Large Cluster Formation through Multiple Substitution with Lanthanide Cations (La, Ce, Nd, Sm, Eu, and Gd) of the Polyoxoanion $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$. Synthesis and Structural Characterization[†]

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Several new large polyoxotungstates have been synthesized by reaction of lanthanide cations with the well-known "As_4W_{40}" anion, $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$ (**1**). The heteropolyanions $[(H_2O)_{11}Ln^{III}(Ln^{III}{}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{20-}$ (Ln = Ce, Nd, Sm, Gd) (**2**−**4**) ($Ln_3As_4W_{40}$) and $[M^m(H_2O)_{10}(Ln^{III}{}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{(18-m)-}$ (Ln = La, Ce, Gd and M = Ba, K, none) (**5**−**7**) ($Ln_4As_4W_{40}$) have been isolated as alkali metal and ammonium salts, respectively, and characterized by single-crystal X-ray analysis, elemental analysis, and IR and ^{183}W-NMR spectroscopy. The X-ray analyses revealed interanionic W−O−Ln bonds between adjacent $Ln_xAs_4W_{40}$ units forming a "dimer" for $x = 3$ and chains for $x = 4$. Upon dissolving in water these bonds hydrolyze and the monomeric species form. The straightforward syntheses which require the use of concentrated NaCl solutions (1−4 M) and the addition of stoichiometric amounts of Ba^{2+} or K^+ reemphasize the importance of the presence of appropriate countercations for the assembly of large polyoxometalate structures.

Introduction

The structures of very large polyoxotungstate anions may be represented in terms of subunits based on lacunary fragments of the Keggin anion or its isomers. The nonatungstoarsenate(III) anion $[B\text{-}\alpha\text{-}AsO_3W_9O_{30}]^{9-}$ "AsW_9" is a lacunary Keggin anion with a coordinative behavior dictated by the lone pair of electrons on As^{III}.[1−6] This anion is a valuable ligand for multiple lanthanide and actinide coordination due to its open structure and therefore has potential for the separation of nuclear waste.[7−9] The cyclic anion $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$ "As_4W_{40}" can be viewed as a derivative of AsW_9, in which four AsW_9 units are linked by additional tungsten atoms. The properties of As_4W_{40}, especially its behavior in solution, have been studied in great detail in the past.[10] It was shown that the anion has the ability to accommodate alkali, alkaline earth, and lanthanide cations in the central cryptate site (S_1) as well as di- or trivalent 3d metal cations and Ag^+ in the four lacunary sites (S_2).[11−14] Most of the knowledge is based on unambiguous spectroscopic data and the early crystal structural analysis obtained for the cobalt(II)-substituted anion $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4Co_2(H_2O)_2]^{24-}$.[14]

In the present paper we report the synthesis and structural characterization of derivatives of As_4W_{40} with multiple lanthanide cations. Polyoxoanions of type $Ln_3As_4W_{40}$ were prepared for Ln = La, Ce, Nd, Sm, Eu, and Gd, and the complete crystal structure analysis is reported for $Na_{40}\{[(H_2O)_{10}Ln^{III}(Ln^{III}{}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\}\cdot nH_2O$, Ln = Ce (**2**), Sm (**3**), and Gd (**4**). Anions of type $BaLn_4As_4W_{40}$ were obtained for Ln = La, Ce, and Gd. Single-crystal data for $Na_{16}\{[Ba(H_2O)_{10}(Ce^{III}{}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 51H_2O$ (**5**) is discussed, along with the structures of $(NH_4)_{15}Na_2\{[K(H_2O)_{10}(Ce^{III}{}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 37H_2O$ (**6**) and $(NH_4)_{18}\{[(H_2O)_{10}(Ce^{III}{}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 46H_2O$ (**7**). The single-crystal structural X-ray analysis of the triple-Ln-substituted anion revealed the linkage between adjacent $Ln_3As_4W_{40}$ units, via two W−O−Ln bonds arranging them in pairs $(Ln_3As_4W_{40})_2$. On the other hand the 4-fold Ln-substituted anion $Ln_4As_4W_{40}$ contains four W−O−Ln bonds and therefore forms chains $(Ln_4As_4W_{40})_\infty$ in the solid state. However, in aqueous solution the anions are present as "monomeric" species $Ln_xAs_4W_{40}$, $x = 3$ or 4, as shown by ^{183}W-NMR analysis. The first X-ray analysis of the parent anion As_4W_{40} discloses the coordination of two chloride ions to the polyoxotungstate−sodium atom framework, $Na_{28}[(AsO_3W_9O_{30})_4(WO_2)_4]\cdot 2NaCl\cdot 55H_2O$ (**1**).

Experimental Section

$\mathbf{Na_{28}[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\cdot 2NaCl\cdot 55H_2O}$ **(1).** The preparation followed essentially the original publication.[11] However, the crude product of 150 g was recrystallized from a 3 M NaCl solution

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[†] Dedicated to Hans-Joachim Lunk on the occasion of his 60th birthday.

[‡] Engelhard Corporation.

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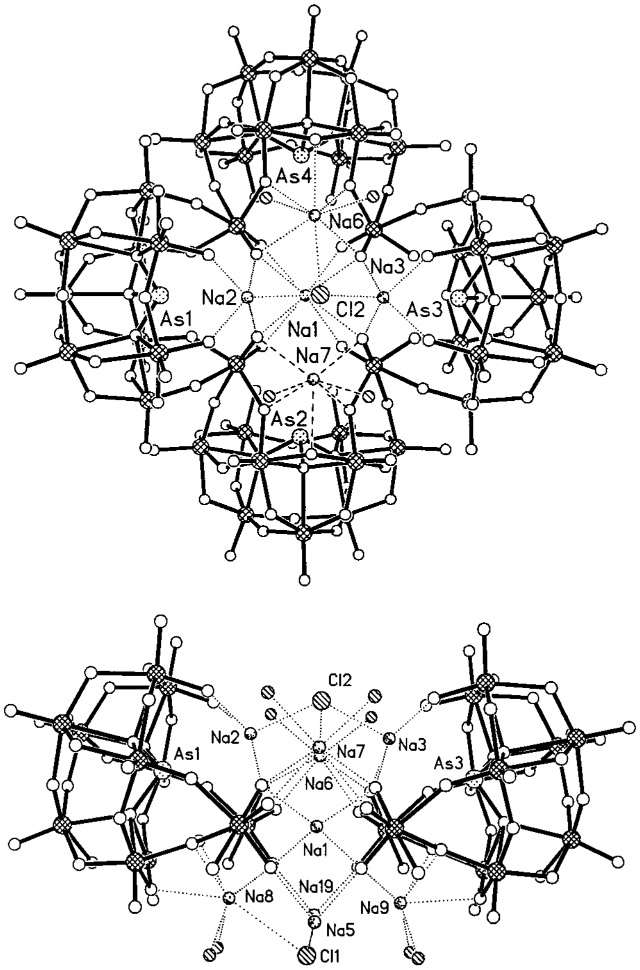

Figure 1. SHELX representation of $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$ (**1**) top and side view; two AsW_9 units have been omitted for clarity in the bottom drawing (small hatched circles = water molecules; open circles = oxygen atoms).

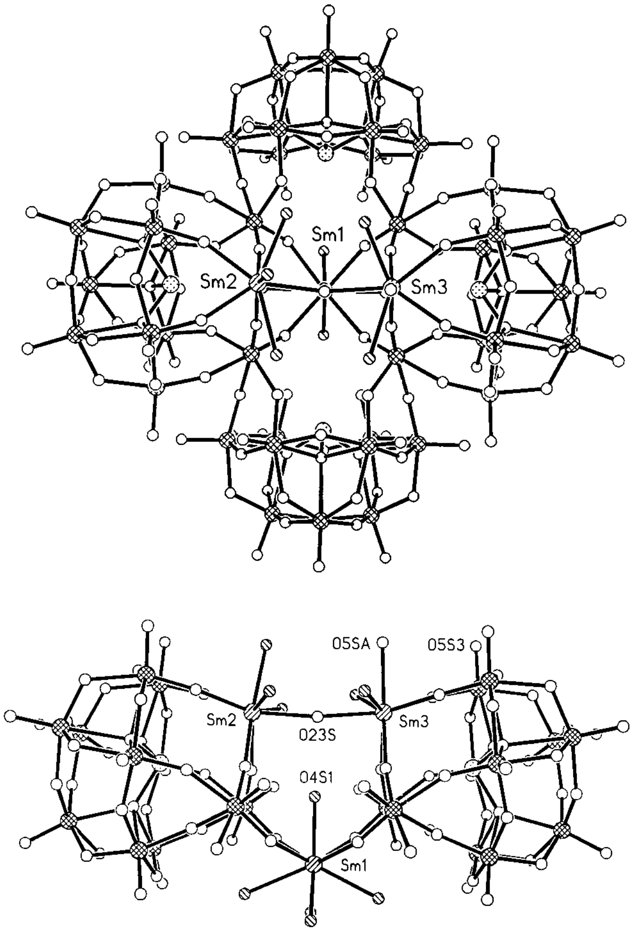

Figure 2. SHELX representation of $[(H_2O)_{10}Ln(Ln_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{20-}$, Ce (**2**), Sm (**3**), Gd (**4**), top and side view; two AsW_9 have been omitted for clarity in the bottom drawing (small hatched circles = water molecules; open circles = oxygen atoms).

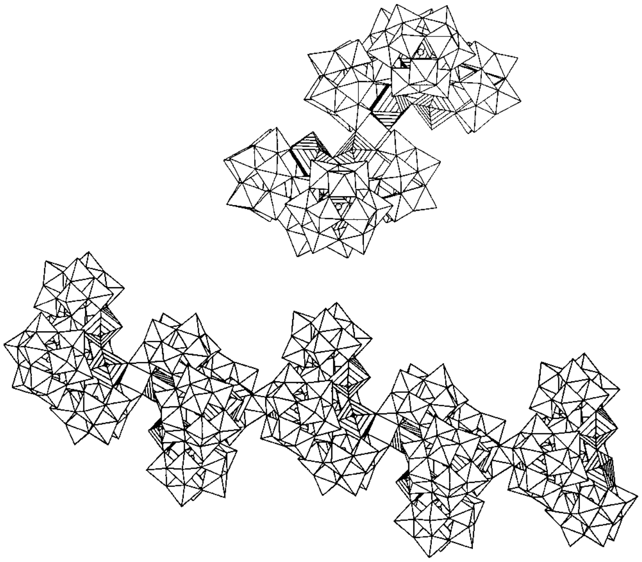

Figure 3. Polyhedral view of the "dimeric" anion $\{[(H_2O)_{11}Ln(Ln_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\}^{40-}$ (Ln = Ce, Nd, Sm, Gd) (**2**−**4**) (top) and the "polymeric" anion $[M^{m}(H_2O)_{10}(Ln^{III}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{(18-m)-}$ (Ln = La, Ce, Gd and M = Ba, K, none) (**5**−**7**) (bottom); LnO_x polyhedra are drawn hatched.

(500 mL, 90 °C, pH 5.0). The next day 80 g (yield ~40%) of a crystalline, needlelike precipitate was isolated and its purity checked by IR spectroscopy. IR (cm^{-1}, KBr disk, metal oxygen region): for **1**, 950 (s), 877 (vs), 802 (s), 746 (sh), 711 (vs), 630 (s). Elemental anal. calcd (found): for **1**, Na 5.92 (5.2), Cl 0.61 (0.86), As 2.57 (2.75), W 63.16 (63.1), H_2O 8.51 (8.5), $n = 55$; for unrecrystallized product, Na (5.3), Cl (0.73), As (2.83), W (65.0).

$Na_{40}[(H_2O)_{10}Ln^{III}(Ln^{III}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\cdot nH_2O$, Ln = La,[15] Ce, Nd,[16] Sm, Eu,[15] and Gd. The general method of synthesis was identical for all employed lanthanides. A sample of 11.62 g (1 mmol) of **1** was dissolved in 75 mL of 2 M NaCl at 90−95 °C, pH ca. 5.0. In a separate beaker containing 12 mL of 2 M NaOAc, 3 mmol of the appropriate lanthanide nitrate was brought into solution (pH 7.0−7.3) and then poured into the rapidly stirred tungstate solution. The resulting clear solution (pH 5.2−5.5) was heated (80 °C) and stirred for 10 min (Gd only 5 min) before 20 g of NaCl (0.34 mol) was added. The resulting precipitates (9−10 g) were isolated a few hours later (1−5 h) and recrystallized first from 1 M NaCl (70 °C, 50−100 mL, pH 5.1−5.8) and then from 3−5 mL of water (65 °C, pH 5.8−6.3). Usually 2 days later large parallelogram-shaped crystals were collected, 3−4 g (yield >30%). IR (cm^{-1}, KBr disk, metal oxygen region): 952 (s), 879 (vs), 855 (sh), 792 (vs), 748 (sh), 709 (vs), 628 (s). Elemental anal. calcd (found): for **Ce**, Na 3.82 (3.26), Ce 3.49 (4.06), As 2.49 (2.6), W 61.04 (58.8), H_2O 10.54 (10.5), $n = 120$; for **Nd**, Na 3.82 (3.2), Nd 3.6 (3.4), As 2.49 (2.49), W 61.18 (60.5), H_2O 10.19 (10.2), $n = 115$; for **Sm**, Na 3.81 (3.3), Sm 3.74 (3.7), As 2.48 (2.5), W 60.94 (60.5), H_2O 10.38 (10.4), $n = 118$; for **Gd**, Na 3.88 (3.4), Gd 3.98 (3.5), As 2.53 (2.66), W 62.04 (61.4), H_2O 8.59 (8.6), $n = 92$.

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(15) Characterized by IR spectroscopy only.

(16) X-ray data for a purple parallelogram-shaped columnar crystal of $Na_{40}\{[(H_2O)_{10}Nd^{III}(Nd^{III}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\}\cdot 115H_2O$: $a = 20.9628(3)$ Å, $b = 20.9718(1)$ Å, $c = 539920(2)$ Å, $\alpha = 84.933(1)°$, $\beta = 84.956(1)°$, $\gamma = 65.743(1)°$, $V = 21521.2(3)$ Å^3, $Z = 2$.

Table 1. Crystallographic Data for $Na_{28}[(AsO_3W_9O_{30})_4(WO_2)_4]\cdot 2NaCl\cdot 62H_2O$ (**1**); $Na_{40}\{[(H_2O)_{10}Ln^{III}(Ln^{III}{}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\}\cdot nH_2O$, Ln = Ce ($n$ = 120) (**2**), Sm (n = 118) (**3**), Gd (n = 92) (**4**); $Na_{16}\{[Ba(H_2O)_{10}(Ce_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 51H_2O$ (**5**); $(NH_4)_{15}Na_2\{[K(H_2O)_{10}(Ce_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 37H_2O$ (**6**); and $(NH_4)_{18}\{[(H_2O)_{10}(Ce_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 46H_2O$ (**7**)

	1	**2**	**3**	**4**	**5**	6	**7**
elemental composition	$H_{124}O_{211}Na_{30}$-$Cl_2As_4W_{40}$	$H_{282}O_{422}Na_{40}$-$As_8Ce_6W_{80}$	$H_{278}O_{420}Na_{40}$-$As_8Sm_6W_{80}$	$H_{266}O_{414}Na_{40}$-$As_8Gd_6W_{80}$	$H_{65}O_{206}Na_{16}$-$As_4BaCe_4W_{40}$	$H_{156}O_{190}N_{16}Na_2K$-$As_4Ce_4W_{40}$	$H_{186}O_{198}N_{18}$-$As_4Ce_4W_{40}$
cryst dimens, mm	0.16 × 0.20 × 0.40	0.13 × 0.15 × 0.40	0.11 × 0.28 × 0.32	0.18 × 0.30 × 0.35	0.08 × 0.10 × 0.20	0.04 × 0.04 × 0.18	0.16 × 0.18 × 0.36
M, g mol^{-1}	11771.26	24103.94	24103.94	24062.58	12116.31	11706.64	11821.83
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$C2/c$
a, Å	19.2004(2)	20.7021(3)	20.6818(2)	19.448(1)	21.101(3)	27.335(2)	35.0164(1)
b, Å	19.5590(2)	21.3722(1)	22.2615(3)	19.630(1)	21.339(3)	19.618(2)	19.5859(1)
c, Å	30.8717(2)	26.9546(3)	25.1353(3)	29.277(2)	26.127(3)	33.380(3)	27.5680(2)
α, deg	94.009(1)	74.190(1)	99.320(1)	81.606(1)	85.477(2)	90.000	90.000
β, deg	99.918(1)	86.783(1)	96.591(1)	74.030(1)	68.241(2)	100.861(2)	101.229(1)
γ, deg	115.966(1)	65.394(1)	109.036(1)	62.996(1)	84.033(2)	90.000	90.000
V, Å^3	10128.3(2)	10410.5(2)	10619.5(2)	9571.6(9)	10856(2)	17580(2)	18544.9(1)
Z	2	1	1	1	2	4	4
d_{calcd}, Mg m^{-3}	3.747	3.845	3.773	4.175	3.707	4.423	4.234
μ, mm^{-1}	23.44	23.43	23.15	25.80	22.85	27.97	26.49
R1 ($>2\sigma(I)$)	0.1078	0.0650	0.0696	0.0580	0.0711	0.1005	0.0810
R1 (all data)	0.1567	0.1031	0.1428	0.0849	0.1573	0.2467	0.1536
wR2 (all data)	0.2559	0.1703	0.1812	0.1680	0.2044	0.2533	0.2225
GOF	1.110	1.117	0.968	1.030	0.956	0.992	1.038
total reflns	47304	48923	49808	45662	52189	42949	22251
ndep reflns	32997	35176	27323	33484	27115	18295	12514
params	1436	1448	1422	1376	1415	1262	642
min transm	0.0267	0.0454	0.0506	0.0120	0.0855	0.2123	0.0241
max transm	0.0963	0.1318	0.1853	0.0479	0.2628	0.4604	0.0789

Table 2. Selected Na−O, Ln−O, and Na−Cl Bond Lengths (Å) for Na and Ln Cations Coordinated to Sites S1, S2, and S3 in Anions **1**−**7**[a]

	1	**2**	**3**	**4**	**5**	**6**	**7**
S1 site	Na−O_8 2.62−2.74				Ba−O_8 2.78−2.90	K−O_8 2.81−2.96	
M−OH					2.82, 2.91	2.94, 3.04	
S2 site	Na−O_4 2.27−2.39 Na−Cl 2.61−2.66	Ce−O_8 2.38−2.76	Sm−O_8 2.32−2.64	Gd−O_8 2.33−2.55	Ce−O_8 2.40−2.66	Ce−O_8 2.31−2.72	Ce−O_8 2.33−2.65
S3 site		Ce−O_9 2.49−2.65	Sm−O_9 2.38−2.65	Gd−O_9 2.36−2.60			

[a] Coordination numbers as subscript values.

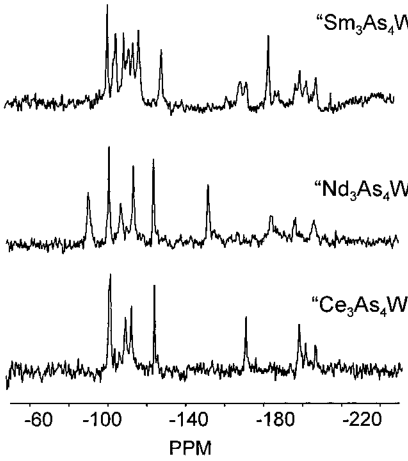

Figure 4. ^{183}W-NMR spectra of $Sm_3As_4W_{40}$, $Nd_3As_4W_{40}$, and $Ce_3As_4W_{40}$ recorded in D_2O.

$\{Na_{16}[(H_2O)_{10}(Ln^{III}{}_2OH)_2Ba(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\}_\infty\cdot nH_2O$, Ln = La, Ce, Gd.[15] Preparation is given for the Ce(III)-containing compound. At first a sample of 122 mg (0.5 mmol) of $BaCl_2$ was dissolved in 50 mL of water at room temperature followed by the addition of 5.81 g (0.5 mmol) of **1**, pH 6.4. To the vigorously stirred clear solution was added 868 mg of $Ce(NO_3)_3\cdot 6H_2O$ (2 mmol) dissolved in 8 mL of 1 M NaOAc/HOAc slowly with a pipet, final pH 4.3. An initial minor precipitate dissolved quickly upon heating to 85 °C on a water bath. The system was kept at this temperature for 5 min. The pH dropped to 4.0 and was then raised to 5.0 with 1 M NaOH (ca. 6.2 mL), and the solution was heated for an additional 5 min. Next, 10 g of NaCl (0.17mol) was added to the clear 40 °C solution at pH 5.2. A precipitate (ca. 5.5 g) formed immediately, was isolated after 15 min, and was then recrystallized from 15 mL of water at 80 °C. Two days later a crystalline product was filtered off at pH 5.7; 2.5 g of orange needles (yield ~45%). IR (cm^{-1}, KBr disk, metal oxygen region): for **5**, 962 (s), 889 (vs), 849 (vs), 783 (vs), 748 (s), 694 (vs), 627 (s). Elemental anal. calcd (found): for **5**, Na 3.17 (2.99), Ba 1.12 (1.1), Ce 4.55 (4.57), As 2.43 (2.5), W 59.72 (61.2), H_2O 10.39 (10.81), n = 51. Chemical shift ^{183}W-NMR in ppm and relative intensities (parentheses): for Ln = La, −110.74 (2), −115.39 (2), −153.08 (2), −194.46 (2); for Ln = Ce, −106.08 (2), −115.49 (2), −191.32 (2), −196.62 (1).

$(NH_4)_{15}Na_2[K(H_2O)_{10}(Ce^{III}{}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\}_\infty\cdot 37H_2O$ (6). The synthesis followed essentially the preparation given for the Ba-containing anion. At first a sample of 38 mg (0.5 mmol) of KCl was dissolved in 50 mL of water at room temperature followed by the addition of 5.81 g (0.5 mmol) of **1**, pH 6.4. To the vigorously stirred clear solution was added 868 mg of $Ce(NO_3)_3\cdot 6H_2O$ (2 mmol) dissolved in 8 mL of 1 M NaOAc/HAc slowly with a pipet, final pH 4.3. At the end of the addition the solution turned cloudy and an orange precipitate formed which dissolved upon heating to 90 °C on a water bath. The system was kept at this temperature for 5 min before the pH was raised from 4.1 to 5.8 with 1 M NaOH (ca. 8.5 mL) and the solution was heated for additional 10 min at 90 °C. Next, 10 g of NaCl (0.17 mol) was added to the clear 40 °C solution at pH 5.9. A precipitate

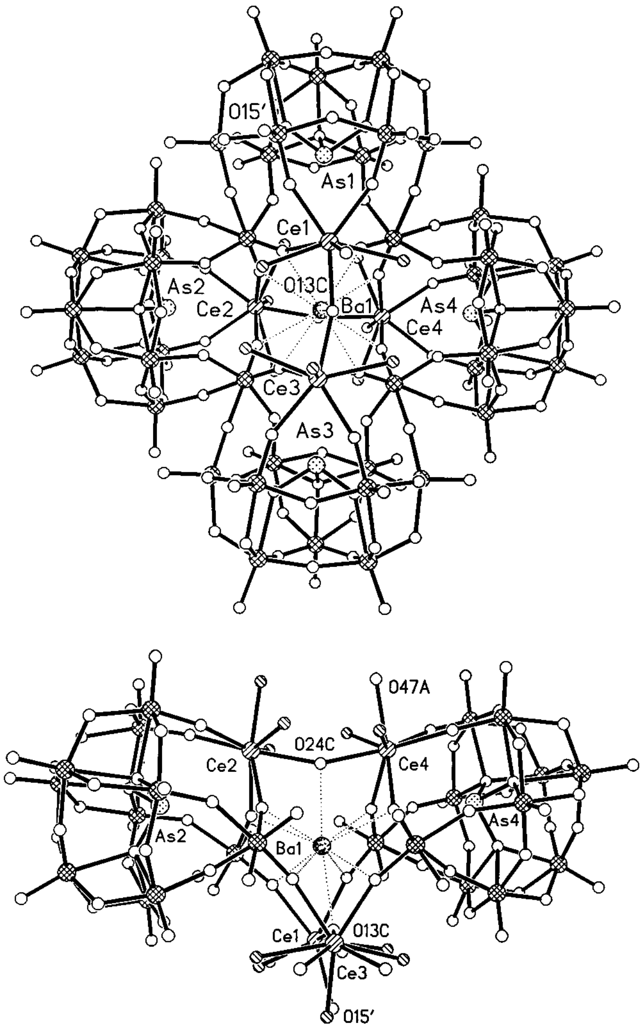

Figure 5. SHELX representation of $[Ba(H_2O)_{10}(Ce_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{16-}$ (**5**), top and side views; two AsW_9 have been omitted for clarity in the bottom drawing (small hatched circles = water molecules; open circles = oxygen atoms).

(ca. 6.5 g) formed immediately, was isolated after 15 min, and was recrystallized twice from water (20 mL and 10 mL) at 80 °C. An orange crystalline product was filtered off at pH 6.1, 2.0 g (yield ~40%). The ammonium salt of **6** was obtained by starting with the one-time-recrystallized sodium salt, which was dissolved in water at room temperature (3.0 g in 20 mL, pH 6.0). The addition of a 4 M NH_4Cl solution (6 mL) led to a pale orange product. This precipitate was recrystallized twice, and fine orange needles were obtained. IR (cm^{-1}, KBr disk, metal oxygen region): for **6**, 958 (s), 889 (sh), 852 (vs), 788 (s), 748 (sh/w), 698 (vs), 628 (s). Chemical shift ^{183}W-NMR in ppm and relative intensities (parentheses): for Ln = Ce, sodium salt, −104.93 (2), −114.10 (2), −183.21 (2?), −194.25 (1).

$(NH_4)_{18}\{[(H_2O)_{10}(Ce^{III}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\}\cdot 92H_2O$ (7). This compound was isolated as a minor product in a synthesis using As_4W_{40}, AsW_9, and Ce^{III} in a 1:2:4 ratio in 2 M NaCl and a NaOAc/HOAc buffer solution (pH 6.0). IR: for **7**, 956 (s), 890 (sh), 844 (vs), 783 (s), 748 (w), 696 (vs), 628 (s).

Aqueous-Organic-Phase-Transfer Procedure. A sample of 1.15 g (0.094 mmol) of **5** was dissolved in 20 mL of water at room temperature (pH 5.9). In a second beaker 0.947 g (1.5 mmol) of dimethyldioctadecylammonium chloride ($DODA^+Cl^-$) was dissolved in 30 mL of CH_2Cl_2. Both solutions were transferred to a separatory funnel, which was then shaken vigorously. The transfer of the polyoxoanion into the organic phase took place immediately. The orange organic phase was separated after a few minutes. In order to record a ^{183}W-NMR spectrum, the solvent was evaporated at room temperature and the resulting glassy yellow product was dissolved in $CDCl_3$.

Instrumental and Analytical Procedures. IR spectra were collected on a Nicolet 7000, KBr disk. The ^{183}W-NMR spectra were recorded in D_2O on a Bruker AM 300 spectrometer (reference 2 M Na_2WO_4 solution). Elemental analyses were carried out by E & R Microanalytical Laboratory, NY, and Kanti Technologies Inc., NY. Water content was determined by weight loss at 400−500 °C measured on TA Instruments TGA 2050 analyzer in air (ceramic pans, heating rate 5 K/min). Single-crystal analyses were carried out on a Siemens SMART CCD single-crystal diffractometer equipped with a Mo anode and graphite monochromator (wavelength = 0.71073 Å). The crystals were mounted under oil (to prevent water loss) on a glass fiber and placed in a nitrogen stream at 173(2) K. An approximate sphere of data was collected out to a $2\theta_{max}$ value of 56°, using ω scans. Routine Lorentz and polarization corrections were applied. An empirical absorption correction was used, based on measured intensities of equivalent reflections at different ϕ and ω values.[17] All structures were solved by direct methods. Refinement was against $|F^2|$ over all reflections. Software used: Siemens SMART, SAINT, SHELXTL.[18−20] No hydrogen atoms were included. Some sodium and crystal-water molecules were disordered. In order to determine the occupancy numbers of these atoms their atomic displacement parameter factors were set to 0.06000 (Na^+) and 0.08000 (H_2O) and the occupancies refined. Then the occupancy numbers were held fixed and the atomic displacement factors refined. Atoms with occupancy numbers below 0.25 were ignored. It was not possible to distinguish between H_2O and NH_4^+ due to disorder and the presence of heavy scatterers. Bond valence sum calculations did indicate water molecules coordinated to the lanthanides and identified bridging oxygens between two Ln atoms as singly protonated.[21,22]

Results and Discussion

$Na_{28}[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\cdot 2NaCl\cdot nH_2O$ (1). This well-known anion was prepared according to the published method. Our experimental results suggested that the recrystallization of the crude product from 3 M NaCl solution is of advantage before further use. The X-ray structural analysis was performed on a crystal isolated from 3 M NaCl solution. A detailed view of the anion $[(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]^{28-}$ is given in Figure 1. The X-ray analysis of the Co-substituted anion is used as a reference with regard to the coordination sites S1 and S2.[14] The X-ray analysis revealed the position of most of the sodium cations surrounding the anion. The central coordination site S1 of eight oxygen atoms formed by terminal oxygen atoms of the WO_6 octahedra, which are bridging the four AsW_9 units, is occupied by a sodium cation (Na1). The four S2 sites, constituted by the terminal oxygen atoms from the bridging WO_6 octahedra and the AsW_9 units, are also occupied by sodium cations (Na 2, 3 and 5, 19). These sodium cations are additionally bridged on each site in pairs by chloride ions (Cl1 and Cl2). The environment of Cl1 is completed by a sodium cation coordinated to an adjacent As_4W_{40} anion, thereby arranging two As_4W_{40} anions in pairs. We propose a similar arrangement for the non-recrystallized material since the chemical analysis revealed the presence of two chloride ions per As_4W_{40} anion as well.

$Na_{40}[(H_2O)_{10}Ln^{III}(Ln^{III}_2OH)(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_2\cdot nH_2O$, Ln = La, Ce, Nd, Sm, Eu, and Gd. The reaction between **1** and 3 equiv of lanthanide in 2 M NaCl solution led to the trisubstituted anion $Ln_3As_4W_{40}$. Figure 2 shows top and

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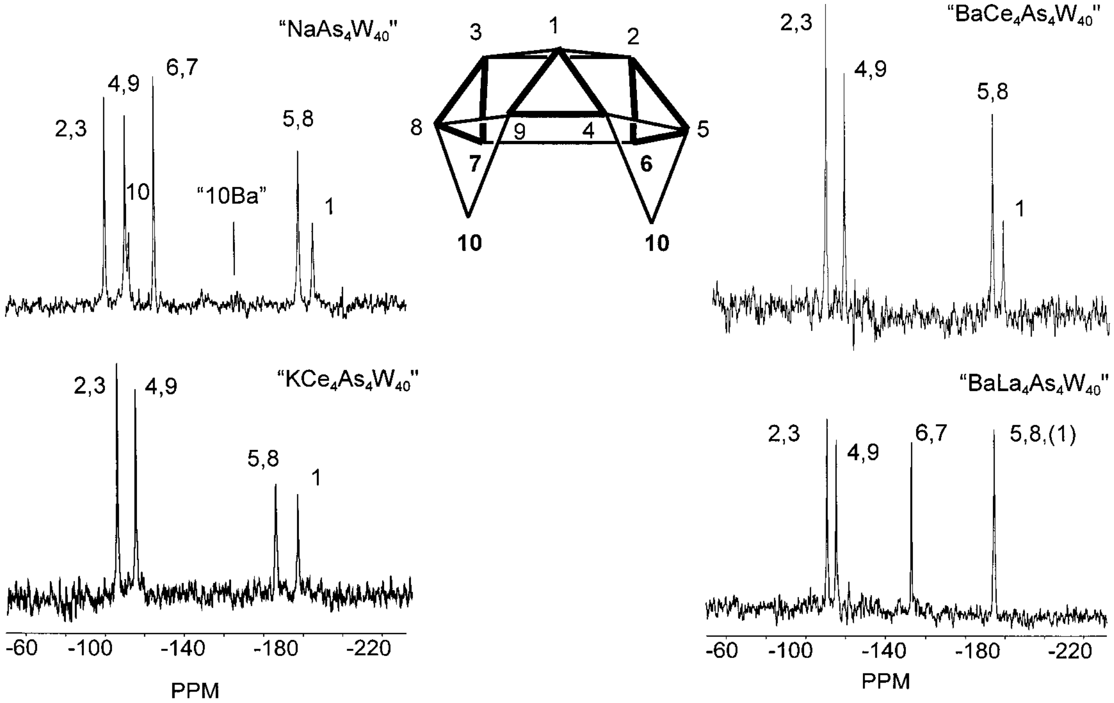

Figure 6. ^{183}W-NMR spectra of $NaAs_4W_{40}$, $BaLa_4As_4W_{40}$, $BaCe_4As_4W_{40}$, and $KCe_4As_4W_{40}$ recorded in D_2O. Inserted line in $NaAs_4W_{40}$ spectrum indicates position for signal of W10 in $BaAs_4W_{40}$. Numbering scheme taken from ref 10.

side views of the novel anion of the Sm derivative. Two adjacent S2 sites are occupied by two Sm atoms (Sm2 and Sm3) which are eight-coordinate to oxygen atoms (distorted square antiprism). The coordination polyhedra share a protonated oxygen atom (O23S) and are completed by four terminal oxygen atoms of site S2, two and three water molecules, respectively, and a terminal oxygen atom (O5SA) from a neighboring $Ln_3As_4W_{40}$ anion, Figures 2 and 3. The third Ln atom Sm1 is nine-coordinate (monocapped square antiprism) to four oxygen atoms and five water molecules. Four oxygen atoms originate from the S1 site opposite to the S2 sites occupied by Sm2 and Sm3. This site is named S3 for future reference. Four of the five water molecules are part of the anion's oxygen surface, while the fifth ligand O4S1 is located inside the anion, placed above the virtual center of the S1 site with respect to Sm1. The protons of O4S1 exchange quickly in D_2O as shown by ^{1}H-NMR. Selected metal−oxygen distances are summarized in Table 2, revealing typical bond lengths for Na−O and Ln−O.

The sodium salts of $(Ln_3As_4W_{40})_2$ are soluble enough to permit the observation of well-resolved ^{183}W-NMR spectra in D_2O solution. On the basis of the crystal structure for the "dimeric" anion and assuming overall C_i symmetry, 40 resonance lines are expected. However, for the "monomeric" unit with overall D_{2d} symmetry only 11 resonances are expected, 9 of intensity 2 and 2 of intensity 1. Between $\delta = -50$ and -250 ppm, 9 lines were observed for Ln = Ce and Nd. The spectrum for the samarium analogue is more congested with at least 18 lines, suggesting D_{2h} symmetry, Figure 4.[24] On the basis of these data it was concluded that the anions of type $(Ln_3As_4W_{40})_2$ are in fact present as two $Ln_3As_4W_{40}$ anions in aqueous solution.

Our experiments revealed that the use of concentrated aqueous NaCl solutions (1−4 M) as solvents favors the stabilization of the parent anion As_4W_{40} and therefore the formation of the anion $Ln_3As_4W_{40}$. When the reactions were carried out in water, the complete decomposition of the precursor anion As_4W_{40} and the formation of the anions $Ln_{16}As_{12}W_{148}$ and $Ln_4As_5W_{39}$ were observed, Ln = La and Ce.[8,9]

$\{Na_{16}[Ba(H_2O)_{10}(Ln^{III}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\}_\infty \cdot nH_2O$, Ln = La, Ce, and Gd, $(NH_4)_{15}Na_2[K(H_2O)_{10}(Ce^{III}_2OH)_2K(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\}_\infty \cdot 37H_2O$, and $(NH_4)_{18}[(H_2O)_{10}(Ce^{III}_2OH)_2K(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]\}_\infty \cdot 46H_2O$. The existence of the 4-fold-substituted anion $Ln_4As_4W_{40}$ was first observed for the cerium-containing anion, which was isolated as a minor product in a synthesis with As_4W_{40}, AsW_9, and Ce in aqueous solution. The single-crystal X-ray analysis revealed the compound $(NH_4)_{18}\{[(H_2O)_{10}(Ce^{III}_2OH)_2(B\text{-}\alpha\text{-}AsO_3W_9O_{30})_4(WO_2)_4]_\infty\} \cdot 46H_2O$ (**7**). In this novel anion all four lacunary S2 sites of the parent anion As_4W_{40} are occupied by cerium atoms. The central cryptate site S1 remained vacant. Attempts at a straightforward synthesis of the anion using As_4W_{40} and Ln in a 1:4 ratio in water or 1−4 M NaCl solution gave variable results. When the reaction was carried out in water only, the formation of the anions $Ln_{16}As_{12}W_{148}$ and $Ln_4As_5W_{39}$ (Ln = La and Ce) was observed, analogous to the previously described results for the experiments using a 1:3 ratio. In NaCl solutions of various concentrations several products were obtained. The isolated products included the cerium salt of $(Ce_3As_4W_{40})_2$ in which additional cerium atoms functioned as cations coordinated to the oxygen surface of the polyoxotungstates, and furthermore a fine crystalline powder. The IR and ^{183}W-NMR spectra of the powder suggested the presence of $Ln_4As_4W_{40}$ (Ln = La, Ce, Sm). However, the product decomposed while being recrystallized or when converted to the ammonium salt. The straightforward preparation of this novel anion type was achieved by the addition of stoichiometric quantities of Ba^{2+} or K^+ to the system. The results of the synthetic procedure confirm earlier solution studies on As_4W_{40} that the anion preferentially binds Ba^{2+} and K^+ ions in its central cryptate site S1.[10] The occupation of site S1 with Ba^{2+} or K^+ prevents

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(24) It has been a general observation of our studies on anions of type $Ln_xAs_yW_z$ (Ln = La, Ce, Nd, Sm, and Eu) that not all expected ^{183}W-NMR resonance lines were detectable.[9]

the formation of $Ln_3As_4W_{40}$, and the formation of the 4-fold-substituted anion becomes more favorable. Attempts to employ a lanthanide cation to occupy site S1, and therefore achieve a 5-fold substitution of As_4W_{40}, showed the most promising results when gadolinium was used. This might be due to the cation's smaller size compared to the earlier lanthanides. However, confirming X-ray structural data are unavailable at present.

Top and side views of the novel anion for the Ce derivative are depicted in Figure 5. All four S2 sites are occupied by cerium cations bridged in pairs by protonated oxygen atoms (O13C and O24C). These Ce cations are eight-coordinate to oxygen atoms (distorted square antiprism) analogous to Sm2 and Sm3 in $(Sm_3As_4W_{40})_2$. The central site S1 is occupied by a Ba^{2+} or K^+ cation. Their coordination sphere extends to the protonated oxygen atoms (O13C and O24C). The X-ray analysis revealed a total of 10 water ligands coordinated to the cerium cations as well as two terminal oxygen atoms (O47A and O15′), originating from two neighboring $Ln_4As_4W_{40}$ anions. These interanionic bonds cause a chain formation in the solid state, Figure 3. The formation of polymeric species in the field of polyoxotungstate research is noteworthy. This feature has been observed before for 3d element substituted Keggin anions and has also recently been found for monosubstituted Keggin anions with lanthanide metals.[25−27]

Upon dissolving the compound in water these bonds hydrolyze as shown by ^{183}W-NMR data in D_2O. The spectra for $BaCe_4As_4W_{40}$, $BaLa_4As_4W_{40}$, and $KLa_4As_4W_{40}$ compared to the spectrum for As_4W_{40} are depicted in Figure 6. In accordance with the anion's D_{2d} symmetry a simple resonance line pattern was found. The lines were assigned on the basis of the observed intensities and chemical shifts and with reference to earlier work.[10] The resonance signal for the bridging tungsten atom W10 between the AsW_9 units could not be detected for any of the three samples.[24,28] The greater intensity of the line for W5 and W8 of $BaLa_4As_4W_{40}$ suggests an overlapping with the signal of W1. The missing resonances for W6 and W7 in $BaCe_4As_4W_{40}$ and $KCe_4As_4W_{40}$ are presumed to be a consequence of several neighboring paramagnetic (Ce) centers.

The 3- and 4-fold lanthanide-substituted anions were successfully transferred into organic solvents by means of $DODA^+Cl^-$. Only the use of a nonsymmetrical tetraalkylammonium salt versus symmetrical tetraalkylammonium salts (C_1-C_7) accomplished the phase transfer of these large polyoxometalate clusters.[29] This experimental procedure was originally developed for the phase transfer of the anions of type $Ln_{16}As_{12}W_{148}$.[30] In all experiments stoichiometric amounts of $DODA^+Cl^-$ were needed to achieve the quantitative transfer into the organic phase. These findings are encouraging in regard to potential applications of the lanthanide-substituted polyoxometalate anions as Lewis acid catalysts.[31] Experiments to record the ^{183}W-NMR spectra of $BaLa_4As_4W_{40}$ in $CDCl_3$ as the $DODA^+$ salt were not successful due to the solution's high viscosity and consequently lower mobility of the polyoxoanion.

The present work shows that the tungstoarsenate As_4W_{40} is a valuable precursor for reactions with lanthanide (and actinide[32]) cations. The substitution of the parent anion with lanthanides was accompanied by the formation of interanionic bonds leading to "dimeric" and "polymeric" species in the solid state. The straightforward syntheses which require the use of concentrated NaCl solutions (1−4 M) and the addition of stoichiometric amounts of Ba^{2+} or K^+ reemphasize the importance of the presence of appropriate countercations for the assembly of large polyoxometalate structures.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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