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$N \rightarrow Sn$ -Coordinated Stannaoxidoborates Containing a SnB_4O_6 Unit

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S Supporting Information

ABSTRACT: We report here the synthesis of new $N \rightarrow Sn$ -coordinated stannaoxidoborates H[LSnB₄O₆R₄] {L = $[2,6-(Me_2NCH_2)C_6H_3]^-$ and R = Ph (6), 4-Br-Ph (7), 3,5-(CF₃)₂-Ph (8), and 4-CHO-Ph (9)} containing a nonsymmetric SnB₄O₆ unit. Compounds 6-9 represent new derivatives of the pentaborates $[B_5O_6R_4]^-$ in which the central boron is substituted by a tin atom. Compounds 6-9 were characterized by means of elemental analysis, electrospray ionization mass spectrometry, and NMR spectroscopy and in the case of 6-8 also by single-crystal X-ray diffraction analysis. The structures of $N \rightarrow$ Sn-coordinated stannaoxidoborates 6-8 consist of a spirobicyclic arrangement, with two six-membered SnB₂O₃ rings at the tin atom providing the new stannaoxidoborate $[LSnB_4O_6R_4]^-$ motif, which is compensated for by



the proton atom coordinated to the Me_2N group of the ligand L. The linear and thermal properties of 6-9 were studied with the help of electronic absorption spectra and differential scanning calorimetry. In addition, the presence of the nonsymmetric stannaoxidoborate SnB_4O_6 unit in 6, 7, and 9 prompted us to investigate their second-order nonlinear-optical properties.

INTRODUCTION

Borate compounds are of considerable interest because of their rich structural chemistry and potential applications in mineralogy, luminescence, and nonlinear-optical (NLO) materials.¹ The chemistry of inorganic borates is widely studied and quite complex. This complexity arises from the flexibility of boron, which can form planar and nonplanar BO3 groups and tetrahedral BO₄ groups. These units may further link together by sharing common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks.^{1,2} In the past, borates have formed the following systems: maingroup and transition-metal (TM) borates,³ rare-earth borates,⁴ and organic-⁵ and TM-complex-⁶templated borates. Most metal borates were made by high-temperature solid-state reaction methods or boric acid flux methods. However, organic- or TMcomplex-templated borates were usually synthesized under moderate-temperature hydrothermal conditions and demonstrated that a useful property of metallo-templated borate can be the function of metal cations.⁶

One of the important applications of borates is based on their optical properties, for example, second-order NLO properties.^{1e} The most well-known examples are the discovery of β -BaB₂O₄ or LiB₃O₅ as useful NLO materials for efficient second harmonic generation (SHG) of Nd:YAG lasers.⁷ Their excellent NLO properties and wide use in industry rekindled the enthusiasm about the study of borates with NLO activities. Being in the same group as boron, aluminum can exist in the AlO₄, AlO₅, and AlO₆ forms and was introduced into the borate

system by Lehmann and Teske, giving porous aluminoborate analogues.⁸ In recent years, attempts to incorporate other heteroatoms into a pure borate framework have resulted in some intriguing systems, such as B-O-P, $^9B-O-V$, $^{10}B-O-Co$, $^{2b}B-O-Zn$, $^{11}B-O-Ga$, $^{12}B-O-Ge$, 13 and B-O-Sn. 14

As mentioned, borates have been studied as NLO materials because of planar ionic groups with π -conjugated systems such as BO3 trigonal planes, which are responsible for efficient SHG coefficients of the materials.¹⁵ However, there are few noncentrosymmetric structures that contain only BO₃ units. It was demonstrated that substitution of the central boron atom in pentaborate $[B_5O_{10}]^{5-}$ by a copper atom is possible to provide a pseudosymmetric [CuB₄O₁₀]⁶⁻ unit.¹⁶ The isolated complex $Li_6[CuB_4O_{10}]$ has been shown to be a new congruently melting NLO material.¹⁶

In addition, while the chemistry of the pentaborates $[B_5O_{10}]^{5-}$ is well explored, analogous *B*-aryl-substituted pentaborates $[B_5O_6R_4]^-$ are rare.¹⁷ In 2002, Nashihara et al. reported the reaction of organoboric acid with a parent rhodium complex to yield $[Rh(PMe_3)_4]^+[B_5O_6R_4]^-$, where the anionic part of the *B*-aryl-substituted pentaborate $[B_5O_6R_4]^-$ is compensated for by the rhodium complex cation.¹⁷ During the reaction, however, no substitution of the central boron atom in the *B*-aryl-substituted pentaborate $[B_5O_6R_4]^-$ has been detected.

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Recently, it was demonstrated that the boron atom of the boroxine ring can be easily substituted by metal atoms to give a variety of metallaboroxines of the general formula $M(O_3B_2R_2)$, where M is Pt,¹⁸ Al,¹⁹ Sb,^{20a} Bi,^{20a} or Sn.^{20b} Later on, we have provided the easy preparation of new stannaboroxines of the general formula $(L-k_3N_2C)PhSn(O_3B_2R_2)$, where L is 2,6-bis(dimethylaminomethy)phenyl and R is an aryl substituent, respectively, containing a six-membered SnB_2O_3 ring.²¹ Our extensive research in the field of stannaboroxine systems has also provided the synthesis of a new type of stannaoxidoborate, $H[(L-k_2NC)SnB_4O_6R_4]$, derivatives of the pentaborates $[B_5O_6R_4]^-$ in which the central boron atom is substituted by a tin atom. In this paper, we report the synthesis, X-ray crystal structure, and optical properties of stannaoxidoborates $H[(L-k_2NC)SnB_4O_6R_4]$ containing a $[SnB_4O_6R_4]^-$ unit.

RESULT AND DISCUSSION

Synthesis and Characterization of Compounds 2–9. The treatment of organotin(IV) carbonate $(L-k_3N_2C)PhSnCO_3$ (1) with organoboric acids $RB(OH)_2$ at a 1:2 molar ratio provided the corresponding organotin(IV) stannaboroxines $(L-k_3N_2C)PhSn(O_3B_2R_2)$, where $L = [2,6-(Me_2NCH_2)C_6H_3]^$ and R = Ph (2),²¹ 4-Br-Ph (3),²¹ 3,5-(CF_3)_2-Ph (4), and 4-CHO-Ph (5)²¹ (Scheme 1). Compounds 2, 3, and 5 were





prepared and characterized according to the literature.²¹ Compound 4 was characterized by NMR spectroscopy. The ¹H NMR spectrum of 4 revealed a AX spin system of methylene CH_2N groups and a single resonance of NMe_2 protons of the chelating ligand L. The ¹¹⁹Sn NMR spectrum of 4 showed single resonances at δ_{Sn} –366.9, suggesting the presence of a six-coordinated tin(IV) center.^{21,22}

Rather surprisingly, compounds 2-5 hydrolyze to give stannaoxidoborates $H[(L-k_2NC)SnB_4O_6R_4]$ {L = [2,6- $(Me_2NCH_2)C_6H_3]^-$, with R = Ph (6), 4-Br-Ph (7), 3,5- $(CF_3)_2$ -Ph (8), and 4-CHO-Ph (9); see Scheme 1}. These compounds were isolated as crystalline materials in low yield (around 10%) when 2-5 were dissolved in toluene and allowed

to stand in air (see the Supporting Information). Reactions of 2-5 with 2 equiv of the parent organoboric acid RB(OH)₂ or of 1 with 4 equiv of $RB(OH)_2$ provided 6–9 in moderate yield (around 60%) along with the elimination of CO₂, H₂O, and C_6H_6 . The formation of 6-9 is remarkable in that the diorganotin(IV) fragment of the starting 2-5 reacts with organoboric acid under the elimination of a benzene molecule. The formation of a monoorganotin(IV) fragment with new Sn-O(B) bonds proceeds readily at ambient conditions despite Sn-C bond cleavage reactions usually occur at elevated temperatures.²³ This suggests that the presence of $N \rightarrow Sn$ coordination in the starting 2-5 facilitates the elimination of a benzene molecule to form a monoorganotin(IV) fragment in 6-9. In addition, the hydrolytic process is accompanied by transformation of a L- k_3N_2C tridentate fashion in starting 2-5 to a L- k_2NC bidentate fashion of ligand L found in 6–9. A second Me₂N group of ligand L is protonated during the reaction, and the Me2NH⁺ group compensates for the stannaoxidoborate $[(L-k_2NC)SnB_4O_6R_4]^-$ fragment in 6–9. This demonstrates the crucial role of ligand L for the formation of **6–9**. To give further support for the importance of ligand L, the reaction of Ph_2SnCl_2 or $BuSnCl_3$ with 4 equiv of $PhB(OH)_2$ was performed. These reactions, however, provided the starting compounds (detected by the ¹H and ¹¹⁹Sn NMR spectroscopy) and an insoluble ill-defined material only.

It should be also noted that studies dealing with the reactions of N \rightarrow Sb-coordinated organoantimony and bismuth oxides [LMO]₂ (M = Sb, Bi) with organoboric acids yielded the pentaborates [B₅O₆R₄]⁻ only.²⁴ Similarly, the complex [Rh-(PMe₃)₄]⁺[B₅O₆R₄]⁻ has been prepared by the reaction of organoboric acids with a parent rhodium complex.¹⁷ This suggests a specific role of the tin atom in the formation of a new class of metalloborates, where substitution of the central boron atom of the pentaborates [B₅O₆R₄]⁻ took place.

All prepared complexes 6-9 are moderately soluble in chlorinated solvents. All of the prepared compounds were characterized by NMR spectroscopy and electrospray ionization mass spectrometry. The molecular structures of 6-8 have been characterized by X-ray diffraction analysis.

The ¹H NMR spectra of compounds 6-9 showed the presence of ligand L and B-aryl substituents R in a 1:4 mutual integration ratio. The 1 H NMR spectra of compounds 6–9 revealed two AX spin systems of methylene CH₂N and four signals for the NMe2 groups of ligand L, suggesting the presence of nonsymmetric character of a tin coordination polyhedron with nonequivalent CH₂NMe₂ arms of ligand L. In addition, the ¹H NMR spectra of compounds 6–9 revealed one broad downfield signal of the $\rm NHMe_2$ proton in the range of δ 11.71 (8) to 12.46 (7) in a 1:4 mutual integration ratio with methylene CH_2N protons. The ¹H NMR spectrum of **9** showed four singlet resonances of CHO protons at δ 10.00, 10.03, 10.06, and 10.09. The nonequivalency of the B-aryl substituents R was also proven by the ¹³C NMR spectra, where signals of four *B*-aryl substituents were observed. The ¹³C NMR spectrum of 9 showed four singlet resonances of CHO carbon atoms at δ 192.6, 192.8, 193.1, and 193.3. Similarly, four signals at δ –62.8, -62.9, -63.0, and -63.2 were detected in the ¹⁹F NMR spectrum of 8.

The ¹¹⁹Sn NMR spectra revealed one signal at δ -554.2 for 6, δ -553.2 for 7, δ -550.1 for 8, and δ -553.2 for 9, and these values are shifted upfield compared with the starting 2-5 (in the range of δ -359.1 to -366.9),²¹ where a diorganotin(IV) fragment is involved in the six-membered SnB₂O₃ ring. On the



Figure 1. POV-ray²⁸ schematic representation of the molecular structures of $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and 8, together with schematic atom numbering. The hydrogen atoms and toluene molecules (for 6 and 7) are omitted for clarity. Selected bond lengths [Å] and angles [deg] for 6: Sn1–N1 2.345(3), Sn1–N2 3.779(3), Sn1–O1 2.035(2), Sn1–O3 2.054(2), Sn1–O4 2.135(2), Sn1–O6 2.012(2). Selected bond lengths [Å] and angles [deg] for 7: Sn1–N1 2.333(5), Sn1–N2 3.744(5), Sn1–O1 2.121(4), Sn1–O3 2.016(4), Sn1–O4 2.046(4), Sn1–O6 2.029(4). Selected bond lengths [Å] and angles [deg] for 8: Sn1–N1 2.309(4), Sn1–N2 3.693(4), Sn1–O1 2.057(2), Sn1–O3 2.052(3), Sn1–O4 2.017(2), Sn1–O6 2.129(2).

other hand, the values are comparable with those found for Y \rightarrow Sn-coordinated monoorganotin(IV) compounds [{C₆H₃(CH₂NMe₂)₂-2,6}SnBr₃] (δ -601),²⁵ [{C₆H₃(CH₂OMe)-2-(CH₂NMe₂)-6}SnBr₃ (δ -531.2),²⁶ and [{C₆H₂[P(O) (OR)₂]₂-1,3-t-Bu-5}SnBr₃] (δ -885).²⁷ The NMR data thus support the transformation of the starting diorganotin(IV) fragment to N \rightarrow Sn-coordinated monoorganotin(IV) moieties containing a negative tin center with a nonsymmetric arrangement.

To establish unambiguously the structural feature of compounds 6–9, single-crystal X-ray structural analysis was carried out. Suitable single crystals of $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and 8 were obtained from a saturated toluene solution of 6–8 at room temperature, and molecular structures of $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and 8 are depicted together with relevant structural parameters in Figure 1 (for crystallographic parameters, see Table S1 in the Supporting Information).

The molecular structures of $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and **8** are widely identical. The tin atom is six-coordinated by four oxygen atoms of two $O_3B_2R_2$ units and by nitrogen and carbon atoms of the ligand L. In fact, established structures of 6-8 showed the presence of two central SnB_2O_3 ring systems and one organic substituent L- k_2NC coordinated to the tin atom, providing the spirobicyclic arrangement. While the nitrogen

atom N1 of the L- k_2NC ligand is coordinated to the tin atom, as indicated from the Sn1-N1 bond distances [in the range of 2.309(4)-2.345(3) Å], the second nitrogen atom N2 is out of the tin coordination sphere [in the range of 3.693(4) - 3.779(3)Å]. The values of Sn–O(B) bond distances in both SnB₂O₃ rings of 6-8 differ substantially. While the values of Sn-O1(B), Sn-O3(B), and Sn-O6(B) [in the range of 2.012(2)-2.054(2) Å] indicate the presence of the Sn–O covalent bonds in 6 [Σ_{cov} (Sn,O) = 2.03],²⁹ the Sn–O4(B) bond distance is prolonged [2.135(2) Å] as a result of O4-H2-N2 hydrogen bonding in **6** [the bond distance of O4-N2 is 2.776(4) Å in **6**]. A similar situation has also been found in 7 and 8, where the bond distances of Sn-O1(B) [2.121(4) Å] in 7 and Sn-O6(B)[2.129(2) Å] in 8 are prolonged in comparison with the remaining Sn-O(B) distances [in the range of 2.016(4)-2.057(2) Å]. These oxygen atoms are again involved in the O1-H2-N2 (7) and O6-H2-N2 (8) hydrogen bonding [the bond distance of O1-N2 is 2.724(8) Å in 7, and that of O6-N2 is 2.763(6) Å in 8].

The structures of 6-8 consist of a spirobicyclic arrangement of two six-membered SnB_2O_3 rings at the tin atom, providing the new stannaoxidoborate $[(L-k_2NC)\text{SnB}_4\text{O}_6\text{R}_4]^-$ motif, which is compensated for by a proton atom coordinated to one Me₂N group of the L- k_2NC ligand. All covalent B–O(Sn)



Figure 2. Distortion of the planarity of both the SnB_2O_3 rings within SnB_4O_6 unit in 6–8.

bonds within the SnB₄O₆ unit are slightly shortened [in the range of 1.323(5)–1.343(5) Å] in comparison with the remaining B–O(B) covalent bond [in the range of 1.380(7)–1.392(5) Å]. All of these values are, however, still a bit shorter than the sum of the covalent radii $\Sigma_{cov}(B,O) = 1.48$ Å.²⁹

The distortion of the planarity of both SnB_2O_3 rings in the SnB_4O_6 unit depends on the *B*-aryl substituents R and provides different mutual orientations of both the SnB_2O_3 rings within SnB_4O_6 unit. In compounds 6 and 7, where R is Ph and 4-BrPh, the oxygen atom O2 of the B1–O2–B2 moiety is bent out by 0.740 Å from the mean plane defined by the O1–Sn1–O3 backbone in 6 (0.604 Å in 7). Similarly, the oxygen atom O5 of the B3–O5–B4 moiety is bent out by 0.663 Å from the mean plane defined by the O4–Sn1–O6 backbone in 6 (0.609 Å in 7; see Figure 2).

A different situation has been found in 8 containing the 3,5-CF₃-Ph group as the *B*-aryl substituent. The oxygen atom O2 of the B1–O2–B2 moiety is strongly bent out by 0.928 Å from the mean plane defined by the O1–Sn1–O3 backbone in 8, while the oxygen atom O5 of the B3–O5–B4 moiety is strongly bent out by 0.737 Å from the mean plane defined by the O4–Sn1–O6 backbone in 8 (see Figure 2). As a result of this puckering of the SnB₄O₆ unit, the O2–B3 and O5–B2 bond distances (the bond distance of the oxygen atoms O2 and O5 involved in B–O–B bonding and the boron atoms B3 and B2 of the opposite SnB₂O₃ rings) are 3.859(7) and 3.930(7) Å, respectively, in 8 [compared with similar bond distances of O2–B4 and O5–B1 of 4.315(6) and 4.121(6) Å found in 6 and 4.465(10) and 4.317(10) Å in 7, respectively].

In addition, the bond distances of B2–B3 and B2C_{ipso}– B3C_{ipso} carbon atoms (C_{ipso} atoms of the *B*-aryl substituent) are 3.289(9) and 3.559(7) Å, respectively, suggesting the presence of a $\pi-\pi$ stacking interaction between the two 3,5-CF₃-Ph groups in 8 (see Figures 2 and 3).

This phenomenon has not been, however, detected in **6** and 7, where the closest contacts of two boron atoms of the opposite SnB_2O_3 rings are 3.759(7) Å (**6**) and 3.945(12) Å (7), respectively, with the bond distances of the parent C_{ipso} atoms of *B*-aryl substituents at 5.015(6) Å (**6**) and 5.402(10) Å (7) (see Figure 2). As a result of the different mutual orientations of both the SnB_2O_3 rings in SnB_4O_6 unit, compound $6 \cdot \text{C}_7\text{H}_8$ belongs to the noncentrosymmetric monoclinic space group $P2_1$, compound $7 \cdot \text{C}_7\text{H}_8$ belongs to the noncentrosymmetric orthorhombic space group $P2_1$ 2_1 2_1 , and compound **8** crystallizes in the centrosymmetric triclinic space group $P\overline{1}$



Figure 3. $\pi - \pi$ stacking interaction between the two 3,5-CF₃-C₆H₃ groups within the stannaoxidoborate $[(L-k_2NC)SnB_4O_6R_4]^-$ unit of 8.

(for a comparison of 6-8 with the structures of related pentaborates $[B_5O_{10}]^{n-}$, see the Supporting Information).

In addition, the thermal behavior of stannaoxidoborates 6-9 was studied by differential scanning calorimetry (DSC). The thermogram of selected compound **6** is shown in Figure 4; the



40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C Temperature / °C



fundamental thermal properties of all target complexes are listed in Table 1. A joint feature of all of the target compounds 6-9 is their solid-solid (s-s) transition, followed by decomposition. The monotropic irreversible s-s transitions are being observed within the range of 170–200 °C and are accompanied by sharp exothermic peaks. The irreversibility of this transition has been verified by cooling the sample upon reaching ca. 240 °C and repeated heating (see the onset in Figure 4). Compounds 6-9 underwent thermal decomposition

Table 1. (Non)linear-Optical and Thermal Properties of 6-9

| compound | λ_{\max} [nm (eV)] | $\varepsilon (\times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$ | $d_{ m eff} \left({ m pm} \atop { m V}^{-1} ight)$ | s—s transition (°C) | $\overset{T_{\mathrm{d}}}{(^{\circ}\mathrm{C})}$ |
|----------|----------------------------|---|--|---------------------------|--|
| 6 | 237 (5.23) | 46.15 | 1.1 | 180 | 320 |
| 7 | 238 (5.21) | 69.95 | 1.4 | 182 | 311 |
| 8 | 237 (5.23) | 54.45 | | 174 | 301 |
| 9 | 259 (4.79) | 74.79 | 1.6 | 200 | 280 |
| | | | | | |

in a similar range of 280–320 °C, which is relatively narrow $(\Delta T \sim 30-40$ °C), indicating the thermal robust behavior of these novel heteroborates.

Linear and NLO Properties. The linear-optical properties of stannaoxidoborates 6-9 were investigated by electronic absorption spectra, as shown in Figure 5.



Figure 5. UV/vis absorption spectra of 6 - 9 measured in CH_2Cl_ (2 \times 10^{-5} M).

Table 1 lists the positions of the longest-wavelength maxima λ_{\max} and corresponding molar absorption coefficients ε . The spectra of 6-9 are dominated by an intensive absorption band, with a position that is a function of the peripheral R substituents and most likely can be attributed to intramolecular charge transfer (ICT) from the central stannaoxidoborate [(L k_2NC)SnB₄O₆R₄]⁻ electron-rich part to peripheral R substituents. Considering the R-substituents as electron deficient ligands, this structural arrangement superficially resembles metal-to-ligand charge transfer. Whereas the longest-wavelength absorption maxima (λ_{max}) of 6–8 are almost identical $(\lambda_{\text{max}} = 237 - 238 \text{ nm})$ and differ mainly in the molar absorption coefficient $\varepsilon = (46.15 - 69.95) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, the formylsubstituted derivative 9 showed a red-shifted band with the maximum appearing at 259 nm ($\varepsilon = 74.79 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). Considering the stannaoxidoborate $[(L-k_2NC)SnB_4O_6R_4]^-$ unit as electron donors, the peripheral formyl groups behave as moderate acceptors placed in conjugated positions. This $D-\pi$ -A arrangement allows the most efficient ICT, and the most bathochromically shifted charge-transfer band is being observed for 9. Unsubstituted and bromine-substituted derivatives 6 and 7 do not bear any electron acceptors (bromine can rather be

considered as the electron donor),³⁰ while the nonconjugated CF_3 groups placed in positions 3 and 5 also have a diminished effect. Compounds **6–9** showed very weak or no emissive properties, however.

As a result of the above-discussed coordination found in 6-8, all of the Sn–O bonds in the SnO₄ polyhedra of 6-8 are of different lengths. Each of the four boron atoms surrounding the central tin atom is on a unique crystallographic site, and each BRO₂ polyhedron contains different B–O bond lengths with various distortions. Additionally, none of the BRO₂ groups are in the same plane. On the basis of the symmetry space groups revealed by the X-ray measurements (Table S1 in the Supporting Information), we have investigated the second-order NLO properties of the noncentrosymmetric molecules 6 and 7 as well as 9 of an unknown arrangement. As mentioned above, the stannaoxidoborate 8 possesses the centrosymmetric space group $P\overline{1}$ and, therefore, delivered no SHG signal. Figure 6 shows the second-order susceptibility of 6, 7, and 9 as a



Figure 6. Dependence of the second-order susceptibility of 6, 7, and 9 versus the applied aligned dc electric field. The saturated dc electric field alignment is indicated by the vertical lines.

function of the applied direct-current (dc) electric field strength, and Table 1 lists the second-order susceptibilities $d_{\rm eff}$. As can be seen, saturation appears at the dc electric field strength of about 4 kV cm^{-1} for all three samples, which indicates the maximal alignment of the studied crystalline powders. The maximal d_{eff} value of 1.6 pm V⁻¹ was achieved for compound 9, which correlates well with its bathochromically shifted longest-wavelength absorption maxima and also confirms its noncentrosymmetric arrangement. Compound 7 showed susceptibility d_{eff} equal to 1.4 pm V⁻¹, whereas this is 1.1 pm V⁻¹ for **6**. Although these values are less than those for α -BiB₃O₆ crystallites (about 4.2 pm V⁻¹),^{28,31} they can further be enhanced by appropriately changing the central anion and its peripheral moieties, defining the principal NLO response. It should be mentioned that in the case of α -BiB₃O₆ as well as the well-known β -BaB₂O₄ such opportunities were already exhausted. However, the SHG output signals are of the same order, and their dc kinetics is almost the same, which confirms the common origins of the observed effects. Some additional effects such as fluorescence scattering, particularly for weakly emissive 7, may also play a role. The second-order susceptibility efficiency correlates with the position of the chrage-transfer band; the less energy of the longest-wavelength absorption maxima favors enhanced second-order susceptibility. It is also

worth noting that the SHG signals for 6, 7, and 9 not only reveal promising and tunable NLO properties but also provide a highly sensitive and definitive test for the absence of the center of symmetry.³²

CONCLUSION

In conclusion, we report here an easy and straightforward synthesis of new N \rightarrow Sn-coordinated stannaoxidoborates H[(L k_2NC)SnB₄O₆R₄] (6-9) containing a nonsymmetric SnB₄O₆ unit. Compounds 6-9 represent new derivatives of the pentaborates $[B_5O_6R_4]^-$ in which the central boron atom is substituted by a tin atom. Compounds 6-9 were characterized by means of elemental analysis and NMR spectroscopy and in the case of 6-8 also by single-crystal X-ray diffraction analysis. The structures of 6-8 consist of a spirobicyclic arrangement of two six-membered stannaboroxine SnB₂O₃ rings at the tin atom, providing a new SnB_4O_6 motif. The presence of a tin atom provided distortion of the planarity of both SnB2O3 rings within the SnB_4O_6 unit in 6–8. The distortion of the planarity depends on the B-aryl substituents R and provides different mutual orientations of both SnB₂O₃ rings within the SnB₄O₆ unit. The linear and thermal properties of 6-9 were studied further, and it was shown that it differs mutually depending on the B-aryl substituents R as well. It is evident that required properties of this new class of heteropentaborates can be tuned by the appropriate B-aryl substituents R. In addition, singlecrystal X-ray diffraction analysis and NMR studies in solution suggested a nonsymmetrical arrangement of the tin atom in the stannaoxidoborate SnB4O6 unit. For this reason, the secondorder NLO properties of complexes 6, 7, and 9 were investigated. The maximal d_{eff} of 1.6 pm V⁻¹ was measured for 9 with the peripheral formyl groups, which also showed the most bathochromically shifted λ_{max} . Unsubstituted and bromine-substituted stannaoxidoborate 6 and 7 possess susceptibilities of 1.1 and 1.4 pm V⁻¹. However, it is crucial that the SHG output signals are of the same order for all of the samples.

EXPERIMENTAL PART

General Methods. All reactions were carried out under argon, using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Compounds 1–3 and 5 were prepared according to the literature, ^{20,21} and organoboric acids were purchased from Sigma-Aldrich. The ¹H, ¹³C, and ¹¹⁹Sn NMR spectra were recorded on a Bruker Avance500 spectrometer at 300 K in CDCl₃. The ¹H, ¹³C, and ¹¹⁹Sn NMR chemical shifts δ are given in ppm and referenced to external Me₄Si and Me₄Sn. Elemental analyses were performed on a LECO-CHNS-932 analyzer. The positive- and negative-ion electrospray ionization mass spectrometry (ESI-MS) spectra were measured on an Esquire 3000 ion-trap analyzer (Bruker Daltonics, Bremen, Germany) in the range m/z 50–2000. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 5 μ L min⁻¹. The ion-source temperature was 300 °C, the tuning parameter compound stability was 100%, and the flow rate and pressure of N₂ were 4 L min⁻¹ and 10 psi, respectively.

Synthesis of $[L-k_3N_2C]$ PhSn{O₃B₂[3,5-(CF₃)₂C₆H₃)]₂} (4). 3,5-(CF₃)₂C₆H₃B(OH)₂ (412 mg, 1.6 mmol) was added to a solution of 1 (357 mg, 0.80 mmol) in CH₂Cl₂ (20 mL) at room temperature. The reaction mixture was stirred for an additional 24 h at this temperature and then evaporated in vacuo. The resulting white solid was washed with hexane (10 mL) and dried in vacuo to give 4 as a white crystalline solid. Yield: 460 mg, 65%. Mp: 172–175 °C. Anal. Calcd for C₃₄H₃₀B₂F₁₂N₂O₃Sn (MW 882.92): C, 46.1; H, 3.3. Found: C, 46.2; H, 3.4. ¹H NMR (CDCl₃, 25 °C): δ 2.44 (s, 12H, NCH₃), 3.20 (AX pattern, 2H, CH₂N), 4.62 (AX pattern, 2H, CH₂N), 7.21 (t, 1H, ArH),

7.35 (d, 2H, ArH), 7.52 (m, 3H, ArH), 7.78 (d, 2H, ArH), 7.97 (s, 2H, ArH), 8.53 (s, 4H, ArH). $^{13}C{^{1}H}$ NMR (CDCl₃, 25 °C): δ 44.7 (CH₃), 62.9 (CH₂N), 123.4 (B-Ar-C), 123.9 (CF₃), 127.9 (Ph-C-3,5), 128.9 (L-C-3,5), 130.1 (Ph-C4), 130.3 (L-C-4), 130.6 (B-Ar-C), 134.3 (B-Ar-C), 134.5 (Ph-C-2,6), 138.5 (L-C1), 140.0 (B-Ar-C), 140.9 (Ph-C-1), 144.9 (L-C-2,6). 19 F NMR (CDCl₃, 25 °C): δ -62.9. 119 Sn NMR (CDCl₃, 25 °C): δ -366.9.

Synthesis of $H[(L-k_2NC)SnB_4O_6Ph_4]$ (6). PhB(OH)₂ (330.1 mg, 2.71 mmol) was added to a stirred solution of 1 (303 mg, 0.67 mmol) in CH₂Cl₂ (20 mL) at room temperature. The reaction mixture was stirred for an additional 5 days at this temperature and then evaporated in vacuo. The resulting white solid was washed with toluene (10 mL) and dried in vacuo to give 6 as a white crystalline solid. Yield: 303.8 mg, 59%. Mp: 171–173 °C. Anal. Calcd for $C_{36}H_{40}B_4N_2O_6Sn$ (MW 758.65): C, 56.9; H, 5.3. Found: C, 56.7; H, 5.2. ¹H NMR (CDCl₃, 25 °C): δ 2.34 (s, 3H, CH₃N), 2.48 (d, 3H, CH₃N), 2.68 (d, 3H, CH₃N), 3.07 (s, 3H, CH₃N), 3.20 and 4.82 (AX pattern, ${}^{2}J_{H-H}$ = 13.6 Hz, 2H, CH_2N), 3.43 and 5.41 (AX pattern, ${}^2J_{H-H} = 11.6$ Hz, 2H, CH_2N), 7.02 (t, 1H, ArH), 7.16-7.51 (m, 14H, ArH),7.74 (d, 2H, ArH), 8.11 (d, 4H, ArH), 8.22 (d, 2H, ArH), 12.39 (s, 1H, NH⁺). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 41.1 (CH₃N), 43.9 (CH₃N), 44.1 (CH₃N), 47.3 (CH₃N), 63.4 (CH₂N), 63.7 (CH₂N), 127.2 (B-Ar-C), 127.3 (B-Ar-C), 127.4 (B-Ar-C), 127.7 (L-C-3), 128.1 (L-C-5), 128.7 (B-Ar-C), 129.5 (B-Ar-C), 129.6 (B-Ar-C), 129.7 (B-Ar-C), 130.0 (B-Ar-C), 130.7 (L-C4), 133.4 (B-Ar-C), 134.8 (B-Ar-C), 135.2 (B-Ar-C), 135.6 (B-Ar-C), 137.9 (B-Ar-C), 138.9 (B-Ar-C), 141.4 (L-C2), 144.4 (L-C6), 150.0 (L-C1). ¹¹⁹Sn NMR (CDCl₃, 25 °C): δ –554.2. Positiveion ESI-MS: 782.2 ($[M + Na]^+$, 29%), 798.0 ($[M + K]^+$, 14%).

Synthesis of H[(L-k₂NC)SnB₄O₆(4-Br-C₆H₄)₄] (7). (4-Br-C₆H₄)-B(OH)₂ (568.7 mg, 2.83 mmol) was added to a stirred solution of 1 (316.5 mg, 0.71 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred for an additional 5 days at this temperature and then evaporated in vacuo. The resulting white solid was extracted with toluene (10 mL) and dried in vacuo to give 7 as a white crystalline solid. Yield: 441.5 mg, 58%. Mp: 194-195 °C. Anal. Calcd for C₃₆H₃₆B₄Br₄N₂O₆Sn (MW 1074.26): C, 40.2; H, 3.4. Found: C, 40.1; H, 3.2. ¹H NMR (CDCl₃, 25 °C): δ 2.38 (s, 3H, CH₃N), 2.56 (d, 3H, CH₃N), 2.78 (d, 3H, CH₃N), 3.03 (s, 3H, CH₃N), 3.48 and 4.72 (AX pattern, ${}^{2}J_{H-H}$ = 14.0 Hz, 2H, CH₂N), 4.58 and 5.55 (AX pattern, ${}^{2}J_{H-H} = 11.5$ Hz, 2H, CH₂N), 7.12 (t, 1H, ArH), 7.14-7.57 (m, 10H, ArH), 7.80-7.91 (m, 8H, ArH), 12.46 (s, 1H, NH⁺). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 41.6 (CH₃N), 44.2 (CH₃N), 44.4 (CH₃N), 47.3 (CH₃N), 63.6 (CH₂N), 64.0 (CH₂N), 124.4 (B-Ar-C), 124.5 (B-Ar-C), 124.9 (B-Ar-C), 127.3 (B-Ar-C), 128.7 (B-Ar-C), 129.2 (L-C-3), 129.7 (L-C-5), 130.2 (B-Ar-C), 130.5 (B-Ar-C), 130.7 (L-C-4), 131.0 (B-Ar-C), 134.5 (B-Ar-C), 134.8 (B-Ar-C), 135.1 (B-Ar-C), 136.3 (B-Ar-C), 136.5 (B-Ar-C), 136.8 (B-Ar-C), 141.5 (L-C-2), 142.5 (L-C-6), 145.1 (B-Ar-C), 149.6 (L-C-1). ¹¹⁹Sn NMR (CDCl₃, 25 °C): δ –553.2. Positive-ion ESI-MS: 1096.8 $([M + Na]^+, 100\%), 1112.0 ([M + K]^+, 21\%).$

Synthesis of H{(L-k₂NC)SnB₄O₆[3,5-(CF₃)₂-C₆H₃)]₄} (8). [3,5-(CF₃)₂-C₆H₃]B(OH)₂ (691.3 mg, 2.68 mmol) was added to a stirred solution of **1** (299.5 mg, 0.67 mmol) in CH₂Cl₂(20 mL) at room temperature. The reaction mixture was stirred for an additional 5 days at this temperature and then evaporated in vacuo. The resulting white solid was extracted with toluene (10 mL) and dried in vacuo to give **8** as a white crystalline solid. Yield: 458.6 mg, 65%. Mp: 194–195 °C. Anal. Calcd for C₄₄H₃₂B₄F₂₄N₂O₆Sn (MW 1302.67): C, 40.5; H, 3.3. Found: C, 40.2; H, 3.1. ¹H NMR (CDCl₃, 25 °C): δ 2.46 (s, 3H, NCH₃), 2.69 (d, 3H, NCH₃), 2.91 (d, 3H, NCH₃), 3.07 (s, 3H, NCH₃), 3.20 and 4.76 (AX pattern, ²J_{H-H} = 14.5 Hz, 2H, CH₂N), 4.55 and 5.62 (AX pattern, ²J_{H-H} = 11.5 Hz, 2H, CH₂N), 7.20 (t, 1H, ArH), 7.70 (d, 2H, ArH), 7.83–8.00 (bs, 4H, ArH), 8.20–8.44 (m, 8H, ArH), 11.71 (s, 1H, NH⁺). ¹⁹F (400 Hz, CDCl₃) = δ –62.8, -62.9, -63.0, -63.2. ¹¹⁹Sn NMR (CDCl₃, 25 °C): δ –550.1. Positive ion ESI-MS: 1326.1 ([M + Na]⁺, 8%), 1342.1 ([M + K]⁺, 16%).

Synthesis of $H[(L-k_2NC)SnB_4O_6(4-CHO-C_6H_4)_4]$ (9). (4-CHO-C₆H₄)B(OH)₂ (482.2 mg, 3.22 mmol) was added to a stirred solution of 1 (359.4 mg, 0.80 mmol) in CH₂Cl₂(20 mL) at room temperature. The reaction mixture was stirred for an additional 2 weeks at this

temperature and then evaporated in vacuo. The solid residue was extracted with toluene (10 mL) and filtered off, and toluene was evaporated in vacuo. The resulting white solid was extracted with CHCl₃ (10 mL), and CHCl₃ was evaporated in vacuo to give 9 as a white crystalline solid. Yield: 420 mg, 60%. Mp: 227-228 °C. Anal. Calcd for C₄₀H₄₀B₄N₂O₁₀Sn (MW 870.67): C, 55.1; H, 4.6. Found: C, 54.9; H, 4.3. ¹H NMR (CDCl₃, 25 °C): δ 2.45 (s, 3H, NCH₃), 2.62 (d, 3H, NCH₃), 2.80 (d, 3H, NCH₃), 3.10 (s, 3H, NCH₃), 3.58 and 4.80 (AX pattern, ${}^{2}J_{H-H}$ = 13.8 Hz, 2H, CH₂N), 4.14 and 5.60 (AX pattern, ${}^{2}J_{H-H} = 11.4 \text{ Hz}, 2\text{H}, CH_{2}\text{N}), 7.19 (t, 1\text{H}, ArH), 7.29 (d, 2\text{H}, ArH),$ 7.78-7.92 (m, 8H, ArH), 8.14 (d, 4H, ArH), 8.21 (d, 4H, ArH), 10.00 (s, 1H, CH=O), 10.03 (s, 1H, CH=O), 10.06 (s, 1H, CH=O), 10.09 (s, 1H, CH=O), 12.27 (s, 1H, NH⁺). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 41.6 (NCH₃), 44.3 (NCH₃), 44.4 (CH₃), 47.4 (NCH₃), 63.5 (CH₂N), 64.1 (CH₂N), 125.3 (L-C3), 128.3 (L-C5), 128.4 (B-Ar-C), 128.6 (B-Ar-C), 128.7 (B-Ar-C), 129.1 (B-Ar-C), 129.4 (B-Ar-C), 133.9 (B-Ar-C), 135.1 (B-Ar-C), 135.5 (B-Ar-C), 130.9 (L-C4), 133.8 (B-Ar-C), 137.5 (B-Ar-C), 137.7 (B-Ar-C), 137.9 (B-Ar-C), 141.6 (L-C2), 142.6 (L-C6), 143.2 (B-Ar-C), 146.0 (B-Ar-C), 149.0 (L-C1), 192.6 (CH=O), 192.8 (CH=O), 193.1 (CH=O), 193.3 (CH=O). ¹¹⁹Sn NMR (CDCl₃, 25 °C): δ –553.2. Positive-ion ESI-MS: 894.2 $([M + Na]^+, 17\%), 910.2 ([M + K]^+, 13\%).$

Second-Order NLO Measurements. Second-order NLO susceptibilities were evaluated using a method similar to that where a polymer served as the matrix for the titled powder.³³ The 20-ns-pulsed Q-switch Nd:YAG laser generating a 1064 nm wavelength and a pulse repetition of about 10 Hz was applied as a fundamental one. Detection of the doubled frequency signal was done using a monochromator of about 2 nm spectral resolution directly connected to the photomultiplier. The latter eliminated the parasitic fluorescence scattering background. As a reference, we applied δ -BiB₃O₆ crystals with known parameters of a second-order optical susceptibility.³⁴ The powdered 6, 7, and 9 were embedded in liquid photopolymer oligoether acrylate composites, which were aligned by an external dc electric field.³⁵

Thermal Properties. The thermal properties of **6–9** were measured by DSC with a Mettler-Toledo STARe System DSC 2/700 equipped with an FRS 6 ceramic sensor and a Hubert TC100-MT RC 23 cooling system. The thermal behavior of the target compounds was measured in open aluminous crucibles under an inert N₂ atmosphere. DSC curves were determined with a scanning rate of 3 °C min⁻¹ within the range 25–400 °C.

Crystallography. Suitable single crystals of $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and 8 were obtained from a saturated toluene solution of 6-8 by slow evaporation of the solvent at room temperature. The X-ray data (Table S1 in the Supporting Information) for colorles crystals 6.C7H8, 7. C₇H₈₁ and 8 were obtained at 150 K using an Oxford Cryostream lowtemperature device on a Nonius Kappa CCD diffractometer with Mo Ka radiation ($\lambda = 0.71073$ Å), a graphite monochromator, and ϕ and χ scan modes. Data reductions were performed with DENZO-SMN.³ The absorption was corrected by integration methods.³⁷ Structures were solved by direct methods $(SIR92)^{38}$ and refined by full-matrix least squares based on F^2 (SHELXL97).³⁹ Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2U_{eq}$ (pivot atom) or $1.5U_{eq}$ for the methyl moiety, with C-H = 0.98, 0.97, and 0.93 Å for methyl, methylene, and hydrogen atoms in the aromatic rings, respectively. There are residual electron maxima and small cavities within the unit cell, probably originating from the disordered solvent (toluene) in the structures of 6·C₇H₈ and 7·C₇H₈. PLATON/SQUEZZE⁴⁰ was used to correct the data for the presence of disordered solvent. Potential solvent volumes of 353 Å³ in the case of $6 \cdot C_7 H_8$ and 1020 Å³ in the case of $7{\cdot}C_7H_8$ were found. A total of 81 electrons $({\bf 6}{\cdot}C_7H_8)$ and 270 electrons $(7 \cdot C_7 H_8)$ per unit cell worth of scattering were located in the void. The calculated stoichiometries of the solvent were calculated to be one and four molecules of toluene per unit cell, respectively. Thermal ellipsoids of the F3, F9, F10, F18, F22, F23, and F24 atoms in 8 were treated with standard ISOR instruction implemented in the SHELXL97 software.³⁹ Crystallographic data for structural analysis

have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1413714–1413716 and 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 and are given in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02505.

Proposed mechanism of the hydrolytic reactions of stannaboroxines 2–5, crystal data and structure refinement for $6 \cdot C_7 H_8$, $7 \cdot C_7 H_8$, and 8, and a comparison of the structures of 6-8 with the related pentaborates $[B_S O_{10}]^{n-}$ (PDF)

X-ray crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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