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Homoleptic Cadmium and Mercury Compounds of Stanna-*closo*-dodecaborate

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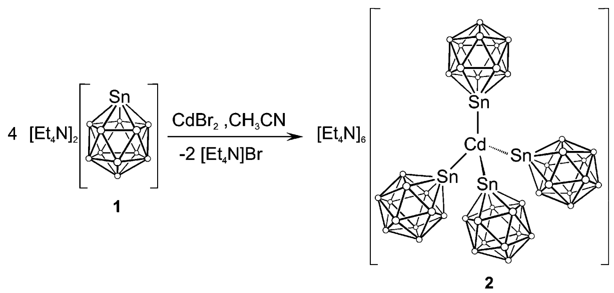
The reaction of stanna-*closo*-dodecaborate $[SnB_{11}H_{11}]^{2-}$ (**1**) with $CdBr_2$ gave the tetrahedrally coordinated compound $[Cd(SnB_{11}H_{11})_4]^{6-}$ (**2**). The same coordination mode can be found in $[Hg(SnB_{11}H_{11})_4]^{6-}$ (**3**), which was obtained by reaction of stannaborate with Hg_2Cl_2. Both compounds were characterized by single crystal X-ray analysis and heteronuclear NMR techniques.

Introduction

Although many silicon complexes of the group 12 metals with the substituents $SiMe_3$, $Si(SiMe_3)_3$, Si^tBu_3, and $Si(SiH^tBu_2)_3$ are known,[1−7] coordination compounds of the heavier congener tin with cadmium and mercury are rare.[8,9] In 2002, the 2-fold coordinated compounds $[M(Me_2N(p\text{-}Tol)_3Sn)_2]$ (M = Zn, Cd, Hg) have been reported as the first crystallographically characterized tin complexes of the group 12 metals.[10] It was shown in recent years that stanna-*closo*-dodecaborate can act as a versatile ligand with nucleophilic properties in the coordination chemistry of various transition metals.[11] Nevertheless, homoleptic complexes of stannaborate are known for the group 10 metals Ni, Pd, and Pt in either square-planar or octahedral coordination modes.[11−13] With Au, the homoleptic square-planar pentaanion $[Au(SnB_{11}H_{11})_4]^{5-}$ has been reported.[13] Herein, the first tetrahedrally coordinated tin complexes of the group 12 metals with stanna-*closo*-dodecaborate are presented.

Scheme 1. Synthesis of $[Et_3NH]_6[Cd(SnB_{11}H_{11})_4]$ (**2**)



Results and Discussion

Syntheses. The reaction product $[Et_3NH]_6[Cd(SnB_{11}H_{11})_4]$ (**2**) was obtained by reaction of $CdBr_2$ with $[Et_4N]_2[SnB_{11}H_{11}]$ in a 1:4 ratio in acetonitrile (Scheme 1). The completeness of the reaction was immediately indicated by one broad signal at −13.8 ppm in the ^{11}B NMR spectrum, since uncoordinated stannaborate exhibits three resonances at −6, −11, and −12 ppm with an intensity ratio of 1:5:5, while the boron atoms

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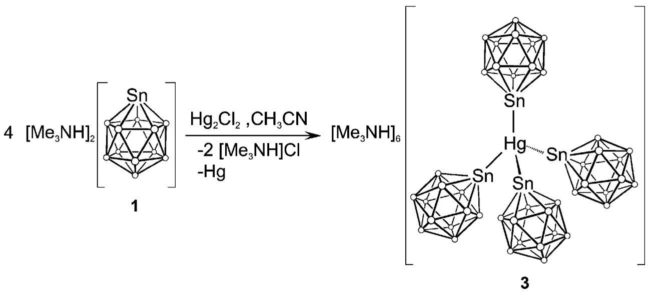
Scheme 2. Synthesis of $[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (**3**)



of coordinated stannaborates have very similar chemical shifts.[11] Slow diffusion of diethylether into the acetonitrile solution yielded **2** as very large colorless crystals in 65% yield.

The synthesis of $[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (**3**) was accomplished by reaction of the $[Me_3NH]^+$ salt of **1** with Hg_2Cl_2 in the ratio 4:1 in acetonitrile (Scheme 2). Again, the immediate formation of **3** was monitored by ^{11}B NMR. In addition, a gray precipitate of elemental mercury occurred, which was filtered from the reaction mixture to yield a clear, pale yellow solution. After slow diffusion of diethylether into this solution, large pale yellow crystals were isolated in 68% yield. It should be noted, that the same compound **3** can be obtained by combination of **1** with $HgCl_2$ and $HgBr_2$. Because the latter reactions yielded unidentified sideproducts, the reaction pathway with Hg_2Cl_2 was chosen.

Solid-State Structure. Compound **2** (Figure 1) crystallizes in the monoclinic space group $C2/c$ with the cadmium atom on the C_2 axis. The tetrahedral coordination environment around the cadmium atom is slightly distorted with Sn−Cd−Sn angles between 98.840(11)° and 119.108(6)°, which can be ascribed to packing effects. The Cd−Sn separations of 2.7462(2) and 2.7655(2) are somewhat longer than the Cd−Sn distance of 2.6758(1) Å in $[Cd(MeSi\{SiMe_2N(p\text{-}Tol)\}_3Sn)_2]$.[10]

The structure refinement of compound **3** (Figure 2) in space group $I\bar{4}2m$ revealed that the asymmetric unit consists of one mercury-coordinated stannaborate moiety with the mercury atom on the 4-fold inversion axis. The residual three heteroborates are generated by symmetry, and the mercury atom is surrounded by a slightly distorted tetrahedral arrangement of stannaborate units with Sn−Hg−Sn angles of 102.610(18)° and 124.29(4)°. The Hg−Sn distance of 2.7152(9) Å is slightly elongated in comparison with the reported Hg−Sn distance of 2.6495(2) Å in $[Hg(MeSi\{SiMe_2N(p\text{-}Tol)\}_3Sn)_2]$.[10] As in compound **2**, the distortion of the tetrahedral coordination environment can be ascribed to packing effects. It should be mentioned that two additional equivalents of $[Me_3NH]Cl$ are included in the unit cell.

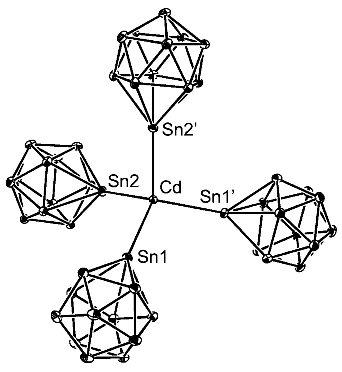


Figure 1. ORTEP plot of the anion of $[Et_3NH]_6[Cd(SnB_{11}H_{11})_4]$ (**2**); H atoms and the cations have been omitted for clarity, ellipsoids at 30% probability. Interatomic distances [Å] and angles [°] Cd−Sn1, 2.7462(2); Cd−Sn2, 2.7655(2); Sn1−Cd−Sn2, 105.344(6); Sn1−Cd−Sn2′, 119.108(6); Sn1−Cd−Sn1′, 109.48(1); Sn2−Cd−Sn2′, 98.84(1).

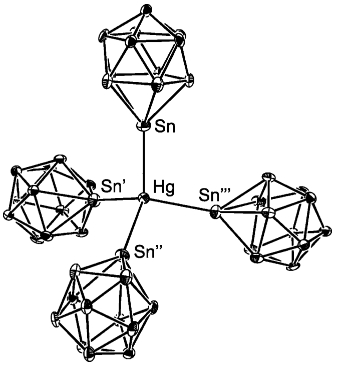


Figure 2. ORTEP plot of the anion of $[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (**3**); H atoms and the cations have been omitted for clarity, ellipsoids at 30% probability. Interatomic distances [Å] and angles [°] Hg−Sn, 2.7152(9); Sn1−Hg−Sn1′, 102.610(3); Sn1−Hg−Sn1", 124.29(4).

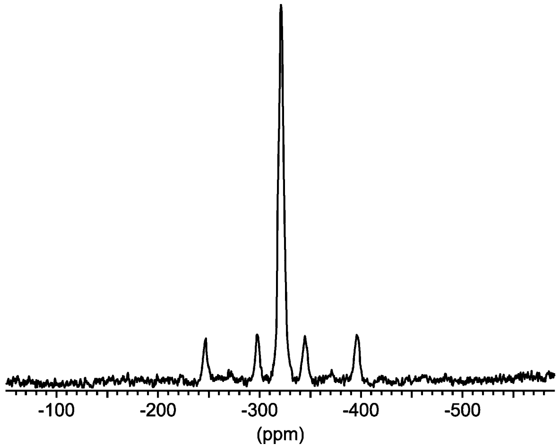


Figure 3. $^{119}Sn\{^1H\}$ NMR spectrum of $[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (**3**).

NMR Spectroscopy. To get more information on the solution behavior of the compounds, heteronuclear NMR studies have been carried out. In the $^{11}B\{^1H\}$ NMR spectra of both compounds, the complete coordination of all four heteroborate units is indicated through broad signals at −13.8 ppm (**2**) and −14.4 ppm (**3**).

These values are significantly shifted toward lower field, since most of the stannaborate transition metal compounds exhibit resonances at about −15 ppm.[11] More information is provided by the $^{119}Sn\{^1H\}$ NMR spectrum of compound **2**, which displays a broad signal at −377 ppm. Additionally, the $^{119}Sn\{^1H\}$ spectrum of **2** shows satellites with $^1J(^{119}Sn-^{113/111}Cd) = 7400$ Hz and $^2J(^{119}Sn-^{117}Sn) = 3500$ Hz. The cadmium satellites are not resolved into ^{111}Cd and ^{113}Cd because of the large line width of the resonances and the similar magnetogyric ratios of both isotopes. A similar coupling pattern can be observed in the $^{119}Sn\{^1H\}$ NMR spectrum of **3** (Figure 3) which consists of a broad resonance at −320 ppm with ^{117}Sn and ^{199}Hg satellites. Thereby, the

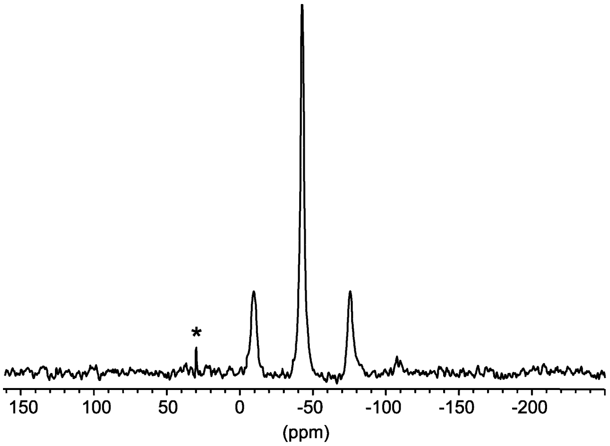


Figure 4. $^{113}Cd\{^1H\}$ NMR spectrum of $[Et_3NH]_6[Cd(SnB_{11}H_{11})_4]$ (**2**), referenced against $CdMe_2$. The asterisk marks the transmitter frequency.

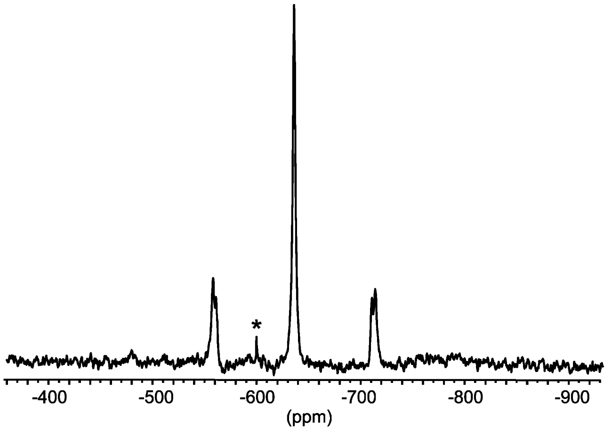


Figure 5. $^{199}Hg\{^1H\}$ NMR spectrum of $[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (**3**), referenced against $HgMe_2$. The asterisk marks the transmitter frequency.

Table 1. Crystal and Structure Refinement Parameters for **2** and **3**

	2	**3**·2[Me$_3$NH]Cl
empirical formula	$C_{36}H_{140}B_{44}CdN_6Sn_4$	$C_{24}H_{124}B_{44}Cl_2HgN_8Sn_4$
formula weight [g/mol]	1720.34	1747.20
wavelength [Å]	0.71073	0.71073
temperature [K]	173	173
Theta range [°]	5.67−25.35	5.72−25.34
crystal system	monoclinic	tetragonal
space group	*C*2/*c*	$I\bar{4}2m$
Z	4	2
a [Å]	29.2531(16)	14.9235(16)
b [Å]	14.6392(5)	14.9235(16)
c [Å]	20.5977(12)	20.3832(16)
β [°]	108.500(4)	90.00
Volume [Å^3]	8365.0(7)	4539.6(8)
ρ_{calc} [g/cm^3]	1.366	1.278
μ [mm^{-1}]	1.460	2.855
reflections collected	51225	25889
independent reflections	7577	2175
parameters/ restraints	430/6	101/0
absorption correction	none	numerical
min./max. transmission	-	0.5292/0.7128
final R indices [$I > 2\sigma$]	$R_1 = 0.0244$, $wR_2 = 0.0559$	$R_1 = 0.0538$, $wR_2 = 0.1382$
R indices all data	$R_1 = 0.0270$, $wR_2 = 0.0569$	$R_1 = 0.0570$, $wR_2 = 0.1396$
GoF on F^2 (all/obs. data)	1.129/1.220	1.208/1.208
largest diff. peak/hole	0.696/−0.746	3.074/−1.130

coupling constants $^1J(^{199}Hg-^{119}Sn) = 13900$ Hz and $^2J(^{119}Sn-^{117}Sn) = 4330$ Hz can be observed.

The $^{113}Cd\{^1H\}$ NMR spectrum of compound **2** exhibits one resonance at −42 ppm (referenced against $CdMe_2$), flanked by $^{119/117}Sn$ tin satellites with the already observed $^1J(^{119/117}Sn-^{113}Cd)$ coupling constant of 7400 Hz (Figure 4). Because of the long T_1 relaxation time of the ^{113}Cd nucleus in **2**, a small amount of $Mn(NO_3)_2$ was added for faster relaxation. The measurement of the ^{113}Cd solid-state VACP-MAS spectrum located a resonance at −38 ppm, which is in good agreement with the solution spectrum.

Unfortunately, the proton relaxation $T_{1\rho}$ (~1 ms) was too small for effective cross polarization, and therefore, the signal-to-noise ratio was very low. However, the presence of tin satellites with the same coupling constant as in solution was observed, and the absence of spinning sidebands indicates a small anisotropy of the ^{113}Cd chemical shift. It has been reported in the literature that the full chemical shift range of ^{113}Cd runs from −740 to +240 ppm ($CdMe_2$ standard) with octahedral oxygen ligands being the most shielding and tetrahedral sulfur ligands the least.[14] In contrast to the ^{195}Pt chemical shift of $[Pt(SnB_{11}H_{11})_6]^{8-}$ (−7724 ppm), which is situated in the highfield region of the ^{195}Pt shift range, the ^{113}Cd chemical shift is located in the lowfield region of the ^{113}Cd chemical shift range.[12] This suggests that stannaborate acts as a weakly shielding ligand in compound **2**.

The high sensitivity of the ^{199}Hg NMR shift to the chemical environment about mercury(II) species, resulting in a large chemical shift range of about 4000 ppm, makes ^{199}Hg NMR spectroscopy a useful tool for the study of mercury complexes. $^{199}Hg\{^1H\}$ NMR measurements located the resonance of **3** at −640 ppm ($HgMe_2$ standard), which is situated in the middle of the ^{199}Hg chemical shift range (Figure 5). This chemical shift agrees well with the chemical shift of K_2HgCN_4 (−502 ppm), whereas other tetrahalogene mercury compounds exhibit chemical shifts at much higher field (K_2HgCl_4: −1331 ppm, K_2HgBr_4: −1921 ppm, K_2HgI_4: −3451 ppm).[15] The resonance is flanked by tin satellites with the already observed $^1J(^{199}Hg-^{119}Sn)$ coupling of 13900 Hz as well as a $^1J(^{199}Hg-^{117}Sn)$ coupling of 13400 Hz.

Conclusion

It can be concluded that stanna-*closo*-dodecaborate reacts readily with Cd and Hg electrophiles, establishing the first coordination compounds of this tin ligand and the group 12

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metals. Futhermore, the complexes **2** and **3** are the first crystallographically characterized group 12 compounds which are coordinated by such a high number of tin ligands.

Experimental Section

General Information. All manipulations were carried out under argon atmosphere in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under argon. NMR spectra were recorded on a Bruker Avance II+ 500 NMR spectrometer equipped with a 5 mm TBI triple resonance probe head. The chemical shifts are reported in δ values in ppm relative to external $BF_3 \cdot Et_2O$ (^{11}B), $CdMe_2$ (^{113}Cd), $SnMe_4$ (^{119}Sn) or $HgMe_2$ (^{199}Hg) using the chemical shift of the solvent ^2H resonance frequency in combination with the unified frequency scale according to paragraph 3.6 of the IUPAC 2001 recommendations.[16] The VACP-MAS NMR spectrum of **2** was measured on a Bruker DSX-200 spectrometer operating at 200.13 MHz (^1H) and 44.39 MHz (^{113}Cd). The powdered sample was spinning about the magic angle at 6 kHz. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Tübingen, using a Vario EL analyzer. $[Me_3NH]_2[SnB_{11}H_{11}]$ and $[Et_3NH]_2[SnB_{11}H_{11}]$ were synthesized using a modified protocol of the original work of Todd et al.[17]

Crystallography. X-ray data for compounds **2** and **3** (Table 1) were collected on an Stoe IPDS 2T diffractometer using Mo Kα radiation and were corrected for Lorentz and polarization effects and absorption by air. The programs used in this work are Stoe's X-Area[18] and the WinGX suite of programs[19] including SHELXS[20] and SHELXL[21] for structure solution and refinement, respectively. Numerical absorption correction based on crystal-shape optimization was applied for **3** with Stoe's X-Red and X-Shape.[22,23]

$[Et_3NH]_6[Cd(SnB_{11}H_{11})_4]$ (2). A 453 mg quantity of (1 mmol) $[Et_3NH]_2[SnB_{11}H_{11}]$ was dissolved in 10 mL of acetonitrile and 68 mg of (0.25 mmol) $CdBr_2$ was added. Large colorless block shaped crystals of **2** (279 mg, 65% yield) can be grown by slow diffusion of Et_2O into the acetonitrile solution. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_3CN): −13.8 (11B). $^{113}Cd\{^1H\}$ NMR (110.99 MHz, CD_3CN): −42 [$^1J(^{119/117}Sn{-}^{113}Cd) = 7400$ Hz]. $^{119}Sn\{^1H\}$ NMR (186.5 MHz, CD_3CN): −377 [$^1J(^{119}Sn{-}^{113/111}Cd) = 7400$ Hz, $^2J(^{119}Sn{-}^{117}Sn) = 3500$ Hz]. Elemental analysis calcd (%) for $C_{36}H_{140}B_{44}CdN_6Sn_4$: C, 25.13; H, 8.20; N, 4.88; found: C, 24.99; H, 7.53; N, 4.78.

$[Me_3NH]_6[Hg(SnB_{11}H_{11})_4]$ (3). A 369 mg quantity of (1 mmol) $[Me_3NH]_2[SnB_{11}H_{11}]$ was dissolved in 10 mL of acetonitrile and 118 mg of (0.25 mmol) Hg_2Cl_2 was added. The solution was filtered to remove the gray precipitate and slow diffusion of Et_2O into the acetonitrile solution yielded 318 mg (68%) large colorless crystals of $\mathbf{3} \cdot 3CH_3CN \cdot 2[Me_3NH]Cl$. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_3CN): −14.4 (11B). $^{119}Sn\{^1H\}$ NMR (186.5 MHz, CD_3CN): −320 [$^1J(^{199}Hg{-}^{119}Sn) = 13900$ Hz, $^2J(^{119}Sn{-}^{117}Sn) = 4330$ Hz]. $^{199}Hg\{^1H\}$ NMR (89.52 MHz, CD_3CN): −630 [$^1J(^{199}Hg{-}^{119}Sn) = 13900$ Hz, $^1J(^{199}Hg{-}^{117}Sn) = 13400$ Hz]. Elemental analysis calcd (%) for $C_{30}H_{133}B_{44}Cl_2HgN_{11}Sn_4$: C, 19.26; H, 7.17; N, 8.24; found: C, 19.27; H, 7.33; N, 8.54.

Supporting Information Available: Crystallographic data for compound **2** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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