The Crystal Structures of Two Hydro-closo-Borates with Divalent Tin in Comparison: Sn(H₂O)₃[B₁₀H₁₀] · 3 H₂O and Sn(H₂O)₃[B₁₂H₁₂] · 4 H₂O

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Abstract
Single crystals of Sn(H₂O)₃[B₁₀H₁₀] · 3 H₂O and Sn(H₂O)₃[B₁₂H₁₂] · 4 H₂O are easily accessible by reactions of aqueous solutions of the acids (H₃O)₂[B₁₀H₁₀] and (H₃O)₂[B₁₂H₁₂] with an excess of tin metal powder after isothermal evaporation of the clear brines. Both compounds crystallize with similar structures in the triclinic system with space group P 1 and Z = 2. The crystallographic main features are electroneutral double chains running along the a-axes. Each Sn²⁺ cation is coordinated by three water molecules of hydration (d(Sn–O) = 221–225 pm for the B₁₀ and d(Sn–O) = 222–227 pm for the B₁₂ compound) and additionally by hydridic hydrogen atoms of the three nearest boron clusters (d(Sn–H) = 281–322 pm for the B₁₀ and d(Sn–H) = 278–291 pm for the B₁₂ compound), which complete the coordination sphere. Between these tin(II)-bonded water and the three or four interstitial crystal water molecules, classical bridging hydrogen bonds are found, connecting the double chains to each other. Furthermore, there is also non-classical hydrogen bonding between the anionic [BₙHₙ]²⁻ (n = 10 and 12) clusters and the crystal water molecules pursuant to B–H⋅⋅⋅H–O interactions often called dihydrogen bonds.

Keywords Divalent tin · Lone-pair cations · Decahydro-closo-decaborates · Dodecahydro-closo-dodecaborates · Hydrates

Introduction
Interactions between soft metal cations, e.g. Cu⁺, Ag⁺ and Hg²⁺, and hydro-closo-borate anions [BₙHₙ]²⁻ (n = 10 and 12) were firstly discussed in the 1960s [1]. The salt-like copper(I) compound Cu₂[B₁₀H₁₀] shows Cu⋅⋅⋅B distances in the range from 214 to 233 pm, indicating a covalent interaction between the Cu⁺ cation and the hydro-closo-borate anion which was suggested as a three-centered two-electron Cu–H–B bond [2]. This assumption was encouraged by the infrared spectra, which unveils two distinct absorption bands in the B–H stretching area, one for the non-coordinating BH groups and another for the BH groups involved in the Cu–H–B interactions [3]. Similar can be found in the infrared spectra of the compounds [Cu₂(bpa)₂B₁₀H₁₀] and [Cu₂(bpa)₂(OH)₂]₂[Cu₂(B₁₀H₁₀)₃] · n CH₃CN, both revealing stretching vibrations of BH groups in three-centered Cu–H–B bonds. Additionally the X-ray crystal structure of [Cu₂(bpa)₂(OF)₂]₂[B₁₀H₁₀] shows Cu–H contacts in the range of 263–273 pm [4]. For the higher homologous salt-like silver(I) compound Ag₂[B₁₀H₁₀] [1, 5], up to now, no crystal structure could be determined, but the presence of three-centered Ag–H–B is supported by infrared spectroscopic data [5]. In the further case of Cu⁺ and Ag⁺ cations the review article by Avdeeva et al. [6] should be mentioned, as it provides a good overview of this field.

Up to now, these kind of connections can be found in several other salt-like hydro-closo-borates, especially with cations of the 6th period possessing lone-pair electrons. All of these compounds unveil interesting properties. The thallium(I) salt Tl₂[B₁₂H₁₂] [7] exhibits a yellow metal-centered luminescence at room temperature, based on an apparent covalent interaction between Tl⁺ and the hydridic hydrogen atoms of the [B₁₁H₁₁]²⁻ anions [8]. Besides Tl₂[B₁₂H₁₂], there can be also found two lead(II) dodecahydro-closo-dodecaborates, Pb[B₁₂H₁₂] [9] with a pure...
For the homologous decahydro-

\[ \text{closo-decaborate anions } \text{[B}_{10}\text{H}_{10}]^{2-}, \text{ interactions between these anions and cations with lone-pair electrons were expected. They could be verified through two lead(II) decahydro-

\[ \text{closo-decaborates } \text{[Pb(bipy)B}_{10}\text{H}_{10}]^{2-} \text{ with a covalent Bi–B single bond (} \text{(Cu–B)} = 218 \text{ pm) } \text{[15], \text{ but with marked differences in the Ti····H coordination spheres, based on stereochemically active lone-pair electrons. All these compounds can be seen as potential precursors for metalated boron clusters such as } \text{[Et3N][Cu(1-B}_{10}\text{H}_{10}\text{N}_{2}]) (} \text{d(Cu–B)} = 218 \text{ pm) } \text{[15], \text{ [P(Cs}_{2}\text{H}_{12}]_{2}[2-\text{SnCl}(\text{Cs}_{2}\text{H}_{12})\text{B}_{10}\text{H}_{10}] \text{ and } \text{[P(C}_{3}\text{H}_{7}]}_{2}[2-\text{SnCl}_{2}(\text{C}_{3}\text{H}_{7})\text{B}_{10}\text{H}_{10}] \text{ (} \text{d(Sn–B)} = 217–219 \text{ pm) } \text{[16, 17], eventually leading to features like in the recently published neutral molecule } \text{[BiB}_{9}\text{H}_{11}] \text{ with a covalent Bi–B single bond (} \text{d(Bi–B)} = 230 \text{ pm) manifesting an inverted polarity as compared to the typical B–H bonds } \text{[18, 19].}\]
(2 ×), from which O₃ is coordinated directly to a tin(II) cation as water molecule of hydration and the other oxygen atoms stand for free interstitial crystal water molecules (Fig. 4).

The higher homologous dodecaborate with the composition Sn(H₂O)₃[B₁₂H₁₂] · 4 H₂O crystallizes also in the triclinic space group P1 with a = 741.72(5) pm, b = 991.56(7) pm, c = 1154.63(8) pm, α = 74.471(2)°, β = 83.430(2)°, γ = 87.483(2)° for two formula units per unit cell (Tables 1 and 3) [13]. The unique Sn²⁺ cation is surrounded by three water molecules of hydration (O₁–O₃, d(Sn–O) = 222–224 pm) again, leading to the already mentioned [Sn(H₂O)₃]²⁺ cation, and three icosahedral [B₁₂H₁₂]²⁻ cluster anions are attached via only one hydrogen atom of each cage (d(Sn–H) = 273–281 pm) providing for a total coordination number of six for the first coordination sphere of the divalent tin (Fig. 5, left). The irregular arrangement of the three oxygen and three hydrogen atoms leaves enough space for a 5sp lone pair of electrons with stereochemical activity. Further tin-hydrogen distances can be found in the range of 315–333 pm, so each of the three boron cages finally coordinates via one triangular face to every Sn²⁺ cation with a total coordination number of 12 for the first and second coordination sphere (Fig. 5, right).

A similar structural motif can be found in the orthorhombic lead(II) salt Pb(H₂O)₃[B₁₂H₁₂] · 3 H₂O, also showing stereochemically active lone pairs (6sp) at the Pb²⁺ cations and direct metal-to-hydrogen interactions (d(Pb–H) = 257–338 pm) [7]. Each quasi-icosahedral [B₁₂H₁₂]²⁻ anion is built up from twelve crystallographically independent boron and hydrogen atoms each (d(B–B) = 177–180 pm, d(B–H) = 106–114 pm) and shows only minor deviations from the ideal values of 178 pm for d(B–B) and 110 pm for d(B–H) for these types of bonds [23]. The pyramidal [Sn(H₂O)₃]²⁺ units are interconnected

| Table 1 | Crystallographic data for Sn(H₂O)₃[B₁₀H₁₀] · 3 H₂O and Sn(H₂O)₃[B₁₂H₁₂] · 4 H₂O |
|---------|----------------------------------------------------------------------------------|
| Empirical formula | Sn(H₂O)₃[B₁₀H₁₀] · 3 H₂O | Sn(H₂O)₃[B₁₂H₁₂] · 4 H₂O |
| Crystal system | triclinic | triclinic |
| Space group | P1 (no. 2) | P1 (no. 2) |
| Lattice constants | | |
| a/pm | 756.49(5) | 741.72(5) |
| b/pm | 948.47(6) | 991.56(7) |
| c/pm | 1034.52(7) | 1154.63(8) |
| α° | 69.141(2) | 74.471(2) |
| β° | 85.364(2) | 83.430(2) |
| γ° | 87.258(2) | 87.483(2) |
| Number of formula units, Z | 2 | |
| Calculated density, D/cm³ | 1.657 | 1.580 |
| Molar volume, V/cm³ | 208.19 | 244.70 |
| Measuring diffractometer | κ-CCD (Bruker Nonius) | |
| Radiation | Mo-Kα (λ = 71.07 pm) | |
| Measuring temperature | 100 K | |
| Measurement limit, Θ max/° | 27.88 | 28.37 |
| Index ranges | 9/12/13 | 9/13/15 |
| F(000) | 340 | 384 |
| Absorption coefficient, μ/mm⁻¹ | 1.847 | 1.583 |
| Data corrections | Empirical, Program Scalepack | |
| Number of measured reflections | 6043 | 7869 |
| Number of unique reflections | 3278 | 4047 |
| Structure solution and refinement | Programs SHELXS-97 and SHELXL-97 | |
| R int | 0.031 / 0.044 | 0.036 / 0.058 |
| R1 for (n) reflections with | 0.024 (2890) | 0.027 (3439) |
| R1 / wR2 for all reflections | 0.032 / 0.046 | 0.037 / 0.041 |
| GoodF | 1.037 | 0.958 |
| Residual electron density, ρ/e⁻ × 10⁻⁶ pm⁻³, min. / max. | − 0.53 / 0.61 | − 0.43 / 0.54 |
Table 2 Atomic positions and equivalent isotropic displacement coefficients for Sn(H2O)3[B10H10] · 3 H2O (all atoms occupy the general Wyckoff position 2).

| Atom   | x/a  | y/b  | z/c  | U(eq)/pm² |
|--------|------|------|------|-----------|
| Sn     | 0.26718(2) | 0.584223(18) | 0.195601(17) | 93(5) |
| O1     | 0.0601(2) | 0.75424(18) | 0.20138(19) | 108(3) |
| H11    | 0.0325(5) | 0.741(4) | 0.274(4) | 370(11) |
| H12    | 0.9615(5) | 0.768(4) | 0.155(4) | 440(10) |
| O2     | 0.4224(2) | 0.7584(2) | 0.22910(18) | 115(3) |
| H21    | 0.5305(5) | 0.775(4) | 0.193(3) | 310(9) |
| H22    | 0.3824(5) | 0.837(4) | 0.205(3) | 280(9) |
| O3     | 0.2065(5) | 0.5261(2) | 0.42537(17) | 121(3) |
| H31    | 0.265(5) | 0.559(4) | 0.465(4) | 440(11) |
| H32    | 0.185(5) | 0.437(5) | 0.4664(4) | 570(13) |
| O4w    | 0.7472(2) | 0.7692(2) | 0.0936(2) | 134(3) |
| H41w   | 0.7424(4) | 0.682(4) | 0.084(4) | 380(10) |
| H42w   | 0.7365(5) | 0.824(4) | 0.024(4) | 310(10) |
| O5w    | 0.1078(3) | 0.2362(2) | 0.55985(18) | 143(3) |
| H51w   | 0.1875(5) | 0.180(4) | 0.576(3) | 390(9) |
| H52w   | 0.0475(5) | 0.216(4) | 0.508(4) | 340(10) |
| O6w    | 0.2757(5) | 0.0365(2) | 0.17935(19) | 143(3) |
| H61w   | 0.3305(3) | 0.083(4) | 0.216(3) | 320(9) |
| H62w   | 0.1765(5) | 0.034(4) | 0.212(4) | 400(10) |
| B1     | 0.6329(3) | 0.3950(3) | 0.3255(3) | 105(5) |
| H1     | 0.571(4) | 0.483(3) | 0.370(3) | 190(7) |
| B2     | 0.5362(3) | 0.2593(3) | 0.286(3) | 105(5) |
| H2     | 0.3954(4) | 0.248(3) | 0.305(3) | 300(8) |
| B3     | 0.6727(3) | 0.4073(3) | 0.1577(3) | 93(5) |
| H3     | 0.6464(5) | 0.507(4) | 0.069(3) | 150(7) |
| B4     | 0.8482(3) | 0.3658(3) | 0.27771(3) | 96(5) |
| H4     | 0.948(3) | 0.438(3) | 0.290(3) | 130(7) |
| B5     | 0.7130(3) | 0.2168(3) | 0.4067(3) | 117(5) |
| H5     | 0.7134(4) | 0.1663(3) | 0.519(3) | 200(7) |
| B6     | 0.6494(3) | 0.2284(3) | 0.1364(3) | 93(5) |
| H6     | 0.5764(5) | 0.228(3) | 0.050(3) | 280(8) |
| B7     | 0.8717(3) | 0.3028(3) | 0.1304(3) | 91(5) |
| H7     | 0.9664(3) | 0.354(3) | 0.042(3) | 200(7) |
| B8     | 0.8985(3) | 0.1678(3) | 0.3066(3) | 102(5) |
| H8     | 0.0164(3) | 0.113(3) | 0.356(3) | 190(7) |
| B9     | 0.6782(3) | 0.0929(3) | 0.3113(3) | 110(5) |
| H9     | 0.6164(4) | 0.980(3) | 0.366(3) | 240(8) |
| B10    | 0.8327(3) | 0.1151(3) | 0.1773(3) | 106(5) |
| H10    | 0.894(3) | 0.033(3) | 0.133(3) | 140(7) |

via [B12H12]2− anions to form electroneutral double chains again, now with the formula \( \frac{1}{3} \) [Sn(H2O)3]3[B12H12]3+3, which run parallel to the a-axis (Fig. 6). These double chains get connected to each other through the four remaining interstitial crystal water molecules (O4w–O7w) erecting the layer structure of Sn(H2O)3[B12H12] · 4 H2O.

These interstitial crystal water molecules are bonded via strong classical O–H\(^{\delta+}\)+O\(^{-}\) hydrogen bonds \(d(O–H⋯O) = 175–221\) pm, \(\angle(O–H⋯O) = 153–174^\circ\) to the tin(II)-attached water molecules of hydration (O1–O3; Fig. 7, left). Furthermore, the hydridic hydrogen atoms of the [B12H12]2− anions interact with the protonic hydrogen atoms of the water molecules of hydration. Each [B12H12]2− anion forms six strong non-classical hydrogen bonds with the nearest water molecules, represented by O2, O4w (2 ×), O5w and O6w (2 ×), with H\(^{\delta+}\)⋯H\(^{\delta+}\) distances ranging from 191 to 225 pm (Fig. 7, right, and Fig. 8).

### Vibrational Spectroscopy

Despite the two different boron clusters the infrared (IR) and Raman spectra of both compounds are very similar to each other (Fig. 9) and all observed peaks could be assigned successfully. The O–H stretching bands at 3596, 3523 and 3440 cm\(^{-1}\) are broadened due to hydrogen bonds (O–H\(^{\delta+}\)+⋯O\(^{-}\)) between the tin(II)-coordinating water molecules of hydration and the free interstitial crystal water molecules.

For the B–H stretching modes between 2400 and 2550 cm\(^{-1}\), there can be found peaks in all four spectra. The sharp peaks in the Raman spectra show no hint for any non-classical hydrogen bonds (B–H\(^{\delta+}\)+⋯H–O), whereas the infrared spectra of Sn(H2O)3[B10H10] · 3 H2O exhibit a band at 2470 cm\(^{-1}\) with a distinct shoulder at 2517 cm\(^{-1}\) and a broad band covering an interval from 2400 to 1800 cm\(^{-1}\). The infrared spectra of Sn(H2O)3[B12H12] · 4 H2O displays a sharp band at 2491 cm\(^{-1}\), with a slight shoulder at 2521 cm\(^{-1}\) and only a weakly broadening between 2390 and 2380 cm\(^{-1}\). The splitting of the B–H stretching mode in a low-frequency and high-frequency region is caused by B–H groups participating in hydrogen bonding (low-frequency shift) and groups that do not participate in hydrogen bonding (high-frequency shift). This clearly signalizing the presence of non-classical hydrogen bonds [24].

Possible occurring B–H⋯Sn stretching vibrations are expected in the low field at 2100 to 2000 cm\(^{-1}\) [25, 26], which is debatable for Sn(H2O)3[B10H10] · 3 H2O, but an existing peak might be covered, whereas the IR spectra of Sn(H2O)3[B12H12] · 4 H2O shows no indication of this.

Furthermore, the H–O–H bending vibrations can also be observed in all the spectra. While the IR spectra show sharp bands at 1626 and 1602 cm\(^{-1}\), in the Raman spectra there are just superficial peaks appearing at 1605 and 1602 cm\(^{-1}\). Also the peaks in the O–H bending area reveal a slight broadening in the IR spectra, indicating classical
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and non-classical hydrogen bonds. The remaining signals encountered in the IR spectra at 1079, 1025, 878 and 713 cm$^{-1}$ can be assigned to B–B stretching vibrations, also visible in the Raman spectra at 1007, 998, 737, 616 and 580 cm$^{-1}$. The very intense peaks at 835 and 744 cm$^{-1}$ are caused by the total symmetric breathing modes of the B$_{10}$ and B$_{12}$ cages.

**Conclusion**

Two tin(II) hydro-closo-borate hydrates were accessible from reactions of elemental tin with aqueous solutions of the acids (H$_3$O)$_2$[B$_{10}$H$_{10}$] and (H$_3$O)$_2$[B$_{12}$H$_{12}$]. Both compounds crystallize in the same triclinic space group (P$\overline{1}$) with Z = 2 and differ only slightly in structure and composition. In both compounds the Sn$^{2+}$ cations are coordinated by three oxygen atoms of the corresponding water molecules of hydration, building up non-planar [Sn(H$_2$O)$_3$]$_2^+$ units with Sn–O distances in an interval of 221 to 225 pm and a 151 pm off-center shift. Furthermore, three [B$_{10}$H$_{10}$]$^{2-}$ and [B$_{12}$H$_{12}$]$^{2-}$ cluster anions establish a second coordination sphere with tin(II)-hydrogen contacts (d(Sn–H) = 273–333 pm), providing enough space for the stereochemically active 5sp lone pair of electrons. The Sn$^{2+}$ cations unveil a coordination behavior very similar to that of the heavier congener Pb$^{2+}$ in its hydrated hydro-closo-borate compounds. Even the metal hydrogen contacts are in the same range (d(Pb–H) = 249–338 pm) [7, 11]. But in comparison, the Sn–H distances are substantially

### Table 3

| Atom  | x/a     | y/b     | z/c     | $U_{eq}$ / pm$^2$ |
|-------|---------|---------|---------|------------------|
| Sn    | 0.21607(2) | 0.870397(15) | 0.701266(14) | 123(5)         |
| O1    | 0.0427(2)  | 0.68534(17)  | 0.72700(15)  | 140(3)         |
| H11   | 0.966(3)   | 0.696(2)    | 0.698(2)    | 60(7)          |
| H12   | 0.092(4)   | 0.611(3)    | 0.726(2)    | 370(9)         |
| O2    | 0.1590(2)  | 0.80620(18) | 0.90177(14) | 153(3)         |
| H21   | 0.076(4)   | 0.752(3)    | 0.935(2)    | 390(9)         |
| H22   | 0.189(4)   | 0.859(3)    | 0.939(3)    | 410(9)         |
| O3    | 0.4205(2)  | 0.69803(15) | 0.75219(15) | 143(3)         |
| H31   | 0.5063(3)  | 0.695(2)    | 0.701(2)    | 230(7)         |
| H32   | 0.467(3)   | 0.684(3)    | 0.824(3)    | 380(8)         |
| O4w   | 0.1727(3)  | 0.43274(18) | 0.73808(16) | 175(4)         |
| H41w  | 0.118(3)   | 0.391(3)    | 0.717(2)    | 130(8)         |
| H42w  | 0.264(4)   | 0.427(3)    | 0.720(3)    | 350(10)        |
| O5w   | 0.55527(2) | 0.63692(2)  | 0.96390(17) | 210(4)         |
| H51w  | 0.5500(7)  | 0.57804(5)  | 0.970(5)    | 130(2)         |
| H52w  | 0.515(3)   | 0.683(3)    | 0.006(2)    | 140(7)         |
| O6w   | 0.7400(2)  | 0.67372(2)  | 0.60933(16) | 181(4)         |
| H61w  | 0.745(4)   | 0.730(3)    | 0.547(3)    | 400(9)         |
| H62w  | 0.7374(1)  | 0.603(3)    | 0.599(3)    | 530(12)        |
| O7w   | 0.9107(2)  | 0.62105(18) | 0.01277(18) | 197(4)         |
| H71w  | 0.899(4)   | 0.614(3)    | 0.083(3)    | 350(9)         |
| H72w  | 0.8396(6)  | 0.6345(8)   | 0.981(4)    | 110(2)         |
| B1    | 0.7925(3)  | 0.0050(2)   | 0.7343(2)   | 114(5)         |
| H1    | 0.854(3)   | 0.898(2)    | 0.770(2)    | 200(6)         |
| B2    | 0.55593(3) | 0.0322(2)   | 0.7773(2)   | 112(5)         |
| H2    | 0.465(3)   | 0.950(2)    | 0.8281(19)  | 160(6)         |
| B3    | 0.6501(3)  | 0.0538(2)   | 0.6248(2)   | 120(5)         |
| H3    | 0.618(3)   | 0.982(2)    | 0.5755(18)  | 140(5)         |
| B4    | 0.8678(3)  | 0.1317(2)   | 0.6069(2)   | 117(5)         |
| H4    | 0.981(3)   | 0.113(2)    | 0.5470(19)  | 190(6)         |
| B5    | 0.9074(3)  | 0.1569(2)   | 0.7493(2)   | 120(5)         |
| H5    | 0.0443(3)  | 0.151(2)    | 0.7767(19)  | 190(6)         |
| B6    | 0.7145(3)  | 0.0949(2)   | 0.8547(2)   | 126(5)         |
| H6    | 0.725(3)   | 0.044(2)    | 0.954(2)    | 210(6)         |
| B7    | 0.5220(3)  | 0.2002(2)   | 0.8043(2)   | 133(5)         |
| H7    | 0.4073(3)  | 0.2202(2)   | 0.8694(19)  | 160(6)         |
| B8    | 0.4836(3)  | 0.1753(2)   | 0.6620(2)   | 122(5)         |
| H8    | 0.3493(3)  | 0.182(2)    | 0.6352(19)  | 170(6)         |
| B9    | 0.6762(3)  | 0.2364(2)   | 0.5578(2)   | 125(5)         |
| H9    | 0.6593(3)  | 0.286(2)    | 0.4628(19)  | 150(5)         |
| B10   | 0.8344(3)  | 0.2998(2)   | 0.6340(2)   | 130(5)         |
| H10   | 0.931(3)   | 0.388(2)    | 0.5864(18)  | 110(5)         |
| B11   | 0.7400(3)  | 0.2783(2)   | 0.7874(2)   | 131(5)         |
| H11   | 0.7693(3)  | 0.350(2)    | 0.8377(19)  | 160(6)         |
| B12   | 0.5984(3)  | 0.3265(2)   | 0.6677(2)   | 122(5)         |
| H12   | 0.5343(3)  | 0.431(2)    | 0.644(2)    | 230(6)         |
longer than the Sn–H distance found in the metallacarborane \[10\text{-endo-(SnPh}_3\text{-})_{10}\mu-H-7,8\text{-nido-C}_2B_9H_{10}][\text{trans-Ir(CO)(PPh}_3\text{)}_2\text{(MeCN)}]\], with \(d(\text{Sn–H}) = 234\) pm [27], as well as the Sn–H contacts found in several dialkylstannylene \([\text{Sn}(H_2O)\text{)}_3[B_{12}H_{12}]\cdot 4H_2O\) [25, 26, 28, 29].

In the same way as the Pb\(^{2+}\) cations, Sn\(^{2+}\) cannot activate the B–H bonds, neither for the \([B_{12}H_{12}]^2^-\) nor for the more reactive \([B_{10}H_{10}]^{2-}\) case. It seems that the desired B–H bond activation is only provided by Bi\(^{3+}\) cations and \([B_{10}H_{10}]^{2-}\) or \([B_{12}H_{12}]^{2-}\) anions [18, 19] under physiological conditions so far.

**Experimental**

Sn\((H_2O)\text{)}_3[B_{10}H_{10}] \cdot 3H_2O

The hydrated decahydro-\textit{closo}-decaborate compound with divalent tin was yielded after the reaction of tin powder (99.9%, Fluka) with an excess of an aqueous solution of the free acid \((H_2O)_2[B_{10}H_{10}]\), obtained by passing an aqueous solution of Cs\([B_{10}H_{10}]\) [30, 31] through a strong acidic ion-exchange column (Merck, Amberlite IR-120). After the hydrogen evolution has concluded, the resulting colorless solution was evaporated at 50 °C to dryness. The white precipitation was again dissolved in water, filtered to remove the remaining tin powder and evaporated.
isothermally at room temperature to obtain crystals within several days. The pristinely colorless and transparent tin(II) salt crystals with the $[\text{B}_{10}\text{H}_{10}]^2-$ anion, for being a much stronger reductant than $[\text{B}_{12}\text{H}_{12}]^2-$, becomes brown and opaque over time due to the continuous precipitation of colloidal tin.

$\text{Sn(H}_2\text{O)}_3[\text{B}_{12}\text{H}_{12}]\cdot 4\text{H}_2\text{O}$

The analogous $[\text{B}_{12}\text{H}_{12}]^2-$ salt was prepared by the reaction of tin powder (99.9%, Fluka) with an aqueous solution of the free acid (H$_3$O)$_2[\text{B}_{12}\text{H}_{12}]$, obtained by passing an aqueous solution of Cs$_2[\text{B}_{12}\text{H}_{12}]$ [1, 32, 33] through a strong acidic ion-exchange column (Merck, Amberlite IR-120). The reaction solution was heated up to 50 $^\circ$C for 2 days, filtered and then evaporated at room temperature to yield colorless single crystals within a few days.

An empirical absorption correction was performed by using the program Scalepack [34]. The crystal structure solutions and refinements were carried out with the program package SHELX-97 [35]. Both structure refinements include the positions of all hydrogen atoms without any constraints. The coefficients of the equivalent isotropic displacement parameters are defined as $U_{eq} = \frac{1}{3} \left[ U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba*b*cos\gamma + 2U_{13}aca*c*cos\beta + 2U_{23}bcb*c*cos\alpha \right]$ in pm$^2$ [36]. Further details of the crystal structure investigations may be
obtained from the CCDC (www.ccdc.cam.ac.uk) and FIZ Karlsruhe (www.fiz-karlsruhe.de) on quoting the depository numbers 1872762 for Sn(H2O)3[B10H10] · 3 H2O and 1872763 for Sn(H2O)3[B12H12] · 4 H2O.

The infrared spectroscopic data were measured as potassium-bromide powder pellets on a Bruker ALPHA FT/IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany). Raman spectra of the single crystals were recorded by using an XploRA Raman microscope (HORIBA Jobin Yvon GmbH, Bensheim, Germany).

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