Low-Temperature Synthesis of Diamminesodium(1+) Triamminesodium(1+) Trithioantimonate(3−) Ammoniate (1:2:1:2) ($[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\,NH_3$), A Solvated Neutral Sodium Trithioantimonate(3−) (3:1) Na_3SbS_3) Ion Complex

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A solution of sodium in liquid ammonia reacts with Sb_2S_3 to form large colorless crystals of the composition $Na_3SbS_3 \cdot 10\,NH_3$. The trigonal-pyramidal SbS_3^{3-} anion is ion-paired with three Na^+ counter ions, the coordination spheres of which are completed by eight ammine ligands. The resulting neutral $[Na(NH_3)_3]_2$-$[Na(NH_3)_2]SbS_3$ molecules crystallize together with two ammonia molecules of solvation in the space group $P2_1/c$ ($a = 9.828(2)$, $b = 6.0702(4)$, $c = 33.4377(6)$ Å, $\beta = 91.362(7)°$, $V = 1994.2(5)$ Å^3, $Z = 4$).

Introduction. – The reduction of main-group elements and compounds with solutions of alkali metals in liquid ammonia is one of the oldest methods for the low-temperature generation of multiply charged anions. *Zintl* and co-workers used this approach in their studies of polyanions of several metallic and semi-metallic elements of group 14 to 16 like Sn_9^{4-} and As_7^{3-} [1]. However, structural studies of the phases which crystallize directly from the ammonia solutions were severely hampered by the fact that they almost invariably contain ammonia molecules of solvation, which causes decomposition of the crystals, even below room temperature. With the modern methods of low-temperature X-ray single-crystal structure analysis available now [2], these ammoniates may be studied systematically, complementing earlier research in extracting and crystallizing *Zintl* anions with solvent like ethylenediamine [3]. Our recent investigations concentrated on the reaction of lithium with several elements in liquid ammonia, resulting in the structural characterization of compounds like $[Li(NH_3)_4]_4P_{14}$ [4], $[Li(NH_3)_4]_3As_7 \cdot NH_3$ [4], and $[Li(NH_3)_4]_4E_9 \cdot NH_3$ (E = Sn, Pb) [5] with cage anions, $[Li(NH_3)_4]_3[Li_2(NH_3)_2Sb_5] \cdot 2\,NH_3$ [6] with a novel ring anion, and $[Li(NH_3)_4]_2Te_2$ [7] with a dumb-bell shaped anion. Analogue studies with binary compounds of main-group elements as starting materials have been initiated; an example is the reduction of As_4Se_4 with lithium in liquid ammonia yielding $[Li(NH_3)_4]_3AsSe_4$ [8]. Due to the relatively high stability of the $[Li(NH_3)_4]^+$ complex, the majority of structure determinations up to now succeeded with this alkali metal. We are interested in broadening the scope of our investigations to include the heavier alkali metals, and report now on the reaction of grey Sb_2S_3 (stibnite) with sodium in liquid ammonia.

Experimental. – All manipulations were executed under dried Ar (Argon 4.6, *Linde*). A mixture of Na (0.615 g, 26.764 mmol; *Merck*, purified by segregation) and Sb_2S_3 (3.031 g, 8.921 mmol; *Merck*) was placed in a

Schlenk-type reaction vessel which had been dried *in vacuo*. On this mixture, *ca.* 30 ml of anh. ammonia (stored as a sodium-ammonia soln.) were condensed at $-78°$. After $2^{1/2}$ months in which the vessel was stored at $-35°$, large colorless rhombic crystals precipitated which are highly sensitive to air and moisture. Due to the loss of ammonia of solvation, they turn opaque at temp. higher than the boiling point of NH_3 ($-33.4°$). Suitable crystalline material was transferred directly from the soln. into cooled perfluorinated polyether (*Galden HT230*, Ausimont). Crystal selection and handling followed the technique described by *Kottke* and *Stalke* [2]. The structure determination was carried out on a *Stoe-IPDS* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71073 Å) at $T-150°$; number of symmetry-independent reflections ($3.16° < \vartheta < 25.04°$): 3236; no. of observed reflections ($I > 2\sigma(I)$) 3103.

Crystal Data for Diamminesodium(1+) Triamminesodium(1+) Trithioantimonate(3−) Ammoniate (1:2:1:2) (=Octaammine(antimony)tris(μ_3-thio)trisodium Ammoniate (1:2) $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\,NH_3$)[1]: Colorless rhombic crystals, M_r 457.24; monoclinic, space group $P2_1/c$ (no. 14); $a = 9.828(2)$, $b = 6.0702(4)$, $c = 33.4377(6)$ Å, $\beta = 91.362(7)°$, $V = 1994.2(5)$ Å^3; $Z = 4$, $D_c = 1.523$ g cm^{-3}; μ (MoK_α) 1.76 mm^{-1}. The crystal structure was solved by direct methods and refined on F^2 using SHELX-program packages [9]; absorption correction by DIFABS [10]. The H-atoms of all NH_3 molecules were located by difference *Fourier* syntheses and refined isotropically, all other atoms anisotropically. For 274 parameters, the refinement converged at a wR_2 value of 0.0608 (corresponding to a conventional R value of 0.0251 taking into account only reflections with $I > 2\sigma(I)$).

Results and Discussion. – The reductive cleavage of the Sb_2S_3 network by a solution of sodium in liquid ammonia yields SbS_3^{3-} molecular anions; the main product has the composition $Na_3SbS_3 \cdot 10\,NH_3$. The trigonal-pyramidal SbS_3^{3-} anion, which is well known from the mineral pyrargyrit Ag_3SbS_3 [11], forms the centre of a neutral ion complex (*Fig. 1*), in which three Na^+ ions are coordinated by two S-atoms respectively in an η^2-like fashion. The coordination sphere of two of the Na^+ ions (Na(1) and Na(2)) are completed by three ammine ligands, while the third Na^+ ion has only two close contacts to ammonia molecules, disturbing the otherwise roughly threefold symmetry of the ion complex. The next closest Na−N distance for Na(3) after these two contacts is 2.849(3) Å to a symmetry-equivalent N(32) atom, which is significantly longer than the medium value for the Na−N contacts of 2.45 Å. The neutral ion complex crystallizes in space group $P2_1/c$ in a molecular packing with two ammonia molecules of solvation. A more precise formula for the compound is thus $[Na(NH_3)_3]_2$-$[Na(NH_3)_2]SbS_3 \cdot 2\,NH_3$ (*Fig. 2*).

There is a significant gap in the values of the N−N distances between the ammonia molecules. Whereas the N−N distances of the free ammonia molecules to their nearest NH_3 neighbours vary between 3.359(3) (N(2)−N(13)), 3.366(3) (N(2)−N(1), and 3.392(3) Å (N(2)−N(1)), distances longer than 3.453(3) Å as a minimum value can be found between all other NH_3 molecules. Regarding the value of 3.38 Å for the N−N distances between NH_3 molecules in solid ammonia as typical for H-bonds [12], the free NH_3 molecules of $Na_3SbS_3 \cdot 10\,NH_3$ form a zig-zag-shaped pattern along the monoclinic *b* axis. The resulting chain is connected to $[Na(NH_3)_3]^+$ fragments by ammonia molecules labeled with N(13). This point of view is supported by the fact that in every H-bridging bond a H-atom can be found pointing to a N-atom of the next ammonia molecule. Typical H−N distances are 2.440(3) (N(1)−H(22)), 2.519(3) (N(2)−H(11)), and 2.524(3) Å (N(2)−H(133)) (*Fig. 3*).

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[1] Further details of the crystal-structure investigation may be obtained from the *Fachinformationszentrum Karlsruhe*, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 411765.

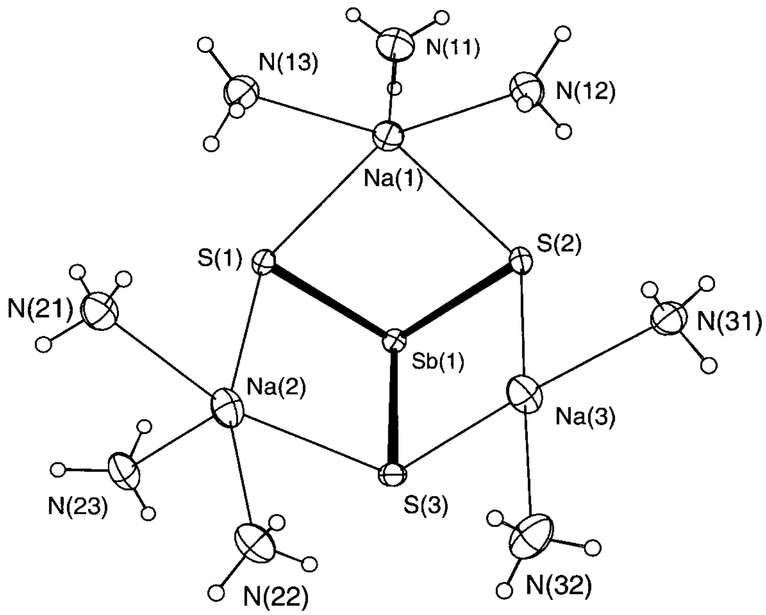

Fig. 1. *ORTEP Plot of the* $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3$ *neutral ion complex in* $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\ NH_3$ (50% probability ellipsoids). Selected interatomic distances [Å] and bond angles [°]: Sb(1)−S(3) 2.4014(5); Sb(1)−S(2) 2.4015(7); Sb(1)−S(1) 2.4021(6); S(1)−Na(1) 2.8813(12); S(1)−Na(2) 2.9357(12); S(2)−Na(1) 2.8723(10); S(2)−Na(3) 2.8879(11); S(3)−Na(3) 2.7871(12); S(3)−Na(2) 2.8886(12); Na(1)−N(11) 2.433(3); Na(1)−N(12) 2.479(2); Na(1)−N(13) 2.476(2); Na(2)−N(21) 2.488(3); Na(2)−N(22) 2.457(3); Na(2)−N(23) 2.460(3); Na(3)−N(31) 2.412(3); Na(3)−N(32) 2.481(3); S(1)−Sb(1)−S(2) 102.35(2); S(1)−Sb(1)−S(3) 100.41(2); S(2)−Sb(1)−S(3) 99.86(2).

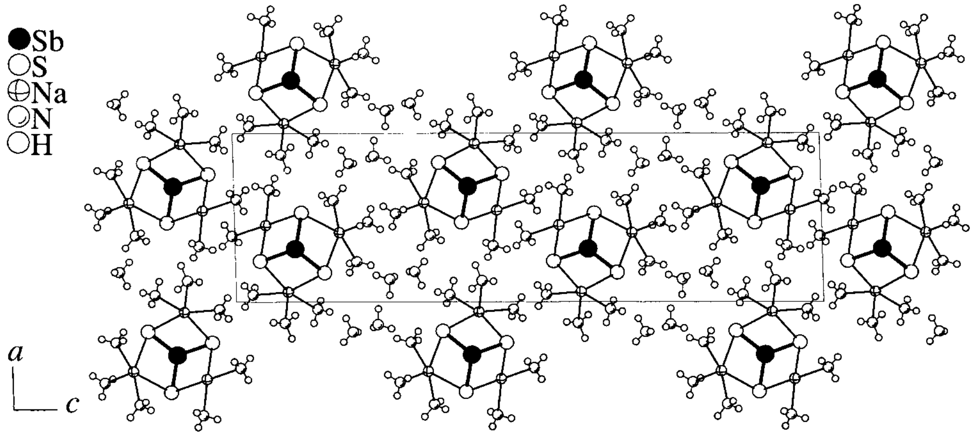

Fig. 2. *Unit cell of* $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\ NH_3$ *viewed in the direction of the* b *axis*

The mean Sb−S bond length in the central SbS_3^{3-} anion is 2.402 Å, which is shorter than the Sb−S bond lengths in Ag_3SbS_3 (2.454 Å) [11] and Tl_3SbS_3 (2.431 Å) [13], and which would be expected for the comparatively more ionic interaction of the anion with

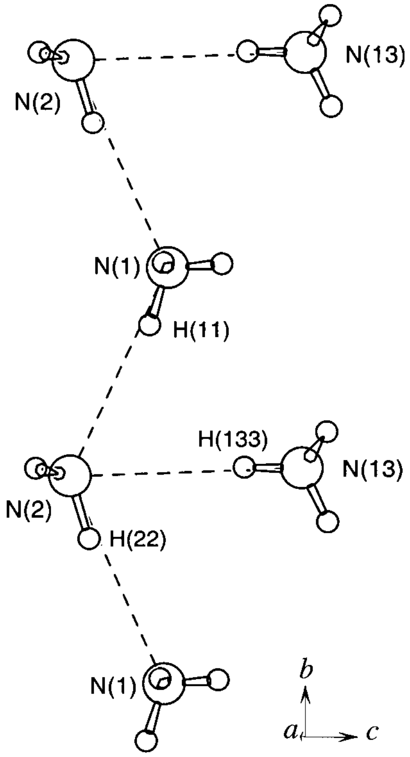

Fig. 3. *Hydrogen bonds of the free ammonia molecules in* $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\ NH_3$

alkali-metal cations. On the other hand, the Sb–S bonds of the same anion in $K_3SbS_3 \cdot 3\ Sb_2O_3$ are significantly shorter (2.362 Å) [14], which is probably due to the better charge separation with potassium counter ions and the fact that only one K–S contact per S-atom exists in this structure. The distances between the Na- and the S-atoms in $[Na(NH_3)_3]_2[Na(NH_3)_2]SbS_3 \cdot 2\ NH_3$ are varying within a range of 2.787(1) (S(3)–Na(3)) to 2.936(1) Å (S(1)–Na(2)), with the Na-atom, the two coordinating S-atoms, and the Sb-atom being approximately coplanar on all three sides of the anion. Thus, a possible description of the Na_3SbS_3 core of the molecule is that of an distorted cube with one missing vertex.

Recently, a compound also containing SbS_3^{3-} anions was synthesized by heating a mixture of CuI, Cu, Sb, and S to 500° in evacuated silica ampoules to yield $(CuI)_2Cu_3SbS_3$ [15]. This indicates that the parallels between liquid ammonia and copper(I) halides as reaction media for the generation of main-group polyanions extend to small, highly charged anions as well.

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