Supporting Information

Na₆TlSb₄: Synthesis, Structure, and Bonding. An Electron-Rich Salt with a Chain Conformation and a Tl–Tl Bond Length Determined by the Cation

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Table S1. Crystal data and structure refinement for Na₆TlSb₄.

Empirical formula	Na ₆ TlSb ₄	
Formula weight	829.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group, Z	C2/c (No. 15), 8	
Unit cell dimensions ^a	$a = 15.154(3)$ Å	$\alpha = 90^\circ$.
	$b = 10.401(2)$ Å	$\beta = 113.57(3)^\circ$.
	$c = 17.413(4)$ Å	$\gamma = 90^\circ$.
Volume	2515.5(9) Å ³	
Density (calculated)	4.380 Mg/m ³	
Absorption coefficient	21.396 mm ⁻¹	
Crystal size	0.15 x 0.15 x 0.25 mm ³	
Theta range for data collection	2.45 to 25.00°	
Index ranges	0 ≤ h ≤ 18, -2 ≤ k ≤ 12, -20 ≤ l ≤ 18	
Reflections collected	4472	
Independent observed reflections	2219 [R(int) = 0.2077]	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2219 / 0 / 101	
Goodness-of-fit on F ²	0.875	
Final R indices [I > 2σ(I)] ^b	R1 = 0.0387, wR2 = 0.0652	
R indices (all data)	R1 = 0.0816, wR2 = 0.0729	
Extinction coefficient	0.000130(8)	
Largest diff. peak and hole	2.283 and -1.765 e ⁻ Å ⁻³	

^a Refined from Guinier data with Si as internal standard, $\lambda = 1.540562$ Å, 23 °C.^b $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^{1/2}$.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Na_6TlSb_4 . $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Tl(1)	912(1)	3587(1)	3254(1)	22(1)
Sb1	964(1)	6000(1)	4231(1)	18(1)
Sb2	840(1)	1198(1)	4180(1)	18(1)
Sb3	2527(1)	3529(1)	2669(1)	19(1)
Sb4	1959(1)	9429(1)	5823(1)	18(1)
Na1	3052(3)	1617(9)	4453(4)	29(2)
Na2	2035(4)	8571(8)	4031(4)	30(2)
Na3	1170(4)	946(9)	2406(4)	28(2)
Na4	3884(4)	1195(9)	2652(4)	30(2)
Na5	9739(4)	8579(8)	4176(4)	28(2)
Na6	9388(4)	3662(9)	4113(4)	29(2)

Table S3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Na_6TlSb_4 . The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl1	30(1)	19(1)	25(1)	1(1)	20(1)	1(1)
Sb1	22(1)	18(1)	17(1)	-3(1)	10(1)	1(1)
Sb2	22(1)	16(1)	15(1)	2(1)	8(1)	-1(1)
Sb3	18(1)	21(1)	21(1)	-3(1)	12(1)	0(1)
Sb4	17(1)	21(1)	15(1)	-3(1)	8(1)	2(1)
Na1	23(3)	31(5)	28(3)	0(4)	6(2)	-10(4)
Na2	41(3)	29(6)	27(3)	-3(4)	21(3)	-3(4)
Na3	29(3)	31(5)	26(3)	0(4)	12(3)	6(4)
Na4	41(3)	28(5)	21(3)	-1(4)	14(3)	6(4)
Na5	22(2)	26(5)	41(4)	2(4)	18(2)	2(4)
Na6	30(3)	37(6)	23(3)	4(4)	14(2)	7(4)

Table S4. Bond lengths [Å] for Na₆TlSb₄.

Tl(1)-Tl(1)#1	2.9541(17)
Tl(1)-Sb(2)	2.9875(15)
Tl(1)-Sb(3)	3.0048(12)
Tl(1)-Sb(1)	3.0152(16)
Tl(1)-Na(6)#2	3.215(5)
Tl(1)-Na(4)#3	3.215(8)
Tl(1)-Na(3)	3.216(8)
Tl(1)-Na(1)#4	3.666(6)
Tl(1)-Na(1)	3.696(7)
Tl(1)-Na(4)#5	3.914(7)
Tl(1)-Na(6)#6	3.963(6)
Tl(1)-Na(3)#1	3.990(7)
Sb(1)-Na(6)#7	3.155(6)
Sb(1)-Sb(4)#8	3.2177(13)
Sb(1)-Na(2)	3.219(8)
Sb(1)-Na(5)#2	3.242(8)
Sb(1)-Na(4)#5	3.255(6)
Sb(1)-Na(2)#8	3.348(6)
Sb(1)-Na(6)#2	3.357(8)
Sb(1)-Na(4)#3	3.384(6)
Sb(1)-Na(1)#4	3.486(8)
Sb(2)-Na(5)#9	3.193(8)
Sb(2)-Na(3)#1	3.202(6)
Sb(2)-Na(1)	3.221(5)
Sb(2)-Na(1)#4	3.234(8)
Sb(2)-Sb(4)#10	3.2499(18)
Sb(2)-Na(5)#7	3.320(6)
Sb(2)-Na(3)	3.330(6)
Sb(2)-Na(2)#10	3.344(8)
Sb(2)-Na(6)#2	3.350(8)
Sb(3)-Na(4)	3.190(8)
Sb(3)-Sb(4)#8	3.2221(18)
Sb(3)-Na(3)#3	3.232(8)
Sb(3)-Na(2)#11	3.282(6)
Sb(3)-Na(6)#6	3.296(6)
Sb(3)-Na(3)	3.302(8)
Sb(3)-Na(5)#12	3.331(6)
Sb(3)-Na(4)#3	3.408(8)
Sb(3)-Na(1)	3.502(7)
Sb(4)-Sb(1)#8	3.2177(13)
Sb(4)-Sb(3)#8	3.2221(18)
Sb(4)-Sb(2)#13	3.2499(18)
Sb(4)-Na(2)	3.291(6)
Sb(4)-Na(5)#14	3.303(7)
Sb(4)-Na(4)#15	3.413(6)
Sb(4)-Na(2)#8	3.437(8)
Sb(4)-Na(3)#15	3.438(6)
Sb(4)-Na(5)#2	3.550(6)

Na(1)-Sb(2)#4	3.234(8)
Na(1)-Na(5)#12	3.452(10)
Na(1)-Na(2)#10	3.470(12)
Na(1)-Sb(1)#4	3.486(8)
Na(1)-Na(1)#4	3.515(14)
Na(1)-Na(3)	3.631(8)
Na(1)-Tl(1)#4	3.666(6)
Na(1)-Na(6)#16	3.691(7)
Na(1)-Na(4)	3.844(8)
Na(2)-Sb(3)#3	3.282(6)
Na(2)-Sb(2)#13	3.344(8)
Na(2)-Sb(1)#8	3.348(6)
Na(2)-Sb(4)#8	3.437(8)
Na(2)-Na(1)#13	3.470(12)
Na(2)-Na(6)#5	3.511(7)
Na(2)-Na(3)#13	3.585(10)
Na(2)-Na(5)#2	3.589(7)
Na(2)-Na(4)#3	3.658(10)
Na(2)-Na(2)#8	3.813(14)
Na(3)-Sb(2)#1	3.202(6)
Na(3)-Sb(3)#11	3.232(8)
Na(3)-Sb(4)#17	3.438(6)
Na(3)-Na(5)#18	3.538(10)
Na(3)-Na(2)#10	3.585(10)
Na(3)-Na(3)#1	3.688(10)
Na(3)-Na(6)#6	3.729(11)
Na(3)-Na(4)	3.970(7)
Na(4)-Tl(1)#11	3.215(8)
Na(4)-Sb(1)#19	3.255(6)
Na(4)-Sb(1)#11	3.384(6)
Na(4)-Sb(3)#11	3.408(8)
Na(4)-Sb(4)#17	3.413(6)
Na(4)-Na(5)#12	3.482(10)
Na(4)-Na(6)#12	3.527(11)
Na(4)-Na(4)#6	3.626(11)
Na(4)-Na(2)#11	3.658(10)
Na(4)-Tl(1)#19	3.914(7)
Na(5)-Sb(2)#20	3.193(8)
Na(5)-Sb(1)#21	3.242(8)
Na(5)-Sb(4)#14	3.303(7)
Na(5)-Sb(2)#7	3.320(6)
Na(5)-Sb(3)#22	3.331(6)
Na(5)-Na(1)#22	3.452(10)
Na(5)-Na(4)#22	3.482(10)
Na(5)-Na(3)#23	3.538(10)
Na(5)-Sb(4)#21	3.550(6)
Na(5)-Na(2)#21	3.589(7)
Na(5)-Na(6)#24	3.592(10)
Na(5)-Na(5)#25	3.971(15)
Na(6)-Sb(1)#7	3.155(6)

Na(6)-Ti(1)#21	3.215(5)
Na(6)-Sb(3)#6	3.296(6)
Na(6)-Sb(2)#21	3.350(8)
Na(6)-Sb(1)#21	3.357(8)
Na(6)-Na(2)#19	3.511(7)
Na(6)-Na(4)#22	3.527(11)
Na(6)-Na(5)#24	3.592(10)
Na(6)-Na(1)#16	3.691(7)
Na(6)-Na(3)#6	3.729(11)
Na(6)-Na(1)#22	3.854(11)
Na(6)-Ti(1)#6	3.963(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2 #2 x-1,y,z #3 -x+1/2,y+1/2,-z+1/2
 #4 -x+1/2,-y+1/2,-z+1 #5 x-1/2,y+1/2,z #6 -x+1,y,-z+1/2
 #7 x-1,y-1,z #8 x,y-1,z #9 -x+1,-y+1,-z+1
 #10 -x+1/2,-y+3/2,-z+1 #11 -x+1/2,y-1/2,-z+1/2
 #12 x-1/2,y-1/2,z #13 x,y+1,z #14 -x+1,-y+2,-z+1
 #15 x,-y+1,z+1/2 #16 -x+3/2,-y+1/2,-z+1 #17 x,-y+1,z-1/2
 #18 -x+1,y-1,-z+1/2 #19 x+1/2,y-1/2,z #20 x+1,y+1,z
 #21 x+1,y,z #22 x+1/2,y+1/2,z #23 -x+1,y+1,-z+1/2
 #24 -x+2,-y+1,-z+1 #25 -x+2,-y+2,-z+1