10 mm high-frequency probe. Typical acquisition parameters included: spectral width, 10 000 Hz; acquisition time, 1.638 s; pulse delay, 0.5 s; pulse width, 15 μs. For all spectra the temperature was controlled to ±0.2°. The ^{31}P spectra were referenced to 85% H_3PO_4, ^{183}W spectra to 2.0 mol dm^{-3}

Table 1 Analytical data for $Na_9[Ln(W_5O_{18})_2]$, $K_{13}[Ln(SiW_{11}O_{39})_2]$ and $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ complexes

		Analysis (%)			
Complex		Calc.	Obs.	TGA	Mass spectrum* (*m*/*z*)
$Na_9[Gd(W_5O_{18})_2]\cdot 21H_2O$	W	58.2	57.6	12.066	
	Gd	5.0	4.85		
	Na	6.55	6.4		
$Na_9[La(W_5O_{18})_2]\cdot 21H_2O$					2528 $[H_3Na_5La(W_5O_{18})_2]^-$
					2550 $[H_2Na_6La(W_5O_{18})_2]^-$
					2572 $[HNa_7La(W_5O_{18})_2]^-$
					2594 $[Na_8La(W_5O_{18})_2]^-$
$K_{13}[La(SiW_{11}O_{39})_2]\cdot 21H_2O$	W	63.5	63.6	6.004	5830 (M^-)
	Si	0.9	0.55		
	K	7.95	7.8		
	La	2.2	1.95		
$K_{13}[Y(SiW_{11}O_{39})_2]\cdot 18H_2O$	W	64.5	64.3	5.187	
	Si	0.9	0.6		
	K	8.1	7.9		
	Y	1.4	1.1		
$K_{13}[Eu(SiW_{11}O_{39})_2]\cdot 19H_2O$	W	63.7	63.5	5.335	
	Si	0.9	0.6		
	K	8.0	7.85		
	Eu	2.4	2.1		
$K_{13}[Yb(SiW_{11}O_{39})_2]\cdot 18H_2O$	W	63.65	63.3	5.079	
	Si	0.9	0.55		
	K	8.0	7.7		
	Yb	2.7	2.5		
$K_{13}[Lu(SiW_{11}O_{39})_2]\cdot 21H_2O$	W	63.1	62.8	5.861	
	Si	0.9	0.65		
	K	7.95	7.65		
	Lu	2.75	2.65		
$K_{17}[\alpha\text{-}2\text{-}La(P_2W_{17}O_{61})_2]\cdot 30H_2O$	W	64.6	64.45	5.561	
	P	1.3	1.25		
	K	6.85	6.7		
	La	1.45	1.35		
$K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]\cdot 27H_2O$	W	64.75	64.5	5.080	8606 $[KLiLu(P_2W_{17}O_{61})_2 - O - WO_3]$
	P	1.3	1.3		
	K	6.9	6.65		4391 $[KLi_2Lu(P_2W_{17}O_{61})]$
	Lu	1.8	1.65		4388 $[KLiH_4Lu(P_2W_{17}O_{61})]$
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}(P_2W_{17}O_{61})]\cdot 4.5H_2O$	W	48.65	50.8		4152 $[KLiLu(P_2W_{17}O_{61}) - WO_3]$
	P	0.95	0.9		
	C	26.9	24.7		
	H	5.2	4.95		
	N	1.95	1.85		

* Negative-ion FAB: see text and SUP 57232. The paratungstate ion is a probable impurity in the $Na_9[La(W_5O_{18})_2]$ preparation. In an attempt to isolate crystals from an aqueous solution of $Na_9[La(W_5O_{18})_2]$, buffered by sodium acetate at pH 7, we obtained crystals of $[W_{12}O_{42}H_2]^{10-}$.[34]

Na_2WO_4 and ^{29}Si spectra to $SiMe_4$. For ^{29}Si, ^{31}P and ^{183}W chemical shifts the convention used is that the more negative chemical shifts denote upfield resonances.

Preparation of complexes

The $Na_9[Ln(W_5O_{18})_2]$ species were prepared following the method of Peacock and Weakley.[14] The $K_{13}[Ln(SiW_{11}O_{39})_2]$ and the $K_{17}[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]$ family of compounds were prepared also using the method of Peacock and Weakley, involving base degradation of the parent compounds, $[SiW_{12}O_{40}]^{4-}$ and $[P_2W_{18}O_{62}]^{6-}$.[14] 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 and co-workers.[28]

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 and co-workers.[28] The salt $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (5 g, 1.02 mmol) was dissolved in water (500 cm^3) to form a clear solution, pH 6.2. The pH was gradually adjusted to 5.65 with sulfuric acid (0.18 mol dm^{-3}). Tetrabutylammonium bromide (3.29 g, 10.2 mmol) was added slowly while the pH of the solution was maintained in the range of 5.5–7.5 with 0.18 mol dm^{-3} sulfuric acid. The resulting white cloudy solution was extracted with CH_3CN (34 cm^3) and CH_2Cl_2 (67 cm^3). The mixture was shaken for 5 min. The clear organic layer was collected and rotary evaporated at 50 °C. Methylene chloride (5 cm^3) was added to dissolve the resulting solid to give a clear faint yellow-green solution. Addition of diethyl ether (25 cm^3) resulted in the precipitation of a white solid. The solid was filtered off and dried *in vacuo*. The compound was recrystallized from acetonitrile.

To collect ^{31}P NMR data in D_2O a metathesis procedure was used.[33] The salt $[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (64 mg) was stirred into a solution of $LiClO_4$ (10 mg) in D_2O (0.5 cm^3). The resulting solution was cooled to 2–3 °C. A solid was separated from the solution by centrifugation.

Elemental analysis, TGA and mass spectral data are given in Table 1, ^{31}P and ^{183}W NMR data in Tables 2 and 3, respectively.

Results and Discussion

Elemental analysis data and thermogravimetric analysis allowed the determination of the exact chemical formula, necessary for accurate concentration determination of biological assays. The elemental analysis, TGA, mass spectrometry and ^{31}P and ^{183}W NMR data are consistent with the formulations $Na_9[Ln(W_5O_{18})_2]$, $K_{13}[Ln(SiW_{11}O_{39})_2]$ and $K_{17}[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$. The negative-ion FAB-mass spectral data (SUP 57232) generally show molecular ion regions followed by frag-

Table 2 Phosphorus-31 NMR data

Compound	δ[a] P(2)	δ[a] P(1)	Solvent[b] (peaks due to protonation)
$K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$[c]	−14.10	−7.28	D_2O
$K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$	−14.15	−8.17	D_2O
$K_{17}[\alpha\text{-}2\text{-}La(P_2W_{17}O_{61})_2]$	−14.15	−8.17	D_2O
$K_{17}[\alpha\text{-}2\text{-}Yb(P_2W_{17}O_{61})_2]$	−22.76	−8.70	D_2O
$K_{17}[\alpha\text{-}2\text{-}Eu(P_2W_{17}O_{61})_2]$	−13.23	+3.14	D_2O
$[N(C_4H_9)_4]_9H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$	−13.60	−9.10	dmso–water
	−11.56	−7.26	dmso, −11.17
	−11.95	−6.55	CH_3CN, −10.47
	−13.63	−7.77	D_2O, $LiClO_4$[d]

[a] See text for data-collection parameters; P(1) is the phosphorus atom closest to the site of substitution, P(2) that remote from the substitution site. [b] In organic solvents, protonation of the oxoanions results in multiple peaks, with addition of water or $[N(C_4H_9)_4]OH$ the peaks disappear, see text. [c] Chemical shifts from ref. 25. [d] See text and ref. 33(*a*).

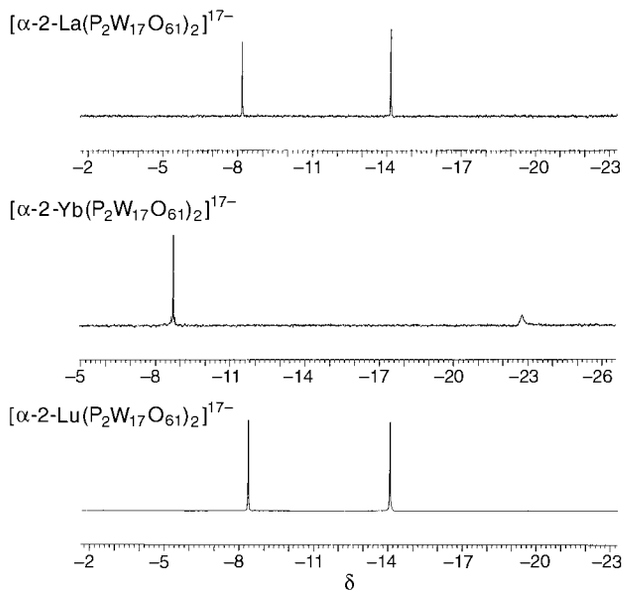


Fig. 2 ^{31}P NMR Spectra of $K_{17}[\alpha\text{-}2\text{-}La(P_2W_{17}O_{61})_2]$, $K_{17}[\alpha\text{-}2\text{-}Yb(P_2W_{17}O_{61})_2]$ and $K_{17}[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]$ in D_2O

mentation of WO_3 groups.[35] The data for $Na_9[Ln(W_5O_{18})_2]$ (SUP 57232) show sets of clusters; a cluster encompassing $m/z = 2594$ $\{[Na_8Ln(W_5O_{18})_2]^-\}$ is the parent ion region. This cluster is separated from clusters of lower m/z by 232, reflecting loss of WO_3 units. Within each cluster are smaller clusters of peaks separated by $m/z = 22$, reflecting the loss of Na^+ and addition of H^+. This mass spectrum shows asymmetry in the cluster of the parent ion, probably due to impurities in the sample.[34]

The ^{31}P NMR data (Fig. 2, Table 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. Phosphorus-31 NMR spectroscopy is an extremely sensitive technique to determine the isomeric purity of the α-1 and α-2 isomers as well as to ascertain any other phosphorus-containing impurities.[28] (The α-1 isomer of the lacunary $[P_2W_{17}O_{61}]^{10-}$ [36] and transition-metal [25,37] and lanthanide complexes [26,38] of $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ generally show chemical shifts of *ca.* δ 9.5–10.5 for P(1) and δ 13–14 for P(2) in water. The α-2 isomers show the resonance for P(1) between δ 7 and 8 and the resonance for P(2) at *ca.* δ 14 in water.)‡ The ^{31}P NMR 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.

Titration experiments performed under acidic conditions using ^{31}P NMR spectroscopy[31] 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. Only the 1:2 $La:[P_2W_{17}O_{61}]^{10-}$ and 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 $Lu:[P_2W_{17}O_{61}]^{10-}$ complex as a potassium salt (elemental analysis, TGA, mass spectrometry). In addition, crystallographic work confirms the 1:2 formulation for $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$.[39] 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 or Lu) complexes by ^{31}P NMR spectroscopy.[39]

Infrared spectroscopy data (SUP 57232) for the lanthanide $\alpha\text{-}2\text{-}P_2W_{17}O_{61}$ derivatives and the tetrabutylammonium salt of the lacunary species show similarity to those for 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 and *ca.* 950 cm^{-1}, characteristic of the P–O and terminal W–O stretches.

^{183}W NMR spectroscopy

Tungsten-183 NMR spectroscopy allow characterization of the solution structure of the molecules. The chemical shifts are given in Table 3. The ^{183}W NMR spectra taken in D_2O at room temperature in a pH range 7–7.6 for $Na_9[La(W_5O_{18})_2]$ and $Na_9[Eu(W_5O_{18})_2]$ are given in SUP 57232. The data are in excellent agreement with the chemical shifts reported recently.[17,18] For each molecule, two peaks in the ratio 4:1 are observed consistent with the structure determined for the analogous complexes of Ce^{IV}, U^{IV} and Eu^{III}, where the lanthanide (or actinide) ion is central to two W_5O_{18} units.[15,16] Four tungsten atoms comprise the 'belt' region with a unique tungsten atom at the cap of each W_5O_{18} unit. We found that $Na_9[Ln(W_5O_{18})_2]$ (Ln = Gd, Eu or Tb) appeared to be quite stable, amenable to crystallization from dimethyl sulfoxide (dmso)–water. The lanthanum(III) analogue was reasonably stable in a pH range of 6.5–8, although we occasionally observed impurity peaks in the ^{183}W NMR spectrum.[34] We could not produce the lutetium(III) analogue in any degree of purity according to ^{183}W NMR spectroscopy.

Fig. 3 shows the ^{183}W NMR spectrum taken at 40 °C for $[La(SiW_{11}O_{39})_2]^{13-}$ and at 23 °C for the $[Lu(SiW_{11}O_{39})_2]^{13-}$ species. For the former compound the resonance at δ −164 is very broad at room temperature (23 °C) and sharpens significantly as the temperature is raised. The spectrum shows six resonances (integration 2:1:2:2:2:2). The lutetium analogue, $[Lu(SiW_{11}O_{39})_2]^{13-}$, as well as the ytterbium analogue (not shown), at room temperature show eleven resonances each integrating for one tungsten. Scheme 1(*a*) represents $[Ln(W_{11}O_{39}Si)_2]^{13-}$, shown in Fig. 1. The corners of the squares represent oxygen atoms forming the defect site in the lacunary $[SiW_{11}O_{39}]^{8-}$ oxoanions 1 and 2. Oxygen atoms A and A′ belong to polyhedra which are edge shared and oxygen atoms B and B′ to those which are corner shared. Scheme 1(*a*) represents the molecule where the oxygen atoms are eclipsed. The point-group symmetry of this molecule is C_{2v} and thus gives rise to six lines in the ^{183}W NMR spectrum with five integrating for two

‡ The literature is very confusing and not systematic in the naming of the $P_2W_{17}O_{61}$ isomer substituted at the 'belt' tungsten octahedra. Most of the literature names this as the α-1 isomer. Ref. 38(*a*) designates it as 'β', an uncommon designation, ref. 38(*b*) as the more common α-1 designation.

Table 3 Tungsten-183 NMR data[a]

Compound	δ
$Na_9[La(W_5O_{18})_2]$	+0.31(4), −13.42(1)
$Na_9[Eu(W_5O_{18})_2]$	−21.10(1), −664.0(4)
$Na_8[SiW_{11}O_{39}]$[b]	−98.0(2), −114.8(2), −119.7(1), −126.2(2), −141.0(2), −174.1(2)
$K_{13}[La(SiW_{11}O_{39})_2]$	−105.19(2), −117.39(1), −133.19(2), −136.60(2), −162.22(2), −169.47(2)
$K_{13}[Yb(SiW_{11}O_{39})_2]$	−91.99(1), −95.62(1), −104.35(1), −113.36(1), −123.29(1), −126.41(1), −146.82(1), −147.15(1), −149.06(1), −152.40(1), −156.61(1)
$K_{13}[Lu(SiW_{11}O_{39})_2]$	−98.08(1), −100.57(1), −107.46(1), −126.70(1), −129.05(1), −130.37(1), −137.77(1), −156.90(1), −159.54(1), −163.02(1), −194.51(1)
$K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$[c]	−127.9(2), −140.8(2), −159.6(2), −175.8(2), −179.6(1), −218.9(2), −222.7(2), −225.0(2), −242.3(2)
$Li_{17}[La(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$[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] Resonances similar to those in ref. 27(*d*). [c] From ref. 27(*c*); we obtained a similar spectrum. [d] Prepared by ion-exchange chromatography at pH 5, see text. [e] Measured in dmso–D_2O.

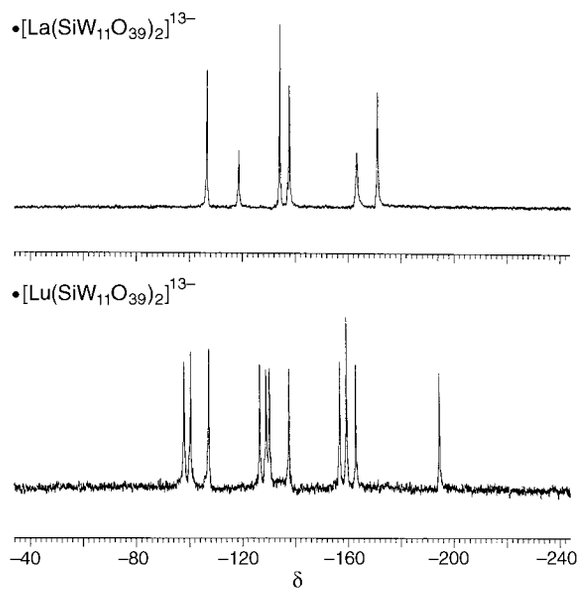
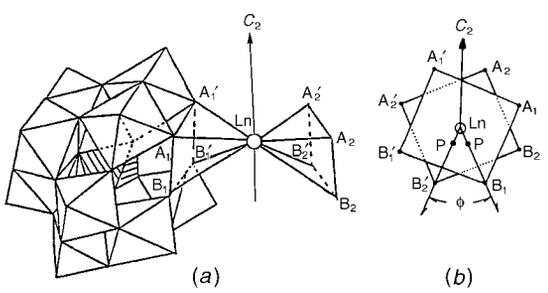


Fig. 3 ^{183}W NMR Spectra of $[La(SiW_{11}O_{39})_2]^{13-}$ (top) as the Li^+ salt in D_2O and $[Lu(SiW_{11}O_{39})_2]^{13-}$ (bottom) as the K^+ salt in D_2O



Scheme 1

tungsten atoms and one integrating for one tungsten atom. Scheme 1(*b*) shows the side view of the complex upon rotation by φ. A rotation where φ = 180° results in a molecule with C_{2h} symmetry; half of each lacunary polyoxoanion is related by a symmetry plane. Each lacunary oxoanion is related to the other by a two-fold rotation; this eclipsed conformation would give rise to six resonances, five integrating for two tungsten atoms and one integrating for one tungsten atom. Rotations where 0 < φ < 180° result in a molecule where no symmetry planes are present. (For φ = 45, 90 and 135° the point-group symmetry of the molecule is C_2.) In this case, as we find with the heavy lanthanides, all eleven tungsten atoms in one lacunary unit are

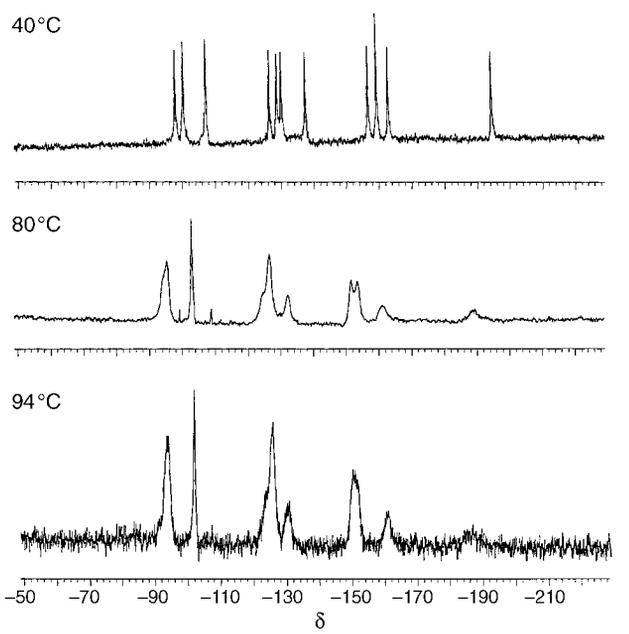


Fig. 4 Variable-temperature ^{183}W NMR spectra of $K_{13}[Lu(SiW_{11}O_{39})_2]$ in D_2O

inequivalent to each other and each lacunary half is related to the other by a two-fold rotation. (The ^{29}Si NMR spectrum shows one resonance at δ −6.77.) The co-ordination geometry about the lutetium and ytterbium is square antiprismatic. This phenomenon has been observed recently for the solutions of the $[Ln(PW_{11}O_{39})_2]^{11-}$ species.[29]

Fig. 4 shows the effect of increasing the temperature of the $[Lu(SiW_{11}O_{39})_2]^{13-}$ solution. At elevated temperatures a broadening and coalescence of peaks is observed. Reducing the temperature to 25 °C results in the original eleven-line pattern. A dynamic effect may be occurring wherein the lacunary $[SiW_{11}O_{39}]^{8-}$ oxoanion halves are rotating; the six-line pattern represents a fast rotation on the NMR time-scale and the eleven-line pattern represents freezing out the structure where the lanthanide ion is in square-antiprismatic co-ordination geometry. Reducing the temperature of the lanthanum analogue, $[La(SiW_{11}O_{39})_2]^{13-}$, does not result in the eleven-line pattern, instead the resonances are broadened, possibly due to increased viscosity of the solution.

The same phenomena occur for the $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ species. Fig. 5 shows the ^{183}W NMR spectra for the lanthanum, ytterbium and lutetium analogues. As in the $[Ln(SiW_{11}O_{39})_2]^{13-}$ species, the oxygen atoms bonded to the Ln in [Ln(α-2-

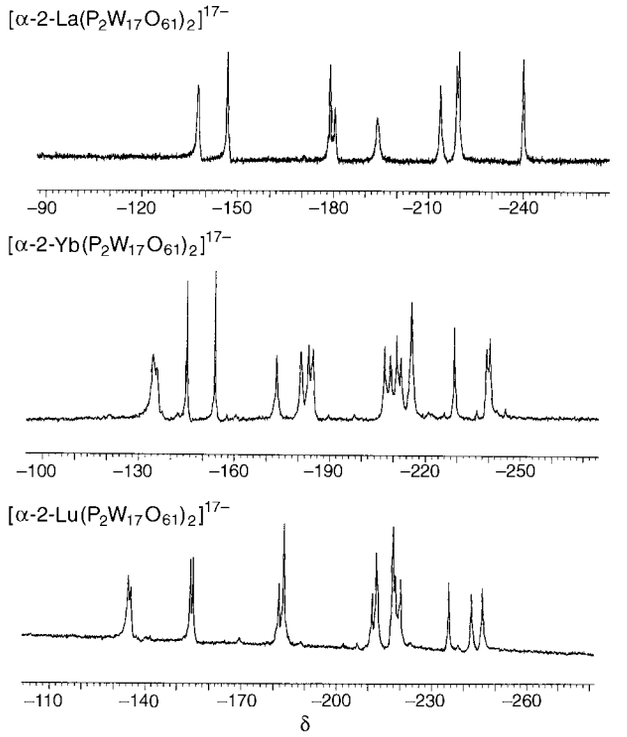


Fig. 5 ^{183}W NMR Spectra of $[\alpha\text{-2-La}(P_2W_{17}O_{61})_2]^{17-}$, $[\alpha\text{-2-Yb}(P_2W_{17}O_{61})_2]^{17-}$ and $[\alpha\text{-2-Lu}(P_2W_{17}O_{61})_2]^{17-}$ in D_2O as the Li^+ salts

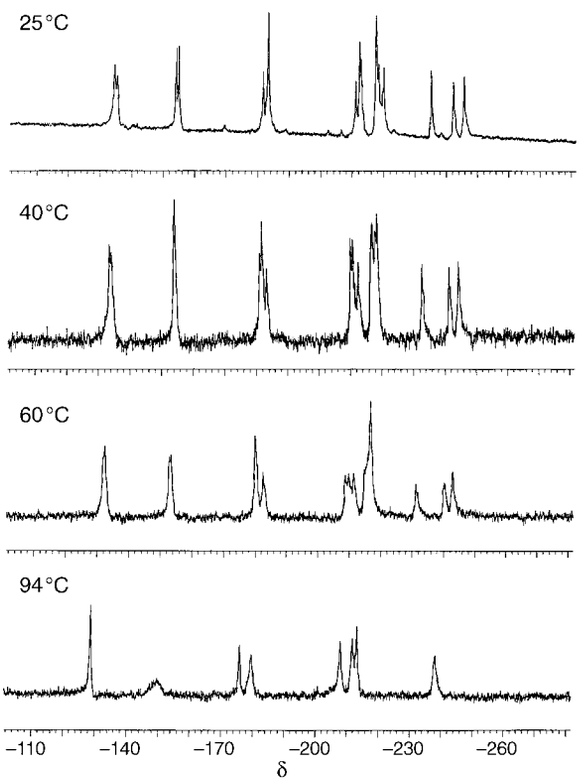


Fig. 6 Variable-temperature ^{183}W NMR spectra of $Li_{17}[\alpha\text{-2-Lu}(P_2W_{17}O_{61})_2]$

$P_2W_{17}O_{61})_2]^{17-}$ species come from two edge-shared polyhedra [A, A′ in Scheme 1(*a*)] and two corner-shared polyhedra (B, B′ in Scheme 1). In the eclipsed form, where $\varphi = 0°$, the molecule has C_{2v} symmetry; the two oxoanion lobes are in a '*syn*' position. The molecule has C_{2h} symmetry when $\varphi = 180°$; this situation corresponds to the conformer where the two oxoanion lobes are disposed in an '*anti*' position. A recent crystal structure of $[O\{Ru^{IV}Cl(\alpha\text{-2-}P_2W_{17}O_{61})\}_2]^{16-}$ shows the two $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ lacunary polyoxoanions in the '*anti*' eclipsed conformation.[40] 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 $0 < \varphi < 180°$ [Scheme 1(*b*)] the resulting structures have two-fold rotation axes, but no symmetry planes, therefore the 17 tungsten atoms in each oxoanion half are inequivalent, and each lacunary $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ 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 co-ordination geometry. The analogues of Yb and Lu 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. The chemical shifts for these species are different from the lacunary $[\alpha\text{-1-}P_2W_{17}O_{61}]^{10-}$ species or the lanthanide derivatives of $[\alpha\text{-1-}P_2W_{17}O_{61}]^{10-}$ which also gave 17 inequivalent tungsten atoms.[25,26] 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. Increasing the temperature of $[Lu(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ (Fig. 6) results in coalescence of many of the resonances, approaching the nine-line spectrum of the lanthanum analogue. Reducing the temperature to 25 °C results in the original spectrum.

The tungsten NMR data for both families of compounds clearly show that as the ionic radius decreases, from lanthanum to lutetium, the solution structures become less symmetrical at room temperature. This is likely due to a dynamic effect; a possible process may be one in which the lacunary oxoanion ligands in the lanthanum analogues rotate relative to each other at room temperature. Higher temperature is required for rotation of the oxoanion halves for the lutetium analogues. The ^{31}P NMR spectrum remains the same at high temperature; there is no evidence of decomposition to the lacunary $[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ and 1:1 Lu:$[\alpha\text{-2-}P_2W_{17}O_{61}]^{10-}$ species formation.[39] We also noticed that, for $[Lu(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$, as the pH is lowered from 3 to 0.3, the ^{183}W NMR peaks broaden and coalesce until, at pH 0.3, the ^{183}W NMR spectrum (SUP 57232) looks similar to that for $[Lu(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ obtained under neutral pH at 94 °C. The ^{31}P NMR spectrum broadens slightly but does not shift significantly at the lower pH values. No evidence of decomposition and formation of $[P_2W_{18}O_{62}]^{6-}$ is observed by ^{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 $[Lu(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ species. It is very likely as at low pH the most basic oxygen atoms bonded to the Lu^{3+} ion,§ 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 we observe 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 time-scale, when facilitated by protonation of the basic oxygen atoms or at high temperature.[42]

The $[Ln(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$ and $[Ln(SiW_{11}O_{39})_2]^{13-}$ families of compounds are stable in a wide pH range. In titrations using HCl and NaOH to adjust the pH, the pH was recorded before and after the measurement; generally it did not shift significantly during the measurement. The complex $[Lu(\alpha\text{-2-}P_2W_{17}O_{61})_2]^{17-}$, discussed above, is stable in the pH range of 8 to 0.3. The lanthanum analogue is stable in the pH range 3–10; at pH *ca.* 2 the peaks begin to broaden and at pH 0.5 the [α-

§ Replacement of the W^{VI} in the parent $[\alpha\text{-}P_2W_{18}O_{61}]^{6-}$ with a lower-valent metal ion increases the basicity of the bridging oxygen atoms adjacent to the lower-valent metal ion. Thus, these bridging oxygen atoms become susceptible to protonation. For a discussion of this phenomenon see ref. 41.

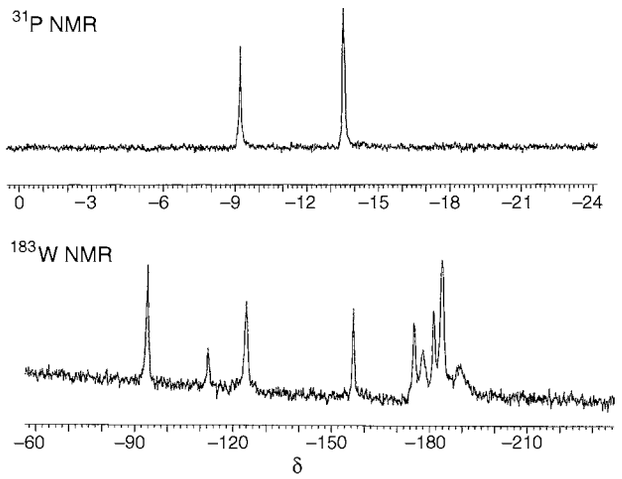


Fig. 7 The ^{31}P NMR spectrum of $[N(C_4H_9)_4]_8H[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (top) in dmso (0.3 cm^3) and D_2O (0.2 cm^3) and the ^{183}W NMR spectrum in dmso (2 cm^3) and D_2O (1 cm^3) containing $[N(C_4H_9)_4]OH$ (bottom)

$P_2W_{18}O_{62}]^{6-}$ species forms. The ^{31}P NMR spectra for $[La(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ remain the same throughout the pH range, but broaden a bit at the lower pH values, and at pH 0.5 the $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ species appears. According to ^{183}W NMR spectroscopy, $[La(SiW_{11}O_{39})_2]^{13-}$ is stable in the range of pH 10 to 1. At pH <1 the Keggin ion forms. The complex $[Lu(SiW_{11}O_{39})_2]^{13-}$ is stable in the pH range 3–10. At pH 2.9 the peaks for this species disappear, a peak at δ −102.55 for the Keggin ion appears and precipitation occurs.

The ^{183}W 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[33] (SUP 57232) confirm the lacunary $\alpha\text{-}2\text{-}P_2W_{17}O_{61}$ structure. Elemental analysis is often unreliable for polyoxoanions and, in this case, we observe high percentages for W and low for C. Phosphorus-31 and ^{183}W NMR spectroscopy are better indicators of the purity of molecules.[28] Using these techniques we observe no evidence of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. Fig. 7 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 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 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.[33] The ^{31}P NMR spectra, taken in pure organic solvents, have additional small peaks due to small amounts of protonated species. This phenomenon has been observed previously.[43] For example, a small peak at *ca.* δ 11 is observed for the tetrabutylammonium salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ 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.[43]

The tetrabutylammonium salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ is >98% isomerically pure; there is no evidence of the α-1 isomer. We did not observe the formation of the tetrabutylammonium salt of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ in this reaction by either ^{31}P or ^{183}W NMR spectroscopy. To avoid formation of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, the pH must be maintained at 5–7 during the metathesis reaction. Reported attempts at the preparation of the tetrabutylammonium salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ resulted in no precipitation in the metathesis reaction or formation of $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ upon acidification.[44] We find that following a modification of a metathesis method developed by Finke and co-workers,[28,33*a*] maintaining the pH in the range 5.5–7 is important in avoiding $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$. Also, extraction with CH_2Cl_2 is necessary as a precipitate does not form upon addition of tetrabutylammonium bromide to $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$.

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 ^{183}W NMR spectra for the lanthanum and europium members of the $Na_9[Ln(W_5O_{18})_2]$ family show two resonances consistent with the solid-state structure found for this family of compounds. The $K_{13}[Ln(SiW_{11}O_{39})_2]$ family of complexes show six-line patterns in the ^{183}W NMR spectra at 40 °C for the lanthanum derivative, consistent with a symmetrical structure (C_{2v} or C_{2h} symmetry), and eleven-line patterns for the ytterbium and lutetium analogues at 23 °C, suggesting that the heavier lanthanide ions, with smaller ionic radii, have a lower symmetry in solution. The same phenomenon is observed for the $[\alpha\text{-}2\text{-}Ln(P_2W_{17}O_{61})_2]^{17-}$ family of compounds. High-temperature ^{183}W NMR experiments on both the $[Lu(SiW_{11}O_{39})_2]^{13-}$ and the $[\alpha\text{-}2\text{-}Lu(P_{21}W_{17}O_{61})_2]^{17-}$ 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 $[\alpha\text{-}2\text{-}Lu(P_2W_{17}O_{61})_2]^{17-}$ compound, indicating that protonation of basic oxygen atoms may facilitate the dynamic effect.

Acknowledgements

We are very grateful to Professors William J. Randall and Richard G. Finke for providing a preprint of ref. 33(*a*). We are grateful to TA Instruments, Inc., Newcastle, Delaware for running TGA experiments and to Mr. Edward Davis for assistance with some experiments. We also thank students in the General Chemistry Laboratories, co-ordinated by Professor P. A. Mills, for preparation of some starting materials. We acknowledge the following sources of support for this research: Eugene Lang Undergraduate Award (S. S.), Olive Stewart Reynolds Undergraduate Chemistry Award (S. S. and M. D.), Gertrude Elion Graduate Fellowship (J. B.), Faculty Research Award Program of the City University of New York, Eugene Lang Faculty Development Award, NSF-CHE9309001, NSF-CHE9502213 (L. C. F.), NIH-Research Centers in Minority Institutions Grant RR03037-08S2, and NSF Grant PCM8111745 for the purchase of the 400 MHz spectrometer.

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Received 10*th September* 1996; *Paper* 6/06250D