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Title

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Journal

Inorganic chemistry, 59(5)

ISSN

0020-1669

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Publication Date

2020-03-01

DOI

10.1021/acs.inorgchem.9b03261

Peer reviewed

Butyltin Keggin ion with a rare 4-coordinate Ca center

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ABSTRACT: Alkyltin clusters are exploited in nanolithography for fabrication of microelectronics. The alkyltin Keggin family is unique amongst Keggin clusters across the periodic table – they appear to favor the lower symmetry β and γ isomers, rather than the highly symmetrical α and ϵ isomers. Therefore, the alkyltin Keggin family may provide important fundamental information about formation and isomerization of Keggin clusters. We have synthesized and structurally characterized a new butyltin Keggin cluster with a tetrahedral Ca^{2+} center, fully formulated $[(\text{BuSn})_{12}(\text{CaO}_4)(\text{OCH}_3)_{12}(\text{O})_4(\text{OH})_8]^{2+}$ (β - CaSn_{12}). The synthesis is a simple one-step process. Extensive solution characterization including electrospray ionization mass spectrometry, small angle x-ray scattering, and multinuclear (^1H , ^{13}C , and ^{119}Sn) NMR shows β - CaSn_{12} is essentially phase-pure and stable. This differs from the prior-reported Na-centered analogues that always form a mixture of β and γ isomers, with facile interconversion. Therefore, this study has clarified prior confusion over complex spectroscopic and crystallographic characterization of the Na-centered analogues. Density functional theory calculations showed a stability order of γ - $\text{CaSn}_{12} < \gamma$ - $\text{NaSn}_{12} < \beta$ - $\text{CaSn}_{12} < \beta$ - NaSn_{12} ; the β -analogue is always more stable than γ , consistent with experiment. Notable outcomes of this study includes a rare tetrahedral Ca-coordination, a Na-free alkyltin cluster (important for microelectronics manufacturing), and a better understanding of Keggin families built of different metal cations.

INTRODUCTION

The Keggin ion is an important structure in inorganic chemistry, which consists of a central tetrahedral $\{\text{MO}_4\}$ unit surrounded by 12 metal-oxo octahedra arranged into four trimers. This structure is formed from metals across the periodic table including W, Mo, Nb, Fe, Al, Cr, Sb, and Sn.^{1–9} There are five rotational isomers of the Keggin ion¹⁰, denoted by the Greek letters α , β , γ , δ , and ϵ , which differ in their symmetry and connectivity between the trimer units. The α isomer has all four trimers connected by corner sharing and has T_d symmetry. Rotating one trimer by 60° reduces the symmetry to C_{3v} in the β isomer, which also has all trimers connected by corners. A second trimer rotation of 60° yields the γ isomer (C_{2v} symmetry), with two trimers corner-linked and two edge-linked. Successive rotation of the third and fourth trimers by 60° results in the δ and ϵ isomers, respectively. The δ isomer has C_{3v} symmetry with three trimers connected by edges and one linked by corners. All four trimers of the ϵ isomer are edge-linked with T_d symmetry.

Recently, we added three new sodium-centered butyltin members to the Sn Keggin family – a β isomer (β - NaSn_{12}), a γ isomer (γ - NaSn_{12}), and a γ isomer capped with an additional Sn (γ - NaSn_{13}).¹¹ Other members of this family include our previously isolated Sn-capped butyltin β isomer (β - NaSn_{13})¹² and the first reported alkyltin Keggin ion – an isopropyltin γ isomer.⁷ More recently, Zhu et al. stabilized the γ isomer of Na-centered butyltin Keggin ion with borate-capping,

including a bicapped NaSn_{14} structure.¹³ The alkyl-Sn Keggin family exhibits differentiating structural features. While the majority of metal cations favor the higher symmetry α (Nb, W, Mo, Fe) and ϵ (Al, Sb) structures, as well as the δ isomer (Cr, Al), we and others have only been able to experimentally isolate alkyltin clusters as the rarer β and γ isomers.^{7,11–13} Isomerization between α and β tungstate Keggin ions has been investigated experimentally¹⁴ and computationally.¹⁵ Both conclude that 1) the α isomer is generally favored, and 2) $\alpha \rightarrow \beta$ isomerization is favored with increasing XO_4^{n-} charge on the central tetrahedron (X =central tetrahedral cation). Meanwhile, the growing alkyltin Keggin cluster family is the only one thus far that favors the lowest symmetry γ isomer. In addition, our previously isolated butyltin Keggin clusters showed evidence of facile interconversion between isomers in solution,¹¹ complicating characterization by tin, carbon, and proton NMR.

In our previous study, we hypothesized that the charge of the 6-coordinate addenda metal may play a role in determining which Keggin isomer would be more favorable.¹¹ We also investigated the influence of capping for enhancing isomerization.¹⁶ However, it is possible that the size and charge of the central atom of the Keggin ion may also be an important factor in promoting isomerization. Zhang *et al.* showed computationally that the central cavity for organoantimonate Keggin ions increases in size when going from the α to β isomer.¹⁷ In addition, the central cavity

increases in size as the charge of the central tetrahedron {MO₄} becomes more positive.¹⁸ It is noteworthy that the Na central cation for our butyltin Keggin clusters has a significantly larger ionic radius and lower charge (0.99 Å, 1+) than the central cations of the most common Keggin structures; e.g. Si (0.26 Å, 4+) and P (0.17 Å, 5+).¹⁹ In order to examine the effect of the central cation on the properties of the Keggin ion, we have crystallized a new butyltin β -Keggin ion with Ca at the center (formulated [(BuSn)₁₂(CaO₄)(OCH₃)₁₂(O)₄(OH)₈]²⁺, **β -CaSn₁₂** henceforth) via a one-step synthesis, and studied its solution behavior. Calcium is similar in size to sodium (ionic radius of 1.00 Å)¹⁹ which allows it to fit in the central cavity of the alkyltin Keggin ion. To our knowledge, β -CaSn₁₂ is the only Keggin ion which has been isolated having a Ca²⁺ ion in the tetrahedral center. The typical coordination number for Ca is 6-8 and it is rare to find examples of Ca with a coordination number as low as 4.²⁰ In fact, there is only one molecular compound in the literature containing the *T_d* {CaO₄} unit, and it required the use of very bulky alkoxide ligands to stabilize the Ca²⁺-centers.²¹ Here we provide complete solution characterization of β -CaSn₁₂ by electrospray ionization – mass spectrometry (ESI-MS), multinuclear (¹H, ¹³C, and ¹¹⁹Sn) NMR, and small angle x-ray scattering (SAXS).

Additionally, we report here room-temperature aging studies in the solution and solid-state for the Ca-centered butyltin Keggin cluster, and heating studies monitored by variable-temperature NMR. Understanding the long-term stability and solution behavior of these organotin materials is important for applications such as high resolution nanolithography.²² These aging and heating studies provided insight to the prior suspected isomerization (or lack thereof) occurring in solution for these alkyl-Sn Keggin clusters. Over time, the methoxy ligands of the clusters (derived by synthesis in methanol) undergo hydrolysis and are replaced with hydroxyl ligands. This was monitored in solution by ¹H NMR and in the solid state by FT-IR. We have also employed density functional theory (DFT) computational studies to compare the relative stabilities of the Ca- and Na- centered clusters.

RESULTS AND DISCUSSION

Synthesis

The Na-centered Keggin clusters used for aging studies were synthesized by combining stock solutions of 0.1M BuSnCl₃ in MeOH and 0.1M NaOH in MeOH at room temperature in a 1:4 ratio, as reported prior.¹¹ β -CaSn₁₂ was synthesized by combining a 0.1M solution of BuSnCl₃ in MeOH with 2 molar equivalents of solid Ca(OH)₂ in a Parr reactor which was heated to 100°C for 24 hours. Though the stoichiometry is the same between the two reactions (1 Sn: 4 OH), the reactant concentrations are much higher in the β -CaSn₁₂ synthesis as Ca(OH)₂ is added as a solid rather than a solution. In addition, the solvothermal conditions are necessary to dissolve the Ca(OH)₂ and force the calcium into the low-coordination environment at the center of the cluster. The reaction does not proceed at room temperature.

Single crystal structure of β -CaSn₁₂

The single crystal x-ray structure of β -CaSn₁₂, fully formulated [(BuSn)₁₂(CaO₄)(OCH₃)₁₂(O)₄(OH)₈]²⁺·2[OH⁻], is shown in **Figure 1** and **S1**. This compound has the same structure and ligand arrangement as our previously reported β -NaSn₁₂, but has Ca at the center instead of Na.¹¹ Elemental analysis by SEM-EDX was used to confirm the presence of Ca and minimal Na (from Ca) in the crystals of β -CaSn₁₂ (**Table S2**). However, the Na is present as NaCl (minimal Cl also observed), and no Na-centered clusters are observed by ESI-MS (discussed later). Each Sn has a terminal butyl ligand and the bridging μ_2 -oxygens between trimers of the Keggin are either oxo or hydroxyl ligands. The bridging μ_3 -oxygens found within each of the four trimers are methoxy ligands which come from the methanol reaction solution. The hydrolysis of these methoxy ligands will be discussed in detail later.

Figure 1: Single crystal x-ray structure of the β -CaSn₁₂ [(BuSn)₁₂(CaO₄)(OCH₃)₁₂(O)₄(OH)₈]²⁺ molecule. Gray and blue polyhedra represent Sn; Ca is shown in teal, O in red, and C in black. Butyl chains have been eliminated with only the Sn-bound carbon shown, for ease of viewing.

β -CaSn₁₂ has a charge of 2+ with two hydroxide counterions. The charge was determined based on ESI-MS data and bond valence sum (BVS) calculations (**Table S1**). Only one OH⁻ was identified in the crystal lattice, but based on SQUEEZE²³ analysis there is room in the crystal packing for an additional hydroxide counterion. As is commonly observed for metal-oxo clusters, the BVS values for bridging oxo ligands are ambiguous, with values ranging from 1.16 to 1.41 (average=1.32), due to disordered protons which cannot be located crystallographically. In order to be consistent with an overall charge of 2+, oxos with a BVS of 1.37 or higher were assigned as O²⁻ and the remaining oxos assigned as OH⁻. In addition, the average BVS of 1.32 is in agreement with the 2/3rd OH⁻ and 1/3rd O²⁻ to correspond with the 2+ charge observed by ESI MS (discussed below).

Table 1: Average bond lengths for O atoms of central tetrahedron

	Avg. Na/Ca-O bond length (Å)	Avg. Sn-central O bond length (Å)
β -NaSn ₁₂	2.32 (1)	2.08 (1)
β -CaSn ₁₂	2.28 (2)	2.11 (1)

Changing the central cation does have a significant effect on the bond lengths of the four central oxos. For β -NaSn₁₂, the average Na-O bond distance is 2.32 Å, and for β -CaSn₁₂ the

average Ca-O bond length is 2.28 Å. The higher charge of Ca²⁺ leads to slightly shorter bonds to the surrounding oxos. Consequently, the Sn-O bonds of the central oxos of β -CaSn₁₂ are lengthened. The average Sn-O bond length for the central oxos of β -CaSn₁₂ is 2.11 Å and for β -NaSn₁₂ it is 2.08 Å. These values are summarized in

Table 1. The BVS of the central Ca is 1.7, while those for the tetrahedral O²⁻ bound to Ca are high (>2.0). Although the BVS for Ca²⁺ is a bit low, this may be due to the fact that the parameters²⁴ used in the BVS calculations are empirically derived from metal oxide lattices, not molecules. As mentioned previously, the coordination environment of the central Ca is unique and there are no other structures in the literature which contain tetrahedral calcium within an inorganic framework.

Electrospray Ionization – Mass Spectrometry (ESI-MS)

ESI-MS of β -CaSn₁₂ crystals dissolved in methanol (**Figure 2a**) shows one main ion species at 1259.85 m/z, corresponding to a molecule with a 2+ charge (based on peak-to-peak separations in the peak envelope). Minor peaks are observed at 1282.83 m/z (2+ charged species) and 2557.63 m/z (1+ charged species). The peak envelopes corresponding to species with a 2+ charge were simulated as a combination of 8 overlapping peaks, shown in **Figure 2b** and listed in **Table 2**. The largest contributor to the overlapping peaks has the formula [(C₄H₉Sn)₁₂(CaO₄)(O)₁₁(OH)₄(OCH₃)₂]²⁺ and comprises 59% of the total peak simulation. Though the intact ion with all ligands present was not detected, all of the assigned peaks have formulae which correspond to species containing 12 butyltin groups, a calcium center, and varying numbers of oxo, hydroxyl, and methoxy ligands. All of the formulae in **Table 2** have fewer than the 40 ligands required for the complete cluster, but this is likely due to the fragmentation process. Unfortunately, the peak at 2557.63 m/z was too low in intensity to accurately assign. No peaks were detected in the negative ionization mode; and

Table 2: ESI-MS peak assignments for β -CaSn₁₂ in methanol

Formula	Observed m/z	Calculated m/z	% Contribution
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₁ (OH) ₆] ²⁺	1245.83	1245.79	6.7%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₀ (OH) ₈] ²⁺	1254.85	1254.79	13.4%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₁ (OH) ₄ (OCH ₃) ₂] ²⁺	1259.85	1259.80	59.0%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₁ (OH) ₃ (OCH ₃) ₃] ²⁺	1266.85	1266.81	7.4%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₈ (OH) ₁₁ (OCH ₃)] ²⁺	1279.84	1279.81	4.0%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₀ (OH) ₄ (OCH ₃) ₄] ²⁺	1282.83	1282.83	3.4%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₈ (OH) ₁₀ (OCH ₃) ₂] ²⁺	1286.83	1286.82	2.7%
[(C ₄ H ₉ Sn) ₁₂ (CaO ₄)(O) ₁₀ (OH) ₃ (OCH ₃) ₅] ²⁺	1289.81	1289.83	3.4%

Nuclear Magnetic Resonance (NMR) Spectroscopy

One of the most important features of CaSn₁₂ is that it predominantly forms the β isomer. The Na-centered clusters always crystallize as a mixture of β and γ isomers, and solution state NMR characterization of these compounds suggests that there may be interconversion between isomers as well.¹¹ Having mainly one isomer present in solution

importantly, no Na-centered clusters were observed. Full peak assignments can be found in **Figures S2-S9**.

Figure 2: a) Full ESI MS spectrum of β -CaSn₁₂ in methanol. Positive ionization mode, 100V fragmentation. b) Experimental (red) and simulated (black) peak envelopes for main ion species. The simulation is a combination of 8 overlapping peaks (see Table 2).

significantly reduces the difficulty of solution characterization. The ¹H and ¹¹⁹Sn NMR spectra for β -CaSn₁₂ in C₆D₆ are shown in **Figure 3a** and **b**, respectively and β , γ -NaSn₁₂ is also included to highlight the difference in the complexity of NMR spectra when multiple isomers are present vs one. Expanded spectral views and ¹³C data can be found in **Figures S10-S12**. The ¹H NMR spectrum for β -

CaSn₁₂ shows much sharper and better-defined peak splitting than does β,γ -NaSn₁₂, but the ¹¹⁹Sn NMR is most telling. Due to the mixture of isomers present in β,γ -NaSn₁₂ as well as suspected isomerization in solution, there are many different Sn environments present, resulting in several Sn peaks in the 6-coordinate region. The ¹¹⁹Sn spectrum of β -CaSn₁₂ has just three sharp peaks in the 6-coordinate region in a 2:1:1 ratio, consistent with the different Sn environments of the β isomer.

The three Sn sites are shown in **Figure 3b**, and each peak has been assigned to its respective site based on integration and ¹¹⁹Sn-¹¹⁷Sn coupling constants. Coupling constants were also used to assign peaks in the ¹⁸³W NMR of the β -AlW₁₂O₄₀ Keggin ion.¹⁴ Site 1 (blue) contains the three Sn of the 60° rotated trimer at the top of the cluster that defines the molecular C₃ axis, site 2 (green) contains the 6 Sn in the middle “belt”, and site 3 (gray) contains the 3 Sn of the trimer opposite to those of site 1. The peak at -469.5ppm with an integrated value of 2 (normalized to peak 1) corresponds to the 6 Sn in the middle belt of the cluster (site 2). The peak at -471.0ppm has a coupling constant of 147 Hz and corresponds to site 3, while the peak at -474.6ppm has a coupling constant of 175 Hz and corresponds to site 1. The larger coupling constant indicates a larger distance between neighboring Sn sites. The Sn-Sn distance between sites 1 and 2 in the crystal structure of β -CaSn₁₂ is 3.8Å and the Sn-Sn distance between sites 2 and 3 is 3.4Å. These values are also summarized in .

Table 3. The asymmetry of the satellites on peaks 2 and 3 of the ¹¹⁹Sn spectrum of β -CaSn₁₂ will be discussed in further detail later. On the other hand, we are unable to assign specific Sn sites for β,γ -NaSn₁₂ due to the multitude of peaks, including satellite peaks from ¹¹⁹Sn-¹¹⁷Sn coupling.

Figure 3: a) ¹H NMR spectrum of β -CaSn₁₂ (red) and β,γ -NaSn₁₂ (blue) in C₆D₆. b) ¹¹⁹Sn NMR spectrum of β -CaSn₁₂ (red) and β,γ -NaSn₁₂ (blue) in C₆D₆. Inset: depiction of three Sn sites of β -CaSn₁₂.

Table 3: Coupling constants, Sn-Sn distances, and peak assignments for ¹¹⁹Sn peaks of β -CaSn₁₂

δ (ppm)	Distance between satellites (Hz)	Sn-Sn distance to middle layer (Å)	Assignment
-469.5	165	-	Site 2
-471.0	147	3.4	Site 3
-474.6	175	3.8	Site 1

Small Angle X-ray Scattering (SAXS)

Shown in **Figure 4**, SAXS of β -CaSn₁₂ in THF (red) shows a pure and monodisperse solution which is consistent with the simulated scattering curve (black) based on the single crystal structure. The deviation between the simulated and experimental curves around $q=0.4\text{\AA}^{-1}$ is due to a structure factor, or ordering of clusters in solution. This behavior has also been observed with our previously isolated β -NaSn₁₃ Keggin cluster.¹² The experimental data were fit with a single-population spherical model which also accounted for the structure factor. The radius determined from this model was 4.92Å, which is consistent with the cluster radius determined from the single crystal structure (5.0Å). This model and its fit to the experimental data can be found in **Figure S13**.

Figure 4: Small angle x-ray scattering data for β -CaSn₁₂ in THF (red) and simulated scattering curve (black).

Aging Studies

Butyl-Sn Keggin clusters are being considered for potential applications in solution-deposited thin films, so it is important to understand the aging behavior of these clusters both in solution and in the solid-state in air. We observed previously that the methoxy ligands of β,γ -NaSn₁₂ exhibited hydrolysis in solution.¹¹ Here we describe the hydrolysis process for β -CaSn₁₂ as a function of solvent composition (C₆D₆, CDCl₃, 9:1 C₆D₆:CD₃OD, and 9:1 CDCl₃:CD₃OD) via ¹H NMR. FT-IR tracks the hydrolysis process in air via the intensity of the methoxy C-O stretch absorbance at ~1050 cm⁻¹.

NMR

^1H NMR is a commonly used technique to monitor and quantify the extent of reactions in the solution state^{25,26} and is ideal for measuring the hydrolysis of methoxy ligands to hydroxyl ligands. The peaks corresponding to bound methoxy and free methanol protons are clearly visible in the ^1H NMR spectrum of $\beta\text{-CaSn}_{12}$. Since methanol is a product of the hydrolysis of methoxy to hydroxyl ligands, the relative integrated areas of the two peaks over time provides information about the reaction rate, and how it is affected by different solvents. **Figure 5** shows the ^1H NMR spectra of $\beta\text{-CaSn}_{12}$ in C_6D_6 and 9:1 $\text{C}_6\text{D}_6\text{:CD}_3\text{OD}$ for fresh solutions (0 days) through day 4 of aging. The analogous spectra recorded in CDCl_3 and 9:1 $\text{CDCl}_3\text{:CD}_3\text{OD}$ are shown in **Figure S14**. The broad peak at approximately 3.6 ppm corresponds to the bound $-\text{OCH}_3$ protons and the sharp peak at 3.0–3.2 ppm corresponds to methanol CH_3 - protons. These peaks were integrated a total of three times each, and their average relative areas compared for each spectrum (**Figure 6**).

Figure 5: ^1H NMR spectra following aging of $\beta\text{-CaSn}_{12}$ in C_6D_6 and 9:1 $\text{C}_6\text{D}_6\text{:MeOD}$.

$\beta\text{-CaSn}_{12}$ exhibits hydrolysis in all of the solvents studied and shows that hydrolysis is the slowest in C_6D_6 and fastest in CDCl_3 . Adding excess deuterated methanol increases the rate of hydrolysis in benzene but does not increase the rate in chloroform. The difference in the rate of hydrolysis in different solvents is most likely due to the amount of residual water present in solution. Due to the proposed application of these clusters, we need to investigate their behavior in non-rigorously controlled environments, so the deuterated solvents

were not dried prior to the aging study. They likely contain trace amounts of water, promoting the hydrolysis process.

Figure 6: Average % methoxy ligands hydrolyzed vs number of days for $\beta\text{-CaSn}_{12}$ in various solvents.

Water is about twice as miscible with chloroform as it is with benzene, consistent with the faster hydrolysis in CDCl_3 .²⁷ Adding MeOD to C_6D_6 likely increases the amount of water in solution, thus increasing the rate of reaction. In the case of $\text{CDCl}_3/\text{MeOD}$, it is possible that the MeOD does not add a significant amount of water compared to what was already present in the CDCl_3 . Unfortunately it is difficult to quantify the amount of residual water in solution, especially in CDCl_3 , as the ^1H NMR peak corresponding to H_2O (~1.56 ppm) overlaps with the butyl ligand protons on the cluster. There is a very small peak at approximately 0.3 ppm in the ^1H spectra of $\beta\text{-CaSn}_{12}$ in C_6D_6 which corresponds to water in solution (**Figure S10**).

Integrating the peaks of interest is straightforward in benzene where the peaks are well-separated, but is more complex in chloroform where the bound and free $-\text{OCH}_3$ peaks overlap. As a further complication, the spectra with excess MeOD exhibit a second free methanol resonance slightly upfield of the main methanol peak, potentially due to the formation of CH_3OD after exchange of CD_3OD with $-\text{OCH}_3$ ligands on the cluster. This is not a major concern for the spectra in $\text{C}_6\text{D}_6/\text{MeOD}$, but does add another layer of complexity to the integration of overlapping peaks in spectra taken in $\text{CDCl}_3/\text{MeOD}$. Peaks also tend to broaden and overlap as aging progresses in all solvents. Despite these difficulties, the deviation between separate integration measurements is estimated to be between 1 and 8%. Perhaps with the exception of CDCl_3 , the curves appear to plateau; suggesting an equilibrium is reached between OH^- and $\text{OCH}_3^-/\text{OCD}_3^-$ ligation. The CDCl_3 perhaps continues to absorb water with aging, driving the equilibrium forward towards more hydrolysis. However, since equilibrium appears to be reached, even in excess methanol, this suggests neither ligand is favored strongly, and both are labile. However, as noted prior, the methoxy-ligand seems necessary for crystallization; as this is the only form we and others have observed the various butyltin Keggin ions.^{11–13}

FT-IR

FT-IR spectra for $\beta\text{-CaSn}_{12}$ were taken at various time intervals after isolating crystals of the compound from the

mother liquor. Spectra were collected at 1 day, 7 days, 14 days, 21 days and 28 days. **Figure 7** shows an overlay of all the spectra focused on the C-O stretch of OCH₃ ligand (normalized to Sn-O absorbance at 530 cm⁻¹). Full spectra are reported in **Figure S15**. The intensity of the C-O peak for β-CaSn₁₂ fluctuates between measurements and does not follow a clear trend. This is consistent with the NMR studies; methanol that is retained in the solid following hydrolysis or from the mother liquor can undergo exchange between OH⁻ and OCH₃⁻ ligation.

Figure 7: FT-IR spectra showing the change in absorbance of the H₃C-O stretch (methoxy ligand) of solid β-CaSn₁₂ over time

In-Situ Heating Monitored by NMR

A solution of β-CaSn₁₂ in C₆D₆ was heated in situ and monitored by ¹H and ¹¹⁹Sn NMR. Beginning at 30°C, ¹H and ¹¹⁹Sn spectra were collected (approximately 1 hour data collection time) and then the temperature was increased by 10°C. ¹H and ¹¹⁹Sn spectra were collected at each temperature. Once the temperature reached 60°C, the temperature was held constant for 3 hours. Three ¹¹⁹Sn spectra and four ¹H spectra were collected during this time. **Figure 8** shows the resulting spectra from this heating experiment.

The ¹H spectra (**Figure 8a**) do not show much change other than the sharpening of peaks upon heating. Interestingly, the ¹¹⁹Sn spectra show the appearance of new peaks (denoted by arrows in **Figure 8b**) upon heating, indicating the formation of additional isomers in solution. The peak at -470.7 ppm in the ¹¹⁹Sn spectrum was originally thought to be a satellite of the neighboring, more intense peak. However, this “satellite” increases in intensity with heating, meaning that it is due to the presence of an additional isomer. The presence of this peak at room temperature indicates that the β-CaSn₁₂ product is not purely β isomer, but additional isomers are only present in trace amounts. As there are four peaks that increase in intensity due to heating, we hypothesize that these are due to formation of the γ isomer at higher temperatures. Upon cooling this heated solution to room temperature, the more complex mixture of isomers is preserved (**Figure S16**). Initially this result was puzzling, since the synthesis performed at elevated temperature yields predominantly the β-form. However, there are multiple differences between the synthesis and the above-described NMR experiment including 1) solvent, 2) excess Ca(OH)₂ in the synthesis, 3) reaction byproducts in the synthesis (i.e. Cl⁻ from the butyltin

trichloride). Despite this isomerization at elevated temperature, the mixture remains predominantly the β-form, illustrating the much slower isomerization of the Ca-centered cluster compared to the Na-centered Keggin.

Figure 8. (a) ¹H NMR spectra of β-CaSn₁₂ in C₆D₆ heated in situ. (b) ¹¹⁹Sn NMR spectra of β-CaSn₁₂ in C₆D₆ heated in situ. Gray arrows indicate growth of the γ isomer with heating.

DFT Computational Analysis

The β and γ isomers of the Na- and Ca-centered Sn Keggin ions were simulated and their hydrolysis Gibbs free energy and HOMO-LUMO gaps were determined using a thermodynamic cycle in which the hydrolysis energy is the sum of the corresponding gas-phase Gibbs free energy (ΔG_{gas}) and the Gibbs free energies of solvation (ΔG_{solv}; **Equation 1**). The gas-phase term contains a correctional value that takes into account the enthalpy, entropy, and temperature of the system when a frequency analysis is performed. Parameterized continuum solvation models were used to determine the solvation energies, modeling the system in water with a dielectric constant of ~78.36. The thermodynamic cycle for the calcium centered Keggin isomers is shown in **Scheme 1**, where “n” is the coefficient of that species.

Equation 1: Hydrolysis Gibbs free energy (ΔG_{aq}) obtained from the thermodynamic cycle in Scheme 1.

$$\Delta G_{\text{aq}} = \Delta G_{\text{gas}} + \sum_{i=1}^{N_{\text{products}}} n_i \Delta G_i^{\text{solv}} - \sum_{j=1}^{N_{\text{reactants}}} n_j \Delta G_j^{\text{solv}}$$

Scheme 1: Thermodynamic cycle for all isomers of CaSn₁₂.

These results are summarized in **Table 4** and are in order from most to least stable. We consider clusters to be more stable if they have a relatively low hydrolysis Gibbs free energy and a large HOMO-LUMO gap. To reduce the number of degrees of freedom, methyl was used as the terminal ligand on each tin rather than butyl. Both isomers of NaSn₁₂ were assigned the same formula and charge: [(MeSn)₁₂(NaO₄)(OCH₃)₁₂(O)₄(OH)₈]¹⁺. Similarly, both isomers of CaSn₁₂ were assigned a formula and charge of [(MeSn)₁₂(CaO₄)(OCH₃)₁₂(O)₄(OH)₈]²⁺. These formulae are consistent with the single crystal structures and species detected by ESI-MS.

Table 4: Calculated hydrolysis Gibbs free energy and HOMO-LUMO gap for β and γ isomers of NaSn₁₂ and CaSn₁₂

Cluster	Hydrolysis Gibbs free energy (kcal/mol)	ΔG (kcal/mol) Normalized to β -NaSn ₁₂ ¹⁺	HOMO-LUMO gap (eV)
β -NaSn ₁₂ ¹⁺	-367.0	0.0	6.21
β -CaSn ₁₂ ²⁺	-354.7	12.3	6.23
α -NaSn ₁₂ ¹⁺	-350.5	16.5	6.18
δ -NaSn ₁₂ ¹⁺	-347.1	19.9	6.00
γ -NaSn ₁₂ ¹⁺	-344.8	22.2	5.67
α -CaSn ₁₂ ²⁺	-342.8	24.2	6.20
γ -CaSn ₁₂ ²⁺	-338.6	28.4	5.73
δ -CaSn ₁₂ ²⁺	-338.3	28.7	6.01
ϵ -NaSn ₁₂ ¹⁺	-306.9	60.1	5.70
ϵ -CaSn ₁₂ ²⁺	-297.2	69.8	5.81

Based on DFT calculations, the Na-centered clusters are more stable than their corresponding Ca-centered analogues, likely due to the fact that Na more easily adopts tetrahedral coordination than Ca. Additionally, the extra positive charge of the Ca-analogue generally decreases the stability. Importantly, the stability of the β -Keggin ion is highest for both the Na and Ca centered clusters, in agreement with experiment. In addition to having lower symmetry, the γ isomer has two edge-sharing trimers with a shorter metal-metal distance between the two Sn centers which decreases the overall stability of the cluster. The difference in hydrolysis Gibbs free energy between the β and γ isomers for NaSn₁₂ is 22.2 kcal/mol and for CaSn₁₂ it is 16.1 kcal/mol, suggesting

that CaSn₁₂ may isomerize more readily than NaSn₁₂. Yet, we observe the opposite to be true in our experimental studies. We hypothesize that this difference may be attributed to kinetic factors related to the interconversion between isomers. A hydrolysis Gibbs free energy difference of more than 10 meV/atom is required to confidently state that one isomer is more stable than another.^{17,28–31} Since these clusters each have 145 atoms, an energy difference of more than 34 kcal/mol signals definitive preference of one isomer over another. The computational stability ordering of the isomers differs slightly from what we observe experimentally, but the differences in hydrolysis Gibbs free energies are below the 34 kcal/mol threshold. Therefore, we can only state with certainty that the β isomers for both systems are more stable than the ϵ analogues. Returning to the isomerization studies of the classic POM Keggin ions^{14,15}, isomerization is more favorable with increasing XO₄ⁿ⁻ charge. Consistent with this, we observe greater isomerization behavior in the {NaO₄}⁷⁻-centered cluster than the {CaO₄}⁶⁻-centered cluster. Another was to view this is, the weaker, longer bond of Na-O compared to Ca-O permits easier lability of the molecule.

CONCLUSION

In summary, we have encapsulated Ca²⁺ into the central tetrahedral cavity of a butyltin β Keggin ion. This is the only member of the growing family of alkyltin Keggin clusters with a central cation other than Na⁺. In addition, β -CaSn₁₂ provides the first example of 4-coordinate Ca²⁺ in an inorganic structure. While alkyltin clusters have been investigated for use in nanolithography, the central Na⁺ in the Keggin clusters has arisen concern about contamination of expensive lithography fabrication facilities. This study shows that other metal substitutions are possible, that may be later exploited in functionality of tin oxide materials. Solution characterization by ESI-MS, SAXS, and multinuclear NMR shows that β -CaSn₁₂ is free of impurities and contains only trace amounts of other isomers. In comparison to the analogous NaSn₁₂ Keggin clusters that always present as mixtures of γ and β isomers, CaSn₁₂ is robustly dominated by the β isomer, and it must be heated in solution to drive conversion to a different isomer, presumably γ . This is consistent with the tungstate Keggin ions, in that the lower-charged central cation promotes $\alpha \rightarrow \beta$ isomerization more readily. In the current study, the Na-centered cluster seems to establish an equilibrium between isomers at room temperature, while the Ca-centered cluster does not isomerize until heat is applied. DFT computations also show a difference in cluster stability with a change in the

central cation. Overall, the size and charge of the central cation has a significant effect on the stability and isomerization of the Sn Keggin cluster as a whole. These experimental and computational studies provide additional fundamental insight into the factors which influence Keggin formation and isomer stability.

MATERIALS AND METHODS

All reagents and solvents were purchased from commercial suppliers and used without further purification.

Synthesis of β -CaSn₁₂: In a Parr reactor, 15 mL of a 0.1 M stock solution of n-BuSnCl₃ (95%, 1.5 mmol) in methanol was combined with 0.22 g solid Ca(OH)₂ (3.0 mmol, 4 eq. OH per Sn) which did not fully dissolve, yielding a cloudy suspension. The suspension was heated solvothermally at 100 °C for 24 hours. Colorless needle crystals were harvested from the walls of the reaction vessel. Yield approx. 200 mg (45%).

Computational Methods. The computational results were obtained using Gaussian 09.³² The geometry of each cluster was first optimized in the gas phase using the B3LYP functional.³³ The basis set 6-31G(d) was used for elements Na, Ca, C, H, and O, while the basis set LANL2DZ was used for Sn.^{34,35} A frequency calculation was done to guarantee that there were no imaginary vibration modes confirming that the system was in a stable/metastable state. The effective core potential LANL2DZ was used for Sn. The geometry was further optimized in water using the continuum solvation model SMD and a solvent accessible surface (SAS).³⁰ The electronic energy was refined using the B3LYP single point with the basis set 6-311+G(d,p) for elements Na, Ca, C, H, and O, and basis set LANL2DZ for Sn.³⁶ The solvation energy was found using B3LYP/6-31G(d) single point with SMD in water and a solvent excluding surface (with minimum radius for added spheres as 0.20 and overlap index as 0.89).

Characterization Techniques

Small Angle X-ray Scattering (SAXS): X-ray scattering data were collected on an Anton Paar SAXSess instrument using Cu-K α radiation (1.54 Å) and line collimation. The instrument was equipped with a 2-D image plate for data collection in the $q = 0.018$ – 2.5 Å^{-1} range. The lower q resolution is limited by the beam attenuator. Approximately 20 mmolar solutions were measured in 1.5 mm glass capillaries (Hampton Research). Scattering data of neat solvent was collected for background subtraction. Scattering was measured for 30 min for every experiment. We used SAXSQUANT software for data collection and treatment (normalization, primary beam removal, background subtraction, desmearing, and smoothing to remove the extra noise created by the desmearing routine). All analyses and curve-fitting to determine R_g , size, shape and size distribution were carried out utilizing IRENA macros with IgorPro 6.3 (Wavemetrics) software.³⁷ To simulate scattering data from the crystal structure, we used SolX software.³⁸

Nuclear Magnetic Resonance Spectroscopy (NMR): ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were collected on a Bruker

Ascend spectrometer (500 MHz for ¹H, 125 MHz for ¹³C, 186 MHz for ¹¹⁹Sn) with a 5 mm BBO probe at 30.0 °C. Chemical shifts are reported in parts per million (δ) and ¹H and ¹³C spectra are referenced to C₆D₆ and CDCl₃ solvent signals.³⁹ ¹¹⁹Sn NMR is referenced to SnCl₄ in C₆D₆.

Electrospray Ionization Mass Spectrometry (ESI-MS): ESI-MS was carried out using an Agilent 6230 ESI-MS system comprised of a Time-of-Flight (TOF) mass spectrometer coupled to an electrospray ionizer. The crystallized Keggin product, β -CaSn₁₂, ([Sn]=1.2 mM), was dissolved in methanol and infused into the ESI-MS system at a flow rate of 0.4 mL min⁻¹ using a syringe pump. The solutions were nebulized with the aid of heated N₂ (325 °C) flowing at 8 L min⁻¹ and a pressure of 35 psig (241 kPa). The voltages of the capillary, skimmer, and RT octopole were set at 3500, 65, and 750 V respectively, while the voltage of the fragmenter was set at 100 V. The data were collected in the positive ionization mode. No ion species were detected in the negative ionization mode.

Single-Crystal X-ray Diffraction Data Collection Analysis: X-ray diffraction intensities for β -CaSn₁₂ (CCDC-1949774) were collected at 173 K on a Bruker Apex2 CCD diffractometer using CuK α radiation, 1.54178 Å. Space group were determined based on systematic absences. Absorption corrections were applied by SADABS.⁴⁰ Structure was solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. All H atoms were refined in calculated positions in a rigid group model. H atoms in bridge –OH groups and in counter-ions were not found and not taken into consideration. The molecule is located in the crystal structure on a mirror plane. The found structure has a low resolution. The terminal t-Bu groups in the structure are significantly disordered and X-ray diffraction at high angles from crystals of this compound is very weak. Even using a strong Incoatec I μ S Cu source reflections with $I/\sigma(I)$ more than 1 were only up to $2\theta_{\text{max}} = 100^\circ$. Only these reflections were used in the final refinement. Anyway it provides appropriate number of reflections per refined parameters, 5031/509. The terminal t-Bu groups are highly disordered and its thermal ellipsoids are significantly elongated. One of these groups was refined as disordered over two positions related by a mirror plane. All terminal groups were refined with restrictions on its geometry; the standard interatomic distances were used as targets for corresponding contacts. Some short H...H contacts in the structure don't correspond to real contacts between the H atoms, but related to the fact that these groups were refined as a solid unit and its disorder was not resolved. One of two -OH counter-ions in the structure is disordered over two positions related by an inversion center. We could not find a position of the second –OH counter-ion needed to provide charge balance. Checking the structure by SQUEEZE²³ indicated that in the structure there is an additional empty space suitable for the second –OH counter-ion. Convergence of the final refinement was not very good due to a lot of highly disordered groups in the structure. RIGU option was used for the final refinement of the structure. Although the found structure has a low resolution it is given the paper because the framework of the

structure seems to be clear and confirms the main chemical results discussed in the work. All calculations were performed by the Bruker SHELXL package.⁴¹

Crystallographic Data for β -CaSn₁₂: C₆₀H₁₅₄CaO₂₉Sn₁₂, M = 2804.18, 0.11 x 0.06 x 0.03 mm, T = 173 K, Orthorhombic, space group *Pbcm*, *a* = 16.1505(6) Å, *b* = 24.9896(11) Å, *c* = 23.5117(11) Å, *V* = 9489.2(7) Å³, *Z* = 4, *D*_c = 1.963 Mg/m³, μ (Cu) = 25.663 mm⁻¹, *F*(000) = 5464, 2 θ _{max} = 100.0°, 20969 reflections, 5031 independent reflections [*R*_{int} = 0.1002], *R*₁ = 0.0856, *wR*₂ = 0.2263 and GOF = 1.042 for 5031 reflections (509 parameters) with *I* > 2 σ (*I*), *R*₁ = 0.1455, *wR*₂ = 0.2640 and GOF = 1.051 for all reflections, max/min residual electron density +0.885/-0.648 eÅ⁻³.

Fourier Transform Infrared Spectroscopy: (FTIR) spectra were recorded on a Nicolet iS10 FTIR spectrometer with a secondary Nicolet iZ 10 module purchased from Thermo Fisher Scientific Inc. The instrument was equipped with a diamond plate for attenuated total reflectance (ATR) measurements. Spectra were collected in air.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS): Electron micrographs and atomic ratios (%) of the crystalline materials were obtained from a Quanta 600F instrument (FEI) combining a scanning electron microscope and an energy-dispersive x-ray spectrometer.

ASSOCIATED CONTENT

Supporting Information. Bond valence sum calculations for β -CaSn₁₂, atomic percentages of β -CaSn₁₂ determined by SEM-EDX, complete ESI-MS peak assignments, expanded ¹H, ¹³C, and ¹¹⁹Sn NMR spectra, model of SAXS data, and expanded FT-IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

This work was funded by the National Science Foundation, Center for Chemical Innovation, grant number CHE-1606982. We also acknowledge the support of the Oregon State University NMR Facility funded in part by the National Institutes of Health, HEI Grant 1S10OD018518, and by the M. J. Murdock Charitable Trust grant #2014162.

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Unlike Na-centered butyltin Keggin clusters which crystallize as a mixture of β and γ isomers, the Ca-centered butyltin Keggin crystallizes pure β isomer.