DOI: 10.1002/ejic.200900630

Synthesis and Structural Characterization of the 28-Isopolytungstate Fragment $[H_2W_{28}O_{95}]^{20-}$ Stabilized by Two External Lanthanide Ions $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$

Amal H. Ismail,[a] Bassem S. Bassil,[a] Andreas Suchopar,[a] and Ulrich Kortz*[a]

Keywords: Cluster compounds / Polyoxometalates / Tungsten / Lanthanides / Structure elucidation

The V-shaped polyanions $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ [Ln = Sm (**1**), and Eu (**2**)] have been synthesized by reaction of Ln^{3+} and WO_4^{2-} in aqueous acidic medium. The sodium salt of **1** and the mixed sodium-europium salt of **2** have been characterized in the solid state by FTIR, single-crystal XRD, thermogravimetric analysis (TGA), and elemental analysis. Single-crystal X-ray analyses were carried out on $Na_{14}[Sm_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 40H_2O$ (**Na-1**) which crystallizes in the triclinic system, space group $P\bar{1}$, a = 14.8727(6) Å, b = 21.7762(11) Å, c = 23.5751(10) Å, α = 89.175(2)°, β = 86.430(2)°, γ = 75.364(2)°, and $Z = 2$ and on $Na_8Eu_2[Eu_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 47H_2O$ (**NaEu-2**) which crystallizes in the monoclinic system, space group $P2_1/n$, a = 25.3862(11) Å, b = 14.6364(5) Å, c = 40.3264(16) Å, β = 96.107(3)°, and Z = 4. The polyanions **1** and **2** consist of a novel isopolyanion unit $[H_2W_{28}O_{95}]^{20-}$ and two $\{Ln(H_2O)_n\}^{3+}$ supporting groups. The $\{W_{28}\}$ cluster coordinates to the two Ln^{3+} ions and acts as a tri- and tetradentate ligand for the two lanthanide ions. The $\{W_{28}\}$ cluster consists of two undecatungstate $\{W_{11}\}$ fragments and a hexatungstate fragment $\{W_6\}$. Furthermore, in the solid state, one $\{W_{28}\}$ fragment is connected to another $\{W_{28}\}$ via lanthanide-oxo bridges forming a $\{W_{56}\}$ aggregate $([Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-})_2$. It was also possible to synthesize other lanthanide derivatives of the $\{W_{28}\}$ cluster (Ln = La, Ce, Pr, Nd, and Gd) as determined by FTIR and preliminary single-crystal X-ray diffraction data.

Introduction

Polyoxometalates (POMs) are a well-known class of anionic metal-oxo clusters of the early (group V and VI) transition metals with molecular and electronic structural versatility. POMs are remarkable due to their reactivity and relevance in fields such as photochemistry, analytical chemistry, clinical chemistry, magnetism, catalysis, biology, medicine, and materials science.[1] POMs, especially polyoxotungstates, are effective homogeneous photocatalysts for the mineralization of organic pollutants (i.e. degradation of organic pollutants to CO_2, H_2O and the corresponding inorganic anions).[2] The ability of POMs to form peroxo derivatives renders them useful in oxidation reactions. Furthermore, chemical modifications in the composition of POMs allow for fine tuning of their Lewis acidity.[3]

Two main types of POMs are known: isopoly- and heteropoly-anions. Isopolyanions are represented with the general formula $[M_mO_y]^{n-}$, where M is the addenda atom in a high oxidation state (e.g. W^{VI}, Mo^{VI}). Heteropolyanions are represented with the general formula $[X_xM_mO_y]^{q-}(x \leq m)$ where X is the heteroatom (e.g. P^V, As^V, Si^{IV}, Ge^{IV}).[1a]

So far, lanthanide-containing POMs have been investigated less than their 3d-transition-metal analogues. The former have also shown interesting properties in the areas of photoluminescence, catalysis, electrochemistry, and magnetism.[4] Most of the lanthanide-containing POMs reported to date are actually heteropolyanions.[5] Our group has also been working on lanthanide-containing heteropolytungstates.[6] We have reported the ytterbium-containing tungstoarsenate $[YbAs_2W_{20}O_{68}(H_2O)_3]^{7-}$ resulting from the interaction of the monolacunary $[As_2W_{20}O_{68}(H_2O)]^{10-}$ with Yb^{3+} ions in acidic aqueous medium. The polyanion consists of two (α-$As^{III}W_9O_{33}$) fragments connected by a V-shaped $(H_2O)Yb[OW(H_2O)]_2$ fragment.[6a] The monolanthanide-containing polyanion family $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = La, Ce, Sm, Eu, Gd, Tb, Yb, Lu) has also been synthesized and structurally characterized.[6c] These polyanions are composed of two chiral (β_2-$SiW_{11}O_{39}$) units sandwiching the Ln^{3+} ion. Recently, we reported the tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ containing 20 cerium atoms and 100 tungsten centers.[6d] We synthesized this polyanion by the reaction of the trilacunary POM precursor $[\alpha\text{-}GeW_9O_{34}]^{10-}$ with Ce^{3+} ions in acidic aqueous medium.

However, to date only two types of lanthanide-containing isopolyanions have been reported. The decatungstate $[Ln(W_5O_{18})_2]^{n-}$ ($\{LnW_{10}\}$) sandwich species (Ln^{3+} = La, Ce, Pr, Nd, Sm, Ho, Yb and Y, and Ce^{4+}), first reported by

[a] School of Engineering and Science, Jacobs University, P. O. Box 750561, 28725 Bremen, Germany
Fax: +49-421-200-3229
E-mail: u.kortz@jacobs-university.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.200900630.

Peacock and Weakley, was synthesized by reaction of the lanthanide ions with WO_4^{2-} in a solution of pH 6.5–7.5.[5a,7a] The structure of the $\{LnW_{10}\}$ family is based on two monolacunary $[W_5O_{18}]^{6-}$ Lindqvist fragments encapsulating a central metal ion in a square-antiprismatic fashion. In particular Yamase's group reported some $\{LnW_{10}\}$ structures with different types of alkali counter cations.[8] Recently our group has reported the synthesis and structure of the yttrium derivative of $\{LnW_{10}\}$ including the use of solution ^{89}Y NMR spectroscopy.[9] The isopolyanion family $[Ln^{III}W_{10}O_{36}]^{9-}$, (Ln = Pr, Nd, Sm, Eu, Tb, Dy), has shown high luminescence quantum efficiency.[7b–7d]

On the other hand, the 22-isopolytungstate $[Ln_2(H_2O)_{10}W_{22}O_{71}(OH)_2]^{8-}$ ($\{Ln_2W_{22}\}$) (Ln^{3+} = La, Ce, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y), has been reported very recently by our group.[10] These $\{Ln_2W_{22}\}$ polyanions were synthesized by the reaction of Na_2WO_4 and the appropriate lanthanide salts in acidic aqueous medium (pH ≈ 2) in an 11:1 ratio. All the $\{Ln_2W_{22}\}$ polyanions are isostructural and crystallize as hydrated sodium salts in the triclinic space group *P*1. The structures of the $\{Ln_2W_{22}\}$ family comprise the isopolyanion $\{W_{22}\}$ coordinated to two $\{Ln(H_2O)_n\}^{3+}$ supporting ions. The $\{W_{22}\}$ structure in turn consists of two undecatungstate units $\{W_{11}\}$ fused by two corner-sharing W–O–W bridges. The $\{Ln_2W_{22}\}$ family can also be described as a dimeric entity composed of two $\{LnW_{11}\}$ half units related by an inversion center, resulting in the point group C_i. These species are the first isopolyanions containing lanthanide ions bearing terminal, labile aqua ligands. This may allow for ligand substitution which could lead to interesting derivatives including chiral ones of interest for catalysis.[10]

Apart from these two classes of compounds, a cerium-containing isopolyanion $[H_6Ce_2(H_2O)ClW_{15}O_{54}]^{7-}$ ($\{Ce_2W_{15}\}$) was reported by Cao's group.[11] The isopolyanion comprises a triangular pentadecatungstate ring capped by two Ce^{3+} ions, with a terminal aqua ligand on one side and a terminal chloro ligand on the other side.

The coordination sphere of the lanthanide ions in the $\{LnW_{10}\}$ family is saturated due to coordination to the monolacunary pentatungstate units. The ability to synthesize isopolyanions containing coordinatively unsaturated lanthanide centers with terminal, labile aqua ligands, such as our $\{Ln_2W_{22}\}$ family, could allow for ligand exchange and resulting applications in (chiral) catalysis. Hence, the synthesis of novel isopolytungstate-supported lanthanides represents a challenge in POM chemistry. Herein, we report the synthesis of a novel class of lanthanide-containing isopolytungstates.

Results and Discussion

Synthesis and Structure

We have synthesized and structurally characterized the V-shaped polyanions $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ [Ln = Sm (**1**), and Eu (**2**)] by one-pot reactions of Ln^{3+} and WO_4^{2-} in aqueous acidic medium. The sodium salt $Na_{14}[Sm_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 40H_2O$ (**Na-1**) and the mixed sodium-europium salt $Na_8Eu_2[Eu_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 47H_2O$ (**NaEu-2**) have been characterized in the solid state by FTIR, single-crystal XRD, thermogravimetric analysis (TGA), and elemental analysis. The polyanions **1** and **2** comprise a novel isopolyanion $[H_2W_{28}O_{95}]^{20-}$ unit and two $\{Ln(H_2O)_n\}^{3+}$ supporting groups (see Figure 1). The $\{W_{28}\}$ cluster, which consists of two undecatungstate $\{W_{11}\}$ fragments and a hexatungstate fragment $\{W_6\}$, coordinates to the two Ln^{3+} ions acting as a tri- and tetradentate ligand, respectively.

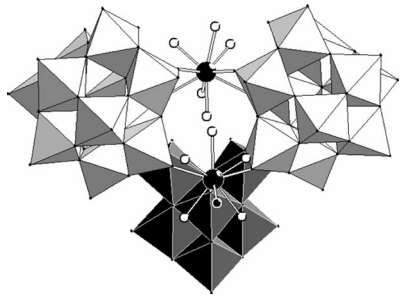

Figure 1. Representation of the V-shaped polyanions $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ (Ln = Sm, **1**; Eu, **2**). The color code is as follows: WO_6 octahedra (gray and black); Ln (big black ball); H_2O (white ball); O (small black ball). In the solid state the "black" oxo ligand links two $\{W_{28}\}$ units via an Ln–O–W′ bridge. The two types of subunits were colored differently for clarity.

The Ln^{3+} ions of **1** and **2** are nine-coordinate with a distorted monocapped square antiprismatic geometry. One of the Ln^{3+} ions is coordinated to the two $\{W_{11}\}$ subunits by four μ-oxo bridges with average Ln–O distances of 2.50(2) Å for **1** and 2.46(2) Å for **2**. The other Ln^{3+} ion is coordinated to the two $\{W_{11}\}$ subunits and the $\{W_6\}$ subunit by three μ-oxo bridges (one O atom from each subunit) with average Ln–O distances of 2.48(1) Å for **1** and 2.46(2) Å for **2**. A fourth oxo-bridge acts as a linker to another $\{W_{28}\}$, forming a $\{Ln_4W_{56}\}$ assembly ($[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-})_2$, see Figure S10 in the Supporting Information. The remaining coordination sphere is filled by aqua ligands. Hence the $\{Ln_4W_{56}\}$ structure can be described as a dimeric entity composed of two half units of $[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ related by an inversion center, resulting in point symmetry C_i.

Polyanions **1** and **2** were formed by following the same synthetic procedure of the $\{Ln_2W_{22}\}$ family reported by us recently.[10] The formation mechanism appears to be a classical tungstate condensation in aqueous acidic medium mediated by lanthanide ions (molar ratio 14:1). Besides **1** and **2** we were also able to synthesize other members of the novel $\{W_{28}\}$ family, namely for Ln = La, Ce, Pr, Nd, and Gd as determined by FTIR and preliminary single-crystal X-ray diffraction analysis, see Figures S1 and S2 (Supporting Information).

Three reaction parameters are crucial for the successful formation of **1** and **2** and to obtain pure compounds in good yields: reaction temperature, concentration of reagents, and pH of the solution.

- The polyanions **1** and **2** as well as the La, Pr, Nd, and Gd analogues were formed at room temperature as well as at 80–90 °C, but resulted in a higher yield at room temperature. On the other hand, the cerium analogue could only be prepared at room temperature.
- The yield of **Na-1** and **NaEu-2** is also affected by the concentration of the starting materials. A tungstate concentration as high as 1.5 M is needed to obtain a pure crystalline product with the reported yields (see Exp. Sect.). Lower reagent concentrations result in lower yields of the products.
- Also the pH of the reaction solution affects the formation and yield of polyanions **1** and **2** and their analogues. A pH window of 2.0–3.7 resulted in a successful synthetic procedure, with pH 3.2 being optimal. A pH lower than 2.0 did not provide any product, and a pH higher than 3.7 gave the well-known paradodecatungstate ($[H_2W_{12}O_{42}]^{10-}$) as the main product.

The synthetic procedures for **1** and **2** are very similar to those of our $\{Ln_2W_{22}\}$ and Weakley's $\{LnW_{10}\}$,[5a,10] except that the synthesis pH of the latter is different (see Figure 2). It is well known that the pH is a crucial parameter in POM synthesis in general. The synthetic procedure for our previously reported $\{Ln_2W_{22}\}$ family was successful for the middle to late lanthanides (Tb–Lu), and also for the early 4d metal ion yttrium. In contrast, the reaction procedure of the $\{Ln_2W_{28}\}$ family reported here was successful for the early lanthanide ions (La–Gd), (see Figure 3). Figure 2 summarizes the lanthanide-containing isopolytungstates reported so far and their respective formation conditions.

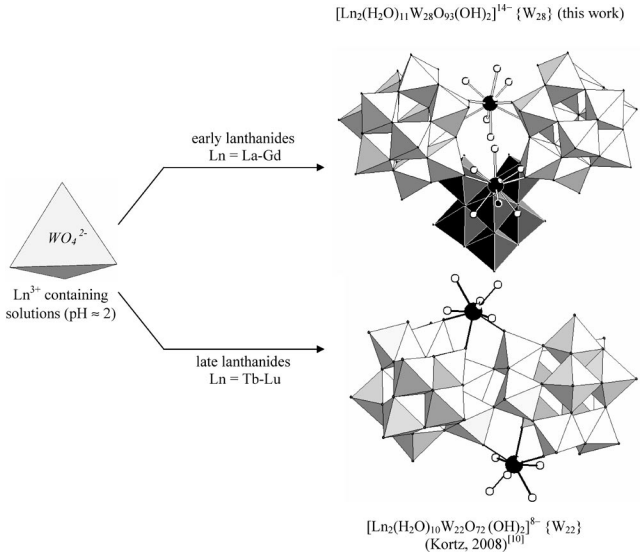

Figure 3. Representation of the two structures of the $\{W_{11}\}$ units containing lanthanides. The color code is as follows: WO_6 octahedra (gray and black); Ln (black big ball); H_2O (white), O (black small ball).

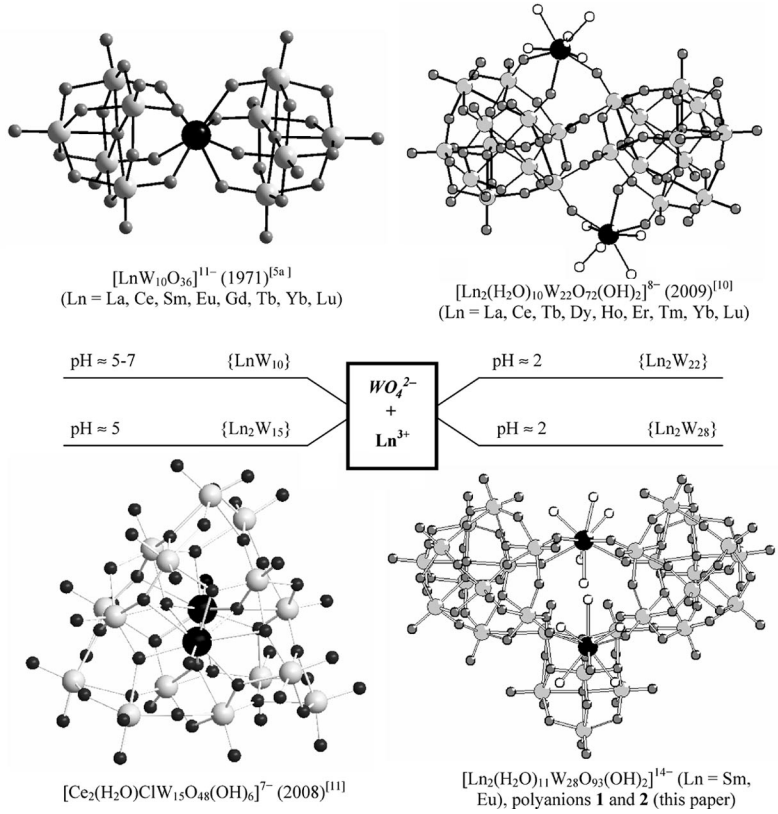

Figure 2. Scheme of different types of lanthanide-containing isopolytungstates and the pH of formation. The color code is as follows: W (faint gray); O (dark gray); Ln (black big ball); H_2O (white); Cl (black small ball).

The single crystals of the La, Ce, Pr, Nd, and Gd analogues of **1** and **2** were not of sufficient quality to finalize the refinements, but the data allowed us to identify the heavy atoms (W and Ln) and enough oxygen atoms to conclude that these polyanions are isostructural with **1** and **2**.[12] On the other hand, the samarium (**1**) and europium (**2**) analogues were fully characterized by single-crystal XRD (see Table 1). The neodymium and gadolinium analogues of the $\{Ln_2W_{28}\}$ family have almost the same unit cell parameters as **Na-1**, and the lanthanum, cerium, and praseodymium analogues have also similar unit cell parameters. All compounds of the $\{Ln_2W_{28}\}$ family (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) have similar IR spectra (see Figure S2).

Table 1. Crystal data and structure refinement for **Na-1** and **NaEu-2**.

	Na-1	**NaEu-2**
Empirical formula	$H_{102}Na_{14}O_{145}Sm_2W_{28}$	$H_{116}Eu_{3.5}Na_{9.5}O_{152}W_{28}$
MW	8193.18	6729.17
Crystal system	triclinic	monoclinic
Space group (no.)	$P\bar{1}$ (2)	$P2_1/n$ (14)
a [Å]	14.8727(6)	25.3862(11)
b [Å]	21.7762(11)	14.6364(5)
c [Å]	23.5751(10)	40.3264(16)
α [°]	89.175(2)	90
β [°]	86.430(2)	96.107(3)
γ [°]	75.364(2)	90
V [Å^3]	7373.2(6)	14898.7(10)
Z	2	4
T [°C]	–100	–100
λ [Å]	0.71073	0.71073
D [Mg m^{-3}]	3.690	3.766
μ [mm^{-1}]	22.68	23.11
$R[I > 2\sigma(I)]$[a]	0.056	0.072
R_w (all data)[b]	0.158	0.203

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $Rw = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

As mentioned above, the $\{W_{28}\}$ unit is an assembly comprising three distinct building blocks (see Figure S11): two undecatungstate subunits $\{W_{11}\}$ and a hexatungstate $\{W_6\}$ subunit. The former consists of four distinct "elementary blocks": one tetratungstate $\{W_4\}$ fragment formed from four edge-shared WO_6 octahedra connected through a μ_4-oxo bridge, one tritungstate $\{W_3\}$ fragment formed from three edge-shared WO_6 octahedra connected through a μ_3-hydroxo bridge, and two ditungstate $\{W_2\}$ fragments, each formed from two edge-shared WO_6 which share corners on one side. The hexatungstate $\{W_6\}$ subunit comprises six edge-shared WO_6 octahedra two of which have three *fac* terminal oxygen atoms. These building blocks have been reported previously. The undecatungstate $[H_4W_{11}O_{38}]^{6-}$ and hexatungstate $[H_3W_6O_{22}]^{5-}$ subunits were first reported by Fuchs et al. in 1988 and 1993, respectively.[13] Recently, Cronin's group reported isopolyanions composed of two or three $\{W_{11}\}$ units.[14] However, to the best of our knowledge the 28-isopolyoxotungstate $\{W_{28}\}$, which comprises two $\{W_{11}\}$ and one $\{W_6\}$ fragment linked via four oxo bridges, has not been reported to date. Notably, the two $\{W_{11}\}$ subunits in $\{W_{28}\}$ are analogous to the framework geometry of $\{W_{22}\}$ in our $\{Ln_2W_{22}\}$ family (see Figure 1).[10] However, they are arranged in C_s symmetry with the extra $\{W_6\}$ acting as a bridge between them as opposed to the C_i symmetry in $\{W_{22}\}$. The $\{W_{28}\}$ isopoly unit as such offers seven sites coordinating to the two Ln^{3+} centers. Polyanions **1** and **2** represent the largest lanthanide-containing isopolytungstates described to date.

We also tried to synthesize the lanthanide-free isopolyanion $[H_2W_{28}O_{93}]^{20-}$ by following the same synthetic procedure as for **1** and **2** and without adding any lanthanide, but so far our attempts have not been successful. On the other hand, we obtained the isopolyanion $[H_{10}W_{34}O_{116}]^{18-}$ $\{W_{34}\}$ which has been reported recently by Cronin's group.[14b] In fact, we identified the crystalline product to be a mixture of Cronin's $\{W_{34}\}$ and our $\{W_{22}\}$ as based on XRD and IR.[10,14b] Our results suggest that lanthanide ions are crucial for the stabilization of the title isopolyanion $\{W_{28}\}$.

Bond valence sum (BVS) calculations for **1** and **2** are consistent with all tungsten atoms being in the +6 oxidation state, and with all Ln ions being +3 as expected.[15] We also checked all polyanion oxygen atoms by BVS for possible protonation. As shown in the respective formulae for **1** and **2**, two monoprotonated oxygen atoms (BVS ≈1.2) were localized in the two $\{W_{11}\}$ subunits, namely the μ_3-oxo bridges of the $\{W_3\}$ fragments. This results in a total of two OH groups per $\{W_{28}\}$ unit leading to a total isopolyanion charge of –20. The two grafted Ln^{3+} ions reduce this charge to –14 in **1** and **2**. The BVS values for nonprotonated oxygen atoms range from 2.2–1.5. The BVS values for terminal W=O oxygen atoms are low (ca. 1.5), which is typical and presumably does not indicate additional protonation.

We also performed TGA on the salts Na-**1** and NaEu-**2** to determine the degree of hydration and thermal stability. The thermograms show the expected weight loss domain between 25 and 400 °C corresponding to dehydration. We calculated 40 and 47 water molecules per formula unit of **Na-1** and **NaEu-2**, respectively. These results are also supported by elemental analysis. The absence of any additional weight loss after dehydration indicated that the salts are thermally stable up to 800–900 °C (see Figures S3 and S4). TGA analysis was also performed on the salts of the La, Ce, Pr, Nd, Sm, Eu, and Gd analogues, see Figures S5–S9.

Conclusions

We have successfully synthesized the V-shaped, lanthanide-containing isopolyanions $[Sm_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ (**1**) and $[Eu_2(H_2O)_{10}W_{28}O_{93}(OH)_2]^{14-}$ (**2**), which were structurally characterized by IR spectroscopy, single-crystal X-ray diffraction, TGA, and elemental analysis. The polyanions **1** and **2** were synthesized in aqueous acidic medium by simple one-pot reaction of sodium tungstate with a lanthanide(III) salt and then isolated as the hydrated sodium and mixed sodium-europium salts **Na-1** and **NaEu-2**, respectively. Polyanions **1** and **2** are composed of a 28-tungsten isopolyanion unit $\{W_{28}\}$ which consists of two undeca $\{W_{11}\}$ and one hexa $\{W_6\}$ fragments coordinated to two

external lanthanide ions bearing five terminal aqua ligands. Polyanions **1** and **2** represent only the second example of lanthanide-containing isopolyanions and they contain exposed lanthanide centers with labile terminal aqua ligands. The latter represent good candidates for ligand substitution with other mono- or polydentate ligands (e.g. carboxylic acids, amino acids), including chiral ones, providing a potential for catalysis. We also tried to isolate **1** and **2** as lipophilic alkyl ammonium salts which would open the door to organic catalysis reactions.

Experimental Section

Instrumentation: Elemental analysis for **NaEu-2** was carried out by Analytische Laboratorien, Lindlar, Germany and for **Na-1** by Kanti Labs, Tirupathi, India. Infrared spectra were recorded with a Nicolet Avatar spectrometer using KBr pellets. Thermogravimetric analysis was performed with a TA Instruments SDT Q600 thermobalance from room temperature to 900 °C with a heating rate of 5° min^{-1} and a 100 mL min^{-1} nitrogen flow.

Figures 1–3 were generated by using the crystal and molecular structure visualization software DIAMOND, Version 3.2, serial number 1.3.1.2004300.2003.[16]

Synthesis: We used reagent-grade chemicals as purchased without further purification.

$Na_{14}[Sm_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 40H_2O$ (Na-1): $Na_2WO_4\cdot 2H_2O$ (10.00 g, 30.30 mmol) was dissolved in H_2O (20 mL) followed by dropwise addition of concentrated aqueous HCl (3 mL) (local formation and redissolution of hydrated tungsten oxide was detected). This was immediately followed by the dropwise addition of $SmCl_3\cdot 6H_2O$ (0.80 g, 2.20 mmol) dissolved in H_2O (5 mL) and the pH was adjusted to 3.2 with HCl (6 M). The mixture was vigorously stirred at room temperature for 1 h. The white precipitate formed was filtered off and the filtrate was kept in an open vial for crystallization. Colorless crystals were obtained after several days, which were filtered off and air dried (yield 3.0 g, 38%). IR data for **Na-1**: $\tilde{\nu}$ = 946 (m), 881 (sh), 833 (s), 801 (s), 756 (sh), 632 (m), 595 (m), 473 (w), 458 (w), 419 (w) cm^{-1}. **Na-1**: calcd. Na 3.9, W 62.8, Sm 3.7; found Na 3.8, W 62.9, Sm 3.9.

$Na_8Eu_2[Eu_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot 47H_2O$ (NaEu-2): $Na_2WO_4\cdot 2H_2O$ (10.00 g, 30.30 mmol) was dissolved in H_2O (20 mL) followed by dropwise addition of concentrated aqueous HCl (3 mL) (local formation and redissolution of hydrated tungsten oxide was detected). This was immediately followed by the dropwise addition of $EuCl_3\cdot 6H_2O$ (0.81 g, 2.20 mmol) dissolved in H_2O (5 mL) and the pH was adjusted to 3.2 with HCl (6 M). The mixture was vigorously stirred at room temperature for 1 h. The white precipitate formed was filtered off and the filtrate was kept in an open vial for crystallization. Colorless crystals were obtained after several days, which were filtered off and air dried (yield 3.4 g, 41%). IR data for **NaEu-2**: $\tilde{\nu}$ = 946 (m), 881 (sh), 833 (s), 801 (s), 756 (sh), 632 (m), 595 (m), 473 (w), 458 (w), 419 (w) cm^{-1}. **NaEu-2**: calcd. Na 2.2, W 60.6, Eu 7.2; found Na 1.3, W 58.4, Eu 7.4. It was not possible to crystallize the Eu POM as a pure Na salt. It was found that the Na content is rather low and that of Eu is slightly high (for every additional 1/3 Eu3+ there is 1 Na+ less).

$Na_{14}[Ln_2(H_2O)_{10}W_{28}O_{93}(OH)_2]\cdot xH_2O$ (Ln = La, Ce, Pr, Nd and Gd): The same procedure as for **Na-1** was followed, but using the respective lanthanide chloride salt instead of $SmCl_3\cdot 6H_2O$.

X-ray Crystallography: The crystals were mounted in Hampton cryoloops using light oil, for data collection at low temperature. Indexing and data collection were performed with a Bruker X8 APEX II CCD diffractometer with kappa geometry and Mo-K_α radiation (λ = 0.71073 Å). Data integration and routine processing were performed using the SAINT software suite. Further data processing, including multi-scan absorption corrections, was performed using SADABS.[17] Direct methods (SHELXS97) solutions successfully located the W atoms, and successive Fourier syntheses (SHELXL97) revealed the remaining atoms.[17] Refinements were full-matrix least-squares against F^2 using all data. Some lanthanides, cations, and waters of hydration were modeled with varying degrees of occupancy, a common situation for polyoxotungstate structures. One disordered europium counter cation was found in addition to the nondisordered Eu^{3+} ions grafted to the $\{W_{28}\}$ polyanion. In the final refinements, all nondisordered heavy atoms (W, Ln) were refined anisotropically, while the O and Na atoms and the disordered europium were refined isotropically. No H atoms were included in the models. The crystallographic data are provided in Table 1.

Supporting Information (see also the footnote on the first page of this article): Two figures with IR spectra, seven thermograms and two figures with different representations of polyanions **1** and **2**.

Acknowledgments

U. K. thanks Jacobs University and the Fonds der Chemischen Industrie for research support. A. I. appreciates the grant from the Ministry of the Higher Education of the Arab Republic of Egypt, allowing her to pursue Ph. D. studies in the laboratory of U. K. in Bremen. We thank Dr. M. H. Dickman for finalizing the CIF files.

[1] a) M. T. Pope, in: *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; c) M. T. Pope, A. Müller, in: *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, The Netherlands, **1994**; d) A. Müller, H. Reuter, S. Dillinger, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2328–2361; e) C. Hill, *Chem. Rev.* **1998** (special thematic issue on polyoxometalates); f) M. T. Pope, A. Müller, in: *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, The Netherlands, **2001**; g) T. Yamase, M. T. Pope, in: *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T. Yamase, M. T. Pope), Kluwer, Dordrecht, The Netherlands, **2002**; h) G. R. J. Choppin, *J. Nucl. Radiochem. Sci.* **2005**, *6*, 1–5.

[2] a) A. Mylonas, A. Hiskia, E. Papaconstantinou, *J. Mol. Catal. A* **1996**, *114*, 191–200; b) A. Hiskia, A. Troupis, E. Papaconstantinou, *Int. J. Photoenergy* **2002**, *4*, 35–40; c) E. Gkika, P. Kormali, S. Antonaraki, D. Dimoticali, E. Papaconstantinou, A. Hiskia, *Int. J. Photoenergy* **2004**, *6*, 227–231; d) A. Hiskia, A. Troupis, S. Antonaraki, E. Gkika, P. Kormali, E. Papaconstantinou, *Int. J. Environ. Anal. Chem.* **2006**, 233–242; e) P. Kormali, A. Troupis, T. Triantis, A. Hiskia, E. Papaconstantinou, *Catal. Today* **2007**, *124*, 149–155.

[3] a) E. Derat, E. Lacôte, B. Hasenknopf, S. Thorimbert, M. Malacria, *J. Phys. Chem. A* **2008**, *112*, 13002–13005; b) C. Boglio, K. Micoine, R. Rémy, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, C. Afonso, J.-C. Tabet, *Chem. Eur. J.* **2007**, *13*, 5426–5432; c) C. Boglio, G. Lemiére, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *Angew. Chem. Int. Ed.* **2006**, *45*, 3324–3327; d) C. Boglio, G. Lenoble, C. Duhayon, B. Hasenknopf, R. Thouvenot, C. Zhang, R. C. Howell, B. P. Burton-Pye, L. C. Francesconi, E. Lacôte, S. Thorimbert, M.

Malacria, C. Afonso, J.-C. Tabet, *Inorg. Chem.* **2006**, *45*, 1389–1398; e) C. Boglio, K. Micoine, E. Derat, R. Thouvenot, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *J. Am. Chem. Soc.* **2008**, *130*, 4553–4561; f) S. Bareyt, S. Piligkos, B. Hasenknopf, P. Gouzerh, E. Lacôte, S. Thorimbert, M. Malacria, *J. Am. Chem. Soc.* **2005**, *127*, 6788–6794; g) K. Micoine, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *Org. Lett.* **2007**, *9*, 3981–3984.

[4] a) M. M. Gresely, W. P. Griffith, A. C. Lämmel, H. I. S. Nogueira, B. C. Parkin, *J. Mol. Catal. A* **1997**, *117*, 185–198; b) W. P. Griffith, N. M-Smith, H. I. S. Nogueira, A. G. F. Shoair, M. Suriaatmaja, A. J. P. White, D. J. Williams, *J. Organomet. Chem.* **2000**, *607*, 146–155; c) J. A. Fernández, X. López, C. Bo, C. de Graaf, E. J. Baerend, J. M. Poblet, *J. Am. Chem. Soc.* **2005**, *127*, 12244–12253; d) W. Chen, Y. Li, Y. Wang, E. Wang, Z. Su, *Dalton Trans.* **2007**, 4293–4301; e) F. Li, L. Xu, Y. Wei, G. Gao, L. Fan, Z. Li, *Inorg. Chim. Acta* **2006**, *359*, 3795–3799; f) W. Huang, L. C. Francesconi, T. Plenova, *Inorg. Chem.* **2007**, *46*, 7861–7869; g) A. Merca, A. Müller, J. van Slageren, M. Läge, B. Krebs, *J. Cluster Sci.* **2007**, *18*, 711–719.

[5] a) R. D. Peacock, T. J. R. J. Weakley, *Chem. Soc. A* **1971**, 1836–1839; b) M. H. Dickman, G. J. Gama, K.-C. Kim, M. T. Pope, *J. Cluster Sci.* **1996**, *7*, 567–583; c) K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445–1448; d) M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem. Int. Ed.* **2000**, *39*, 2914–2916; e) M. Sadakane, M. H. Dickman, M. T. Pope, *Inorg. Chem.* **2001**, *40*, 2715–2719; f) Q. H. Luo, R. C. Howell, M. Dankova, J. Bartis, C. W. Williams, W. D. Horrocks, V. G. Young, A. L. Rheingold, L. C. Francesconi, *Inorg. Chem.* **2001**, *40*, 1894–1910; g) G. L. Xue, J. Vaissermann, P. J. Gouzerh, *J. Cluster Sci.* **2002**, *13*, 409–421; h) Q. H. Luo, R. C. Howell, J. Bartis, M. Dankova, W. D. Horrocks, A. L. Rheingold, L. C. Francesconi, *Inorg. Chem.* **2002**, *41*, 6112–6117; i) P. Mialane, L. Lisnard, A. Mallard, J. Marrot, E. Antic-Fidancev, P. Aschehoug, D. Vivien, F. Sécheresse, *Inorg. Chem.* **2003**, *42*, 2102–2108; j) F. Li, L. Xu, Y. Wei, G. Gao, L. Fan, Z. Li, *Inorg. Chim. Acta* **2006**, *359*, 3795–3799; k) Y. Lu, Y. Li, E. Wang, X. Xeu, Y. Ma, *Inorg. Chim. Acta* **2007**, *360*, 2063–2070; l) R. C. Howell, F. G. Perez, S. Jain, W. D. Horrocks Jr., A. L. Rheingold, L. C. Francesconi, *Angew. Chem. Int. Ed.* **2001**, *113*, 4155–4158; m) G. L. Xue, J. Vaissermann, P. Gouzerh, *J. Cluster Sci.* **2002**, *13*, 409–421; n) K. Fukaya, T. Yamase, *Angew. Chem. Int. Ed.* **2003**, *42*, 654–658; o) Y. Lu, Y. Li, E. Wang, X. Xe, Y. Ma, *Inorg. Chim. Acta* **2006**, *360*, 2063–2070; p) M. Zimmermann, N. Belai, R. J. Butcher, M. T. Pope, E. V. Chubarova, M. H. Dickman, U. Kortz, *Inorg. Chem.* **2007**, *46*, 1737–1740; q) A. Merca, A. Müller, J. van Slageren, M. Läge, B. Krebs, *J. Cluster Sci.* **2007**, *18*, 711–719; r) X. Fang, P. Kögerler, *Chem. Commun.* **2008**, 3396–3398.

[6] a) U. Kortz, C. Holzapfel, M. Reicke, *J. Mol. Struct.* **2003**, *656*, 93–100; b) U. Kortz, *J. Cluster Sci.* **2003**, *14*, 205–214; c) B. S. Bassil, M. H. Dickman, B. Kammer, U. Kortz, *Inorg. Chem.* **2007**, *46*, 2452–2458; d) B. S. Bassil, M. H. Dickman, I. Römer, B. Kammer, U. Kortz, *Angew. Chem. Int. Ed.* **2007**, *46*, 6192–6195.

[7] a) J. Iball, J. N. Low, T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.* **1974**, 2021–2024; b) T. Yamase, H. Naruke, Y. Sasaki, *J. Chem. Soc., Dalton Trans.* **1990**, 1687–1696; c) F. A. Almeida Paz, M. S. S. Balula, A. M. V. Cavaleiro, J. Klinowski, H. I. S. Nogueira, *Acta Crystallogr., Sect. E* **2005**, *61*, i28–i31; d) M. J. Stillman, A. J. J. Thomson, *J. Chem. Soc., Dalton Trans.* **1976**, 1138–1144.

[8] a) T. Ozeki, M. Takahashi, T. Yamase, *Acta Crystallogr., Sect. C* **1992**, *48*, 1370–1374; b) T. Ozeki, T. Yamase, *Acta Crystallogr., Sect. B* **1994**, *50*, 128–134; c) T. Ozeki, T. Yamase, *Acta Crystallogr., Sect. C* **1993**, *49*, 1574–1577; d) T. Ozeki, T. Yamase, *Acta Crystallogr., Sect. C* **1994**, *50*, 327–330; e) T. Yamase, T. Ozeki, K. Ueda, *Acta Crystallogr., Sect. C* **1993**, *49*, 1572–1574; f) T. Yamase, T. Ozeki, *Acta Crystallogr., Sect. C* **1993**, *49*, 1577–1580; g) T. Yamase, T. Ozeki, M. Tosaka, *Acta Crystallogr., Sect. C* **1994**, *50*, 1849–1852; h) T. Ozeki, M. Takahashi, T. Yamase, *Acta Crystallogr., Sect. C* **1992**, *48*, 1370–1374.

[9] M. Barsukova, M. H. Dickman, E. Visser, S. S. Mal, U. Kortz, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2423–2427.

[10] A. Ismail, M. H. Dickman, U. Kortz, *Inorg. Chem.* **2009**, *48*, 1559–1565.

[11] T. Li, F. Li, J. Lü, Z. Guo, S. Gao, R. Cao, *Inorg. Chem.* **2008**, *47*, 5612–5615.

[12] a) The lanthanum derivative of the $\{Ln_2W_{28}\}$ family crystallizes in the triclinic system, space group $P\bar{1}$, with a = 20.577(14) Å, b = 27.020(15) Å, c = 31.090(19) Å, α = 81.511(19)°, β = 75.062(3)°, γ = 77.11(2)°, V = 16205.7 Å^3, and Z = 2; b) The cerium derivative of the $\{Ln_2W_{28}\}$ family crystallizes in the triclinic system, space group $P\bar{1}$, with a = 21.629(2) Å, b = 26.869(3) Å, c = 31.611(3) Å, α = 80.463(3)°, β = 72.936(4)°, γ = 75.999(4)°, V = 16951.2 Å^3, and Z = 2; c) The praseodymium derivative of the $\{Ln_2W_{28}\}$ family crystallizes in the triclinic system, space group $P\bar{1}$, with a = 21.110(8) Å, b = 26.903(8) Å, c = 31.154(10) Å, α = 81.125(11)°, β = 73.771(13)°, γ = 76.903(12)°, V = 16467.77 Å^3, and Z = 2; d) The neodymium derivative of the $\{Ln_2W_{28}\}$ family crystallizes in the triclinic system, space group $P\bar{1}$, with a = 14.837(3) Å, b = 21.803(4) Å, c = 23.596(4) Å, α = 88.899(7)°, β = 86.092(6)°, γ = 75.540(7)°, V = 7374.23 Å^3, and Z = 2; e) The gadolinium derivative of the $\{Ln_2W_{28}\}$ family crystallizes in the triclinic system, space group $P\bar{1}$, with a = 14.8426(19) Å, b = 21.779(3) Å, c = 23.581(3) Å, α = 89.059(4)°, β = 86.325(4)°, γ = 75.426(4)°, V = 7362.12 Å^3, and Z = 2.

[13] a) T. Lehmann, J. Fuchs, *Z. Naturforsch., Teil B* **1988**, *43*, 89–93; b) H. Hartl, R. Palm, J. Fuchs, *Angew. Chem.* **1993**, *105*, 1545; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1492–1494.

[14] a) D.-L. Long, H. Abbas, P. Kögerler, L. Cronin, *J. Am. Chem. Soc.* **2004**, *126*, 13880–13881; b) H. N. Miras, J. Yan, D.-L. Long, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 8420–8423.

[15] D. Altermatt, I. D. Brown, *Acta Crystallogr., Sect. B* **1985**, *41*, 244–247.

[16] *DIAMOND*, Version 3.2, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany (URL: http://www.crystalimpact.com/diamond).

[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Received: July 4, 2009
Published Online: September 16, 2009

