Reaction of Sn_4^{4-} in liquid ammonia: Synthesis and characterization of $Rb_6[(\eta^2\text{-}Sn_4)Zn(\eta^3\text{-}Sn_4)] \cdot 5NH_3$

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Supplementary Information

Experimental procedure

All manipulations were performed under argon atmosphere using standard Schlenk and Glovebox techniques. Liquid ammonia was dried over elemental potassium prior to use. Diphenylzinc, $ZnPh_2$, and [2.2.2]-cryptand (systematic name: 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) were commercially purchased from Sigma Aldrich and used without further drying.

50 mg Rb_4Sn_4 [1] (0.06 mmol) were dissolved in approximately 5 mL liquid ammonia together with 13 mg $ZnPh_2$ (0.06 mmol) and 23 mg [2.2.2]-cryptand (0.06 mmol). The solution immediately turned deeply red after the addition of liquid ammonia and was stored at 236 K for about 6 months until crystallization. Crystals of $Rb_6[(\eta^2\text{-}Sn_4)Zn(\eta^3\text{-}Sn_4]\cdot 5NH_3$ **(1)** (major product) and $(Rb@[2.2.2]\text{-crypt})ZnPh_3\cdot NH_3$ **(2)** were obtained.

Crystal structure determination

Thermally unstable, air- and moisture- sensitive crystals of **1** and **2** suitable for X-ray structure analysis were isolated and directly transferred from the mother liquor into perfluorether oil at 213 K. The crystals were mounted onto an Agilent SuperNova diffractometer and analytical absorption correction respectively multiscan absorption correction was applied. Data collection was carried out at 123 K by using graphite-monochromated Mo-Kα-radiation (λ=0.71073Å). The data reductions were performed with the Crysalis program package.[2] The structures of **1** and **2** were determined with the SIR92[3] respectively OLEX2[4] program packages and refined anisotropically with SHELXL-97[5] against $|F^2|$ for all non-hydrogen atoms.

The crystal of **1** showed non-merohedral twinning. Due to only few overlapping reflections (200) the reflections from the main domain (indexing of 75%) allowed the solution of the structure. Hydrogen atoms of one ammonia molecule could be located in the difference fourier maps, for 2 ammonia molecules, the hydrogen atoms were placed in geometrically reasonable positions. For one disordered ammonia molecule constructed positions did not seem reasonable. This results in a discrepancy of reported sum formula and calculated values for the hydrogen atoms in the .cif-file. Rb4 showed disordering, which allowed the introduction of split positions. Rb5 is located on a general position but a s.o.f. of 0.5 was fixed (after a careful examination by using a second free variable which refined to a value of 0.5) and allowed the electro neutral formulation of **1**. The selected X-ray data and refinement parameters for **1** are shown in Table 1. Atomic coordinates and displacement parameters are listed in Table 3 to Table 5.

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[1] further information concerning synthesis and characterization see Supplementary Information of the previously published article, *Angew. Chem. Int. Ed.*, **2013**, *52*, 4483–4486

[2] CrysAlisPro, Agilent Technologies, Version 1.171.36.28 (release 01-02-2013 CrysAlis171 .NET)

[3] L. J. Farrugia, *J. Appl. Cryst.*, **1999**, *32*, 837. Sluis, P. van der & Spek, A.L., *Acta Cryst.*,**1990**, *A46*, 194–201

[4] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, **2009**, *42*, 339–341

[5] G. Sheldrick, SHELX97 – Programs for solution and refinement of crystal structures, Universität Göttingen, 1997

Table 1 Selected X-ray data collection and refinement parameters for $Rb_6Sn_8Zn{\cdot}5NH_3$ (Deposition number CSD 426039)

FW/g mol^{-1}	1612.88
Space group, Z	$I2/m$, 4
a/Å	19.7142(3)
b/Å	7.82480(10)
c/Å	21.0029(3)
β/°	105.632(2)
V/Å^3	3120.06(8)
ρ_{calc}/g cm^{-1}	3.434
Radiation, λ/Å	MoKα, 0.71073
T/K	123.15
μ/cm^{-1}	16.339
Reflections collected	26678
Independent reflections	3416
R_{int}	0.0347
R_1/w R_2, $I \geq 2\sigma_1$	0.0198/0.0509
R_1/w R_2, all data	0.0228/0.0520

For the crystal structure of **2**, the hydrogen atoms of the cryptand molecule and the phenyl substituents of $ZnPh_3$ were placed using HFIX 23 respectively HFIX 43. The hydrogen atoms of the ammonia molecule could be located in the fourier difference maps and were refined isotropically. For further information on structure determination see table 2.

Table 2 Selected X-ray data collection and refinement parameters for (Rb@[2.2.2]-crypt)$ZnPh_3 \cdot NH_3$ (Deposition number CCDC 939282)

FW/g mol^{-1}	775.66
Space group, Z	$P2_1/c$, 4
a/Å	15.12530(10)
b/Å	13.62330(10)
c/Å	18.76700(10)
β/°	99.3590(10)
V/Å^3	3815.59(4)
ρ_{calc}/g cm^{-1}	1.350
Radiation, λ/Å	MoKα, 0.71073
T/K	123.15
μ/cm^{-1}	1.956
Reflections collected	23861
Independent reflections	6967
R_{int}	0.0188
R_1/w R_2, $I \geq 2\sigma_1$	0.0225/0.0516
R_1/w R_2, all data	0.0263/0.0533

Table 3 Atomic Coordinates and Isotropic Displacement Parameters for $Rb_6Sn_8Zn{\cdot}5NH_3$

Atom	**x [Å]**	**y[Å]**	**z[Å]**	**s.o.f.**	**U*eq*[Å²]**
Sn04	0.66397(2)	0.00000	0.14159(2)	1	0.0172(1)
Sn02	0.48552(2)	-0.50000	0.23844(2)	1	0.0168(1)
Sn03	0.36543(2)	-0.50000	0.29134(2)	1	0.0161(1)
Sn01	0.48594(1)	0.30741(4)	0.36446(1)	1	0.0145(1)
Sn05	0.72250(1)	0.30429(4)	0.38612(1)	1	0.0139(1)
Sn06	0.81540(2)	-0.50000	0.49156(2)	1	0.0151(1)
Zn1	0.60008(3)	-0.50000	0.34796(3)	1	0.0116(2)
N03	0.4012(5)	0.00000	0.4868(4)	1	0.059(3)
N02	0.2300(2)	-0.2542(6)	0.3639(2)	1	0.0237(12)
N01	0.4388(3)	0.00000	0.1866(3)	1	0.0291(19)
N4A	0.6062(7)	-0.50000	0.0217(14)	0.50(10)	0.020(6)
N4B	0.5976(7)	-0.50000	0.0575(12)	0.50(10)	0.017(5)
Rb01	0.58652(3)	0.00000	0.28525(3)	1	0.0150(2)
Rb02	0.33234(3)	0.00000	0.32606(4)	1	0.0235(2)
Rb03	0.67859(3)	-0.50000	0.20650(3)	1	0.0173(2)
Rb4B	0.773(2)	0.00000	0.5320(10)	0.52(16)	0.043(4)
Rb5	0.48785(4)	-0.23123(12)	0.07888(5)	0.500	0.0195(3)
Rb6	0.37206(4)	-0.50000	0.47736(4)	1	0.0406(3)
Rb4A	0.7508(10)	0.00000	0.5247(5)	0.48(16)	0.0251(15)

Table 4 Atomic Coordinates of Hydrogen Atoms and Isotropic Displacement Parameters for $Rb_6Sn_8Zn \cdot 5NH_3$

Atom	x [Å]	y[Å]	z[Å]	s.o.f.	U*eq*[Å²]
H03A	0.43400	-0.05380	0.47040	0.5	0.0740
H4AA	0.60340	0.05590	0.47690	0.5	0.0740
H03B	0.41490	-0.10960	0.49730	0.5	0.0740
H02A	0.25210	-0.31840	0.34200	1	0.05(2)
H4AB	0.79820	0.33620	0.61620	1	0.040(17)
H02B	0.19410	-0.21310	0.33010	1	0.06(2)
H01B	0.44040	-0.01230	0.23020	0.5	0.0740
H01A	0.43290	-0.10440	0.16690	0.5	0.0740
H01C	0.40120	-0.06790	0.16690	0.5	0.0740

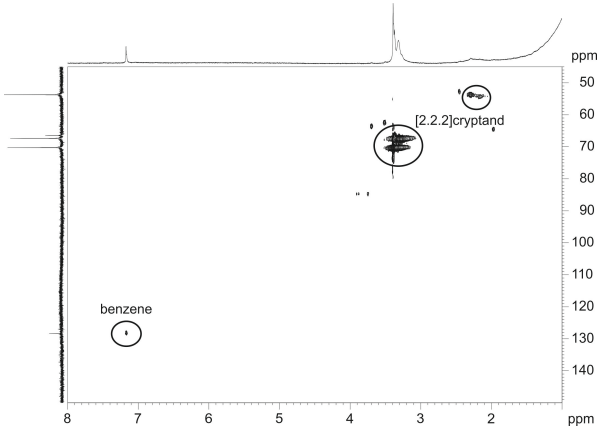
Table 5 Atomic Coordinates and Anisotropic Displacement Parameters for $Rb_6Sn_8Zn \cdot 5NH_3$

Atom	U_{11} [Å²]	U_{22}[Å²]	U_{33}[Å²]	U_{23}[Å²]	U_{13}[Å²]	U_{13}[Å²]
Sn04	0.0123(2)	0.0243(3)	0.0172(2)	0.0000	0.0078(2)	0.0000
Sn02	0.0165(2)	0.0236(2)	0.0110(2)	0.0000	0.0051(2)	0.0000
Sn03	0.0102(2)	0.0195(2)	0.0176(2)	0.0000	0.0020(2)	0.0000
Sn01	0.0138(2)	0.0107(2)	0.0196(2)	0.0036(1)	0.0055(1)	0.0002(1)
Sn05	0.0124(1)	0.0092(2)	0.0189(2)	-0.0014(1)	0.0024(1)	-0.0006(1)
Sn06	0.0155(2)	0.0173(2)	0.0107(2)	0.0000	0.0007(2)	0.0000
Zn1	0.0073(3)	0.0154(4)	0.0124(3)	0.0000	0.0034(3)	0.0000
N03	0.071(6)	0.045(5)	0.044(5)	0.0000	-0.012(4)	0.0000
N02	0.028(2)	0.022(2)	0.023(2)	0.0038(19)	0.0102(19)	-0.0008(19)
N01	0.018(3)	0.036(4)	0.029(3)	0.0000	-0.001(3)	0.0000
N4A	0.020(6)	0.021(7)	0.022(14)	0.0000	0.011(6)	0.0000
N4B	0.024(6)	0.019(6)	0.013(11)	0.0000	0.013(6)	0.0000
Rb01	0.0144(3)	0.0145(3)	0.0169(3)	0.0000	0.0058(2)	0.0000
Rb02	0.0181(3)	0.0151(3)	0.0386(4)	0.0000	0.0097(3)	0.0000
Rb03	0.0210(3)	0.0165(3)	0.0161(3)	0.0000	0.0080(2)	0.0000
Rb4B	0.089(10)	0.0177(12)	0.037(3)	0.0000	0.042(5)	0.0000
Rb5	0.0136(4)	0.0178(4)	0.0239(5)	0.0027(4)	-0.0003(3)	0.0007(3)
Rb6	0.0200(4)	0.0881(7)	0.0151(3)	0.0000	0.0072(3)	0.0000
Rb4A	0.049(4)	0.0127(12)	0.0221(19)	0.0000	0.024(2)	0.0000

NMR-Data Collection and Processing

NMR spectra were recorded on a Bruker Avance 600 (600.13 MHz) spectrometer with a 5 mm broadband triple resonance Z-gradient (53.5 G cm^{-1}). The temperature was controlled by a Bruker BVTE 3000 unit. NMR data were processed with the Bruker TOPSPIN 3.2 program.

For $ZnPh_2$ four signals would be expected in ^{13}C NMR-experiments (148.1, 137.7, 127.8, 127.6 ppm).[6] These could be neither detected in 1D-^{13}C spectrum nor in the $^{1}H^{13}C$-HSQC spectrum. We only observed signals at 7.17 ppm and 128.33 ppm, which fit the literature known values for benzene (Figure 1).[7] The remaining ^{13}C signals can be assigned to the [2.2.2]-cryptand molecule.



[6] These data have been obtained by own measurements of $ZnPh_2$ in CD_2Cl_2.
[7] Predicted NMR data calculated using Advanced Chemistry Development, Inc. (ADC/Labs) Software V11.01 (© 1994-2013 ADC/Labs).

Figure 1: $^{1}H^{13}C$-HSQC spectrum of Rb_4Sn_4 + [2.2.2]-cryptand + $ZnPh_2$ in liquid NH_3 at 233 K, shows the signal for benzene, but none for $ZnPh_2$ are detected in this solution.