Coordination of Rare-Earth Elements in Complexes with Monovacant Wells−Dawson Polyoxoanions

Qun-Hui Luo,[†] Robertha C. Howell,[†] Michaela Dankova,[†] Judit Bartis,[†] Clayton W. Williams,[‡] William DeW. Horrocks, Jr.,[§] Victor G. Young, Jr.,[||] Arnold L. Rheingold,[⊥] Lynn C. Francesconi,*[,†] and Mark R. Antonio*[,‡]

Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439, Department of Chemistry, Hunter College and the Graduate School of the City University of New York, 695 Park Avenue, New York, New York 10021, Department of Chemistry, The University of Delaware, Newark, Delaware 19716, Department of Chemistry, X-ray Crystallographic Laboratory, University of Minnesota, Minneapolis, Minnesota 55455, and Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received December 17, 2000

The α-1 and α-2 isomers of the monovacant Wells−Dawson heteropolyoxoanion $[P_2W_{17}O_{61}]^{10-}$ are complexants of trivalent rare-earth (RE) ions and serve to stabilize otherwise reactive tetravalent lanthanide (Ln) and actinide (An) ions in aqueous solution. Aspects of the bonding of Ln ions with α-1-$[P_2W_{17}O_{61}]^{10-}$ and α-2-$[P_2W_{17}O_{61}]^{10-}$ were investigated to address issues of complex formation and stability. We present structural insights about the Ln(III) coordination environment and hydration in two types of stoichiometric complexes, $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ and $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ (for Ln ≡ Sm, Eu, Lu; X ≡ P, As). The crystal and molecular structures of $[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ (**1**) and $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ (**2**) were solved and refined through use of single-crystal X-ray diffraction. The crystallographic results are supported with corresponding insights from XAFS (X-ray absorption fine structure) for a series of nine solid-state complexes as well as from optical luminescence spectroscopy of the Eu(III) analogues in aqueous solution. All the Ln ions are eight-coordinate with oxygen atoms in a square antiprism arrangement. For the 1:1 stoichiometric Ln/α-1-$[P_2W_{17}O_{61}]^{10-}$ complexes, the Ln ions are bound to four O atoms of the lacunary polyoxometalate framework in addition to four O atoms from solvent (water) molecules as $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. This structure (**1**) is the first of its kind for any metal complex of α-1-$[P_2W_{17}O_{61}]^{10-}$, and the data indicate that the general stoichiometry $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ is maintained throughout the lanthanide series. For the 1:2 stoichiometric Ln/α-2-$[X_2W_{17}O_{61}]^{10-}$ complexes, no water molecules are in the Ln−O_8 coordination sphere. The Ln ions are bound to eight O atoms—four from each of two heteropolyanions—as $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$. The average Ln−O interatomic distances decrease across the lanthanide series, consistent with the decreasing Ln ionic radius.

Introduction

The Wells−Dawson heteropolyanion α-$[P_2W_{18}O_{62}]^{6-}$ [1] forms coordination complexes with rare-earth (RE) cations, which bind to oxygen atoms of the P−W−O framework. The stability constants for the binding of selected RE ions with $[P_2W_{18}O_{62}]^{6-}$ are low and suggest the formation of weak, labile complexes.[2−6] The poor complexant behavior of α-$[P_2W_{18}O_{62}]^{6-}$ is attributed to the weakly basic oxygen atoms on the anion's surface in combination with the lack of suitable inner-sphere coordination sites.

In contrast, the monovacant, lacunary Wells−Dawson polyoxoanion $[P_2W_{17}O_{61}]^{10-}$, which is obtained by removal of one $[W(VI)=O]^{4+}$ group from the plenary anion $[P_2W_{18}O_{62}]^{6-}$, binds RE ions to form coordination complexes that are considerably more stable than those formed with the plenary anion.[7] Two isomers, α-1 and α-2, of $[P_2W_{17}O_{61}]^{10-}$ can be prepared. These are known to function as tetradentate ligands with four strongly basic O donor atoms directed at the vacant site left by the removal of $[WO]^{4+}$.[8−17] For both isomers of $[P_2W_{17}O_{61}]^{10-}$, the

[†] Hunter College and the Graduate School of the City University of New York.
[‡] Argonne National Laboratory.
[§] The Pennsylvania State University.
[||] University of Minnesota.
[⊥] The University of Delaware.

(1) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113−126.
(2) Saito, A.; Choppin, G. R. *Inorg. Chem.* **1991**, *30*, 4563−4566.
(3) Shilov, V. P.; Astafurova, L. N.; Krot, N. N. *Radiochemistry (Engl. Transl.)* **1994**, *36*, 266−267.
(4) Lis, S. *Acta Phys. Pol. A* **1996**, *90*, 275−283.
(5) Van Pelt, C. E.; Crooks, W. J., III.; Choppin, G. R. *Inorg. Chim. Acta*, in press.
(6) Van Pelt, C. E.; Crooks, W. J., III.; Choppin, G. R. *Inorg. Chim. Acta*, submitted.
(7) Yusov, A. B.; Shilov, V. P. *Sov. Radiochemistry (Engl. Transl.)* **1999**, *41*, 1−23.
(8) Bartis, J.; Dankova, M.; Lessmann, J. J.; Luo, Q.-H.; Horrocks, W., Jr.; Francesconi, L. C. *Inorg. Chem.* **1999**, *38*, 1042−1053.
(9) Ciabrini, J. P.; Contant, R. *J. Chem. Res., Synop.* **1993**, 391.
(10) Haraguchi, N.; Okaue, Y.; Isobe, T.; Matsuda, Y. *Inorg. Chem.* **1994**, *33*, 1015−1020.
(11) Jorris, T. L.; Kozik, M.; Casan-Pastor, N.; Domaille, P. J.; Finke, R. G.; Miller, W. K.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 7402−7408.
(12) Keita, B.; Girard, F.; Nadjo, L.; Contant, R.; Canny, J.; Richet, M. *J. Electroanal. Chem* **1999**, *478*, 76−82.
(13) Lyon, D. K.; Miller, W. K.; Novet, T.; Domaille, P. J.; Evitt, E.; Johnson, D. C.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7209−7221.
(14) Mansuy, D.; Bartoli, J. F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222−7226.

10.1021/ic001427+ CCC: $20.00
Published on Web 03/13/2001

available data reveal high formation constants with transition metal and RE ions.[5,6,9,13,18−23] The α-1- and α-2-$[P_2W_{17}O_{61}]^{10-}$ isomers are useful ligands for stabilizing tetravalent cations, especially the otherwise reactive ones of the lanthanide (Ln) and actinide (An) elements.[24−29] As such, these polyoxometalates, specifically, the α-2-$[P_2W_{17}O_{61}]^{10-}$ isomer, find applications to selected aspects of An separations science in nuclear waste processing.[30−39]

As reported in 1971 by Peacock and Weakley,[40] the first RE complexes of $[P_2W_{17}O_{61}]^{10-}$ were prepared with what is now known as the α-2 isomer and had a 1:2 stoichiometry, $[RE^{n+}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{n-20}$. These complexes, with one RE^{n+} ion[8−10,41,42] ($n = 3, 4$) or one alkaline earth ion[43] and two α-2-$[P_2W_{17}O_{61}]^{10-}$ anions, are of contemporary interest. Complexes of the α-1 isomer have also been prepared; the prevalent ones form with the 1:1 stoichiometry, $[RE^{n+}(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{n-10}$, with one RE ion[8,9] or one transition metal ion[11,21] and one α-1-$[P_2W_{17}O_{61}]^{10-}$ anion. Despite considerable research activity throughout the past 30 years, there is a dearth of metrical information about the coordination of RE ions in these otherwise well-characterized complexes of the α-1 and α-2 isomers of $[P_2W_{17}O_{61}]^{10-}$. No complete single-crystal X-ray diffraction structures have been determined before now because of difficulties in obtaining suitable-quality crystals. The sole available structure determination, showing the tungsten framework only, was reported in 1979 for the 1:2 Ce^{4+} complex $K_{16}[Ce(P_2W_{17}O_{61})_2]\cdot 50H_2O$.[44] No Ce−O distances were reported because the O atoms were not located in the low-grade ($R =$ 19%) structure determination. We have solved and refined the complete crystal and molecular structures of two lutetium complexes, $K_7[Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]$ (**1**) and $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ (**2**). The former structure (**1**) is the first of its kind for any metal complex of α-1-$[P_2W_{17}O_{61}]^{10-}$. Both structures provide information on the Lu^{3+}−O coordination environments, which are described along with metrical results from the XAFS (X-ray absorption fine structure) analyses of the corresponding Sm and Eu complexes as well as the optical luminescence spectroscopy of the Eu analogues in aqueous solution. Our results are discussed in light of available crystallographic information for related RE polyoxoanions and RE aquo complexes.

Experimental Section

Preparation of Complexes. Nine Ln(III)-containing heteropolyoxotungstates, including six $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ (for Ln ≡ Sm, Eu, Lu; X ≡ P, As) and three $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ (for Ln ≡ Sm, Eu, Lu) complexes, were prepared according to literature methods as the Li and K salts.[8,41,42] ^{31}P and ^{183}W NMR spectroscopy revealed the preparation of single-phase and isomerically pure complexes.[8,41,42] Selected compounds were checked by elemental analysis and TGA.[8,42]

Crystallization of $[Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ (1). Crystals of **1** for X-ray diffraction were grown by a modification of the synthesis reported earlier.[8] $K_9Li[\alpha\text{-}1\text{-}P_2W_{17}O_{61}]$ (2.0 g) was dissolved in 20 mL of lithium acetate buffer (0.285 M, pH = 4.7). An aqueous solution of $LuCl_3$ (1 M, 0.6 mL) was added, and the solution was stirred for 30 min. Potassium chloride (1.4 g) was added. The resulting suspension was cooled in the freezer for 10 h and filtered. The filtrate was cooled in the freezer for another 2 days to yield colorless crystals. Elemental analysis *on the crystals* were performed (University of Illinois Microanalytical Laboratory) to determine the chemical species that are disordered in the channels in the crystal structure. $K_7[Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]\cdot 18.7H_2O\cdot {}^1/_2CH_3COOK$. Anal. Calcd for $K_8W_{17}P_2LuO_{80.7}H_{38.9}$: W, 62.34; Lu, 3.49; P, 1.23; K, 5.85; C, 0.24; H, 0.77. Found: W, 59.49; Lu, 3.01; P, 1.15; K, 5.80; C, 0.16; H, 0.40. TGA on the crystals shows 18.7 H_2O. Lithium was not detected by elemental analysis.

Crystallization of $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ (2). Crystals of **2** were prepared as described previously.[42] One milliliter of a saturated aqueous solution of $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ was diluted with 0.3 mL of water and one drop of a saturated KCl solution. The solution was allowed to evaporate at room temperature over a period of 3 days to yield colorless crystals.

Laser Excitation Luminescence Spectroscopy. A Continuum YG581 pulsed Nd:YAG laser pumped TDL50 tunable dye laser was used to obtain the excitation spectra and luminescence lifetimes. The $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ion in $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ was excited as the $^5D_0 \rightarrow {}^7F_2$ emission band was monitored.[45] All measurements were carried out at 25.0 ± 0.1 °C. The commercially available Peakfit program, which employs a nonlinear regression

(15) Qu, L.; Wang, S.; Peng, J.; Chen, Y.; Wang, G. *Polyhedron* **1992**, *11*, 2645−2649.
(16) Qu, L.; Wang, S.; Peng, J.; Chen, Y.; Yu, M. *Chin. Sci. Bull.* **1993**, *38*, 1087−1091.
(17) Venturelli, A.; Nilges, M. J.; Smirnov, A.; Belford, R. L.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans.* **1999**, 301−310.
(18) Spitsyn, V. I.; Orlova, M. M.; Krot, N. N.; Saprykin, A. S. *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.)* **1978**, *23*, 677−680.
(19) Nomiya, K.; Miwa, M. *Polyhedron* **1985**, *4*, 89−95.
(20) Hamlaoui, M. L.; Vlassenko, K.; Messadi, D. *C. R. ′Acad. Sci., Ser. II* **1990**, *311*, 795−798.
(21) Bartis, J.; Kunina, Y.; Blumenstein, M.; Francesconi, L. C. *Inorg. Chem.* **1996**, *35*, 1497−1501.
(22) Bion, L.; Moisy, P.; Vaufrey, F.; Meot-Reymond, S.; Simoni, E.; Madic, C. *Radiochim. Acta* **1997**, *78*, 73−82.
(23) Bion, L.; Mercier, F.; Decambox, P.; Moisy, P. *Radiochim. Acta* **1999**, *87*, 161−166.
(24) Chistyakov, V. M.; Baranov, A. A.; Karbovnichii, P. N.; Erin, E. A.; Timofeev, G. A. *Sov. Radiochem. (Engl. Transl.)* **1990**, *32*, 334−337.
(25) Erine, E. A.; Baranov, A. A.; Yu, V. A.; Chistyakov, V. M.; Timofeev, G. A. *J. Alloys Compd.* **1998**, *271−273*, 782−785.
(26) Isobe, T.; Okaue, Y. In *New Development of Studies on Rare Earth Complexes*; Adachi, G., Yamase, T., Inanaga, J., Komiyama, M., Machida, K., Eds.; The Rare Earth Society of Japan: Osaka, 1997; pp 67−74.
(27) Kosyakov, V. N.; Timofeev, G. A.; Erin, E. A.; Andreev, V. I.; Kopytov, V. V.; Simakin, G. A. *Sov. Radiochem. (Engl. Transl.)* **1977**, *19*, 418−423.
(28) Myasoedov, B. F.; Lebedev, I. A. *Sov. Radiochem. (Engl. Transl.)* **1977**, *19*, 69−71.
(29) Saprykin, A. S.; Shilov, V. P.; Spitsyn, V. I.; Krot, N. N. *Dokl. Chem. (Transl. of Dokl. Akad. Nauk)* **1976**, *226*, 114−116.
(30) Bion, L.; Moisy, P.; Madic, C. *Radiochim. Acta* **1995**, *69*, 251−257.
(31) Kamoshida, M.; Fukasawa, T.; Kawamura, F. *J. Nucl. Sci. Technol.* **1998**, *35*, 185−189.
(32) Madic, C.; Bourges, J.; Dozol, J.-F. *AIP Conf. Proc.* **1995**, *346*, 628−638.
(33) Malikov, D. A.; Milyukova, M. S.; Myasoedov, B. F. *Sov. Radiochem. (Engl. Transl.)* **1989**, *31*, 425−430.
(34) Malikov, D. A.; Milyukova, M. S.; Kuzovkina, E. V.; Myasoedov, B. F. *Sov. Radiochem. (Engl. Transl.)* **1993**, *35*, 465−471.
(35) Milyukova, M. S.; Varezhkina, N. S.; Myasoedov, B. F. *J. Radioanal. Nucl. Chem.* **1986**, *105*, 249−256.
(36) Milyukova, M. S.; Varezhkina, N. S.; Myasoedov, B. F. *J. Radioanal. Nucl. Chem.* **1988**, *121*, 403−408.
(37) Milyukova, M. S.; Varezhkina, N. S.; Myasoedov, B. F. *Sov. Radiochem. (Engl. Transl.)* **1990**, *32*, 361−367.
(38) Myasoedov, B. F.; Milyukova, M. S.; Malikov, D. A. *Solvent Extr. Ion Exch.* **1984**, *2*, 61−77.
(39) Varezhkina, N. S.; Milyukova, M. S.; Myasoedov, B. F. *J. Radioanal. Nucl. Chem.* **1989**, *135*, 67−76.
(40) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, 1836−1839.
(41) Bartis, J.; Dankova, M.; Blumenstein, M.; Francesconi, L. C. *J. Alloys Compds.* **1997**, *249*, 56−68.
(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) Spitsyn, V. I.; Orlova, M. M.; Saprykina, O. P.; Saprykin, A. S.; Krot, N. N. *Russ. J. Inorg. Chem. (Transl. of Zh. Neorg. Khim.)* **1977**, *22*, 1355−1357.
(44) Molchanov, V. N.; Kazanskii, L. P.; Torchenkova, E. A.; Simonov, V. I. *Sov. Phys. Crystallogr. (Engl. Transl.)* **1979**, *24*, 96−97.
(45) Horrocks, W. D., Jr.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334−340.

Table 1. Crystal Data and Structure Refinement for **1** and **2**

empirical formula	$K_8LuO_{80.7}C_1P_2W_{17}$ (**1**)	$K_{17}LuO_{176}P_4W_{34}$ (**2**)
fw	4858.70	10030.45
temp, K	173(2)	293(2)
wavelength, Å	0.710 73	0.710 73
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	18.6997(2)	14.4722(6)
b, Å	26.1617(4)	22.3719(8)
c, Å	19.2653(1)	24.4501(9)
α, deg	90	95.103(2)
β, deg	106.417(1)	102.618(2)
γ, deg	90	99.954(3)
vol, Å^3	9040.6(2)	7542.3(5)
Z	4	2
calcd density, Mg/m^3	3.570	4.417
abs coeff, mm^{-1}	22.977	27.101
F(000)	8418	8756
cryst size, mm	0.40 × 0.25 × 0.11	0.2 × 0.05 × 0.03
θ range for data collection, deg	1.34−24.93	1.18−28.31
limiting indices	$-21 \le h \le 21, 0 \le k \le 30, 0 \le l \le 22$	$-19 \le h \le 18, -29 \le k \le 28, 0 \le l \le 32$
reflns collected/unique	53627/15174 [R(int) = 0.0749]	65797/34303 [R(int) = 0.0000]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	15171/243/577	34303/0/1199
GOF on F^2	1.054	1.063
final R indices [$I > 2\sigma(I)$]	R1 = 0.0732, wR2 = 0.1915	R1 = 0.0860, wR2 = 0.2303
R indices (all data)	R1 = 0.1065, wR2 = 0.2076	R1 = 0.0964, wR2 = 0.2424
largest diff peak and hole, e/Å^3	6.103 and −3.303	7.575 and −6.735

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Selected Atoms (Lu and Oxygen Atoms in Lu Coordination Sphere) for Compounds **1** and **2**

	x	y	z	U(eq) [a]	SOF
$K_7[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]$ (**1**)					
Lu(14)	2585(1)	1075(1)	5240(1)	24(1)	0.826(4)
O(63)	2287(14)	1610(10)	6122(14)	37(6)	0.826(4)
O(64)	2212(13)	477(9)	6056(13)	36(6)	0.826(4)
O(65)	3263(14)	1831(9)	5810(13)	37(6)	0.826(4)
O(66)	3686(15)	763(10)	6089(15)	46(7)	0.826(4)
O(9)	1305(9)	956(7)	4734(9)	22(4)	1
O(19)	2539(10)	282(7)	4669(10)	26(4)	1
O(20)	2138(10)	1720(7)	4474(9)	27(5)	1
O(26)	3393(10)	1153(7)	4566(10)	31(5)	1
$K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ (**2**)					
Lu(1)	−463(1)	2429(1)	8959(1)	10(1)	1
O(1A)	−1556(12)	2155(7)	9504(7)	12(3)	1
O(2A)	−624(12)	3340(8)	9432(7)	15(3)	1
O(10A)	1078(12)	2909(7)	9471(7)	14(3)	1
O(11A)	191(10)	1775(6)	9516(6)	6(3)	1
O(1B)	−1411(13)	1495(8)	8421(7)	17(3)	1
O(2B)	−1851(12)	2686(7)	8448(7)	12(3)	1
O(10B)	86(13)	3137(8)	8447(8)	19(3)	1
O(11B)	526(13)	2007(8)	8451(7)	18(3)	1

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

method, was used for data analyses. The concentration of the sample used to obtain the excitation spectrum was 250 μM. For lifetime measurements of the Eu excited state in D_2O, the complex was recrystallized once and lyophilized twice from 99.99% D_2O.

XAFS. The XAFS experiments were performed at wiggler station 4-3 at SSRL with a Si⟨220⟩ monochromator and ca. 0.8 mm vertical entrance slits. With ca. 80% detuning of the incident X-ray intensity, the Ln L_3-edge fluorescence XAFS was collected using a 13-element detector (Canberra) without filters. The powdered samples were maintained at 17 K in a continuous-flow LHe cryostat (Oxford CF-1208). The EXAFS was analyzed with the EXAFSPAK programs.[46] Single-scattering phase and amplitude functions were calculated with FEFF7.02[47,48] and a scale factor of 1. We performed single-shell (Ln−O) best integer fits of the $k^3\chi(k)$ EXAFS. In these, the oxygen coordination numbers (N_O) were refined as integer values and the interatomic distances (r), Debye−Waller factors (σ^2), and energy shifts (ΔE_0) were refined as real values.

Table 3. Bond Lengths [Å] for the Immediate Coordination Sphere about the Lu(III) in **1** and **2**

$K_7[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]$ (**1**)			
Lu(14)−O(26)	2.26(2)	Lu(14)−O(20)	2.24(2)
Lu(14)−O(19)	2.34(2)	Lu(14)−O(9)	2.34(2)
Lu(14)−O(63)	2.39(3)	Lu(14)−O(66)	2.38(3)
Lu(14)−O(64)	2.45(2)	Lu(14)−O(65)	2.44(2)
$K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ (**2**)			
Lu(1)−O(10B)	2.249(18)	Lu(1)−O(10A)	2.325(17)
Lu(1)−O(11A)	2.272(14)	Lu(1)−O(2B)	2.314(16)
Lu(1)−O(1A)	2.321(16)	Lu(1)−O(2A)	2.326(17)
Lu(1)−O(11B)	2.349(17)	Lu(1)−O(1B)	2.388(18)

Crystal Structure Solution and Refinement. 1. Data collection and structure solution of $K_7[Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]\cdot 18.7H_2O\cdot {}^1/_2CH_3COOK$ were conducted at the X-ray Crystallographic Laboratory, University of Minnesota. A single crystal of **1** was attached to a glass fiber and mounted on a Siemens SMART system for data collection at 173(2) K with Mo Kα radiation (0.710 73 Å). The space group $P2_1/n$ was determined on the basis of systematic absences and intensity statistics (SHELXTL-Plus, version 5.0, Siemens Industrial Automation, Inc., Madison, WI). A successful direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Several full-matrix least-squares/difference Fourier cycles were performed that located the remainder of the non-hydrogen atoms. All non-hydrogen and non-oxygen atoms were refined with anisotropic displacement parameters. Crystal data and structure refinement parameters are listed in Table 1. Final atomic coordinates and displacement parameters for the significant atoms are given in Table 2. All atomic coordinates are given in Table S1 of Supporting Information. Selected bond distances and angles about the Lu(III) ion are given in Tables 3 and 4, respectively. A complete set of bond distances and angles are given in Tables S2 and S3 of Supporting Information, respectively.

The crystal structure shows positional disorder in the tungsten framework. The Lu(14) atom is disordered over two sites Lu(14)W(5) and W(6)Lu(15) sites. The model constructed and refined successfully

(46) George, G. N.; Pickering, I. J. In http://www-ssrl.slac.stanford.edu/exafspak.html.

(47) Rehr, J. J.; de Leon, J. M.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135−5140.

(48) de Leon, J. M.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev.* **1991**, *B44*, 4146−4156.

Table 4. Bond Angles (deg) for the Immediate Coordination Sphere about the Lu(III) in **1** and **2**[a]

$K_7[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]$ (**1**)		$K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]$ (**2**)	
O(20)−Lu(14)−O(26)	74.9(7)	O(10B)−Lu(1)−O(11A)	135.8(6)
O(26)−Lu(14)−O(9)	122.9(6)	O(10B)−Lu(1)−O(2B)	76.0(6)
O(26)−Lu(14)−O(19)	75.6(7)	O(11A)−Lu(1)−O(2B)	147.2(5)
O(20)−Lu(14)−O(66)	143.0(8)	O(10B)−Lu(1)−O(1A)	145.4(6)
O(9)−Lu(14)−O(66)	145.7(8)	O(11A)−Lu(1)−O(1A)	75.1(5)
O(20)−Lu(14)−O(63)	84.7(8)	O(2B)−Lu(1)−O(1A)	77.9(6)
O(9)−Lu(14)−O(63)	87.6(7)	O(10B)−Lu(1)−O(10A)	73.5(6)
O(66)−Lu(14)−O(63)	92.5(9)	O(11A)−Lu(1)−O(10A)	70.7(5)
O(26)−Lu(14)−O(65)	80.7(8)	O(2B)−Lu(1)−O(10A)	139.0(6)
O(19)−Lu(14)−O(65)	151.3(7)	O(1A)−Lu(1)−O(10A)	114.8(6)
O(63)−Lu(14)−O(65)	53.1(8)	O(10B)−Lu(1)−O(2A)	77.0(6)
O(26)−Lu(14)−O(64)	141.4(7)	O(11A)−Lu(1)−O(2A)	115.6(5)
O(19)−Lu(14)−O(64)	75.9(7)	O(2B)−Lu(1)−O(2A)	73.4(6)
O(63)−Lu(14)−O(64)	75.7(8)	O(1A)−Lu(1)−O(2A)	74.1(6)
O(20)−Lu(14)−O(9)	71.2(6)	O(10A)−Lu(1)−O(2A)	73.5(6)
O(20)−Lu(14)−O(19)	113.6(7)	O(10B)−Lu(1)−O(11B)	72.3(6)
O(9)−Lu(14)−O(19)	77.8(6)	O(11A)−Lu(1)−O(11B)	75.4(6)
O(26)−Lu(14)−O(66)	80.6(8)	O(2B)−Lu(1)−O(11B)	117.8(6)
O(19)−Lu(14)−O(66)	85.9(8)	O(1A)−Lu(1)−O(11B)	141.2(6)
O(26)−Lu(14)−O(63)	133.2(8)	O(10A)−Lu(1)−O(11B)	77.7(6)
O(19)−Lu(14)−O(63)	150.6(8)	O(2A)−Lu(1)−O(11B)	142.6(6)
O(20)−Lu(14)−O(65)	74.6(8)	O(10B)−Lu(1)−O(1B)	115.2(6)
O(9)−Lu(14)−O(65)	129.6(7)	O(11A)−Lu(1)−O(1B)	82.3(5)
O(66)−Lu(14)−O(65)	74.4(9)	O(2B)−Lu(1)−O(1B)	74.3(6)
O(20)−Lu(14)−O(64)	141.3(7)	O(1A)−Lu(1)−O(1B)	78.6(6)
O(9)−Lu(14)−O(64)	74.9(7)	O(10A)−Lu(1)−O(1B)	144.3(6)
O(66)−Lu(14)−O(64)	71.9(9)	O(2A)−Lu(1)−O(1B)	141.2(6)
O(65)−Lu(14)−O(64)	115.8(8)		

[a] For **1**, symmetry transformations used to generate equivalent atoms: (#1) $x - {}^1/_2, -y + {}^1/_2, z - {}^1/_2$; (#2) $-x + 1, -y, -z + 1$; (#3) $-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_2$; (#4) $-x, -y, -z$; (#5) $x + {}^1/_2, -y + {}^1/_2, z + {}^1/_2$; (#6) $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$; (#7) $x + {}^1/_2, -y + {}^1/_2, z - {}^1/_2$; (#8) $x - {}^1/_2, -y + {}^1/_2, z + {}^1/_2$. For **2**, symmetry transformations used to generate equivalent atoms: (#1) $x - 1, y, z + 1$; (#2) $x, y, z + 1$; (#3) $x + 1, y, z$; (#4) $-x + 1, -y, -z + 2$; (#5) $-x, -y, -z + 2$; (#6) $-x + 1, -y + 1, -z + 2$; (#7) $x - 1, y - 1, z$; (#8) $x - 1, y, z$; (#9) $-x + 1, -y + 1, -z + 1$; (#10) $-x, -y + 1, -z + 2$; (#11) $-x, -y + 1, -z + 1$; (#12) $x, y, z - 1$; (#13) $x + 1, y, z - 1$; (#14) $-x + 2, -y + 1, -z + 1$; (#15) $x, y - 1, z$; (#16) $x + 1, y + 1, z$; (#17) $x, y + 1, z$.

has Lu(14) sharing the position $^5/_6$ of the time with W(5) occupying the position $^1/_6$ of the time. This type of positional disorder is common in polyoxoanion crystal structures, and in fact, severe positional disorder has been observed before for the lacunary α-2-$[P_2W_{17}O_{61}]^{10-}$ species and the $Co(H_2O)$ derivative.[49] Disorder in the countercations and water molecules are also common in heteropolyoxometalate crystal structures.[50]

Five of the seven potassium ions required for neutrality were found in the crystal structure in proximity to the anion. The other potassium ions (at least eight per unit cell, two per molecule) are likely disordered along with an unknown amount of water in the channels. The program PLATON/SQUEEZE[51] found a potential solvent volume of 1788.8 Å^3 per unit cell volume of 9040.6 Å^3, or 19.8% of the total. The elemental analyses of the crystals are consistent with this assessment; two to three potassium ions, water, and some acetate per molecule are disordered in the infinite channels that lie parallel to the *b* axis in the unit cell (Figure S1 of Supporting Information).

2. The data for $K_{17}[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]\cdot 54H_2O$ were collected at the University of Delaware, and the structure was solved at the University of Delaware and Hunter College. A single crystal of **2** was attached to a glass fiber and mounted on a Siemens SMART system for data collection at 173(2) K with Mo Kα radiation (0.710 73 Å). The raw data were corrected for Lorentz polarization and absorption effects (face-indexed numerical correction) using SAINT/SADABS. The structure was solved by direct methods. Tungsten, lutetium, and the

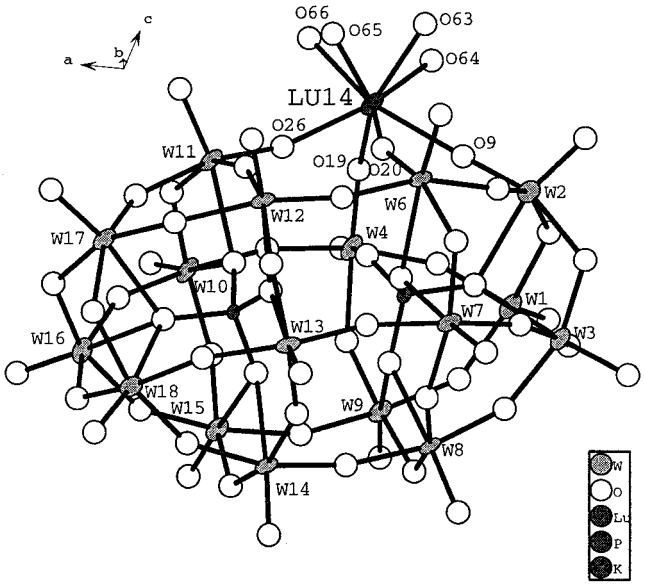

Figure 1. Ball and stick structure of the anion $[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$, **1**.

17 potassium atoms were refined anisotropically by full-matrix least squares on the F^2 data (SHELXTL-Plus, version 5.0). All atoms were not refined anisotropically because of a low data/parameters ratio and absorption effects. The resulting structure was triclinic and of the $P\bar{1}$ space group. The data were further subjected to an empirical absorption correction by means of the program DIFABS;[52] the refinement continued after this correction was applied. The largest residual peaks are located close to the metal atoms in a final difference map. We collected data on two crystals of this compound, and we have experienced the same difficulties with absorption effects and high residual peaks. Large residual peaks in the final difference map are a common problem encountered in the solution and refinement of polyoxotungstate structures.[50,53−58]

The details of data collection and refinement are contained in Table 1. Final atomic coordinates and displacement parameters for the significant atoms are given in Table 2. All atomic coordinates are given in Table S1. Selected bond distances and angles about the Lu(III) ion are given in Tables 3 and 4, respectively. A complete set of bond distances and angles is given in Tables S2 and S3, respectively.

Results

Single-Crystal X-ray Diffraction. A. $[Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. The crystal structure of anion **1** (Figure 1) shows that the Lu(III) ion is substituted for a $[WO]^{4+}$ unit in the "belt" region of the tungsten−oxygen framework of the parent Wells−Dawson ion α-$[P_2W_{18}O_{62}]^{6-}$.[1] The bond lengths from Lu to the four oxygen atoms of the framework are 2.26(2), 2.34(2), 2.24(2), and 2.34(2) Å. Moreover, the crystal structure shows that four water molecules are bound to Lu(III), with Lu−O distances of 2.38(3), 2.44(2), 2.39(3), and 2.45(2) Å, so that Lu is fully coordinated with eight O atoms in a square antiprism geometry. The presence of four H_2O molecules bound to Lu(III) is consistent with luminescence lifetime measurements of the

(49) Weakley, T. J. R. *Polyhedron* **1987**, *6*, 931−937.
(50) Casañ-Pastor, N.; Gomez-Romero, P.; Jameson, G. B.; Baker, L. C. W. *J. Am. Chem. Soc.* **1991**, *113*, 5658−5663.
(51) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.
(52) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166.
(53) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939−943.
(54) Ortega, F.; Pope, M. T.; Evans, H. T., Jr. *Inorg. Chem.* **1997**, *36*, 2166−2169.
(55) Xin, F.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 5693−5695.
(56) Wasserman, K.; Lunck, H. J.; Palm, R.; Fuchs, J.; Steinfeldt, N.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 5.
(57) Zhang, X. Y.; O'Connor, C. J.; Jameson, G. B.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 30−34.
(58) Jeannin, Y.; Launay, J. P.; Seid Sedjadi, M. A. *Inorg. Chem.* **1980**, *19*, 2933−2935.

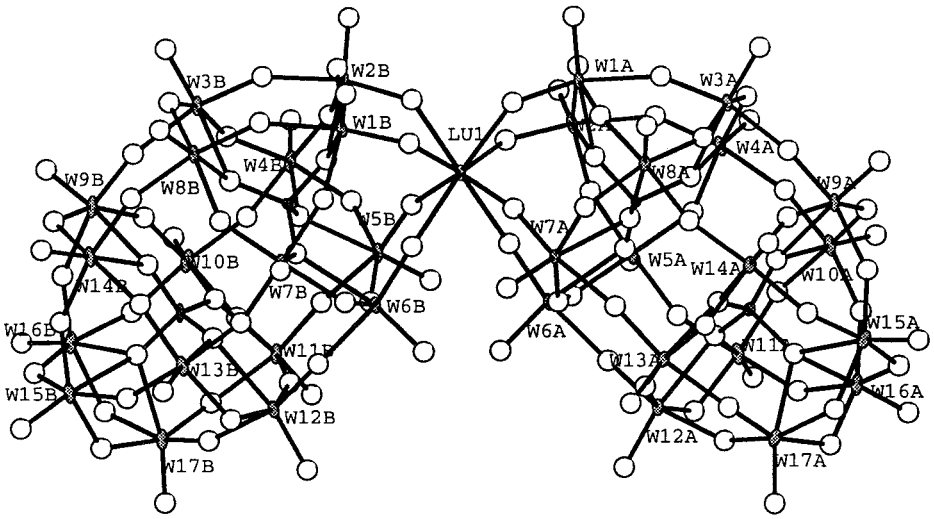

Figure 2. Ball and stick structure of the anion $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$, **2**.

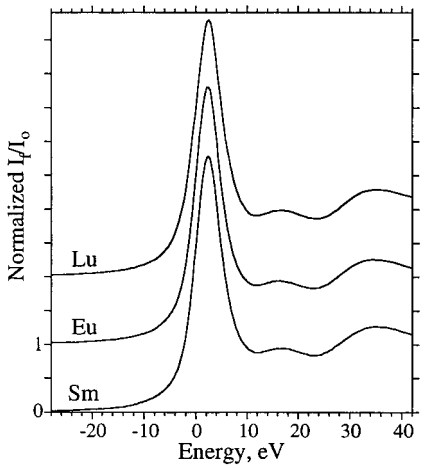

Figure 3. Normalized Ln L_3-edge XANES, I_f/I_0, for the solid salts of $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ at 17 K. The intense edge peaks at ca. +2.4 eV reveal that all the Ln ions (Sm, Eu, and Lu) are trivalent in the heteropolyoxoanion complexes. The energy origins for the individual spectra are defined as the inflection point energies, which were obtained from the first differential XANES. These are 6718.5 ± 0.1, 6979.3 ± 0.1, and 9246.0 ± 0.1 eV for the Sm, Eu, and Lu spectra, respectively. The spectra for the Eu^{3+} and Lu^{3+} complexes have been offset for clarity.

analogous Eu complex, which has four water molecules bound to Eu(III).[8] The water molecules are clearly an integral part of the coordination environment of Lu in **1**. As such, the anion's stoichiometry is best described by the formula $[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$, which will be designated hereon as **1**. Substitution of Lu(III) into the belt region results in a structure of C_1 symmetry, consistent with the solution ^{183}W NMR data for a series of lanthanide analogues.

B. $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$. The crystal structure of anion **2** shown in Figure 2 demonstrates that the Lu(III) ion substitutes for two $[WO]^{4+}$ units in the "cap" regions of two α-2-$[P_2W_{17}O_{61}]^{10-}$. The Lu(III) ion is in a square antiprismatic coordination environment with eight oxygen atoms, four from each of the two α-2-$[P_2W_{17}O_{61}]^{10-}$ ligands. Unlike **1**, no water molecules are bound to the Lu(III) ion in this molecule. As shown in Table 3, the Lu−O bond lengths exhibit a range 2.249(18)−2.388(18) Å. The two polyoxometalate "lobes" are disposed in a syn fashion. This structure is similar to the partial structure of $[Ce^{4+}(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$. The tungsten−oxygen and the phosphate bonds and angles of the two polyoxoanion ligands (Supporting Information) are consistent with the structure of α-2-$[P_2W_{17}O_{61}]^{10-}$ and its Co(III) complex.[49] The molecule has C_2 point group symmetry, consistent with the ^{31}P and ^{183}W solution NMR spectroscopic results.[42]

Luminescence Spectroscopy. The excitation spectrum of $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ revealed a peak at 580.44 nm, which is due to the $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ion. The experimentally determined luminescence lifetime τ (ms) of Eu^{3+} was measured separately in H_2O and D_2O solutions. This was done to determine the number of water molecules coordinated to Eu^{3+} in $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$. We obtained the following values: $\tau(H_2O) = 3.0$ ms and $\tau(D_2O) = 4.8$ ms. According to the method of Horrocks and Sudnick,[45,59] these values provide a hydration number of 0.1 for Eu^{3+} in $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$. This result indicates that in aqueous solution no water molecules are coordinated to Eu^{3+} in the complex. This finding is consistent with the absence of water molecules in the Lu^{3+} coordination of **2**, vide supra. The excitation spectrum and luminescence lifetime of Eu^{3+} in $[Eu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ have been reported previously.[8] The data indicate that in aqueous solution four water molecules are bound to Eu^{3+} in the complex. This finding is consistent with the number (four) of water molecules bound to Lu^{3+} in **1** reported here, vide supra.

XAFS. A. $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$. The Ln L_3 XANES (X-ray absorption near-edge structure) for the 1:2 Sm, Eu, and Lu complexes with $[\alpha\text{-}2\text{-}P_2W_{17}O_{61}]^{10-}$ is shown in Figure 3. The corresponding XANES for the $[Ln(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ complexes is indistinguishable (see Figure S2 of Supporting Information). The intense edge peaks at +2.4 eV of ca. 6.5 fwhm are typical for the trivalent lanthanide ions.[60] These are primarily due to an electronic transition from the full Ln $2p_{3/2}$ manifold to the empty 5d orbitals.[61] There is no evidence for divalent Sm or Eu, which would be apparent in the XANES of Figure 3 at some 8 eV below the edge peaks.[62] Two less intense, broad peaks at ca. +17 and +35 eV arise from photoelectron backscattering. The first one was previously shown to be diagnostic of the oxygen near-neighbor environment. From

(59) Horrocks, W. D., Jr.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384−392.
(60) Lytle, F. W.; van der Laan, G.; Greegor, R. B.; Larson, E. M.; Violet, C. E.; Wong, J. *Phys. Rev. B* **1990**, *41*, 8955−8963.
(61) Röhler, J. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr, Eyring, L., Hüfner, S., Eds.; North-Holland: Amsterdam, 1987; Vol. 10, pp 453−545.
(62) Antonio, M. R.; Soderholm, L.; Song, I. *J. Appl. Electrochem.* **1997**, *27*, 784−792.

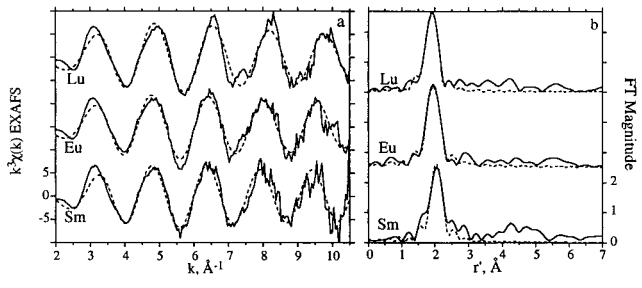

Figure 4. Ln L_3-edge (a) $k^3\chi(k)$ EXAFS and (b) FT data for the solid salts of $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ at 17 K. The solid lines are the primary experimental data, and the dashed lines illustrate the fit with a single Ln−O coordination sphere. The data for $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ and $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ have been offset for clarity.

Table 5. Curve-Fitting Results for the Ln L_3-Edge Fluorescence EXAFS, $k^3\chi(k)$, of $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ (X ≡ P, As) and $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ Obtained at 17 K[a]

anion	N_O [b]	r,[c] Å	σ^2,[d] Å^2	ΔE_0 [e]
$[Sm(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$	8	2.44(1)	0.002(1)	1.9
$[Sm(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$	8	2.44(1)	0.001(1)	1.8
$[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$	8	2.39(1)	0.003(1)	0.9
$[Eu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$	8	2.42(1)	0.005(1)	2.3
$[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$	8	2.31(1)	0.003(1)	1.1
$[Lu(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$	8	2.31(1)	0.002(1)	1.0
$[(H_2O)_4Sm(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$	8	2.41(2)	0.006(2)	1.4
$[(H_2O)_4Eu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$	8	2.38(2)	0.005(1)	−0.7
$[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$	8	2.27(1)	0.008(1)	−0.1

[a] The numbers in parentheses represent the estimated standard deviations (σ) obtained from the least-squares fits. The number of curve-fitting parameters (four: N_O, r, σ^2, ΔE_0) was less than the number of independent data points, $N_{idp} = 2\Delta k\Delta r/\pi = 10$, where $\Delta k \approx 8$ Å^{-1} and $\Delta r \approx 2$ Å. [b] The average number of oxygen atoms coordinated to the Ln(III) ions obtained from best integer fits. The esd for N_O is ±1 O atom. [c] The average Ln−O bond length. [d] The Debye−Waller factor, which is the mean square deviation in the average Ln−O bond length. [e] The energy difference between the EXAFS experiment and FEFF7.02 theory.

studies of Ln L_3 XANES of Ln_2CuO_4 and $LnBa_2Cu_3O_7$ (Ln ≡ trivalent lanthanide), such a peak is observed when the Ln^{3+} ion is eight-coordinate with O atoms.[63] The EXAFS results presented below serve to confirm the XANES of Figure 3, indicating that the Ln ions in $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ are eight-coordinate, and to provide the Ln−O interatomic distances.

The $k^3\chi(k)$ EXAFS and the corresponding Fourier transform (FT) data for the trivalent Ln complexes $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ are shown in Figure 4. The primary data of Figure 4a (solid lines) are essentially indistinguishable from the corresponding data for the $[Ln(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$ complexes (see Figure S3 of Supporting Information). The Ln(III)−O coordination in the heteropolytungstate complexes is evident in the FTs of Figure 4b (solid lines) as the single, intense peak at ca. 2 Å (before phase shift correction). Fitting the $k^3\chi(k)$ EXAFS provides the metrical information shown in Table 5. The best fits to the EXAFS data are shown as dashed lines in Figure 4. It is clear from Figure 4b that the conservative model we have used to fit the experimental Ln−O interactions is a good representation of the data. The effects of the lanthanide contraction are evident from the distances of Table 5. The average Ln(III)−O interatomic distances for the complexes with Sm and Eu (2.44 ± 0.01 and 2.41 ± 0.01 Å, respectively) are significantly longer than the average Lu−O distance of 2.31 ± 0.01 Å. The oxygen coordination numbers of 8 are consistent with the square antiprism structure about Lu^{3+} in **2** (vide supra), which is typical of the entire series of complexes, $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$.

B. $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. The Ln L_3 XANES data for the 1:1 Sm, Eu, and Lu complexes (Figure S4 of Supporting Information) are essentially the same as those of Figure 3 for $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$, except for a slight flattening of the weak, broad postedge peak at ca. +16 eV. As noted above, the presence of this feature suggests that the Ln ions in $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ are eight-coordinate. The positions and shapes of the intense edge peaks at +2.4 eV are typical of the trivalent Ln ions. There is no evidence for divalent Sm or Eu.

The $k^3\chi(k)$ EXAFS and the corresponding FT data for $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ (Figure S5 of Supporting Information) are comparable to the data of Figure 4 for $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$. Metrical parameters were obtained using the best integer approach that was used to model the EXAFS data for the 1:2 α-2 complexes. The interatomic distance resolution of our data is estimated to be 0.2 Å, so Ln−O distances separated by less than this amount will produce a single peak in the FT. For this reason, it was not possible to distinguish between O backscattering from H_2O and $[P_2W_{17}O_{61}]^{10-}$. Consequently, the Ln−O interactions were treated as a single (averaged) coordination sphere in the fits. The metrical results obtained from the best fits (shown as Figure S5) are listed in Table 5. In these three complexes, there are eight nearest oxygen atoms about the Ln ions at an average distance of 2.41(2), 2.38(2), and 2.27(1) Å for the Sm, Eu, and Lu heteropolyanions, respectively. The oxygen coordination numbers are consistent with the environment of Lu^{3+} in **1**, and the distance variation is typical of the lanthanide contraction effect.

Discussion

$[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ (1). The Lu(III) ion in **1** is eight-coordinate with a square antiprismatic environment of oxygen atoms. Four O atoms are from the W−O framework of one α-1-$[P_2W_{17}O_{61}]^{10-}$ ligand, and the remaining four O atoms are from four bound water molecules. The average $Lu-(OH_2)_4$ bond distance, 2.42(5) Å, is 0.12 Å larger than the average $Lu-O_4(\alpha\text{-}1\text{-}P_2W_{17}O_{61})^{10-}$ distance, 2.30(4) Å. The average distance for all eight Lu−O interactions is 2.36(6) Å. Because Lu is not bound to an oxygen of a phosphate group, the Lu^{3+} ion is displaced outward and away from the normal 18th position in the Wells−Dawson framework. This type of bonding, also seen in $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ (**2**) and for $[Ce(IV)(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{16-}$, has been observed for crystal structures of lanthanide derivatives of the α-monovacant Keggin ions and $[Ln(III)W_{10}O_{36}]^{9-}$ derivatives.[64,65] In contrast, transition metal ions bound to a phosphate oxygen and to another axial ligand, such as a water molecule, to complete the octahedral coordination sphere are seen in the Co derivative of the lacunary α-2-$[P_2W_{17}O_{61}]^{10-}$ species.[49] The eight-coordinate $[Lu(OH_2)_8]^{3+}$ aquo ion has bond lengths of 2.31−2.338 Å.[66,67] The $Lu-OH_2$ bond lengths in **1** are longer than in the aquo ion, and the Lu−O bonds with the W−O framework in **1** are approximately the same as those of the aquo ion. The combination of the crystallographic results for **1** and the luminescence results for $[(H_2O)_4Eu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ [8] demonstrate that the $Ln^{3+}-O_8$

(63) Tan, Z. Q.; Heald, S. M.; Cheong, S. W.; Hwang, H. Y.; Cooper, A. S.; Budnick, J. I. *Physica C* **1991**, *184*, 229−234.
(64) Ozeki, T.; Yamase, T. *Acta Crystallogr.* **1994**, *B50*, 128−134.
(65) Sugeta, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 444−449.
(66) Yamaguchi, T.; Nomura, M.; Wakita, H.; Ohtaki, H. *J. Chem. Phys.* **1988**, *89*, 5153−5159.
(67) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1979**, *70*, 2797−2806.

coordination in the 1:1 Ln/α-1 complexes is the same for the solids and their aqueous solutions.

The bond lengths in the P−W−O framework of **1** compare favorably with those reported for the Wells−Dawson parent structure[1] and the crystal structures of the lacunary α-2-$[P_2W_{17}O_{61}]^{10-}$ isomer and the Co(III)H_2O adduct.[49] Table S2 (Supporting Information) shows the complete list of bond lengths. For the two phosphate tetrahedra, the range of bond lengths (1.53(2)−1.64(2) Å) and angles (106.7(9)−114.0(10)°) are well within the ranges observed in the previous structures. Terminal W−O bonds are in the 1.73(2)−1.80(2) Å range. The W−O (phosphate) bonds extend from 2.34(2) to 2.43(2) Å. The W−O bond lengths in the belt containing the Lu atom have a range 1.83(2)−2.03(2) Å. These bonds show a significant trans alternation where each W atom in the ring is involved in a "short" W−O bond trans to a "long" W−O bond (see Figure S6 of Supporting Information). This phenomenon is not significant for the second W_6 ring. Oxygen atoms O19 and O20 bridge the Lu14 atom and W4 and W6, respectively; the W4−O19 and W6−O20 bonds are shorter than for other bridging oxygen atoms with bond lengths (1.78(2) and 1.80(2) Å, respectively) approaching terminal W−O bond lengths. In the two caps, bridging W−O bonds range from 1.93(2) to 1.99(2) Å. The pattern of edge-shared WO_6 octahedra and corner-shared WO_6 octahedra, observed in the Wells−Dawson ion and the lacunary α-2-$[P_2W_{17}O_{61}]^{10-}$ isomer, is retained in this structure. Both of the cap regions show edge-shared octahedra, while the belt regions show the alternating pattern of corner- and edge-shared octahedra. This pattern is obvious from the W−W distances in the two cap and two belt regions. The W−W distances in the two cap regions range from 3.41 to 3.48 Å. In the belt regions, the edge-shared octahedra show W−W distances of 3.37 to 3.42 Å, and the W−W distances for the corner-shared octahedra range from 3.72 to 3.79 Å. The presence of the $[Lu(III)(H_2O)_4]^{3+}$ unit in one belt disrupts the pattern of edge and corner sharing because the Lu is connected to the two W atoms in the belt by single bridging oxygen atoms. Overall, the $Lu(III)(H_2O)_4$ unit introduces a relatively minor perturbation into the parent Wells−Dawson framework.

$[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ (2). The Lu^{3+} ion is eight-coordinate in a square antiprismatic oxygen coordination environment. The average Lu−O bond length is 2.32(5) Å, consistent with the XAFS result of 2.31(1) Å, and essentially the same as that in the $[Lu(OH_2)_8]^{3+}$ aquo ion. The two polyoxometalate "lobes" are disposed in a syn fashion, and the structure is similar to that found for the Ce(IV) analogue.[44] As for structure **1**, the details of the bond lengths and angles in the W−O framework are consistent with the α-2-$[P_2W_{17}O_{61}]^{10-}$ isomer and the cobalt (III) complex.[49] The combination of the crystallographic results for **2** and the luminescence results for $[Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{7-}$ demonstrate that the $Ln^{3+}-O_8$ coordination in the 1:2 Ln/α-2 complexes is the same for the solids and their aqueous solutions.

$[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ and $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$. The average Ln−O bond lengths (Table 5) for all nine complexes (six $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ complexes and three $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ complexes) are similar to those for the Ln(III) aquo ions. In aqueous solutions at room temperature, Sm(III) is coordinated to eight to nine H_2O molecules at distances of 2.45−2.47 Å.[66,68−70] Aqueous Eu(III) is reported to have eight to nine water molecules at 2.43−2.45 Å,[66,70] and the eight-coordinate Lu(III) aquo ion has bond lengths of 2.31−2.338 Å.[66,67] These are comparable to the average $Ln-O_8$ distances for the solid polyoxometalate complexes at 17 K, wherein the Sm−O, Eu−O, and Lu−O distances are 2.41(2)−2.44(1), 2.38(2)−2.42(1), and 2.27(1)−2.31(1) Å, respectively.

For all complexes in Table 5, there are eight O atoms about Sm, Eu, and Lu. Our Ln L_3−EXAFS is insufficient to resolve the O atoms of the water molecules from the O atoms of the Wells−Dawson framework in the 1:1 series of complexes $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. The X-ray crystal structure of **1** reveals a difference of 0.12 Å, which is smaller than the EXAFS resolution, between the average Lu−O(water) and Lu−O(framework) bond lengths. From the crystal structure of **1**, we know that four O atoms are from the tetradentate α-1-$[P_2W_{17}O_{61}]^{10-}$ framework and that the remaining four are from O atoms of water molecules. For the 1:1 α-1 anions, the Sm, Eu, and Lu EXAFS results corroborate the conclusions from luminescence measurements of $[(H_2O)_4Eu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ [8] and $[(H_2O)_4Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ (vide supra) as well as the crystal structure of **1**, all of which reveal that the Ln hydration number (*n*) is 4. The general stoichiometry $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ is maintained throughout the lanthanide series. From the crystal structure of **2**, we know that all eight O atoms about Sm, Eu, and Lu in the 1:2 series of complexes $[Ln(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ are from two tetradentate α-2-$[P_2W_{17}O_{61}]^{10-}$ anions. There are no water molecules bound to the Ln(III) ions.

The Ln−O bond lengths of Table 5 are also in agreement with other known Ln-to-polyoxoanion-O framework distances. For example, the isomorphous Sm(III) and Eu(III) complexes of the tetradentate Lindquist isopolyanion $[W_5O_{18}]^{6-}$ reveal $Ln-O_8$ coordination environments with average Sm−O and Eu−O distances of 2.43−2.47[71,72] and 2.41−2.43 Å[65,73] for $[Sm(W_5O_{18})_2]^{9-}$ and $[Eu(W_5O_{18})_2]^{9-}$, respectively. Other direct comparisons are similarly illuminating. We have found an average Ce(III)−O distance of 2.52(4) Å for $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ in an aqueous electrolyte.[74] This long bond distance is consistent with the large ionic radius of 1.143 Å for eight-coordinate Ce(III).[75] The ionic radius of 1.079 Å for eight-coordinate Sm(III)[75] is 0.064 Å smaller than for Ce(III), which is consistent with the 0.08 Å bond length contraction between the EXAFS-determined Ce−O and Sm−O interatomic distances of 2.52(4) and 2.44(1) Å for $[Ce(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ and $[Sm(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$, respectively. The shortening of the Ln−O distances along the Sm, Eu, and Lu series for the 1:2 α-2 and 1:1 α-1 complexes is consistent with the effects of the lanthanide contraction.

Conclusions

We have solved and refined the crystal and molecular structures of $[Lu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})_2]^{17-}$ and $[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$. Until now, complete single-crystal X-ray diffraction results have not been available. The $Lu^{3+}-O$ coordination environments were compared with those for the corresponding Sm and Eu complexes with the isomerically pure heteropolyanions α-2-$[X_2W_{17}O_{61}]^{10-}$ (X ≡ P, As) and α-1-$[P_2W_{17}O_{61}]^{10-}$ through use of XAFS and optical luminescence spectroscopies. The coordination of trivalent rare-earth ions to

(68) Cossy, C.; Helm, L.; Powell, D. H.; Merbach, A. E. *New J. Chem.* **1995**, *19*, 27−35.
(69) Johansson, G.; Wakita, H. *Inorg. Chem.* **1985**, *24*, 3047−3052.
(70) Habenschuss, A.; Spedding, F. H. *J. Chem. Phys.* **1980**, *73*, 442−450.
(71) Ozeki, T.; Yamase, T. *Acta Crystallogr.* **1994**, *C50*, 327−330.
(72) Ozeki, T.; Yamase, T. *Acta Crystallogr.* **1993**, *C49*, 1574−1577.
(73) Yamase, T.; Ozeki, T.; Ueda, K. *Acta Crystallogr.* **1993**, *C49*, 1572−1574.
(74) Antonio, M. R.; Soderholm, L.; Williams, C. W.; Ullah, N.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans.* **1999**, 3825−3830.
(75) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

the Wells−Dawson framework structures of the α-1 and α-2 isomers provides Ln−O distances that are consistent with literature values. Neither unusually long nor short distances were found that would suggest a bonding mismatch or otherwise odd interactions between the Ln orbitals and the O atoms of the heteropolyanion structure. The Ln(III) ions in $[Ln(\alpha\text{-}2\text{-}X_2W_{17}O_{61})_2]^{17-}$ are eight-coordinate. No water molecules are in the $Ln-O_8$ coordination sphere, which is the same for the solid clusters and their aqueous solutions. The Ln(III) ions in $[Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ are also eight-coordinate. The crystallographic results for $[(H_2O)_4Lu(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$ as well as the luminescence results for $[(H_2O)_4Eu(\alpha\text{-}2\text{-}P_2W_{17}O_{61})]^{7-}$ reveal that four water molecules participate in the $Ln-O_8$ coordination, which is the same for the solid clusters and their aqueous solutions. The variation of Ln−O distances along the Sm, Eu, and Lu series is consistent with the effects of the lanthanide contraction.

Acknowledgment. We thank L. Soderholm for assistance and Craig Van Pelt for preprints of his work (refs 5 and 6) prior to publication. The work at Argonne is supported by the Environmental Management Science Program, Office of Science and Technology, Office of Environmental Management, U.S. DOE, under Contract No. W-31-109-ENG-38. The work at Hunter College is supported by the National Science Foundation. SSRL is operated by the DOE, Office of Basic Energy Sciences. Research Infrastructure at Hunter College is supported by NIH−Research Centers in Minority Institutions Grant RR03037-08. The SSRL Biotechnology Program is supported by the NIH, Biomedical Resource Technology Program, Division of Research Resources and by the Department of Energy, Office of Health and Environmental Research.

Supporting Information Available: Table S1 of atom coordinates (including esds) and displacement parameters for **1** and **2**, Table S2 of bond lengths for **1** and **2**, Table S3 of bond angles for **1** and **2**, an X-ray crystallographic file (CIF format), Figure S1 of a view of unit cell for **1** wherein counterions and water are disordered in infinite channels, Figure S2 of Ln L_3-edge XANES of $[Ln(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$, Figure S3 of Ln L_3-edge $k^3\chi(k)$ EXAFS and FT data of $[Ln(\alpha\text{-}2\text{-}As_2W_{17}O_{61})_2]^{17-}$, Figure S4 of Ln L_3-edge XANES of $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$, Figure S5 of Ln L_3-edge $k^3\chi(k)$ EXAFS and FT data of $[(H_2O)_4Ln(\alpha\text{-}1\text{-}P_2W_{17}O_{61})]^{7-}$, Figure S6 of tungsten−oxygen bond lengths in the rings of the two belt regions of **1** showing trans-bond alternation with Lu substitution. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001427+