A Trihydroxy Tin Group That Resists Oligomerization in the Trinuclear Nickel Cluster \([\text{Ni}_3(\mu-\text{P},\text{P}’-\text{PPh}_2\text{CH}_2\text{PPh}_2)_3(\mu_3-\text{L})-(\mu_3-\text{Sn(OH)}_3)]\)**

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The conversion of tin chloride reagents into the corresponding hydroxides typically results in the formation of oligomeric tin oxides.[1–3] We report herein the preparation and reactivity of a trinuclear nickel cluster that is capped by a \(\mu_3-\text{Sn(OH)}_3\) group. This is a rare example of a complex that contains an intact trihydroxy tin group, thus allowing the study of the chemistry of tin hydroxides without interference from competing reactions that form oligomeric tin oxides.

The trichlorostannyl-capped cluster \([\text{Ni}_3(\mu-\text{dppm})_3(\mu_3-\text{Cl})(\mu_3-\text{Sn(Cl)}_3)]\) (1; dppm = bis(diphenylphosphino)methane) is a dark-green diamagnetic species, the \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum of which displays a singlet at } \delta = -2.3 \text{ ppm that is flanked by satellites arising from coupling to the trichlorostannyl group } (J_{\text{31P}-119\text{Sn},117\text{Sn}} = 138 \text{ Hz (unresolved)}). The properties of cluster 1 are similar to the closely related \(\mu\)-iodo-capped cluster that was reported recently.[4] The molecular structure of the trichlorostannyl-capped precursor 1 is presented in Figure 1. The three chlorine atoms of the \(\mu_3-\text{SnCl}_3\) are staggered with respect to the three nickel atoms, resulting in an approximately octahedral coordination environment at the tin atom and approximate \(C_3\) symmetry for the cluster.

Cluster 1 may be converted into the trihydroxystannyl-capped cluster \([\text{Ni}_3(\mu-\text{dppm})_3(\mu_3-\text{Cl})(\mu_3-\text{Sn(OH)}_3)]\) (2) in high yield by treatment with in situ hydrolyzed NaH in a CH\(_2\)Cl\(_2\)/THF solvent mixture [Eq. (1)]. Use of NaH provides higher yields than direct use of NaOH, most likely because the NaH powder gives more highly dispersed NaOH than the poorly soluble NaOH pellets.

Cluster 2 is a deep-blue diamagnetic solid whose \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum displays a singlet with satellites at } \delta = -0.1 \text{ ppm } (J_{\text{31P}-119\text{Sn},117\text{Sn}} = 122 \text{ Hz (unresolved)}). The unit cell of crystals of 2 has three independent molecules per unit cell and was solved in space group \(P3\). The molecular structure of 2 is presented in Figure 2. The structure reveals a \(\mu_3-\text{Sn(OH)}_3\) group capping a triangular Ni\(_3\) cluster in a staggered conformation. Overall, the bond parameters of 2 are quite similar to the \(\mu_3-\text{SnCl}_3\)-capped precursor 1 and the cluster \([\text{Ni}_4(\mu-\text{dppm})_4(\mu_3-\text{I})(\mu_3-\text{SnCl}_3)]\).[5] However, the solid-state crystal structure of 2 reveals that the clusters are organized in pairs with the two Sn(OH)\(_3\) groups facing each other in a crystallographically imposed threefold staggered conformation (Figure 3).

The face-to-face arrangement of pairs of Sn(OH)\(_3\) groups suggests partial intermolecular hydrogen bonding in the solid state. The intermolecular distances between pairs of O atoms of the hydroxy groups (Figure 3 A) fall in the narrow range of 2.983(10)–3.003(10) Å. This is at the long end of the range.

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**Supporting information for this article (ORTEP diagram for complex 6, spectroscopic data, and MS data) is available on the WWW under http://www.angewandte.org or from the author.**

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normally associated with relatively weak O–H···O hydrogen bonding.\(^5\) The fact that the \(\mu_3\)-Sn(OH)\(_3\) group of the cluster \(2\) resists oligomerization is likely to be the result of the considerable steric influences of the \(\text{Ni}_3\text{(dppm)}_3\) framework. A space-filling diagram of the structure of \(2\) shows that the \(\mu_3\)-Sn(OH)\(_3\) group sits in a hydrophobic pocket created by the phenyl rings of the three dppm ligands (Figure 4).

![Figure 2](image2.png)  
**Figure 2.** ORTEP diagram of complex \(2\) (thermal ellipsoids set at 50% probability). Selected bond lengths [\(\text{Å}\)] and angles [\(^\circ\)]: \(\text{Sn}(1)-\text{O}(1)\) 2.039(7), \(\text{Sn}(1)-\text{Ni}(1)\) 2.6355(17), \(\text{Ni}-\text{P}\) (average) 2.193(3), \(\text{Ni}(1)-\text{C}(1)\) 2.429(4), \(\text{Ni}(1)-\text{Ni}(1A)\) 2.451(2); \(\text{O}(1)-\text{Sn}(1)-\text{O}(1A)\) 94.0(3), \(\text{O}(1)-\text{Sn}(1)-\text{Ni}(1)\) 105.4(2), \(\text{Ni}(1)-\text{Sn}(1)-\text{Ni}(1A)\) 55.4(5), \(\text{Ni}(1)-\text{Ni}(1A)-\text{Ni}(1B)\) 60.0.

![Figure 3](image3.png)  
**Figure 3.** Packing diagram for the crystal structure of complex \(2\) showing the pairing-up of the clusters: A) side view, B) top view.

The \(\mu_3\)-Sn(OH)\(_3\) group of cluster \(2\) exhibits nucleophilic addition to carbon dioxide and epoxides. Bubbling CO\(_2\) through solutions of complex \(2\) in CH\(_2\)Cl\(_2\) or THF results in an immediate color change from deep-blue to purple and the quantitative formation of the \(\eta^1\)-carbonate complex \(3\) [Eq. (2)].

![Figure 4](image4.png)  
**Figure 4.** Two projections of the space-filling diagram of the structure of complex \(2\); the three oxygen atoms of the \(\mu_3\)-Sn(OH)\(_3\) groups are shown in darker gray.

![Figure 5](image5.png)  
**Figure 5.** ORTEP diagram for complex \(3\) (thermal ellipsoids set at 50% probability). Selected bond lengths [\(\text{Å}\)] and angles [\(^\circ\)]: \(\text{Sn}(1)-\text{O}(3)\) 2.121(3), \(\text{Sn}(1)-\text{Ni}(3)\) 2.5197(7), \(\text{Ni}(1)-\text{Ni}(3)\) 2.4344(8), \(\text{Ni}(1)-\text{C}(1)\) 2.4705(14), \(\text{Ni}(3)-\text{C}(1)\) 2.3543(13), \(\text{O}(4)-\text{C}(4)\) 1.232(6), \(\text{O}(2)-\text{C}(4)\) 1.325(6), \(\text{O}(3)-\text{Sn}(1)-\text{O}(3)\) 90.39(9), \(\text{O}(3)-\text{Sn}(1)-\text{O}(2)\) 61.80(13), \(\text{Ni}(3)-\text{Sn}(1)-\text{Ni}(2)\) 57.42(2), \(\text{Ni}(2)-\text{Ni}(1)-\text{Ni}(3)\) 61.01(3), \(\text{O}(3)-\text{C}(4)-\text{O}(2)\) 111.8(4).

Characteristic bands for carbonate, \(\nu_{\text{CO}} = 1634\) and 1669 cm\(^{-1}\), are observed in the solid-state and solution IR spectra of cluster \(3\). The \(^{31}\text{P}\left[\text{H}\right]\) NMR spectrum is a singlet flanked by two satellites at \(\delta = \pm 1.1\) ppm (\(2\text{J}(\text{P}-\text{Sn},\text{Sn}) = 128\) Hz (unresolved)). Formation of the carbonate cluster is accompanied by H\(_2\)O elimination, and the reaction between the \(\mu_3\)-Sn(OH)\(_3\) cluster \(2\) and the \(\mu_3\)-Sn(OH)(\(\eta^1\)-CO\(_3\)) cluster \(3\) is completely reversible [Eq. (2)]. The molecular structure of cluster \(3\) is presented in Figure 5.

The carbonate-capped cluster \(3\) exhibits one of the most distorted angles yet observed in a carbonate complex, \(\tau_{\text{CO}} = 61.80(13)\)\(^\circ\), and a highly distorted octahedral coordination geometry around the tin atom.\(^6\) The carbonate group is also highly distorted from ideal \(D_{3d}\) symmetry (ideal: all C–O \(\approx 1.28–1.29\) Å) with longer C–O bond lengths for the oxygen atoms coordinated to tin (average: 1.330(3) Å), and a shorter C–O bond lengths for the uncoordinated oxygen atom (1.223(6) Å). The O(3)-C(4)-O(2) bond angle is narrow (111.8(4)), reflecting a strained four-membered ring.
Cluster 2 also undergoes ring-opening addition of 1,2-epoxybutanate to give the 1,2-diolate tin cluster $[\text{Ni}_3(\mu_3-PPh_3CH_2PPh_3)_3(\mu_3-Sn)(\eta^2-O-CH_2CH(CH_2H)_3-O)]$ (4). Cluster 4 was characterized by mass spectrometry and NMR spectroscopy (see Supporting Information). This reaction results in isomeric mixtures, and we were unable to isolate a suitable crystal of 4 for X-ray characterization. However, the closely related $\mu_3$-Br derivative $[\text{Ni}_3(\mu_3-PPh_3CH_2PPh_3)_3(\mu_3-\text{Br})](\mu_3-Sn(OH))]$ (5; see Experimental Section) reacts with 1,2-epoxybutanate to afford the 1,2-diolate cluster $[\text{Ni}_3(\mu_3-PPh_3CH_2PPh_3)_3(\mu_3-\text{Br})]\{\mu_3-Sn(OH)[\eta^2-O-CH_2CH(CH_2H)_3O]\}$ (7) as a crystalline material [Eq. (3)].

Complexes 2 and 5 constitute rare examples of tin trihydroxy compounds. A search of more than 250000 structures in the Cambridge Crystallographic Data Center[7–9] does not yield any structurally characterized compounds that have an intact Sn(OH)$_3$ fragment. The search recalls only one example of a Sn($\eta^2$-CO$_2$H) group. Of course, the usual tendency for such groups is to dimerize or even polymerize.[1–3]

In conclusion, we report a straightforward synthetic pathway that leads to a new series of trihydroxy tin trinuclear nickel clusters. The reactivity of these clusters is centered at the octahedrally coordinated tin atom. The Sn(OH)$_3$ groups of clusters 2 and 5 resist oligomerization and display high nucleophilicity leading to reversible formation of an $\eta^2$-carbonato-tin-capped cluster in the presence of CO$_2$ and ring opening of 1,2-epoxybutanate to the corresponding tin-coordinated diolate.

**Experimental Section**

1: A solution of SnCl$_2$ (274 mg, 1.46 mmol) dissolved in THF was added to a mixture of [Ni(cod)$_2$] (400 mg, 1.46 mmol; cod = cyclooctadiene), dpmm (845 mg, 2.2 mmol), and [Ni(acac)$_2$] (186 mg, 0.73 mmol; acac = 2,4-pentanedionato) in THF (20 mL). The solution turned dark-green immediately and a green precipitate appeared. The solid was collected by filtration and washed with diethyl ether. Recrystallization from CH$_2$Cl$_2$/diethyl ether gave pure 1 (690 mg, 59%). Elemental analysis (%) calcld for C$_{75}$H$_{66}$Cl$_4$Ni$_3$P$_6$Sn: C 56.66, H 4.62; $\delta$ (31P–$\eta^2$-Sn,117Sn) = 98 Hz (unresolved). The molecular structure of complex 7 shows a OCH$_2$CH(C$_2$H$_5$)O diolate group coordinated to the tin atom in a chelated $\eta^2$ fashion (Figure 6). The large thermal parameter for the C(5) atom in the direction perpendicular to the O(1)-O(2)-C(5)-C(4) plane is the result of superposition of two different orientations of the molecule in the crystal lattice. The centrosymmetric $P2(1)/c$ space group confirms the presence of a 50:50 $R/S$ racemide mixture in the crystal.

**Figure 6.** ORTEP diagram for complex 7 (thermal ellipsoids set as 50% probability). Selected bond lengths [Å] and angles [°]: Ni(1)–Ni(3) 2.4307(14), Ni(1)–Br(1) 2.4470(16), Ni(1)–Sn(1) 2.6238(12), Ni(2)–Sn(1) 2.6173(12), Ni(3)–Sn(1) 2.5873(11), Sn(1)–O(2) 2.020(7), Sn(1)–O(1) 2.043(7), Sn(1)–O(3) 2.178(7); Ni(3)–Ni(1)–Ni(2) 59.60(4), Ni(3)–Ni(1)–Sn(1) 61.44(4), Ni(3)–Ni(2)–Ni(1) 60.17(4).

52.11, H 4.13. $^{31}$P{¹H} NMR (121 MHz, [D₈]THF, 295 K): $\delta = -2.1$ (s, sat. $J_{\text{31P,119Sn,117Sn}} = 140$ Hz (unresolved)).

7: 1,2-Epoxybutane (30 mg, 0.22 mmol) was added to a solution of cluster 5 (250 mg, 0.16 mmol) in THF (10 mL). The solution was gently heated and an immediate color change from deep-blue to turquoise was observed. The $^{31}$P NMR spectrum shows no signal for the starting cluster 5 and only one singlet at $\delta = -1.9$ ppm (185 mg, 63%). MALDI-MS $[\text{Ni}_3(\text{dppm})_3\text{Br}\{\text{Sn(OH)}\{\text{OCH}_2\text{CH-}
(C_2\text{H}_5)\text{O}\}\}\text{H}]^+$ 1633 m/z; $^{31}$P{¹H} NMR (121 MHz, [D₈]THF, 295 K): $\delta = -1.9$ ppm (s, sat. $J_{\text{31P,119Sn,117Sn}} = 98$ Hz (unresolved)).

CCDC-250075–CCDC-250079 (1, 2, 3, 6, and 7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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