Dimethyltin-Functionalized Cyclic Selenotungstates based on {Se₂W₁₂} Units

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Section 1 Synthesis, Crystal Data, and Structures of 1 and 2

1.1 Synthesis

General Considerations. All commercially obtained reagent, including Na₂WO₄·2H₂O, K₂SeO₃, acetic acid, (CH₃)₂SnCl₂, NaCl, and HCl were purchased from Aldrich and used without further purification. Deionized water was used throughout the study. The reaction mixtures were heated and agitated in the round bottomed flasks with reflux condensing tubes on a CL-1A-type agitator purchased from GongYi Company in China. A pHS-25B pH meter was used for pH measurements.

Synthesis of 1: Na₂WO₄·2H₂O (1.84 g, 5.76 mmol) and K₂SeO₃ (0.20 g, 0.96 mmol) were dissolved in 40 mL water. The pH value of the solution was adjusted to 4.5-5.5 by acetic acid solution. After the solution was stirred for around 30 min, solid (CH₃)₂SnCl₂ (0.15 g, 0.68 mmol) and NaCl (0.50 g, 8.56 mmol) were successively added. The final pH was kept at 4.5-5.5 by 2 M HCl. This solution was stirred for another 60 min, then filtered and left to evaporate slowly. Colorless block-shaped crystals were obtained after four weeks, which were then collected by filtration and air-dried. Yield: 0.23 g, (13.2 %, based on W). IR (in cm⁻¹): 3436 (w), 1625 (s), 944 849 (m), (w), 809 (w), 767 (w). Elemental analysis, calc. for C₂H₃₈K₄Na₁₄O₁₁₀Se₆SnW₂₄: K 2.14, Na 4.41, Sn 1.63, W 60.4 %; Found K 1.92, Na 4.29, Sn 1.75, W 59.4 %.

Synthesis of 2: The synthesis process of 2 is similar to 1, but the pH of the solution was adjusted to 3.5 by the addition of aqueous 2 M HCl before stirring for another 60 min. Slow evaporation of the solution results in the colorless needle-shaped crystals 2 forming in two months. Yield: 0.12 g, (6.20 %, based on W). IR (in cm⁻¹): 3433 (w), 1622 (s), 956 (w), 894 (w), 843 (w), 784 (w). Elemental analysis, calc. for $C_2H_{92}Cl_2K_8Na_{18}O_{188}Se_6SnW_{40}$: K 2.64, Na 3.49, Sn 1.00, W 62.0 %; Found K 2.51, Na 3.63, Sn 1.21, W 61.1 %.

1.2 Synthesis Discussion

The precise control of the one-pot reaction conditions of combining $(CH_3)_2Sn^{2+}$ groups with the SeO₃²⁻ anion templates at proper pH was employed for the assembly of **1** and **2**. The SeO₃²⁻ anion templates have a lone pair of electrons and only form three bonds through oxygen atoms in trigonal configurations owing to the inducing effect of the lone pair of electrons.¹ Moreover, the electrophile $(CH_3)_2Sn^{2+}$ groups possess the stability of the Sn–C bond in aqueous media and also the fact that Sn^{IV} can substitute for addenda metals in POM skeletons². Significantly, diverse $(CH_3)_2Sn^{2+}$ moieties realize that dimethyltin–containing POMs develop abundant architectures². Therefore, according to previous literatures, a synergistic effect between $(CH_3)_2Sn^{2+}$ groups and the anion template effect of SeO₃²⁻ may guide the construction of unprecedented dimethyltin-functionalized selenotungstates.

First, we chose Na₂WO₄ and K₂SeO₃ as the W– & Se–sources, which could provide K⁺ and Na⁺ counterions simultaneously. The acidification of them (W/Se molar ratio 6:1) by acetic acid was necessary.¹ Acetic acid has already been proven to be a suitable reagent for acidifying Se–based POTs clusters^{1b,1i}, and the molar ratio also plays an important role that is in accordance with the final {Se₂W₁₂} building blocks in **1** and **2**.

Subsequently, dimethyltin species ((CH₃)₂Sn²⁺) and NaCl were introduced to the acid solution. Among several factors (e.g., reaction solvents etc.) during the synthesis, the features of the countercation constitute a key factor in the formation of several POMs, and therefore, choosing desirable counteraction may allow for a rational design of tailored POM assemblies². **1** and **2** were also realized through the use of extra Na⁺ not only because the sodium cations are usually beneficial to the isolation of POMs anion, but also sodium cations could be ligated by the cluster surface (bonding for the formation of the macrocycle (**1**); binding into the vacancy in the macrocycle (**2**)) for further stabilizing the whole clusters during the assemblies.

Finally, different pH value leads to the formation of **1** and **2** thus the impact of the pH should be considered during the one-pot synthesis. From the previously reported

studies, the pH value is a known crucial parameter in POTs chemistry: a series of available building units toward the formation of the final structures are driven by it. Thus, we analyze the formation of **1** and **2** with the pH value as the single variable: the reaction solution changes to be turbid particularly when the pH > 6.0 and pH < 3.0, and even no crystal products could be isolated, this is in line with the previous works that the dimethyltin-functionalized selenotungstates are obtained at the pH range from 3.5 to 5.0. Available Wells–Dawson–type {Se₂W₁₂} building blocks linked by *trans*-(CH₃)₂Sn²⁺ groups at pH 4.5-5.5 for **1** and stabilized by *trans*-(CH₃)₂Sn²⁺ groups at pH 4.5-5.5 for **1** and stabilized by *trans*-(CH₃)₂Sn²⁺ groups at pH values leads to the assemblies of dimethyltin-functionalized selenotungstates from dimeric to trimeric wheels.

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1.3 Crystal Data

	1	2
Empirical formula	$C_2H_{38}K_4Na_{14}O_{110}Se_6SnW_{24}$	$C_2H_{92}Cl_2K_8Na_{18}O_{188}Se_6SnW_{40}$
M	7305.43	11868.72
$\lambda/{ m \AA}$	0.71073	0.71073
T/K	296(2)	296(2)
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/n	Pmmn
$a/{ m \AA}$	18.766(5)	21.458(4)
b/Å	19.585(5)	21.507(4)
$c/{ m \AA}$	21.347(5)	23.317(5)
$lpha/^{\circ}$	90	90
$eta/^{\circ}$	114.046(4)	90
$\gamma/^{\circ}$	90	90
$V/Å^3$	7165(3)	10761(4)
Ζ	2	2
$D_c/\mathrm{Mg}~\mathrm{m}^{-3}$	3.386	3.663
μ/mm^{-1}	21.121	22.727
<i>F</i> (000)	6380	10412
θ Range/°	1.579–25.452	1.894–27.270
Measured reflections	41485	73713
Independent reflections	13032	12657
<i>R_{int}</i> after SQUEEZE	0.1043	0.0743
Goodness-of-fit on F^2	1.040	1.033
$R_1(I > 2\sigma(I))^a$	0.0725	0.0471
wR_2 (all data) ^b	0.2168	0.1311
${}^{a}R_{1} = \sum F_{0} $	$- F_{\rm c} /\sum F_{\rm o} $. ^b $wR_2 = \{\sum [w(F_{\rm o}^2 -$	$F_{\rm c}^{2})^{2}]/\sum[w(F_{\rm o}^{2})^{2}]\}^{1/2}.$

Table S1. Crystal Data and Structure Refinements for 1 and 2.

Single-crystal X-ray diffraction: Single-crystal X-ray diffraction data for **1** and **2** were recorded on a Bruker Apex CCD II area-detector diffractometer with graphitemonochromated Mo_{*K*α} radiation ($\lambda = 0.71073$ Å) at 296(2) K. Absorption corrections were applied using multiscan technique and performed by using the SADABS program¹. The structures of **1** and **2** were solved by direct methods and refined on *F*² by full-matrix leastsquares methods by using the SHELXTL package.² The numbers of lattice water molecules and counter cations for **1** and **2** was estimated by the results of elemental analyses, TG curves, and calculations of electron count in the voids with SQUEEZE³. Detailed interpretation for **1** and **2** was shown in CIF files. CCDC 1584541 (**1**) and 1584542 (**2**) contain the supplementary crystallographic data for this paper.

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1.4 Structures of 1 and 2



Fig. S1. The structures of the neutral $\{Mn(H_2O)_2(SeO_3)\}\$ complex units (a) in $[Mn_4Se_6W_{24}O_{94}Cl(H_2O)_6]^{13-}$ and the electronegative $\{Na(H_2O)_2(SeO_3)\}\$ complex units (b) in 1.



Fig. S2. The packing arrangement of 1.



Fig. S3. The structure of the $\{Se_6W_{38}\}$ wheel in 2.



Fig. S4. The coordination modes of four crystallography equivalent Na ions inside $\{Se_6W_{38}\}$ wheel in 2.



Fig. S5. The coordination modes of Cl ions in 2.



Fig. S6. The chain connection modes outside $\{Se_6W_{38}\}$ wheel in 2.



Fig. S7. The packing arrangement of 2.

	1
Sn(1)-C(1)	2.18(6) Å
Sn(1)-O(22) ^{#2}	2.289(18) Å
Sn(1)-O(32)	2.295(18) Å
Sn(1)-O(36)	2.331(19) Å
Sn(1)-O(42) ^{#2}	2.337(18) Å
Sn(1)-C(2)	2.45(6) Å
C(2)-Sn(1)-C(1)	<i>169(2)</i> °
^{#2} -x+1,-y+1,-z-1	
	2
Sn(1)-O(43)	2.20(2) Å
Sn(1)-O(43) ^{#2}	2.20(2) Å
Sn(1)-O(36)	2.202(10) Å
Sn(1)-O(36) ^{#2}	2.202(10) Å
Sn(1)-C(1)	2.09(5) Å
Sn(1)-C(2)	2.17(5) Å
C(1)-Sn(1)-C(2)	<i>173.1(17</i>)°
#2 -x+1/2,y,z	

1.5 Selected Bond Lengths and Angles for the Tin Atoms in 1 and 2.

 Table S2. Selected bond lengths [Å] and angles [°] for the tin atoms in 1 and 2.

Section 2 Experimental Section

2.1 Materials and Physical Measurements

Characterization: Elemental analysis of K, Na, Sn, and W were performed with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were recorded on an Alpha Centauri FTIR spectrophotometer on pressed KBr pellets in the range 400~4000 cm⁻¹. Water contents were determined by TG analyses on a PerkinElmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C min⁻¹. Electrospray ionization mass spectrometry was carried out on a Bruker Micro TOF-QII instrument (1 mg/mL).

Electrochemical experiments: Electrochemical measurements were carried out on a CHI 660 electrochemical workstation at room temperature. Thrice-distilled water was used throughout the experiments. All solutions were deaerated by bubbling pure argon prior to the experiments and the electrochemical cell was kept under an argon atmosphere throughout the experiment. A conventional three-electrode system was used with a 1.5 mm glassy carbon working electrode, an Ag/AgCl used as electrode, and a platinum wire counterelectrode. The glassy carbon working electrodes were polished with alumina on polishing pads, rinsed with distilled water, and sonicated in H₂O before each experiment. The scan rate was 50~500 mV s⁻¹. All potentials were measured and reported versus Ag/AgCl. Solutions **1** and **2** in 0.5 M H₂SO₄/Na₂SO₄ (pH = 2.50 or 3.50) were used. A pHS-25B pH meter was used for pH measurements.

2.2 Cyclic Voltammetry

Fig. S8a shows the CV pattern of 1 (5 × 10⁻⁴ M) at a scan rate of 100 mV s⁻¹ in the region from –1.000 to +0.600 V of potential values *vs.* Ag/AgCl. The cathodic part features two separated quasi-reversible redox couples of waves at $E_{1/2} = -0.602$ V (II/II') and $E_{1/2} = -0.883$ V (III/III') [$E_{1/2} = (E_{pa} + E_{pc})/2$] (*vs* Ag/AgCl), and one distinct reduction wave appeared at –0.342 V (I/I'), they all belong to W-centered redox processes. It is worth raising that two redox couples of waves both demonstrate a quasi-reversible one-electron process (Table S5) in terms of the ΔE_p values according to a reversible electron transfer with its theoretical value of ΔE_p remains 59 mV. Different scan rates (Fig. S8b, from 100 to 500 mV s⁻¹) experiments reveal that diffusion-controlled is dominative during the redox process in view of the peak currents were proportional to the square root of the scan rate.



Fig. S8. CVs of **1** in aqueous 0.5 M H_2SO_4/Na_2SO_4 electrolyte solutions (pH = 2.50). POM concentrations = 5 × 10⁻⁴ M. The scan rate was 100 mV s⁻¹ (Top). CVs of **1** at different scan rates (Bottom): from inside to out: 100, 200, 300, 400 and 500 mV s⁻¹. Inset: representation of the current as a function of the square root of the scan rate. The working electrode was glassy carbon, and the reference electrode was Ag/AgCl.

	$E_{\rm pa}\left({ m V} ight)$	$E_{\rm pc}$ (V)	$E_{1/2}$ (V)	$\Delta E_{\rm p}~({\rm mV})$
	-	-0.342	-	-
1	-0.557	-0.647	-0.602	90
	-0.850	-0.916	-0.883	66
	-0.304	-0.409	-0.357	105
2	-0.657	-0.744	-0.701	87
	-	-0.979	-	-
	POM co	ncentrations = 5	× 10 ⁻⁴ M.	

Table S3. Redox Peak Potentials for all the Tungsten Waves Determined by CyclicVoltammetry in 0.5 M H_2SO_4/Na_2SO_4 solution for 1 (pH = 2.50) and 2 (pH = 3.50).



Fig. S9. UV-Vis spectra of 1 (a) and 2 (b) kept at room temperature for 24 hours.

2.4 ESI-MS



Table S4. Assignment of peaks in negative mode Mass spectrum of 1.

Observed m/z	Calculated m/z	Charge	Molecular mass	Polyanion
1708.4	1708.3	-4	6833.0	$\{K_4Na_5H_5[Sn(CH_3)_2W_{24}Se_6O_{94}](H_2O)\}^{4-2}$
2280.6	2280.6	-3	6841.8	$\{K_2Na_8H_5[Sn(CH_3)_2W_{24}Se_6O_{94}](H_2O)_2\}^{3-2}$



Observed m/z	Calculated m/z	Charge	Molecular mass	Polyanion
2179.6	2179.9	-5	10899.7	$\{K_7Na_{12}[Sn(CH_3)_2Se_6W_{40}O_{145}(H_2O)_2](H_2O)\}^{5-1}$
2728.8	2729.2	-4	10916.6	$\{K_6Na_{12}H_2[Sn(CH_3)_2Se_6W_{40}O_{145}(H_2O)_2](H_2O)_4\}^{4-1}$

 Table S5. Assignment of peaks in negative mode Mass spectrum of 2.



Fig. S12. The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV)of1(a)and2(b).

2.5 Photocatalytic Hydrogen Evolution

Photocatalytic Measurements: Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N_2 several times to ensure complete air removal and then irradiated by using a 500 W mercury lamp. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 mm) using N_2 as carrier gas.

The proposed mechanism of photocatalytic H₂ production of **1** and **2** are shown in Fig. S13. They both have appropriate band gaps (3.23 eV and 2.92 eV), which are suitable for water splitting (*Adv. Mater.* **2012**, *24*, 2014–2018). Firstly, **1** yields its excited-state (**1***) after a certain wavelengths of UV light irradiation; Secondly, **1*** obtains electrons from CH₃OH (electron donor, oxidized to HCHO), and donates the excited electrons; Thirdly, the H⁺ in water obtains the electron to be reduced to H atom to form H₂. The proposed mechanism of photocatalytic H₂ production of **2** is similar as **1**. (*J. Am. Chem. Soc.* **2012**, *134*, 19716–19721)



Fig. S13. The proposed mechanism of photocatalytic H₂ production.



Fig. S14. Dependence of H_2 production on irradiation time with the use of 1 (blue), 2(green), {Se₆W₃₉} (red), and blank (black) as photocatalysts (75 mg). Theexperiments were performed under 500 W mercury lamp irradiation in methanol (30 mL)in120 mLofwater(4/1,v/v).

Section 3 Supplementary Physical Characterizations



Fig. S15. IR spectrum of **1**: The characteristic peaks at 944, 849, 804, and 767 cm⁻¹ are ascribed to vibrations of v(Se-O), $v(\text{W=O}_d)$, $v(\text{W-O}_b)$, and $v(\text{W-O}_c)$, respectively. The broad peak at 3436 cm⁻¹ and the strong peak at 1625 cm⁻¹ are attributed to the lattice water molecules and aqua ligands.



Fig. S16. IR spectrum of **2**: The characteristic peaks at 956, 894, 843, and 784 cm⁻¹ are ascribed to vibrations of v(Se–O), v(W=O_d), v(W–O_b), and v(W–O_c), respectively. The broad peak at 3433 cm⁻¹ and the strong peak at 1622 cm⁻¹ are attributed to the lattice water molecules and aqua ligands.



Fig. S17. The XRPD patterns for simulated (a) and as-synthesized (b) of 1.



Fig. S18. The XRPD patterns for simulated (a) and as-synthesized (b) of 2.



Fig. S19. TG/DTA curve of 1.



Fig. S20. TG/DTA curve of 2.