Tin Coordination Chemistry

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1,1,1-Tris(distanna-*closo*-dodecaborate)stannate: A Tripodal Tin Ligand**

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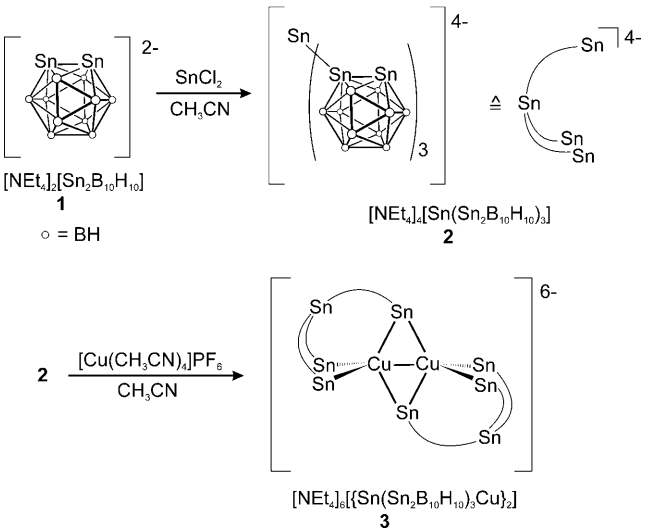
1,2-Distanna-*closo*-dodecaborate, the highest known homologue of *ortho*-carborane, was synthesized in 2006.[1] Since then, we have been investigating this promising bidentate tin ligand. Sn^{II} and Sn^{IV} ligands are widely used in reactions with transition metals,[2] but multidentate tin ligands are fairly scarce.[3–5] Some related polynuclear tin frameworks can only be found in tin cluster chemistry. The Zintl anions Sn_5^{2-}, Sn_9^{3-}, and Sn_9^{4-} have delocalized electrons and also coordinate transition metals, for example $[Sn_9Pt_2(PPh_3)]^{2-}$, $[Sn_9Ir(cod)]^{3-}$ (cod = 1,5-cyclooctadiene), and $[Sn_9Zn(C_6H_5)]^{3-}$.[6] Tris(pyrazolyl)hydroborates and variations thereof (-methanes and -methanides) are the most prominent class of face-capping tripodal ligands.[7] They have been thoroughly explored and widely used since its first introduction by Trofimenko in 1967.[8] Herein we present a heavier structural analogue thereof that is built up of a skeleton of seven tin atoms. This facial triad of strongly σ-donating Sn^{II} units is an unprecedented and extraordinary coordination unit. We also present a coordination compound of this ligand formed by reaction with a Cu^{I} electrophile.

The reaction of the dianionic cluster 1,2-distanna-*closo*-dodecaborate (**1**) with tin(II) chloride resulted in a substitution of the two chloride ions by three cluster anion equivalents. The terminal tin atom remains in the oxidation state +II, giving rise to $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$ (**2**) with an unprecedented tetraanion $[Sn(Sn_2B_{10}H_{10})_3]^{4-}$ with a Sn_7 skeleton (Scheme 1). This SnX_3^{2+3n}-type molecule (n = charge of X), which bears three $[Sn_2B_{10}H_{10}]^{2-}$ clusters, each of which provides a free Sn^{II} vertex with a lone pair, forms a tripodal coordination pocket (Scheme 1). When exposed to air, the *closo*-$[B_{10}H_{10}]^{2-}$ cluster anion and tin oxide result within hours. Reaction of the electron-rich cluster aggregate **2** with tetrakis(acetonitrile)copper(I) gave the hexaanionic cluster **3** within one hour (Scheme 1). A Cu^{I}–Cu^{I} bond is formed, resulting in a typical isolated dicopper unit.[9] This unit is surrounded by two equivalents of the tin ligand $[Sn(Sn_2B_{10}H_{10})_3]^{4-}$, forming a fairly distorted octahedral Sn_6 coordination pocket. The three tin vertices of $[Sn(Sn_2B_{10}H_{10})_3]^{4-}$ each chelate one Cu^{I} center in a tripodal, pincer-like manner. Whilst two of the tin donors of each ligand coordinate in a terminal chelating η^1 fashion, the third tin site bridges the two copper centers in a μ_2 fashion. This ligation of the dicopper unit gives rise to a distorted Sn_4 coordination polyhedron around each copper center, resulting in two edge-sharing Sn_4 tetrahedra.



Scheme 1. Reaction of 1,2-distanna-*closo*-dodecaborate (**1**) with tin(II) chloride to give **2** and subsequent reaction with tetrakis(acetonitrile)-copper(I)to give **3**.

Complex **3** is isolated as a red solid, which is poorly soluble in common organic solvents and is fairly sensitive to oxidation by air. Crystals of **2** and **3** that were suitable for single crystal x-ray analysis were grown by slow vapor diffusion of diethyl ether into an acetonitrile solution of **2** or **3**.[10] One conformer of the disordered tetraanion of **2** is shown in Figure 1.[11]

The interatomic distances from Sn1 to the cluster tin atoms Sn2, Sn4, and Sn6 are non-equivalent and range from 2.887(2) to 2.915(2) Å. These bonds are slightly longer than the Sn–Sn distances found in elemental tin (2.81 Å in α-Sn).[12] The intracluster Sn–Sn bonds range from 2.797(2) to

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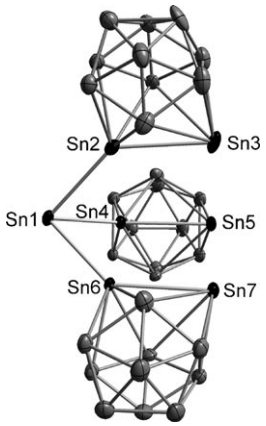

Figure 1. Diamond plot of the molecular structure of $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$ (**2**). H atoms and cations are omitted for clarity; ellipsoids are set at 30% probability. Selected distances [Å] and angles [°]: Sn1–Sn2 2.915(2), Sn1–Sn4 2.898(2), Sn1–Sn6 2.887(2), Sn2–Sn3 2.797(2), Sn4–Sn5 2.807(2), Sn6–Sn7 2.817(2); Sn2-Sn1-Sn6 81.20(5), Sn2-Sn1-Sn4 80.95(5), Sn4-Sn1-Sn6 81.69(4), Sn1-Sn2-Sn3 134.73(7), Sn1-Sn4-Sn5 134.17(6), Sn1-Sn6-Sn7 133.95(6).

2.817(2) Å. These distances are very similar to the intracluster Sn–Sn distances determined in $[NEt_3H]_2[(Sn_2B_{10}H_{10})_2]$, which are 2.795(1) and 2.794(1) Å.[1] Sn1 is in a pseudo tetrahedral environment, with an average angle of 81°.

The molecular structure of the coordination compound **3** is shown in Figure 2.[11] The Cu–Cu distance (2.457(2) Å) is within the typical range of Cu–Cu distances in organocopper compounds.[13] The shortest Cu–Cu distance to date was reported (2.3059(11) Å) in a hydride-bridged copper dimer with carbene ligands.[14] Copper metal has an interatomic distance of 2.56 Å in cubic close packing.[15] The bond lengths between the μ-bridging tin atoms (Sn3 and Sn3′) and the respective copper ions are 2.632(2) Å and 2.620(1) Å and are thus about 0.08 Å longer than the terminal Cu–Sn bonds,

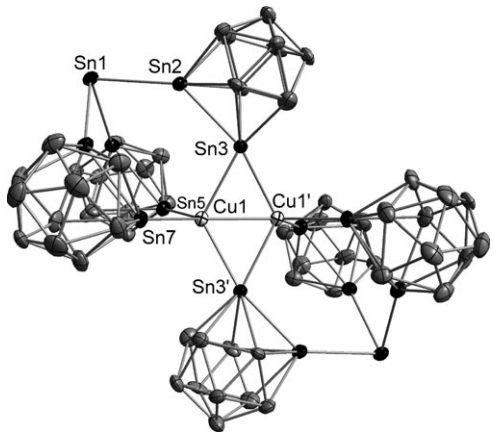

Figure 2. Diamond plot of the molecular structure of $[NEt_4]_6[\{Sn(Sn_2B_{10}H_{10})_3Cu\}_2]$ (**3**). H atoms and cations are omitted for clarity; ellipsoids are set at 30% probability. Selected distances [Å] and angles [°]: Cu1–Cu1′ 2.457(2), Cu1–Sn3 2.632(2), Cu1–Sn5 2.547(2), Cu1–Sn7 2.545(2), Sn1–Sn2 2.882(1), Sn2–Sn3 2.766(1); Sn2-Sn1-Sn4 82.24(3), Sn1-Sn2-Sn3 137.42(4), Sn2-Sn3-Cu1 107.42(4), Sn3-Cu1-Sn5 101.48(5), Sn3-Cu1-Sn3′ 122.45(5), Cu1-Sn3-Cu1′ 55.78(5).

which are 2.547(2) Å (Cu1–Sn5) and 2.545(2) Å (Cu1–Sn7). Coordination compounds with Cu–Sn bonds are very rare; however, many ternary copper stannides are known in the field of intermetallics. The intracluster Sn–Sn distances in **2** are slightly shortened upon coordination to the copper center and range from 2.766(1)–2.779(1) Å in **3**. The interatomic distances of Sn1 to the cluster tin atoms Sn2, Sn4, and Sn6 (2.861(1)–2.882(1) Å) are similarly shorter than found in **2**. The tetrahedral angles Sn-Cu-Sn range from 101.48(5)° (Sn3-Cu1-Sn5) to 122.45(5)° (Sn3-Cu1-Sn3′). The Cu1-Sn3-Cu1′ angle (55.78(5)°) is similar to related M-E-M angles of coinage metal coordination compounds with bridging stanna-, carbastanna- and germa-*closo*-dodecaborate.[16]

The $^{11}B\{^1H\}$ NMR spectrum of 1,2-distanna-*closo*-dodecaborate has four signals between $\delta = 1.6$ and -11.7 ppm with an intensity ratio of 2:2:4:2, in accordance with the C_{2v} symmetry of **1**. The asymmetrically substituted clusters in **2** should show six distinct signals. Instead, only three signals ($\delta = -1.7$, -7.8, and -13.7 ppm) with an intensity ratio of 4:4:2 are observed, and these signals are shifted to lower frequency compared to the starting material. These signals do not show a temperature- or solvent-dependent splitting. Furthermore, from a ^1H–^{11}B HSQC experiment, only three groups of cluster protons could be identified.

The $^{119}Sn\{^1H\}$ NMR spectrum exhibits three signals for the three distinct homotopic groups of tin atoms (Figure 3). The atoms Sn2, Sn4, and Sn6 correspond to the signal at $\delta = -273$ ppm with $^{117/119}Sn$ satellites from coupling to the central

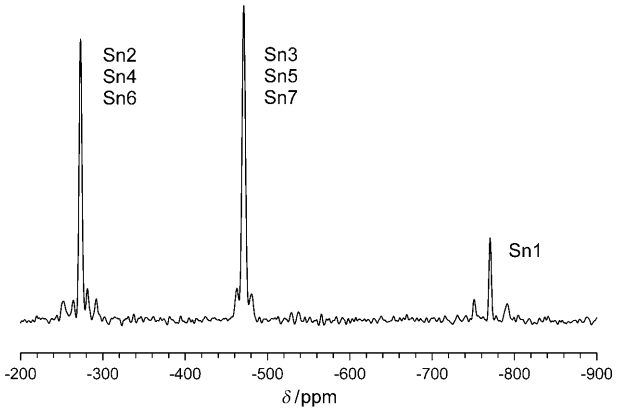

Figure 3. $^{119}Sn\{^1H\}$ NMR spectrum of **2** at 243 K.

Sn1 (7600 Hz) and to the outer cluster tin atoms, Sn3, Sn5, and Sn7 (3300 Hz). Consequently the other signals exhibit only one coupling. The signal at $\delta = -471$ ppm conforms to the cluster tin atoms Sn3, Sn5, and Sn7 with the small coupling. The third signal at $\delta = -770$ ppm shows only one third of the intensity of the other two signals and shows only the larger coupling of 7600 Hz. The resonances show relatively strong temperature-dependent chemical shifts. Cooling from room temperature to −30 °C resulted in a shift of approximately 60 ppm for the signal at $\delta = -770$ ppm. Smallest impurities of 1,2-distanna-*closo*-dodecaborate lead to a total collapse of the two cluster signals at $\delta = -273$ and -471 ppm and result in a spectrum with only one signal at $\delta = -770$ ppm. Upon

addition of further 1,2-distanna-*closo*-dodecaborate, a broad resonance emerges at about $\delta = -350$ ppm. Taking all spectral information into account, a fast dynamic process could explain the apparently higher symmetry of the $^{11}B\{^1H\}$ NMR spectrum on a timescale that cannot be seen in the $^{119}Sn\{^1H\}$ NMR spectrum. Addition of 1,2-distanna-*closo*-dodecaborate leads to an associative–dissociative exchange mechanism, which can be monitored in the $^{119}Sn\{^1H\}$ NMR spectrum.

Owing to the poor solubility of the copper complex **3** in common solvents, only a $^{11}B\{^1H\}$ NMR spectrum could be recorded. Three resonances were measured at chemical shifts of $\delta = -4.1$, -11.1, and -13.4 ppm with an intensity ratio of 4:4:2.

The ^{119}Sn Mössbauer spectrum of $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$ (**2**) is presented in Figure 4, together with an integral fit of the transmission;[11] the corresponding fitting parameters are listed in Table 1. The complex spectrum of **2** was well-reproduced by three superimposed signals that are all

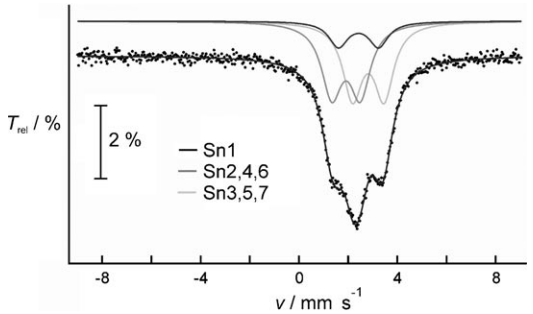

Figure 4. Experimental (●) and simulated ^{119}Sn Mössbauer spectrum (——) of $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$ (**2**) at 77 K.

Table 1: Fitting parameters of ^{119}Sn Mössbauer spectroscopic measurements for $K_2[Sn_2B_{10}H_{10}]$ and $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$.[a]

Sn site	δ [mm s^{-1}]	ΔE_Q [mm s^{-1}]	Γ [mm s^{-1}]
$K_2[Sn_2B_{10}H_{10}]$[11]	2.50(1)	1.53(1)	0.87(1)
Sn1 (black)[b]	2.42(4)	1.63(5)	0.93(9)
Sn2,4,6 (gray)[b]	1.91(1)	1.16(2)	1.00(2)
Sn3,5,7 (light gray)[b]	2.82(1)	1.28(2)	0.95(2)

[a] Numbers in parentheses represent the statistical errors in the last digit. δ = isomer shift, ΔE_Q = electric quadrupole splitting, Γ = experimental line width. The ratio of intensities of Sn1/Sn2,4,6/Sn3,5,7 was fixed at 1:3:3. [b] See Figure 4.

subjected to significant quadrupole splitting. From the results of the crystal structure analysis, we fixed the signal intensities at a ratio of 1:3:3. Data fitting then allowed an independent refinement of the isomer shifts, the experimental line widths, and the quadrupole splitting parameters (Table 1). The three signals can then be unambiguously assigned to the distinct tin sites. The black signal (Figure 4) with the smallest intensity corresponds to the central tin atom of the Sn_7 cluster. The strong quadrupole splitting parameter of Sn1 is due to its strong lone-pair activity, similar to the tin centers in $K_2[Sn_2B_{10}H_{10}]$. The tin atoms Sn2,4,6 and Sn3,5,7 have comparable quadrupole splitting parameters but distinctly different isomer shifts (Table 1). The tin atoms Sn2,4,6 are bound to the central tin atom Sn1 and lose some electron density, in line with the smaller isomer shift of 1.91 mm s^{-1} (gray signal in Figure 4). The light gray signal can be attributed to Sn3,5,7. The higher isomer shift of 2.82 mm s^{-1} corresponds to a higher electron density at the Sn3,5,7 nuclei, which is even higher than in the starting material.[17] Therefore, the Sn_7 anion is more nucleophilic than the starting cluster **1**.

In conclusion, we present the synthesis and characterization of the first tripodal tin ligand. The tridentate nature of the ligand can be seen in the reaction with a Cu^I electrophile, forming an unprecedented novel Cu–Cu complex. The presence of the remaining terminal Sn^{II} vertex will potentially lead to the formation of extended network structures by coordination to various transition-metal ions. Such homo- and heterometallic complexes are currently under study. They will possibly exhibit unprecedented forms of metal–metal interactions by such novel tin-based ligand systems, which can give rise to various further applications of these systems.

Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by established methods and stored under argon. NMR spectra were recorded by using a Bruker Avance II + 500 NMR spectrometer. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Tübingen using a Vario MICRO EL from Elementar Co. operating in CHNS mode.

2: A solution of $[NEt_4]_2[Sn_2B_{10}H_{10}]$ (216.6 mg, 0.352 mmol) in acetonitrile (20 mL) was treated with a solution of $SnCl_2$ (22.2 mg, 0.117 mmol) in THF (5 mL). The resulting mixture turned intense yellow in color. After stirring for 30 min at room temperature, the solvent was removed in vacuo. The orange-colored solid was washed with water (3 × 5 mL) and diethyl ether (3 × 5 mL) and dried under reduced pressure. Single crystals in form of red cubes of $[NEt_4]_4[Sn(Sn_2B_{10}H_{10})_3]$ (171.7 mg, 86 %) suitable for X-ray analysis were grown by slow diffusion of diethyl ether into an acetonitrile solution of **2**. $^1H\{^{11}B\}$ NMR (500 MHz, CD_3CN): $\delta = 3.8$ (s, 12 H; BH), 3.2 (q, $J = 7.3$ Hz, 32 H; NCH_2), 2.4 (s, 12 H; BH), 2.1 (s, 6 H; BH), 1.2 ppm (t, $J = 7.3$ Hz, 48 H; NCH_2CH_3); $^{11}B\{^1H\}$ NMR (160 MHz, CD_3CN): $\delta = -1.7$ (4 B), -7.8 (4 B), -13.7 ppm (2 B); $^{119}Sn\{^1H\}$ NMR (186 MHz, CD_3CN, -30 °C): $\delta = -273$ (s, $^1J(^{119}Sn(2,4,6), ^{117/119}Sn(1)) = 7600$ Hz, $^1J(^{119}Sn(2,4,6), ^{117/119}Sn(3,5,7)) = 3300$ Hz, 3 Sn; Sn2,4,6), -471 (s, $^1J(^{119}Sn(3,5,7), ^{117/119}Sn(2,4,6)) = 3300$ Hz, 3 Sn; Sn3,5,7), -770 ppm (s, $^1J(^{119}Sn(1), ^{117/119}Sn(2,4,6)) = 7600$ Hz, 1 Sn, Sn1). Elemental analysis (%) calcd for **2**·4 CH_3CN ($C_{40}H_{122}B_{30}N_8Sn_7$, 1870.76 g mol^{-1}): C 25.68, H 6.57, N 5.99; found: C 25.64, H 6.45, N 5.92; calcd for **2** ($C_{32}H_{110}B_{30}N_4Sn_7$, 1706.55 g mol^{-1}): C 22.52, H 6.50, N 3.28; found: C 22.45, H 6.58, N 3.62.

3: A solution of **2** (43.5 mg, 0.025 mmol) in acetonitrile (10 mL) was added to a solution of $[Cu(CH_3CN)_4]PF_6$ (9.5 mg, 0.025 mmol) in acetonitrile (5 mL). The yellow-colored mixture was stirred for 1 h at room temperature. By slow diffusion of diethyl ether into the acetonitrile solution, single crystals of $[NEt_4]_6[\{Sn(Sn_2B_{10}H_{10})_3Cu\}_2]$ (38.9 mg, 95 %) suitable for X-ray analysis were grown. $^{11}B\{^1H\}$ NMR (160 MHz, CD_3CN): $\delta = -4.1$ (4 B), -11.1 (4 B), -13.4 ppm (2 B). Elemental analysis (%) calcd for **3** ($C_{48}H_{180}B_{60}Cu_2N_6Sn_{14}$,

3279.69 g mol^{-1}): C 17.58, H 5.53, N 2.56; found: C 17.43, H 5.48, N 2.74.

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[10] CCDC 811135 (**2**) and 811136 (**3**) 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.

[11] Details are given in the Supporting Information.

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