Polyoxometalates

DOI: 10.1002/anie.200701422

The Tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$: A Polyoxometalate Containing 20 Cerium(III) Atoms**

*Bassem S. Bassil, Michael H. Dickman, Isabella Römer, Bernd von der Kammer, and Ulrich Kortz**

Polyoxometalates (POMs) are anionic metal oxide clusters with a wide structural variety and interesting properties,[1] and have potential applications in diverse areas such as catalysis, magnetism, bio- and nanotechnology, medicine, and materials science.[2] POMs are usually synthesized through condensation reactions in aqueous, acidic solution. These reactions can be influenced by careful variation of the synthetic conditions, for example, the ratio and concentration of reagents, solvent, pH, countercations, and temperature. Under suitable synthetic conditions, POMs usually form quickly by self-assembly processes.

Lanthanide ions incorporated into POM frameworks show interesting luminescence, magnetic, and Lewis acid catalytic properties. Because of their larger coordination numbers relative to 3d transition metals, lanthanides are suitable for linking POM fragments into discrete POMs or extended metal–oxygen frameworks.[3] In recent years, there has been a significant increase in the number and also the size of the lanthanide-containing polytungstates.[4] In 1997 Pope and co-workers reported a POM containing 148 tungsten and 16 cerium atoms, $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$, which remains the largest discrete, molecular polytungstate known to date.[5] A few years later, Francesconi and co-workers reported the large, europium-containing phosphotungstate $[(PEu_2W_{10}O_{38})_4(W_3O_{14})]^{30-}$.[6] Gouzerh and co-workers described two large cerium-containing polyanions, $[Ce(H_2O)_5As_4W_{40}O_{140}]^{25-}$ and $[(SbW_9O_{33})_4\{WO_2(H_2O)\}_2Ce_3(H_2O)_8(Sb_4O_4)]^{19-}$.[7] Also, Fukaya and Yamase reported two crown-shaped, europium-containing tungstoarsenates(III), $[K\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_6]^{35-}$ and $[Cs\subset\{Eu(H_2O)_2(\alpha\text{-}AsW_9O_{33})\}_4]^{23-}$.[8] Our group has also been interested in the interaction of lanthanide ions with lacunary POMs.[9] In 2003, we reported the ytterbium-substituted tungstoarsenate(III) $[YbAs_2W_{20}O_{68}(H_2O)_3]^{7-}$ and also the La-containing Wells–Dawson dimer $[\{La(CH_3COO)(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$ with two acetates bridging the La^{3+} ions.[9a,b] In 2007 we prepared the chiral Peacock–Weakley-type POMs $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = La, Ce, Sm, Eu, Gd, Tb, Yb, Lu).[9c]

We then decided to focus on the trilacunary polyanion precursor $[\alpha\text{-}GeW_9O_{34}]^{10-}$, first reported by Hervé and Tézé in 1977.[10] No lanthanide-containing derivative of this POM precursor has been reported so far. The trilacunary nature of $[\alpha\text{-}GeW_9O_{34}]^{10-}$ may allow coordination with several lanthanide centers, perhaps resulting in the formation of very large POMs.

Herein we report the 20-cerium(III) ion tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ (**1**). Polyanion **1** was synthesized by reaction of the trilacunary POM precursor $[\alpha\text{-}GeW_9O_{34}]^{10-}$ with Ce^{III} ions in a 1:1 ratio in water at pH 5.0 and isolated as the mixed cesium-sodium salt $Cs_{28}Na_{28}[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]\cdot n\,H_2O$ ($n \approx 180$; CsNa-**1**), which crystallizes in the monoclinic space group $P2_1/n$ (Figure 1).[11] It has a crystallographic inversion center resulting in point group symmetry C_i. The polyanion could also be obtained as the sodium salt $Na_{56}[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]\cdot n\,H_2O$ ($n \approx 180$; Na-**1**) by using an aqueous 1 M NaCl solution instead of water as the solvent but otherwise analogous reaction conditions. Although these conditions resulted in a better yield (see the Experimental Section), the crystals were not suitable for X-ray diffraction. However, the similarity of the IR spectra of the sodium and mixed cesium-sodium salts suggests that the same polyanion is present in both compounds.

Polyanion **1** can be described as a dimeric entity composed of two half units of $[Ce_{10}Ge_5W_{50}O_{188}(OH)_2(H_2O)_{15}]^{28-}$ (**1a**) related by an inversion center (Figure 2). The two units **1a** are linked to each other through long Ce–O(W) bridges (2.61(4) Å), which suggests that **1** might dissociate readily in solution to provide two equivalents of **1a**. Our preliminary ^{183}W NMR measurements on re-dissolved Na-**1** (CsNa-**1** was not soluble enough) are not conclusive. We realize that NMR spectroscopy will most likely not allow us to conclude if **1** or **1a** or both (in equilibrium) are actually present in solution.[12]

Besides Pope's cyclic W_{148}-POM $[As_{12}Ce_{16}(H_2O)_{36}W_{148}O_{524}]^{76-}$ [5] and our ball-shaped dimethyltin-containing W_{108}-POM $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A\text{-}XW_9O_{34})_{12}]^{36-}$ (X = P, As),[13] polyanion **1** is the third-largest (in terms of the number of W centers) polytungstate reported to date. The roughly dumbbell-shaped **1** has a maximum dimension of about 4.2 nm.

Each half unit **1a** comprises five $\{\beta(4,11)\text{-}GeW_{10}O_{38}\}$ units (i.e., β-Keggin fragments that have lost a WO_6 group from position 4 in the belt and position 11 in the rotated triad, according to the IUPAC rules for POMs) [2b] linked asymmetrically by ten Ce^{3+} centers, resulting in an asymmetric

---

[*] B. S. Bassil, Dr. M. H. Dickman, I. Römer, B. von der Kammer, Prof. U. Kortz
Jacobs University Bremen
School of Engineering and Science
P.O. Box 750 561, 28725 Bremen (Germany)
Fax: (+49) 421-200-3229
E-mail: u.kortz@jacobs-university.de

[**] U.K. thanks Jacobs University for research support. I.R. is thankful for financial support from the Nanomolecular Science graduate program at Jacobs University. We thank Can F. Bilgin for preparing the cover art. Figures 1–3 were generated by Diamond Version 3.1e (Crystal Impact GbR).

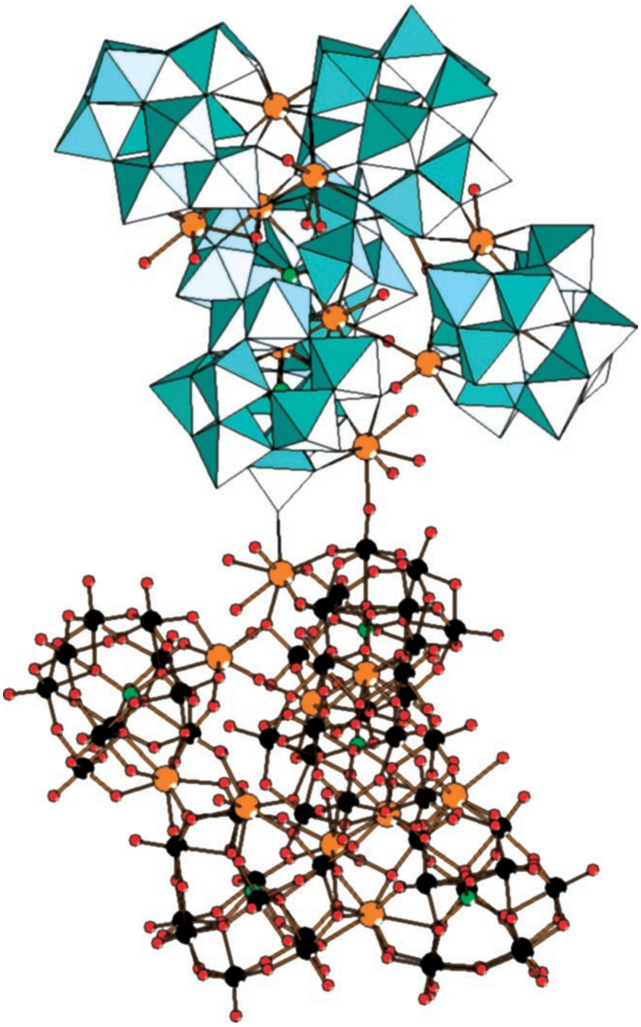

Figure 1. Combined polyhedral/ball-and-stick representation of $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ (**1**). Color code: W black, Ce orange, Ge green, O red, WO_6 octahedra light blue.

assembly with C_1 symmetry (see Figure 2). The dilacunary $\{\beta(4,11)\text{-}GeW_{10}O_{38}\}$ Keggin unit is unprecedented. Recently we reported the dimeric and trimeric zirconium-containing tungstosilicates $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ and $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ with lacunary Keggin fragments closely related to those in **1**.[15] However, the Zr_4-POM is based on $\{\beta(1,9)\text{-}SiW_{10}O_{37}\}$ and $\{\beta(4,9)\text{-}SiW_{10}O_{37}\}$ units, and the Zr_6-POM on $\{\beta(4,10)\text{-}SiW_{10}O_{37}\}$ units. Close inspection of the structure of **1a** indicates that essentially five dicerium-containing $\{\beta(4,11)\text{-}GeW_{10}O_{38}\}$ building blocks are linked to each other. In other words, each of the dilacunary β(4,11)-Keggin units has two cerium ions coordinated to the respective vacant sites in the rotated triad and the belt.

The same linkage mode through a cerium ion incorporated in the Keggin "belt" has been seen previously in the lanthanide-containing tungstosilicates $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln = La, Ce, Sm, Eu, Gd, Tb, Yb, Lu).[9c] These observations allow us to suggest a likely mechanism of formation for **1a** by initial formation of the monomeric building blocks ($\beta(4,11)\text{-}Ce_2GeW_{10}O_{38}$), which then (most likely gradually) self-assemble in an asymmetric fashion to give **1a**. Then two

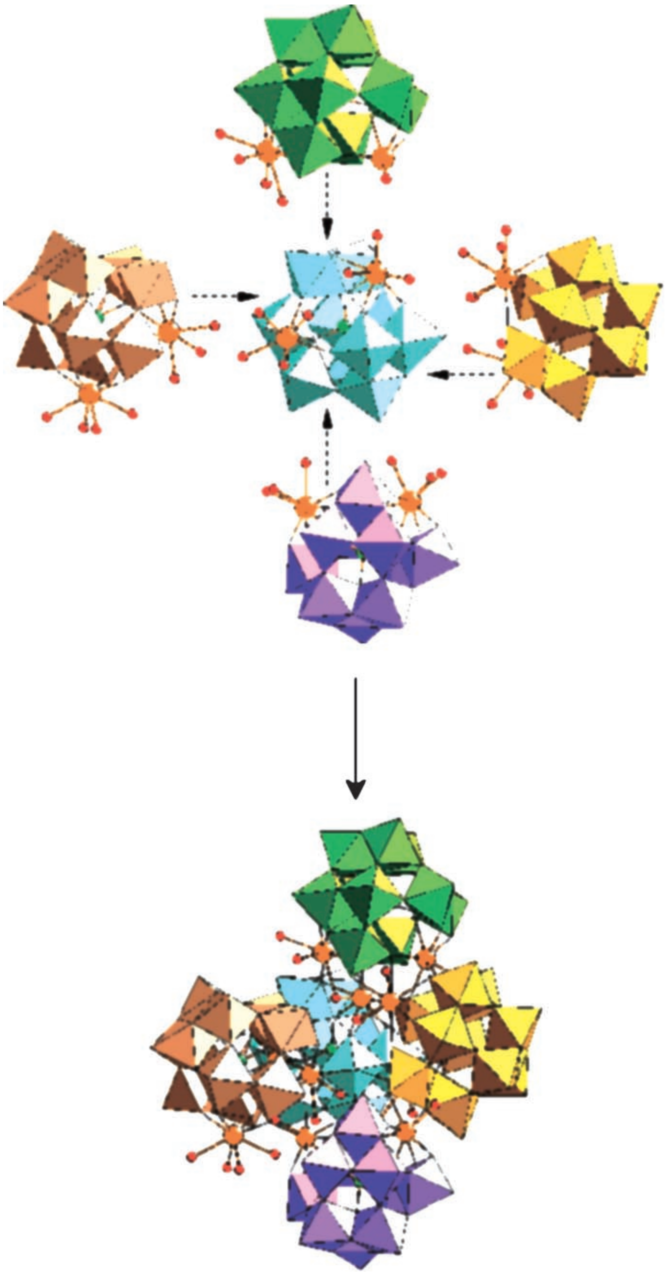

Figure 2. Left: Exploded view of the half unit $[Ce_{10}Ge_5W_{50}O_{188}(OH)_2(H_2O)_{15}]^{28-}$ (**1a**); right: arrangement of the five equivalent "Ce_2GeW_{10}" Keggin building blocks in **1** (shown in different colors for clarity).

enantiomers of **1a** (*R*,*S* or *S*,*R*) dimerize through two Ce–O(W′) bonds to give **1** (which has C_i symmetry).

We have already pointed out above that **1** contains exclusively dilacunary "GeW_{10}" Keggin units, although the reaction was carried out with the trilacunary "GeW_9" precursor. Gain (and also loss) of tungsten during a reaction involving lacunary polytungstate precursors has been observed, for example, in the reaction of Mn^{II} ions with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ to give the trimeric, cyclic, chiral POM $[(\beta_2\text{-}SiW_{11}MnO_{38}OH)_3]^{15-}$.[16]

To find a more rational synthetic procedure for **1**, we tried several other reactions, for example, with $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$ [17] as precursor or starting with $[\alpha\text{-}GeW_9O_{34}]^{10-}$ and adding one equivalent of sodium tungstate. When the same reaction conditions (solvent, pH value, etc.) are used as for the original reaction, neither pathway resulted in **1** on the basis of IR spectroscopy.

We performed bond valence sum (BVS) calculations to test for the presence of hydroxo groups in **1a**.[18] We identified two hydroxo bridges, one between W17 and Ce4 and one between W38 and Ce8 (see Figure 3). Therefore, a more detailed molecular formula of **1** is: $[\{[Ce_{10}(H_2O)_{15}][\beta(4,11)\text{-}GeW_{10}O_{37}(OH)]_2[\beta(4,11)\text{-}GeW_{10}O_{38}]_3\}_2]^{56-}$. The total charge of **1** is therefore −56, which is balanced equally by cesium and sodium ions in the solid state. We also performed TGA measurements on CsNa-**1** and Na-**1** from room temperature to 900 °C. These results are fully consistent with the formulae provided above.

The 10 cerium(III) ions in **1a** exhibit two coordination numbers: nine for Ce8 and Ce9, and eight for all others, with Ce−O bond lengths ranging from 2.20(3) to 2.88(3) Å. The cerium centers are linked either directly to each other through oxo or aqua bridges, or indirectly through O-W-O bridges, leading to an asymmetric assembly in **1a** (Figure 3). Eight of the ten cerium atoms are linked through O bridges, resulting in four pairs (Ce1 and Ce10, Ce2 and Ce3, Ce6 and Ce7, and Ce8 and Ce9); Ce4 bridges to Ce8 over a very long distance (2.87(3) Å) through a tungstate oxo atom, whereas Ce5 is "isolated", bound only to tungstate oxygen atoms or water not bridging to another Ce atom. There are no terminal water ligands on Ce2 or Ce9; Ce5 and Ce6 have one terminal water ligand each; and Ce3, Ce4, and Ce8 have two terminal water ligands each. The lanthanides Ce1 and Ce10 are bridged by a water molecule: Ce1 has no terminal ligands and the Ce10 has two extra terminal water ligands. This leaves Ce7, which has three terminal water ligands and is linked to a tungsten atom of the second half unit of **1** through a long oxo bridge (2.61(4) Å).

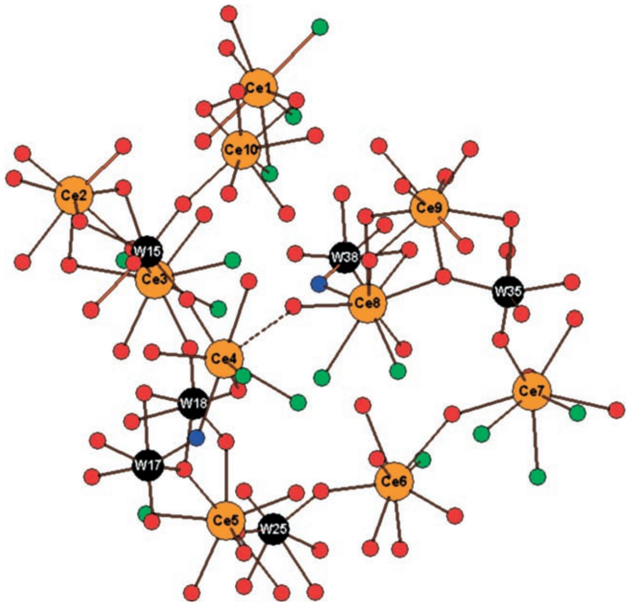

Figure 3. Ball-and-stick representation of all 10 Ce^{III} centers in **1a**. The figure also shows the inner coordination sphere of the Ce^{III} ions and their connectivity through WO_6 units, which leads to asymmetric assembly. The 15 terminal water ligands of the 10 cerium centers are shown as green balls, the two bridging hydroxo groups are blue, and the remaining oxygen atoms are red. The weak interaction between Ce4 and the bridging oxo to Ce8 is shown as a dotted line.

In summary, we have synthesized the large, dimeric, 20 cerium(III) ion tungstogermanate $[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]^{56-}$ (**1**) under conventional reaction conditions from the trilacunary POM precursor $[\alpha\text{-}GeW_9O_{34}]^{10-}$ and Ce^{III} ions. Investigations of physical and catalytic properties of **1** are planned. The terminal water ligands on the cerium centers in **1** allow ligand substitution, which could lead to interesting derivatives. Our work reemphasizes that lanthanides or other large cations are ideal linkers for lacunary POM fragments to form very large assemblies.

Experimental Section

CsNa-**1**: A sample of $CeCl_3\cdot 7H_2O$ (0.064 g; 0.17 mmol) was dissolved in water (20 mL) at pH 5.0, and then $Na_{10}[GeW_9O_{34}]$ (0.5 g; 0.17 mmol; synthesized according to reference [10]) was added. This solution was heated to 50 °C for 30 minutes, allowed to cool to room temperature, and then filtered. 1 M CsCl solution (0.5 mL) was added to the solution, which was allowed to evaporate in an open vial at room temperature. After about one week a yellow, crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product, which was filtered off and air-dried. Yield: 0.1 g (16 %). IR: $\tilde{\nu}$ = 1619(s), 941(m), 892(sh), 787(s), 752(sh), 702(sh), 671(w), 594(w), 521(w), 501(w) cm^{-1}. Anal. calcd for CsNa-**1**: Cs 10.3, Na 1.8, Ce 7.8, W 50.9, Ge 2.0; found: Cs 9.1, Na 2.2, Ce 7.4, W 52.0, Ge 1.7. Polyanion **1** could also be synthesized in higher yield under analogous reaction conditions using a 1 M solution of NaCl instead of water (no 1 M CsCl solution was added this time). The crystalline product $Na_{56}[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]\cdot 180H_2O$ (Na-**1**) was obtained after two weeks, but the single crystals were not suitable for XRD analysis. The identity of Na-**1** was established by comparison if its IR spectrum with that of CsNa-**1**, and the degree of hydration was determined by thermogravimetric analysis. Yield: 0.2 g (36 %). IR: $\tilde{\nu}$ = 1628(s), 937(m), 897(sh), 800(s), 765(sh), 714(sh), 625(w), 602(w), 518(w) cm^{-1}. Elemental analysis was performed by Analytische Laboratorien, Industriepark Kaiserau, 51789 Lindlar (Germany).

Received: April 2, 2007

Keywords: cerium · lanthanides · polyoxometalates · self-assembly · supramolecular chemistry · tungsten

---

[1] a) J. Berzelius, *Poggendorff's Ann. Phys.* **1826**, *6*, 369; b) J. F. Keggin, *Nature* **1933**, *131*, 908–909; c) J. F. Keggin, *Proc. R. Soc. London Ser. A* **1934**, *144*, 75–77; d) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.

[2] a) *Polyoxometalates: from Platonic Solids to Anti Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**; b) *Chem. Rev.* **1998**, *98*, 1–389 (Special Thematic Issue on Polyoxometalates); c) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **2001**; *Polyoxometalate Chemistry for Nano-Composite Design* (Eds.: T. Yamase, M. T. Pope), Kluwer, Dordrecht, **2002**; d) M. T. Pope, *Compr. Coord. Chem. II* **2003**, *4*, 635–678; e) C. L. Hill, *Compr. Coord. Chem. II* **2003**, *4*, 679–759; f) *Polyoxometalate Molecular Science* (Eds.: J. J. Borras-Almenar, E. Coronado, A. Müller, M. T. Pope), Kluwer,

Dordrecht, **2004**; g) N. Casan-Pastor, P. Gomez-Romero, *Front. Biosci.* **2004**, *9*, 1759 – 1770.

[3] a) C. Zhang, R. C. Howell, K. B. Scotland, F. G. Perez, L. Todaro, L. C. Francesconi, *Inorg. Chem.* **2004**, *43*, 7691 – 7701; b) R. C. Howell, F. G. Perez, S. Jain, W. D. Horrocks, Jr., A. L. Rheingold, L. C. Francesconi, *Angew. Chem.* **2001**, *113*, 4155 – 4158; *Angew. Chem. Int. Ed.* **2001**, *40*, 4031 – 4034.

[4] Recent examples: a) F. Li, L. Xu, Y. Wei, G. Gao, L. Fan, Z. Li, *Inorg. Chim. Acta* **2006**, *359*, 3795 – 3799; b) C. Boglio, G. Lenoble, C. Duhayon, B. Hasenknopf, R. Thouvenot, C. Zhang, R. C. Howell, B. P. Burton-Pye, L. C. Francesconi, E. Lacote, S. Thorimbert, M. Malacria, C. Afonso, J. C. Tabet, *Inorg. Chem.* **2006**, *45*, 1389 – 1398; c) C. Zhang, L. Bensaid, D. McGregor, X. Fang, R. C. Howell, B. Burton-Pye, Q. Luo, L. Todaro, L. C. Francesconi, *J. Cluster Sci.* **2006**, *17*, 389 – 425; d) P. Mialane, A. Dolbecq, E. Rivière, J. Marrot, F. Sécheresse, *Eur. J. Inorg. Chem.* **2004**, 33 – 36; e) N. Belai, M. H. Dickman, M. T. Pope, R. Contant, B. Keita, I. Mbomekalle, L. Nadjo, *Inorg. Chem.* **2005**, *44*, 169 – 171; f) C. Zhang, R. C. Howell, D. McGregor, L. Bensaid, S. Rahyab, M. Nayshtut, S. Lekperic, L. C. Francesconi, *C. R. Chim.* **2005**, *8*, 1035; g) C. Zhang, R. C. Howell, Q. H. Luo, H. L. Fieselmann, L. Todaro, L. C. Francesconi, *Inorg. Chem.* **2005**, *44*, 3569 – 3578.

[5] K. Wassermann, M. H. Dickman, M. T. Pope, *Angew. Chem.* **1997**, *109*, 1513 – 1516; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1445 – 1448.

[6] R. C. Howell, F. G. Perez, S. Jain, W. D. Horrocks, Jr., A. L. Rheingold, L. C. Francesconi, *Angew. Chem.* **2001**, *113*, 4155 – 4158; *Angew. Chem. Int. Ed.* **2001**, *40*, 4031 – 4034.

[7] G. L. Xue, J. Vaissermann, P. Gouzerh, *J. Cluster Sci.* **2002**, *13*, 409 – 421.

[8] K. Fukaya, T. Yamase, *Angew. Chem.* **2003**, *115*, 678 – 682; *Angew. Chem. Int. Ed.* **2003**, *42*, 654 – 658.

[9] 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. von der Kammer, U. Kortz, *Inorg. Chem.* **2007**, *46*, 2452 – 2458.

[10] a) G. Hervé, A. Tézé, *Inorg. Chem.* **1977**, *16*, 2115 – 2117; b) A. Tézé, G. Hervé, *J. Inorg. Nucl. Chem.* **1977**, *39*, 999 – 1002; c) A. Tézé, G. Hervé, *J. Inorg. Nucl. Chem.* **1977**, *39*, 2151 – 2154.

[11] Crystal data for $Cs_{28}Na_{28}[Ce_{20}Ge_{10}W_{100}O_{376}(OH)_4(H_2O)_{30}]\cdot n\,H_2O$ ($n \approx 180$; CsNa-**1**): A yellow rod of CsNa-**1** with dimensions $0.17 \times 0.03 \times 0.03$ mm^3 was mounted in a Hampton cryoloop for indexing and intensity data collection at 173 K on a Bruker D8 APEX II CCD single-crystal diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). Of the 331 397 reflections collected ($2\theta_{max} = 41.6°$, 99.4 % complete), 27 826 were unique ($R_{int} = 0.278$) and 16 425 reflections were considered observed ($I > 2\sigma(I)$). Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program (G. M. Sheldrick, Siemens Analytical X-ray Instrument Division: Madison, WI, **1995**). Direct methods were used to locate the tungsten and cerium atoms (SHELXS-97). Then the remaining atoms were found from successive Fourier maps (SHELXL-97). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (W, Ce, Ge, and Cs atoms), and isotropic thermal parameters (O and Na atoms) converged at $R = 0.069$ ($I > 2\sigma(I)$) and $R_w = 0.212$ (all data). Residual electron density min./max.: -2.85 e Å^{-3}/ 3.98 e Å^{-3} (0.74 Å from O34W/0.88 Å from Cs5). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-391392.

[12] To resolve this issue, we are planning size-exclusion chromatography and electrochemistry experiments. Furthermore, we will make use of laser-light scattering, which should also shed light on the question of whether **1** and/or **1a** form the supramolecular, spherical agglomerates called "blackberries" in solution (see G. Liu, T. Liu, S. S. Mal, U. Kortz, *J. Am. Chem. Soc.* **2006**, *128*, 10 103 – 10 110).

[13] U. Kortz, F. Hussain, M. Reicke, *Angew. Chem.* **2005**, *117*, 3839 – 3843; *Angew. Chem. Int. Ed.* **2005**, *44*, 3773 – 3777.

[14] A. Tézé, G. Hervé, *Inorg. Synth.* **1990**, *27*, 85.

[15] B. S. Bassil, M. H. Dickman, U. Kortz, *Inorg. Chem.* **2006**, *45*, 2394 – 2396.

[16] U. Kortz, S. Matta, *Inorg. Chem.* **2001**, *40*, 815 – 817.

[17] N. H. Nsouli, B. S. Bassil, M. H. Dickman, U. Kortz, B. Keita, L. Nadjo, *Inorg. Chem.* **2006**, *45*, 3858- 3860.

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