Synthesis and Structures of 1,3,5,7-Tetraazaheptatrienylsodium and -thallium(I)**

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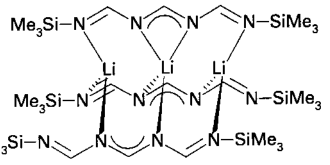
Organolithium compounds are important as reagents in both organic and inorganic chemistry. For this reason their structures have been extensively investigated in solution and in the solid state.[1] Structures of the heavier alkali metal organic compounds are also attracting increasing interest.[2] Although the chemistry of thallium(I) compounds bears some resemblance to that of alkali metal analogues, thallium(I) bis(trimethylsilyl)amide was only recently structurally characterized,[3] whereas the alkali metal bis(trimethylsilyl)amides have been known since the 1960s.[4] The alkali metal amides have proved their versatility as bulky bases, amido-ligand transfer reagents, polymerization initiators, and in insertion reactions with unsaturated polar organic compounds containing C–O or C–N multiple bonds.

We have described the reaction of $LiN(SiMe_3)_2$ with 1,3,5-triazine (**1**) yielding the 1,3,5,7-tetraazaheptatrienyllithium complex **2**, involving both formally an α → ω Me_3Si shift and ring opening.[5] We now report on the reactions of the corresponding sodium and thallium(I) amides $MN(SiMe_3)_2$ (M = Na, Tl) with **1**, and the structures of the novel products, 1,3,5,7-tetraazaheptatrienylsodium (**3**) and -thallium(I) (**4**).



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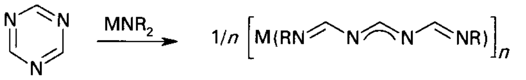
1,3,5-Triazine (**1**) was allowed to react at −20 °C in tetrahydrofuran with sodium bis(trimethylsilyl)amide, or in toluene with thallium(I) bis(trimethylsilyl)amide, to give a green-gray or black suspension which afforded colorless crystals of **3** or **4** in 70% and 66% yield, respectively [Eq. (1)].



(1)

M = Li, n = 3 [5] **2**
Na, n = 3 **3**
Tl, n = 8 **4**
R = $SiMe_3$

Compounds **3** and **4** are both air- and moisture-sensitive, and very soluble in hydrocarbons. Each was characterized by elemental analysis, multinuclear NMR spectroscopy, and single crystal X-ray structure analysis.

The X-ray molecular structure of the crystalline sodium complex **3** shows the presence of two crystallographically independent, trinuclear molecules and a disordered cyclohexane molecule in the unit cell. Each of the three-coordinate sodium atoms Na1 and Na3 is in a distorted trigonal planar environment (the sum of the angles being 349.6(2) and 349.2(2)°, respectively); the average Na–N bond length is 2.46 Å (Figure 1). The remaining sodium atom Na2 is at the center of a distorted trigonal prism (the central lithium atom in **2** is at the center of a distorted tetrahedron),[5] comprising the two triangular faces N2, N10, N6 and N3, N7, N11 (the sum of the angles subtended by each of these atoms at Na2 is 298.1(2) and 298.5(2)°, respectively); the average Na–N bond length is 2.42 Å, and thus similar to the Na–N bond length in benzamidinate systems.[6] Each organic ligand has very similar bond lengths (also when compared to the ligands in the lithium complex **2**, although in **2** they have slipped with respect to each other);[5] N1–C1 and N4–C3 are double bonds (ca. 1.27 Å), C3–N3 and C1–N2 are short single bonds (ca. 1.37 Å); and N3–C2 and C2–N2 have bond lengths characteristic for a delocalized system (ca. 1.31 Å).[7] These assignments are consistent with the coplanarity of the atoms Si1, N1, C1, N2, C2, N3, C3, N4, and Si2; the largest deviation from the mean plane is 0.080 Å. In summary, we conclude that this novel structural type comprises three sodium cations forming an axis to which the three anionic ligands coordinate. The projection of **3** along its Na–Na–Na axis shows the molecule to have approximate C_3 symmetry (Figure 2). To the best of our knowledge, only two other trinuclear sodium amides, $[Na\{\mu\text{-}N(SiMe_3)_2\}]_3$,[8] and $[Na\{\mu\text{-}\overline{NC(Me)_2(CH_2)_3C}Me_2\}]_3$,[9] and one aryl-ligand complex, $[Na\{\mu\text{-}2,6\text{-}(CH_2NMe_2)_2C_6H_3\}]_3$,[10] were previously known; each of these three complexes are, unlike trinuclear **3**, divisible into three identical monomeric units.

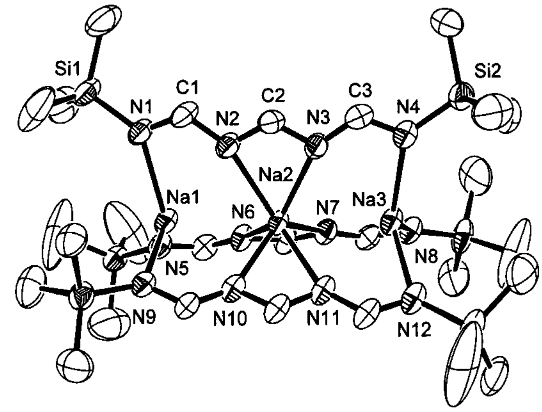


Figure 1. ORTEP representation of **3** with selected bond lengths [Å] and angles [°]: N1-C1 1.275(7), C1-N2 1.380(7), N2-C2 1.316(7), C2-N3 1.311(7), N3-C3 1.360(7), C3-N4 1.269(7), Na1-N1 2.462(5), Na1-N5 2.475(5), Na1-N9 2.440(5), Na2-N2 2.452(5), Na2-N3 2.397(5), Na2-N6 2.432(5), Na2-N7 2.404(5), Na2-N10 2.381(5), Na2-N11 2.466(5); N2-C2-N3 122.4(5), N1-Na1-N5 118.1(2), N1-Na1-N9 111.3(2), N5-Na1-N9 120.2(2), N2-Na2-N3 56.7(2), N2-Na2-N6 99.3(2), N3-Na2-N6 132.4(2).

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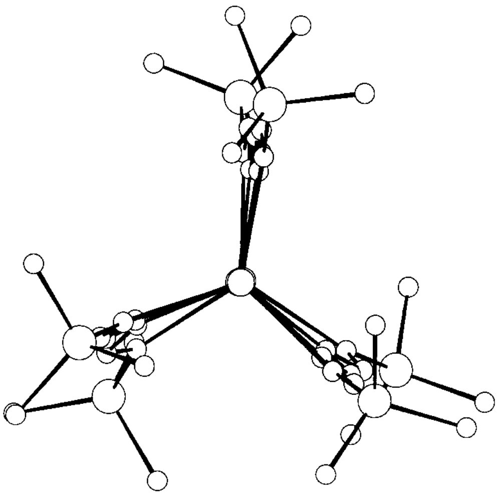

Figure 2. Projection of **3** along its Na-Na-Na axis showing pseudo-C_3 symmetry.

The thermal stability of this trinuclear sodium complex **3** is remarkable. The EI mass spectrum showed the molecular ion and more intense fragment ions corresponding to loss of one ligand; the dinuclear ion was the base peak. The ^{23}Na{^{1}H} NMR spectrum of **3** at ambient temperature in [D$_8$]toluene showed a signal at $\delta = 25.0$ ($w_{1/2} = 0.36$ kHz) and another centered at $\delta = 9$ ($w_{1/2} = 2.2$ kHz) in a ratio of approximately 1:2, and these signals coalesced at around 98 °C. Thus, compound **3**, like **2**,[5] evidently retains its trinuclear structure in solution and in the gas phase. The excellent coordination of the ligands to the sodium cations is also apparent from the fact that **3**, like **2**, is unresponsive to strongly coordinating, neutral donor molecules, such as tetramethylethylenediamine and pentamethyldiethylenetriamine.

The molecular structure of crystalline **4** consists of two symmetry-related tetranuclear units that form a rather asymmetric and unprecedented structure (Figure 3). The atom Tl1 is four-coordinate (distances to Tl2 3.76; Tl3 3.68; N41 2.59; N63 2.51 Å), Tl2 is three-coordinate (distances to Tl1 3.76; N1 2.655; N25 2.49 Å), Tl3 is five-coordinate (distances to Tl1 3.84; Tl4′ 3.89; N45 2.54; N65 2.75; N67 2.60 Å), and Tl4 is three-coordinate (distances to Tl3′ 3.57; N5 2.495; N21 2.58 Å). The structure is best described as comprising four units each consisting of two thallium atoms and two [{Me$_3$SiNC(H)N}$_2$CH]$^-$ ligands with Tl–N bond lengths in the unexceptional range of 2.49–2.75 Å. Each ligand bonds to two thallium atoms, and each thallium atom bonds to two ligands, that is, two ligands to Tl1 and Tl3 and two to Tl2 and Tl4. Short internuclear Tl1–Tl2, Tl1–Tl3 and Tl3–Tl4 distances of around 3.76, 3.65, and 3.89 Å, respectively, and additional metal–ligand contacts lead to the formation of a "cluster". Although polynuclear thallium(I) compounds are well known and often have relatively short Tl···Tl contacts,[11] only one octanuclear structure, [{TlS*t*Bu}$_8$], was previously reported.[12] Recent examples of thallium(I) amides having Tl$^{\mathrm{I}}$···Tl$^{\mathrm{I}}$ contacts of about 3.7 Å and Tl$^{\mathrm{I}}$–N bond lengths of about 2.45 Å include [{TlN(SiMe$_3$)CH$_2$}$_2$CH$_2$][13] and [{TlN(SiMe$_3$)CH$_2$}$_3$CR′]$_2$ (R′ = Me,[14] Ph[15]).

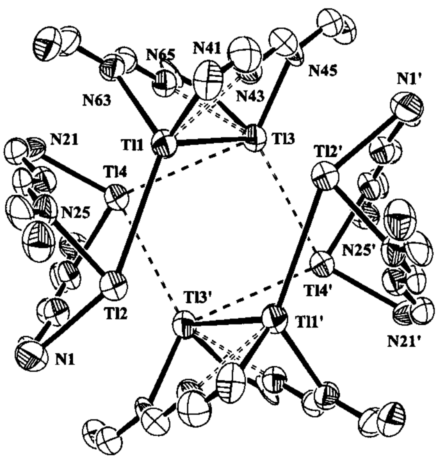

Figure 3. The core of the molecular structure of **4**. Hydrogen atoms and Me$_3$Si groups are omitted. Selected bond lengths [Å] and angles [°]: Tl1-Tl2 3.7591(9), Tl1-Tl3 3.6788(9), Tl3-Tl4 3.887(1), Tl1···Tl4 3.965(1), Tl2···Tl3′ 3.947(1), Tl3···Tl4′ 4.000(1), Tl2···Tl4 4.601(2), Tl1-N41 2.592(14), Tl1-N43 2.794(13), Tl1-N63 2.511(10), Tl2-N1 2.65(14), Tl2-N25 2.489(12), Tl3-N45 2.541(11), Tl3-N65 2.747(11), Tl3-N67 2.602(14), Tl4-N5 2.495(12), Tl4-N21 2.582(12), N1-C2 1.24(2), C2-N3 1.38(2), N3-C4 1.332(19), C4-N5 1.335(19), N5-C6 1.38(2), C6-N7 1.253(19); N3-C4-N5 121.6(15), N5-Tl4-N21 89.5(4), N45-Tl3-N67 87.8(4), N63-Tl1-N41 91.0(4), N65-Tl3-N67 50.9(4), Tl1-Tl3-Tl4′ 109.8, Tl2-Tl1-Tl3 112.44(2).

The ligand [{Me$_3$SiNC(H)N}$_2$CH]$^-$ coordinates differently to thallium in **4** than to sodium in **3**, in that only N1 and N5, but not N7, bind to the metal in **4**. This, however, is not reflected in the intraligand bond lengths which are similar in **2**–**4**; thus, for **4** the approximate bond lengths for N1–C2 and C6–N7 are 1.25 Å, for C2–N3 and C6–N5 1.38 Å, and for C4–N3 and C4–N5 1.33 Å.

In the ^{1}H and ^{13}C{^{1}H} NMR solution spectra at ambient temperature, ^{203}Tl or ^{205}Tl couplings were not observed, possibly due to a dynamic exchange process or because Tl–CH interactions were absent.

Each of **2**–**4** consists of cationic metal atoms and anionic, planar, delocalized [{Me$_3$SiNC(H)N}$_2$CH]$^-$ ligands. Their structures differ, however, due to weak metal–metal interactions present in **4**, but not in **2** or **3**. We expect **3** and **4** to be significant additions to **2** as ligand-transfer reagents for the synthesis of new unusual, highly thermally stable and lipophilic metal complexes.

Experimental Section

3: 1,3,5-Triazine (**1**) (1.07 g, 13.2 mmol) was added to a solution of NaN(SiMe$_3$)$_2$ (2.42 g, 13.2 mmol) in THF (75 mL) at −20 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 4 h. Volatiles were removed in vacuo, and the residue was extracted with pentane (2 × 200 mL) to give the analytically pure solid **3** (2.46 g, 70 %). Recrystallization from hexane yielded colorless single crystals suitable for X-ray structure analysis. Mp 201–204 °C (decomp); elemental analysis $C_{27}H_{63}Na_3N_{12}Si_6$ (%): calcd: C 40.9, H 8.00, N 21.2; found: C 41.3, H 7.97, N 21.2; ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 293 K): $\delta = 8.30$ (s, 6H), 8.08 (s, 3H), 0.32 (s, 54H, SiMe$_3$); ^{13}C{^{1}H} NMR (75.47 MHz): $\delta = 180.2$ [{Me$_3$SiNC(H)N}$_2$CH]$^-$, 170.9 [{Me$_3$SiN*C*(H)N}$_2$CH]$^-$, 0.5 (SiMe$_3$); ^{23}Na{^{1}H} NMR (66.17 MHz): $\delta = 25.0$ ($w_{1/2} = 0.36$ kHz, 1Na), 9 ($w_{1/2} \approx 2.2$ kHz, 2Na); MS (EI; M = L$_3$Na$_3$): *m/z* (%): 792 ([L$_3$Na$_3$]$^+$, 4), 551 ([L$_2$Na$_3$]$^+$, 44), 287 ([LNa$_2$]$^+$, 100).

4: 1,3,5-Triazine (**1**) (1.24 g, 15.3 mmol) was added to a solution of TlN(SiMe$_3$)$_2$ (freshly sublimed, 6.18 g, 17.0 mmol) in toluene at −20 °C. The mixture was protected from light, and stirring was continued at ambient temperature for 12 h. The organic layer was filtered and volatiles were evaporated in vacuo from the filtrate to afford the air-sensitive, analytically pure **4** (4.48 g, 66 %). Colorless, single crystals suitable for X-ray structure analysis were obtained from hexane. Elemental analysis $C_{72}H_{168}N_{32}Si_{16}Tl_8$ (%): calcd: C 24.25, H 4.75, N 12.6; found: C 25.9, H 4.80, N 12.4; ^{1}H NMR (500.13 MHz, $C_6D_5CD_3$, 293 K): $\delta = 9.72$ (s, 2H), 8.45 (s, 1H), 0.21 (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz): $\delta = 175.5$, 167.45, 0.6.

Crystal data for **3**: $C_{27}H_{63}Na_3N_{12}Si_6(C_6H_{12})_{1/2}$, $M_r = 835.5$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.372(8)$, $b = 22.57(2)$, $c = 23.50(2)$ Å, $\alpha = 92.76(6)$, $\beta = 102.75(5)$, $\gamma = 103.25(6)^\circ$, $V = 5194(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.07$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 2.2$ cm^{-1}. Data for a specimen of dimensions $0.4 \times 0.4 \times 0.4$ mm^3 were collected at 173(2) K on an Enraf-Nonius CAD-4 diffractometer, 14448 unique reflections for $2^\circ < \theta < 23^\circ$, $R1 = 0.078$ (for 9400 reflections with $I > 2\sigma(I)$), $wR2 = 0.235$ (all data). In **3** there are two independent molecules of the trimer and one poorly defined cyclohexane solvent molecule. For **4**: $C_{72}H_{168}N_{32}Si_{16}Tl_8$, $M_r = 3566.8$, monoclinic, space group $C2/c$, $a = 15.6556(4)$, $b = 30.3470(9)$, $c = 30.2663(3)$ Å, $\beta = 96.195(1)^\circ$, $V = 14295.6(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.657$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.9159$ cm^{-1}. Data for a specimen of dimensions $0.33 \times 0.21 \times 0.12$ mm^3 were collected at 193 K in the hemisphere mode on a Siemens P4 instrument fitted with a CCD area detector, 8557 unique reflections for $4.6^\circ < \theta < 54^\circ$, $R1 = 0.0565$ (for 6019 reflections with $I > 2\sigma(I)$), $wR2 = 0.1443$ (all data). Each of the structures **3** and **4** was solved by using the heavy atom method and refined with full-matrix least-squares on all F^2 (SHELXL-93 and 97, respectively) with non-hydrogen atoms anisotropic.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133067 and -133068. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Genetic Engineering of *Streptomyces coelicolor* A3(2) for the Enantioselective Reduction of Unnatural *β*-Keto-Ester Substrates[**]

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The use of whole cells for the biotransformation of organic substrates is a well-documented technique[1] which has a number of benefits over conventional, reagent-based methods. For example, bakers' yeast is routinely used for the reduction of *β*-keto-esters, and the resulting *β*-hydroxy-esters are obtained with predictably high chemo- and enantioselectivities, under mild and neutral conditions.[2] With the huge advances made in molecular biology over the last 20 years it has become possible to manipulate microbial biosynthetic pathways at the genetic level.

For a number of years Hopwood et al.[3] and others[4] have been studying the genetics of *Streptomyces coelicolor* A3(2), a soil bacterium that produces the dimeric benzoisochromanequinone antibiotic actinorhodin (**1**). The biosynthesis of **1** proceeds by the polyketide pathway outlined in Scheme 1,[5] where key features involve a type II minimal *act* polyketide synthase (PKS)—consisting of *β*-ketoacyl synthase (KS), chain length factor (CLF), and acyl carrier protein (ACP)—and associated aromatase and cyclase enzymes to assemble the naphthol **2**, which undergoes selective reduction to **3** and cyclization to the yellow pigment (*S*)-DNPA (**4**). Recently we have provided definitive proof that the *act*VI genetic region of *S. coelicolor* A3(2) is involved in the stereospecific construction of the pyran ring of **1**.[6] More specifically it was found that the engineered strain CH999/pIJ5660 (a pRM5-based plasmid[4b] containing the *act* minimal PKS, aromatase (ARO), and cyclase (CYC) genes as well as the *act*VI-

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