

# Mono- and Di-Lanthanide Derivatives of 19-Tungsto-2-Arsenate(III)

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70<sup>th</sup> birthday

Two types of lanthanide-containing derivatives of the 19-tungsto-2-arsenate(III)  $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$  (**As<sub>2</sub>W<sub>19</sub>**) have been synthesized in mildly acidic aqueous media and characterized in the solid state. The ytterbium(III)-containing anion  $[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**1**) was formed by reaction of  $\text{Yb}^{3+}$  with the potassium salt of **As<sub>2</sub>W<sub>19</sub>**, while the lanthanum(III) derivative  $[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$  (**2**) was formed by reaction of  $\text{La}^{3+}$  with the sodium salt of the trilacunary precursor  $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$  (**AsW<sub>9</sub>**). The polyanions **1** and **2** crystallize as hydrated salts in the triclinic system, space group  $P\bar{1}$ :  $\text{K}_{0.5}\text{Na}_{0.5}[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 25\text{H}_2\text{O}$  (**KNa-1**) with cell dimensions  $a = 12.4730(5)$ ,  $b = 17.4630(9)$ ,  $c = 21.1990(10)$  Å,  $\alpha = 72.568(3)^\circ$ ,  $\beta = 85.442(2)^\circ$ ,  $\gamma = 89.147(3)^\circ$ ,  $Z = 2$ ;  $\text{Na}_8[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 17\text{H}_2\text{O}$  (**Na-2**) with cell dimensions  $a = 14.929(2)$ ,  $b = 17.769(3)$ ,  $c = 20.754(4)$  Å,  $\alpha = 77.203(10)^\circ$ ,  $\beta = 80.273(9)^\circ$ ,  $\gamma = 72.670(9)^\circ$ ,  $Z = 2$ . Both compounds **KNa-1** and **Na-2** were characterized in the solid state by FTIR spectroscopy, TGA and single-crystal X-ray diffraction analyses. In polyanion **1**, the **As<sub>2</sub>W<sub>19</sub>** unit sandwiches one ytterbium and one potassium ion leading to a structure with idealized  $C_s$  symmetry, whereas polyanion **2** incorporates two lanthanum ions leading to a structure with idealized  $C_{2v}$  symmetry. Compositional analogs of polyanions **1** ( $Ln = \text{La, Ce, Eu, Gd}$  and  $\text{Lu}$ ) and **2** ( $\text{Ce}$ ) were also synthesized and identified by FTIR spectroscopy.

**Key words:** Arsenic, Lanthanides, Polyoxometalates, Tungsten, X-Ray Crystal Structure

## Introduction

Polyoxometalates (POMs) are a diverse class of anionic metal-oxygen cage complexes formed predominantly of early transition metals (groups V and VI) in high oxidation states. The large compositional and structural versatility of POMs gives rise to various applications in fields such as catalysis, medicine, analytical chemistry, and material science [1]. Although the first polyanion has been made already in 1826, the mechanism of POM formation is still not well understood and usually described as self-assembly [1]. POMs are usually formed *via* condensation of mononuclear metalate ions in acidic aqueous solutions. In particular, polyoxotungstates are effective homogeneous photocatalysts useful for the degradation of organic pollutants [2].

Lanthanide-containing POMs are in general less investigated than their 3*d*-transition-metal analogs, but recently there have been more reports on the former class [3]. POMs-containing lanthanides show inter-

esting properties in areas such as photoluminescence, catalysis, electrochemistry, and magnetism [4, 5]. Due to their larger sizes and consequently larger coordination numbers compared to 3*d* transition metal ions, lanthanide ions exhibit a different coordination mode to lacunary POM precursors resulting in novel and sometimes unexpected structures [6].

Lacunary POM precursors containing a hetero group with a lone pair of electrons (*e. g.*  $\text{As}^{\text{III}}$ ,  $\text{Sb}^{\text{III}}$ ) are of particular interest, because the lone pair does not allow the closed Keggin unit to form, resulting in a very different reactivity as compared to lacunary POMs with a tetrahedral hetero group. The claw-shaped  $[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$  (**As<sub>2</sub>W<sub>19</sub>**) precursor is a member of this subclass, and its structure can be rationalized as two  $[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]^{9-}$  (**AsW<sub>9</sub>**) units linked through a  $\text{WO}_6$  group *via* four equatorial W-O-W bonds and *trans*-related terminal oxo and aqua ligands (see Fig. S1; Supporting Information: online only). The dilacunary polyanion **As<sub>2</sub>W<sub>19</sub>** was first reported by Tourné *et al.* in 1973 [7], and its structure

was confirmed later by our group using single-crystal X-ray diffraction [8]. Incorporation of an additional W-bridge in the dilacunary  $\text{As}_2\text{W}_{19}$  unit results in the monolacunary  $[\text{As}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})]^{10-}$  ( $\text{As}_2\text{W}_{20}$ ), which was first reported by Hervé and coworkers (see Fig. S2) [9]. Interaction of  $\text{As}_2\text{W}_{19}$  with di- and trivalent transition metal and main group elements has been investigated by different groups and has resulted in the expected disubstituted products  $[\text{M}_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})_3]^{n-}$  ( $n = 10$ ;  $M = \text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{VO}^{2+}$ ;  $n = 8$ ;  $M = \text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ) [10].

Our group has also been working in the area of lanthanide-containing polyoxotungstates, and we have isolated species incorporating between one and twenty lanthanide centers [11]. We have also investigated the interaction of both  $\text{As}_2\text{W}_{19}$  and  $\text{As}_2\text{W}_{20}$  with ytterbium(III) ions in aqueous acidic ( $\text{pH} = 2$ ) medium, resulting in both cases in  $[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{7-}$  [11a]. This polyanion consists of two  $\text{AsW}_9$  units connected by a triangular  $[\text{YbW}_2\text{O}_2(\text{H}_2\text{O})_3]^{11+}$  unit which is composed of two 6-coordinated tungsten centers and a 7-coordinated  $\text{Yb}^{\text{III}}$  ion, all carrying one terminal water ligand [11a].

Now, we have focused on the reactivity of lanthanide ions with lone pair-containing lacunary POM precursors such as  $\text{As}_2\text{W}_{19}$  and  $\text{AsW}_9$ . This work has resulted in the synthesis and structural characterization of two lanthanide-containing 19-tungsto-2-arsenates(III) reported herein.

## Results and Discussion

We have synthesized and structurally characterized the mono- and di-lanthanide-containing polyanions  $[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**1**) and  $[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$  (**2**). The mixed potassium-sodium salt of **1**  $\text{K}_{9.5}\text{Na}_{0.5}[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})] \cdot 25\text{H}_2\text{O}$  (**KNa-1**) and the sodium salt of **2**  $\text{Na}_8[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})] \cdot 17\text{H}_2\text{O}$  (**Na-2**) have been characterized in the solid state by FTIR spectroscopy, single-crystal X-ray diffraction and TGA analyses. Both polyanions are based on the  $\text{As}_2\text{W}_{19}$  skeleton with one (**1**) or two (**2**) incorporated lanthanide ions.

The ytterbium(III)-containing polyanion  $[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**1**) consists of two  $\text{AsW}_9$  subunits sandwiching an ytterbium and a tungsten ion and a weakly bound, stabilizing potassium ion, leading to a structure with idealized  $C_s$

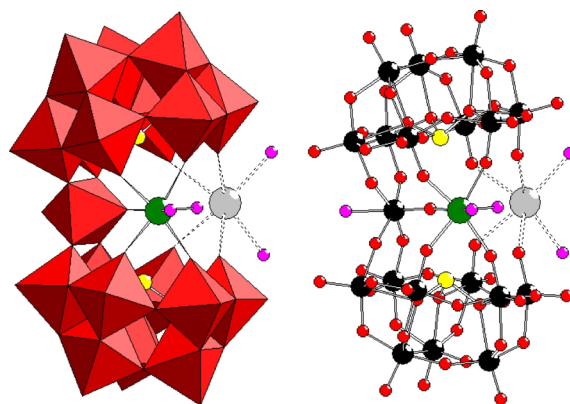


Fig. 1. Polyhedral (left) and ball-and-stick (right) representation of  $[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**1**). The color code is as follows:  $\text{WO}_6$  octahedra (red), W (black), As (yellow), Yb (green), K (grey), O (red),  $\text{H}_2\text{O}$  (pink). (color online).

symmetry (Fig. 1). The tungsten and potassium ions in the central ‘belt’ of the structure are six-coordinated, whereas the ytterbium ion is seven-coordinated. The ytterbium and potassium ions have two terminal aqua ligands each while the unique tungsten atom has just one, and all aqua ligands point away from the polyanion. We checked for possible protonation of polyanion **1** by bond valence sum (BVS) calculations [12], but no additional protonation sites besides the terminal aqua ligands described above were identified. The three metal ions in the central ‘belt’ of **1** are all coordinated to both  $\text{AsW}_9$  fragments *via* four  $\mu_2$ -oxo bridges involving corner-sharing  $\text{WO}_6$  octahedra of each  $\text{AsW}_9$  subunit. The average Yb–O and K–O distances in **1** are 2.266(14) and 2.836(16) Å, respectively.

Polyanion **1** was synthesized using simple and conventional open beaker conditions by interaction of the dilacunary precursor  $\text{As}_2\text{W}_{19}$  with  $\text{Yb}^{3+}$  ions in aqueous acidic ( $\text{pH} = 6$ ) medium. It is known that interaction of  $\text{As}_2\text{W}_{19}$  or  $\text{AsW}_9$  with transition metal ions or organometallic species at a proper pH usually results in mono- or disubstituted products based on the  $\text{As}_2\text{W}_{19}$  framework [10]. For example, our group has already reported di-manganese(II)/cobalt(II)/zinc(II) [10c], diphenyltin [10e], mono-palladium(II) [10f], and dititanium(IV) derivatives [10g, h]. At  $\text{pH} = 2.0$ , reaction of  $\text{As}_2\text{W}_{19}$  with ytterbium(III) led to the formation of  $[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{7-}$  [11a], whereas the same reaction at  $\text{pH} = 6.5$  resulted in polyanion **1**. This is fully consistent with the known fact that  $\text{pH} \sim 2$  induces condensation of an extra tungsten center at the lacu-

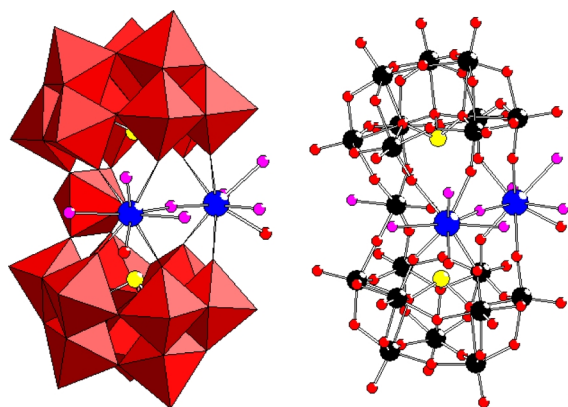


Fig. 2. Polyhedral (left) and ball-and-stick (right) representation of  $[\text{La}_2(\text{H}_2\text{O})_8\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$  (**2**). The color code is the same as in Fig. 1, and La (blue). (color online).

nary site of  $\text{As}_2\text{W}_{19}$  resulting in  $\text{As}_2\text{W}_{20}$  [9], whereas at mildly acidic pH the  $\text{As}_2\text{W}_{19}$  framework is maintained, and the vacant site in the central ‘belt’ is occupied by a potassium ion as seen in **1**. We also tried to obtain the di-ytterbium analog of **1** using different synthetic pathways involving  $\text{As}_2\text{W}_{19}$ , but without success. We believe that the potassium ion in the  $\text{As}_2\text{W}_{19}$  framework inhibits incorporation of an additional  $\text{Yb}^{3+}$  ion. It is interesting to note that when the same reaction was performed at pH = 2.0 in a 1M KCl solution (instead of water), anion **1** is obtained rather than the expected  $[\text{YbAs}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})_3]^{7-}$ , which confirms the role of potassium in mediating the reaction pathway. We were also able to synthesize other lanthanide containing analogs of **1**, namely  $[\text{Ln}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Eu}, \text{Gd}$ ). The IR spectra of these analogs are all very similar and virtually identical with that of **1** (see Fig. S3).

The di-lanthanum(III) polyanion  $[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$  (**2**) consists of two  $\text{AsW}_9$  subunits sandwiching one tungsten and two lanthanum(III) ions leading to a structure with  $C_{2v}$  symmetry (Fig. 2). The unique tungsten atom in the central ‘belt’ is six-coordinated, whereas the two lanthanum ions are nine-coordinated with an average La–O distance of 2.555(17) Å. Both lanthanum ions are linked by a bridging water molecule, and they also have three terminal aqua ligands each, whereas the tungsten ion has an inner oxo and an outer aqua terminal ligand. BVS calculations indicate that no other oxygen atoms of **2** are protonated. In analogy with polyanion **1**, all three metal atoms in the ‘belt’

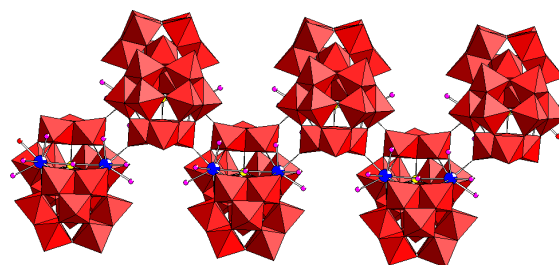


Fig. 3. Polyhedral representation of **2** forming a 1D chain in the solid state. The color code is the same as in Fig. 2. (color online).

of **2** connect both  $\text{AsW}_9$  fragments *via* four  $\mu_2$ -oxo bridges involving corner-sharing  $\text{WO}_6$  octahedra. The coordination sphere of each lanthanum ion is completed through a La–O–W’ bridge, where W’ belongs to a neighboring polyanion, leading to a zigzag 1D chain formation in the solid state (Fig. 3).

The structures of polyanions **1** and **2** are very similar as both are based on the lacunary  $\text{As}_2\text{W}_{19}$  unit. However, the potassium ion in **1** is replaced by a lanthanum(III) ion in **2**. No potassium ions were present during the synthesis of **2**, and a different precursor was used ( $\text{AsW}_9$  *vs.*  $\text{AsW}_{19}$ ). As expected, the coordination number of  $\text{La}^{3+}$  in **2** is larger than that of  $\text{Yb}^{3+}$  in **1** (9 *vs.* 7), reflecting the larger size of the former.

Polyanion **2** was synthesized under mild, conventional conditions by interaction of the sodium salt of the trilacunary precursor  $\text{AsW}_9$  with  $\text{La}^{3+}$  ions in aqueous acidic (pH = 5) medium. A high concentration of NaCl (1.0 M) was needed in order to obtain the desired crystalline product. The same reaction performed in water did not result in any crystalline product. Also, polyanion **2** cannot be prepared when using  $\text{As}_2\text{W}_{19}$  as precursor instead of  $\text{AsW}_9$ . Several variations of the synthetic procedure with  $\text{As}_2\text{W}_{19}$  (pH, solvent, temperature, ratio of reactants) always led to the mono-lanthanum polyanion. This observation indicates the importance of the POM precursor and the type of counterion during the synthesis of polyanions **1** and **2**. As stated above, a potassium ion preferentially coordinates to the lacunary site of the  $\text{As}_2\text{W}_{19}$  precursor, thereby blocking insertion of a second lanthanide ion. On the other hand, using the sodium salt of  $\text{AsW}_9$  allowed us to prepare the di-lanthanide derivative **2**. The different role of potassium *vs.* sodium ions in the stabilization of lacunary polyanion fragments in aqueous solution is well known [13]. Following the same synthetic procedure as for **2**, we were able to prepare the

cerium(III) analog  $[\text{Ce}_2(\text{H}_2\text{O})_8\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$ , as confirmed by FTIR studies (Fig. S4).

The bonding modes of the lanthanide centers in **1** ( $\text{Yb}^{3+}$ ) and **2** ( $\text{La}^{3+}$ ) are different. The ytterbium ion in **1** is connected to the unique ‘belt’ tungsten atom *via* a  $\mu_2$ -oxo bridge, whereas both lanthanum ions in **2** are bound to each other *via* a  $\mu_2$ -aqua bridge, but not to the unique ‘belt’ tungsten atom. The  $\text{W}\cdots\text{Yb}$  distance in **1** is *ca.* 4.0 Å whereas the average  $\text{W}\cdots\text{La}$  distance in **2** is *ca.* 5.2 Å, which can be correlated with the size difference of  $\text{Yb}^{3+}$  *vs.*  $\text{La}^{3+}$ . The smaller ytterbium(III) ion is incorporated more deeply into the  $\text{As}_2\text{W}_{19}$  framework than the lanthanum(III) ion.

We also performed thermogravimetric analyses (TGA) on the salts **KNa-1** and **Na-2** to determine the degree of hydration and thermal stability. The thermograms showed the expected weight loss domain between 25 and 400 °C corresponding to dehydration. We calculated 25 and 16 water molecules per formula unit of **KNa-1** and **Na-2**, respectively.

## Conclusions

The mono-ytterbium(III) and di-lanthanum(III) 19-tungsto-2-arsenates(III)  $[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (**1**) and  $[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{8-}$  (**2**), have been structurally characterized in the solid state by IR spectroscopy, single-crystal X-ray diffraction and TGA. Polyanions **1** and **2** were synthesized in simple, one-pot reactions of  $\text{Yb}^{3+}$  and  $\text{La}^{3+}$  ions with the dilacunar and trilacunar polyanion precursors  $\text{As}_2\text{W}_{19}$  and  $\text{AsW}_9$ , respectively. The structure of **1** comprises an  $\text{As}_2\text{W}_{19}$  fragment with one incorporated  $\text{Yb}^{3+}$  ion, whereas **2** contains two  $\text{La}^{3+}$  ions in the vacant site of  $\text{As}_2\text{W}_{19}$ . Different synthetic strategies were needed to deliberately and selectively prepare mono- and di-lanthanide derivatives of  $\text{As}_2\text{W}_{19}$ . In this context it was discovered that countercations ( $\text{K}^+$  *vs.*  $\text{Na}^+$ ) play an important role. The terminal, labile water ligands in **1** and **2** are of interest for structural modifications and applications. We plan to explore aqua ligand substitution by other mono- and polydentate ligands, including chiral ones, and we envision potential applications in Lewis acid catalysis. Efforts to isolate lipophilic salts of **1** and **2** in order to study their catalytic properties in organic media are also underway.

## Experimental Section

### Instrumentation

Infrared spectra were recorded on a Nicolet Avatar spectrometer using KBr pellets. Thermogravimetric (TGA) analyses were performed using a TA Instruments SDT Q600 thermobalance from r. t. to 900 °C with a heating rate of 5°  $\text{min}^{-1}$  and a 100  $\text{mL min}^{-1}$  flow of nitrogen. The elemental analysis was performed by Analytische Laboratorien Lindlar, Germany.

### Synthesis

The precursors  $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$  and  $\text{Na}_9[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]$  used for the synthesis of the reported species were synthesized according to the procedures published by Kortz [8] and Pope [14], respectively. All other reagent-grade chemicals were used without further purification.

### $\text{K}_{9.5}\text{Na}_{0.5}[\text{Yb}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 25\text{H}_2\text{O}$ (**KNa-1**)

0.10 g (0.21 mmol) of  $\text{Yb}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$  was added to 20 mL  $\text{H}_2\text{O}$  with stirring followed by addition of 1.0 g (0.19 mmol) of  $\text{K}_{14}[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]$ , and then the pH was adjusted to 5.5–6.5 with 1 M  $\text{NaOH}_{(\text{aq})}$ . The solution was stirred at 60 °C for 20 min, allowed to cool to r. t. and then filtered. 0.5 mL of 1 M  $\text{KCl}_{(\text{aq})}$  was added to the filtrate, which was kept in an open vial for crystallization. After about three weeks colorless crystals were obtained, which were filtered off and air-dried (yield 1.1 g, 95 %). The IR spectrum for **KNa-1** showed metal-oxygen bands at 948(m), 891(m), 792(sh), 720(s), 615(s), 479(w), 471(w)  $\text{cm}^{-1}$ . –  $\text{H}_{60}\text{As}_2\text{K}_{10.5}\text{Na}_{0.5}\text{W}_{19}\text{Yb}$  (5850.6): calcd. K 7.02, Na 0.20, Yb 2.96, As 2.60, W 59.71; found K 6.99, Na 0.18, Yb 2.76, As 2.60, W 58.84.

### $\text{Na}_8[\text{La}_2(\text{H}_2\text{O})_6\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]\cdot 16\text{H}_2\text{O}$ (**Na-2**)

0.07 g (0.19 mmol) of  $\text{LaCl}_3\cdot 6\text{H}_2\text{O}$  was added to 20 mL of 1 M  $\text{NaCl}_{(\text{aq})}$  with stirring, followed by addition of 0.50 g (0.20 mmol) of  $\text{Na}_9[\text{B-}\alpha\text{-AsW}_9\text{O}_{33}]$ , and then the pH was adjusted to 5.0 with 1 M  $\text{HCl}$ . The solution was stirred at 50 °C for 30 min, allowed to cool to r. t. and then filtered. The filtrate was kept in an open vial for crystallization. After *ca.* three weeks colorless crystals were obtained, which were filtered off and air-dried (yield 0.41 g, 71 %). The IR spectrum for **Na-2** showed metal-oxygen bands at 953(m), 878(w), 859(s), 796(m), 728(s), 615(w), 500(w), 484(w), 458(w)  $\text{cm}^{-1}$ .

### X-Ray structure determination

The crystals were mounted in Hampton cryoloops using light oil for data collection at  $T = 173$  K. Indexing and data collection were performed using a Bruker X8 APEX II

Table 1. Crystal and Structure Refinement Data for **KNa-1** and **Na-2**.

	<b>KNa-1</b>	<b>Na-2</b>
Emp. formula	K <sub>9.5</sub> Na <sub>0.5</sub> [Yb(H <sub>2</sub> O) <sub>2</sub> -K(H <sub>2</sub> O) <sub>2</sub> As <sub>2</sub> W <sub>19</sub> O <sub>67</sub> -(H <sub>2</sub> O)]·25H <sub>2</sub> O	Na <sub>8</sub> [La <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> -As <sub>2</sub> W <sub>19</sub> O <sub>67</sub> -(H <sub>2</sub> O)]·16H <sub>2</sub> O
<i>M<sub>r</sub></i>	5850.6	5591.1
Crystal system	triclinic	triclinic
Space group (no.)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> , Å	12.4730(5)	14.929(2)
<i>b</i> , Å	17.4630(9)	17.769(3)
<i>c</i> , Å	21.1990(10)	20.754(4)
$\alpha$ , deg	72.568(3)	77.203(10)
$\beta$ , deg	85.442(2)	80.273(9)
$\gamma$ , deg	89.147(3)	72.670(9)
<i>V</i> , Å <sup>3</sup>	4391.3(4)	5093.6(15)
<i>Z</i>	2	2
<i>T</i> , K	173	173
$\lambda$ , Å	0.71073	0.71073
<i>D</i> , g cm <sup>-3</sup>	4.42	3.65
$\mu$ (MoK $\alpha$ ), mm <sup>-1</sup>	27.2	23.0
$\theta_{\max}$ , deg	27.48	26.43
Unique data / ref. param.	20018 / 641	20612 / 670
<i>R</i> [ $I \geq 2 \sigma(I)$ ] <sup>a</sup>	0.069	0.065
<i>R<sub>w</sub></i> (all data) <sup>b</sup>	0.197	0.236
GOF <sup>c</sup>	1.009	0.995
$\Delta\rho_{\text{fin}}$ (max / min), e Å <sup>-3</sup>	6.1 / -4.2	4.7 / -3.4

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>b</sup>  $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$  and A and B are constants adjusted by the program; <sup>c</sup>  $\text{GoF} = S = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ , where  $n_{\text{obs}}$  is the number of data and  $n_{\text{param}}$  the number of refined parameters.

CCD diffractometer with kappa geometry and MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data integration and routine processing were performed using the SAINT software suite [15]. Direct Methods (SHELXS-97 [16]) solutions successfully located

the W atoms, and successive Fourier syntheses (SHELXL-97 [17]) revealed the remaining atoms. Refinements were done with full-matrix least-squares methods against  $F^2$  using all data. Multi-scan absorption corrections were performed using SADABS [18]. Some water molecules of hydration were modeled with varying degrees of occupancy, a common procedure in POM chemistry. In the final refinements, all heavy atoms (W, La, Yb, K) and non-disordered Na atoms were refined anisotropically, while O atoms as well as disordered Na atoms were refined isotropically. No H atoms were included in the models. The crystallographic data are shown in Table 1. Figs. 1–3 were generated with the program DIAMOND, Version 3.2c (copyright Crystal Impact GbR) [19].

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-informationsdienste.de/en/DB/icsd/depotanforderung.html>) on quoting the deposition numbers CSD-421225 (**KNa-1**) and CSD-421226 (**Na-2**).

#### Supporting information

Figs. S1–S4 are provided as Supporting Information online only (<http://www.znaturforsch.com/ab/v65b/c65b.htm>).

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## Supporting Information

### Mono- and Di-Lanthanide Derivatives of 19-Tungsto-2-Arsenate(III)

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#### Figure captions

**Figure S1.** Ball-and-stick representation of the dilacunary polyanion precursor

$[\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{14-}$  (**As<sub>2</sub>W<sub>19</sub>**). The color code is as follows: W (black), As (yellow), H<sub>2</sub>O (pink), O (red).

**Figure S2.** Ball-and-stick representation of the monolacunary polyanion precursor

$[\text{As}_2\text{W}_{20}\text{O}_{68}(\text{H}_2\text{O})]^{10-}$  (**As<sub>2</sub>W<sub>20</sub>**). The color code is the same as in Fig. S1.

**Figure S3.** IR spectra of **KNa-1** (black line) and its four compositional analogues

$[\text{Ln}(\text{H}_2\text{O})_2\text{K}(\text{H}_2\text{O})_2\text{As}_2\text{W}_{19}\text{O}_{67}(\text{H}_2\text{O})]^{10-}$  (from top to bottom  $\text{Ln} = \text{La}, \text{Ce}, \text{Eu}, \text{Gd}$ ).

**Figure S4.** IR spectra of **Na-2** (top) and its cerium analogue (bottom).



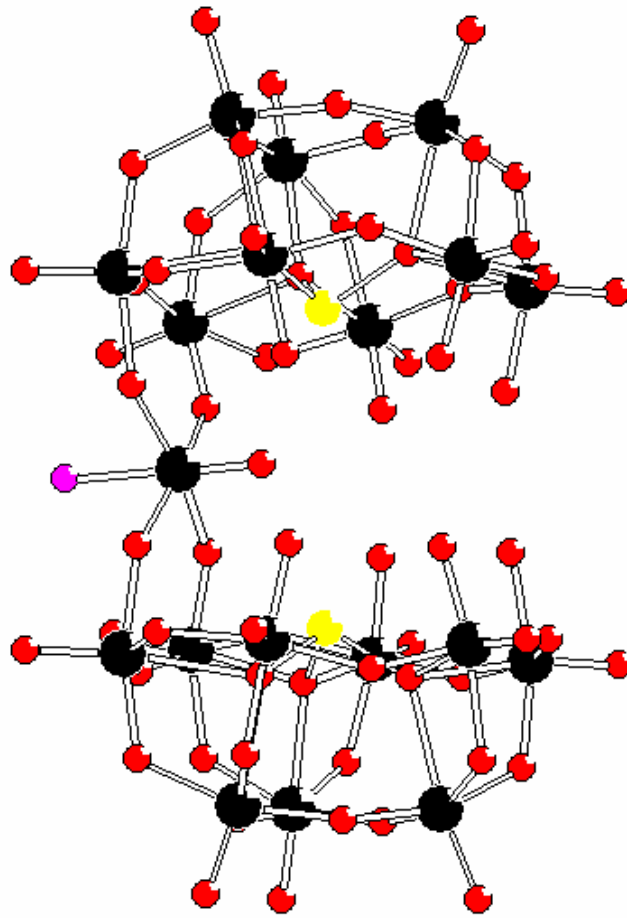


Figure S1.

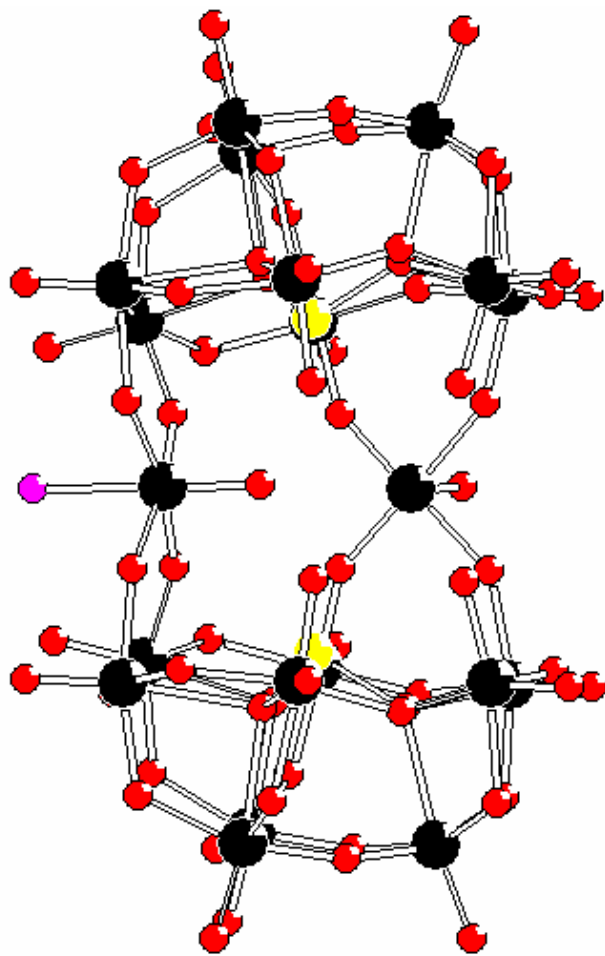


Figure S2.

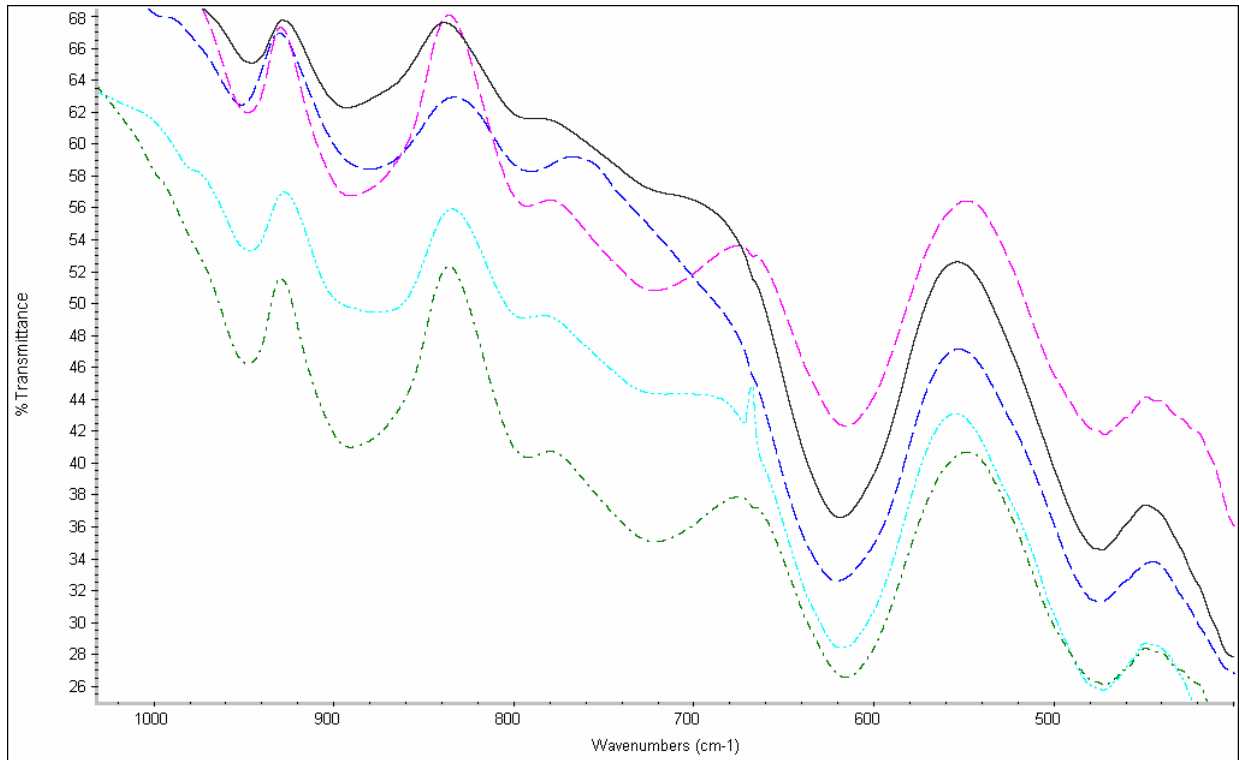


Figure S3.

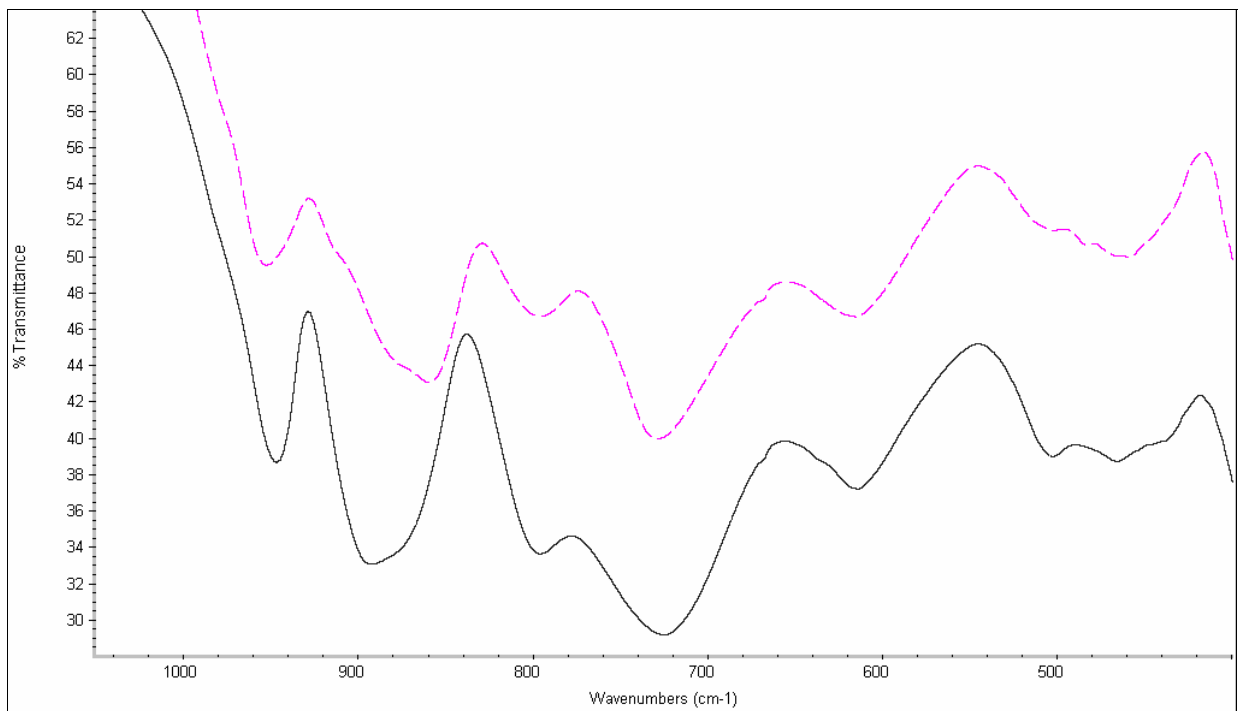


Figure S4.