

Rigid Nonlabile Polyoxometalate Cryptates $[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-}$ That Exhibit Unprecedented Selectivity for Certain Lanthanide and Other Multivalent Cations

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Received June 11, 1992

Reaction of aqueous solutions of the heteropolytungstate $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ with various cations Z^{n+} in a sealed container at 120–180 °C for several hours leads to cation exchange and the formation of $[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-}$ when $\text{Z} = \text{Ca}^{2+}$, trivalent Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, or Bi, or tetravalent Ce or U. No exchange occurred for $\text{Z} = \text{Cd}^{2+}$, Sn^{2+} , Hg^{2+} , Tl^{3+} , Ce^{3+} , Pr^{3+} , or Th^{4+} at temperatures up to 180 °C. The lanthanide selectivity appears to be determined by ionic radius. The new complexes, which are hydrolytically stable from pH 0 to pH 9–10, are characterized by cyclic voltammetry, IR spectra, and ^{31}P NMR spectra (single line in all cases except when $\text{Z} = \text{Y}^{3+}$ which shows $^2J(^{31}\text{P}-\text{O}-^{89}\text{Y}) = 1.6$ Hz); $\delta = -68.1$ to $+17.6$ ppm. The lanthanide-induced shifts of the ^{31}P nucleus are predominantly pseudocontact in origin. The ^{183}W NMR spectrum of the Eu^{3+} derivative has four doublets at $+62.5$, -201.7 , -209.5 , and -297.5 ppm (1:2:1:1) consistent with the C_{5v} structure found for the Na derivative. The emission spectrum of the Eu derivative and the ESR spectrum of the Gd derivative are reported. The low proton relaxivity of the latter complex (ca. 1.0 mM s^{-1} at 300 MHz) is consistent with the presumed structure in which Gd^{3+} is inaccessible to solvent water.

Introduction

Some large heteropolytungstate anions have structures which permit the binding and exchange of various alkali and alkaline earth metal cations within a central cavity of an appropriate size. The complexes $[(\text{Na})\text{Sb}_9\text{W}_{21}\text{O}_{86}]^{18-}$ and $[(\text{K})\text{As}_4\text{W}_{40}\text{O}_{140}]^{27-}$ are examples which favor Na^+ and K^+ respectively^{1,2} and are viewed as inorganic analogues of crown ethers and other organic cryptands. In other heteropolyanion species, such as $[(\text{Na})(\text{HF}_3)_2\text{W}_{18}\text{O}_{56}]^{7-}$,³ the sodium ion occupies a central interstitial site and is not accessible to exchange.

A crystallographic investigation⁴ of the so-called Preyssler tungstophosphate anion has revealed it to be $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ ($\text{NaP}_5\text{W}_{30}$) and not $[\text{HP}_3\text{W}_{18}\text{O}_{66}]^{8-}$ as first assigned by Preyssler.⁵ The anion has approximate D_{5d} symmetry (Figure 1) and consists of five PW_6O_{22} units derived from the Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$, arranged in a crown so that the $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ anion has an unusual 5-fold symmetry axis. The tungsten atoms are distributed in four parallel planes perpendicular to this axis. The two outer planes each contain five tungsten atoms and the two inner planes ten tungsten atoms. The structure leaves a cylindrical vacancy along the 5-fold axis, and the sodium ion is positioned in this vacancy, not in the center as might be expected, but in one of the inner oxygen planes, so that it is coordinated to five oxygens in this plane and to five oxygens in an outer plane at a larger distance; see Figures 2 and 3. The structure rationalized previously-recorded ^{31}P NMR,⁶ which showed a single line for the five equivalent phosphorus atoms, and ^{183}W NMR,⁷ which gave four lines in a 2:2:1:1 ratio as expected from the dissymmetry introduced by the sodium ion. Sodium-23 NMR showed separate signals for internal and free cationic Na^+ indicating relatively slow exchange.⁴

Under severe experimental conditions (heating in aqueous solution at 120 °C in a bomb) the sodium ion could apparently be replaced by Ca^{2+} , which has a radius (1.14 Å)⁸ similar to that of Na^+ (1.16 Å). The ionic radii of the trivalent lanthanides (Ln) ($r = 1.17$ – 1.00 Å) are similar to those of Na^+ and Ca^{2+} , and Ln^{3+} ions are often used to replace Ca^{2+} in complexes in biological studies. Because of their higher charge the lanthanide complexes would be expected to be even more stable than those of Na^+ and Ca^{2+} . Early attempts⁴ to insert Ln^{3+} proved inconclusive, and we report here a reinvestigation of this system.

Experimental Section

$\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}] \cdot 15\text{H}_2\text{O}$ was prepared either according to ref 9 or by the following method which gives an improved yield. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (33 g) was dissolved in water (30 mL), and 85% H_3PO_4 (26.5 mL) was added. The mixture was placed in a sample preparation bomb (Parr Model 4748), which was heated at 120 °C overnight. After the bomb was cooled to room temperature, water (15 mL) was added to the slightly yellow solution, followed by solid KCl (10 g). The precipitate was filtered off and washed with 2 M potassium acetate and methanol. When dry, it was dissolved in hot water (30 mL). When this solution was cooled to room temperature, white crystals formed. A second recrystallization gave the pure product. Yield: 8.8 g (33% based on Na_2WO_4). The IR spectrum and cyclic voltammogram were as previously reported.⁴

$[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{n-}$ Salts. In a typical experiment $\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}] \cdot 15\text{H}_2\text{O}$ (1 g) was dissolved in 12 mL of water or dilute acid (<1 M HCl) and the solution was heated to 60–70 °C. To this solution was dropwise added two equivalents of Z^{n+} , the replacing cation, as the chloride or nitrate salt dissolved in water (3 mL). If a persistent precipitate appeared ($\text{Z} = \text{Ce}^{4+}$, U^{4+}) the addition was stopped after 1 equiv of Z^{n+} had been added. The mixture was placed in a Parr Model 4746 or Model 4748 sample preparation bomb and heated to 140–180 °C overnight. After the solution had cooled to room temperature, the product was isolated by the addition of 4 g of solid KCl. In some cases when the exchange was not complete (monitored by cyclic voltammetry), unreacted $\text{NaP}_5\text{W}_{30}$ was precipitated first by addition of a small amount of KCl. After

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- (8) The "ionic radius" of a cation is known to depend upon its coordination number. In order to compare sizes of the different cations discussed in this paper, we have chosen the set of effective ionic radii of Shannon and Prewitt [*Acta Crystallogr.*, **1976**, *A32*, 751] appropriate for 6-fold coordination by oxide. The effective coordination number of the central atom in P_5W_{30} is larger than six, of course, but sufficient reliable data are not available for larger coordination numbers.
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filtration, the filtrate was treated with additional KCl to precipitate the product, which was filtered off, washed with ice water, and air-dried. Yields varied from 45 to 90% of isolated material (see Results).

All products were colorless except $\text{CeP}_5\text{W}_{30}$, which was light yellow, and UP_5W_{30} , which was light yellow-green. They were identified by cyclic voltammetry, IR, ^{31}P NMR, ^{183}W NMR, ^{23}Na NMR, electronic spectra of $\text{EuP}_5\text{W}_{30}$ and UP_5W_{30} , and EPR and elemental analysis of $\text{GdP}_5\text{W}_{30}$. Anal. Calcd (found) for $\text{K}_{12}[\text{GdP}_5\text{W}_{30}\text{O}_{110}]\cdot 54\text{H}_2\text{O}$: K, 5.3 (5.2); W, 61.1 (61.1); Gd, 2.1 (1.7); P, 2.2 (1.7). Elemental analysis was performed by E+R Microanalytical Laboratory, Inc., Corona, NY.

The free acid of $\text{EuP}_5\text{W}_{30}$ was prepared by ion exchange of a solution of the potassium salt on a column of Bio-Rad AG 50W-X2 resin, 50–100 mesh. The eluate was concentrated for electronic and NMR spectroscopy on a rotary evaporator.

Physical Measurements. Electrochemical measurements were made using a BAS-100A electrochemical analyzer with a PWR-3 power module/potentiostat. CV (cyclic voltammetry) measurements were performed using a glassy-carbon working electrode and a Ag/AgCl reference electrode. Unless otherwise stated all potentials quoted in this paper are vs Ag/AgCl. For controlled-potential electrolysis a platinum-gauze electrode was used vs a saturated calomel reference electrode. NMR spectra were recorded on a Bruker AM-300 WB spectrometer operating at a magnetic field of 300.10 MHz for protons. The resonance frequencies were 12.505 MHz for ^{183}W , 121.496 MHz for ^{31}P , and 79.391 MHz for ^{23}Na . The chemical shift standards were saturated Na_2WO_4 in D_2O for ^{183}W , 85% H_3PO_4 for ^{31}P , and 1 M NaNO_3 for ^{23}Na . All NMR spectra were recorded at 21 °C on samples dissolved in water containing ca. 15% D_2O . ESR spectra were recorded on a Varian E-4 spectrometer. A Spex Fluorolog spectrofluorimeter equipped with a xenon lamp was used for the emission measurements.

Results and Discussion

Preparation and Chemical Properties. The reaction between Ca^{2+} and $\text{NaP}_5\text{W}_{30}$ has been shown⁴ to be accompanied by the appearance of Na^+ in the solution as measured with a sodium electrode, leading to the conclusion that Ca^{2+} had replaced Na^+ in the cavity of the heteropolyanion. By reaction of a neutral or slightly acid aqueous solution of $\text{K}_{12.5}\text{Na}_{1.5}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ at 145–180 °C with 1–2 equiv of a variety of lanthanide and other metal ions having radii similar to that of Na^+ , products were obtained which contained the reacting cations and which were characterized by cyclic voltammograms and ^{31}P NMR spectra that differed from that of $\text{NaP}_5\text{W}_{30}$; see below. The yields varied with the metal ion and temperature and are summarized in Table I. While Gd^{3+} and Tb^{3+} reacted practically quantitatively at 145 °C, Eu^{3+} reacted only partly at this temperature but almost quantitatively at 165 °C. The smaller lanthanide ions Yb^{3+} and Lu^{3+} required still higher temperatures and reacted only partly even at 180 °C.

All lanthanide ions with ionic radii smaller or equal to that of Nd^{3+} ($r = 1.12 \text{ \AA}$) were found to react with $\text{NaP}_5\text{W}_{30}$, but no reaction was observed for the larger lanthanide ions Pr^{3+} ($r = 1.13 \text{ \AA}$) and Ce^{3+} ($r = 1.15 \text{ \AA}$) even at temperatures up to 180 °C. An experiment in which an equimolar solution of Nd^{3+} and Pr^{3+} was reacted with P_5W_{30} yields only the Nd^{3+} derivative. Assuming that the cations have replaced Na^+ in the central cavity, this behavior indicates an extraordinary and, to our knowledge, unprecedented¹⁰ size selectivity, since Nd^{3+} and Pr^{3+} differ in ionic radius by only 0.01 Å. In contrast, other lanthanide-containing heteropolyanions such as $[\text{Ln}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ and $[\text{Ln}(\text{SiW}_{11}\text{O}_{39})_2]^{13-}$ can be made with all lanthanide ions.^{11,12} These complexes, however, are more flexible with the lanthanide ions sandwiched between two lacunary heteropolyanion ligands, while in the $\text{P}_5\text{W}_{30}\text{O}_{110}$ heteropolyanion the size of the central

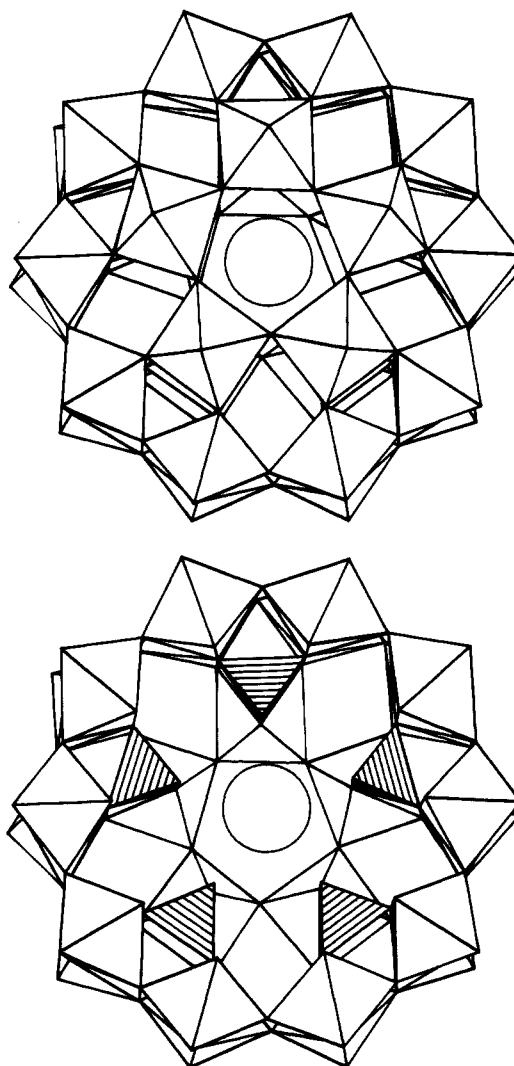


Figure 1. Top: (a) Structure of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ in polyhedral form showing WO_6 octahedra and the central Na (open circle). Bottom: (b) $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ from same perspective as in part a but with nearest ring of five WO_6 octahedra removed, revealing PO_4 tetrahedra (shaded).

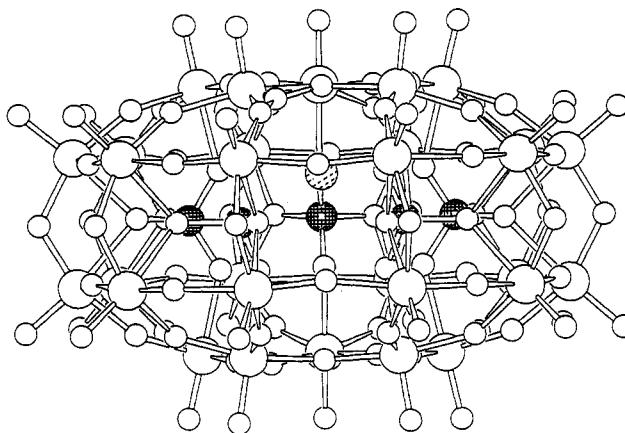


Figure 2. $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ viewed perpendicular to the anion's C_3 axis. Tungsten and oxygen atoms are represented by large and small circles, respectively, phosphorus atoms are represented by shaded circles, and the sodium atom is represented by a broken-hatched circle.

(10) Size-controlled differences in reactivity of lanthanides have been observed, but these generally involve a greater range of radii. Recent examples include Y vs Yb ($\Delta r = 0.03 \text{ \AA}$) [Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* 1986, 5, 263] and Y vs Lu ($\Delta r = 0.04 \text{ \AA}$) [Alvarez, D., Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* 1990, 5674].

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cation is restricted by the diameter of the cavity, which may not have the flexibility to expand beyond a certain well-defined size.

At the other end of the lanthanide series, Yb^{3+} ($r = 1.01 \text{ \AA}$) and Lu^{3+} ($r = 1.00 \text{ \AA}$) replaced Na^+ only partly. Presumably these ions are too small to compete effectively with Na^+ .

The smaller yields with Ce^{4+} and U^{4+} were partly due to the small solubility of the tetravalent cations with the heteropolyanion

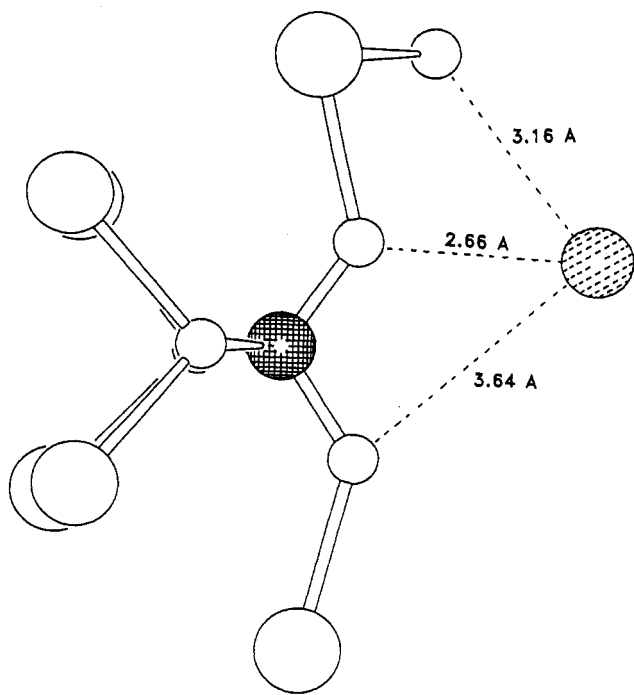


Figure 3. Part of the $[\text{NaP}_5\text{W}_{30}\text{W}_{110}]^{14-}$ structure, viewed perpendicular to C_5 axis, which is aligned vertically through the sodium atom (broken-hatched circle) as in Figure 2. One-fifth of the coordination sphere of the sodium atom is depicted. Tungsten and oxygen atoms are shown as large and small circles, respectively, and the phosphorus atom is shown as a shaded circle.

Table I. Conditions and Yields for Preparation of ZP_5W_{30} anions^a

Z^{n+}	$T/^\circ\text{C}$	% yield
Pr^{3+}	180	no reaction
Nd^{3+}	180	<80
Sm^{3+}	160	90
Eu^{3+}	145–165	45–90
Gd^{3+}	145	90
Tb^{3+}	145	90
Dy^{3+}	160	90
Ho^{3+}	160	90
Er^{3+}	160	90
Tm^{3+}	160	90
Yb^{3+}	160–180	50–70
Lu^{3+}	180	40
Ce^{4+}	160	50
Y^{3+}	160	90
Bi^{3+}	160	90
U^{4+}	160	30
Ca^{2+}	140	90

^a $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-} + \text{Z}^{n+} \rightarrow [\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-} + \text{Na}^+$. $C_{[\text{NaP}_5\text{W}_{30}]} = 8.0 \text{ Mm}$; $C_{\text{Z}^{n+}} = 8\text{--}16 \text{ mM}$.

necessitating using smaller concentrations of cations (<1 equiv compared to 2 equiv for the other metal ions). Not only did Ce^{3+} not react with $\text{NaP}_5\text{W}_{30}$ as mentioned above, but no reduction of $\text{Ce}^{\text{IV}}\text{P}_5\text{W}_{30}$ could be observed in aqueous solution (see below), further illustrating the point that Ce^{3+} might be too large for the cavity.

While ease of substitution of Na^+ by lanthanide ions seems to follow the size of their ionic radii strictly, substitution by other metal ions of similar size did not always proceed as expected. While Y^{3+} ($r = 1.04 \text{ \AA}$), U^{4+} ($r = 1.03 \text{ \AA}$), Bi^{3+} ($r = 1.17 \text{ \AA}$), and Ce^{4+} ($r = 1.01 \text{ \AA}$) did react, other metal ions with similar radii such as Cd^{2+} ($r = 1.09 \text{ \AA}$), Tl^{3+} ($r = 1.03 \text{ \AA}$), Sn^{2+} , Hg^{2+} ($r = 1.16 \text{ \AA}$), and Th^{4+} ($r = 1.08 \text{ \AA}$) did not, under the same conditions. The fact that Cd^{2+} did not react is especially surprising as the similarly sized Ca^{2+} reacted readily. It is possible that stereochemical (Hg^{2+} , Sn^{2+}) and "hard-soft" preferences might also contribute to reactivity—the polyanion cavity is lined with "hard" oxide ions.

The ZP_5W_{30} ions were stable in aqueous solution for at least 3 weeks in 1 M HCl at 25 °C, but a slow decomposition ($[\text{ZP}_5\text{W}_{30}\text{O}_{110}]^{(15-n)-} \rightarrow \text{WO}_4^{2-}$, HPO_4^{2-} , $\text{Z}(\text{OH})_n$) took place at pH 9–10 with a half-life of about 2 days in a pH 10, 0.025 M borax buffer and several weeks at pH 9, as measured voltammetrically with $\text{GdP}_5\text{W}_{30}$ using a supporting electrolyte of 1 M Na_2SO_4 .

When a solution containing $\text{EuP}_5\text{W}_{30}$ in 1 M NaCl was heated at 160 °C for 24 h, no detectable amount of $\text{NaP}_5\text{W}_{30}$ was observed although $\text{LuP}_5\text{W}_{30}$ under the same conditions gave mostly $\text{NaP}_5\text{W}_{30}$. These observations combined with the yields in the preparations of ZP_5W_{30} (Table I) shows increased stability of $\text{LnP}_5\text{W}_{30}$ over $\text{NaP}_5\text{W}_{30}$, as expected from the more highly charged Ln^{3+} ions, and that $\text{LuP}_5\text{W}_{30}$ is less stable than $\text{EuP}_5\text{W}_{30}$. This was further shown by the observation that Eu^{3+} replaced ca. 85% of Lu^{3+} in $\text{LuP}_5\text{W}_{30}$ when a 2:1 mixture was heated at 160 °C for 20 h.

The observation that different Ln^{3+} ions reacted with $\text{NaP}_5\text{W}_{30}$ with different efficiency suggested that $\text{NaP}_5\text{W}_{30}$ might be used to separate mixtures of lanthanides. To test this notion some competition experiments were performed in which mixtures of two Ln^{3+} ions and $\text{NaP}_5\text{W}_{30}$ in 1:1:1 ratio were heated at 160 °C for 20 h and the products examined by ^{31}P NMR of the reaction mixture. Solutions containing Sm^{3+} and the smaller Yb^{3+} gave only $\text{SmP}_5\text{W}_{30}$ as product, while the neighboring Sm^{3+} and Eu^{3+} reacted to give a mixture of $\text{SmP}_5\text{W}_{30}$ and $\text{EuP}_5\text{W}_{30}$ in a 1:4 ratio. When mixtures of Eu^{3+} and Tb^{3+} were used $\text{EuP}_5\text{W}_{30}$ was the only product. It thus appears that $\text{NaP}_5\text{W}_{30}$ efficiently separates smaller Ln^{3+} ions from larger ones and preferentially reacts with Eu^{3+} rather than Sm^{3+} . Once incorporated in the heteropolyanion, the free Ln^{3+} ions can be recovered by basic hydrolysis.

IR Spectroscopy. The IR spectra of all the products were practically identical and differed only slightly from the parent $\text{NaP}_5\text{W}_{30}$ heteropolyanion; the only consistent differences being in the position and size of one of the P–O stretching bands (1073 cm^{-1} (m) for $\text{NaP}_5\text{W}_{30}$ and 1060 cm^{-1} (s) for ZP_5W_{30}) and a better resolved peak at 980 cm^{-1} for $\text{NaP}_5\text{W}_{30}$. The splitting of the 1160-cm^{-1} P–O stretching band reported⁴ for $\text{CaP}_5\text{W}_{30}$ was not seen and may have been due to an impurity or artifact in the earlier spectrum.

NMR Spectroscopy. In the ^{23}Na NMR spectrum of $\text{NaP}_5\text{W}_{30}$ it was found that the coordinated sodium ion gave rise to a broad line at a slightly different frequency from that of the free sodium ion.⁴ In order to test whether Na^+ had indeed been replaced by the reacting cations in the ZP_5W_{30} complexes ^{23}Na NMR spectra of the acid (more soluble) forms of YP_5W_{30} and $\text{NaP}_5\text{W}_{30}$ were attempted using the same conditions of concentration and instrumentation. The Y^{3+} complex was chosen because it is diamagnetic so that no significant shift from $\text{NaP}_5\text{W}_{30}$ or line broadening would be expected if Na^+ were still coordinated. No Na resonances were observed for YP_5W_{30} supporting the notion that the observed reaction is indeed a displacement of Na^+ by the reacting cations and not attachment at another site of the heteropolyanion.

The ^{31}P NMR chemical shifts of ZP_5W_{30} are shown in Table II. A single ^{31}P NMR line was observed for all complexes except for YP_5W_{30} which gave a doublet with a coupling constant of 1.6 Hz. These data confirm that all the phosphorus atoms are equivalent (as expected) in ZP_5W_{30} , the doublet in YP_5W_{30} presumably being due to splitting caused by ^{89}Y (100%, $I = 1/2$). ^{31}P NMR spectra of the ZP_5W_{30} ions (Table II) gave shifts for diamagnetic Z^{3+} ions of -8.2 to -10.2 ppm, for $\text{NaP}_5\text{W}_{30}$ -9.4 ppm, for $\text{CaP}_5\text{W}_{30}$ -11.1 ppm, for $\text{CeP}_5\text{W}_{30}$ -16 ppm, and for UP_5W_{30} -15.5 ppm. For the paramagnetic Ln^{3+} ions the shifts varied from $+18$ to -68 ppm and widths varied from $5\text{--}240$ Hz except for $\text{GdP}_5\text{W}_{30}$, which gave no observable spectrum.

Some of the lanthanides induced shifts to higher frequency, others to lower frequency, as was also observed for $[\text{Ln}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$.¹² The lanthanide induced shifts, LIS_{obs} , taken as the

Table II. ^{31}P NMR Spectral Data for ZP_5W_{30}

Z^{n+}	δ/ppm	$\Delta\nu_{1/2}/\text{Hz}$	$\text{LIS}_{\text{obs}}^a$
Nd $^{3+}$	-15.0	8.8	+4.9
Sm $^{3+}$	-9.5	4.6	+0.6
Eu $^{3+}$	0.7	5.0	+10.8
Gd $^{3+}$
Tb $^{3+}$	-27.2	175	-17.1
Dy $^{3+}$	-68.1	241	-58.0
Ho $^{3+}$	-40.0	222	-29.9
Er $^{3+}$	1.8	151	+11.9
Tm $^{3+}$	17.6	68	+27.7
Yb $^{3+}$	9.1	16	+19.2
Lu $^{3+}$	-10.1		...
Y $^{3+}$	-10.2 (d) ^b		
Bi $^{3+}$	-8.2		
Ce $^{4+}$	-16.0	4.5	
U $^{4+}$	-15.5	5.5	
Na $^+$	-9.4		
Ca $^{2+}$	-11.1		

^a Lanthanide induced shift, $\delta(\text{Ln}) - \delta(\text{Lu})$. ^b $^2J(\text{P-O-Y}) = 1.6$ Hz.

observed shifts for $\text{LnP}_5\text{W}_{30}$ minus the observed shift for $\text{LuP}_5\text{W}_{30}$, are known¹³⁻¹⁵ to be expressed as a sum of the pseudocontact (dipolar, through space) shift, LIS_{pc} , and the contact (scalar, through bonds) shift, LIS_{c} .

$$\text{LIS}_{\text{obs}} = \text{LIS}_{\text{pc}} + \text{LIS}_{\text{c}} \quad (1)$$

$$\text{LIS}_{\text{pc}} = C_j \frac{[\beta^2 \langle r^2 \rangle 2A_2^0 (3 \cos^2 \theta - 1) + \beta^2 \langle r^2 \rangle 2A_2^2 \sin^2 \theta \cos 2\phi]}{60(kr)^2 r^3} \quad (1a)$$

$$\text{LIS}_{\text{c}} = \frac{\left(\frac{A}{h}\right) \langle S_z \rangle}{\frac{\gamma B_0}{2\pi}} \quad (1b)$$

where

$$C_j = g^2 J(J+1)(2J-1)(2J+3) \langle J \| a \| J \rangle$$

and r , θ , ϕ are spherical coordinates of the observed nucleus (P) with respect to the lanthanide, β is the Bohr magneton, A is the electron-nuclear hyperfine coupling constant, γ is the magnetogyric ratio, $\langle r^2 \rangle 2A_2^0$ and $\langle r^2 \rangle 2A_2^2$ are ligand field terms, and the other symbols have their usual significance. Values of C_j , which determine shifts to higher or lower frequency, have been calculated by Bleaney¹⁴ for each lanthanide ion. The spin expectation values $\langle S_z \rangle$ have been tabulated by Golding and Halton.¹⁵

According to eqs 1a and 1b a plot of the measured LIS_{obs} values versus Bleaney's C_j values should be linear if the origin of the shift is purely pseudocontact and the complexes are isostructural. Deviation from linearity indicates that the measured LIS_{obs} values are not purely pseudocontact. Similarly a linear plot of LIS_{obs} versus $\langle S_z \rangle$ would be expected for purely contact shifts. It has been suggested¹⁶ that isotropic shifts of nuclei four or more bonds removed from the lanthanide may be considered exclusively pseudocontact in origin. In $[\text{Ln}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ the phosphorus atom is four bonds away from Ln, and the LIS dependence is found to be appreciable if not predominantly pseudocontact by comparison of C_j and LIS_{obs} values.¹² The

observed deviation from linearity in that case was ascribed to structural changes of the heteropolyanion as the lanthanide varied. In the present series of $\text{LnP}_5\text{W}_{30}\text{O}_{110}$, the lanthanide is separated from the phosphorus atoms by only two bonds. A plot of LIS_{obs} versus C_j showed a fairly good linear dependence ($r^2 = 0.97$) with only $\text{TbP}_5\text{W}_{30}$ deviating from the line. A plot of LIS_{obs} versus $\langle S_z \rangle$ showed random scattering ($r^2 = 0.52$). It thus seems that pseudocontact term predominates for $\text{LnP}_5\text{W}_{30}\text{O}_{110}$ as well, even if the distance between Ln^{3+} and P is only two bonds.

Rewriting eqs 1a and 1b as $\text{LIS}_{\text{obs}} = GC_j + F\langle S_z \rangle$ or $\text{LIS}_{\text{obs}}/\langle S_z \rangle = G(C_j/\langle S_z \rangle) + F$ allows one to determine G and F graphically and to calculate the pseudocontact contribution to LIS_{obs} .¹⁷ A plot of $\text{LIS}_{\text{obs}}/\langle S_z \rangle$ versus $C_j/\langle S_z \rangle$ gave a fairly linear plot ($r^2 = 0.89$) with $G = 0.36$ and $F = -0.36$. The fraction of LIS that may be ascribed to a pseudocontact contribution may be estimated from $|GC_j|/(|F\langle S_z \rangle| + |GC_j|)$. Values ranging from 75 to 94% pseudocontact were calculated for the coordinated lanthanide ions except for Eu^{3+} , which gave 44%. The LIS of the Sm derivative was too small to be evaluated accurately, and the Gd complex should only have a contact shift, if it could have been observed. It is not inconceivable that some minor structural changes occur along the lanthanide-heteropolyanion series due to the differences in ionic radius of Ln^{3+} , but no obvious pattern was evident.

The ^{183}W NMR spectrum of $\text{EuP}_5\text{W}_{30}$ gave four lines at 62.5 ppm (d, 5W, $J(\text{P-O-W}) = 3.8$ Hz), -201.7 ppm (s, 10W), -209.5 ppm (s, 10W), and -297.5 ppm (d, 5W, $J(\text{P-O-W}) = 1.9$ Hz) with an intensity ratio of 1:2:2:1. This spectrum is comparable to that of $\text{NaP}_5\text{W}_{30}$ which consists of four lines at -209.6 ppm (d, 10W, $J(\text{P-O-W}) = 1.25$ Hz), -211.6 ppm (d, 10W, $J(\text{P-O-W}) = 1.28$ Hz), -277.25 ppm (d, 5W, $J(\text{P-O-W}) = 1.27$ Hz), and -289.6 ppm (d, 5W, $J(\text{P-O-W}) = 1.32$ Hz). The major difference between the two ^{183}W NMR spectra is in the downfield shift of one of the 5W lines by ca. 350 ppm. In the $[\text{Ln}(\text{PW}_{11}\text{O}_{39})_2]$ series it was observed that only resonances for the tungsten atoms that were two bonds away from the paramagnetic ion were shifted significantly in comparison to the diamagnetic analogs.¹² The observation that the ^{183}W spectrum of $\text{EuP}_5\text{W}_{30}\text{O}_{110}$ displays the same pattern as that of $\text{NaP}_5\text{W}_{30}\text{O}_{110}$ with only one of the 5W lines displaced significantly to a different frequency confirms that Eu^{3+} has replaced Na^+ and occupies a similar site in the complex as did Na^+ , being closer to one of the outer 5-tungsten planes than to the other (Figure 2). As illustrated in Figure 3, the sodium in $\text{NaP}_5\text{W}_{30}$ is connected to tungsten in the closest outer plane via oxygen atoms which are 2.66 Å from the metal ion, while the Na-O distance in Na-O-W to the other outer ring was 3.64 Å. Tungstens in the inner 10-tungsten rings are four bonds removed from the central ion and by comparison to $\text{Ln}(\text{PW}_{11}\text{O}_{39})_2$ would not be expected to be strongly shifted by a paramagnetic species.

Electrochemistry. As for the parent $\text{NaP}_5\text{W}_{30}$, several reduction steps to heteropoly blue species were observed for ZP_5W_{30} . In 1 M HCl there are five reduction steps between 0 and -0.6 V for all ZP_5W_{30} anions except $\text{EuP}_5\text{W}_{30}$ and $\text{CaP}_5\text{W}_{30}$ which showed only four reductions; see Table III. This pattern contrasts with that of $\text{NaP}_5\text{W}_{30}$ under the same conditions, which showed two reduction steps of four electrons each at -0.18 and -0.30 V and one additional multielectron step at -0.52 V (Figure 4). It thus appears that the first two reduction steps of the $\text{NaP}_5\text{W}_{30}$ ion have split into four two electron steps in the ZP_5W_{30} ions, (except for $\text{EuP}_5\text{W}_{30}$ and $\text{CaP}_5\text{W}_{30}$, where only the first step was split).

At higher pH, further splitting of the reduction steps occurs, as is commonly observed for other heteropolyanions¹⁸ and is attributed to the deprotonation of the reduced species. At pH

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Table III. Voltammetric Reduction Potentials^a for [ZP₅W₃₀O₁₁₀]ⁿ⁻

Z ⁿ⁺	E/V vs Ag/AgCl				
Nd ³⁺	-0.12	-0.22	-0.35	-0.41	-0.50
Sm ³⁺	-0.11	-0.20	-0.32	-0.40	-0.50
Eu ³⁺	-0.12	-0.22	-0.32 ^b		-0.49
Gd ³⁺	-0.11	-0.21	-0.33	-0.41	-0.49
Tb ³⁺	-0.10	-0.20	-0.32	-0.41	-0.48
Dy ³⁺	-0.12	-0.21	-0.34	-0.41	-0.50
Ho ³⁺	-0.12	-0.21	-0.32	-0.41	-0.50
Er ³⁺	-0.11	-0.20	-0.32	-0.40	-0.49
Tm ³⁺	-0.10	-0.20	-0.31	-0.39	-0.49
Yb ³⁺	-0.13	-0.22	-0.34	-0.41	-0.50
Lu ³⁺	-0.10	-0.20	-0.31	-0.38	-0.49
Y ³⁺	-0.11	-0.20	-0.32	-0.40	-0.49
Bi ³⁺	-0.11	-0.19	-0.27	-0.34	-0.45
Ce ⁴⁺	-0.10	-0.20	-0.31	-0.39	-0.46
U ⁴⁺	-0.08	-0.18	-0.32	-0.46	-0.53
Na ⁺	-0.18 ^b		-0.30 ^b		-0.52
Ca ²⁺	-0.16	-0.21	-0.33 ^b		-0.49

^a $1/2(E_{pc} + E_{pa})$, 1.0 M HCl; All are 2-electron steps except where noted. ^b 4-electron step.

5–10 eight reductions were observed between 0 and -1400 mV for most ZP₅W₃₀, the first two reductions involving one-electron processes; see Figure 4. While the one-electron steps were nearly reversible ($\Delta E \sim 60$ mV), the others were less so (ΔE varied from 80 to 160 mV).

No oxidations of the central cation were observed for any ZP₅W₃₀ in aqueous solution, which is surprising for Z = U^{IV}. Heteropolyanions are known¹⁹ to stabilize higher oxidation states of coordinated metal ions probably because of the high negative charges of the polyanion. A reversible U^{4+/5+} oxidation state has been observed²⁰ at +0.94 V vs SCE (+0.96 V vs Ag/AgCl) for [U^{IV}(PW₁₁O₃₉)₂]¹⁰⁻ in 1 M H₂SO₄. No such step was observed for the present UP₅W₃₀ at potentials as high as +1.8 V vs Ag/AgCl.

The question arises as to whether the isolated CeP₅W₃₀ contains Ce(III) or Ce(IV). No Ce(IV/III) CV reduction waves were observed between +1.8 and -0.1 V. Between -0.1 and -1.4 V several W(VI/V) waves appear, but this part of the cyclic voltammogram was identical to those of other LnP₅W₃₀. Also an attempted controlled-potential electrolysis at +0.1 V in a 1 M HCl solution showed no evidence of reduction. Cerium(IV) compounds are generally known to be strong oxidants ($E^{\circ}_{Ce(IV/III)} = +1.44$ V vs NHE) in 1 M H₂SO₄ and several Ce(IV) heteropolyanions, such as [CeW₁₀O₃₆]⁸⁻, [Ce(SiW₁₁O₃₉)₂]¹²⁻, [Ce(PW₁₁O₃₉)₂]¹⁰⁻, [Ce(P₂W₁₇O₆₁)₂]¹⁶⁻ have Ce(III/IV) redox potentials of +1.1 to +0.8 V.²¹ Although most Ce(III) compounds are colorless, the Ce(III) heteropolyanions are light brown due to Ce^{III} → W^{VI} charge transfer. That the present light yellow CeP₅W₃₀ complex is indeed a Ce(IV) compound is thus not evident from its color only. The ³¹P NMR spectrum shows a fairly small downfield shift (5 ppm) from the diamagnetic LuP₅W₃₀. This shift is similar in magnitude to the shift observed for paramagnetic [Ce^{III}(PW₁₁O₃₉)₂]¹¹⁻ and is also similar to the ³¹P chemical shift of UP₅W₃₀ which has two unpaired electrons. However, these shifts are relatively small so ³¹P NMR does not solve the question of the oxidation state of cerium in CeP₅W₃₀. The most compelling evidence for Ce^{IV}P₅W₃₀ comes from its method of preparation. Cerium(III) did not react with NaP₅W₃₀ while Ce(IV) did so readily. Indeed by comparison with the other lanthanide ions, Ce(III) ($r = 1.15$ Å) should be too big to enter the heteropolyanion while Ce(IV) ($r = 1.01$ Å) has the right size. That no reduction of Ce^{IV}P₅W₃₀ was observed down to -1.4 V shows an extraordinary stabilization of the Ce(IV) oxidation state by the P₅W₃₀O₁₁₀ anion, a stabilization which seems likely to be due to the inability of the ligand to expand its cavity to accommodate the larger Ce(III) ion.

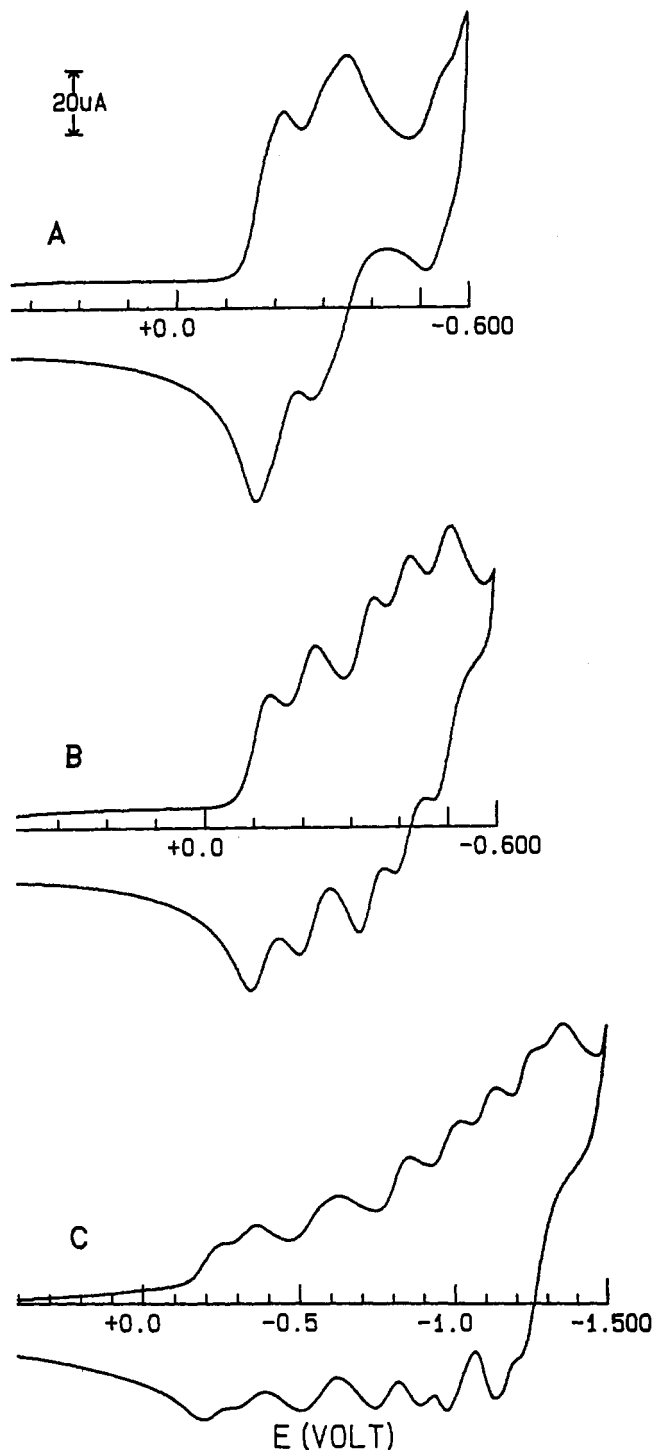


Figure 4. Cyclic voltammograms recorded with a glassy carbon working electrode, Ag/AgCl reference electrode, and a sweep rate of 200 mV s⁻¹ (concentration of heteropolyanion, 1.0 mM): (A) [NaP₅W₃₀O₁₁₀]¹⁴⁻, 1.0 M HCl; (B) [GdP₅W₃₀O₁₁₀]¹²⁻, 1.0 M HCl; (C) [GdP₅W₃₀O₁₁₀]¹²⁻, pH 10.0 (0.025 M borax/NaOH, 1 M Na₂SO₄).

ESR Spectroscopy. The room-temperature X-band ESR spectrum of GdP₅W₃₀, recorded on a polycrystalline sample of GdP₅W₃₀, diluted 1:2 in a TbP₅W₃₀ matrix, is shown in Figure 5. The spectrum arises from transitions between the four Kramers doublets of the ⁸S_{7/2} ground state of Gd(III).²² When the zero-field splitting is small as is the case here, seven allowed transitions are observed at each orientation of the crystal. The powder spectrum represents the sum of individual spectra of all possible orientations. A spectrum recorded at 77 K showed no additional features.

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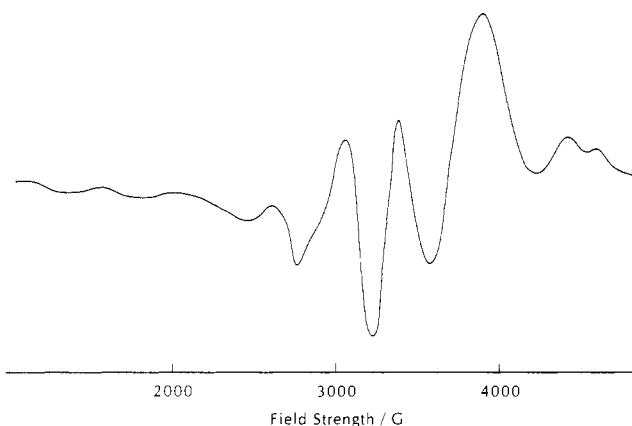


Figure 5. X-Band ESR spectrum of powdered $K_{12}[GdP_5W_{30}O_{110}]$ at 298 K.

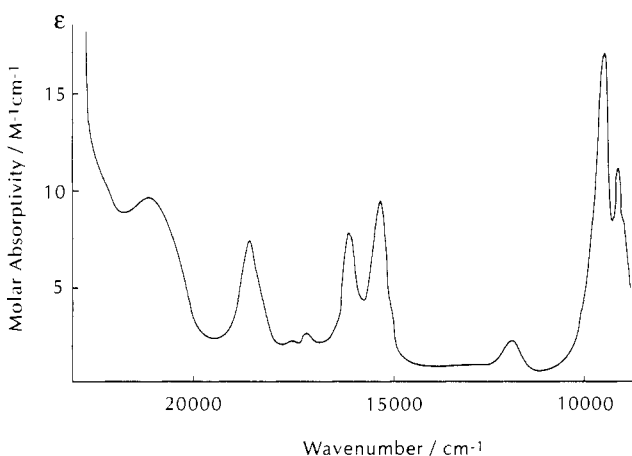


Figure 6. Visible-near-IR absorption spectrum of $[UP_5W_{30}O_{110}]^{11-}$ in 1 M H_2SO_4 .

Electronic Spectroscopy. All ZP_5W_{30} complexes absorb strongly in the UV. The low intensity electronic absorption spectrum of UP_5W_{30} is shown in Figure 6. It is broadly similar, but not identical, to that of $[U^{IV}Mo_{12}O_{42}]^{8-}$.²⁰ A concentrated solution of EuP_5W_{30} showed weak absorbances at 464 and 525 nm. Intense polytungstate absorption below 400 nm obscured further Eu bands.

Emission Spectroscopy. Excitation of a ca. 0.2 M aqueous solution of $H_{12}EuP_5W_{30}O_{110}$ into the 464.7 nm Eu^{3+} absorption line at 30 °C gave the emission spectrum presented in Figure 7. The spectrum shows broad bands at positions characteristic for Eu^{3+} luminescence arising from transitions ${}^5D_0 \rightarrow {}^7F_J$. The strongest emissions are in the ${}^5D_0 \rightarrow {}^7F_1$ and 7F_2 transition regions which have about equal intensity while the ${}^5D_0 \rightarrow {}^7F_3$ transition is weak and the ${}^5D_0 \rightarrow {}^7F_0$ is either absent or obscured by the ${}^5D_0 \rightarrow {}^7F_1$ band. The poor resolution of the bands does not allow any detailed analysis of the symmetry and structural nature of the Eu^{3+} coordination site.²³ No emission was observed from solid powdered samples at room temperature or at 0 °C. In this respect it resembles $K_{17}Eu(P_2W_{17}O_{61})_2$.²⁴

Relaxation Studies. Labile Gd^{3+} complexes with inner sphere coordinated water are known to catalyze the proton relaxation of water. A measure of this effect is the relaxivity, R , which is obtained as the slope of T_1^{-1} versus concentration of the Gd complex. The relaxivity is dependent on the hydration number so that for $[Gd(H_2O)_{8-9}]^{3+}$, $R = 9.1 \text{ mM s}^{-1}$ measured at 20 and 90 MHz, for $[Gd(H_2O)_{2-3}]^{3+}$, $R = 4.6 \text{ mM s}^{-1}$ (90 MHz), and for $[Gd(H_2O)_{cav}]^{3+}$, $R = 2.0 \text{ mM s}^{-1}$ (20 MHz).²⁵ One way to determine whether Gd^{3+} is indeed situated in the cavity of the

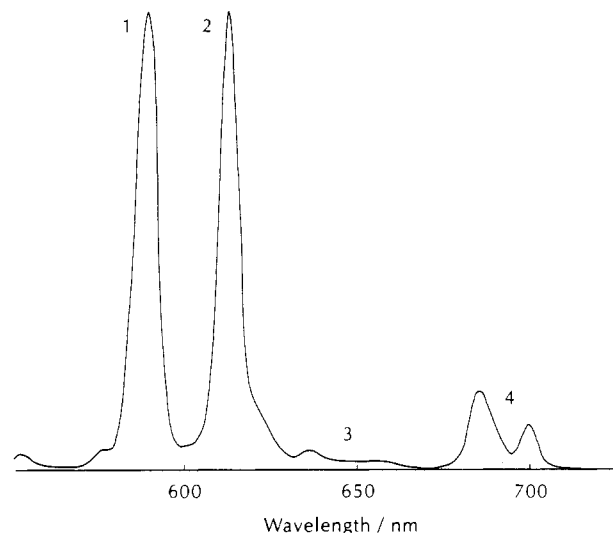


Figure 7. Emission spectrum of $H_{12}[EuP_5W_{30}O_{110}]^{(12-n)-}$ in a concentrated aqueous solution. Excitation wavelength is 464.7 nm at 303 K. Values of J for the transitions ${}^5D_0 \rightarrow {}^7F_J$ are given.

P_5W_{30} heteropolyanion where it would have no possibility to be coordinated by water, is to measure its relaxivity. At 21 °C a preliminary value of ca. 1.0 mM s^{-1} was obtained at 300 MHz using an inversion-recovery sequence. Relaxivities are frequency dependent, but the very low value found seems to confirm that Gd^{3+} in GdP_5W_{30} does not have the ability to exchange coordinated water with bulk water and is indeed situated in the cavity.

Conclusions

It has proven possible to replace Na^+ in the stable $[NaP_5W_{30}O_{110}]^{14-}$ with various (but not all) lanthanide and other metal ions having ionic radii similar to that of Na^+ . That the observed reactions were actual substitution reactions of Na^+ and not substitution of the metal ions at another site of the heteropolyanion was shown by a variety of techniques. The lanthanide ions reacted with different efficiency; the medium sized ions were the most reactive, the smallest reacted with difficulty, and the largest, Pr^{3+} , and Ce^{3+} , not at all under equivalent conditions (≤ 180 °C). The difference in reactivity may prove useful in separating mixtures of lanthanides. Cerium(IV) reacted readily, but the product could not be reduced to $Ce^{III}P_5W_{30}$ at potentials more positive than -1.4 V , probably because the cavity in the heteropolyanion was too small to accommodate the larger Ce(III) ion. This is an unprecedented stabilization of a Ce(IV) compound.

Despite the large negative charge on $UP_5W_{30}O_{110}^{11-}$ no oxidation of $U^{IV}P_5W_{30}$ to $U^{VP_5W_{30}}$ was observed. While it is conceivable that the cavity cannot expand to hold the larger Ce(III) ion, it is not clear why a smaller U(V) ion cannot be generated, as it has been observed in other heteropolyanions of similar charge.

The complexes exhibited extraordinary stability toward hydrolysis for heteropolyanions, covering a range from 6 M HCl to pH 9–10.

Acknowledgment. This work has been supported in part by a grant from ARCO Chemical Co. We are indebted to Chaoying Rong for measurement of NMR spectra and to Dr. Michael Dickman and Feibo Xin for assistance in preparation of the figures. Figures 2 and 3 were generated by SCHAKAL 88B/V16 (copyright Egbert Keller, University of Freiburg).

Supplementary Material Available: Stereoview versions of parts a and b of Figure 1 (2 pages). Ordering information is given on any current masthead page.

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