Na$_7$RbTl$_4$

New Ternary Alkali Metal Thallide Including Tl$_4^{8-}$ Tetrahedra

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Trying To Fill The Gaps

\[ A:Tr \ (A=\text{alkali metal}, \ Tr=\text{trielide}) \ 2:1 \]

**Li\(_2\)Ga type structure** (\(\rightarrow\) zigzag chains)
- Li\(_2\)Al [1]
- Li\(_2\)Ga [2]
- Li\(_2\)In [3]
- Li\(_2\)Tl [4]

**Na\(_2\)Tl type structure** (\(\rightarrow\) tetrahedra)
- Na\(_2\)In [5]
- Na\(_2\)Tl [6]

**Only known compounds in** \(A:Tr\) **ratio of 2:1 so far**

\[ \text{Na}_7\text{RbTl}_4 \]

**Sample Preparation**

Stoichiometrical inwight for \(\text{Na}_4\text{RbTl}_{2.5}\) in a tantalum ampoule and reaction started under following temperature program.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>RT</td>
<td>3</td>
</tr>
</tbody>
</table>

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**Picture:** S. Gärtner, *Crystals* 2020, 10(11), 1013.

Crystallographic Difficulties

Symmetry Descent: tetragonal to orthorhombic

Tetragonal $P_{int}=0.051$
Orthorhombic $P_{int}=0.034$

No structure solution possible in any tetragonal space group. Also no twinning could be observed.

### Crystallographic Data

<table>
<thead>
<tr>
<th>Property</th>
<th>Na₂TI [*]</th>
<th>Na₇RbTI₄</th>
<th>Na₂TI</th>
<th>Na₇RbTI₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>1063.88</td>
<td>1063.88</td>
<td>0.099 × 0.096 × 0.067</td>
<td>0.1 × 0.08 × 0.07</td>
</tr>
<tr>
<td><strong>Temperature [K]</strong></td>
<td>123</td>
<td>123</td>
<td>AgKα (λ = 0.56087)</td>
<td>AgKα (λ = 0.56087)</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>orthorhombic</td>
<td>orthorhombic</td>
<td>4.326 to 65.822</td>
<td>4.846 to 55.73</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C₂₂₂₁</td>
<td>Pbam</td>
<td>1.140</td>
<td>1.086</td>
</tr>
<tr>
<td><strong>a [Å]</strong></td>
<td>8.81020(10)</td>
<td>16.3584(4)</td>
<td>0.0297</td>
<td>0.0588</td>
</tr>
<tr>
<td><strong>b [Å]</strong></td>
<td>13.8277(2)</td>
<td>16.3581(4)</td>
<td>R₁ = 0.0142, wR₂ = 0.0278</td>
<td>R₁ = 0.0231, wR₂ = 0.0392</td>
</tr>
<tr>
<td><strong>c [Å]</strong></td>
<td>11.60330(10)</td>
<td>11.3345(3)</td>
<td>R₁ = 0.0150, wR₂ = 0.0280</td>
<td>R₁ = 0.0282, wR₂ = 0.0402</td>
</tr>
<tr>
<td><strong>α = β = γ [°]</strong></td>
<td>90</td>
<td>90</td>
<td>1.05/-1.75</td>
<td>1.73/-1.95</td>
</tr>
<tr>
<td><strong>Volume [Å³]</strong></td>
<td>1413.57(3)</td>
<td>3033.04(14)</td>
<td>-0.013(6)</td>
<td></td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>16</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ρ(calc) [g/cm³]</strong></td>
<td>4.705</td>
<td>4.660</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>µ [mm⁻¹]</strong></td>
<td>24.694</td>
<td>24.713</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>F(000)</strong></td>
<td>1648.0</td>
<td>3504.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparison of $\text{Na}_2\text{TI}$ and $\text{Na}_7\text{RbTI}_4$

23 Na in coordination sphere

16 Na und 5 Rb in coordination sphere
This type of coordination could not be observed in Na₇RbTl₄.
## Alkali Metal Coordination

<table>
<thead>
<tr>
<th>Symmetry Independent Alkali Metal (Wyckoff)</th>
<th>Number of Na/Rb Neighbors (Distances[Å])</th>
<th>Number of Tl Neighbors (Distances[Å])</th>
<th>Symmetry Independent Alkali Metal (Wyckoff)</th>
<th>Number of Na/Rb Neighbors (Distances[Å])</th>
<th>Number of Tl Neighbors (Distances[Å])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1 (4a)</td>
<td>Na: 6 (&lt;3.7) + 2 (&lt;4.1)</td>
<td>4 (&lt;3.5) → CN=12</td>
<td>Na1 (8i)</td>
<td>Na: 5 (&lt;3.7) Rb: 1 (&lt;4.1) + 1 (&lt;4.6)</td>
<td>3 (&lt;3.3) + 1 (&lt;3.5) → CN=11</td>
</tr>
<tr>
<td>Na2 (4h)</td>
<td>Na: 6 (&lt;3.7)</td>
<td>6 (&lt;3.7) → CN=12</td>
<td>Na2 (4h)</td>
<td>Na: 4 (&lt;3.51) + 1 (&lt;4.0) Rb: 2 (&lt;4.5)</td>
<td>4 (&lt;3.4) → CN=11</td>
</tr>
<tr>
<td>Na3 (8c)</td>
<td>Na: 7 (&lt;3.7) + 2 (&lt;4.2)</td>
<td>5 (&lt;3.8) → CN=14</td>
<td>Na3 (4h)</td>
<td>Na: 1 (&lt;3.0) + 7 (&lt;4.0), Rb: 1 (&lt;3.8)</td>
<td>5 (&lt;3.5) → CN=14</td>
</tr>
<tr>
<td>Na4 (8c)</td>
<td>Na: 7 (&lt;3.7) + 1 (&lt;4.2)</td>
<td>4 (&lt;3.3) → CN=12</td>
<td>Na4 (4f)</td>
<td>Na: 4 (&lt;3.6) + 2 (&lt;3.8), Rb: 2 (&lt;4.7)</td>
<td>4 (&lt;3.5) → CN=12</td>
</tr>
<tr>
<td>Na5 (8c)</td>
<td>Na: 7 (&lt;3.8) + 3 (&lt;4.2)</td>
<td>3 (&lt;3.5) + 1 (&lt;4.2) → CN=14</td>
<td>Na5 (8i)</td>
<td>Na: 6 (&lt;3.8) Rb: 2 (&lt;4.1)</td>
<td>4 (&lt;3.5) → CN=12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na6 (8i)</td>
<td>Na: 3 (&lt;3.6) + 2 (&lt;3.9), Rb: 2 (&lt;4.2)</td>
<td>5 (&lt;3.5) → CN=12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na7 (4e)</td>
<td>Na: 4 (&lt;3.51) + 2 (&lt;3.9), Rb: 2 (&lt;3.7)</td>
<td>4 (&lt;3.5) → CN=12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na8 (4g)</td>
<td>Na: 1 (&lt;3.0) + 5 (&lt;3.9), Rb: 1 (&lt;3.8)</td>
<td>5 (&lt;3.5) → CN=12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na9 (4g)</td>
<td>Na: 2 (3.5) + 3 (&lt;3.9), Rb: 2 (&lt;4.6)</td>
<td>3 (&lt;3.3) + 1 (&lt;3.6) → CN=11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Na10 (8i)</td>
<td>Na: 3 (&lt;3.6) + 4 (&lt;3.8), Rb: 2 (&lt;4.3)</td>
<td>3 (&lt;3.3) → CN=12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rb1 (4h)</td>
<td>Na: 13 (&lt;4.5)</td>
<td>5 (&lt;4.3) → CN=18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rb2 (4g)</td>
<td>Na: 3 (&lt;3.8), 6 (&lt;4.2), 4 (&lt;4.6)</td>
<td>4 (&lt;4.1) + 1 (&lt;4.3) → CN=18</td>
</tr>
</tbody>
</table>

While in Na₂Tl the coordination number (CN) of sodium only differs in 12 and 14, in Na₇RbTl₄ the coordination numbers of the alkali metals vary from 11, 12, 14 to 18.
Closer Look On The Tl$_4$ Tetrahedra

<table>
<thead>
<tr>
<th>Na$_2$Tl tetrahedra</th>
<th>Na$_7$RbTl$_4$ tetrahedra 1</th>
<th>Na$_7$RbTl$_4$ tetrahedra 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\angle 1,1,2$=58.569(4)$^\circ$</td>
<td>$\angle 1,2,3$=58.223(7)$^\circ$</td>
<td>$\angle 4,5,6$=58.124(7)$^\circ$</td>
</tr>
<tr>
<td>$\angle 2,1,1$=62.282(4)$^\circ$</td>
<td>$\angle 3,1,2$=56.140(7)$^\circ$</td>
<td>$\angle 6,4,5$=61.820(7)$^\circ$</td>
</tr>
<tr>
<td>$\angle 1,2,1$=59.150(5)$^\circ$</td>
<td>$\angle 2,3,1$=65.637(8)$^\circ$</td>
<td>$\angle 5,6,4$=60.056(4)$^\circ$</td>
</tr>
<tr>
<td>$\angle 2,1,2$=59.455(6)$^\circ$</td>
<td>$\angle 3,1,3$=61.174(10)$^\circ$</td>
<td>$\angle 6,4,6$=62.757(9)$^\circ$</td>
</tr>
<tr>
<td>$\angle 1,2,2$=62.118(4)$^\circ$</td>
<td>$\angle 3,3,1$=59.413(5)$^\circ$</td>
<td>$\angle 6,6,4$=58.621(5)$^\circ$</td>
</tr>
<tr>
<td>$\angle 2,2,1$=58.428(4)$^\circ$</td>
<td>$\angle 3,2,3$=62.788(9)$^\circ$</td>
<td>$\angle 6,5,6$=60.215(9)$^\circ$</td>
</tr>
<tr>
<td>$\angle 3,3,2$=58.606(5)$^\circ$</td>
<td>$\angle 6,6,5$=59.893(5)$^\circ$</td>
<td></td>
</tr>
</tbody>
</table>
Powder Diffraction Pattern at Room Temperature

Na₂Tl (impurities: Na₆Tl)

Na₇RbTl₄ is the main compound (impurities: Na₄Rb₆Tl₁₃, Na₂₃Rb₉Tl₁₅.₃, Na₁₅Rb₆Tl₁₈H)
First Theoretical Calculations: DOS

$\text{Na}_2\text{Tl}$

$\text{Na}_7\text{RbTl}_4$

→ Band structure calculations planned
→ Calculations on the Tl$_4$ cluster unit planned
Solvation Test in Liquid Ammonia

Motivation: Polyanionic salts right to the Zintl border normally dissolve either colorful or show no solubility in liquid ammonia.

\[
\begin{align*}
\text{Na}_2\text{Tl} & \quad \text{and} \quad \text{Na}_7\text{RbTl}_4 \quad \text{in liquid ammonia} \\
\rightarrow \text{Solvated electrons} & \quad \rightarrow \text{Tl}_4^{8-} \quad \text{cluster unstable in solution} \\
\rightarrow \text{Degradation of} \quad \text{Na}_2\text{Tl} & \quad \text{and} \quad \text{Na}_7\text{RbTl}_4
\end{align*}
\]