

## Syntheses and Structural Characterization of the Heavier Alkali-Metal Stannates Bearing the Tripodal Triamino Framework: Structural Trends in the Series of $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{M}]$ ( $\text{M} = \text{Na}, \text{K}, \text{Rb}$ )

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Treatment of the lithium stannate  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{SnLi}(\text{OEt}_2)]$  (**1**) with AgCl yielded the corresponding distannane  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}]_2$  (**2**) as the product of an oxidative coupling in good yield. The distannane (**2**) underwent reductive cleavage with the heavier alkali metals (sodium, potassium, rubidium) in a non-coordinating solvent (toluene or cyclohexane), to afford the solvate-free stannates(II)  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{M}]$  ( $\text{M} = \text{Na}$  (**3**),  $\text{K}$  (**4**), and  $\text{Rb}$  (**5**)), which were structurally characterized. The Na atom in **3** is directly bonded to two of the three amido-N atoms of the stannate cage and additionally solvated by  $\pi$ -coordination of a tolyl substituent of a neighboring stannate cage. In contrast, the group 1 metal cations in the two isomorphous compounds **4** and **5** are further removed from the nitrogen functions and are  $\pi$ -coordinated by three tolyl arene rings. The Sn–K distances in **4** were found to be 3.635 and 3.870 Å, whereas the Sn–Rb contacts in **5** are 3.708 and 3.908 Å; these are the first such Sn–Rb bonding contacts to be characterized in a molecular compound by X-ray diffraction.

### Introduction

In recent years, the structural chemistry of anionic trisubstituted metalate(II) compounds of the group 14 elements has emerged as a topical field of molecular main group chemistry.<sup>1,2</sup> This progress is due to significant improvements in crystal preparation techniques and low-temperature crystal data collection.<sup>3</sup> In early work dating from the late 1980s, Veith and co-workers characterized an entire series of lithium trisalkoxygermanates(II), stannates(II), and plumbates(II) that display characteristic cage structures, such as  $[\text{Li}(\text{dioxane})_4]\text{-}[\text{Li}\{\mu\text{-C}_4\text{H}_9\text{O}\}_3\text{Sn}]_2$  and  $[\{\text{Sn}(\text{OtBu})_3\text{M}\}_2]$ .<sup>4–6</sup> More recently, Wright et al. reported the structure of  $[\text{Pb}(2\text{-py})_3\text{-}$

$\text{Li}(\text{thf})]_7$  and Stalke and co-workers published the synthesis and X-ray diffraction (XRD) study of several tris(pyrazolyl)-germanates(II) and stannates(II), such as  $[\{\text{Pz}\}_3\text{SnNa}(\text{thf})_3\text{-}(\text{PzH})\}_2]$ , in which the heteroatom donor ligands at the p-block atom also serve as bridging units between the cations and metalate anions.<sup>8</sup> A particularly interesting class of alkali-metal group 14 and group 15 metalates includes those containing a direct metal–metal contact between the cationic and anionic metal centers, as was found in the crystal structures of  $[\text{Ph}_3\text{Si-Li}(\text{thf})_3]$ ,<sup>9</sup>  $[\text{Ph}_3\text{Sn-Li}(\text{pmdeta})]$ ,<sup>10</sup> and  $[\text{Ph}_3\text{Pb-Li}(\text{pmdeta})]$ .<sup>11</sup> A direct K–Sn bond was established by both NMR spectroscopy [<sup>119</sup>Sn–<sup>39</sup>K-coupling] and XRD for the complex  $[(\text{Me}_3\text{CCH}_2)_3\text{Sn-K}(\text{toluene})_3]$  (**8**), which Lappert and co-workers isolated from the reaction of the distannane  $[(\text{Me}_3\text{CCH}_2)_3\text{Sn}]_2$  with potassium metal.<sup>12</sup> Nev-

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ertheless, metalates of the heavier alkali metals, which are characterized by XRD, remain extremely rare.

We recently began to study the structural details of anionic tripodal triaminostannates(II) and their use as "ligands" in transition-metal chemistry.<sup>13–25</sup> In this paper, we report the synthesis and structural characterization of a novel trisilyl-silane-derived hexaaminodistannane and its conversion by reductive cleavage to the corresponding heavier alkali-metal (sodium, potassium, rubidium) stannates(II). This allowed us to conduct a systematic, comparative structural study of the interactions between the group 1 cations and the stannate cages.

## Experimental Section

**Materials and Equipment.** All manipulations were performed under a nitrogen atmosphere (Granusic desiccant (P<sub>4</sub>O<sub>10</sub>), J. T. Baker), using standard Schlenk/vacuum line techniques, or in a glovebox. All reaction flasks were flame-dried prior to use, and solvents as well as solutions were transferred by cannula-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. Benzene-*d*<sub>6</sub>, used for the NMR spectroscopic measurements, was distilled from sodium benzophenone prior to use and stored over 4 Å molecular sieves. Solids were separated from suspensions by filtration through rigorously dried Celite. The <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>119</sup>Sn NMR spectra were recorded on Bruker model Avance 250 and model AMX 400 FT-NMR spectrometers. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR data are listed in parts per million (ppm), relative to tetramethylsilane, and were referenced using the residual protonated solvent peak (<sup>1</sup>H), the carbon resonance (<sup>13</sup>C), and the silicon resonance (<sup>29</sup>Si, external standard). <sup>119</sup>Sn NMR data are given in units of ppm, relative to tetramethyltin as an external standard. Elemental analyses were performed with a CE-Instruments model EA 1110 CHNS–O microanalyzer. The triaminostannate [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(OEt<sub>2</sub>)<sub>2</sub>] (1)<sup>17,18</sup> was prepared according to a published procedure. All other chemicals used as starting materials were obtained commercially and used without further purification.

**Preparation of the Compounds.** a. [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (2). To a solid mixture of MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(OEt<sub>2</sub>)<sub>2</sub>} (1) (1.00 g, 1.36 mmol) and AgCl (1.00 g,

6.98 mmol) was added toluene (20 mL) that was precooled at –78 °C. The solution was slowly warmed to room temperature and subsequently sonicated for 90 min in an ultrasound bath. After the solution was filtered through Celite, the filtrate was evaporated to total dryness, redissolved in pentane (5 mL), and stored at –30 °C to afford compound 2 as an orange crystalline solid. The supernatant solution was discarded, and the crystals were washed with cold pentane (2 mL) and dried under vacuum to yield 620 mg (70%) of 2. <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): 0.00 (s, 6H, SiCH<sub>3</sub>), 0.28 (s, 36H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.33 (s, 18H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.69 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 12H, H<sup>2,6</sup> of CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.08 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 12H, H<sup>3,5</sup> of CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –13.4 (SiCH<sub>3</sub>), 4.0 (Si(CH<sub>3</sub>)<sub>2</sub>), 21.0 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 125.1 (C<sup>2,6</sup>), 129.7 (C<sup>3,5</sup>), 129.8 (C<sup>4</sup>), 147.8 (C<sup>1</sup>). {<sup>1</sup>H}<sup>29</sup>Si NMR (49.7 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –85.0 (SiMe), 6.4 (SiMe<sub>2</sub>). {<sup>1</sup>H}<sup>119</sup>Sn NMR (93.28 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –157.4. Anal. Calcd for C<sub>56</sub>H<sub>84</sub>N<sub>6</sub>Si<sub>8</sub>Sn<sub>2</sub>: C, 51.61; H, 6.50; N, 6.45. Found: C, 51.82; H, 6.61; N, 6.35.

b. [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn][Na] (3). A suspension of finely dispersed sodium (50.0 mg, 2.17 mmol) in toluene (20 mL), together with [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (0.50 g, 384 μmol) (2), was sonicated for 30 min in an ultrasound bath at room temperature. The dark solution was filtered through Celite, and the filtrate was evaporated to total dryness. The residual yellow solid was redissolved in toluene (2 mL) and cooled (–30 °C) to afford colorless crystals of the sodium stannate 3 (270 mg, 52%). <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): 0.23 (s, 3H, SiCH<sub>3</sub>), 0.49 (s, 18H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.12 (s, 9H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.85 (s, 12H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –14.3 (SiCH<sub>3</sub>), 4.1 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.7 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 126.3 (C<sup>2,6</sup>), 129.3 (C<sup>4</sup>), 130.1 (C<sup>3,5</sup>), 152.5 (C<sup>1</sup>). {<sup>1</sup>H}<sup>29</sup>Si NMR (49.7 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –86.6 (SiMe), –4.7 (SiMe<sub>2</sub>). Anal. Calcd for C<sub>28</sub>H<sub>42</sub>N<sub>3</sub>NaSi<sub>4</sub>Sn: C, 49.85; H, 6.27; N, 6.23. Found: C, 50.12; H, 6.53; N, 6.24.

c. [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn][K] (4). A suspension of NaK<sub>2</sub> (100 mg, 0.99 mmol) in cyclohexane (20 mL) containing [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (0.50 g, 384 μmol) (2) was sonicated for 20 min in an ultrasound bath at room temperature. The dark solution was filtered through Celite, and the filtrate was evaporated to total dryness. The residual off-white solid was redissolved in toluene (2 mL) and cooled (–30 °C) to afford colorless crystals of compound 4 (360 mg, 68%). <sup>1</sup>H NMR (400.13 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): 0.32 (s, 3H, SiCH<sub>3</sub>), 0.60 (s, 18H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.15 (s, 9H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.85 (s, 12H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –14.0 (SiCH<sub>3</sub>), 4.0 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.6 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 125.5 (C<sup>2,6</sup>), 127.3 (C<sup>3,5</sup>), 129.9 (C<sup>4</sup>), 153.9 (C<sup>1</sup>). {<sup>1</sup>H}<sup>29</sup>Si NMR (49.7 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –87.5 (SiMe), –5.4 (SiMe<sub>2</sub>). Anal. Calcd for C<sub>28</sub>H<sub>42</sub>N<sub>3</sub>KS<sub>4</sub>Sn: C, 48.68; H, 6.13; N, 6.08. Found: C, 48.95; H, 6.57; N, 5.83.

d. [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn][Rb] (5). In an analogous procedure to that described previously for the preparation of 4, a mixture of 164 mg (1.92 mmol) of rubidium and 0.50 g (384 μmol) of [Me{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (2) in cyclohexane (20 mL) was sonicated for 5 min in an ultrasound bath. The dark solution was filtered through Celite, and the filtrate was evaporated to dryness. The residual off-white solid was redissolved in toluene (2 mL) and cooled (–30 °C) to afford colorless crystals of compound 5 (300 mg, 53%). <sup>1</sup>H NMR (250.13 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): 0.34 (s, 3H, SiCH<sub>3</sub>), 0.64 (s, 18H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.14 (s, 9H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.82 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 6H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 6.90 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 6H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>). {<sup>1</sup>H}<sup>13</sup>C NMR (62.9 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –13.8 (SiCH<sub>3</sub>), 4.1 (Si(CH<sub>3</sub>)<sub>2</sub>), 20.6 (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 125.5 (C<sup>2,6</sup>), 126.7 (C<sup>4</sup>), 129.8 (C<sup>3,5</sup>), 154.3 (C<sup>1</sup>). {<sup>1</sup>H}<sup>29</sup>Si NMR (49.7 MHz, C<sub>6</sub>D<sub>6</sub>, 295 K): –86.8 (SiMe), –5.6 (SiMe<sub>2</sub>). Anal. Calcd for C<sub>28</sub>H<sub>42</sub>N<sub>3</sub>RbSi<sub>4</sub>Sn: C, 45.62; H, 5.74; N, 5.70. Found: C, 45.79; H, 6.08; N, 6.12.

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**Table 1.** Summary of Crystallographic Details for Compounds **2**, **3**, **4**, and **5**

	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
empirical formula	C <sub>56</sub> H <sub>84</sub> N <sub>6</sub> Si <sub>8</sub> Sn <sub>2</sub> ·2Tol	C <sub>28</sub> H <sub>42</sub> N <sub>3</sub> NaSi <sub>4</sub> Sn·C <sub>6</sub> D <sub>6</sub>	C <sub>28</sub> H <sub>42</sub> N <sub>3</sub> KSi <sub>4</sub> Sn <sup>1/2</sup> C <sub>6</sub> D <sub>6</sub>	C <sub>28</sub> H <sub>42</sub> N <sub>3</sub> RbSi <sub>4</sub> Sn <sup>1/2</sup> C <sub>6</sub> D <sub>6</sub>
fw	1487.66	758.83	733.87	780.24
temp (K)	120 ± 2	150 ± 2	150 ± 2	150 ± 2
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> (Å)	24.6311(4)	11.0978(2)	24.7876(4)	25.4510(3)
<i>b</i> (Å)	22.0716(4)	13.9804(3)	13.34100(10)	13.30710(10)
<i>c</i> (Å)	14.7615(2)	24.6348(5)	21.9895(3)	21.7466(2)
α (deg)	90	90	90	90
β (deg)	105.6270	93.7570(10)	90	90
γ (deg)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	7728.4(2)	3813.92(13)	7271.74(16)	7365.12(12)
<i>Z</i> , calcd density (g/cm <sup>3</sup> )	4, 1.279	4, 1.322	8, 1.341	8, 1.407
μ(Mo Kα) (mm <sup>-1</sup> )	0.812	0.833	0.973	2.161
R <sub>1</sub> <sup>a</sup> ( <i>I</i> ≥ 2σ)	0.0501	0.0366	0.0300	0.0281
wR <sub>2</sub> <sup>b</sup> ( <i>I</i> ≥ 2σ)	0.1109	0.0886	0.0742	0.0536

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

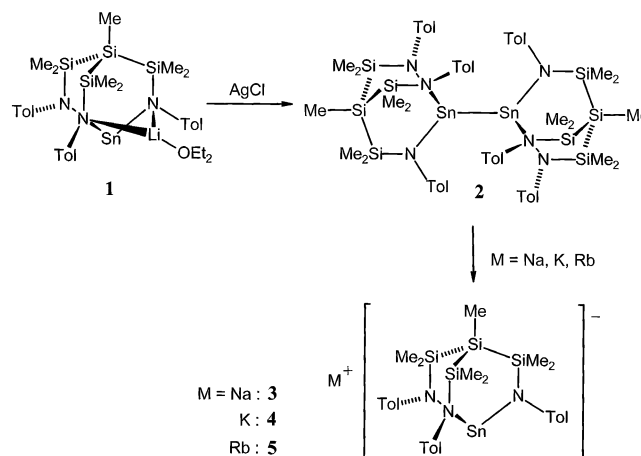
**Crystal Structure Determination.** Data of compounds **2–5** were collected on a Nonius Kappa CCD diffractometer using Mo K<sub>α</sub> radiation ( $\lambda = 0.71073$  Å). The Denzo-Scalepack<sup>26</sup> program package was used for cell refinements and data reduction. Structures were solved by direct methods, using the SHELXS-97 program.<sup>27</sup> An empirical absorption correction based on equivalent reflections<sup>28</sup> was applied to all data ( $T_{\min}/T_{\max} = 0.17671/0.20249, 0.12884/0.16689, 0.11960/0.15740, \text{ and } 0.23478/0.27184$  for compounds **2**, **3**, **4**, and **5**, respectively). Structures were refined with the SHELXL-97 program<sup>29</sup> and the WinGX graphical user interface.<sup>30</sup> All H atoms were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data of compounds **2–5** are summarized in Table 1.

## Results and Discussion

**Synthesis and Structural Characterization of the Hexaaminodistannane [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (2).** Treatment of the previously reported lithium stannate [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(OEt<sub>2</sub>)] (**1**)<sup>17,18</sup> with AgCl at ambient temperature afforded the product of an oxidative coupling, the distannane [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub> (**2**), in good yield. The <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra indicate the expected threefold molecular symmetry of the distannane in solution, as shown in Scheme 1.

The <sup>119</sup>Sn NMR resonance, which is attributed to the triamino-Sn unit, is observed at  $\delta -157.4$  ppm. The coupling between the <sup>117</sup>Sn and <sup>119</sup>Sn nuclei was not detectable, which is an effect that we attribute to the rapid relaxation of the <sup>117</sup>Sn and <sup>119</sup>Sn nuclei in a coordination environment in which the metal atom is surrounded by three quadrupolar <sup>14</sup>N nuclei. We note that the trisilylmethane-derived stannate [HC{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>SnLi(thf)<sub>3</sub>]<sup>16</sup> reacts analogously with AgCl to afford the corresponding trisilylmethane-derived

**Scheme 1.** Syntheses of the Hexaaminodistannane **2** and Its Reductive Cleavage To Give the Heavy Alkali-Metal Stannates(II) [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn][M] (M = Na (**3**), K (**4**), and Rb (**5**))

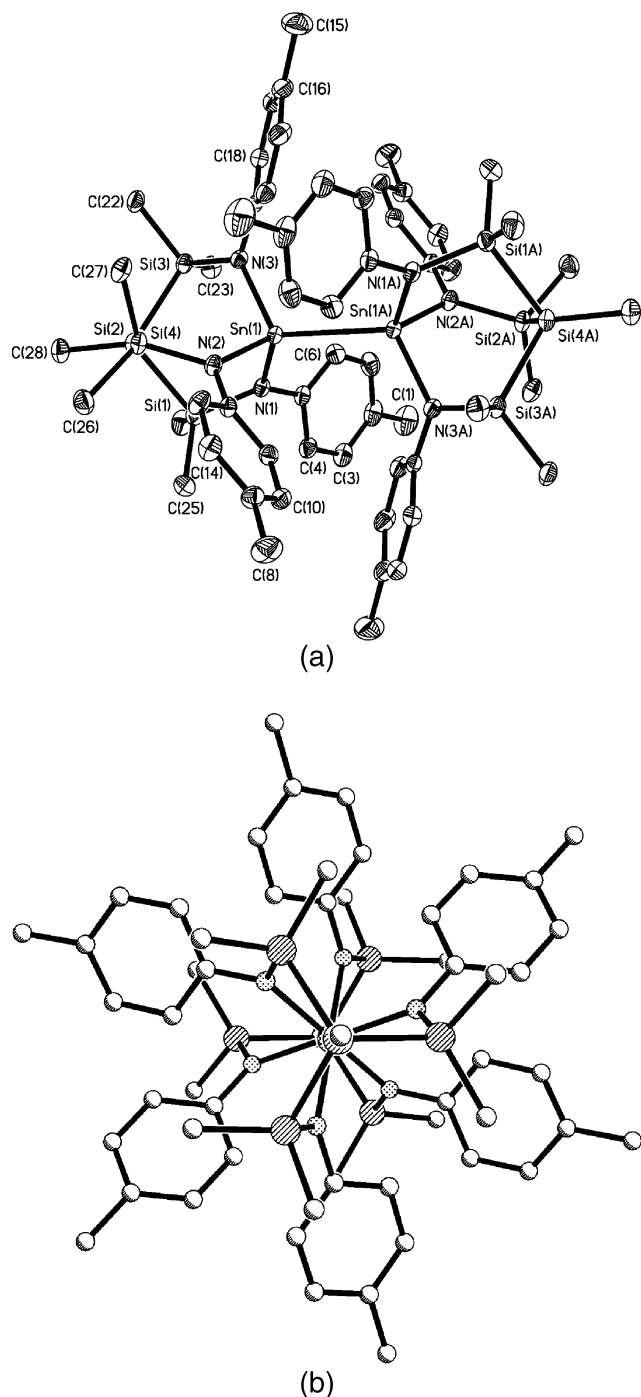


fused cage structure of the hexaaminodistannane [HC{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]<sub>2</sub>.<sup>31</sup> Compound **2** crystallizes in the centrosymmetric monoclinic space group *P2<sub>1</sub>/c*, and its crystal structure contains two independent molecules in the asymmetric unit. The structure is depicted in Figure 1 and the principal metric parameters are shown in Table 2.

In both of the crystallographically independent but structurally very similar molecules, the two {MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn} units are staggered with respect to each other, with a crystallographic center of inversion at the midpoint of the Sn–Sn' vector (*C<sub>i</sub>* symmetry). The overall molecular structure is therefore related to those of the recently reported Sn–M–Sn (M = Hg, Cd) heterodimetallic complexes.<sup>24</sup> As found for previously studied tripodal triamidotin compounds, the structural building block is the [2,2,2]-bicyclo-octane-related cage comprising the trisilylsilane unit and the triamidotin unit. These two structural units are twisted with respect to each other (torsion angle Si(4)–Si(1)–N(1)–Sn(1) of 35.4(3)°, which is to be seen as a consequence of the steric repulsion of the methyl groups within the trisilylsilane unit rather than being due to the geometrical require-

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**Figure 1.** (a) Molecular structure of the hexaaminodistannane **2** in the crystal. (b) View along the Sn–Sn bond axis, showing the staggered arrangement of the two triamidotin units. The principal bond lengths and angles are given in Table 2.

ments of Sn–N binding in the molecule. The Sn–Sn bond distances were found to be 2.8568(6) Å for Sn(1)–Sn(1') and 2.8837(7) Å for Sn(1B)–Sn(1B'), which is in the range of those of previously characterized distannanes.<sup>31–44</sup> A related distannane derivative was previously reported by

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**Table 2.** Selected Bond Lengths and Angles for Compound **2**

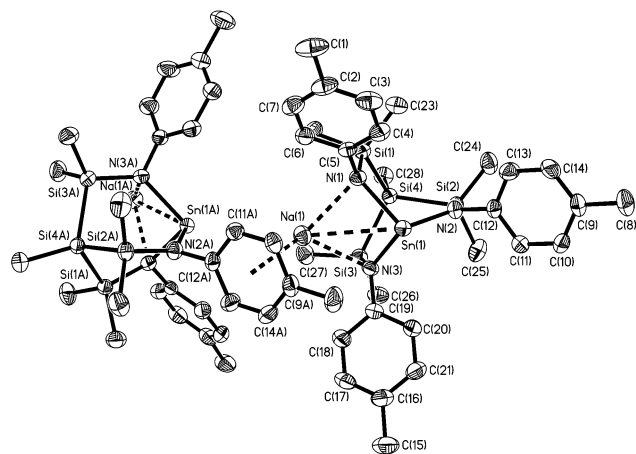
Bond Distances (Å)			
N(1)–Sn(1)	2.050(4)	N(1B)–Sn(1B)	2.069(4)
N(2)–Sn(1)	2.062(4)	N(2B)–Sn(1B)	2.065(4)
N(3)–Sn(1)	2.062(4)	N(3B)–Sn(1B)	2.072(4)
Sn(1)–Sn(1A)	2.8568(6)	Sn(1B)–Sn(1C)	2.8837(7)
Bond Angles (deg)			
N(1)–Sn(1)–N(2)	102.65(16)	N(1B)–Sn(1B)–N(2B)	102.43(18)
N(1)–Sn(1)–N(3)	102.49(16)	N(1B)–Sn(1B)–N(3B)	102.39(17)
N(2)–Sn(1)–N(3)	102.66(16)	N(2B)–Sn(1B)–N(3B)	103.14(18)
N(1)–Sn(1)–Sn(1A)	115.88(11)	N(1B)–Sn(1B)–Sn(1C)	117.41(12)
N(2)–Sn(1)–Sn(1A)	114.57(11)	N(2B)–Sn(1B)–Sn(1C)	113.71(13)
N(3)–Sn(1)–Sn(1A)	116.61(11)	N(3B)–Sn(1B)–Sn(1C)	115.80(12)

Wrackmeyer, Herberhold, and co-workers, who described the synthesis and crystallographic study of [Me<sub>2</sub>Si(N-*t*Bu)<sub>2</sub>Sn(N-*t*Bu)]<sub>2</sub>( $\mu$ -Se), in which the Sn–Sn bond distance was found to be 2.852(1) Å.<sup>45</sup>

**Synthesis and Structural Characterization of the Alkali-Metal Triaminostannates [MeSi{SiMe<sub>2</sub>N(4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>Sn]–[M] (M = Na (3), K (4), Rb (5)).** Treatment of a solution of the hexaaminodistannane **2** in toluene or cyclohexane with the alkali metals sodium, potassium, and rubidium in an ultrasound bath afforded, in all three cases, dark reaction mixtures, from which the corresponding solvate-free heavy alkali-metal stannates(II) **3**, **4**, and **5** were isolated by extraction with pentane and subsequent recrystallization from toluene as highly air- and moisture-sensitive colorless crystalline solids. The signal patterns in the <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra of compounds **3**, **4**, and **5**, recorded in C<sub>6</sub>D<sub>6</sub>, are consistent with the expected threefold molecular symmetry of the tripodal aminostannates(II) in solution, as represented in Scheme 1. This is consistent with a highly fluxional alkali-metal cation–stannate interaction. It is noteworthy that the aromatic protons of compounds **3** and **4** appear as a pseudo-singlet resonance in the <sup>1</sup>H NMR spectrum (degenerate AB-spin system), whereas the <sup>1</sup>H NMR spectrum of **5** exhibits, as expected, two doublet resonances for the aromatic protons. As for many of the previously characterized lithium triaminostannates(II), the <sup>119</sup>Sn NMR resonances of the heavier alkali-metal stannates(II) **3**, **4**, and **5** were not detectable.

To obtain detailed structural information on these novel compounds and, in particular, to establish the nature of the

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**Figure 2.** Molecular structure of a pair of the sodium stannate molecules  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{Na}]$  (**3**) in the crystal. The principal bond lengths and angles are given in Table 3.

**Table 3.** Selected Bond Lengths and Angles for Compound **3**

Bond Distances (Å)			
N(1)–Sn(1)	2.200(3)	N(1)–Na(1)	2.564(3)
N(2)–Sn(1)	2.134(3)	N(3)–Na(1)	2.570(3)
N(3)–Sn(1)	2.204(3)	Na(1)–Sn(1)	3.2551(15)
Bond Angles (deg)			
N(1)–Sn(1)–N(2)	101.52(11)	N(1)–Sn(1)–Na(1)	51.77(8)
N(1)–Sn(1)–N(3)	89.61(10)	N(2)–Sn(1)–Na(1)	135.14(8)
N(2)–Sn(1)–N(3)	100.58(10)	N(3)–Sn(1)–Na(1)	51.93(8)

cation–anion aggregation in their solvent-free crystal structures, XRD studies of all three stannates **3–5** were performed.

The sodium stannate  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{Na}]$  (**3**) crystallizes in the monoclinic space group  $P2_1/c$ . The molecular structures of two molecules, which are part of a weakly aggregated infinite chain, are depicted in Figure 2, and the principal bond lengths and angles are summarized in Table 3.

The mode of coordination of the  $\text{Na}^+$  cation to the stannate cage is similar to that observed previously for lithium group 14 metalates(II) bearing the same type of triamido tripod ligand. The  $\text{Na}^+$  cation occupies a bridging position between two amido N atoms ( $\text{Na}(1)\text{--N}(1)$  2.564(3),  $\text{Na}(1)\text{--N}(3)$  2.570(3) Å) and, consequently, distorts the stannate cage. The alkali metal “ties” the two amido functions, to which it is bonded, together, generating an N-donor arrangement that deviates from the otherwise more-or-less undistorted trigonal-monopyramidal geometry of the  $\text{N}_3\text{Sn}$  unit (with the angles  $\text{N}(1)\text{--Sn}(1)\text{--N}(3)$  = 89.61(10)°,  $\text{N}(1)\text{--Sn}(1)\text{--N}(2)$  = 101.52(11)°, and  $\text{N}(2)\text{--Sn}(1)\text{--N}(3)$  = 100.58(10)°). Another structural consequence of the direct bonding of the  $\text{Na}^+$  cation to the N-donor groups is the rotation of the  $\text{SiMe}_2$  groups at Si(1) and Si(3) to an almost eclipsed arrangement, which is observed only rarely in tripod amido complexes containing a trisilylsilane backbone, because of steric repulsion of the methyl groups. The  $\text{Na}^+$  cation is additionally stabilized by an attractive metal–metal contact with the Sn atom in the stannate cage. The Sn–Na distance was found to be 3.2551(15) Å and is close to the sum of the covalent radii of the Sn and Na ions (1.40 + 1.83 = 3.23 Å) and the intermetallic distance of an unsupported Na–Sn bond in

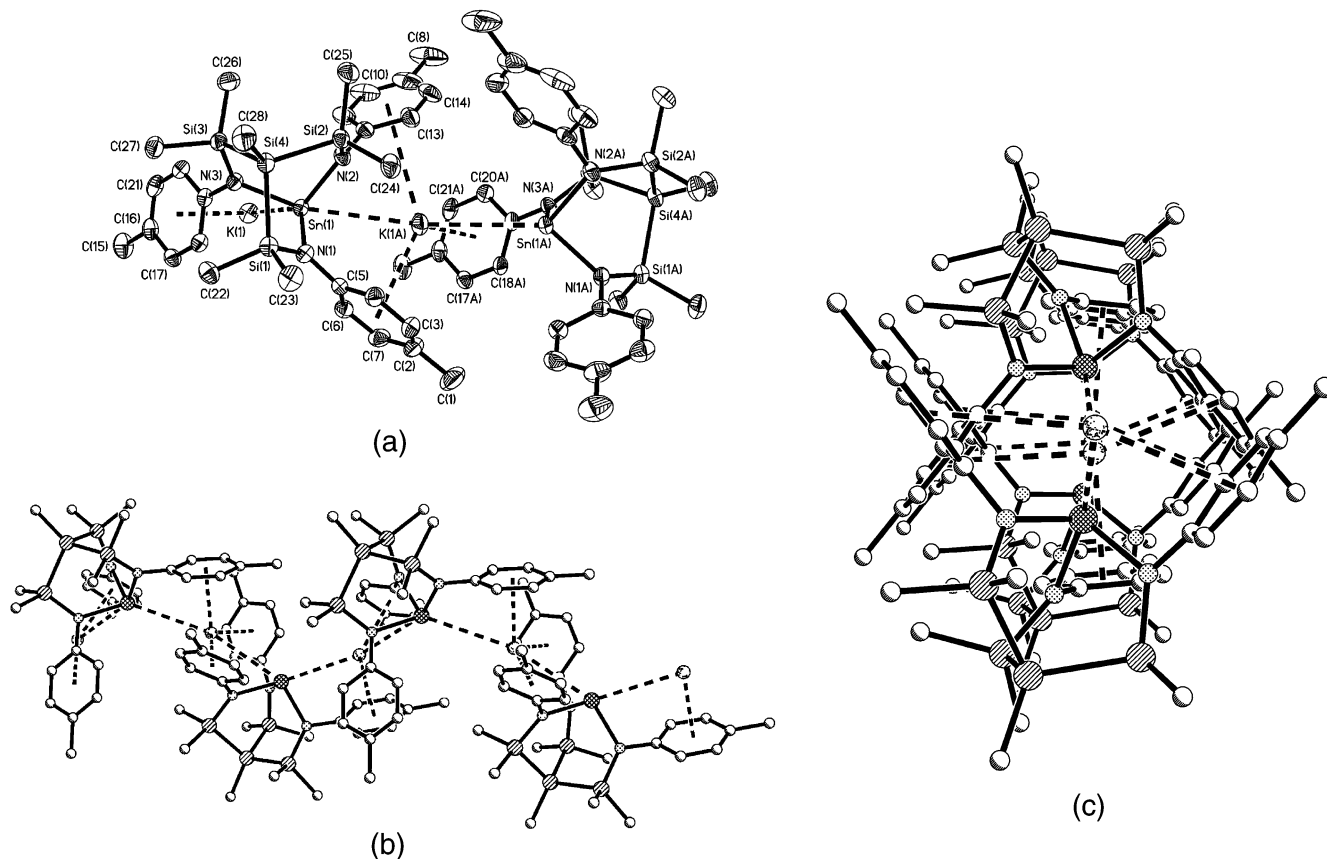
$[(\text{thf})_3\text{Na}\{\text{Sn}(\text{C}_6\text{H}_3\text{-2,6-Trip}_2)\}]$  (3.240(7) Å) reported by Power et al.<sup>46</sup> Two other examples of unsupported Na–Sn bonds previously reported by Klinkhammer and Wiberg were found to be ca. 0.02 Å shorter.<sup>47,48</sup> We would like to point out that the relative arrangement of the Sn and Na atoms in **3** and the presence of the bridging amido functions make a covalent bonding component in the metal–metal interaction most probably insignificant, and the Na–Sn contact should be viewed as essentially electrostatic.

The exposed  $\text{Na}^+$  cation is additionally solvated through a slightly slipped  $\pi$ -arene coordination of a tolyl group of a neighboring stannate unit (Na(1) centroid: 2.707 Å). This type of  $\pi$ -arene solvation is quite common in the chemistry of the heavier alkali metals.<sup>49–61</sup>

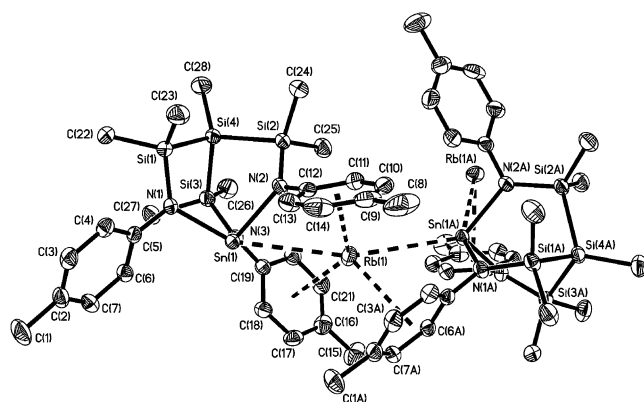
The orthorhombic crystals of **4** and **5** were found to be isomorphous and both compounds are thus isostructural. As can be seen in Figure 3a and b, the solvent-free potassium stannate **4** aggregates to form a polymeric array in the solid state, consisting of a zigzag chain of alternating  $\text{K}^+$  and stannate(II) units ( $\angle(\text{K}\text{--Sn}\text{--K})$  = 126.52° and  $\angle(\text{Sn}\text{--K}\text{--Sn})$  = 165.18°).

The  $\text{K}^+$  cation formally adopts a distorted, five-coordinate coordination geometry, in which the metal is solvated by three tolyl groups, two of which are coordinated to a  $\text{K}^+$  cation in an  $\eta^6$ -fashion ( $d(\text{K}\text{--centroid})$  = 2.879 and 2.888 Å) and a third is coordinated in a slipped  $\eta^2$ -fashion ( $d(\text{K}\text{--centroid})$  = 3.017 Å). The amido-N–K distances are >3 Å (3.068(2)–3.6409(2) Å); thus, a direct bridging interaction between the nitrogen functions similar to that found for the sodium derivative **3** is, at best, weak. The bond angles (N–Sn–N) deviate from the idealized trigonal-monopyramidal arrangement in the  $\text{N}_3\text{Sn}$  unit ( $\text{N}(1)\text{--Sn}(1)\text{--N}(2)$  = 92.38(8)°,  $\text{N}(1)\text{--Sn}(1)\text{--N}(3)$  = 97.88(7)°, and  $\text{N}(2)\text{--Sn}(1)\text{--N}(3)$  = 100.60(7)°). (Table 4 shows the bond distances and angles for compound **4**.) This deviation is less pronounced than for the sodium derivative and is probably largely due to the

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**Figure 3.** (a) Molecular structure of a pair of the potassium stannate molecules  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{K}]$  (**4**) in the crystal; the  $\text{K}^+$ -arene and  $\text{K-Sn}$  contacts are highlighted by the dashed lines. The principal bond lengths and angles are given in Table 4. (b) Polymeric chain of molecules of compound **4** in the crystal showing the aggregation via metal-metal and metal-arene contacts. (c) View of the polymeric aggregate along the chain of metal-metal contacts, showing the "encapsulation" of the metals by the tolyl arene rings.



**Figure 4.** Molecular structure of a pair of the rubidium stannate molecules  $[\text{MeSi}\{\text{SiMe}_2\text{N}(4\text{-CH}_3\text{C}_6\text{H}_4)\}_3\text{Sn}][\text{Rb}]$  (**5**) in the crystal featuring the same intra- and intermolecular interactions as the potassium analogue.

electrostatic interaction with the arene groups involved. The  $\text{Sn-K}$  contacts in this type of polymeric array were found to have distances of 3.6347(6) and 3.8697(6) Å, respectively, and are in the same range as those of the previously characterized  $\text{Sn-K}$  bonds.<sup>12,62</sup>

The relative arrangement of the tolyl groups in the polymeric chain leads to an "encapsulation" of the  $\text{K}^+$  cation, as can be appreciated in the view along such an "ion channel", which is depicted in Figure 3c.

**Table 4.** Selected Bond Lengths and Angles for Compound **4**

Bond Distances (Å)			
$\text{N}(1)\text{-Sn}(1)$	2.1745(19)	$\text{K}(1\text{A})\text{-Sn}(1)$	3.6347(6)
$\text{N}(2)\text{-Sn}(1)$	2.177(2)	$\text{K}(1)\text{-Sn}(1)$	3.8697(6)
$\text{N}(3)\text{-Sn}(1)$	2.1389(19)	$\text{K}(1\text{A})\text{-N}(2)$	3.068(2)
Bond Angles (deg)			
$\text{N}(1)\text{-Sn}(1)\text{-N}(2)$	92.38(8)	$\text{N}(2)\text{-Sn}(1)\text{-K}(1)$	132.52(6)
$\text{N}(1)\text{-Sn}(1)\text{-N}(3)$	97.88(7)	$\text{N}(3)\text{-Sn}(1)\text{-K}(1)$	76.97(5)
$\text{N}(2)\text{-Sn}(1)\text{-N}(3)$	100.60(7)	$\text{K}(1)\text{-Sn}(1)\text{-K}(1\text{A})$	126.518(5)
$\text{N}(1)\text{-Sn}(1)\text{-K}(1)$	135.11(5)	$\text{Sn}(1)\text{-K}(1)\text{-Sn}(1\text{A})$	165.18(2)

**Table 5.** Selected Bond Lengths and Angles for Compound **5**

Bond Distances (Å)			
$\text{N}(1)\text{-Sn}(1)$	2.139(2)	$\text{Rb}(1\text{A})\text{-Sn}(1)$	3.9080(3)
$\text{N}(2)\text{-Sn}(1)$	2.183(2)	$\text{Rb}(1)\text{-Sn}(1)$	3.7076(3)
$\text{N}(3)\text{-Sn}(1)$	2.179(2)		
Bond Angles (deg)			
$\text{N}(1)\text{-Sn}(1)\text{-N}(2)$	99.81(8)	$\text{N}(2)\text{-Sn}(1)\text{-Rb}(1)$	60.07(6)
$\text{N}(1)\text{-Sn}(1)\text{-N}(3)$	97.82(8)	$\text{N}(3)\text{-Sn}(1)\text{-Rb}(1)$	74.26(6)
$\text{N}(2)\text{-Sn}(1)\text{-N}(3)$	93.46(8)	$\text{Rb}(1)\text{-Sn}(1)\text{-Rb}(1\text{A})$	122.898(5)
$\text{N}(1)\text{-Sn}(1)\text{-Rb}(1)$	157.04(5)	$\text{Sn}(1)\text{-Rb}(1)\text{-Sn}(1\text{A})$	164.00(1)

Figure 4 displays the molecular and solid-state structure of compound **5**, which is isomorphous to the potassium stannate **4**. Consequently, the main structural features are very similar to those discussed previously. Because of its larger ionic radius, the  $\text{Rb}^+$  cation moves even farther away from the amido-N units. The distortion of the stannate cage induced by this bridging coordination of the metal cation is, therefore, even less pronounced than that for the potassium

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analogue. The N–Sn–N bond angles in the N<sub>3</sub>Sn unit of **5** were found to be N(2)–Sn(1)–N(3) = 93.46(8)°, N(1)–Sn(1)–N(3) = 97.82(8)°, and N(1)–Sn(1)–N(2) = 99.81(8)°. (Table 5 shows the bond distances and angles for compound **5**.) The Sn–Rb bonding contacts of 3.708 and 3.908 Å are the first to be characterized by XRD. These intermetallic distances should be compared with the sum of the covalent radii of the Sn and Rb ions, which is given as 1.40 + 2.43 = 3.88 Å.

### Conclusion

In this first systematic study of the structural chemistry of the heavier alkali-metal triaminostannates(II), we have shown how the transition to the heavier group 1 cations leads to crystal structures that differ markedly from those established for their lithium analogues. Although the latter retain a molecular identity in their solid-state structures, with the Li cations tightly bonded to the amido-N functions of the stannate cage (a situation that is still apparent in the sodium stannate **3**), the increase in the size of the cation leads to infinite aggregates in the crystal. Moving out of the immedi-

ate proximity of the electronegative amido functions, the heavier alkali metals are preferentially solvated by  $\pi$ -coordination of the tolyl ligand periphery.

The reductive cleavage of a hexaaminodistannane such as compound **2** is the method of choice for the synthesis of the heavier alkali-metal stannates. However, the analogous reaction of **2** with lithium metal leads to different reaction products, because of redox and redistribution reactions. This aspect of stannate reactivity is the focus of our current studies.

**Acknowledgment.** We thank the University of Joensuu (Inorganic Materials Chemistry Graduate Program) and the CNRS (France) for financial support of this work.

**Supporting Information Available:** Details of the structure determinations and tables of crystallographic data, the positional and thermal parameters, and the interatomic distances and angles for compounds **2–5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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