Inorg. Chem. **2006**, *45*, 1389−1398

Inorganic Chemistry

Article

Production and Reactions of Organic-Soluble Lanthanide Complexes of the Monolacunary Dawson $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ Polyoxotungstate

Cécile Boglio,[†,‡] Géraldine Lenoble,[†] Carine Duhayon,[†] Bernold Hasenknopf,*[,†] René Thouvenot,[†] Cheng Zhang,[§] Robertha C. Howell,[§] Benjamin P. Burton-Pye,[§] Lynn C. Francesconi,*[,§] Emmanuel Lacôte,[‡] Serge Thorimbert,[‡] Max Malacria,[‡] Carlos Afonso,[||] and Jean-Claude Tabet[||]

Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie, Case Courrier 42, 4 place Jussieu, 75005 Paris, France, Department of Chemistry, Hunter College and the Graduate School of the City University of New York, New York, New York 10021, Laboratoire de Chimie Organique, UMR CNRS 7611, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie, Case Courrier 229, 4 place Jussieu, 75005 Paris, France, and Laboratoire Structure et Fonction de Molécules Bioactives, UMR CNRS 7613, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie, Case Courrier 45, 4 place Jussieu, 75005 Paris, France

Received September 29, 2005

The incorporation of lanthanides into polyoxometalates provides entry to new classes of potentially useful materials that combine the intrinsic properties of both constituents. To utilize the $[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]^{7-}$ species in applications of catalysis and development of luminescent materials, the chemistry of this family of lanthanide polyoxometalates in organic solvents has been developed. Organic-soluble polyoxometalate–lanthanide complexes $TBA_5H_2[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]$ (Ln = La(III), Sm(III), Eu(III), Yb(III)) were prepared and characterized by elemental analysis, acid–base titration, IR, ^{31}P NMR, and mass spectrometry. The synthetic procedure involves a cation metathesis reaction in aqueous solution under strict pH control. A solid–liquid-phase transfer protocol yielded a unique species $(TBA)_8K_3[Yb(\alpha_1\text{-}YbP_2W_{17}O_{61})_2]$ with three ytterbium ions and two $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ polyoxotungstates. A centrosymmetric dimeric complex $[\{\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ was crystallized from aqueous solution and characterized by X-ray diffraction. ESI mass spectral analysis of the complexes $TBA_5H_2[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]$ shows that similar dimers exist in organic solution, in particular for the early lanthanides. Fragmentation in the mass spectrometer of the complexes from dry acetonitrile solution involves double protonation of an oxo ligand and loss of one water molecule. Low mass tungstate fragments combine into $[(WO_3)_n]^{2-}$ ($n = 1$–5) ions and their condensation products with phosphate. Reaction of $TBA_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]$ with 1,10-phenanthroline or 2,2′-bipyridine showed an increase of the europium luminescence. This result is explained by the formation of a ternary complex of $[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]^{7-}$ and two sensitizing ligands.

Introduction

The incorporation of lanthanides into polyoxometalates, early transition metal clusters (POMs), may provide an entry to new classes of materials that combine the intrinsic properties of both constituents.[1] Lanthanides can impart useful functionality such as luminescent,[2] magnetic,[3] or Lewis acid catalytic centers[4] to POMs, thus extending their range of physical and chemical properties and gaining access to an array of new potential applications of the resulting complexes.

This study focuses on elucidating the chemistry in organic solvents of the monolacunary $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ ion and its

---

* To whom correspondence should be addressed. E-mail: hasen@ccr.jussieu.fr (B.H.); lfrances@hunter.cuny.edu (L.F.).

[†] Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR CNRS 7071, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie.

[‡] Laboratoire de Chimie Organique, UMR CNRS 7611, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie.

[§] Department of Chemistry, Hunter College and the Graduate School of the City University of New York.

[||] Laboratoire Structure et Fonction de Molécules Bioactives, UMR CNRS 7613, Institut de Chimie Moléculaire FR 2769, Université Pierre et Marie Curie.

(1) Yusov, A. B.; Shilov, V. P. *Radiochemistry* **1999**, *41*, 3−24.
(2) Dossing, A. *Eur. J. Inorg. Chem.* **2005**, 1425−1434.
(3) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369−2387.
(4) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227−2302.

10.1021/ic051679g CCC: $33.50

complexes with several lanthanide ions that traverse the lanthanide series. In water, we found that the 1:1 Ln:[α_1-$P_2W_{17}O_{61}$]$^{10-}$ species, formally [$(H_2O)_4$Ln(α_1-$P_2W_{17}O_{61}$)]$^{7-}$, is favored with high selectivity for the midlater lanthanides.[5] Organic soluble 1:1 Ln:[α_1-$P_2W_{17}O_{61}$]$^{10-}$ and corresponding "ternary complexes" formed by replacement of the solvent molecules are attractive synthetic targets for a number of reasons. (1) The lanthanide ion, coordinated to the chiral [α_1-$P_2W_{17}O_{61}$]$^{10-}$ framework, should be Lewis acidic and well reactive toward substrates. Moreover, the 1:1 Ln:[α_1-$P_2W_{17}O_{61}$]$^{10-}$ offers a substantial chiral space for the entrance of substrates and additives that can be modulated by the Ln(III) ionic radii, auxiliary molecules, and even counterions. Therefore, applications in chiral catalysis can be envisioned. (2) Replacement of the solvent molecules of the lanthanide with an appropriate sensitizing organic ligand should enhance the luminescence of the lanthanide via photosensitization and thus provide novel strategies to prepare luminescent POM complexes for incorporation into films and other materials for display applications. The polyoxometalate ligand can circumvent quenching of the lanthanide excited state through C−H, N−H, and O−H vibrations associated with conventional organic ligand architectures.

Our approach, which employs the monolacunary [α_1-$P_2W_{17}O_{61}$]$^{10-}$ species, differs from and should complement the approaches taken by other investigators for the development of luminescent materials. In one approach, recently reported by a number of investigators, the well-known 1:2 Ln:monolacunary POMs (Peacock and Weakley ions[6]) are directly incorporated into films to confer electrochromic, electroluminescent, photochromic, and photoluminescent behavior.[7−16] Indeed, the Ln POMs in these materials retain their intrisic weak luminescence properties. We have also incorporated [α_1-Eu$(H_2O)_4P_2W_{17}O_{61}$]$^{7-}$ into mesoporous MCM-41 with retention of the luminescence, albeit low, as expected.[17] Our target molecules should show enhanced luminescence over the POMs used in these studies because the Ln will be sensitized by a strongly absorbing organic ligand and not the weakly absorbing POM framework.

Another approach to the synthesis of lanthanide polyoxometalate materials is the reaction of plenary or polylacunary POMs with lanthanides. Plenary POMs can weakly coordinate other metal ions; indeed, solid-state materials can be obtained from these building blocks and lanthanide ion linkers.[18−21] The lacunary polyoxometalates form strong complexes with transition metals and lanthanides.[22−26] Large assemblies have been obtained with polylacunary POMs and lanthanides because of the large number of basic oxygens in these POMs and the high coordination number requirement of lanthanide ions.[27−31] The strategy to use lanthanides as "linkers" to form nanomaterials has not yet proven positive for production of luminescent or catalytic materials probably because the lanthanide center is often (1) highly hydrated, leading to quenching in the case of luminescence, or (2) highly coordinated to other POM ligands that will neither produce effective sensitization nor allow substrates to enter the Ln coordination sphere, in the case of catalytic applications.

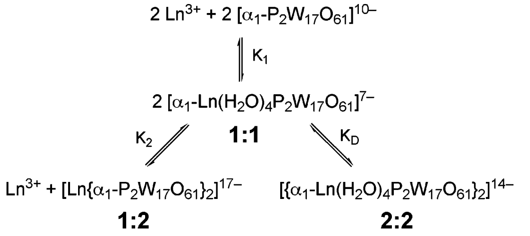
Our strategy involves the formation of simple, discrete, organic-soluble monolacunary [α_1-$P_2W_{17}O_{61}$]$^{10-}$ lanthanide complexes. Such complexes can react with organic ligands to form organic−inorganic hybrid complexes for photoluminescence or for catalytic organic transformations. However, transferring POM chemistry and lanthanide chemistry from aqueous to organic media is a complex issue. Both POMs and lanthanides exhibit dynamic behavior in aqueous and organic solutions; speciation is dependent on solvents, concentrations, counterions, aging, and other factors. This study was designed to understand the chemistry of Ln[α_1-$P_2W_{17}O_{61}$]$^{10-}$ complexes in organic solution as an important first step for the development of their applications in the rational synthesis of functional materials or as catalysts for transformation of organic reactions.

We present here solid-state and solution chemistry that elucidates the organic solution behavior of the monolacunary Dawson ion [α_1-$P_2W_{17}O_{61}$]$^{10-}$ and its complexes with several lanthanide ions that traverse the lanthanide series (La^{3+}, Sm^{3+}, Eu^{3+}, and Yb^{3+}). We also present preliminary results

---

(5) Zhang, C.; Howell, R. C.; Luo, Q.-H.; Fieselmann, H. L.; Todaro, L. J.; Francesconi, L. C. *Inorg. Chem.* **2005**, *44*, 3569−3578.
(6) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836−1839.
(7) Yamase, T. *Chem. Rev.* **1998**, *98*, 307−325.
(8) Katsoulis, D. E. *Chem. Rev.* **1998**, *98*, 359−388.
(9) Liu, S.; Kurth, D. G.; Möhwald, H.; Volkmer, D. *Adv. Mater.* **2002**, *14*, 225−228.
(10) Mo, Y.-G.; Dillon, R. O.; Snyder, P. G.; Tiwald, T. E. *Thin Solid Films* **1999**, *355−356*, 1−5.
(11) Xu, L.; Zhang, H.; Wang, E.; Kurth, D. G.; Li, Z. *J. Mater. Chem.* **2002**, *12*, 654−657.
(12) Xu, L.; Zhang, H.; Wang, E.; Wu, A.; Li, Z. *Mater. Chem. Phys.* **2002**, *77*, 484−488.
(13) Wang, Y.; Wang, X.; Hu, C.; Shi, C. *J. Mater. Chem.* **2002**, *12*, 703−707.
(14) Wang, J.; Liu, F.; Fu, L.; Zhang, H. *Mater. Lett.* **2002**, *56*, 300−304.
(15) Wang, Y.; Wang, X.; Hu, C. *J. Colloid Interface Sci.* **2002**, *249*, 307−315.
(16) Wang, J.; Wang, H. S.; Fu, L. S.; Liu, F. Y.; Zhang, H. J. *Thin Solid Films* **2002**, *414*, 256−261.
(17) Xu, W.; Luo, Q.; Wang, H.; Francesconi, L. C.; Stark, R. E.; Akins, D. L. *J. Phys. Chem. B* **2003**, *107*, 497−501.
(18) Shivaiah, V.; Reddy, P. V. N.; Cronin, L.; Das, S. K. *J. Chem. Soc., Dalton Trans.* **2002**, (20), 3781−3782.
(19) Drewes, D.; Limanski, E. M.; Krebs, B. *Dalton Trans.* **2004**, 2087−2091.
(20) An, H.; Lan, Y.; Li, Y.; Wang, E.; Hao, N.; Xiao, D.; Duan, L.; Xu, L. *Inorg. Chem. Commun.* **2004**, *7*, 356−358.
(21) Niu, J.-Y.; Guo, D.-J.; Wang, J.-P.; Zhao, J.-W. *Cryst. Growth Des.* **2004**, *4*, 241−247.
(22) Pope, M. T. In *Comprehensive Coordination Chemistry II*; Wedd, A. G., Ed.; Elsevier: Oxford, U,K., 2004; Vol. 4, pp 635−678.
(23) Wassermann, K.; Pope, M. T. *Inorg. Chem.* **2001**, *40*, 2763−2768.
(24) Lu, Y. W.; Keita, B.; Nadjo, L. *Polyhedron* **2004**, *23*, 1579−1586.
(25) Kortz, U.; Holzapfel, C.; Reicke, M. *J. Mol. Struct.* **2003**, *656*, 93−100.
(26) Tomsa, A. R.; Muresan, L.; Koutsodimou, A.; Falaras, P.; Rusu, M. *Polyhedron* **2003**, *22*, 2901−2909.
(27) Yamase, T.; Naruke, H.; Sasaki, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 1687−1696.
(28) Howell, R. C.; Perez, F. G.; Jain, S.; Horrocks, W. D., Jr.; Rheingold, A. L.; Francesconi, L. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4031−4034.
(29) Cronin, L.; Beugholt, C.; Krickemeyer, E.; Schmidtmann, M.; Bögge, H.; Kögerler, P.; Luong, T. K. K.; Müller, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 2805−2808.
(30) Müller, A.; Beugholt, C.; Bögge, H.; Schmidtmann, M. *Inorg. Chem.* **2000**, *39*, 3112−3113.
(31) Xue, G.; Vaissermann, J.; Gouzerh, P. *J. Cluster Sci.* **2002**, *13*, 409−421.

Scheme 1



on the application of the 1:1 Eu:$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ species for the preparation of a ternary complex wherein a sensitizing ligand is bound to the 1:1 Eu:$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ species.

Previous Results. Since the first report of Ciabrini and Contant in 1993,[32] studies from our laboratories[5,33,34] and others[35] have established that Ln(III) ions form different complexes with $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ in aqueous solution. The most important equilibria are summarized in Scheme 1. Similar solution equilibria have been investigated for complexes with the isomeric $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$.[24,36-39]

In all of these complexes, the Ln(III) ion occupies the lacuna of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$. As this lacuna provides only four basic oxygen donor atoms, and lanthanides are commonly 8 or 9 coordinated, further coordination sites are available on the lanthanide. The complexes are denoted **1:1**, **2:2**, or **1:2** indicating the stoichiometry of the Ln:$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$, as shown in Scheme 1. In the **1:1** complex, the free coordination sites are occupied by water molecules. These **1:1** complexes can dimerize into the **2:2** complexes through coordination of the lanthanide to terminal oxo ligands of a second POM unit. Alternatively, the lanthanide can be sandwiched between two $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ POMs in the **1:2** complexes.

The equilibria of the **1:1** and **1:2** complexes and their constituents are slow enough to observe all species separately by ^{31}P NMR. This allowed some of us to determine the complexation constants K_1 and K_2 for the lanthanides La, Nd, Eu, Dy, Er, Yb, and Lu in different buffer solutions.[5] In general, K_1 increases across the lanthanide series and K_2, while much smaller than K_1, peaks at Nd and decreases for the late lanthanides. Thus, **1:2** complexes could only be isolated and crystallized with La, Nd, Eu, and Er but not with Yb and Lu.

The dimerization equilibrium between **1:1** and **2:2** is fast on the NMR time scale. Using the concentration dependence of the chemical shift, Pope established a dimerization constant of $K_D = 20 \pm 4\ \text{mol}^{-1}\cdot\text{L}$ at 22 °C for the compound $[\alpha_1\text{-}Ce(H_2O)_4P_2W_{17}O_{61}]^{7-}$.[35]

Results and Discussion

1. Preparation of Complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ and Ln(III) with 1:1 Stoichiometry in Aqueous Solution. The optimal stability of the $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ isomer is in the pH range 4−5. At higher pH, it isomerizes to $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, and at lower pH, it is converted into $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$.[40] We therefore prepared the complexes $[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]^{7-}$ by mixing equal amounts of $Ln(NO_3)_3$ (Ln = La, Sm, Eu, Yb) and $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ in acetate buffer (0.5 M) solutions at pH 4.5. The buffer cations were Li^+, Na^+, or K^+. This selection of lanthanides is representative of the series as it includes early, middle, and late elements. ^{31}P NMR showed in each case one set of signals for the two phosphorus atoms (see Table 1) in accordance with previous results.[5,33]

If any free $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ or **1:2** complexes were present, these species would be below the NMR detection limit, in these cases ca. 2−5%. However, the chemical shifts observed correspond certainly to the average value of the **1:1** and **2:2** complexes. The tendency to dimerize decreases for complexes $[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]^{7-}$ with late lanthanides, as discussed below.

Isolation of a 2:2 Complex: Crystal Structure of the 2:2 Complex $[\{\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ (1). In the presence of KCl, the lanthanum complex crystallizes as a $[\{\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ dimer (**1**, Figure 1). Single-crystal X-ray diffraction revealed a molecular structure similar to but not identical with that of $[\{\alpha_1\text{-}Ce(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ reported by Pope.[35] In both cases, a centrosymmetric dimer is formed through the coordination of the lanthanide to two POM units. La(III) and Ce(III) occupy each a distorted monocapped square antiprism defined by the four oxygens of the lacuna, four water molecules, and a terminal oxo ligand of the second POM unit. The nature of this W═O group is different in $[\{\alpha_1\text{-}Ce(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ and $[\{\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$. Whereas a belt W═O is bound to Ce in the former case, a cap W═O is bound to La in the latter case. The reason for this difference is not clear. The La−O bond distances are in the range of 2.45−2.52 Å for La−oxo bonds and 2.50−2.72 Å for water ligands; these are reasonable bond lengths for La−O bonds. The W−O bond distance in the W−O−La bridge is 1.79 Å, which is about 0.1 Å longer than for W═O terminal oxo ligands, as expected.

In contrast to the Ce(III) and La(III) structures, the crystal structure of $[\alpha_1\text{-}Lu(H_2O)_4P_2W_{17}O_{61}]^{7-}$ is a monomeric structure where the 8 coordinate Lu(III) is bound to the 4 oxygen atoms of the defect site and to 4 water molecules.[34] The dimerization to form the **2:2** structures may satisfy the coordination requirements of the lanthanide ions; the early lanthanides require 9 coordination whereas the later lanthanides require 8 coordination. We observe a stronger signal

---

(32) Ciabrini, J.-P.; Contant, R. *J. Chem. Res.* **1993**, 2719−2745.

(33) Bartis, J.; Dankova, M.; Lessmann, J. J.; Luo, Q.-H.; Horrocks, W. D., Jr.; Francesconi, L. C. *Inorg. Chem.* **1999**, *38*, 1042−1053.

(34) Luo, Q.-H.; Howell, R. C.; Dankova, M.; Bartis, J.; Williams, C. W.; Horrocks, W. D., Jr.; Young, V. G.; Rheingold, A. L.; Francesconi, L. C.; Antonio, M. R. *Inorg. Chem.* **2001**, *40*, 1894−1901.

(35) Sadakane, M.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2001**, *40*, 2715−2719.

(36) Sadakane, M.; Ostuni, A.; Pope, M. T. *J. Chem. Soc., Dalton Trans.* **2002**, 63−67.

(37) Luo, Q.-H.; Howell, R. C.; Bartis, J.; Dankova, M.; Horrocks, W. D., Jr.; Rheingold, A. L.; Francesconi, L. C. *Inorg. Chem.* **2002**, *41*, 6112−6117.

(38) Bion, L.; Mercier, F.; Decambox, P.; Moisy, P. *Radiochim. Acta* **1999**, *87*, 161−166.

(39) VanPelt, C. E.; Crooks, W. J.; Choppin, G. R. *Inorg. Chim. Acta* **2003**, *346*, 215−222.

(40) Contant, R.; Richet, M.; Lu, Y. W.; Keita, B.; Nadjo, L. *Eur. J. Inorg. Chem.* **2002**, 2587−2593.

Table 1. ^{31}P NMR Data for Ln(III) Complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$

compd	DMSO-d_6[a]		CD_3CN + 10% D_2O[a]		D_2O[b]	
	δ[P(1)]	δ[P(2)]	δ[P(1)]	δ[P(2)]	δ[P(1)]	δ[P(2)]
$(^nBu_4N)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ (**4**)	−9.0	−13.0	−8.6	−12.2	−10.6	−13.1
$(^nBu_4N)_5H_2[\alpha_1\text{-Sm}(H_2O)_4P_2W_{17}O_{61}]$ (**5**)	−12.2	−14.0	−11.5	−13.2	−13.6	−12.6
$(^nBu_4N)_5H_2[\alpha_1\text{-Eu}(H_2O)_4P_2W_{17}O_{61}]$ (**6**)	4.0	−9.3	4.8	−11.7	6.2	−11.3
$(^nBu_4N)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]$ (**3a**)	12.6	−1.7	33.8	−1.7	27.0	−6.8
$(^nBu_4N)_6H_4[\alpha_1\text{-}P_2W_{17}O_{61}]$ (**2**)	−10.6	−12.4	−10.5	−11.9	−8.5	−12.8

[a] All spectra were recorded at a concentration of 100 mg/0.5 mL. [b] Data obtained with the potassium salts of the lanthanides complexes.

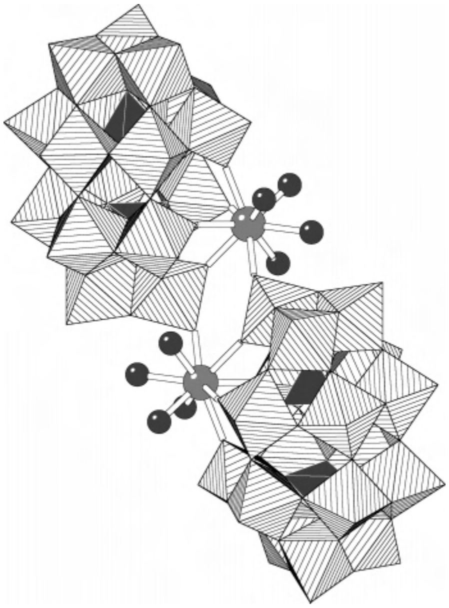


Figure 1. Single-crystal X-ray structure of $[\{\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}\}_2]^{14-}$ (**1**). A lanthanum cation occupies the lacuna of one lacunary Dawson ion and is coordinated to a cap oxo ligand of a second Dawson ion. Four water molecules complete the coordination sphere of each La.

for the **2:2** dimer in the mass spectral data of the $La^{III}[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ complex than for the Yb analogue, vide infra, suggesting that the dimerization may be weaker for the later lanthanides in accordance with our crystal structure observations.

2. Preparation of Lanthanide $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ Complexes with Organic Cations. The cation exchange from K^+ to tetrabutylammonium (TBA^+) in POM salts can often be accomplished by metathesis reactions in solution. Addition of (TBA)Br to an aqueous solution of a POM yields an insoluble salt which can be recovered by filtration or by extraction with an organic solvent. In the present case of lanthanide complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$, the addition of (TBA)Br shifts equilibria in solution, and the TBA POM salts isolated do not always correspond to the major compounds in aqueous solution. Although we started in all cases with a solution that was checked by ^{31}P NMR to verify the existence of only the **1:1**/**2:2** complexes, we obtained mixtures of compounds after metathesis in some preparations. We therefore focused on one lanthanide complex—$[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]^{7-}$—to optimize the conditions for a clean conversion to the TBA salt. The paramagnetic influence of Yb^{3+} allows us to distinguish compounds with and without ytterbium easily in the ^{31}P NMR spectra. A more detailed description of unsuccessful procedures can be found as Supporting Information.

The equilibria of Scheme 1 depend on the composition of the buffer solution. We therefore tested the preparation of the $Yb^{III}[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ complex in the absence of buffer, monitoring the pH with a glass electrode and adjusting it to 4.5 with dilute HCl during the addition of (TBA)Br. We also switched to $YbCl_3$ because the reaction with $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ results in a solution of lower pH compared to that obtained with $Yb(NO_3)_3$. In this way, we decreased the amount of lacunary $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ ligand as impurity in the final TBA salt of $[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ considerably. The use of a small excess (5−10%) of $YbCl_3$ finally gave a pure compound, characterized by only two peaks in the ^{31}P NMR spectrum. Subsequent analysis proved it to be the organic salt $(TBA)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]$ (**3a**).

We applied the same procedure to obtain also the TBA salts of $[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**4**), $[\alpha_1\text{-Sm}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**5**), and $[\alpha_1\text{-Eu}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**6**). With minor modifications, we also obtained $(BnEt_3N)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**3b**) and $(MePh_3P)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**3c**). The $(TBA)_6H[\alpha_1\text{-Lu}(H_2O)_4P_2W_{17}O_{61}]$ analogue was prepared previously by a similar method.[33]

Composition of the Compounds Obtained. We have titrated acidic protons of all TBA salts of $[\alpha_1\text{-Ln}(H_2O)_4P_2W_{17}O_{61}]^{7-}$ in acetonitrile solution with (TBA)OH in methanol. In potentiometric titrations, no clear end point could be detected due to the degradation of the POMs by the base. With phenolphthalein as indicator, we found repeatedly between 1.85 and 2.25 acidic protons. Again, the lack of precision is due to POM degradation. Nevertheless, these values agree well with the elemental analysis, and we therefore formulate our compounds as $(TBA)_5H_2[\alpha_1\text{-Ln}(H_2O)_4P_2W_{17}O_{61}]$. The given number of water molecules bound to the lanthanide is based on elemental analysis of the solids, and these molecules are likely to be exchanged with solvent molecules in organic solutions. Five solvent ligands are expected for the early lanthanide complexes in solution.

IR Analysis. IR spectral data for all new compounds are compiled in the Experimental Section. The lacunary compound $(TBA)_6H_4[\alpha_1\text{-}P_2W_{17}O_{61}]$ (**2**) is characterized by strong IR bands between 740 and 960 cm^{-1} for the W−O−W and W═O groups, two weak bands at 1018 and 1062 cm^{-1}, a strong band at 1090 cm^{-1}, and a medium band at 1145 cm^{-1} corresponding to P−O stretching vibrations. This spectrum is in agreement with the reported data for $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ (1020, 1090, and 1140 cm^{-1}).[41]

All these bands are found with little variations in the lanthanide complexes $(TBA)_5H_2[\alpha_1\text{-Ln}(H_2O)_4P_2W_{17}O_{61}]$ (**3**−

---

(41) Contant, R. *Inorg. Synth.* **1990**, *27*, 104−111.

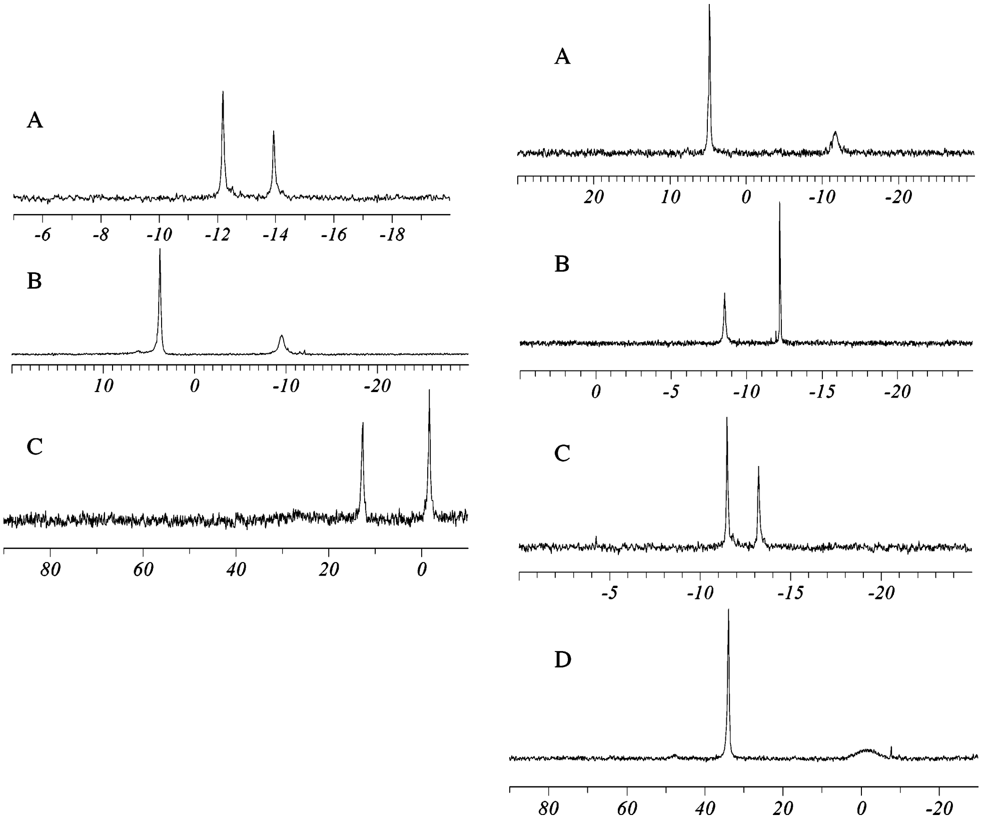


Figure 2. Left: ^{31}P NMR spectra of (A) [α_1-Sm(H_2O)$_4P_2W_{17}O_{61}$]$^{10-}$, (B) [α_1-Eu(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$, and (C) [α_1-Yb(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$ in DMSO. Right: ^{31}P NMR spectra of (A) [α_1-Eu(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$, (B) [α_1-La(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$, (C) [α_1-Sm(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$, and (D) [α_1-Yb(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$ in acetonitrile/10% water.

6). The only significant difference concerns the vibration seen at 1145 cm^{-1} in the lacunary compound. This band is much weaker and shifted to higher energy in the lanthanide complexes. A second very weak band around 1125 cm^{-1} is sometimes detected as a shoulder of the band at 1093 cm^{-1}. Thus, the spectra of (TBA)$_5H_2$[α_1-Ln(H_2O)$_4P_2W_{17}O_{61}$] bear a resemblance to that of (TBA)$_6$[α-$P_2W_{18}O_{62}$], proving the tight inclusion of the lanthanide into the lacuna. The spectra of the potassium salts K_7[α_1-Ln(H_2O)$_4P_2W_{17}O_{61}$] with a band of medium intensity between 1130 and 1145 cm^{-1} are closer to that of the lacunary compound [α_1-$P_2W_{17}O_{61}$], which might be a hint to a weaker binding of the lanthanide in these cases.

The combination of different organic cations (MePh$_3$P)$^+$ and (BnEt$_3$N)$^+$ with [α_1-Yb(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$ (compounds **3a**−**c**) is not reflected by any change in the IR spectra, apart from the additional signals of the cations.

^{31}P NMR Analysis. ^{31}P NMR is a useful tool to characterize our complexes as the resonance of the two phosphorus atoms are very sensitive to any change in the POM framework. The chemical shifts observed for all [α_1-Ln(H_2O)$_4P_2W_{17}O_{61}$]$^{7-}$ are compiled in Table 1, and representative spectra are reproduced in Figure 2.

The phosphorus atom near the lacuna is denoted by P(1), and P(2) denotes the remote phosphorus atom. The values are reproducible within ±0.1 ppm between different batches of compounds.

It should be noted that spectra taken in reasonably dry acetonitrile show several overlapping signals for P(1) and P(2). Spectra with two narrow peaks are obtained in DMSO (Figure 2, left). On addition of 10% water to the acetonitrile solution (Figure 2, right), clean spectra with two signals are obtained. However, the broadness of the signals indicates exchange processes in solution. Such a behavior is not unprecedented and can be explained by the concommitance of several factors: (i) slow exchange of different protonation states in dry acetonitrile;[42,43] (ii) coordination of different solvent molecules on the lanthanide; (iii) association of the POM−lanthanide complexes into small aggregates with each other or with cations. Such aggregates would be favored in solvents with lower dielectric constant such as acetonitrile. In the presence of dissociating solvents such as DMSO or water, exchange of protons occurs more rapidly and all ions are solvated more individually as well. The phenomenon of cation−anion aggregates is also seen by mass spectrometry of these compounds, as discussed below.

All spectra, and namely those with paramagnetic lanthanide ions, are strongly concentration dependent. Furthermore, the chemical shifts vary—sometimes considerably—with change of the solvent or change of the counterion. This behavior certainly reflects not only the intrinsic solvent properties which influence the chemical shifts but also the change in the chemical equilibrium between **1:1** and **2:2** complexes.

---

(42) Bartis, J.; Sukal, S.; Dankova, M.; Kraft, E.; Kronzon, R.; Blumenstein, M.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans.* **1997**, 1937−1944.

(43) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947−2960.

Mass Spectrometric Analysis. Mass spectrometry techniques based on desorption/ionization processes such as matrix-assisted laser desorption ionization (MALDI) or electrospray ionization (ESI) are becoming important tools in the study of polyoxometalates.[44−50] In this work, ESI was used as it allows the direct study of these species in various solvents such as water, methanol, or acetonitrile. Furthermore, this technique offers unique features that allow obtaining a global view of intact polyoxometalates together with few characteristic fragments. Such an analysis requires a careful tuning of the electrospray source. In particular, the voltage difference between the orifice and the first skimmer has to be set such to avoid decomposition of the anions in the ion source. As a result, the attribution of the observed signals to complex stoichiometries is formulated readily, and the spectra reflect the solution composition.

The ESI mass spectra recorded in negative ion mode of a 5×10^{-5} M solution of $(TBA)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ (**4**) in acetonitrile and acetonitrile/water are presented in Figure 3 a,b. These spectra are representative for all $(TBA)_5H_2[\alpha_1\text{-Ln}(H_2O)_4P_2W_{17}O_{61}]$ complexes **3a**−**6** of this study. The **1:1** complex is detected as $[LaP_2W_{17}O_{61}]^{7-}$ (loss of water coordinated to La) and with the required number of TBA^+ and H^+ cations to obtain a charge state distribution from 5− to 3−. No reduction of the tungstates is observed. In the case of acetonitrile solution (Figure 3a), singly and doubly protonated species are detected, whereas almost only monoprotonated species are found in the presence of water (Figure 3b). This result is consistent with our observation in ^{31}P NMR where we found broad peaks in acetonitrile indicating exchange of different protonation states, although care has to be taken when comparing protonation states in solution and in the mass spectrometer. A similar deprotonation as reported here has been observed earlier by ESI-MS of $[HSiMo_{12}O_{40}]^{3-}$ on addition of water to an organic solution.[46] The three species in Figure 3a can undergo loss of one water molecule. A close examination of the signals reveals that this tendency increases for the higher charged species. The signal of the 3− species at *m*/*z* 1596.6 is narrow and corresponds to $\{(TBA)_2H_2[LaP_2W_{17}O_{61}]\}^{3-}$. The signal of the 4− species at *m*/*z* 1136.6 is broadened toward lower masses (Figure 3a, inset), indicating the coexistence of $\{(TBA)_1H_2[LaP_2W_{17}O_{61}]\}^{4-}$ and $\{(TBA)_1[LaP_2W_{17}O_{60}]\}^{4-}$ (loss of H_2O). The 5− species is found at *m*/*z* 856.9, which corresponds to $\{LaP_2W_{17}O_{60}\}^{5-}$, i.e., a complete loss of one H_2O from the doubly protonated $\{H_2[LaP_2W_{17}O_{61}]\}^{5-}$. This observation indicates a particular desolvation pathway of POMs in the mass spectrometer: the double protonation of the same oxo ligand with concomitant loss of water. Similar observations have been made on other polyoxotungstates.[48,51] No such fragmentation occurs in samples in 50:50 acetonitrile/water (Figure 3b, inset), as these conditions favor monoprotonated species.

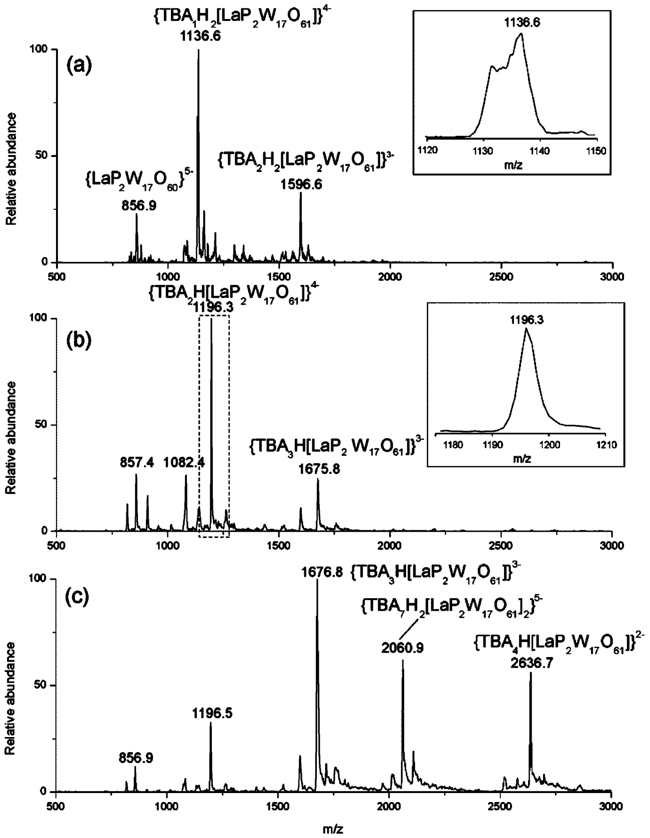


Figure 3. ESI-mass spectra of $(TBA)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ in negative ion mode. Concentration: 5×10^{-5} M. Key: (a) acetonitrile; (b) 50:50 acetonitrile/water; (c) 50:50 acetonitrile/water using conditions for trapping high *m*/*z* ions. Insets: (a) expansion of *m*/*z* 1136.6 signal for the 4− species indicating loss of one H_2O; (b) expansion of *m*/*z* 1196.3 signal of the 4− species showing no loss of H_2O.

The same MeCN/H_2O solution of $(TBA)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ (**4**) as for Figure 3b was analyzed under conditions allowing the transmission and trapping of high mass-to-charge ratio ions (Figure 3c). Under these conditions, a strong signal corresponding to the dimeric species $\{(TBA)_7H_2[LaP_2W_{17}O_{61}]_2\}^{5-}$ was detected at $m/z = 2060.9$ (70%). Note that the signals at *m*/*z* 2636.7 and 1676.8 can be attributed to even charged states 4− and 6− of the **2:2** complex as well as to 2− and 3- **1:1** species. The dimeric **2:2** complex is therefore present in solution but in relatively low amount, which is consistent with the NMR data. It should be stressed again that this analysis of $(TBA)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ (**4**) is representative for the series of compounds **3a**−**6**. However, in the spectra of $(TBA)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]$ (**3a**), only a relatively weak signal can be attributed unequivocally to a **2:2** form: *m*/*z* 1978.1 (20%) for $\{(TBA)_5H_4[YbP_2W_{17}O_{61}]_2\}^{5-}$. This indicates a weaker dimerization for the late lanthanides, in accordance with the results discussed above.

---

(44) Dablemont, C.; Proust, A.; Thouvenot, R.; Afonso, C.; Fournier, F.; Tabet, J. C. *Dalton Trans.* **2005**, 1831−1841.

(45) Dablemont, C.; Proust, A.; Thouvenot, R.; Afonso, C.; Fournier, F.; Tabet, J.-C. *Inorg. Chem.* **2004**, *43*, 3514−3520.

(46) Lau, T.-C.; Wang, J.; Guevremont, R.; Siu, K. W. M. *J. Chem. Soc., Chem. Commun.* **1995**, 877−8.

(47) Deery, M. J.; Howarth, O. W.; Jennings, K. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4783−4788.

(48) Truebenbach, C. S.; Houalla, M.; Hercules, D. M. *J. Mass Spectrom.* **2000**, *35*, 1121−1127.

(49) Bonchio, M.; Bortolini, O.; Conte, V.; Sartorel, A. *Eur. J. Inorg. Chem.* **2003**, 699−704.

(50) Mayer, C. R.; Roch-Marchal, C.; Lavanant, H.; Thouvenot, R.; Sellier, N.; Blais, J.-C.; Secheresse, F. *Chem.*—*Eur. J.* **2004**, *10*, 5517−5523.

(51) Easterly, C. E.; Hercules, D. M.; Houalla, M. *Appl. Spectrosc.* **2001**, *55*, 1665−1670.

Table 2. Negative Ions Observed in ESI-MS of $TBA_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (**3a**) under High Declustering Conditions

m/*z* (% rel intensity)[a,b]	composn of the ions
248.8 (50)	$[HWO_4]^-$
239.8 (17)	$[W_2O_7]^{2-}$
480.9 (23)	$[HW_2O_7]^-$
518.9 (11)	$[KW_2O_7]^-$
537.0 (9)	$[(H_2O)KW_2O_7]^-$
722.3 (64)	$[(^nBu_4N)W_2O_7]^-$
355.9 (100)	$[W_3O_{10}]^{2-}$
954.3 (7)	$[(^nBu_4N)W_3O_{10}]^-$
471.9 (93)	$[W_4O_{13}]^{2-}$
587.9 (20)	$[W_5O_{16}]^{2-}$
542.9 (12)	$[PW_2O_9]^-$
774.8 (12)	$[PW_3O_{12}]^-$
512.1 (6)	$[HPW_4O_{16}]^{2-}$
495.5 (20)	$[PW_6O_{22}]^{3-}$

[a] *m*/*z* given for the most intense peak in the isotopic distribution. [b] Observed values given. The calculated *m*/*z* agree within 0.1 Da.

The analysis of low *m*/*z* signals in the spectra give further insight into the fragmentation pathways of these POMs. Experiments using a relatively high declustering potential were carried out with $(TBA)_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (**3a**) in acetonitrile. Under these conditions signals corresponding to the decomposition of the POMs are displayed in the mass spectrum (Table 2 and Supporting Information). Using the enhanced resolution mode of the instrument, it was possible to resolve the isotopic clusters and attribute unequivocally the observed signals. $[(WO_3)_nO]^{2-}$ ions ($n = 1-5$) and their association with protons, potassium, or TBA cations are recognized in the spectrum. These compositions correspond to chains of corner-sharing tetrahedra of WO_4^{2-}, identified earlier in ESI spectra of isopolyoxotungstates.[52] In addition, we find their condensation products with PO_4^{3-}. None of the fragments observed contains a lanthanide ion. We suppose that the aggregation of WO_4^{2-} with PO_4^{3-} units resulting from fragmentation of **3**−**6** takes place in the instrument in analogy to the mechanism postulated for isopolyoxotungstates.[52] Aggregation processes have also been observed for the related lacunary POM $Li_7[\alpha\text{-}PW_{11}O_{39}]$,[49] although the reported species were different.

Solid−Liquid-Phase Transfer Synthesis. Functionalization of POMs can be achieved in solid−liquid-phase transfer reactions. We have recently applied this strategy to prepare organotin derivatives of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$.[53] This technique relies on the use of a soluble reactant together with insoluble $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ in an organic solvent. The easy workup of this procedure prompted us to apply it to the preparation of lanthanide complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$. Thus, we added $Yb(OTf)_3$ and (TBA)Br to a suspension of $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ in acetonitrile. The lacunary POM slowly reacted with the soluble Yb^{3+}, and the resulting complex stayed in solution. It was isolated by precipitation with ethanol and ether.

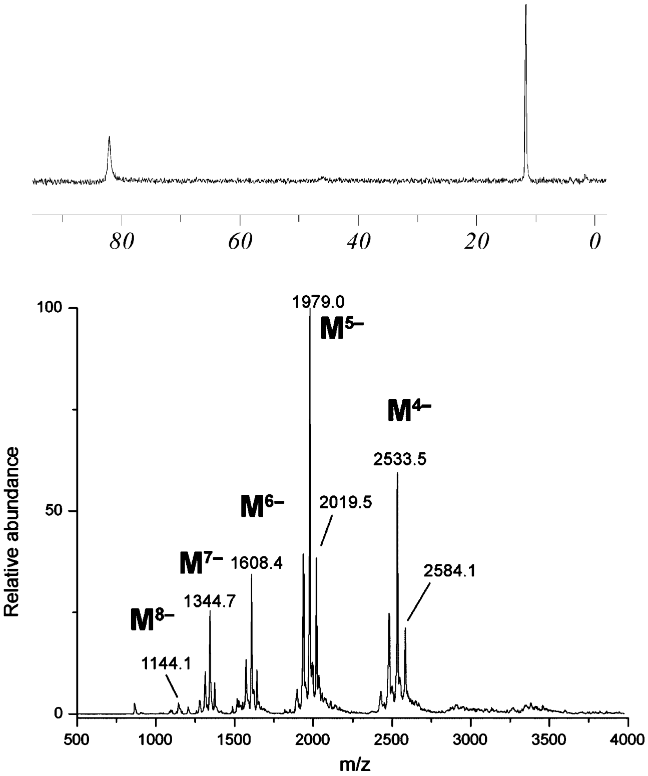


Figure 4. Analysis of the **3:2** compound $(TBA)_8K_3[Yb(\alpha_1\text{-}YbP_2W_{17}O_{61})_2]$ (**7**). Top: ^{31}P NMR spectrum in acetonitrile. Bottom: ESI-mass spectrum from acetonitrile solution. The charge states 4− to 8− are observed, each with 0−3 K^+ ions and the corresponding number of TBA^+ ions.

Elemental analysis of the compound, recrystallized to constant composition, indicates a formulation of $(TBA)_8K_3[Yb(\alpha_1\text{-}YbP_2W_{17}O_{61})_2]\cdot 8H_2O$ with three ytterbium atoms/two lacunary Dawson tungstates. In line with our abbreviations given above for the other complexes, we designate this complex (**7**) as **3:2**. The extra ytterbium atom might play the role of counterion together with eight TBA^+ and three K^+ found by elemental analysis. The IR spectrum of compound **3:2** is very close to that of $(TBA)_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (**3a**). This shows that the **3:2** compound contains the intact fragment $\{\alpha_1\text{-}YbP_2W_{17}O_{61}\}^{7-}$. One should note however for the **3:2** compound a new band at 1032 cm^{-1} and a shift of the strongest P−O band from 1093 to 1087 cm^{-1} compared to that for **3a**−**c**.

The ^{31}P NMR (Figure 4, top) gives strong evidence that the **3:2** compound, **7**, is a new complex. Indeed, the spectrum in acetonitrile shows two narrow lines at 82.0 and 11.6 ppm. The chemical shifts are concentration and solvent dependent, as seen before. However, the chemical shifts of the **3:2** complex, in organic solution, are not close to those of $[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]^{7-}$ (**3a**). Only in aqueous $LiClO_4$ solution, the ^{31}P NMR of **3:2** and **3a** were identical, as would be expected for the decomposition of the **3:2** complex into Yb(III) and $\{\alpha_1\text{-}YbP_2W_{17}O_{61}\}^{7-}$ units. Therefore, compound **3:2** should be considered to be a new species formed by the association of two $\{\alpha_1\text{-}YbP_2W_{17}O_{61}\}^{7-}$ units and one additional Yb^{3+}. The presence of the third paramagnetic Yb^{3+} also explains the deshielding of the NMR signals. We formulate compound **3:2** as $(TBA)_8K_3[Yb(\alpha_1\text{-}YbP_2W_{17}O_{61})_2]$ (**7**) although one or more of the potassium ions and additional water molecules might be tightly bound to the complex.

---

(52) Walanda, D. K.; Burns, R. C.; Lawrance, G. A.; Von Nagy-Felsobuki, E. I. *J. Cluster Sci.* **2000**, *11*, 5−28.

(53) Bareyt, S.; Piligkos, S.; Hasenknopf, B.; Gouzerh, P.; Lacôte, E.; Thorimbert, S.; Malacria, M. *J. Am. Chem. Soc.* **2005**, *127*, 6788−6794.

Further evidence for the presence of only one discrete complex is obtained by mass spectrometry. All signals in the mass spectrum can be attributed to $[Yb(\alpha_1\text{-}YbP_2W_{17}O_{61})_2]^{11-}$. Each charge state from 3− to 8− (4− to 8− shown in Figure 4 bottom) is observed with 0−3 K^+ and the corresponding number of TBA^+ associated with the anion. We have shown above that $[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]^{7-}$ can be observed by mass spectrometry under these conditions. The absence of any signal related to this compound in the spectrum of **7** proves that the latter is a stable compound and does not dissociate in organic solution.

At the present stage, we can only speculate on the structure of the **3:2** compound **7**. The two line ^{31}P NMR spectrum demonstrates that both P(1) and P(2) atoms in the two Dawson entities are equivalent. One should therefore envisage a symmetric structure of two $\{\alpha_1\text{-}YbP_2W_{17}O_{61}\}^{7-}$ fragments which hold an Yb^{3+} ion tightly in the middle. We are currently investigating the compound further by ^{183}W NMR and trying to grow diffraction-quality crystals to resolve the structure.

We could not isolate any clean compound from the phase-transfer reaction of $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ and other lanthanide triflates (La^{3+}, Eu^{3+}, Sm^{3+}). In all of these cases, we do get acetonitrile-soluble lanthanide complexes of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$. ^{31}P NMR analyses of the solutions show multiple lines, indicating mixtures of compounds. Addition of 10% water yields spectra identical with the corresponding **1:1**/**2:2** complexes. This demonstrates that even if **3:2** complexes might be formed with other lanthanides, they are not as stable as with ytterbium.

3. Reactivity of 1:1 $[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]^{7-}$. To investigate the formation of soluble ternary organic Eu(III) POM species and their luminescent properties, the **1:1** $(TBA)_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]$ (**6**) was reacted with organic ligands in acetonitrile. Complex **6** was chosen because it was clear, according to stability constant measurements, that the **1:1** formulation is maintained across the lanthanide series in aqueous solution and also in organic solution without contamination of the **1:2** species.[5,33] Experiments wherein 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy) is titrated into the solution of $(TBA)_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]$ (**6**) in CH_3CN with $\lambda_{exc} = 350$ nm show an increase in emission ($\lambda_{emission} = 614$ nm) of the Eu(III) that levels off at 2 equiv of organic ligand/equiv of complex **6**, consistent with 2:1 organic ligand:$[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]^{7-}$ formulation and energy transfer from the organic sensitizing ligand to the Eu(III) center (Figure 5). This is expected because two bidentate organic ligands bind to the $[Eu(\alpha_1\text{-}P_2W_{17}O_{61})]^{7-}$ unit to complete the eight coordination of Eu(III). Excitation spectra taken at each titration point confirm the energy transfer process from the organic moiety to the Eu(III). Quantum yields are 0.12 for the bipy:Eu:$[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ compared to <0.01 for $[Eu(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{17-}$ and other **1**:**2** Ln:POM complexes, measured against a rhodamine dye standard.[54,55]

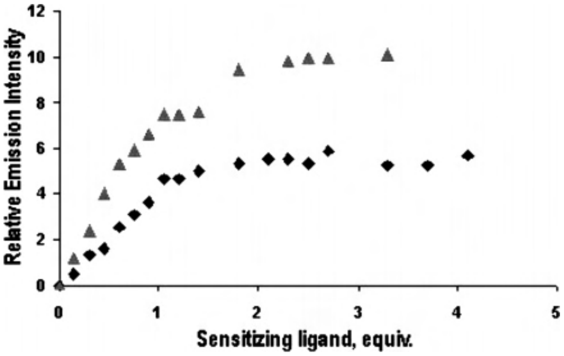


Figure 5. Relative emission intensity of $[Eu(\alpha_1\text{-}P_2W_{17}O_{61})]^{7-}$ upon addition of (▲) 2,2′-bipyridine and (◆) 1,10-phenanthroline in CH_3CN. Concentration of $(TBA)_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61})]$: 7.02×10^{-4} M. $\lambda_{exc} = 319$ nm.

^{31}P NMR shows slight shifts for both resonances from the parent **1:1** $[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61})]^{7-}$ complex upon addition of 2 equiv of phenanthroline, suggesting that the Eu−POM remains intact during the titration. The control, $Eu(ClO_4)_3$, shows a peak at 4−5 equiv of organic ligand added, consistent with all of the 8−9 coordination sites taken up by the bidentate ligand. Similar luminescence titrations have been performed for crown ether lanthanide complexes with sensitizing organic ligands to indicate ternary Ln (crown ether) (sensitizer ligand) complexes.[56]

Conclusion

This work elucidates fundamental aspects of the chemistry in organic solvents of the $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ in combination with lanthanides. The aqueous solution chemistry shows **1:1** complexes in equilibrium with **2:2** dimers. These species can be rendered soluble in organic solvent by metathesis with (TBA)Br under strict pH control. The formulation of $(TBA)_5H_2[\alpha_1\text{-}Ln(H_2O)_4P_2W_{17}O_{61}]$ has been determined by elemental analysis, acid−base titration, IR, ^{31}P NMR, and mass spectral analysis. Moreover, the mass spectral data show the presence of the **2:2** species as well and suggest a mode of decomposition by double protonation and elimination of water.

A **3:2** complex of Yb has been isolated by reaction of $Yb(OTf)_3$ and (TBA)Br to a suspension of $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ and characterized by elemental analysis, IR, ^{31}P NMR, and mass spectral analysis.

We have thus established the synthetic protocols to obtain discrete Ln−POM species of different stoichiometries in organic solvents. This is the prerequisite for the use of such compounds as building blocks for the rational synthesis of molecular materials. Moreover, the reaction of $(TBA)_5H_2[\alpha_1\text{-}Eu(P_2W_{17}O_{61})]^{7-}$ with bidentate ligands (phenanthroline and bipyridine) that sensitize the luminescence of the Eu(III) by formation of ternary species indicates the way to enhance the luminescence properties of these building blocks. We are currently studying these properties to develop new

---

(54) Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. *J. Phys. Chem. A* **2003**, *107*, 1697−1702.

(55) Huignard, A.; Gacoin, T.; Boilot, J.-P. *Chem. Mater.* **2000**, *12*, 1090−1094.

(56) Magennis, S. W.; Craing, J.; Gardner, A.; Fucassi, F.; Cragg, P. J.; Robertson, N.; Parsons, S.; Pikramenou, Z. *Polyhedron* **2003**, *22*, 745−754.

luminescent materials. Furthermore, the understanding of the solution chemistry is necessary to explore the Lewis acid catalytic activities of these compounds. Our promising results on this topic will be reported subsequently.

Experimental Section

Materials and Methods. Reagents and chemicals were purchased from commercial sources and used as received. The lacunary Dawson complex $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ was prepared as reported in the literature.[41] Aqueous solutions of $[\alpha_1\text{-}P_2W_{17}O_{61}]^{10-}$ were standardized by titration with standardized $CoCl_2$ solutions, monitoring the absorbance at $\lambda = 540$ nm. The $LnCl_3$ solutions are standardized by titration with EDTA with xylenol orange indicator. *Infrared spectra* were recorded from KBr pellets with a BioRad FTS 165 FT-IR spectrophotometer. *^{31}P NMR spectra* were obtained in 5 mm o.d. tubes at 298 and 300 K at 121.5 and 162 MHz, respectively, by use either of a Bruker AC 300 or of a Bruker AVANCE 400 at a concentration of 100 mg/0.5 mL. Some 85% H_3PO_4 in a coaxial tube was used as external reference. *Elemental analysis* were carried out by the "Service Central d'Analyse", CNRS, Vernaison, France. Some tungsten analysis were obtained by atomic absorption spectroscopy on a Perkin-Elmer Analyst 100 spectrometer. *Mass spectrometry* experiments have been carried out on an electrospray-ion trap instrument (Bruker, Esquire 3000). The 50 pmol·μL^{-1} solutions of POMs were infused using a syringe pump (160 μL·min^{-1}). The negative ion mode was used with a capillary high voltage of 3500 V. The orifice/skimmer voltage difference was set to 40 V to avoid decomposition of the POMs. The low-mass-cutoff (LMCO) of the ion trap was set to 50 Th or 100 Th to trap preferentially low or high mass to charge ions, respectively. For *solution luminescence spectroscopy*, steady-state emission and excitation spectra were acquired using a Fluorolog ISA JOBIN YVON SPEX spectrofluorometer.

Titration of $(TBA)_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61}]$ (6) with 1,10-Phenanthroline and 2,2′-Bipyridine. The following example is typical of the experimental procedure: 358 μL of 0.015 89 M $(TBA)_5H_2[\alpha_1\text{-}Eu(H_2O)_4P_2W_{17}O_{61})]$ stock solution (concentration was determined by ICP measurements of Eu, P, W) and 2142 μL of CH_3CN were placed in a clean 0.5 mL of luminescence cuvette. Using a volumetric pipette, a total of 22.77 mmol of 1,10-phenanthroline solution was added in 15 μL (1−8), 20 μL (9−14), and 40 μL (15−18) increments of 0.056 93 M 1,10-phenanthroline stock solution. The excitation (monitored at 614 nm) and emission (excited at 319 nm) spectra were collected at each data point. The relative luminescence intensity was plotted as a function of added ligand.

Single-Crystal X-ray Structure Determination. Crystals were mounted on glass fibers and sealed with an epoxy cement. Crystal structure data are summarized in Table 3. Full presentation of the information is deposited as part of the crystallographic information format (CIF) file as Supporting Information.

$K_7[\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}]\cdot 9H_2O$ (1). The complex was prepared as published.[33] X-ray-quality crystals were obtained from an aqueous solution at 3 °C. Yield: 40%. ^{31}P NMR (162 MHz, D_2O): $\delta = -10.6$ (s, 1 P, PW_8La) and -13.1 ppm (s, 1 P, PW_9). IR: $\tilde{\nu} = 1135$ (m), 1083 (s), 1058 (w), 1013 (w), 944 (s), 896 (s) cm^{-1}. Anal. Calcd for $H_{26}K_7LaO_{74}P_2W_{17}$ ($M_r = 4810.15$): K, 5.69; La, 2.89; P, 1.29; W, 64.98. Found: K, 5.63; La, 2.38; P, 1.11; W, 60.07.

$(^nBu_4N)_6H_4[\alpha_1\text{-}P_2W_{17}O_{61}]$ (2). The lacunary $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ (1.0 g, 0.2 mmol) was dissolved in 25 mL of water at 20 °C. The suspension was stirred until a clear solution was obtained. A solution of (TBA)Br (750 mg, 2.3 mmol) in 10 mL of water was added dropwise. After complete addition, the solution was allowed to stir for an additional 2 min and 0.1 mL of AcOH (1 M) was added. The white precipitate was then collected by filtration. Yield: 1.05 g (93%). ^{31}P NMR (162 MHz, $c = 0.036$ mol·L^{-1}, CD_3CN): $\delta = -10.5$ (s, 1 P, PW_8) and -11.9 ppm (s, 1 P, PW_9). IR: $\tilde{\nu} = 2963$ (m), 2935 (m), 2875 (m), 1485 (m), 1469 (w), 1381 (w), 1145 (w), 1090 (s), 1062 (vw), 1018 (w), 961 (w), 950 (s), 904 (s), 786 (vs) cm^{-1}. Anal. Calcd for $C_{96}H_{220}N_6O_{61}P_2W_{17}$ ($M_r = 5622.19$): C, 20.50; H, 3.94; N, 1.49; P, 1.10; W, 55.52. Found: C, 20.44; H, 3.96; N, 1.44; P, 1.13; W, 55.15.

Table 3. Crystallographic Data for $K_{14}[\{\alpha_1\text{-}La(H_2O)_4P_2W_{17}O_{61}\}_2]$ (1)

formula	$H_{44}K_{14}La_2O_{144}P_4W_{34}$
M_r	9548.24
color	colorless
cryst system	monoclinic
space group	$P2_1/n$
T (K)	295
a (Å)	13.008(2)
b (Å)	21.225(4)
c (Å)	28.835(6)
α (deg)	90
β (deg)	92.857(17)
γ (deg)	90
V (Å^3)	7951(3)
Z	2
μ (cm^{-1})	255.1
ρ_{calcd} (g cm^{-3})	3.99
R^a	0.0686
$R_w{}^a$	0.0779

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma wF_o{}^2]^{1/2}$. Weighting scheme is of the form $w = w'[1 - ((||F_o| - |F_c||)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ with coefficients 0.677, 0.480, and 0.367 for a Chebychev series for which $X = F_c/F_c(\max)$.

$(^nBu_4N)_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (3a). The lacunary $K_9Li[\alpha_1\text{-}P_2W_{17}O_{61}]$ (1.0 g, 0.2 mmol) was dissolved in 25 mL of water at 20 °C. The suspension was stirred until a clear solution was obtained. $YbCl_3$ (89.6 mg, 0.22 mmol) was dissolved in 2 mL of water and added dropwise to the stirring solution (pH = 4.5). After 2 min, a solution of (TBA)Br (750 mg, 2.3 mmol) in 10 mL of water was added dropwise and the pH maintained at 4.5 with 1 M HCl. After complete addition, the solution was allowed to stir for an additional 2 min. The white precipitate was then collected by filtration. Yield: 1.03 g (93%). ^{31}P NMR (162 MHz, $c = 0.036$ mol·L^{-1}, CD_3CN + 10% D_2O): $\delta = 33.8$ (s, 1 P, PW_8Yb) and -1.7 ppm (s, 1 P, PW_9). IR: $\tilde{\nu} = 2963$ (m), 2936 (m), 2874 (s), 1484 (m), 1470 (m), 1382 (w), 1154 (vw), 1147 (sh), 1093 (s), 1067 (sh), 1018 (w), 955 (s), 906 (s), 793 cm^{-1} (vs) cm^{-1}. Anal. Calcd for $C_{72}H_{146}N_{4.5}K_{0.5}O_{65}P_2W_{17}Yb$ ($(^nBu_4N)_{4.5}K_{0.5}H_2[Yb(H_2O)_4(\alpha_1\text{-}P_2W_{17}O_{61})]$) ($M_r = 5521.13$): C, 15.66; H, 3.14; N, 1.14; K, 0.35; P, 1.12; W, 56.60; Yb, 3.13. Found: C, 15.59; H, 3.17; N, 1.04; K, 0.49; P, 1.15; W, 54.95; Yb, 3.01.

$(BnEt_3N)_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (3b). Yield: 1.03 g (96%). ^{31}P NMR (121.5 MHz, $c = 0.037$ mol·L^{-1}, DMSO-d_6): $\delta = 21.6$ (s, 1 P, PW_8Yb), -3.8 ppm (s, 1 P, PW_9). IR: $\tilde{\nu} = 2986$ (w), 1480 (m), 1457 (w), 1395 (w), 1155 (w), 1093 (s), 1066 (vw), 1013 (w), 948 (s), 904 (s), 793 (vs), 751 (vw), 708 (vw) cm^{-1}. Anal. Calcd for $C_{65}H_{120}N_5O_{65}W_{17}Yb$ ($M_r = 5372.10$): C, 14.53; H, 2.25; N, 1.30; P, 1.15; W, 58.18; Yb, 3.22. Found: C, 14.46; H, 2.23; N, 1.22; P, 1.05; W, 48.83; Yb, 2.69.

$(MePh_3P)_5H_2[\alpha_1\text{-}Yb(H_2O)_4P_2W_{17}O_{61}]$ (3c). Yield: 1.15 g (99%). ^{31}P NMR (121.5 MHz, $c = 0.035$ mol·L^{-1}, DMSO-d_6): $\delta = 24.7$ (s, 1 P, PW_8Yb), 23.4 (s, 5 P, $MePh_3P$), -2.4 ppm (s, 1 P, PW_9). IR: $\tilde{\nu} = 2918$ (w), 1588 (vw), 1485 (w), 1440 (m), 1408 (vw), 1340 (vw), 1322 (vw), 1193 (vw), 1156 (vw), 1117 (m), 1092 (s), 1066 (sh), 1014 (vw), 998 (vw), 947 (s), 901 (s), 791 (vs), 746 (w), 720 (vw), 690 (m) cm^{-1}. Anal. Calcd for $C_{95}H_{100}O_{65}P_7W_{17}Yb$ (M_r = 5797.10): C, 19.68; H, 1.74; P, 3.74; W, 53.91; Yb, 2.98. Found: C, 20.61; H, 1.85; P, 3.66; W, 47.95; Yb, 2.62.

$(^nBu_4N)_5H_2[\alpha_1\text{-La}(H_2O)_4P_2W_{17}O_{61}]$ (4). Yield: 996 mg (89%). ^{31}P NMR (162 MHz, $c = 0.036$ mol·L^{-1}, CD_3CN + 10% D_2O): $\delta = -8.6$ (s, 1 P, PW_8La) and -12.2 ppm (s, 1 P, PW_9). IR: $\tilde{\nu}$ = 2964 (m), 2936 (m), 2876 (m), 1485 (m), 1469 (m), 1380 (w), 1147 (sh), 1121 (vw), 1092 (s), 1064 (vw) 1018 (w), 956 (s), 906 (s), 792 (vs) cm^{-1}. Anal. Calcd for $C_{80}H_{190}N_5LaO_{65}P_2W_{17}$ (M_r = 5588.68): C, 17.19; H, 3.43; N, 1.25; La, 2.48; P, 1.11; W, 55.92. Found: C, 15.97; H, 3.26; N, 1.12; La, 2.16; P, 1.19; W, 55.39.

$(^nBu_4N)_5H_2[\alpha_1\text{-Sm}(H_2O)_4P_2W_{17}O_{61}]$ (5). Yield: 940 mg (84%). ^{31}P NMR (162 MHz, $c = 0.036$ mol·L^{-1}, CD_3CN + 10% D_2O): $\delta = -11.54$ (s, 1 P, PW_9) and -13.2 ppm (s, 1 P, PW_8Sm). IR: $\tilde{\nu}$ = 2965 (m), 2936 (m), 2876 (m), 1485 (m), 1469 (w), 1382 (w), 1147 (vw), 1126 (sh), 1093 (s), 1063 (vw) 1018 (w), 953 (s), 905 (s), 793 (vs) cm^{-1}. Anal. Calcd for $C_{80}H_{190}N_5O_{65}P_2SmW_{17}$ (M_r = 5600.13): C, 17.16; H, 3.42; N, 1.25; P, 1.11; Sm, 2.68; W, 55.81. Found: C, 16.74; H, 3.37; N, 1.18; P, 1.17; Sm, 2.69; W, 53.72.

$(^nBu_4N)_5H_2[\alpha_1\text{-Eu}(H_2O)_4P_2W_{17}O_{61}]$ (6). Yield: 986 mg (88%). ^{31}P NMR (162 MHz, $c = 0.036$ mol·L^{-1}, CD_3CN + 10% D_2O): $\delta = 4.8$ (s, 1 P, PW_8Eu) and -11.7 ppm (s, 1 P, PW_9). IR: $\tilde{\nu}$ = 2963 (m), 2936 (m), 2875 (m), 1485 (m), 1459 (m), 1382 (w), 1147 (sh), 1127 (vw), 1092 (s), 1066 (vw) 1018 (w), 951 (s), 904 (s), 792 (vs) cm^{-1}. Anal. Calcd for $C_{80}H_{190}N_5EuO_{65}P_2W_{17}$ (M_r = 5601.74): C, 17.15; H, 3.42; N, 1.25; Eu, 2.71; P, 1.10; W, 55.79. Found: C, 16.74; H, 3.35; N, 1.17; Eu, 2.37; P, 1.12; W, 55.05.

$(^nBu_4N)_8K_3[Yb\{\alpha_1\text{-YbP}_2W_{17}O_{61}\}_2]$ (7). $Yb(OTf)_3$ (490 mg, 0.8 mmol) and (TBA)Br (1.93 g, 6.0 mmol) were added to a suspension of $K_9[Li(\alpha_1\text{-}P_2W_{17}O_{61})]$ (4.0 g, 0.8 mmol) in acetonitrile (20 mL). The mixture was stirred for 36 h at room temperature under argon atmosphere. The remaining solid was filtered off, and the product was isolated by precipitation (1:10 EtOH/Et_2O). Yield: 1.7 g (57%). ^{31}P NMR (121.5 MHz, $c = 0.018$ mol·L^{-1}, CD_3CN): $\delta = 82.0$ (s, 1 P, PW_8Yb) and 11.6 ppm (s, 1 P, PW_9). IR: $\tilde{\nu}$ = 2964 (m), 2936 (m), 2876 (m), 1485 (m), 1470 (m), 1383 (w), 1262 (), 1153 (vw), 1087 (s), 1032 (w), 957 (s), 902 (s), 798 (vs) cm^{-1}. Anal. Calcd for $C_{128}H_{304}N_8K_3O_{130}P_4W_{34}Yb_3$ (**7**·$8H_2O$, M_r = 11047.06): C, 13.83; H, 2.83; N, 1.00; K, 1.05; P, 1.11; W, 56.22; Yb, 4.21. Found: C, 13.87; H, 2.75; N, 0.96; K, 1.08; P, 0.79; W, 53.17; Yb, 4.21.

Acknowledgment. We gratefully acknowledge financial support from the UPMC and CNRS. A doctoral fellowship (C.B.) of the Ministère de l’Education Nationale, de l’Enseignement supérieur et de la Recherche was made possible by the support of the Institut Universitaire de France, of whom M.M. is a senior member. L.C.F. acknowledges NSF Grant No. CHE 0414218 and Grant NIH-S06 GM60654 (SCORE). Research Infrastructure at Hunter College is partially supported by NIH-Research Centers in Minority Institutions Grant RR03037-08.

Supporting Information Available: A description of “unsuccessful” synthetic procedures and the ESI-MS spectrum of $(TBA)_5H_2[\alpha_1\text{-Yb}(H_2O)_4P_2W_{17}O_{61}]$ (**3a**) under highly declustering conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051679G