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Lanthanide Complexes of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$: Solid State and Solution Studies

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We have isolated the 1:1 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ complexes for a series of lanthanides. The single-crystal X-ray structure of the Eu^{3+} analogue reveals two identical $[Eu(H_2O)_3(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ moieties connected through two Eu–O–W bonds, one from each polyoxometalate unit. An inversion center relates the two polyoxometalate units. The Eu(III) ion is substituted for a $[WO]^{4+}$ unit in the "cap" region of the tungsten–oxygen framework of the parent Wells–Dawson ion. The point group of the dimeric molecule is C_i. The extended structure is composed of the $[Eu(H_2O)_3(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]_2^{14-}$ anions linked together by surface-bound potassium cations. The space group is $P\bar{1}$, $a = 12.7214(5)$ Å, $b = 14.7402(7)$ Å, $c = 22.6724(9)$ Å, $\alpha = 71.550(3)°$, $\beta = 84.019(3)°$, $\gamma = 74.383(3)°$, $V = 3883.2(3)$ Å^3, $Z = 1$. The solution studies, including ^{183}W NMR spectroscopy and luminescence lifetime measurements, show that the molecules dissociate in solution to form monomeric $[Ln(H_2O)_4(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ species.

Introduction

Polyoxometalates may be versatile inorganic building blocks for the construction of molecular-based materials. By means of their multiple coordination requirements and oxophilicity, lanthanide (Ln) cations are suitable to link polyoxometalates to form new classes of materials with potentially useful magnetic and luminescent properties.

Lanthanide ions link polyoxometalates (Nb, Mo) by binding to surface bridging or terminal oxygen atoms. For example, Er(III) ions complexed to a triad of surface bridging oxygen atoms of the $UMo_{12}O_{40}^{8-}$ anion form an oligomeric species.[1] Clusters of Eu(III) ions bind to the bridging Nb−O oxygen atoms of the isopolyanion, $Nb_6O_{19}^{8-}$, in $\{[Eu_3O(OH)_3(H_2O)_3]_2Al_2(Nb_6O_{19})_5\}^{26-}$.[2] Complexes of lanthanide ions bound to the surface of $(Mo_8O_{26})^{4-}$ units via terminal Mo=O oxygen atoms have been reported.[3] Each Eu(III) in the cluster $[Eu_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})\ _4]^{16-}$ binds to four terminal Mo=O oxygen atoms of $[Mo_7O_{24}]^{6-}$ polyoxometalates.[4] Lanthanide ions may bind to terminal W=O bonds of a basic polyoxotungstate, formed by replacement of a $[W{=}O]^{4+}$ moiety by a lower charged unit.[5] Such bonding is found in the extended polymeric solid state structures where the Ln ion in the $(H_2O)_nLn(SiW_{11}O_{39})^{5-}$ species (Ln = La(III), Ce(IIII)) binds to terminal tungsten oxygen atoms of two different $(H_2O)_nLn(SiW_{11}O_{39})^{5-}$ units.[6]

Lanthanide ions also bind to the basic oxygen atoms at a defect site in *lacunary* polyoxometalates. For example, $Eu_3(H_2O)_3(W_5O_{18})_3(SbW_9O_{33})]^{18-}$ clusters have been formed by linking lacunary XW_9 ($SbW_9O_{33}^{7-}$ and $AsW_9O_{34}^{9-}$) units and $W_5O_{18}^{6-}$ units with lanthanide ions.[7] The largest tungstate recorded, a cyclic assembly $[Ln_{16}As_{12}W_{148}O_{524}(H_2O)_{36}]^{76-}$, is composed of lacunary $AsW_9O_{34}^{9-}$ units and $W_5O_{18}^{6-}$ units linked by Ln(III) cations.[8] We reported a new family of

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tungstates, stable in the solid state and in solution, assembled from $(PW_9O_{34})^{9-}$ clusters and Ln(III) cations.[9]

We have studied lanthanide(III) complexes of the monovacant $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ and $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ isomers, derivatives of the well-known *plenary* heteropolytungstate, $(\alpha\text{-}P_2W_{18}O_{62})^{6-}$ (Wells−Dawson ion).[10−13] We report here an extension of our work on the solution (Ln = Nd−Lu) and solid state chemistry (Ln = Eu) of Ln complexes of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$. In the solid state two $[(H_2O)_4Eu[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{7-}$ species are linked to each other via Eu bonding to terminal W−O oxygen atoms to form a centrosymmetric dimer. The "dimers" are linked by potassium cations binding to surface (bridging and terminal W−O bonds) of the polyoxometalate. The dimer dissociates upon dissolution in aqueous solution.

Two crystal structures of lanthanide $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ derivatives have been reported: $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$ (tungsten framework found only) shows the 1:2 Ce(IV):α-2-heteropolyanion formulation.[14] We have recently reported the crystal structure for the $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ species.[13] The 1:1 complexes have been observed by titration but have not been isolated. Spectrophotometric titrations and electrochemical data suggest the existence of $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ as well as the 1:2 complex, $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$.[15,16] The 1:1 and 1:2 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ species have been observed in ^{31}P NMR titration experiments.[17] In this study, where the titration data was collected under highly acidic conditions, conclusions were drawn that the early lanthanide ions formed 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. Recently, the 1:1 La and Ce:$SiW_{11}O_{39}$ species, polymeric in the solid state and monomeric in solution, have been reported.[6]

Experimental Section

General Comments. All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Distilled, deionized water was used throughout. The "Wells−Dawson" ion, $(P_2W_{18}O_{62})^{6-}$ as the potassium salt, was prepared using literature methods.[18] The α-2 lacunary isomer, $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$, was prepared following the method of Finke.[19] The potassium salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ 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.[20] The standardization of the Li^+ or Na^+ salt of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ was accomplished by spectrophotometric titration with cobalt(III) as described previously for the $[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]^{10-}$ complex.[12] Elemental analysis was performed by Kanti Industries, Tonawanda, NY. Infrared spectra were measured from KBr pellets using a Perkin-Elmer series 1600 FTIR.

Preparation of Complexes. 1:1 Eu:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ Complex; $K_7[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]$ (1). The lacunary $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ (5 g, 1.017 mmol) was dissolved in 50 mL of 0.5 M sodium acetate buffer at pH = 5.5 at 70 °C to form a clear solution. $EuCl_3$ (1.20 g, 3.08 mmol) was dissolved in a minimum amount of water and added dropwise to the stirring $K_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ solution. KCl (5 g) was added to the reaction mixture, and the clear solution was cooled in the refrigerator. After 2 h, a white precipitate formed, which contained a small impurity of the 1:2 sandwich complex, according to ^{31}P NMR spectroscopy. The precipitate was dissolved in 50 mL of sodium acetate buffer at pH 5.5 at 70 °C, and 1.5 mL of 1.0 M $EuCl_3$ was added, followed by the addition of 3 g of KCl. The clear solution was cooled to 0 °C. A white precipitate formed after a few hours and was collected and recrystallized twice from hot water at 70 °C.

Crystallization of 1 To Give $K_{13}(H_3O)[Eu(H_2O)_3(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]_2\cdot 2KCl\cdot 50H_2O$. To a solution of $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ (0.01 g in 1 mL of water) was added one drop of saturated KCl; the solution remained clear. The solution was evaporated at room temperature slowly to yield colorless crystals after 3 days. Elemental analysis was performed on a sample obtained from a bulk crystallization experiment that was carried out in a similar fashion as the experiment that yielded the crystal selected for the X-ray analysis. Generally, the number of H_2O molecules varies from 40 to 60 between different crystallization experiments. Elemental anal. of the crystals. Calcd for $K_{13}(H_3O)[Eu(H_2O)_3(P_2W_{17}O_{61})]_2\cdot 2KCl\cdot 50H_2O$: W, 60.70; Eu, 2.95; P, 1.20; K 5.70. Found: W, 61.2; Eu, 3.10; P, 1.32; K, 5.67.

1:1 Lu:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ Complex; $K_7[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]$ (2). This compound was prepared similarly to **1**, above. Calcd for $K_7[Lu(P_2W_{17}O_{61})]\cdot 16\ H_2O$: W, 63.78; Lu, 3.57; P, 1.26; K, 5.58. Found: W, 62.04; Lu, 3.06; P, 1.18; K, 5.50. TGA data shows 16.0 H_2O.

Laser Excitation Luminescence Spectroscopy. Luminescence experiments were performed at Penn State University using equipment and the Peakfit program that was described in previous references.[12,13,21] All measurements were carried out at 25.0 ± 0.1 °C. The concentration of the samples used for the measurements was in the 100 nM to 250 μM range. For lifetime measurements of the Eu(III) excited state in D_2O, the complexes were recrystallized once and lyophilized two times from 99.99% D_2O.

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

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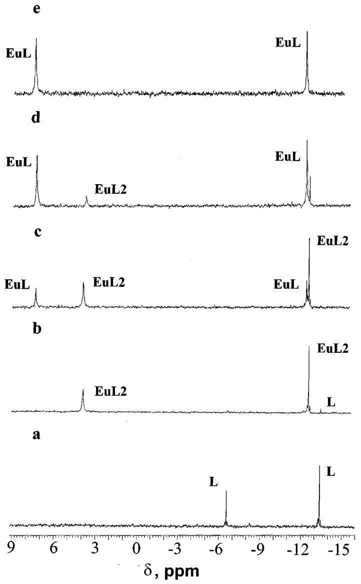

Figure 1. ^{31}P NMR titration data for $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ with Eu^{3+} at pH = 4.7. L = lacunary $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$; EuL2 = 1:2 Eu^{3+}:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$; EuL = 1:1 Eu^{3+}:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$. Ratio of Eu^{3+}:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$: (a) 0, (b) 1:2, (c) 3:4, (d) 1:1, (e) 6:4.

included the following: spectral width, 10000 Hz; acquisition time, 0.8 s; pulse delay, 1s; pulse width, 15 μs (50° tip angle). From 200 to 500 scans were required. For ^{183}W spectra, typical conditions included the following: spectral width, 10000 Hz; acquisition time, 1.6 s; pulse delay, 0.5 s; pulse width, 50 μs (45° tip angle). From 1000 to 30000 scans were acquired. For all spectra, the temperature was controlled to ±0.2 deg. ^{31}P spectra were referenced 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.

Titration of $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ with $LnCl_3$ Monitored by ^{31}P NMR Spectroscopy. Standardized buffered $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ solution (0.5 mL) was placed into a 5 mm NMR tube. The concentrations were in the range 0.022−0.025 M, buffered with lithium acetate for Eu and sodium acetate for La, Lu; the solution contain 30% D_2O. The ^{31}P NMR spectrum was recorded. Aliquots of 25−30 μL of the standardized $LnCl_3$ solution (concentration is ca. 0.1 M) were added, the resulting solution was shaken well in the NMR tube, and the ^{31}P NMR spectrum was recorded immediately upon mixing. The titration data for Eu, are shown in Figure 1. ^{31}P NMR chemical shifts for the 1:1 and 1:2 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ species are given in Table 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 furthest from the site of substitution (or defect).

Solution of Crystal Structure. A single crystal of **1** was attached to a glass fiber and mounted on a Brüker Siemens diffractometer equipped with a SMART CCD detector and a graphite monochromator (Kα wavelength = 0.71073 Å) for data collection at 173(2) K**.** The raw data was corrected for Lorentz−polarization and absorption effects (face-indexed numerical correction) using SAINT/SADABS. The crystal structure solution was performed as described elsewhere.[13] The largest residual peaks are located close to the metal atoms in a final difference map. The highest residual electron density from the difference electron map is 4.274 e Å^{-3}. Large residual peaks in the final difference map are a common problem encountered in the solution and refinement of polyoxotungstate structures.[22−27]

Table 1. Multinuclear NMR Data for the 1:1 and 1:2 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ Complexes: Ln = Lanthanide, $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ as the Na^+ Salt in 0.5 M Sodium Acetate Buffer at pH = 4.7

	^{31}P NMR data: δ ppm^a			
	1:2 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$		1:1 Ln:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$	
Ln	P1	P2	P1	P2
Lu	−7.72	−13.42	−8.03	−13.52
La	−7.42	−13.58	−7.52	−13.56
Y	−7.68	−13.49	−7.83	−13.51
Eu^b	3.73	−12.73	7.32	−12.43
Nd	−18.50	−14.36	−20.84	−14.64

compd	^{183}W NMR data: δ ppm (integration)
1:1 Lu:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-\ c}$	−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)
1:2 Lu:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-\ d}$	−134.66 (1), −135.46 (1), −154.26 (1), −155.10 (1), −181.75 (1), −183.44 (2), −211.81 (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)
$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-\ e}$	−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)
1:1 Nd:$[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$	626.63 (2), −139.87 (2), −174.17 (1), −195.06 (2), −214.22 (2), −216.68 (2), −216.68 (2), −219.53 9 (4)

[a] P1 denotes the phosphorus atom close to the lanthanide. P2 is attributed to the remote phosphorus atom. [b] $Li_{10}[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]$ in 0.5 M lithium acetate buffer, pH = 4.7 [c] NMR measured in D_2O as the Li^+ salt. [d] From: Bartis, J.; et al. *J. Chem. Soc., Dalton Trans.* **1997**, 1937. [e] From: Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384. We obtained a similar spectrum.

Table 2. Crystal Data and Structure Refinement for $(H_3O)K_{13}[Eu(H_2O)_3(P_2W_{17}O_{61})]_2\cdot 2KCl\cdot 56H_2O$

empirical formula	$(H_3O)K_{13}[Eu(H_2O)_3(P_2W_{17}O_{61})]_2\cdot 2KCl\cdot 56H_2O$
fw	10184.10
temp, K	173(2)
wavelength, λ, Å	(Mo Kα) 0.71073
a, Å	12.7214(5)
b, Å	14.7402(7)
c, Å	22.6724(9)
α, deg	71.550(3)
β, deg	84.019(3)
γ, deg	74.383(3)
vol, Å^3	3883.2(3)
Z; calcd density, Mg/m^3	1; 4.355
abs coeff, mm^{-1}	26.466
F(000)	4445
cryst size, mm	0.2 × 0.2 × 0.3
θ range, deg	1.50−28.54
limiting indices	$-15 \le h \le 16$, $-18 \le k \le 19$, $0 \le l \le 29$
reflns collected/unique	17930/17930 [*R*(int) = 0.0000]
completeness to θ = 28.54°	90.7%
refinement meth	full-matrix least-squares on F^2
data/restraints/params	17930/0/605
GOF on F^2	1.098
R indices [$I > 2\sigma(I)$]	R1 = 0.0520, wR2 = 0.1287
R indices (all data)	R1 = 0.0679, wR2 = 0.1450
largest diff peak and hole, e Å^{-3}	4.156 and −4.274

The details of data collection and refinement are contained in Table 2. Selected bond distances and angles about the Eu(III) are given in Table 3. Final atomic coordinates and isotropic displacement parameters for significant atoms are given in Table S1 (Supporting Information). Table S2 (Supporting Information) gives anisotropic displacement parameters.

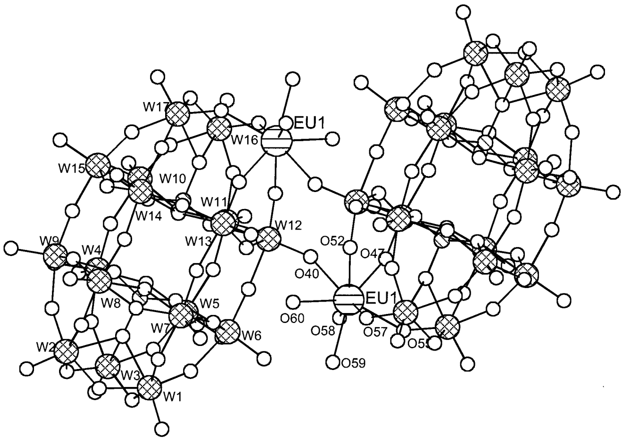

Figure 2. Ball and stick representation of the anion $[Eu(H_2O)_3(P_2W_{17}O_{61})]_2^{14-}$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(H_3O)K_{13}[Eu(H_2O)_3(P_2W_{17}O_{61})]_2\cdot 2KCl\cdot 56H_2O$, **1**

Eu(1)−O(47)	2.338(11)	Eu(1)−O(57)	2.391(10)
Eu(1)−O(58)	2.368(13)	Eu(1)−O(59)	2.415(13)
Eu(1)−O(52)	2.370(11)	Eu(1)−O(40)#1	2.433(11)
Eu(1)−O(55)	2.373(11)	Eu(1)−O(60)	2.453(11)

O(47)−Eu(1)−O(58)	80.1(4)	O(57)−Eu(1)−O(59)	77.7(4)
O(47)−Eu(1)−O(52)	72.7(4)	O(47)−Eu(1)−O(40)#1	72.9(4)
O(58)−Eu(1)−O(52)	139.7(4)	O(58)−Eu(1)−O(40)#1	71.4(4)
O(47)−Eu(1)−O(55)	75.3(4)	O(52)−Eu(1)−O(40)#1	72.6(4)
O(58)−Eu(1)−O(55)	81.5(4)	O(55)−Eu(1)−O(40)#1	141.0(4)
O(52)−Eu(1)−O(55)	118.1(4)	O(57)−Eu(1)−O(40)#1	139.6(4)
O(47)−Eu(1)−O(57)	117.2(4)	O(59)−Eu(1)−O(40)#1	119.9(4)
O(58)−Eu(1)−O(57)	146.1(4)	O(47)−Eu(1)−O(60)	140.0(4)
O(52)−Eu(1)−O(57)	74.0(4)	O(58)−Eu(1)−O(60)	110.0(4)
O(55)−Eu(1)−O(57)	75.9(4)	O(52)−Eu(1)−O(60)	76.2(4)
O(47)−Eu(1)−O(59)	142.0(4)	O(55)−Eu(1)−O(60)	143.1(4)
O(58)−Eu(1)−O(59)	72.3(4)	O(57)−Eu(1)−O(60)	76.4(3)
O(52)−Eu(1)−O(59)	143.7(4)	O(59)−Eu(1)−O(60)	75.5(4)
O(55)−Eu(1)−O(59)	75.2(4)	O(40)#1−Eu(1)−O(60	74.3(4)

Results and Discussion

Synthesis. The 1:1 Ln:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ complexes can be easily prepared at room temperature by reacting a Ln salt with the ligand in water using a slight excess of the Ln salt. Occasionally, the crude solid showed a small impurity of the 1:2 Ln:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ sandwich complex according to ^{31}P NMR data. In these cases, addition of Ln salt results in the conversion of the 1:2 impurity to the desired 1:1 Ln:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ complex.

Crystal Structure. The crystal structure of the anion, [Eu (α-2-$P_2W_{17}O_{61}$)]$^{7-}$, Figure 2, shows that two identical [Eu(H_2O)$_3$(α-2-$P_2W_{17}O_{61}$)]$^{7-}$ moieties are connected through two Eu−O−W bonds, one from each polyoxometalate unit. An ORTEP diagram is shown in Figure S1 (Supporting Information). An inversion center relates the two polyoxometalate units. The Eu(III) ion is substituted for a [WO]$^{4+}$ unit in the "cap" region of the tungsten−oxygen framework of the parent Wells−Dawson ion. The point group of the dimeric molecule is C_i.

The Eu(III) is in a square antiprismatic coordination geometry, bound to four oxygen atoms of the tungsten oxygen framework, to three water molecules, and to an oxygen atom of a terminal W═O of another [Eu(H_2O)$_3$(α-2-$P_2W_{17}O_{61}$)]$^{7-}$ moiety. The Eu(III) is not bound to an oxygen of a phosphate. Thus, the Eu(III) is displaced outward and away from the normal eighteenth position in the Wells−Dawson framework.

The bond lengths from Eu(III) to the oxygen atoms of the polyoxometalate framework are similar and average 2.369 Å. The average bond length of the Eu(III) to the three water molecules is 2.413 Å. The Eu−O (oxygen atom of a terminal W═O) bond length is 2.434(12) Å, in the range of the Eu−O(H_2O) bond distances. The bond length of 1.736(4) Å for the terminal W═O bound to the Eu(III) is at the high end of the range typically found for terminal W═O bonds. The bond lengths of the atoms in the tungsten−oxygen framework of [Eu(H_2O)$_3$(α-2-$P_2W_{17}O_{61}$)]$^{7-}$ compare favorably with those reported for the Wells−Dawson parent structure, the crystal structures of the [α-2-$P_2W_{17}O_{61}$]$^{10-}$ isomer, and the Co^{III}-(H_2O) adduct[28] and with the [Ln(α-2-$P_2W_{17}O_{61}$)]$^{14-}$ complexes.[13,29]

The structure of 1:1 Eu:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ (**1**) can be compared with the structures of the 1:1 La/Ce:$SiW_{11}O_{39}^{8-}$ complexes, see below, [6] and to the crystal structure of [Lu-(H_2O)$_4$(α-1-$P_2W_{17}O_{61}$)]$^{7-}$, another 1:1 lanthanide polyoxometalate. In the latter case four water molecules are bound to the Lu(III) ion.[13] There is no bonding between the Lu(III) ion and a terminal oxygen atom of another [Lu(α-1-$P_2W_{17}O_{61}$)]$^{7-}$ moiety possibly due to the high basicity of the oxygens at the α-1 defect site and steric encumbrance at the α-1 defect site. [16] Recently, the 1:1 Ce(III):(α-1-$P_2W_{17}O_{61}$)$^{10-}$ complex was characterized by single-crystal X-ray analysis among other techniques. In contrast to the monomeric [Lu(H_2O)$_4$(α-1-$P_2W_{17}O_{61}$)]$^{7-}$, this anion consists of a centrosymmetric head-to-head dimer, [{Ce(H_2O)$_4$(α-1-$P_2W_{17}O_{61}$)}$_2$]$^{14-}$, where each Ce(III) cation is bound to four oxygen atoms of one (α-1-$P_2W_{17}O_{61}$)$^{10-}$ unit, to four water molecules, and to one of the terminal oxygen atoms of the other [Ce(H_2O)$_4$(α-1-$P_2W_{17}O_{61}$)]$^{7-}$ unit.[30]

Both the La and Ce cations in the 1:1 La/Ce:α-$SiW_{11}O_{39}^{8-}$ complexes reported recently[6] are coordinated by nine oxygen atoms in a distorted monocapped square antiprism environment, involving bonding to the four oxygen atoms of the lacunary polyoxoanion; the cerium analogue is additionally coordinated by two neighboring α-$SiW_{11}O_{39}^{8-}$ moieties and to three oxygen atoms of water molecules. Two types of La ions alternate in the lanthanum analogue: one La(III) is

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coordinated to two α-$SiW_{11}O_{39}^{8-}$ moieties and three water molecules, and the second La(III) is coordinated to one α-$SiW_{11}O_{39}^{8-}$ moiety and four water molecules. In both the Ce and La analogues, the bonding to two terminal tungsten oxygen atoms each from a different α-$SiW_{11}O_{39}^{8-}$ species allows these species to form polymeric chains connected by Ln−O−W bonding in the solid state.

The extended structure of **1** is composed of the anions linked together by surface-bound potassium cations. The potassium ions bind to terminal oxygen atoms of two dimers giving rise to chains along the crystallographic *a* axis and a meshlike structure along the crystallographic *b* and *c* axes. The surface-bound potassium ions result in the formation of discrete channels forming a porous 3D structure (Figure S2, Supporting Information).[31,32] The approximate cross-sectional areas of the gaps in **1** are of the order of 19 × 12 $Å^2$. The K−O distances of terminal bound K cations range from 2.75 to 2.85 Å. The separations between adjacent layers are 12.7, 14.7, and 22.7 Å for the crystallographic *a*, *b*, and *c* axes, respectively.

Solution Chemistry. The solution data suggests that the dimeric unit found in the solid state dissociates into a monomer, $[Eu(H_2O)_4(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$, upon dissolution in water. $[Eu(H_2O)_3(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]_2^{14-}$, **1**, is slightly soluble in water compared with polyoxometalates of similar size, perhaps due to the network formed by the lanthanide linkages and cation surface binding.

Luminescence Data. Since the $^7F_0 \rightarrow {}^5D_0$ transition occurs between nondegenerate energy levels, neither of which can be split by a ligand field, a single environment gives rise to only a single transition. If more than one Eu(III) environment is present, each will have its characteristic transition energy. Figure 3 shows the excitation spectrum resulting from dilute solutions (100 nM to 250 μM) of the 1:2 $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ "sandwich" complex. Two peaks are observed: the peak at 580.44 nm corresponds to the $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ complex; the peak at 579.81 nm corresponds to the 1:1 $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ species. The observation of two species at these concentrations indicates that the formation constant for the following equilibrium is in the micromolar range:

$$[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-} + [\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-} \rightleftharpoons [Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$$

This is consistent with our work in the determination of equilibrium constants for a series of lanthanide $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ complexes and with the measurements of other workers for the Eu(III) and Ce(III) complexes.[16,29,33]

Luminescent lifetime measurements in H_2O and D_2O solutions allow determination of the number of coordinated water molecules, *q*, according to the following equation.[34,35]

$$q = 1.11[\tau^{-1}(H_2O) - \tau^{-1}(D_2O) - 0.31]$$

For $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$, $\tau(H_2O) = 3.02$ ms and $\tau(D_2O) = 4.79$ ms, whereas for the 1:1 complex, $\tau(H_2O) = 0.23$ ms and $\tau(D_2O) = 2.8$ ms. Solving the equation, $q = 0.21$ for $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$, consistent with the crystal structure, where no water molecules are coordinated to the Ln(III).[13] For the $K_7[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]$ complex, $q = 4.09$, consistent with four water molecules coordinated to the Eu(III) for the 1:1 complex. Previously, the solution excitation spectrum and luminescence lifetime data of the $[Eu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ species have been reported,[12] leading to $q = 4$ for that species, consistent with the crystal structure of that species. The luminescence lifetime data provide compelling evidence that the $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]_2^{14-}$ dimeric complex dissociates in aqueous solution to form the monomeric $[Eu(H_2O)_4(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ complex.

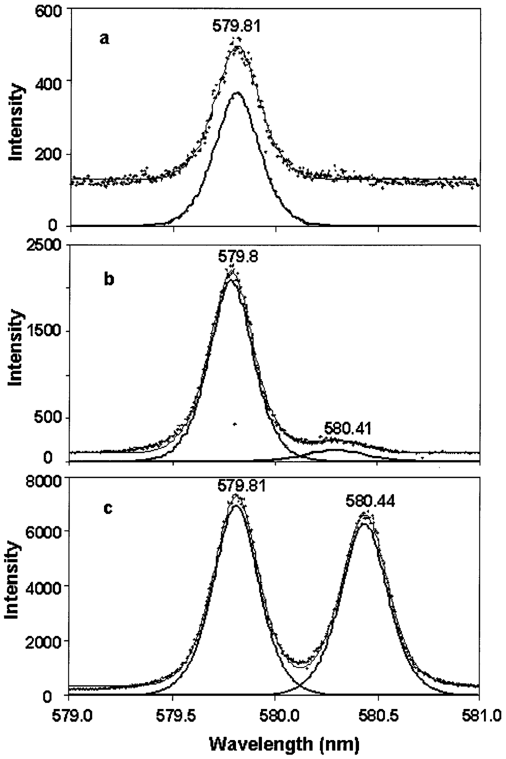

Figure 3. Excitation spectra of a dilute aqueous solution (100 nM to 250 μM) of the 1:2 $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ complex. The Eu^{3+} emission due to the $^5D_0$ to $^7F_2$ transition was monitored at 614 nm. Concentrations: (a) 100 nM, (b) 10 μM, (c) 250 μM.

Multinuclear NMR Data. The ^{183}W NMR spectroscopy also give cogent data suggesting that the dimeric $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]_2^{14-}$ complexes dissociate in aqueous solution. Figure S3 (Supporting Information) compares the ^{183}W NMR spectrum of the $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ complex with that of the "sandwich" $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ complex.[11] As expected due to the C_s symmetry of the $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ unit, 9 resonances (integration ratio: 2:2:1:2:2:2:2:2:2) are observed (Table 1). The chemical shifts of the ^{183}W NMR resonances are different from the chemical shifts from the lacunary species.[10,36] If the dimer remained intact in solution,

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all 17 tungsten atoms in one lacunary unit would be inequivalent to each other while each lacunary half would be related to the other by an inversion center. Therefore, 17 peaks of equal intensity would be observed in the ^{183}W NMR spectrum. Nine peaks are observed, clearly indicating C_s symmetry of the lacunary [α-2-$P_2W_{17}O_{61}$]$^{10-}$ unit. The ^{183}W NMR spectrum of the Nd analogue is also consistent with C_s symmetry showing eight resonances (two overlapping). The ^{31}P chemical shifts for the 1:1 Ln:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ complexes are also presented in Table 1

Conclusion

We have synthesized the 1:1 Ln:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ species and characterized this species in the solid state and in solution. In the solid state the [Eu(H_2O)$_3$(α-2-$P_2W_{17}O_{61}$)]$_2^{14-}$ is a dimer where the Eu is bound to the four oxygen atoms in the cap vacancy of the heteropolyanion and to three water molecules and to a terminal tungsten oxygen. Potassium ions bind to the surface of the dimer to connect the dimers into chains. The assembly disassociates in solution according to the luminescence spectroscopy and ^{183}W NMR spectroscopy to form a monomeric species wherein the lanthanide is bound to four water molecules and one [α-2-$P_2W_{17}O_{61}$]$^{10-}$ moiety. We are pursuing reactivity studies of the potentially interesting 1:1 Ln^{3+}:[α-2-$P_2W_{17}O_{61}$]$^{10-}$ complexes.

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Note Added in Proof: While this manuscript was in preparation, a report on the 1:1 cerium(III):[α-2-$P_2W_{17}O_{61}$]$^{10-}$ complex appeared. This study finds that the complex crystallizes in a head to head dimer in the solid state and establishes an equilibrium with the monomer in aqueous solution. Sadakane, M.; Ostuni, A.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **2002**, 63−67.

Supporting Information Available: Figures S1 and S2 showing an ORTEP diagram and the packing diagram for [Eu(H_2O)$_3$(α-2-$P_2W_{17}O_{61}$)]$_2^{14-}$. Figure S3 showing the ^{183}W NMR data for the [Lu(α-2-$P_2W_{17}O_{61}$)]$^{7-}$ complex. Tables S1 and S2 giving the atomic coordinates and anisotropic displacement parameters, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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