The first ternary tin(II) nitride: NaSnN

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NaSnN with the non-centrosymmetric layered structure type of KSnAs and featuring the new layered Zintl ion $[SnN]^-$ is the first example of a ternary nitride containing Sn–N bonds, and the first example of a nitride containing formally divalent tin.

Ternary nitrides[1] are a growing class of material and are expected to exhibit properties complementary to those of the better known oxides and chalcogenides. Binary, ternary and higher nitrides of the elements are less thermodynamically stable than the corresponding oxides as the greater energy cost associated with breaking the strong bond in N_2 relative to that in O_2 is not compensated for by a corresponding increase in bonding in the nitride product relative to an oxide product. The effects of this are familiar to those working in the area of nitride chemistry: nitrides are often subject to aerial oxidation or hydrolysis, although many are kinetically stable at ambient temperatures and are of increasing technological importance.

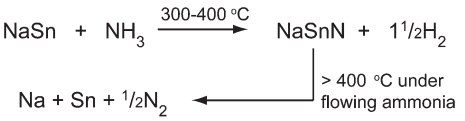
Many elements in the periodic table, notably several heavy late transition metals and some heavy p-block metals such as lead, do not form binary nitrides because these are of low thermodynamic stability with respect to the elements partly due to weak M–N bonding. The first and, until now, the only known nitride containing Sn–N bonds is the binary spinel phase Sn_3N_4. This was synthesised in crystalline form[2] by reacting tin(IV) halides with potassium amide in liquid ammonia and with subsequent annealing under vacuum at 300 °C (thermal decomposition occurred at higher temperatures). Sn_3N_4 had previously been prepared in amorphous form by thermal decomposition of $Sn(NH_2)_2NH$[3] derived from $SnBr_4$ and KNH_2 in liquid ammonia, and in crystalline thin film form by using the vapour phase reaction between $Sn(NMe_2)_4$ and ammonia.[4]

At the other end of the periodic table, although Li_3N is well characterised, the nitrides of the heavier alkali metals K–Cs are unknown and Na_3N, with the anti-ReO_3 structure, was reported only recently,[5] synthesised by a novel low-temperature route and subject to thermal decomposition to the elements above 90 °C. The instability of the heavier alkali metal nitrides is likely to be associated with the difficulty in satisfying the coordination requirements of both ions in a compound with the A_3X stoichiometry.

We have recently reported a new route to ternary nitrides which relies on the oxidation of a highly electropositive intermetallic binary with ammonia gas. $BaSiN_2$ was synthesised by the reaction between BaSi and flowing NH_3 at the comparatively low temperature of 550 °C.[6] However, this ternary nitride is quite thermally stable and may be synthesised at much higher temperatures using more conventional methods such as the reaction between the binary nitrides under anaerobic conditions. The true value of the reaction between an intermetallic and ammonia is in the bulk synthesis of nitrides which are so thermally unstable with respect to the elements or an intermetallic that they cannot be made by routes (such as the reaction between two binary nitrides) in which a large amount of heat energy is required to overcome the activation barrier to reaction. (Such reactions also preclude the use of thermally unstable binaries such as Na_3N and Sn_3N_4 as reactants.)

Here we report the synthesis of NaSnN, the first ternary nitride containing Sn–N bonds, using the reaction between the highly reactive intermetallic Zintl phase NaSn and ammonia gas (Scheme 1). NaSn was synthesised† from the elements[7] and pulverised in an argon-filled glove box with an O_2 and H_2O content <1 ppm. The grey intermetallic was placed in an alumina boat and reacted with flowing ammonia gas (1 cm^3 s^{-1}) at temperatures of between 100 and 700 °C for periods of 12–24 h. No reaction was observed at 100 °C while at 700 °C the only remaining product was elemental tin, the sodium having sublimed from the boat and reacted downstream with the silica tube. The main product of a reaction of 16 h duration at the optimal temperature of 400 °C was a dark red solid (NaSnN) which was distributed over the entire inner surface of the alumina boat, indicating that some transport of the product in the vapour phase had occurred. Some lumps of elemental tin were observed in the product and overall there was a slight decrease in the mass of the sample by 2.4% indicating that partial decomposition occurs at this temperature (*i.e.* about 15% of the NaSnN product formed in the reaction goes on to decompose thermally during a 16 h treatment at 400 °C). The red NaSnN was separated fairly readily from the excess tin produced by decomposition and the material which had transported to the walls of the crucible was found to consist of well-formed single crystals of NaSnN.

Laboratory powder X-ray diffraction measurements showed the presence of a new phase which was readily indexed by hand on a primitive hexagonal unit cell with a = 3.333(2) Å and c = 5.4513(4) Å. Chemical analysis† on the bulk powder and on individual single crystals showed that the Na : Sn ratio in the crystals was 1 : 1 and that the overall stoichiometry was NaSnN containing the chemically sensible Sn^{II} species. Single crystal X-ray diffraction data showed weak superstructure reflections which



Scheme 1 The formation and thermal decomposition of NaSnN.

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Table 1 Structural parameters for NaSnN‡

Atom	Site	x	y	z	$U(\mathrm{eq})^a/\mathrm{Å}^2$
Sn	2*a*	0	0	0.0000(2)	0.0069(1)
Na	2*b*	1/3	2/3	0.2466(7)	0.0128(2)
N	2*b*	2/3	1/3	0.0980(4)	0.0081(5)

[a] U(eq) is defined as one third of the orthogonalised U_{ij} tensor.

were consistent with a doubling of the *c* axis and this was confirmed by analysis of high intensity powder X-ray diffraction data collected on Station 9.1 at the UK Synchrotron Radiation Source (SRS) at the Daresbury Laboratory. The systematic absences in the X-ray diffraction patterns were consistent with the space groups $P6_3mc$, $P\bar{6}2c$ and $P6_3/mmc$. Location of the tin atoms by direct methods, followed by the location of the sodium and nitrogen atoms from the Fourier difference map and subsequent refinement‡ showed that NaSnN adopts the KSnAs structure type[8,9] crystallising in the non-centrosymmetric space group $P6_3mc$ (No. 186) (see Table 1 for structural parameters). The inversion symmetry is only broken by the light atoms (Na and N), but the lack of inversion symmetry was demonstrated by measuring the second harmonic generation (SHG) of 1064 nm laser light:‡ the SHG efficiency was 2–5 times that of α-quartz. Single crystal analysis of several crystals produced in different reactions showed that in some the absolute polarity could not be determined with certainty (Flack parameter of ~0.5 with a large esd). This suggests that some crystals of the compound may be twinned. In the case of the high-quality crystal reported here, the absolute polarity was determined satisfactorily (Flack parameter = 0.0(2)).[10]

One way to view the structure, shown in Fig. 1, is as slabs of edge-shared N-centred NNa_3Sn_3 octahedra obtained by an abc stacking of Sn–N–Na atomic layers with the slabs then stacked in A(abc)B(acb)A(abc) fashion. This description suggests an analogy with a cation-ordered variant of the Ca_2N structure[11] and the antitypes of the CdI_2 and $CdCl_2$ structure types.

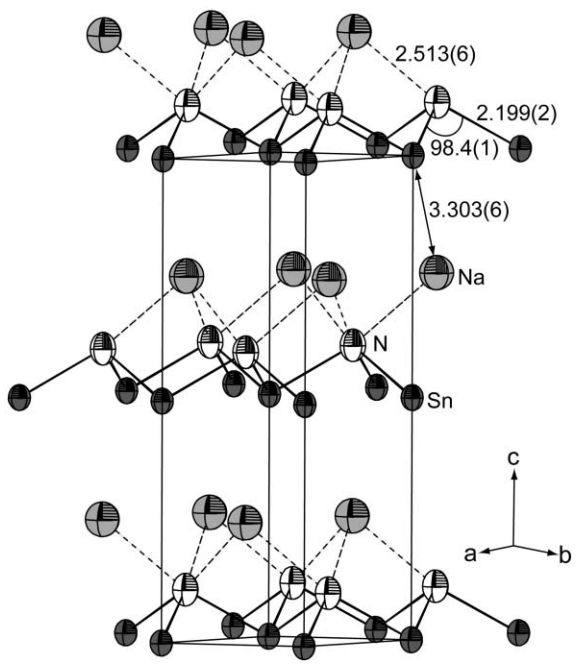

Fig. 1 Crystal structure of NaSnN showing the two-dimensional $[SnN]^-$ Zintl anions (isoelectronic and isostructural with the layers in elemental arsenic) separated by Na^+ ions. Interatomic separations in Å and angles in degrees; 99% displacement ellipsoids are shown.

The most useful formulation for NaSnN is as Na[SnN] with the $[SnN]^-$ Zintl anion forming a puckered hexagonal layer isoelectronic and isostructural with the layers in elemental arsenic[12] and a high pressure form of black phosphorus.[13] Such Zintl anions are found in $CaSi_2$,[14] $CaGe_2$,[15] a high pressure form of $SrGe_2$,[16] and several ternary compounds including the heavier pnictide analogues of NaSnN: Na[SnP],[17] K[SnAs][8,9] (first described with this structure), K[SnSb][9,18] and the halide analogue [BiTe]Cl.[19]

The three identical Sn–N distances of 2.199(3) Å are close to the average of the Sn–Sn distances of 2.973 Å in NaSn[7] and the N–N distance of 1.45 Å in molecular hydrazine H_2NNH_2. There are no other Sn^{II} nitrides for comparison, but the Sn–N distances in NaSnN are slightly larger than the Sn–N distances for Sn^{IV} in tetrahedral (2.105 Å) or octahedral (2.177 Å) coordination by N in the spinel Sn_3N_4.[2] Three-coordinate Sn^{II} compounds are rare, but the mean Sn–N distance of 2.15 Å in the 1,3-diaza-2,4-distanna-cyclobutanediide $[Sn(N(SiMe_3)_2)Cl]_2$[20] is comparable to the Sn–N distance in NaSnN, and slightly shorter Sn–N distances of 2.09 Å have been measured in the Sn^{II} amide $Sn[N(SiMe_3)_2]_2$[21] in which Sn is only 2-coordinate by nitrogen. The N–Sn–N and Sn–N–Sn angle of 98.4(2)° in NaSnN is similar to the angle of 96.6° in elemental arsenic.[12] The three Na–N distances of 2.513(6) Å are consistent with the 2.509 Å found for octahedral coordination of Na by N in $NaTaN_2$[22] and to the 2.366 Å distance for octahedral coordination of N by Na in Na_3N.[5] The three Na–Sn separations of 3.303(6) Å are fairly consistent with the Na–Sn distances of 3.445 Å in NaSn[7] and 3.417 Å in NaSnP.[17] The Sn–Sn separation of 3.33 Å suggests there is no direct Sn–Sn interaction; the pyramidal coordination of the Sn^{II} centre by nitrogen suggests a stereochemically-active lone pair protruding into the interlamellar space between the Na and Sn layers.

The extreme sensitivity of the compound to aerial hydrolysis (with evolution of ammonia gas) has prevented bulk property measurements, but the dark red colour suggests a semiconductor with a band gap of around 2.5 eV. The possibility of performing soft oxidative intercalation into the interlamellar space between the Na and Sn layers of the structure to produce a Sn^{IV} species is under investigation. This would be analogous to the intercalation demonstrated for the layered nitride Ca_2N.[11]

The synthesis of NaSnN suggests that the nitridation of reactive intermetallic compounds using ammonia is a viable route of particular value in the isolation of new phases containing weak element–nitrogen bonds which are expected to decompose with loss of N_2 at elevated temperatures. Syntheses of further nitrides of the heavy p-block metals are in progress.

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Notes and references

† NaSn was synthesised by reacting together equimolar quantities of Na (Aldrich 99+%) and Sn shot (Alfa 99.99+%) at 800 °C in a stainless steel tube that was welded closed in an argon atmosphere and sealed inside an evacuated silica jacket. Quantitative elemental analysis on single crystals of NaSnN for sodium and tin was carried out on a JEOL JSM-840A scanning electron microscope equipped with an Oxford Instruments ISIS300 energy dispersive X-ray analyser. A normalised Sn : Na ratio of 50.6(6) : 49.4(6) was determined from twelve spot readings on several crystals. Combustion analysis for nitrogen was carried out using a Carlo Erber Strumentazione 1106 CHN analyzer: the measured N content of 7.2% by mass is lower than the expected 9.0% due to some contamination of the bulk sample by the decomposition product: elemental tin, and partial hydrolysis during analysis. No hydrogen was detected in this analysis.

‡ NaSnN: space group $P6_3mc$ (No. 186), a = 3.3306(1) Å, c = 10.8919(5) Å, Z = 2, ρ_{calc} = 4.942 g cm^{-3}, T = 220 K, M = 155.7. Single crystal XRD data were collected on a 0.04 mm diameter, 0.02 mm thick well-formed hexagonal red crystal using a Nonius Kappa CCD diffractometer: MoKα radiation (λ = 0.71073 Å); angular range $7° \leqslant \theta \leqslant 42°$; completeness to θ_{max}: 99.4%; R_{int} = 0.034; 4545 reflections measured (247 independent). Structure solution (direct methods): SHELXS-97,[23] absorption correction: numerical based on face indexing[24] (μ = 11.94 mm^{-1}; max/min transmission: 0.62/0.44). Full matrix refinement on F using 12 parameters and no restraints using CRYSTALS[25] (R_1 = 0.0176, wR = 0.0133 for $I > 2\sigma(I)$, Goodness of fit on F = 1.107, Flack parameter = 0.0(2) from 93 Friedel pairs). CCDC 269578. See http://dx.doi.org/10.1039/b505208d for crystallographic data in CIF or other electronic format.

Powder SHG measurements were performed on a modified Kurtz-NLO[26] system using 1064 nm light from a Continuum Minilite II laser, operating at 15 Hz.[27] Powder samples were sealed in glass capillary tubes.

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