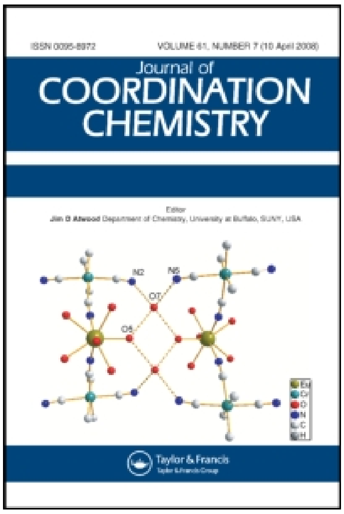

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# Tin derivatives of A-α-$AsW_9O^{9-}_{34}$ : Synthesis and characterization of $[Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$, $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ and $[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]^{12-}$

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# Tin derivatives of A-α-$AsW_9O_{34}^{9-}$: Synthesis and characterization of $[Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$, $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ and $[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]^{12-}$

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Complexes [ $Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ (**1**) and $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ (**2**) were synthesized by the reaction of tin(II) sulfate and phenyltintrichloride with $A - \alpha - AsW_9O_{34}^{9-}$ in aqueous solution. Complex $[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]^{12-}$ (**3**) is synthesized by the oxidation of **1** by $Br_2$. The complexes were characterized by elemental analysis, IR, $^{119}Sn$ NMR, UV–Vis spectroscopy, TGA, and single crystal analysis. The single crystal analysis was carried out on $K_{12}[Sn_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2] \cdot 12H_2O$ which crystallizes in the triclinic system, space group *P-1* with $a = 13.4503$ Å, $b = 20.393$ Å, $c = 28.898$ Å, $\alpha = 87.376(2)^\circ$, $\beta = 81.504(2)^\circ$, $\gamma = 86.335(3)^\circ$, $V = 7818.2$ Å$^3$, and $Z = 4$. Complex **1** consists of three $Sn^{II}$ cations sandwiched between two $AsW_9O_{34}^{9-}$ units. The coordination of each Sn is pseudo trigonal bipyramidal with the "equatorial" unshared electron pair directed toward the center of the anion. The 21° rotation of one $AsW_9O_{34}^{9-}$ group with respect to the other $AsW_9O_{34}^{9-}$ results in inequality of the equatorial (2.124 Å) and axial (2.486 Å) Sn–O bond lengths. The overall anion symmetry is $D_3$. The **2** and **3** complexes display one-line $^{119}Sn$ NMR corresponding to the three symmetry-equivalent Sn atoms.

*Keywords*: Polyoxometalates; Tin derivatives; Sandwich-type complexes; $^{119}Sn$ NMR; Single crystal structure analysis

## 1. Introduction

Polyoxometalates are discrete early transition metal–oxide cluster anions and comprise a class of inorganic complexes of unrivaled versatility and structural variation in both symmetry and size, with applications in many fields of science [1–5]. In each of these application areas it would be desirable to have chiral polyoxometalates, since much biological activity is expected to depend on the chiral configuration, and chiral-selectivity in catalysis is also a major goal [6]. The existence of a lone pair in the coordination environment of tin(II) induces nucleophilic and chirality properties in tin(II) polyoxometalates. In 1987, Chorghade and Pope [7] produced tin(II) monosubstituted polyoxotungstates which act as nucleophiles toward organic and

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organometallic compounds. In 1996, Xin and Pope [6] reported syntheses and structural characterization of three tin(II) complexes derived from the trivacant lacunary anions of $\alpha-PW_9O_{34}^{9-}$ and $\alpha$- and $\beta$-$SiW_9O_{34}^{10-}$. Due to stereochemical demand of $Sn^{II}$, these complexes are chiral and interact with chiral amino acids such as lysine, histidine and isoleucine. Organotin derivatives of polyoxometalates are prepared by direct reaction of $\{SnR\}^{3+}$ groups with lacunary polyoxometalates [8–12]. Due to similar size of Sn(IV) and W(VI), in the polytungstate structure, terminal $WO^{4+}$ groups are replaced by $\{SnR\}^{3+}$ [13, 14]. We report here the syntheses and structural characterization of Sn(II) and Sn(IV) complexes derived from the lacunary anions A-$\alpha$-$AsW_9O_{34}^{9-}$.

## 2. Experimental

### 2.1. *Chemical and apparatus*

All reagents were commercially available and used without purification. Phenyltintrichloride was purchased from Aldrich Company. $Na_8H$[A-$\alpha$-$AsW_9O_{34}$]$\cdot xH_2O$ was prepared according to the literature [15]. Infrared spectra were recorded in KBr plate on a Thermo Nicolet FT-IR model Nexus-670 and NMR were recorded on a BRX-500 AVANCE spectrometer. Resonance frequency for $^{119}Sn$ is 111.924 MHz and a solution of $SnCl_2$ in 12 M HCl (chemical shift −388.1 *vs.* tetramethyltin) was used as external standard, but the chemical shifts are reported with respect to $(CH_3)_4Sn$. The $H_2O$ and carbon contents of the complexes have been determined by Thermogravimetric Analysis (TGA) using PL-1500 TGA apparatus. Analysis of As, Sn, and W were carried out by ICP and K by flame photometric method using a Corning Flame photometer 410 apparatus. Electronic spectra were recorded on a Varian, CARY 1E UV–visible spectrophotometer. The strongly acidic (Dowex HCR-W2 $H^+$ form) resin packed into a column (20 cm length; 1 cm diameter) was used for ion exchange chromatography. For acidification, solutions of the complexes were eluted through the acidic form of the cationic resin column. The eluants were collected and studied by IR spectroscopy after solvent evaporation.

### 2.2. *Preparation of complexes*

**2.2.1. $K_{12}[Sn_3$(A-$\alpha$-$AsW_9O_{34})_2]\cdot 12H_2O$ (1).** Powdered $Sn^{II}SO_4$ (0.67 g, 3 mmol) was added to 60 mL of water with stirring. Nitrogen was bubbled through this slightly turbid solution to remove oxygen. Solid $Na_8H$[A-$\alpha$-$AsW_9O_{34}$]$\cdot xH_2O$ (5.7 g, 2 mmol) was quickly added to the above solution; after a few minutes, the tungstoarsenate dissolved and the solution turned orange. The solution was stirred for an additional 10 min under nitrogen and then traces of insoluble material were filtered out. Potassium chloride was added in small portions until no more precipitation was observed. The precipitate was collected on a medium porosity sintered glass frit and dried under suction for 10 min, then washed with saturated KCl solution and dried overnight under vacuum. Suitable single crystals were obtained by dissolving the product in distilled water and by slow evaporation in a refrigerator for 20 days. Yield 4 g (70%).

Anal. Calcd for $K_{12}[Sn_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]\cdot 30H_2O$ (%): As, 2.53; K, 7.94; Sn, 6.02; W, 55.97; $H_2O$, 9.13. Found: As, 2.38; K, 7.83; Sn, 6.10; W, 55.47; $H_2O$, 9.07.

The ammonium salt of **1** was prepared according to the above synthetic procedure, but KCl was replaced by $NH_4Cl$.

#### 2.2.2. $K_{11}H[(PhSnOH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]\cdot 29H_2O$ (2).

To a solution of 0.6 mL of $PhSnCl_3$ (3 mmol) in 60 mL of water at room temperature was added sodium acetate to adjust the pH to 1.5; at this stage the solution is slightly turbid. Powered $Na_8H[A\text{-}\alpha\text{-}AsW_9O_{34}]\cdot xH_2O$ (5.7 g, $x$ mmol) was added quickly to the solution with stirring. Within a few seconds, most of the tungstoarsenate dissolved and the solution was clarified. The final pH was 5.0. Traces of the insoluble material were filtered out after 10 min. Solid KCl was added to the filtrate in small portions until no more precipitation was observed and the precipitate was collected. Yield 2 g (35%). Anal. Calcd for $K_{11}H[(PhSnOH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]\cdot 29H_2O$ (%): As, 2.44; C, 3.52; K, 7.01; Sn, 5.80; W, 53.91; $H_2O$, 8.50. Found: As, 2.50; C, 3.47; K, 6.95; Sn, 5.55; W, 54.00; $H_2O$, 8.48.

#### 2.2.3. $K_{11}H\ [(HOSn^{IV}OH)_3(AsW_9O_{34})_2]\cdot 20H_2O$ (3).

Complex **3** was synthesized by the addition of 1.0 mL of bromine to 40 mL of a water solution containing 3 g of $K_{12}[Sn_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]\cdot 30H_2O$ (**1**). This solution was stirred for 5 min, then the excess $Br_2$ was removed by extracting with $CCl_4$. Addition of potassium chloride yielded a white precipitate which was filtered out and dried under vacuum. Yield 2 g (67%). Anal. Calcd for $K_{11}H[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]\cdot 20H_2O$ (%): As, 2.59; K, 7.42; Sn, 6.14; W, 57.09; $H_2O$, 6.21. Found: As, 2.46; K, 7.39; Sn, 6.00; W, 56.29; $H_2O$, 6.19.

### 2.3. *X-ray crystallographic structure determination*

Crystal data collection and refinement parameters for **1** are given in table 1. The data were collected at 100 K on a Bruker APEX 1000 CCD area detector single crystal diffractometer with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). Data collection, indexing, and initial cell refinements were all handled using APEX2 software [16]. The final cell parameters were determined from least-squares refinement on 41711 reflections. The multi-scan method was used to carry out absorption corrections. The structure was solved using direct methods and difference maps techniques (SHELXTL, V5.1) [17]. All metal atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [18]. Structure solution, refinement, and generation of publication materials were performed by using SHELXTL, V5.1 software. Selected bond lengths and angles of **1** are given in table 2.

## 3. Results and discussion

### 3.1. *Structure*

The X-ray structure of **1** reveals that three tin(II) ions are sandwiched between two A-type $\alpha\text{-}AsW_9O_{34}^{9-}$ moieties into an assembly of virtual $D_3$ symmetry (figure 1).

Table 1. Crystal data and structure refinement for **1**.

| | |
|---|---|
| Empirical formula | $H_{24}As_2K_{12}O_{80}Sn_3W_{18}$ |
| Formula weight | 5588.60 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 13.4503 |
| $b$ | 20.393 |
| $c$ | 28.898 |
| $\alpha$ | 87.376 |
| $\beta$ | 81.504 |
| $\gamma$ | 86.335 |
| Volume ($Å^3$) | 7818.2 |
| $Z$ | 4 |
| Crystal size ($mm^3$) | 0.17 × 0.13 × 0.05 |
| Density (Calcd) | 4.748 $Mg\,m^{-3}$ |
| Absorption coefficient ($mm^{-1}$) | 28.896 |
| $F(000)$ | 9760 |
| $2\theta_{max}$ | 58.32° |
| Reflections collected | 114,916 |
| Crystal description | plate |
| Independent reflections | 41,711 [$R(\text{int}) = 0.1067$] |
| Absorption correction | Multi-scan |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 41,711/78/2134 |
| Goodness-of-fit on $F^2$ | 0.975 |
| Final $R$ indices [with $I > 2\sigma(I)$] | $R_1 = 0.0769$, $wR_2 = 0.1311$ [for 41,711 reflns.] |
| $R$ indices (all data) | $R_1 = 0.1475$, $wR_2 = 0.1443$ |
| Largest different peak and hole ($e\,Å^{-3}$) | 5.323 and −3.017 |

Note: The weighting used is $w = 1/[\sigma^2(F_o^2) + (0.0780P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

| | Bond lengths (Å) | Average (Å) |
|---|---|---|
| W=O | 1.650–1.750 | 1.715 |
| W–O(W) | 1.747–2.100 | 1.92 |
| W–O(As) | 2.261–2.370 | 2.330 |
| As–O(W) | 1.610–1.700 | 1.668 |
| W–O(Sn) equatorial Sn-O | 1.789–1.851 | 1.830 |
| W–O(Sn) axial Sn-O | 1.746–1.803 | 1.776 |
| Sn–O(W) equatorial | 2.110–2.138 | 2.124 |
| Sn–O(W) axial | 2.400–2.570 | 2.486 |
| | Bond angles (°) | Average (°) |
| O–Sn–O equatorial | 94.2–98.0 | 96.5 |
| O–Sn–O axial | 142.0–146.0 | 144.1 |

In A-type sandwich, polyoxometalates $M_3(PW_9O_{34})_2$, $M_3(SiW_9O_{34})_2$, and $M_3(AsW_9O_{34})_2$ two $PW_9O_{34}^{9-}$, $SiW_9O_{34}^{10-}$, or $AsW_9O_{34}^{9-}$ units are related by a mirror plane, i.e., they are "eclipsed" [10–14, 19–26]. In compound **1**, one $AsW_9O_{34}^{9-}$ group is rotated by 21° around the $C_3$ axis from the eclipsed position (figure 2). The corresponding amounts for [ $Sn_3^{II}(\alpha\text{-}PW_9O_{34})_2]^{12-}$ and [ $Sn_3^{II}(\alpha\text{-}SiW_9O_{34})_2]^{14-}$ are

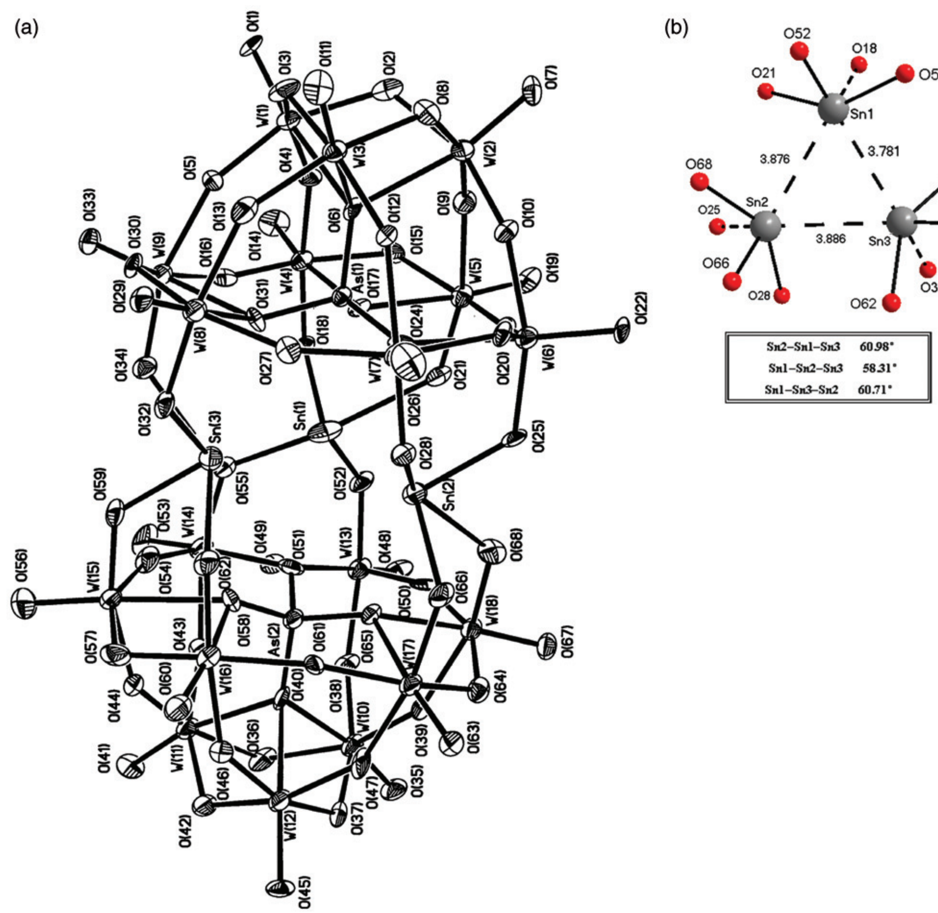

Figure 1. (a) Structure of [ $Sn_3^{II}(AsW_9O_{34})_2]^{12-}$ (**1**) showing 50% probability thermal ellipsoids. (b) The coordination sphere of the tin in **1**.

7 and 10°, respectively [6]. Each $Sn^{II}$ is coordinated by two terminal oxygens of an edge-shared pair of $WO_6$ octahedra to each $AsW_9O_{34}^{9-}$ unit. Because of the relative rotation of the $AsW_9O_{34}^{9-}$ groups, each $Sn^{II}$ has pseudo-trigonal-bipyramidal coordination with two long axial Sn–O bonds (2.486 Å), two short equatorial Sn–O bonds (2.124 Å), and the lone-pair of electrons occupying the third equatorial position pointing toward the anion's $C_3$ axis. The axial O–Sn–O bond angle is about 141.1° (142.0–146.0°) and the equatorial O–Sn–O angle is about 96.5° (94.2–98.0°) (table 2). Although, twisting from an eclipsed structure is much more than phosphorus base complex, the bond lengths and angles are consistent with reported values for other trigonal-bipyramidal tin(II) structures [27]. The large twist angle in **1** can be attributed to the size and electronic properties of $As^V$. Since the rotation of the two $AsW_9$ units can occur either to the left or to the right, **1** is chiral [2, 6]. The space groups of the X-ray structure of **1** is $P\bar{1}$, therefore each unit cell contains four complete sandwich structures (two pairs of enantiomers), related by the center of symmetry.

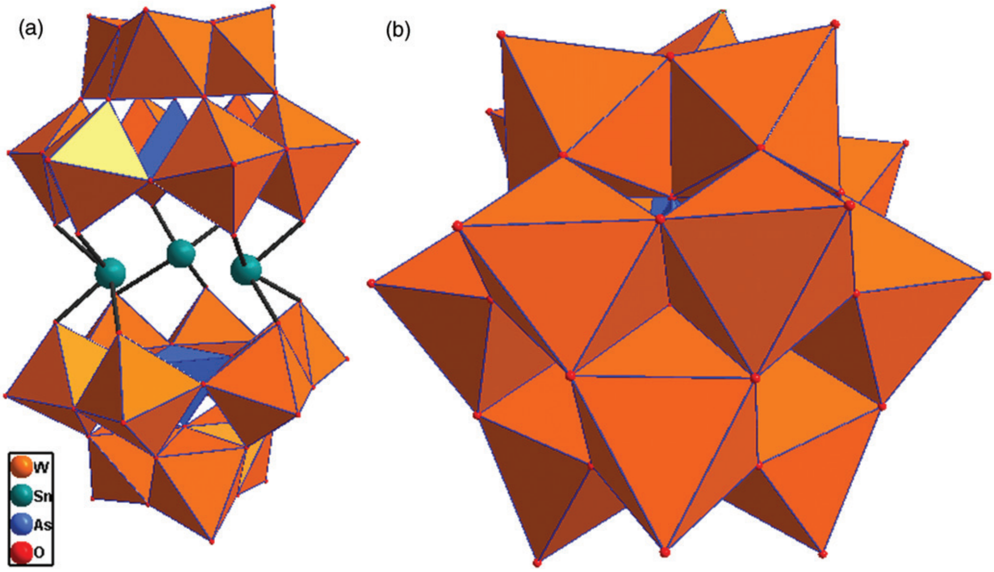

Figure 2. (a) Combination ball-and-stick/polyhedral representation of **1**. (b) View of **1** along the $C_3$ axis represents the twisting of one $AsW_9O_{34}{}^{9-}$ with respect to another.

### 3.2. *Syntheses and stabilities*

Solid $Na_8H[A\text{-}\alpha\text{-}AsW_9O_{34}]^{9-}$ at room temperature and under a constant stream of $N_2$ reacts with $SnSO_4$ to form **1**. Addition of $NaHCO_3$ was necessary to synthesize $[Sn_3(\alpha$ or $\beta\text{-}XW_9O_{34})_2]^{n-}$ ($X = P, Si$) compounds [6], whereas pH adjustment for synthesis of **1** was not necessary. Addition of $NaHCO_3$ did not affect the pH of the solution and the yield of product was decreased. Anion (**1**) is stable in the solid state and aqueous solution, but can be oxidized to its tin(IV) derivative (**3**) by bromine. Iodometric titration (addition of known and excess $Br_2$ to the solution containing **1** and then inverse titration of $Br_2$ by $S_2O_3^{2-}$ standard solution) confirms that all three tin(II) atoms in **1** are oxidized to tin(IV). The mole ratio of bromine and **1** was 2.90 : 1. In compound **3**, in addition to four bonds of $AsW_9O_{34}^{9-}$, each $Sn^{IV}$ has two terminal ligands. The common ligands are $H_2O$ but due to high charge on the $Sn^{IV}$ these ligands are $OH^-$ [12, 24, 26]. In compound **2**, one $OH^-$ of each $Sn^{IV}$ is replaced by a phenyl. When the complex solution is eluted through strongly acidic ion exchange the product is the Dawson anion, $\alpha\text{-}As_2W_{18}O_{62}^{6-}$, isolated as $H_6[As_2W_{18}O_{62}]$ [20] and confirmed by IR spectrum and cyclic voltammogram (CV). This confirms the presence of $A\text{-}\alpha\text{-}AsW_9O_{34}^{9-}$ Keggin moieties in the complexes [28]. Consistent with the elemental analysis, acid/base titrations show that **2** and **3** each have one acidic hydrogen. The TGA of **2** shows two mass loss regions below 500°C. The first region, 30–230°C with 8.48% weight loss, is assigned to lattice water. The second region, 410–470°C, with approximately 3.76% weight loss, is assigned to the loss of three molecules of benzene from Ph groups and protic hydrogen (S1 Supplementary information). There are other minor weight losses of 1.3% in the temperature range 470–520°C, which might be attributable to the loss of oxygen from the residual metal oxides.

### 3.3. *IR and NMR spectra*

As expected, IR spectra of **1–3** A-type sandwich complexes have very similar patterns (S2 Supplementary information). Comparing the IR spectra of the complexes and trivacant lacunary A-$AsW_9O_{34}^{9-}$, the following points can be drawn: (i) All characteristic vibrational frequencies increased compared with those of A-$\alpha$-$AsW_9O_{34}^{9-}$, attributed to the decrease of negative charge per A-$\alpha$-$AsW_9O_{34}^{9-}$ moiety in the anions. (ii) The asymmetry stretching vibration frequency of W–$O_c$–W in the anion is clearly split into three peaks in the complexes, attributed to the presence of tin(II) and tin(IV) cation (directly bound to the terminal oxygen of an edge-shared pair of $WO_6$). (iii) The vibrational frequency of As–O bonds overlaps those W–$O_b$–W bonds. In the range 950–700 $cm^{-1}$, characteristic bands were assigned to the asymmetric stretching vibrations of terminal W–$O_d$ (950 $cm^{-1}$), bridging W–$O_b$–W and As–O (900–850 $cm^{-1}$), and bridging W–Oc–W (800–700 $cm^{-1}$) [15, 29]. The $O_d$, $O_b$, and $O_c$ are representative of terminal, corner-shared, and edge-shared oxygen, respectively. The $^{119}Sn$ NMR spectra of **2** and **3** show one peak at −656.6 and −691.1 ppm, respectively, corresponding to the three symmetry-equivalent Sn atoms (S3 and S4 Supplementary information). The values for the chemical shifts are similar to the values observed for $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}PW_9O_{34})_2]^{12-}$, −609.6 ppm, and $[(HOSn^{IV}OH)_3(PW_9O_{34})_2]^{12-}$, −659.4 ppm [6]. Based on these results, the three complexes have A-type sandwich structures in which three $Sn^{II}$ (**1**), ($PhSn^{IV}OH$) (**2**), and ($HOSn^{IV}OH$) (**3**) groups are sandwiched between two A-$\alpha$-$AsW_9O_{34}^{9-}$ Keggin moieties.

### 3.4. *Electronic spectroscopy*

The UV spectra of **1–3** exhibit characteristic bands at ~200 and 260 nm, assigned to $O_d \rightarrow W$ and $O_b/O_c \rightarrow W$ charge transfer transitions, respectively [1] (S5 Supplementary information). These bands are shifted to higher wavelength compared to A-$AsW_9O_{34}^{9-}$ ($O_b/O_c \rightarrow W$ 247 nm). The UV spectra of **2** and **3** are more similar, indicating their similar electronic structures. Compound **1** exhibits a metal-to-ligand charge transfer band at 382 nm ($\varepsilon = 550\ cm^{-1}\ M^{-1}$) (S5 Supplementary information). This band is absent in the tin(IV) derivatives.

## 4. Conclusion

Three tin derivatives $[Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$, $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$, and $[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]^{12-}$ were synthesized and characterized by elemental analysis, IR, $^{119}Sn$ NMR, UV–Vis spectroscopy, TGA, and single crystal analysis. Compounds **1** and **2** were synthesized by the reaction of $AsW_9O_{34}^{9-}$ with $SnSO_4$ and $PhSnCl_3$, respectively, but **3** was synthesized by the oxidation of $[Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ with $Br_2$. The X-ray structure of $[Sn_3^{II}(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ reveals that three tin ions are sandwiched between two A-type $\alpha$-$AsW_9$ moieties. One $AsW_9O_{34}^{9-}$ group was rotated by 21° around the $C_3$ axis from the eclipsed position, and hence anion symmetry is reduced to $D_3$. The results also confirm that the complexes of $[(HOSn^{IV}OH)_3(AsW_9O_{34})_2]^{12-}$ and $[(PhSn^{IV}OH)_3(A\text{-}\alpha\text{-}AsW_9O_{34})_2]^{12-}$ have A-type sandwich structure in which three ($HOSn^{IV}OH$) and ($PhSn^{IV}OH$) groups, respectively, are sandwiched between two A-$\alpha$-$AsW_9O_{34}^{9-}$ Keggin moieties.

## Supplementary information

The PDF file of figures of TGA. FTIR, UV–Vis, XPRD pattern, and $^{119}$Sn NMR spectra with respect to the solution of $SnCl_2$ in HCl 12 M (6 pages). Crystallographic data (CIF file) for the structural analysis have been deposited with the Fachinformationszentium Karlsruhe (FIZ), CSD-number 419702 ($H_{24}As_2K_{12}O_{80}Sn_3W_{18}$). These data can be obtained free of charge via Email: crysdata@FIZ-Karsruhe.de; Tel.: +49 7247 808 310; Fax: +49 7247 808 136.

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## References

[1] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York (1983).
[2] M.T. Pope, A. Müller (Eds). *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers: Dordrecht, The Netherlands (1994).
[3] C.L. Hill (Ed.). *Chem. Rev.* (special edition on polyoxometalates), 98 (1998).
[4] M.T. Pope, A. Müller (Eds). *Polyoxometallate Chemistry: From Topology via Self-assembly to Applications*, Kluwer Academic Publishers, Dordrecht, The Netherlands (2001).
[5] T. Yamase, M.T. Pope (Eds). *Polyoxometalate Chemistry for Nano-Composite Design*, Kluwer Academic Publishers: Dordrecht, The Netherlands (2002).
[6] F. Xin, M.T. Pope. *J. Am. Chem. Soc.*, **118**, 7731 (1996).
[7] G.S. Chorghade, M.T. Pope. *J. Am. Chem. Soc.*, **109**, 5134 (1987).
[8] V.W. Day, W.G. Klemperer. *Science*, **228**, 4699, 533 (1985).
[9] R.G. Finke, B. Rapko, R.J. Saxton, P.J. Domaille. *J. Am. Chem. Soc.*, **108**, 2947 (1986).
[10] W.H. Knoth, P.J. Domaille. *Inorg. Chem.*, **22**, 818 (1983).
[11] W.H. Knoth, P.J. Domaille, D.C. Roe. *Inorg. Chem.*, **22**, 198 (1983).
[12] F. Xin, M.T. Pope. *Organometallics*, **13**, 4881 (1994).
[13] F. Zonnevijlle, M.T. Pope. *J. Am. Chem. Soc.*, **101**, 2731 (1979).
[14] W.H. Knoth. *J. Am. Chem. Soc.*, **101**, 2211 (1979).
[15] L.H. Bi, R.D. Hung, J. Peng, E.B. Wang, Y.H. Wang, C.W. Hu. *J. Chem. Soc., Dalton Trans.*, 121 (2001).
[16] Bruker. *APEX2 software package*, *Bruker AXS Inc., 5465*, East Cheryl Parkway, Madison, WI (2005).
[17] G.M. Sheldrick. *SHELXTL v. 5.10, Structure Determination Software Suite*, Bruker AXS, Madison, WI, USA (1998).
[18] A.J.C. Wilson (Ed.).*International Tables for X-ray Crystallography*, Vol. C, Tables 4.2.6.8 (pp. 219–222) and 6.1.1.4, pp. 500–502, Kluwer Academic, Dordrecht (1992).
[19] R.G. Finke, B. Rapko, T.J.R. Weakley. *Inorg. Chem.*, **28**, 1573 (1989).
[20] R. Contant, R. Thouvenot. *Inorg. Chim. Acta*, **212**, 41 (1993).
[21] R. Khoshnavazi, A. Salimi, A. Ghiasi Moaser. *Polyhedron*, **27**, 1303 (2008).
[22] R. Khoshnavazi, R. Sadeghi, L. Bahrami. *Polyhedron*, **27**, 1855 (2008).
[23] Y. Lin, T.J.R. Weakley, B. Rapko, R.G. Finke. *Inorg. Chem.*, **32**, 5095 (1993).
[24] W.H. Knoth, P.J. Domaille, R.D. Farlee. *Organometallics*, **4**, 62 (1985).
[25] T. Yamase, T. Ozeki, H. Sakamoto, S. Nishiya, A. Yamamoto. *Bull. Chem. Soc. Jpn*, **66**, 103 (1993).

[26] F. Xin, M.T. Pope, F.J. Long, U. Russo. *Inorg. Chem.*, **35**, 1207 (1996).
[27] M. Gielen, O. Recktenwald, Z.M.O. Rzaev, M. Veith. In *Topics in Current Chemistry 104. Organotin Compounds*, F.L. Boschke (Ed.), pp. 22–86, Springer-Verlag, Berlin, Heidelberg, New York (1982).
[28] G. Hervé, A. Tézé. *Inorg. Chem.*, **16**, 2115 (1977).
[29] (a) R. Contant, R. Thouvenot. *Can. J. Chem.*, **69**, 1498 (1991); (b) M. Rocchiccioli-Deltcheff, M. Fournier, R. Franck. *Inorg. Chem.*, **22**, 207 (1983).